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Complexes of Lanthanum, Gadolinium, and Erbium Iodides with Acetamide: Synthesis and Structure

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Abstract—New acetamide complexes of lanthanum, gadolinium, and erbium iodides of the composition $LnI_3 \cdot 4AA \cdot 4H_2O$ (Ln = La, Gd, Er; AA = CH_3CONH_2) are synthesized and studied. The synthesized complexes are characterized by the data of chemical analysis and IR spectroscopy and are studied by X-ray diffraction analysis. The coordination of the ligands (water and acetamide molecules) by the lanthanum, gadolinium, or erbium atom occurs through the oxygen atoms. The coordination polyhedron of the Ln atom is a distorted square antiprism. The iodide ions are not coordinated and exist in the external sphere.

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INTRODUCTION

Acetamide CH_3CONH_2 (**AA**), as well as carbamide $CO(NH_2)_2$, serves as an ambidentate ligand in complexes and can be coordinated by the complexing atom both through the oxygen atom of the carbonyl group and the nitrogen atom of the NH_2 group. The ability to the formation of a hydrogen bond system is less pronounced in acetamide than in carbamide [1]. However, the crystalline acetamide complexes with salts containing high-charged cations can serve as model systems of the supramolecular type.

Amide compounds of lanthanides (**Ln**) (particularly, those of erbium and gadolinium) are promising as catalysts in organic synthesis, in medicine (as contrast materials in X-ray diagnostics), and in the production of various additives (burning out neutron absorbers based on the erbium and gadolinium compounds, plasticizers, and pore-forming agents) introduced into the nuclear fuel composition [2].

Complexes of Ln salts with acetamide are difficultly formed and, hence, poorly studied. Data are available on the acetamide complexes of some lanthanide chlorides and acetates containing also water ligands, probably, supplementing the internal coordination sphere of the central Ln atom [3, 4]. Note that the acetate ones in addition to acetamide and water can evidently act as ligands in the cerium acetate complex $Ce(CH_3COO)_3 \cdot 3AA \cdot H_2O$. Since the chloride ions are less prone to be coordinated by lanthanide atom than the acetate ions, the coordination environment of the central lanthanum atom in the $LaCl_3 \cdot 5AA \cdot 5H_2O$ complex requires the higher (than in the case of acetates) number of the acetamide ligands and water molecules.

Published data on the composition and structure of the acetamide complexes of lanthanide iodides are lacking. The purpose of the present work is to synthesize and characterize new acetamide complexes of lanthanum, gadolinium, and erbium iodides.

EXPERIMENTAL

The starting substances for the synthesis were acetamide (reagent grade) and lanthanum, gadolinium, or erbium iodide nonahydrates of the composition $LnI_3 \cdot 9H_2O$ (Ln = La, Gd, Er) prepared by the reaction of oxides or carbonates of the corresponding lanthanides with hydroiodic acid, which was preliminarily purified from an iodine admixture according to a described procedure [5].

Synthesis of complexes $LnI_3 \cdot 4AA \cdot 4H_2O$ (Ln = La (I), Cd (II), Er (III); AA = CH_3CONH_2). Acetamide and $LnI_3 \cdot 9H_2O$ were mixed in specified molar ratios (6 : 1. 8 : 1, and 10 : 1, respectively) and without water addition. Several drops of concentrated hydroiodic acid were added to the reaction mixture to prevent the precipitation of the basic salts due to hydrolysis. The interaction of the crystalline reactants leads to the dissolution of the mixture in water, which is partially displaced from the internal coordination sphere of the lanthanide aquacomplexes by the acetamide molecules. In the case of the 10 : 1 molar ratio of the reactants, a transparent viscous yellow solution is formed. The solution was stored for 4–6 weeks in a desiccator over phosphorus(V) oxide to precipitate prismatic (La, Gd) or yellow plate-like (Er) rather hygroscopic crystals (become blurred in air). At molar ratios of 6 : 1 and 8 : 1, the crystalline complexes were also isolated in the absence of

Table 1. Frequencies of the maxima of selected absorption bands (cm^{-1}) in the IR spectra of acetamide and compounds **I–III**

