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Complexes of Heavy Lanthanides with *o*-Aminobenzoic Acid

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Anthranilates of Tb – Lu prepared in the reaction of the rare earth hydroxides with *ortho*-aminobenzoic acid (anthranilic acid) have the general formula $Ln(C_6H_4NH_2COO)_3 \cdot 2H_2O$ where Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu. The water molecules in the hydrated compounds are in the outer coordination sphere. On heating in air at 493 K dehydration occurs and the anhydrous anthranilates $Ln(C_6H_4NH_2COO)_3$ are formed. On the basis of the IR spectra it was found that the metal in dihydrated anthranilates was simultaneously coordinated through amino and carboxyl groups whereas in anhydrous anthranilates only through the bidentate carboxyl group. From X-ray analysis it was stated that the anthranilates $Ln(C_6H_4NH_2COO)_3 \cdot 2H_2O$ are isostructural, whereas the anhydrous compounds $Ln(C_6H_4NH_2COO)_3$ are isostructural in the two groups Tb – Er and Tm – Lu.

(Keywords: Anthranilic acid; Heavy lanthanides, complexes)

Die Komplexe der schweren Selteneerdmetalle mit Orthoaminobenzoesäure

Zur Darstellung der Verbindungen des Typs $Ln(C_6H_4NH_2COO)_3 \cdot 2H_2O$ (mit Ln = Tb bis Lu) wurde die berechnete Menge von $Ln(OH)_3$ und $C_6H_4NH_2COOH$-Lösung gemischt und bei 363 K schnell zur Kristallisation gebracht. Die Produkte werden schnell abfiltriert, mit Wasser gewaschen und bis zur Gewichtskonstanz getrocknet. Die Verbindungen $Ln(C_6H_4NH_2COO)_3 \cdot 2H_2O$ sind isostrukturell mit der Dichte ungefähr $1.6 g \cdot cm^{-1}$ und geringer Löslichkeit in Wasser bei Raumtemperatur. Beim Erhitzen folgt zunächst Entwässerung bei 493 K, später Zersetzung zu Tb_4O_7 und Ln_2O_3. Die wasserfreien Verbindungen $Ln(C_6H_4NH_2COO)_3$ sind isostrukturell in 2 Strukturtypen: Tb – Er and Tm – Lu. Die Infrarotspektren von wasserfreien Verbindungen und Doppelhydraten wurden registriert. Es wurde festgestellt, daß die Koordinierung der Seltenerdmetalle mit Liganden in den Dihydraten sowohl durch die Amino- als auch durch Carboxylgruppen erfolgt. In den wasserfreien Komplexen tritt die Koordinierung nur durch Carboxylgruppen auf.

Introduction

Ortho-aminobenzoic acid (anthranilic acid), as an important precursor of tryptophan (one of the biologically important α-amino-acids) forms with monovalent metals compounds used in the investigation of the behaviour of potassium in biological systems [1].

The anion of anthranilic acid is a unique ligand which forms highly insoluble complexes suitable for gravimetric determination of the transition metals [2, 3]. On the other hand the insoluble bis-anthranilato copper(II) complex is pharmacologically active as an antiinflammatory agent [4] and other metal complexes (e.g. Rh) with the anthranilic acid having unusual catalytic properties [5]. A number of studies report the chromatographic separation of ferrous and ferric anthranilates by differential extraction with *n*-pentanol [6] or by paper chromatography of adducts of iron anthranilates with pyridine [7].

The studies on the divalent metal complexes with anthranilic acid in solids tending towards elucidation of their structures lead to the conclusion that the anthranilic ligand may act as bidentate [8–10] or tridentate one [11, 12] which, as it was found by *Karasev* [9], depends on the nature of the competitive ligands (e.g. H_2O, pyridine).

Some of the NH_2 groups may not take part in the metal coordination but form intra- or intermolecular hydrogen bonds and the metal is coordinated only through the bidentate carboxyl group.

Sandhu et al. [11] proposed a structure in which the *ortho*-aminobenzoate acted as a tridentate ligand, giving rise to a distorted octahedral coordination around the central divalent metal, *Hill* and *Curran* [10] suggested a square planar structure, *Lange* and *Haendler* [12] reported the crystal and molecular structure of bis-anthranilato-copper(II). The local coordination geometry is a distorted octahedron, in which each *ortho*-aminobenzoate group acts as a tridentate ligand, but the three sites of attachment on the ligand are not associated with the same copper atom. From the papers on rare earth complexes with anthranilic acid [13–16] the studies on the manner of coordination do not appear to be so extensive as in the case of d-electron elements.

