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## ACETAMIDE COMPLEXES FOR CHLORIDES AND BROMIDES OF SOME LANTHANIDES: SYNTHESIS AND PROPERTIES\*

**L.Yu. Alikberova<sup>1,@</sup>, D.V. Al'bov<sup>2</sup>, P.S. Kibal'nikov<sup>1</sup>, M.I. Vergeles<sup>1</sup>,  
G.A. Fedorova<sup>1</sup>, E.V. Volchkova<sup>1</sup>**

<sup>1</sup> Moscow Technological University (Institute of Fine Chemical Technologies), Moscow, 119571 Russia

<sup>2</sup> Lomonosov Moscow State University, Moscow, 119234 Russia

@Corresponding author e-mail: alikberovalyu@mail.ru

*The aim of the this work is the synthesis and study (IR, single crystal XRD, DTG) of complex compounds of chlorides and bromides of lanthanum, neodymium, holmium, and erbium with acetamide,  $[Ln(AA)_4(H_2O)_4]Cl_3 \cdot H_2O$  ( $Ln = La, Nd, Ho, Er$ ) and  $[La(AA)_4(H_2O)_4]Br_3 \cdot H_2O$ . Ligands ( $Ln$ ) coordination occurs through the oxygen atoms, and the coordination polyhedra of the  $Ln$  atoms are distorted tetragonal antiprisms or two-capped trigonal prisms ( $CN = 8$ ). All the studied complexes are characterized by a developed system of hydrogen bonds with the bromide or chloride ions (and outer-sphere water molecules) in the cavities of the structure formed by the complex cations. The features of the complexes thermal decomposition are discussed.*

**Keywords:** lanthanum, neodymium, holmium, erbium, chloride, bromide, acetamide, complexes, structure.

Oxygen-containing amide compounds are known for the ability to form numerous hydrogen bonds combining their molecules into supramolecular assemblies, structures of tunnel or clathrate type. In some cases such features are also typical of complexes of amide compounds with various salts. That is why such objects draw the attention of many researchers. In particular, complex derivatives of one of the simplest amides, acetamide  $CH_3CONH_2$  (AA), which is in most cases coordinated by the atoms of *s*-, *p*- or *d*-elements via the oxygen atom [1] are actively studied, though there are examples of coordination via the nitrogen atom of the amide group [2].

So far, the interaction of REE salts with AA was studied insufficiently. Thus, there are data on compounds  $Ce(CH_3COO)_3 \cdot 3AA \cdot H_2O$  [3],  $LaCl_3 \cdot 5AA \cdot 5H_2O$  [4] and  $YCl_3 \cdot 4AA \cdot 5H_2O$  [5]. However, their structures were not studied. Complex compounds of REE iodides of composition  $[Ln(AA)_4(H_2O)_4]I_3$  ( $Ln=La, Gd, Er$  [6],  $Nd, Eu, Dy, Ho, Y$  [7] and  $Ce, Pr, Sm, Tb, Tm, Yb, Lu$  [8]) were isolated. According to X-ray analysis these compounds have the same type of structure. It includes complex cations  $[Ln(AA)_4(H_2O)_4]^{3+}$  (coordination number 8, the coordination polyhedron is a distorted square antiprism) and outer-sphere iodide ions. Analysis of the stereochemical characteristics of the cations allowed the authors [8] to conclude that the metal–ligand (AA) bond is highly ionic. They used the criteria suggested in [9, 10].

It was found that erbium and lutetium bromides react with acetamide to form complexes of composition  $[\text{Ln}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Cl}_3$  [11] similar to derivatives of REE iodides in composition and structure. In case of acetamide complex compounds of neodymium bromide, samarium bromide and samarium chloride there is an additional outer-sphere molecule of water in the crystal structure:  $[\text{Nd}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Br}_3 \cdot \text{H}_2\text{O}$ ,  $[\text{Sm}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Br}_3 \cdot \text{H}_2\text{O}$  and  $[\text{Sm}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$  [12, 13]. The form of the coordination polyhedrons is transitional between the tetragonal antiprism and dodecahedron, the coordination number is 8. We also synthesized and studied an yttrium chloride complex of composition  $[\text{Y}(\text{AA})_5(\text{H}_2\text{O})_2]\text{Cl}_3$  [14]. It was found that the chloride ions are not a part of the internal sphere of the complex, and the coordination of acetamide in the complex cation occurs via the oxygen atoms. The coordination polyhedron is a distorted pentagonal bipyramid (the coordination number is 7). There are no data in the literature on complex compounds of other chlorides and REE bromides with acetamide. The purpose of this work is to synthesize and study the structure of acetamide complexes of lanthanum chloride and bromide, neodymium, holmium and erbium chlorides.

