

Faculty of Chemistry Marie Curie-Skłodowska University  
Department of Inorganic and General Chemistry

Wanda BRZYSKA, Barbara PASZKOWSKA

### Preparation and Properties of Rare Earth Element Capronates

Preparatyka i właściwości kapronianów pierwiastków ziem rzadkich

Hexanoic acid known as capronic or caproic acid is a liquid, soluble in water ethanol and ether. The rare earth element complexes with capronic acid are little known. From the survey of the literature it follows that there are some papers on the preparation of the capronates of some rare earth elements [1–5]. Paul *et al.* [1, 2] prepared anhydrous capronates of La(III) to Sm(III) and studied their thermal decomposition. They studied also magnetic properties [1] of La(III) and Ce(III) complexes. It was also found that capronates of La(III)—Sm(III) are sparingly soluble in water [5].

Gushichina and Kotenko [4] prepared capronates of La, Gd, Dy, Ho and Yb as hydrates with different degree of hydration ( $n=1.6; 2.7; 2.2; 2.1; 3.7$ , respectively). In the literature there are not the papers on the systematical study on the rare earth capronates.

The aim of our work was to obtain in solid state the capronates of yttrium and all lanthanides in the same conditions and to examine some of their properties.

#### EXPERIMENTAL

##### PREPARATION OF COMPLEX

Rare earth element capronates were prepared by adding equivalent quantities of solution of ammonium salt ( $pH$  6.5) to a hot solution of rare earth element chlorides ( $pH$  4.5) (cerium was used as its nitrate). The precipitate formed was heated for 0.5 h at 345–353 K, then was filtered off, washed with hot water to remove  $NH_4^+$  and  $Cl^-$  ions and dried at 303 K to a constant mass.

## ANALYTICAL DATA

The content of carbon and hydrogen in capronates prepared was determined on the basis of elemental analysis by using  $V_2O_5$  — as oxidizing agent. The content of rare earth elements was determined from TG curve and by ignition of the preparations to oxides at 1273 K. The water contents were determined from TG curve. The results obtained are presented in Table 1.

Table 1. Analytical data

Complex	%C		%H		%M	
	Calcd	Found	Calcd	Found	Calcd	Found
$YI_3 \cdot 2H_2O$	46.01	46.40	7.94	7.95	18.42	18.27
$LaL \cdot H_2O$	43.07	43.40	7.03	7.23	27.67	27.47
$CeL_3 \cdot H_2O$	42.97	42.65	7.01	7.20	28.75	28.49
$PrL_3 \cdot H_2O$	42.90	43.22	7.00	7.40	27.46	27.24
$NdL_3 \cdot 2H_2O$	41.16	41.47	7.10	7.50	27.45	27.42
$SmL_3 \cdot 2H_2O$	40.68	40.95	7.02	7.10	28.30	27.95
$EuL_3 \cdot 2H_2O$	40.56	40.84	7.00	7.47	28.51	28.33
$GdL_3 \cdot 2H_2O$	40.17	39.82	6.93	6.53	29.00	28.89
$TbL_3 \cdot 2H_2O$	38.72	38.45	6.68	6.45	28.47	28.57
$DyL_3 \cdot 2H_2O$	39.78	39.98	6.86	6.54	29.89	29.62
$HoL_3 \cdot 2H_2O$	39.59	39.80	6.83	6.96	28.00	27.92
$ErL_3 \cdot 2H_2O$	39.36	39.05	6.79	6.43	30.63	30.62
$TmL_3 \cdot 3H_2O$	38.04	38.49	6.92	6.64	29.71	29.40
$YbL_3 \cdot 3H_2O$	37.77	37.37	6.87	6.65	30.22	30.10
$LuL_3 \cdot 3H_2O$	37.67	37.45	6.85	6.48	30.48	30.51

$L^* - (C_3H_{11}COO^-)$

## IR SPECTRA AND DIFFRACTOGRAMS

IR spectra of capronic acid, its sodium salt and rare earth element complexes were recorded. The measurements were made on a UR-20 spectrophotometer within the range  $4000-400\text{ cm}^{-1}$ . The samples were prepared as KBr discs.

The diffractograms of prepared capronates were recorded on a DRON-2 diffractometer by using  $CuK_{\alpha}$  (Ni filtered) radiation.

The measurements were made by means of the Debye—Scherrer method over the range  $2\Theta = 4-60^\circ$ . The results are presented in Fig. 1.