Acetamide	$LnI_3 \cdot 4AA \cdot 4H_2O$			Assignment of bands
	I (La)	**II** (Gd)	**III** (Er)	
1048	1047	1046	1046	$\nu_s(CN)$
1150	1115	1116	1115	$\rho(NH_2)$
1398	1392	1393	1391	$\nu(CN)$
1458 w	1469	1465	1470	$\delta(CH_3)$
1606	1589	1590	1586	$\delta(NH_2) + \nu(CO)$
1631	1649	1638	1636	$\delta(NH_2)$
1677 w	1656	1654	1653	$\nu(CO) + \delta(NH_2) + \delta(HOH)$
2819	2853 w	2852	2852	$\nu(CH)$
	2920	2920	2919	
3168	3169	3187	3171	
3354	3321	3302	3312	$\nu(OH) + \nu(NH)$
	3419	3420	3394	

drying agents. This difference in the properties of the reaction mixture during the synthesis can be due to the affinity of acetamide to form oversaturated solutions, which exerts a strong effect in the case of its excess in solutions.

The composition of the synthesized complexes at all used molar ratios of the reactants corresponds to the formula $LnI_3 \cdot 4AA \cdot 4H_2O$.

For $LaI_3 \cdot 4AA \cdot 4H_2O$ (**I**)

anal. calcd, %: La, 16.78; I, 45.98.

Found, %: La, 16.26; I, 45.34.

For $GdI_3 \cdot 4AA \cdot 4H_2O$ (**II**)

anal. calcd, %: Gd, 18.58; I, 44.98.

Found, %: Gd, 18.24; I, 44.54.

For $ErI_3 \cdot 4AA \cdot 4H_2O$ (**III**)

anal. calcd, %: Er, 19.53; I, 44.46;

Found, %: Er, 19.21; I, 44.23.

In complexes **I–III**, the Ln : I ratio is 1 : 3.05, 1 : 3.02, and 1 : 3.03, and the melting point is 99.0, 110.4, and 99.5°C (visual polythermal method, PTP instrument), respectively.

The results of the IR spectroscopic study of complexes **I–III** (EQUINOX 55 FT-IR spectrometer, Bruker) are given in Table 1. The absorption bands observed in the spectra of the complexes at 1586–1590 and 1653–1654 cm^{-1} should be interpreted, evidently, as the shifted bands at 1606 and 1677 cm^{-1}, respectively, including the $\nu(CO)$ and $\delta(NH_2)$ vibrations. These shifts of the absorption bands are caused by the weakening of the CO band due to the coordination of the acetamide by the Ln atom.

X-Ray diffraction data. The experimental intensities of the diffraction reflections were obtained at room temperature (293(2) K) on a CAD-4 diffractometer [6] (MoK_α radiation, graphite monochromator, ω scan mode). The unit cell parameters were determined and refined by 25 reflections in the θ range from 14° to 15° (for **I** and **II**) and from 13° to 14° (for **III**). Selected experimental parameters and crystallographic characteristics of compounds **I–III** are listed in Table 2. An absorption correction was applied by the ψ scan method of particular reflections. The experimental data set was primarily processed using the WinGX program package [7]. All subsequent calculations were performed in the framework of the SHELX-97 program package [8]. Crystal structures **I–III** were determined by direct methods followed by the refinement of positional and thermal parameters in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were introduced in the calculated positions and refined by the riding model. The structures of compounds **I–III** and atomic numeration are shown in Figs. 1–3, which were drawn using the MERCURY program [9].