## Experimental

In order to obtain complex compounds of lanthanum chloride and bromide, neodymium, holmium and erbium chlorides we used chemically pure acetamide  $\text{CH}_3\text{CONH}_2$ .  $\text{LaBr}_3 \cdot 7\text{H}_2\text{O}$  and  $\text{LnCl}_3 \cdot 7\text{H}_2\text{O}$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Ho}, \text{Er}$ ) were synthesized from the corresponding lanthanide oxides or carbonates (technic specifications 6-09-4770-79) using the reaction with  $\text{HBr}$  (analytical grade) or with  $\text{HCl}$  (chemically pure) taken in 35–40% surplus. The obtained solutions of halogenides were evaporated upon heating until crystals started forming. Then the solutions were cooled. The crystals were separated from the filtrate by vacuum filtration on a porous glass filter and kept in a dessicator over potassium hydroxide to attain a constant weight.

The synthesis of the acetamide complex compounds was carried out by mixing lanthanide halogenides heptahydrates and acetamide in molar ratios 1:4 and 1:6. Several drops of water were added to homogenize the solution. After 2–3 weeks crystals precipitated from the obtained transparent solutions. The shape of the crystals conforms to a combination of a prism and a pinacoid: colourless (La), lilac (Nd), pink (Er) or light yellow (Ho). The crystals are hygroscopic and deliquesce in moist air. However, longtime keeping in a dessicator over phosphorus(V) oxide results in the loss of a part of water.

The content of the metals in crystallohydrates of the corresponding halogenides was checked by the trilonometric method [15]. The content of nitrogen, carbon and hydrogen was determined with the use of an elemental analyzer CHNS Flash EA1112 made by Thermo Finnigan (Italy). The measurement error was 0.2–0.3% for C, H, N. The composition of the

compounds obtained at both ratios of the initial reagents turned out to be identical, the molar ratio of  $\text{LnX}_3 : \text{AA}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) is 1: 4.

The obtained compounds conform to the formulas given in Table 1, namely:  $[\text{La}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$  (**I**),  $[\text{Nd}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$  (**II**),  $[\text{Ho}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$  (**III**),  $[\text{Er}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$  (**IV**),  $[\text{La}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Br}_3 \cdot \text{H}_2\text{O}$  (**V**).

**Table 1.** Results of chemical analysis of  $[\text{La}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$  (**I**),  $[\text{Nd}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$  (**II**),  $[\text{Ho}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$  (**III**),  $[\text{Er}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$  (**IV**) and  $[\text{La}(\text{AA})_4(\text{H}_2\text{O})_4]\text{Br}_3 \cdot \text{H}_2\text{O}$  (**V**)

Compound	Empiric formula	Molar weight	$w_i(\text{calculated})\% / w_i(\text{experimental})\%$			
			C	H	N	Ln
<b>I</b>	$\text{C}_8\text{H}_{30}\text{Cl}_3\text{LaN}_4\text{O}_9$	571.62	<u>16.80</u>	<u>5.25</u>	<u>9.80</u>	<u>24.31</u>
			18.0	4.70	10.2	24.3
<b>II</b>	$\text{C}_8\text{H}_{30}\text{Cl}_3\text{NdN}_4\text{O}_9$	576.95	<u>16.65</u>	<u>5.20</u>	<u>9.71</u>	<u>25.01</u>
			17.1	5.18	10.0	24.2
<b>III</b>	$\text{C}_8\text{H}_{30}\text{Cl}_3\text{HoN}_4\text{O}_9$	597.64	<u>16.07</u>	<u>5.02</u>	<u>9.38</u>	<u>27.67</u>
			16.3	4.98	9.62	27.2
<b>IV</b>	$\text{C}_8\text{H}_{30}\text{Cl}_3\text{ErN}_4\text{O}_9$	599.97	<u>16.01</u>	<u>5.00</u>	<u>9.34</u>	<u>27.89</u>
			15.7	4.80	9.76	28.1
<b>V</b>	$\text{C}_8\text{H}_{30}\text{Br}_3\text{LaN}_4\text{O}_9$	705.00	<u>13.62</u>	<u>4.26</u>	<u>7.95</u>	<u>19.71</u>
			14.4	3.48	8.30	19.5

The deviations in the content of Ln, N, C, H, are probably caused by the high hygroscopicity of the substances.