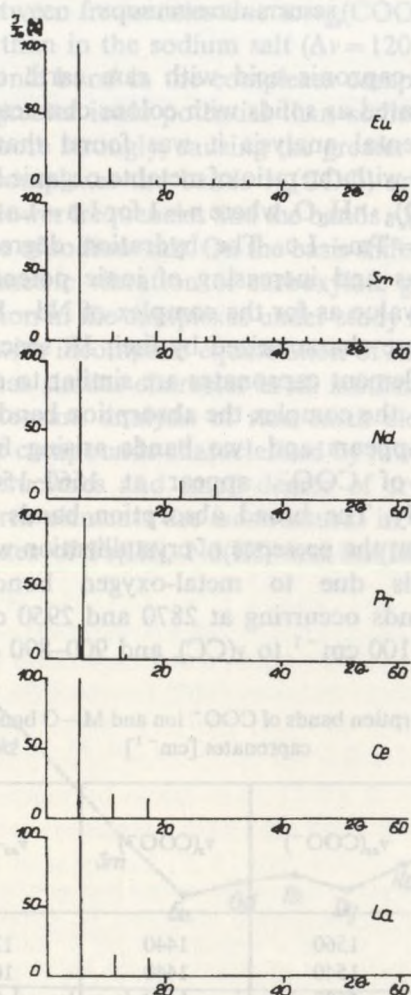


Fig. 1. Radiogram sheet of rare earth capronates

#### DETERMINATION OF SOLUBILITY

The solubilities in water of obtained complexes at 298 K were determined. The saturated solutions were prepared under constant conditions. The content of rare earth elements in saturated solution was determined by using spectrophotometric method, with arsenazo III. The measurements were made on a spectrophotometer SPECORD M-40. On the basis of 3-4 results the solubilities of complexes were determined.

## RESULTS AND DISCUSSION

The complexes of capronic acid with rare earth elements (Y, La—Lu without Pm) were prepared as solids with colour characteristic of Ln(III) ions. On the basis of elemental analysis it was found that rare earth element capronates are hydrates with the ratio of metal to organic ligand 1:3 and general formula  $\text{Ln}(\text{C}_5\text{H}_{11}\text{COO})_3 \cdot n\text{H}_2\text{O}$ , where  $n = 1$  for  $\text{Ln} = \text{La} - \text{Pr}$ ;  $n = 2$  for  $\text{Ln} = \text{Y}$ ,  $\text{Nd} - \text{Er}$ ;  $n = 3$  for  $\text{Ln} = \text{Tm} - \text{Lu}$ . The hydration degree increases with decreasing of ionic radius and increasing of ionic potential, and for yttrium complex has the same value as for the complex of Nd—Er.

The compounds were characterized by their IR spectra (Table 2). The IR spectra for rare earth element capronates are similar to each other. When the acid is converted into the complex the absorption band of the COOH group at  $1725 \text{ cm}^{-1}$  [3] disappears and two bands arising from asymmetric and symmetric vibrations of  $\text{COO}^-$  appear at  $1560 - 1540 \text{ cm}^{-1}$  and  $1450 - 1430 \text{ cm}^{-1}$ , respectively. The broad absorption bands with the maxima at  $3400 - 3300 \text{ cm}^{-1}$  confirm the presence of crystallization water molecules in the complexes. The bands due to metal-oxygen bond are observed at  $425 - 415 \text{ cm}^{-1}$ . The bands occurring at  $2870$  and  $2950 \text{ cm}^{-1}$  are assigned to  $\nu(\text{C}-\text{H})$ , at  $1220$  and  $1100 \text{ cm}^{-1}$  to  $\nu(\text{CC})$ , and  $900 - 890 \text{ cm}^{-1}$  to  $\delta(\text{CC})$ .

Table 2. Frequencies of absorption bands of  $\text{COO}^-$  ion and M—O bond for Na, Y and lanthanide capronates [ $\text{cm}^{-1}$ ]

Complex	$\nu_{as}(\text{COO}^-)$	$\nu_s(\text{COO}^-)$	$\nu_{as} - \nu_s$	M—O
NaL	1560	1440	120	
YL <sub>3</sub> · 2H <sub>2</sub> O	1540	1440	100	415
LaL <sub>3</sub> · H <sub>2</sub> O	1530	1440	90	420
CeL <sub>3</sub> · H <sub>2</sub> O	1530	1445	185	425
PrL <sub>3</sub> · H <sub>2</sub> O	1545	1430	115	425
NdL <sub>3</sub> · 2H <sub>2</sub> O	1545	1445	100	420
SmL <sub>3</sub> · 2H <sub>2</sub> O	1545	1445	100	420
EuL <sub>3</sub> · 2H <sub>2</sub> O	1545	1445	100	420
GdL <sub>3</sub> · 2H <sub>2</sub> O	1550	1445	105	420
TbL <sub>3</sub> · 2H <sub>2</sub> O	1545	1445	100	425
DyL <sub>3</sub> · 2H <sub>2</sub> O	1545	1450	95	420
HoL <sub>3</sub> · 2H <sub>2</sub> O	1545	1445	100	420
ErL <sub>3</sub> · 2H <sub>2</sub> O	1545	1440	105	420
TmL <sub>3</sub> · 3H <sub>2</sub> O	1540	1445	195	420
YbL <sub>3</sub> · 3H <sub>2</sub> O	1540	1445	95	420
LuL <sub>3</sub> · 3H <sub>2</sub> O	1545	1440	105	420