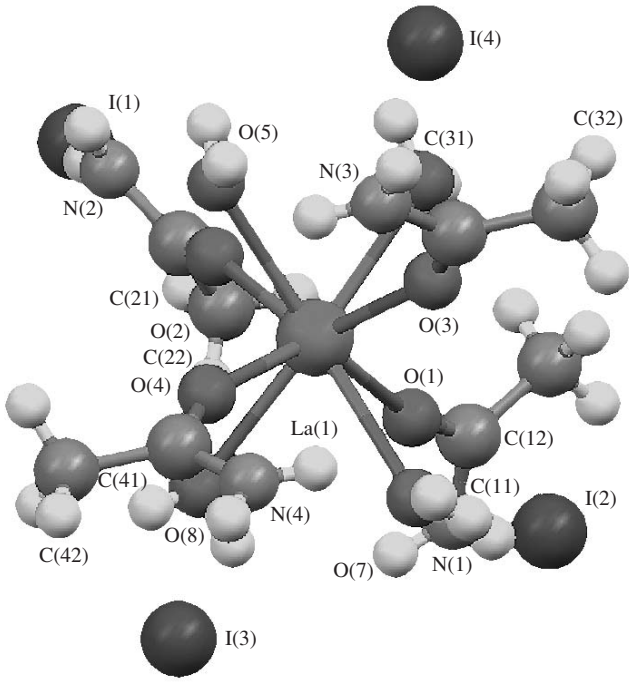

Fig. 1. Structure of the compound $LaI_3 \cdot 4AA \cdot 4H_2O$ (**I**): selected bond lengths La(1)–O(2) 2.423(6), La(1)–O(1) 2.438(6), La(1)–O(4) 2.442(6), La(1)–O(3) 2.453(5), La(1)–O(5) 2.514(6), La(1)–O(7) 2.528(7), La(1)–O(6) 2.556(5), and La(1)–O(8) 2.564(5) Å and bond angles C(11)O(1)La(1) 166.1(7)°, C(21)O(2)La(1) 157.3(7)°, C(31)O(3)La(1) 154.5(6)°, C(41)O(4)La(1) 158.4(7)°, O(1)C(11)N(1) 118.3(10)°, O(1)C(11)C(12) 125.3(10)°, and N(1)C(11)C(12) 116.1(9)°.

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

Parameter	Value		
	I	**II**	**III**
Empirical formula	$C_8H_{28}I_3LaN_4O_8$	$C_8H_{28}GdI_3N_4O_8$	$C_8H_{28}ErI_3N_4O_8$
FW	827.95	846.29	856.30
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2/*c*	*P*2/*c*	*P*2/*c*
a, Å	16.283(8)	16.138(4)	16.126(8)
b, Å	10.823(2)	10.488(5)	10.505(4)
c, Å	15.831(7)	15.648(8)	15.668(7)
β, deg	112.53(4)	112.83(4)	112.66(4)
V, Å^3	2577.0(18)	2441.1(11)	2449.3(19)
Z	4	4	4
ρ_{calcd}, g/cm^3	2.134	2.281	2.322
μ, mm^{-1}	5.283	6.544	7.241
θ range, deg	1.35–25.97	1.94–27.97	5.24–7.97
Range of indices *h*, *k*, *l*	$0 \le h \le 20$ $-13 \le k \le 0$ $-19 \le l \le 18$	$-20 \le h \le 20$ $-13 \le k \le 0$ $-20 \le l \le 0$	$0 \le h \le 21$ $0 \le k \le 13$ $-20 \le l \le 19$
Crystal sizes, mm	0.2 × 0.2 × 0.2	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
Independent reflections	5067	5926	5948
Number of reflections with $I \ge 2\sigma(I)$	2963	4630	4314
Refined parameters	222	222	246
Goodness-of-fit	0.926	1.044	1.039
R factor ($I \ge 2\sigma(I)$) R_1/wR_2	0.0426/0.0628	0.0595/0.1553	0.0585/0.1579
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	0.747/–0.792	1.270/–1.078	1.250/–1.090

The coordinates of atoms and other parameters of crystal structures **I–III** were deposited with the Cambridge Crystallographic Data Centre (nos. 682947 (**I**), 682946 (**II**), and 682945 (**III**); deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The structures of compounds **I–III** include the $[Ln(AA)_4(H_2O)_4]^{3+}$ complex cations. The Ln atoms coordinate eight oxygen atoms of four water molecules and four monodentate AA ligands at the vertices of the distorted square antiprism. The Ln–O(H_2O) bonds are longer than Ln–O(AA): on the average, 2.540 and 2.439 Å (La), 2.366 and 2.284 Å (Gd), and 2.367 and 2.261 Å (Er). This indicates a stronger binding of the acetamide ligand than that of the water molecules. Analogous ratios of the Ln–O bond lengths for the water and carbamide (Ur) molecules are also observed for the earlier studied complexes $[LnUr_4(H_2O)_4]I_3$ (Ln = Nd, Gd, Er) [10, 11].