The IR spectra of the synthesized complexes were recorded with the use of an EQUINOX 55 IR Fourier spectrometer, "Bruker" (Germany).

Experimental intensities of diffraction reflections were obtained at room temperature with the use of a CAD-4 diffractometer [16],  $\text{AgK}_\alpha$ - ( $\lambda=0.56087 \text{ \AA}$ ) or  $\text{MoK}_\alpha$ - radiation ( $\lambda=0.71072 \text{ \AA}$ ), graphite monochromator,  $\omega/\theta$  scanning. The unit cell parameters were determined and refined with the use of 25 reflections in the range of angles  $\theta = 11^\circ - 12^\circ$ . Error correction taking into account absorption was made by the method of  $\Psi$ -scanning of individual reflections.

Preprocessing of the experimental data array was carried out with the use of WinGX software system [17]. All subsequent calculations were carried out within SHELX97 software system [18]. The crystal structure was determined by direct methods followed by refinement of positional and thermal parameters at anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms in acetamide molecules were entered into the calculated positions and included in the refinement by “rider's” method. We did not succeed in finding the hydrogen atoms of water from residual electronic density. Their correct calculation is impossible. All subsequent calculations were carried out with the use of SHELXTL PLUS 5.0 program [19]. The structures of the compounds were visualized by means of Mercury program [20]. Crystallographic characteristics are presented in Table 2.

**Table 2.** Crystallographic characteristics, details of the X-ray diffraction experiment and refinement of the structure of complexes **I–V**

Parameter	Value				
	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>	<b>V</b>
Empiric formula	C <sub>8</sub> H <sub>30</sub> Cl <sub>3</sub> LaN <sub>4</sub> O <sub>9</sub> '	C <sub>8</sub> H <sub>30</sub> Cl <sub>3</sub> N <sub>4</sub> NdO <sub>9</sub> '	C <sub>8</sub> H <sub>30</sub> Cl <sub>3</sub> HoN <sub>4</sub> O <sub>9</sub>	C <sub>8</sub> H <sub>30</sub> Cl <sub>3</sub> ErN <sub>4</sub> O <sub>9</sub>	C <sub>8</sub> H <sub>30</sub> Br <sub>3</sub> LaN <sub>4</sub> O <sub>9</sub> '
Molar weight.	571.62	576.95	597.64	599.97	705.00
Crystallographic system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> /n	<i>P</i> 2 <sub>1</sub> /n	<i>P</i> 2 <sub>1</sub> /n	<i>P</i> 2 <sub>1</sub> /n	<i>P</i> 2 <sub>1</sub> /n
<i>a</i> , Å	10.398(3)	10.3241(18)	10.2136(3)	10.2052(5)	10.582(2)
<i>b</i> , Å	14.597(5)	14.5674(17)	14.5671(4)	14.5671(5)	15.086(4)
<i>c</i> , Å	15.328(5)	15.2525(19)	15.1730(6)	15.1460(8)	15.595(4)
$\alpha$ , °deg.	90	90	90	90	90
$\beta$ , deg.	99.86(3)	99.636(12)	99.242(3)	99.171(4)	99.31(3)
$\gamma$ , deg.	90	90	90	90	90
<i>V</i> , Å <sup>3</sup>	2292.0(12)	2261.5(6)	2228.17(13)	2222.82(18)	2456.7(11)
<i>T</i> , K	293(2)	293(2)	293(2)	293(2)	293(2)
<i>Z</i>	4	4	4	4	4
<i>P</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.657	1.695	1.782	1.793	1.906
Radiation	AgK $\alpha$	AgK $\alpha$	MoK $\alpha$	MoK $\alpha$	AgK $\alpha$
$\mu(K\alpha)$ , mm <sup>-1</sup>	1.187	1.424	3.952	4.178	3.554

