THE COMPLEXES OF NEODYMIUM AND DYSPROSIUM WITH GLUTAMIC ACID

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The interaction of neodymium and dysprosium chlorides with glutamic acid at pH 7 is studied. The complexes are isolated and characterized with X-ray spectroscopy and FTIR. The complexes of neodymium were characterized with elemental and thermal analysis.

Keywords: neodymium, dysprosium, glutamic acid, coordination chemistry

The ability of rare earths for formation complexes with polydentate organic ligands as well as their significant similarity to calcium, which belongs to the biometal group, causes great interest to this field of chemistry. It is well known nowadays that vital significant metals in living organism are included to the coordination complexes. Though not more than 3 % of mass of the human body is the mass of all metals, they are of great significance in the processes proceeding in the organism. All organism presents a harmoniously functioning polymetallic and polyligand system [1].

One can say with certainty that complexes of rare earths with glutamic acid will be widely adopted in very different fields and branches of industry and in the first place in pharmacology as anti-inflammatory [2] and antitumor preparations [2, 3]. They can also be used in radioelectronics as pyroelectric materials [4, 5].

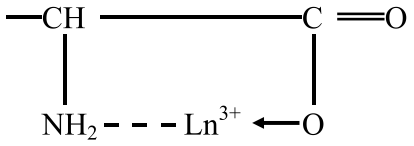

Fig. 1

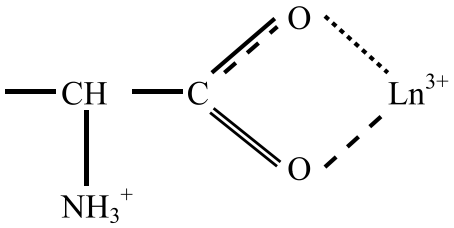

Fig. 2

A whole interest to the complexes of rare earths with glutamic acid was shown about 20 years ago, but the glutamates of rare earths are still studied insufficiently.

Glutamic acid is a low-dentate (potential tridentate) ligand in formation of the coordination compounds with rare earths. The molecule has three donor groups that are amino group and two carboxylic groups. In accordance with its structure glutamic acid can form two different chelate cycles. They are five-membered glycinate cycle and four-membered carboxylic cycle (fig. 1, 2).

In accordance with the Chugaev rule (cycles with five or six links are the most stable) the glycinic cycle is much more stable than the carboxylic one.

The aim of the work was the synthesis and investigation of the coordination complexes of neodymium and dysprosium with glutamic acid.

Materials and methods of research

Glutamic acid, neodymium chloride hexahydrate, dysprosium oxide, 25 % ammonia and concentrated hydrochloric acid were taken as initial substances and used without further purification.

The solution of dysprosium chloride was prepared by dissolution of dysprosium oxide in concentrated hydrochloric acid. Then the solution was softened by steam and diluted with distilled water to volume of 100 ml. The concentration of dysprosium chloride was determined by titration with EDTA.

For the synthesis of the complexes the initial substances were mixed in proportions 1:1, 1:2 and 1:3. The pH value of the solutions was adjusted to 6–8 with ammonia solution.

Thermal analysis was done by means of a derivatograph Q-1500D Paulik-Paulik-Erdey, temperature interval 20–500 °C, heating velocity 10 °C per minute, sample mass 20 mg. After that the sample was heated in electrical oven at 750 °C until its mass became constant.

Results of research and their discussion

The results of physico-chemical analyses of the complexes presented in the Table 1 and Table 2 allow us to make conclusions of chemical pureness of the complexes of neodymium (lacks of stripes of admixtures in X-ray diffraction patterns) and variable hydrate composition and to ascribe definite formulae to them.

Table 1

The results of elemental analysis of the complexes of neodymium with glutamic acid

Sample	Content of Nd, mass %		Formulae of the compounds
	found	calculated	
(1)	33,46	33,31	$Nd(Glu)Cl \cdot 6H_2O$
(2)	23,83	24,01	$Nd(HGlu)_3 \cdot 2H_2O$
(3)	35,02	34,75	$Nd(Glu)Cl \cdot 5H_2O$

Table 2

The results of FTIR analysis of the complexes of neodymium and dysprosium with glutamic acid (s – strong intensity of a peak, m – middle intensity of a peak, w – weak intensity of a peak)

Compound	ν C=O COOH	δ_{COOH}	ν C–O as	ν C–O s	δ^{N-H}	ν^{C-N}	ν^{C-H}, ν^{N-H}, ν^{O-H}
1	2	3	4	5	6	7	8
H_2Glu	1695	1310	1630	1425	1545	1020–1080	2800–2900
The complexes of neodymium							
Compound	ν C=O COOH	δ_{COOH}	ν C–O as	ν C–O s	δ^{N-H}	ν^{C-N}	ν^{C-H}, ν^{N-H}, ν^{O-H}
$Nd(HGlu)_3 \cdot 3H_2O$			1550–1560	1405		1045–1080	2500–3600
$Nd(HGlu)Glu \cdot 5H_2O$			1550–1680	1410		1045–1080	2500–3600
Nd(HGlu)Glu			1550–1660	1410		1045–1080	2950 3100–3400
$Nd(HGlu)_3 \cdot 7H_2O$			1550–1670	1410		1040–1080	2500–3600
$Nd(HGlu)_3$			1570–1660	1420		1045–1080	2900–3300
$Nd(Glu)Cl \cdot 5H_2O$			1554 s	1408 s		1036 m	2782 m 2930 m 3158 s 3354 s
$Nd(HGlu)_3 \cdot 2H_2O$			1556 s	1408 m		1034 m, 1076 m	2404 m 2590 m 2782 m 2926 m 3080 m 3158 m 3384 m
$Nd(Glu)Cl \cdot 6H_2O$			1582 s	1408 m		1076 m	2552 w 2588 w 2738 w 2782 m 2856 m 2926 m 3080 m 3158 m 3386 m
The complexes of dysprosium							
Compound	ν C=O COOH	δ_{COOH}	ν C–O as	ν C–O s	δ^{N-H}	ν^{C-N}	ν^{C-H}, ν^{N-H}, ν^{O-H}
1			1632 m, 1666 m	1406 m			2502 w 2598 w 2624 w 2666 w 2784 m 2856 m 2926 m 2960 m 3050 m 3154 m 3352 m