The complex cations form double layers of the alternating tetraaquatetraacetamide cations, and the NH_2 planar groups of the coordinated acetamide molecules of the adjacent layers are opposite to each other with the shift and almost perpendicular turn. The iodide ions forming triple columns are localized between the layers of the complex cations. The iodide ions form hydrogen bonds with the coordinated water molecules and amide fragments of the acetamide ligands.

The crystals of complexes **I–III** are isostructural. The mutual arrangement of the ligands and iodide ions in the unit cell of the lanthanum and gadolinium complexes is the same, and the distinction of the erbium complex is the different orientation of one of the acetamide ligands (Fig. 4).

It is noteworthy that the molecular volume changes nonmonotonically in the series of the complexes studied (the *V* value is minimum in the case of gadolinium), whereas for analogous carbamide complexes this value changes monotonically in the series Nd–Gd–Er (1184, 1161, and 1131 Å^3, respectively). In addition, in the case of the carbamide ligand, all studied complexes of

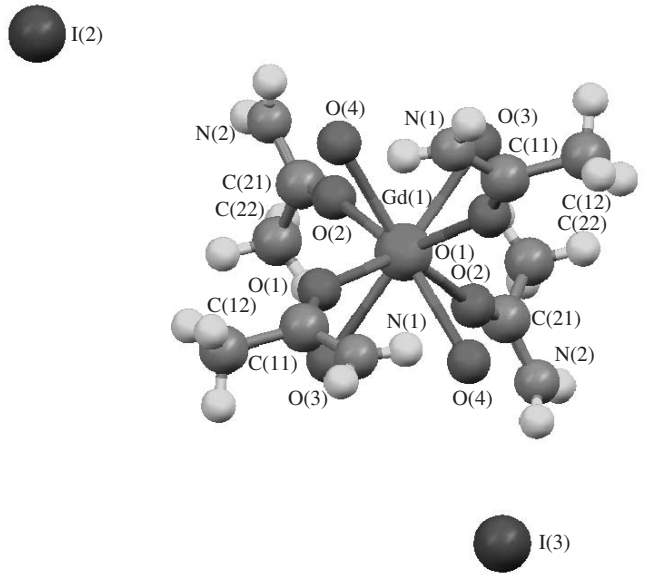

Fig. 2. Structure of the compound $GdI_3 \cdot 4AA \cdot 4H_2O$ (**II**): selected bond lengths Gd(1)–O(2) 2.255(7), Gd(1)–O(1) 2.314(7), Gd(1)–O(4) 2.344(6), and Gd(1)–O(3) 2.389(7) Å and bond angles C(11)O(1)Gd(1) 151.7(7)°, C(21)O(2)Gd(1) 164.4(8)°, O(1)C(11)N(1) 125.0(10)°, O(1)C(11)C(12) 121.2(11)°, N(1)C(11)C(12) 113.6(10)°, O(2)C(21)N(2) 127.1(11)°, O(2)C(21)C(22) 125.5(11)°, and N(2)C(21)C(22) 106.0(11)°.