Range of angles $\theta$ , deg.	1.531–21.968	1.536–20.969	3.901–30.709	3.903–30.673	1.492–19.976
Range of indexes $h, k, l$	$-13 \leq h \leq 13$ ; $-17 \leq k \leq 19$ ; $-18 \leq l \leq 20$	$-13 \leq h \leq 12$ ; $0 \leq k \leq 18$ ; $0 \leq l \leq 19$	$-12 \leq h \leq 14$ ; $-13 \leq k \leq 20$ ; $-21 \leq l \leq 21$	$-14 \leq h \leq 5$ ; $-20 \leq k \leq 20$ ; $-8 \leq l \leq 21$	$-12 \leq h \leq 12$ ; $-18 \leq k \leq 18$ ; $0 \leq l \leq 18$
Dimensions of crystal, mm	0.30×0.30×0.30	0.30×0.30×0.30	0.25×0.22×0.20	0.21×0.19×0.17	0.30×0.30×0.30
Experiment size	5692	4908	6794	6634	4649
The number of independent reflections	4807	4137	4234	3812	3807
The number of reflections with $I \geq 2\sigma(I)$	4807	4137	4234	3812	3807
The number of reflections in the least square method /the number of refined parameters	5692/271	4908/271	6794/271	6634/271	4649/261
GooF	1.075	1.068	0.817	0.800	1.024
$R$ -factor [ $I \geq 2\sigma(I)$ ] $R_1/wR_2$	0.0452/0.0362	0.0428/0.0325	0.0715/0.0413	0.0898/0.0488	0.0464/0.0339
$\Delta\rho_{\max}/\Delta\rho_{\min}$ , $e/\text{\AA}^3$	1.305/–1.163	1.149/–1.205	3.796/–2.926	3.676/–3.319	1.172/–0.699

DTA curves were recorded with the use of a Q-D1500 derivatograph in the range of temperatures 20–500 °C at heating rate about 5 °C/min. Decomposition of the compounds starts at 62–85 °C and proceeds in several stages difficult to divide. Finally it results in the formation of amorphous mixtures of oxides and oxohalides of corresponding lanthanides.

## Results and Discussion

It can be seen from the presented data that complexes **I–V** synthesized by us for the first time are generally similar to the previously studied acetamide complexes of halides of other lanthanides of similar composition.

The IR spectra of the studied complexes **I–V** generally turned out to be of the same type (Table 3).

The nature of the IR spectra allows drawing preliminary conclusions on the type of the ligand coordination. Thus, it is possible to explain the shift of the absorption bands at 1606 and 1672  $\text{cm}^{-1}$  including the valence vibrations of the CO bonds and the deformation vibrations of the  $\text{NH}_2$  bonds towards the lower frequencies (1597–1600 and 1652–1661  $\text{cm}^{-1}$ , respectively) by weakening of the CO bond resulting from the formation of the bond of the ligand with the metal via the oxygen atom [1, 6].

Therefore, it can be concluded that acetamide is coordinated by REE atoms via the oxygen atom of the carbonyl group.

**Table 3.** Frequencies ( $\text{cm}^{-1}$ ) of the main absorption bands in the IR spectra of acetamide AA and complex compounds **I–V**

AA	I	II	III	IV	V	Assignment of the main absorption bands
1048	1048	1048	1048	1048	1048	$\nu_s(\text{CN})$
1150	1148	1150	1138	1142	1138	$\rho(\text{NH}_2)$
1396	1399	1401	1401	1397	1401	$\nu(\text{CN})$
1450	1471	1469	1468	1466	1468	$\delta(\text{CH}_3)$
1606	1600	1605	1600	1597	1600	$\delta(\text{NH}_2) + \nu(\text{CO})$
1672	1659	1661	1657	1652	1657	$\nu(\text{CO}) + \delta(\text{NH}_2) + \delta(\text{HOH})$
2820	2786 2851 2920	2798 2923	2778	2787 2853 2924	2778	$\nu(\text{CH})$
3202 3374	3211 3351	3209 3351	3193 3355	3212 3366	3193 3355	$\nu(\text{OH}) + \nu(\text{NH})$

X-Ray structural analysis of the crystals showed that there are complex cations  $[\text{Ln}(\text{H}_2\text{O})_4(\text{AA})_4]^{3+}$  in the structure of **I–V**. The coordination number is 8 (Figures 1 and 2). Acetamide is coordinated via the oxygen atom. The halide ions are not included in the sphere of the complex and are kept in the structure by hydrogen bonds. In addition, the crystals contain an outer-sphere molecule of water.