The values  $\Delta\nu$  between frequencies due to  $\nu_{as}(\text{COO})$  and  $\nu_s(\text{COO})$  in these complexes are lower than in the sodium salt ( $\Delta\nu = 120 \text{ cm}^{-1}$ ) which indicates a smaller degree of ionic bond in the complexes compared to that of sodium (Table 2). Having a greater ionic potential than sodium ion, lanthanide ions influence the ligand more strongly, causing the greater deformation. In the IR spectra of prepared complexes the bands  $\nu_{as}(\text{COO})$  are shifted insignificantly ( $\Delta\nu = 15\text{--}20 \text{ cm}^{-1}$ ) to lower frequencies and the bands  $\nu_s(\text{COO})$  do not change in comparison with those of sodium salt. On the basis shifts of absorption bands of asymmetric and symmetric vibration of carboxylate group, as well as of  $\Delta\nu$  values the carboxylic ion in the complexes under study is found to be bidentate ligand but probably with incomplete equalization of its bond lengths [6]. The bond metal—ligand has similar character in all lanthanide series.

From the diffractogram analysis of rare earth element capronates were found to be crystalline compounds characterized by low symmetry, large size of unit cells, different structures and small degree of crystallinity (Fig. 1). The complexes of rare earth elements are isostructural in the group: La, Ce and Eu—Lu. The complexes of Pr(III), Nd(III) and Sm(III) are characterized by different structure.

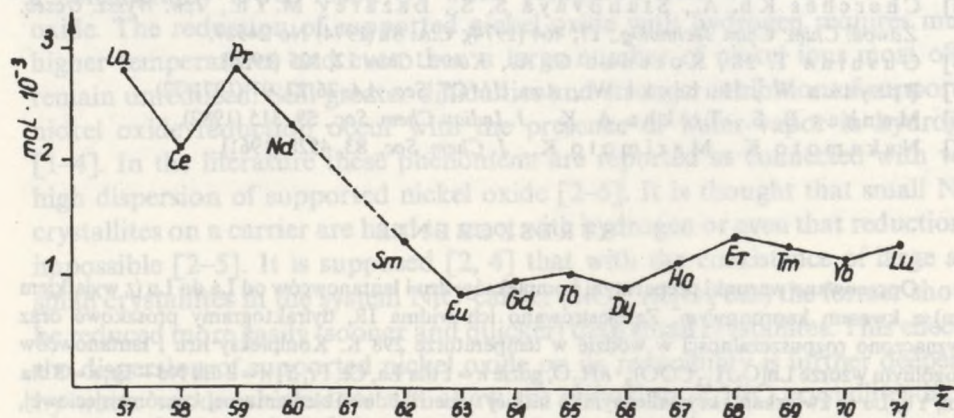


Fig. 2. Relationship between solubilities of rare earth element capronates and  $Z$

The rare earth element capronates are sparingly soluble in water. Their solubilities at 298 K are of the order  $10^{-3}\text{--}10^{-4} \text{ mol} \cdot \text{dm}^{-3}$  and change in the lanthanide series (Fig. 2) with an increase in the atomic number of metal ( $Z$ ). Capronates of light lanthanides (La—Sm) are better soluble than those of heavy lanthanides. The solubility of heavy lanthanide capronates are similar to each other. Solubility of La capronate has the highest value (Table 3).

Table 3. Solubilities of rare earth element capronates in water at 298 K

Complex	Solubility [ $\text{mol} \cdot \text{dm}^{-3} \cdot 10^{-3}$ ]	Complex	Solubility [ $\text{mol} \cdot \text{dm}^{-3} \cdot 10^{-3}$ ]
Y	1.52	Tb	1.00
La	2.82	Dy	0.88
Ce	2.13	Ho	1.10
Pr	2.80	Er	1.33
Nd	2.30	Tm	1.20
Sm	1.29	Yb	1.14
Eu	0.84	Lu	1.23
Gd	0.94		

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## STRESZCZENIE

Opracowano warunki preparatyki kompleksów itru i lantanowców od La do Lu (z wyjątkiem Pm) z kwasem kapronowym. Zarejestrowano ich widma IR, dyfraktogramy proszkowe oraz wyznaczono rozpuszczalności w wodzie w temperaturze 298 K. Kompleksy itru i lantanowców o ogólnym wzorze  $\text{Ln}(\text{C}_5\text{H}_{11}\text{COO})_3 \cdot n\text{H}_2\text{O}$ , gdzie  $n=1$  dla La, Ce, Pr, Y;  $n=2$  dla Nd—Er;  $n=3$  dla Tm, Yb, Lu są związkami krystalicznymi o niskiej symetrii i dużej elementarnej komórce sieciowej, trudno rozpuszczalne w wodzie. Ich rozpuszczalność wynosi  $10^{-3}$ – $10^{-4}$   $\text{mol} \cdot \text{dm}^{-3}$ .