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THERMIC STUDIES OF THE RARE EARTH ELEMENT COORDINATION COMPOUNDS WITH THIOSEMICARBAZIDEDIACETIC ACID

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ABSTRACT

The thermogravimetric investigation of rare earth elements coordination compounds with tetradentate tripod ligand, containing N,O,O,N donor atoms - thiosemicarbazidediacetic acid (H_2L) of the composition $Na[LnL_2]\cdot 3H_2O$ ahd $LnLX\cdot 4H_2O$. The thermic decomposition of complexes proceeds in two stages: at 40-130°C proceeds their one step dehydratation and at 185-250°C takes place exothermic destruction of complexes.

INTRODUCTION

Thiosemicarbazidediacetic acid $H_2N-C(S)-NH-N(CH_2COOH)_2$ (H_2L) concerns to polydentate polyfunctional ligands of complexon type. Combination of carboxilic ahd thiosemicarbazidic branches communicates to H_2L the properties of carboxilate and thiosemicarbazide ligands. Having the possibility to use for coordination sulphur atom, amine group nitrogen and the hydrazine rest nitrogen atoms and the oxigen atom of carboxilic groups and being extremly flexible ligand H_2L gives complexes with a majority of periodic system of elements. H_2L forms with rare earth elements some types of coordination compounds of the composition $Na[LnL_2]\cdot 3H_2O$ (I) and $LnLX\cdot 4H_2O$ (II), where Ln = La, Pr, Nd, Sm, Eu, Gd, Ho, Er; X = Cl, Br, OH in which H_2L is coordinated as tetradentate N,O,O,N - ligand [1-3].

RESULTS AND DISCUSSION

By TG and DTA methods it was established the compounds of type II to be characterised with lowtemperature (~40-130°C) endothermic effects, which proceed in one stage independently from the heating rate and exothermic in the region 185-250°C (Fig) The dehydratation process proceeds by mean of solid phase of variable composition formation without a structural recombination of

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solid complexes. The maximal development of the dehydratation process proceeds at ~90°C. A complete dehydratation is reached only at 200–240°C, i.e. before the intense development of exothermic effect of the complex destruction.

Table. The results of thermic analysis of the rare earth element with H_2L

Element	Dehydratation stage			Exothermic decomposition stage	
	temper. interval, t, °C	t of DTA, C	t of complete dehydratation	temper. interval t°, C	t of DTA pear, °C
			$LnLCl \cdot 4H_2O$		
La	35–170	90	170	205–245	227
Ce	30–160	93	160	197–240	223
Pr	32–160	97	207	200–240	222
Nd	45–122	92	210	195–240	222
Sm	45–122	87	200	195–240	222
Eu	45–132	95	210	200–240	227
Gd	45–120	85	200	205–245	227
Ho	35–160	93	160	200–245	225
Er	45–135	92	180	200–255	228
			$LnLOH \cdot 4H_2O$		
La	40–135	95	203	175–225	203
Pr	45–130	105	225	175–225	205
Nd	35–150	90	150	185–237	217
Sm	45–130	95	210	175–230	210
Eu	35–120	90	215	190–300	245
Gd	30–140	90	200	185–235	212
Ho	45–130	92	240	180–230	210
Er	45–117	87	212	155–240	212
Y	45–135	93	200	160–240	220