It is known [21] that the square anti-prism, the two-cap trigonal prism and the dodecahedron are most stable among all the possible polyhedrons for a complex of composition

[M(monodentate ligand A)<sub>4</sub>(monodentate ligand B)<sub>4</sub>]. In order to determine the shape of the coordination polyhedron it is possible to use the known criterion [22] based on the measurement of dihedral angles between the hedra which are crossed at edges of *b* type. The  $\delta$ -criterion allows establishing the formation of a dodecahedron, square anti-prism or trigonal prism with two additional vertices over the centers of two rectangular hedra. In a dodecahedron, 4 edges meet at vertices of *A* type, and 5 edges, at vertices of *B* type. Edges *b* connect vertices of *B* type. The corresponding angles between the hedra in ideal polyhedrons should have the values presented in Table 4.

**Table 4.** The values of angles  $\delta$  (deg.) in ideal polyhedrons

Polyhedron type	$\delta_1$	$\delta_2$	$\delta_3$	$\delta_4$
Ideal dodecahedron	29.5	29.5	29.5	29.5
Trigonal prism	0	21.7	48.2	48.2
Antiprism	0	0	52.5	52.5

The measured values of dihedral angles for complexes **I–V** studied by us presented in Table 5 indicate the complex shape of the coordination polyhedrons: it is intermediate between the dodecahedron and the two-cap trigonal prism.

**Table 5.** The values of angles  $\delta$  (deg.) in the studied polyhedrons

Compound	$\delta_1$	$\delta_2$	$\delta_3$	$\delta_4$
[La(AA) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O ( <b>I</b> )	18.75	23.39	42.17	44.16
[Nd(AA) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O ( <b>II</b> )	18.27	21.93	43.10	44.16
[Ho(AA) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O ( <b>III</b> )	17,95.	24.56	35.41	38.45
[Er(AA) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O ( <b>IV</b> )	22.13	25.98	34.84	35.77
[La(AA) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]Br <sub>3</sub> ·H <sub>2</sub> O ( <b>V</b> )	22.69	27.05	39.00	41.50

The structural characteristics of the complex cation can be used to evaluate the nature of the metal-acetamide chemical bond [9, 10]. Thus, in case of a purely covalent bond the overlap of electronic clouds between the metal and the  $sp^2$ -hybridized orbitals of oxygen is optimal, angle M–O–C is close to 120°, and the metal cation belongs to the plane of the amide ligand.

(The methyl group of acetamide is not considered.) If the bond is purely ionic, the optimal interaction corresponds to the metal atom position on the vector of the dipole moment of the ligand, when the value of angle M–O–C is 154°, and the distance between the metal and oxygen atoms of close to 2.50 Å. Comparing the results of determination of angles Ln–O–C in the structures of the acetamide complexes of lanthanide iodides with these extreme values for M–O–C, the authors of [8] conclude that the lanthanide-acetamide chemical bond in complex cations  $[\text{Ln}(\text{AA})_4(\text{H}_2\text{O})_4]^{3+}$  is mostly ionic.

Analyzing the data on the Ln–O bond lengths (Table 6) and the Ln–O–C angle values (Table 7) for complexes **I–V** studied by us we concluded that these objects of study can be considered too by means of the above criteria.

**Table 6.** The values of some bond lengths  $d$ , Å for complexes **I–V**

Bond	Value, Å				
	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>	<b>V</b>
Ln(1) – O(1)	2.53(8)	2.46(2)	2.31(8)	2.30(3)	2.518(4)
Ln(1) – O(2)	2.50(4)	2.46(3)	2.32(2)	2.31(6)	2.504(4)
Ln(1) – O(3)	2.51(8)	2.49(2)	2.34(1)	2.33(3)	2.519(4)
Ln(1) – O(4)	2.51(4)	2.43(3)	2.32(2)	2.31(8)	2.507(3)
Ln(1) – O(5)	2.44(1)	2.40(2)	2.36(9)	2.35(5)	2.440(3)
Ln(1) – O(6)	2.46(1)	2.40(2)	2.35(8)	2.35(1)	2.447(3)
Ln(1) – O(7)	2.44(3)	2.38(2)	2.37(1)	2.35(9)	2.455(4)
Ln(1) – O(8)	2.43(4)	2.37(2)	2.35(6)	2.34(5)	2.437(4)
N(5) – C(51)	1.29(9)	1.33(9)	1.30(2)	1.28(6)	1.309(7)
C(51) – C(52)	1.48(1)	1.35(8)	1.49(4)	1.54(4)	1.466(8)
N(6) – C(61)	1.30(4)	1.32(2)	1.30(6)	1.32(4)	1.308(6)
C(61) – C(62)	1.48(3)	1.38(5)	1.50(2)	1.50(1)	1.463(8)
N(7) – C(71)	1.29(8)	1.25(5)	1.31(1)	1.30(9)	1.292(6)
C(71) – C(72)	1.49(1)	1.480	1.47(2)	1.47(1)	1.483(7)
N(8) – C(81)	1.30(6)	1.28(2)	1.31(5)	1.32(3)	1.292(7)
C(81) – C(82)	1.48(7)	1.50(9)	1.49(1)	1.46(8)	1.503(8)