The aim of this paper on rare earths *ortho*-anthranilates is to determine some of their physicochemical properties and to characterise the manner of the metal-ligand coordination.

Experimental

Anthranilates of Tb – Lu were obtained by adding the anthranilic acid solution at 363 K to newly precipitated colloidal hydroxides of Tb – Lu with the molar ratio of the acid to Ln^{3+} 3 : 1. The complexes precipitated immediately as fine powders, were filtered off, washed with water and dried at 303 K to constant weight.

The percentage of carbon, hydrogen and nitrogen was determined on the basis of the elemental analysis. The content of the rare earth elements and water was established by a derivatographic method (Q-1500D derivatograph, heating rate of 2.5 $\mathrm{deg\,min^{-1}}$) from TG curves as well as gravimetrically by ignition of the complexes to the oxides Tb_4O_7 and Ln_2O_3 at 1273 K. The density of the compounds was determined using a pycnometer.

IR spectra of anthranilates of Tb – Lu and anthranilic acid were recorded on UR-20 spectrophotometer over the range 4000–400 $\mathrm{cm^{-1}}$. The samples were prepared as KBr discs. X-ray diffraction patterns were taken on a DRON-2 diffractometer using Ni filtered CuKα radiation. The measurements were made by means of the powder *Debye-Scherrer* method.

Result and Discussion

Anthranilates of Tb – Lu are obtained in solid states as light-cream dihydrates. They are sparingly soluble in water. The anthranilates of Er – Lu are more soluble than those of Tb – Ho. Their density is about 1.6 $\mathrm{g\cdot cm^{-1}}$ (Table 1). They are stable under normal conditions but heated in air they lose crystallization water at 323–455 K and decompose exothermically in the range of 589–986 K to the oxides Tb_4O_7 and Ln_2O_3 [17]. In order to study the types of the bonding between the ligand and metal ions and to elucidate the structure of the obtained complexes their IR spectra were recorded.

For the interpretation of IR spectra the literature data on IR spectra of aminocarboxylic acid compounds with various metals were used [8–

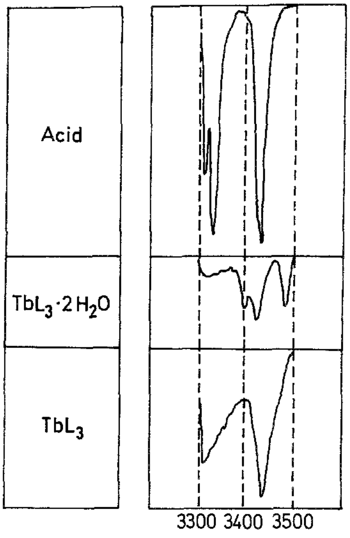

Fig. 1. IR spectra of anthranilic acid, terbium anthranilate $TbL_3\cdot 2H_2O$ and TbL_3

Table 1. *Analytical data*

Complex*	% C Calcd.	% C Found	% H Calcd.	% H Found	% N Calcd.	% N Found	% M Calcd.	% M Found	Solubility in water mol $dm^{-1} \cdot 10^{-4}$	Density g cm^{-1}
$TbL_3 \cdot 2\,H_2O$	41.80	41.54	3.67	3.43	6.96	6.96	26.34	26.02	4.217	1.603
$DyL_3 \cdot 2\,H_2O$	41.56	41.54	3.65	3.58	6.92	6.54	26.77	26.92	6.546	1.729
$HoL_3 \cdot 2\,H_2O$	41.39	41.98	3.64	3.55	6.90	6.80	27.06	27.00	6.913	1.688
$ErL_3 \cdot 2\,H_2O$	41.23	41.43	3.62	3.51	6.87	6.56	27.34	27.31	14.534	1.595
$TmL_3 \cdot 2\,H_2O$	41.09	41.42	3.61	3.99	6.85	6.53	27.59	27.14	14.512	1.620
$YbL_3 \cdot 2\,H_2O$	40.85	40.49	3.59	3.47	6.80	6.68	28.02	27.89	13.880	1.644
$LuL_3 \cdot 2\,H_2O$	40.72	41.26	3.54	3.76	6.78	7.07	28.25	27.99	11.681	1.670