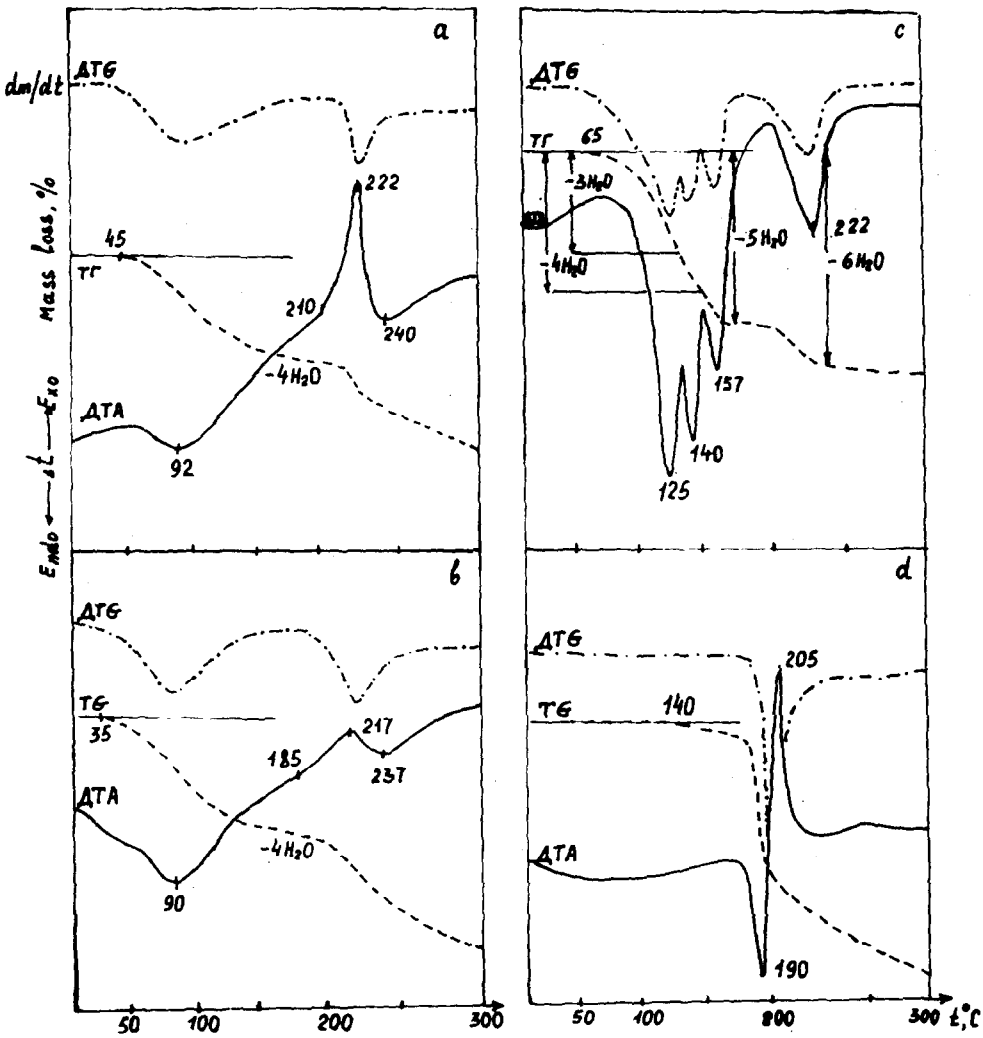

Fig. The curves of thermic analysis

a - $NdLCl \cdot 4H_2O$

b - $NdCl \cdot 6H_2O$

c - $NdLOH \cdot 4H_2O$

d - H_2L

The thermogramms of studied complexes differ from the thermogrammes of the initial compounds - rare earth salts and thiosemicarbazidediacetic acid (Fig.). The latter on heating melting at 180-185°C with decomposition, while the coordination compound is distructed at a higher temperature with exothermic peak at 220-225°C. Exothermic decomposition of hydroxocomplexes proceeds at some lower temperature (~ 180°C), than of chlorocomplexes (~ 200°C) and is less intensive. Introduction of hydroxile in the complex instead of Cl-ion lowers the distruction temperature of the comlex. On changing of Cl-ion for Br-ion the character of decomposition and the temperature intervals of the thermic transformations don't change. A temperature dehydratation and the further thermolysis don't depend on the ordinal number of rare earth element.

CONCLUSIONS

The thermic decomposition of crystallohydrates has a stepped character and encludes the followings stages: monostepped dehydration and the thermic decomposition of the complex coordination sphere. The dehydratation proceeds in a wide of temperature interval (from ~ 40 to 210°C and nigher) (see table). Elimination of last portions of water involves the decomposition of complex compound with elimination of the ligand and subsequent its de - sintegration.

The thermic stability of compound was studied on the derivatograph of Paulic-Paulic-Erday system to 300°C in the air atmosphere.

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