**Table 7.** Bond angles  $\omega$  (deg.) in the structure of complexes **I–V**

Angle	Value (deg.)				
	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>	<b>V</b>
Ln(1) – O(5) – C(51)	154.5(3)	156.3(4)	169.5(4)	168.9(1)	156.0(9)
Ln(1) – O(6) – C(61)	155.1(7)	150.4(8)	156.1(1)	156.2(1)	158.0(9)
Ln(1) – O(7) – C(71)	155.5(3)	174.7(1)	155.5(1)	155.2(7)	156.3(6)
Ln(1) – O(8) – C(81)	173.3(2)	154.7(9)	154.6(7)	153.9(8)	170.1(8)

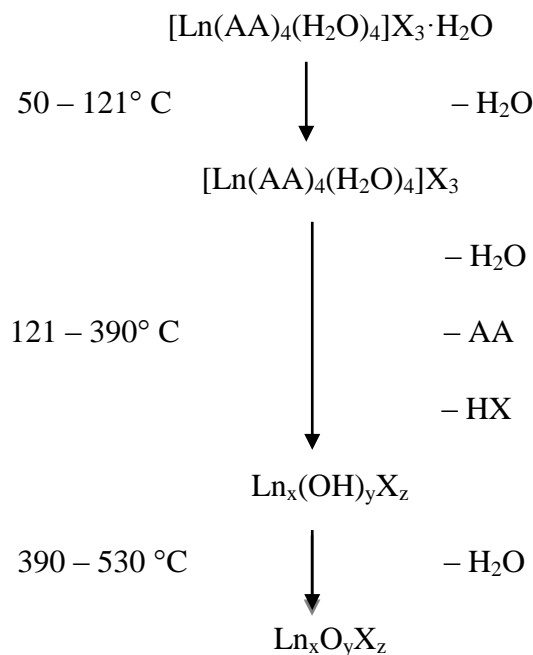
It was found that angles Ln–O–C in complexes **I–V** take values from 154° to 173° (Table 7). Obviously, the metal ligand bond in the compounds synthesized by us, as well as in complex [Ln(AA)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]<sub>3</sub> [7, 8], is to a great extent ionic.

Thus, the acetamide complexes of lanthanum, neodymium, holmium and erbium chlorides and bromides are very similar to the analogous complexes of iodides of these elements, but differ in the existence of an additional outer-sphere molecule of water. It is not impossible that this is caused by the sterical factor (the smaller sizes of the chloride and bromide ions as compared to the iodide ion).

Compounds **I–V** are characterized by a large number of hydrogen bonds in the structure, the length of which is 2.10–2.66 Å.

Thermal decomposition of the compounds starts at 62–85°C and occurs in several stages difficult to divide. According to the results of studying the decomposition of the compounds upon heating we concluded that water is gradually eliminated (first from the outer sphere, then from the inner sphere) with simultaneous elimination of AA followed by its decomposition. Obviously, this process is followed by high-temperature hydrolysis resulting in hydrogen chloride (or hydrogen bromide) elimination and formation of the main salt. Subsequent heating results in the elimination of constitutional water and transformation of hydroxy derivatives into oxo derivatives. Finally, amorphous mixtures of oxides and oxochlorides (oxobromides) of the corresponding lanthanides are formed at 500 – 520 °C.

Thus, we can suggest a general scheme of the decomposition of the studied acetamide complexes of REE chlorides and bromides.



The thermogravimetric data confirm the existence of outer-sphere water weakly bonded in the crystalline structure of the complex compounds.

## Conclusions

Five previously undescribed complex compounds of REE were synthesized and studied, their compositions and structures were established. The existence of an additional outer-sphere molecule of water in the crystals was found. Specific features of the structure of the crystalline acetamide derivatives of rare-earth halides and the nature of their thermal decomposition were discussed.

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