* $L = C_6H_4NH_2COO^-$

10, 18, 19]. IR spectra of the compounds and anthranilic acid were also recorded (Fig. 1 and Tables 2, 3). In the spectrum of anthranilic acid the absorption bands arising from asymmetric and symmetric vibrations of amino group appear at 3468 cm^{-1} and 3370 cm^{-1}, respectively and the absorption band resulting from the deformation vibration δNH_2 occurs at 1618 cm^{-1}. The value of the splitting for the absorption band of valency vibrations is equal to 102 cm^{-1} because of the interaction of two $N-H$ bands [9, 10]. Owing to the complexation disruption of $N-H \ldots O$ bonds existing in the dimer of acid takes place with simultaneous formation of other bonds. In the IR spectra of dihydrated Tb – Lu anthranilates the absorption bands of ν_{as} and ν_s of NH_2 group are displaced to lower frequencies with respect to those of the free acid (Table 2). The values of the shifts for the compounds $LnL_3 \cdot 2H_2O$ equal 95–102 cm^{-1} for ν_{as} and 55–65 cm^{-1} for ν_s.

Hill and *Curran* [10] classified the compounds of anthranilic acid with metals into two groups. The anthranilates of Na, K, Ca, Ba and Sr belong to the group of salts whereas the anthranilates of Mg, Zn, Cd, Ni and Cu to the group of complexes.

In the group of salts the maximum of absorption bands due to ν_{as} and ν_s NH_2 appears to be in close agreement with those for the acid, while the spectra of complexes reveal their shift to lower frequencies (149–187 cm^{-1}). The large value of the shift points to strong N-M coordination bond formation. The values of the shifts for anthranilates $LnL_3 \cdot 2H_2O$ are smaller than those obtained by *Hill* for the anthranilates of d-electron elements. The data may indicate a weaker N-M bond between the atom of nitrogen and the central atom of lanthanides in dihydrated anthranilates. It seems to be a result of the strong influence of the filled $5s^2$ $5p^6$ electron shells on 4f electrons of lanthanides [20]. The value of the shift 20–30 cm^{-1} was obtained by *Karasiev* [9] for terbium anthranilate and 100–200 cm^{-1} for chloroanthranilate of lanthanides by *Deshande* [13].

The absorption band at c.a. 3475 cm^{-1} (Table 2) reveals the water in the $LnL_3 \cdot 2H_2O$ complexes as well as in *p*-anthranilates of lanthanides [21] to be outer sphere water.

In the group of anhydrous lanthanide anthranilates LnL_3 the maximum of absorption bands ν_{as} and ν_s appears to be near those for the acid (Table 2, Fig. 1).

The values of shifts ν_{as} to greater frequencies are 10–20 cm^{-1}, ν_s to lower frequencies are 4–5 cm^{-1}. Simultaneously, the value of the splitting for the absorption band of valency vibrations ν_{as} and ν_s $(\nu_{as} - \nu_s)$ is close to those in a free dimer of the acid.

The data may indicate absence of a coordination bond between nitrogen and lathanides atoms.

Table 2. *Frequencies of absorption bands of the* NH_2 *group of*

Compound[a]	δ OH	ν OH	ν_{as} NH_2
$C_6H_4NH_2COOH$	–	–	3470
K*L* 25	–	–	3420
$\mathrm{Tb}L_3 \cdot 2\ \mathrm{H_2O/Tb}L_3$	1652/–	3480/–	3375/3485
$\mathrm{Dy}L_2 2\ \mathrm{H_2O/Dy}L_3$	1652/–	3480/–	3375/3480
$\mathrm{Ho}L_3 \cdot 2\ \mathrm{H_2O/Ho}L_3$	1652/–	3475/–	3374/3480
$\mathrm{Er}L_3 \cdot 2\ \mathrm{H_2O/Er}L_3$	1652/–	3480/–	3375/3480
$\mathrm{Tm}L_3 \cdot 2\ \mathrm{H_2O/Tm}L_3$	1652/–	3475/–	3472/3485
$\mathrm{Yb}L_3 \cdot 2\ \mathrm{H_2O/Yb}L_3$	1652/–	3470/–	3370/3490
$\mathrm{Lu}L_3 \cdot 2\ \mathrm{H_2O/Lu}L_3$	1652/–	3468/–	3368/3488

[a] $L = C_6H_4NH_2COO^-$

[b] $\Delta\nu_{as}$ = shift of absorption band γ_{as} NH_2 compared with γ_{as} of free acid