End of Table 2

1	2	3	4	5	6	7	8
2			1552 m, 1630 m, 1674 m			1040 w, 1080 m	2502 m 2602 m 2624 m 2646 m 2722 m 2814 s 2860 s 3046 s 3142 s 3350 s
3			1552 m, 1584 m, 1628 s			1040 m, 1080 m	2502 s 2600 m 2624 m 2646 m 2806 m 3046 s 3132 s 3354 s

N o t e s : All the complexes isolated are X-ray amorphous.

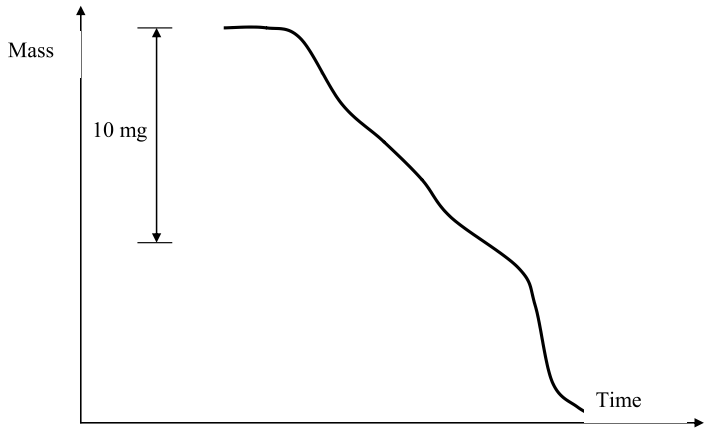

Fig. 3

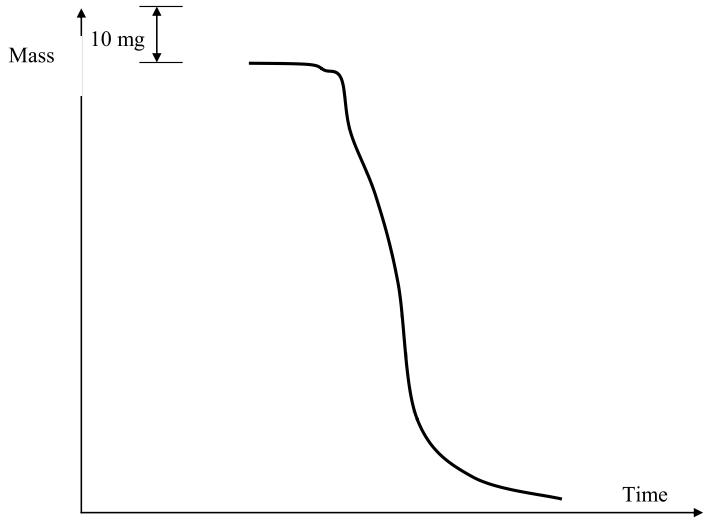

Fig. 4

FTIR spectra of these compounds in the wavenumber region 400–4000 confirm generation of the complexes (lack of stripes belonging to glutamic acid, splitting and displacement of other stripes).

The results of physico-chemical analyses of the complexes of dysprosium allow us to make conclusions of insufficient chemical pureness of the complexes (stripes of ammonium chloride and glutamic acid in X-ray diffraction patterns). The complexes of dysprosium obtained in proportion of the initial substances 1:2 and 1:3 are sticky substances. Hence it can be supposed that they have polymeric structure. The results of thermal analysis of the complexes are presented in the Fig. 3–4 and in the Table 3.

Table 3

Thermal analysis of the complexes of neodymium with glutamic acid

Compound	No. of the dehydration stage	Interval, ºC	Mass decrease, %	Mass decrease in moles of H_2O
$Nd(Glu)Cl \cdot 3H_2O$	1	55–170	8,3	1,8
	2	170–265	5,6	1,2
$Nd(Glu)Glu \cdot 5H_2O$	1	50–175	8,9	2,6
	2	175–260	8,4	2,4
$Nd(HGlu)_3 \cdot 7H_2O$	1	70–170	9,8	3,9
	2	170–220	7,9	3,1
$Nd(Glu)Cl \cdot 5H_2O$	1	80–160	2,5	0,6
	2	160–240	11,0	2,5
	3	240–310	44,5	–
$Nd(HGlu)_3 \cdot 2H_2O$	1	80–130	1,2	0,2
	2	130–380	3,5	0,7
	3	380–470	1,7	0,3

It can be said in conclusion that in spite of difficulties, which the studying such complexes cause, nowadays, when we have real possibilities for studying them, it is quite possible to reach significant success and clearness in studying many vital significant processes. Such complexes are of great importance in processes proceeding in biological systems.

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