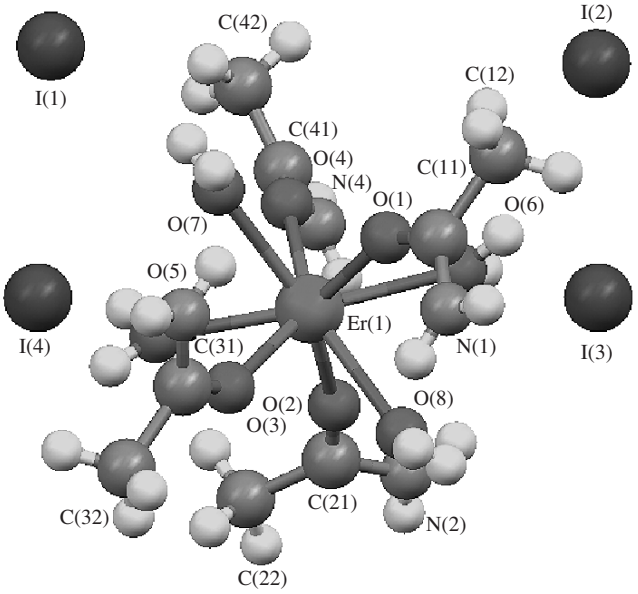

Fig. 3. Structure of the compound $ErI_3 \cdot 4AA \cdot 4H_2O$ (**III**): selected bond lengths Er(1)–O(4) 2.235(14), Er(1)–O(2) 2.249(16), Er(1)–O(1) 2.276(11), Er(1)–O(3) 2.283(9), Er(1)–O(7) 2.351(19), Er(1)–O(6) 2.360(11), Er(1)–O(8) 2.372(19), and Er(1)–O(5) 2.384(10) Å and bond angles C(11)O(1)Er(1) 152.5(16)°, C(21)O(2)Er(1) 168.9(18)°, C(31)O(3)Er(1) 149.1(17)°, C(41)O(4)Er(1) 158.1(16)° O(1)C(11)N(1) 118.3(10)°, O(1)C(11)C(12) 118.1(19)°, and N(1)C(11)C(12) 117.0(19)°.

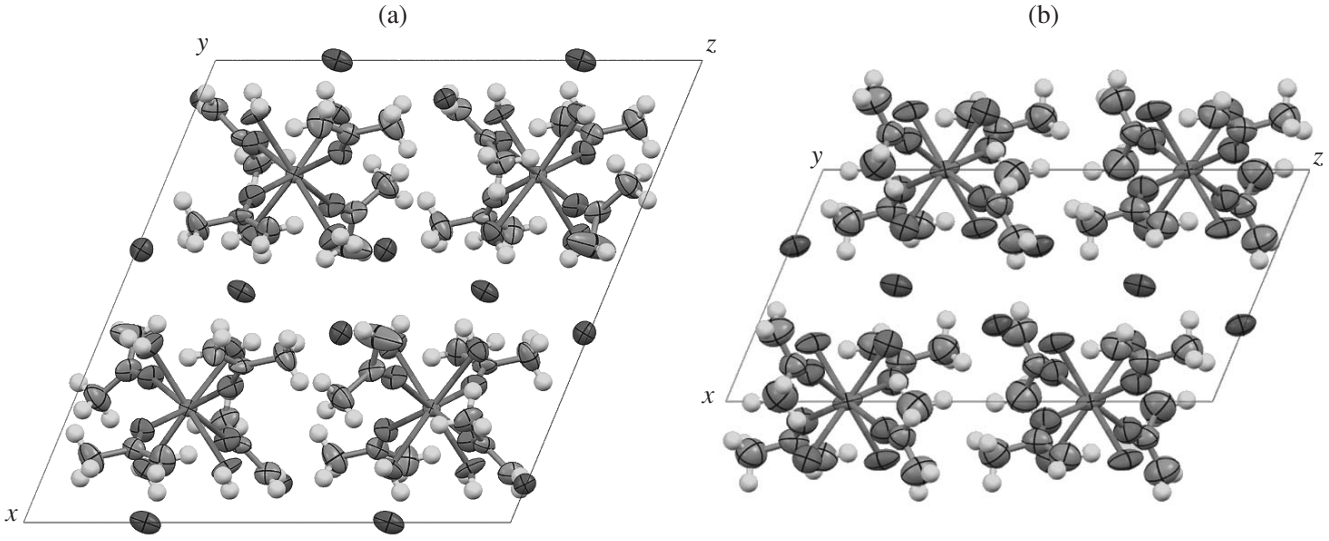

Fig. 4. Crystal packings of compounds (a) **I** and (b) **II**: view along the *y* axis.

lanthanide iodides (neodymium [11], gadolinium, and erbium [10]) are characterized by $Z = 2$. Obviously, the arrangement of the planar ligand (carbamide) in the composition of the complex cation meets no such steric hindrances as in the case of the nonplanar acetamide molecule. These hindrances change the mutual orientation of the ligands on going from gadolinium to erbium.

When explaining these differences, one should take into account, probably, the so-called secondary periodicity, or the tetrad effect [12]. The reasons for this effect

are considered to be the nonuniform rate of deepening of the 4*f* orbitals in the series of lanthanides resulting in the "gadolinium break," the spin-orbital interaction that divides the whole series of lanthanides into four segments, and the additional stabilization by the crystalline field that is maximum in the beginning and in the end of two subgroups of the lanthanide family. This is, most likely, a reason for a more compact structure of the acetamide complex of gadolinium (**II**).

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