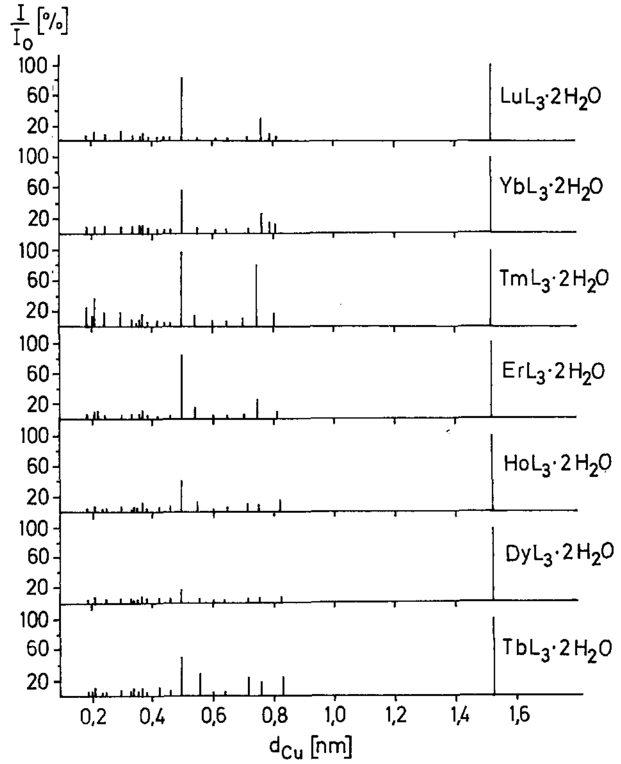

Fig. 2. Powder photograph of anthranilates $Ln(C_6H_4NH_2COO)_3 \cdot 2H_2O$ where $Ln = Tb - Lu$

anthranilic acid and their compounds with rare earth elements

$\Delta\nu_{as}{}^{b}$	γ_s NH_2	$\Delta\nu_s{}^{c}$	$\nu_{as} - \gamma_s$	δ NH_2
–	3370	–	100	1618
50	3380	10	60	1620
−95/+15	3314/3366	−56/−4	61/119	1620/1618
−95/+10	3315/3365	−55/−5	60/115	1621/1615
−96/+10	3310/3365	−60/−5	64/115	1621/1613
−95/+12	3310/3365	−60/−5	65/110	1622/1614
−98/+15	3310/3365	−60/−5	62/120	1621/1613
−100/+20	3309/3365	−61/−5	61/125	1622/1612
−102/+18	3305/3365	−65/−5	63/123	1620/1613

[c] $\Delta\nu_s$ = shift of absorption band γ_s NH_2 compared with γ_s of free acid

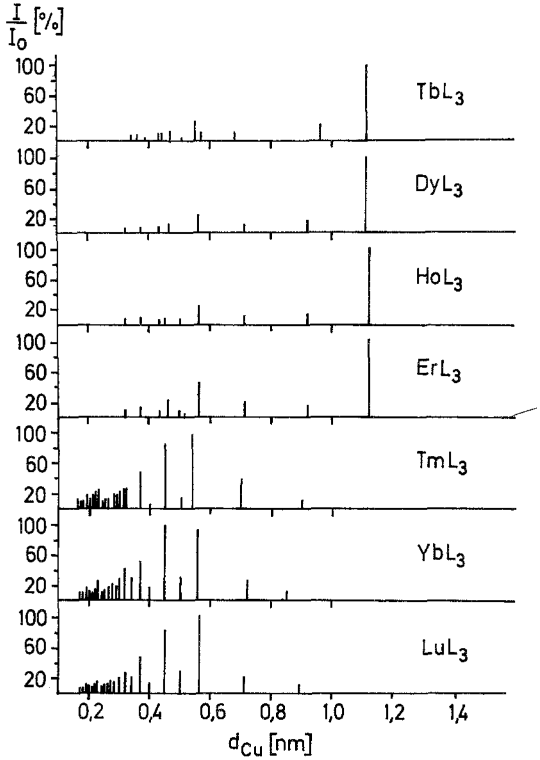

Fig. 3. Powder photograph of anhydrous anthranilates $Ln(C_6H_4NH_2COO)_3$ where Ln = Tb − Lu

Table 3. *Frequencies of absorption bands of* COO^- *of anthranilic acid and compounds with rare earth elements*

Compound[a]	γ C=O	γ_{as} COO^-	Δv_{as}[b] COO^-	γ_s COO^-	Δv_s[c] COO^-	$\gamma_{as} - \gamma_s$ COO^-	γ *M*-O
$C_6H_4NH_2COOH$	1670	1585	–	1420		–	–
K*L* [25]	–	1560	25	1400	20	160	–
$TbL_3 \cdot 2\,H_2O/TbL_3$	–	1521/1510	65/75	1405/1395	15/25	115/115	400/400
$DyL_3 \cdot 2\,H_2O/TbL_3$	–	1520/1511	65/74	1406/1396	14/24	114/115	400/420
$HoL_3 \cdot 2\,H_2O/TbL_3$	–	1521/1510	64/75	1406/1395	14/25	115/115	420/420
$Er \cdot 2\,H_2O/ErL_3$	–	1525/1511	60/74	1410/1398	10/22	115/113	420/420
$Tm \cdot 2\,H_2O/TmL_3$	–	1525/1511	60/74	1410/1398	10/22	115/113	420/420
$Yb \cdot 2\,H_2O/TbL_3$	–	1522/1510	63/75	1412/1397	8/23	110/113	420/430
$Lu \cdot 2\,H_2O/LuL_3$	–	1525/1510	60/75	1412/1400	8/20	113/110	420/430

[a] $L = C_6H_4NH_2COO^-$

[b] Δv_{as} COO^- = shift of absorption band γ_{as} COO^- compared with γ_{as} of free acid

[c] Δv_s COO^- = shift of absorption band v_s COO^- compared with γ_s of free acid

The carboxylic group is the second group participating in the bond of the anthranilic acid with lanthanides. Its characteristic bands in the IR spectra obtained for the free dimer of acid appear at 1670 cm^{-1} (ν_{as} C=O), 1585 cm^{-1} (ν_{as} COO$^-$) and 1420 cm^{-1} (ν_s COO$^-$) (Table 3).

In the spectra of the obtained complexes the band due to the C=O vibration at 1670 cm^{-1} disappears entirely. Just as in the spectra of anthranilates of d-electronic metals [10, 19] the bands of asymmetric and symmetric vibrations of the COO$^-$ group in the spectra of lanthanide anthranilates are displaced to lower frequencies.

According to *Hill* and *Curan* [10] the COO$^-$ ... M^{2+} bonds in the anthranilate complexes are essentially electrostatic. The shift of ν_{as} and ν_s bands to lower frequency supports the assumption that the carboxyl group in the anthranilate complexes is bridging bidentately [18]. The shift values of the bands to lower frequency indicate the degree of bond covalency. The shift of the peak ν_{as} COO$^-$ (1 585 cm^{-1}) in Na, K, Ca, Sr, Ba anthranilates are equal 2–5 cm^{-1} (*Hill* [10]) and in Cd, Ni, Co, Zn, Cu anthranilates 40–50 cm^{-1} [10, 18] whereas in lanthanide anthranilates 60–65 cm^{-1} for dihydrates and 75 cm^{-1} for anhydrous compounds was found (Table 3).

The highest value of the shifts for the lanthanide anthranilates may be connected with the higher degree of covalency of the COO$^-$ ... Ln^{3+} bond. It is also confirmed by the lower values of $\Delta\nu (\Delta\nu = \nu_{as} - \nu_s)$ for the complexes Tb – Lu (c.a. 115 cm^{-1}) compared to those for potassium salt (160 cm^{-1}) (Table 3).

On the basis of IR spectra interpretation the lanthanide ions were found to coordinate the anthranilate ligands in dihydrate complexes $LnL_3 \cdot 2H_2O$ through a nitrogen atom of the NH_2 group and oxygen atoms of the carboxylate group forming sixmembered rings. It seems to be necessary to take into account the fact proved by *Lange* [12] for the anthranilate of Cu(II) that each oxygen atom coördinates a different lanthanide ion.

In the anhydrous lanthanide complexes LaL_3 coordination of the anthranilate ligands by lanthanides atom takes place through two atoms of oxygen of the carboxylic group. Coordination by the NH_2 group is absent as in *p*-anthranilates of lanthanides (*Efremova* [21]).

From the recorded diffractograms (Figs. 2, 3), the anthranilate Tb – Lu were found to be crystalline compounds of low symmetry and big unit cells. The hydrated complexes forms the group of isostructural compounds $LnL_3 \cdot 2H_2O$. The anhydrous anthranilate, LnL_3, obtained by heating the hydrated complexes at 493 K forms the two group of isostructural compounds: Tb – Er and Tm – Lu (Fig. 3). Single crystals of Tb – Lu anthranilate dihydrates have been grown and a full X-ray structure determination is in progress.

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