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RESEARCH ARTICLE

Coordination compounds of indium, gadolinium, and erbium nitrates with low urea content

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Abstract

Objectives. To date, compounds of rare earth nitrates with urea in a ratio of 1:4 and indium in a ratio of 1:6 have been synthesized and structurally characterized. However, there is a lack of research into similar compounds having a lower urea content. The purpose of this work was to continue the search for regularities of structure formation for complexes of various elements with urea.

Methods. Novel coordination compounds were synthesized and characterized by powder- and single-crystal X-ray diffraction analysis, as well as infrared spectroscopy.

Results. The interaction of indium, gadolinium and erbium nitrates with urea (Ur) in an aqueous solution under conditions of ligand deficiency produces the previously unknown coordination compounds $\text{cis-[In(Ur)}_4(\text{NO}_3)_2]\text{NO}_3$, $[\text{Gd}(\text{H}_2\text{O})_2(\text{Ur})_2(\text{NO}_3)_3]$, and $[\text{Er}(\text{H}_2\text{O})_2(\text{Ur})(\text{NO}_3)_3]$. The indium complex is shown to have an ionic structure, whereas the gadolinium and erbium

complexes have a molecular structure. In the indium complex, the coordination number is 6; the cation has an octahedral structure; it involves two *cis*-arrange monodentate nitrate groups and four monodentate urea molecules. The coordination number of gadolinium is 10; here, the coordination polyhedron is a distorted pentagonal bipyramid at the vertices of which there are two water molecules, while in the internal polygonal base there are two monodentate urea molecules and three bidentate chelating nitrate groups oriented perpendicular to the polygonal base of the bipyramid. The coordination number of erbium is 9; the coordination polyhedron is a distorted tricapped trigonal prism.

Conclusions. In contrast with the gadolinium complex, one urea molecule is coordinated in the erbium complex instead of two, decreasing the coordination number from 10 to 9. In the indium complex cation, the coordination number is 6; unlike the gadolinium and erbium complexes, the cation does not contain water, and the nitrate groups are monodentate.

Keywords: indium nitrate, gadolinium nitrate, erbium nitrate, urea, complexes, crystal structure, X-ray diffraction analysis

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НАУЧНАЯ СТАТЬЯ

Координационные соединения нитратов индия, гадолиния и эрбия с низким содержанием мочевины

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Аннотация

Цели. В настоящее время синтезированы и структурно охарактеризованы соединения нитратов редкоземельных элементов с мочевиной в соотношении 1:4 и индия — в соотношении 1:6, однако практически не изучены подобные соединения с меньшим содержанием мочевины. Целью настоящей работы является продолжение поиска закономерностей образования и строения комплексов различных элементов с мочевиной.

Методы. Новые координационные соединения синтезированы и охарактеризованы методами рентгенофазового анализа, инфракрасной спектроскопии и рентгеноструктурного анализа.

Результаты. Взаимодействие нитратов гадолиния и эрбия с карбамидом (мочевиной, Ur) в водном растворе в условиях недостатка лиганда приводит к образованию ранее неизвестных координационных соединений *cis*-[In(Ur)₄(NO₃)₂]NO₃, [Gd(H₂O)₂(Ur)₂(NO₃)₃] и [Er(H₂O)₂(Ur)(NO₃)₃]. Показано, что комплекс индия имеет ионное, а комплексы гадолиния и эрбия — молекулярное строение. Координационное число индия равно 6; комплексный катион имеет октаэдрическое строение с *cis*-расположением двух монодентатных нитратных групп. Вершины октаэдра заняты атомами кислорода четырех

монодентатных молекул карбамида. Координационное число гадолиния равно 10, координационный полиэдр можно представить как искаженную пентагональную пирамиду, в вершинах которой расположены две молекулы воды, а в плоскости — две мондентатные молекулы мочевины и три бидентатно-хелатирующие нитратные группы, ориентированные перпендикулярно плоскости бипирамиды. Координационное число эрбия равно 9, координационный полиэдр — искаженная трехшапочная тригональная призма.

Выводы. При переходе от гадолиния к эрбию наблюдается координация одной молекулы мочевины вместо двух, координационное число уменьшается от 10 до 9. В комплексе индия координационное число равно шести; в отличие от комплексов гадолиния и эрбия комплексный катион не содержит воды, а нитратные группы являются не бидентатными, а монодентатными.

Ключевые слова: нитрат индия, нитрат гадолиния, нитрат эрбия, карбамид, комплексы, кристаллическая структура, рентгеноструктурный анализ

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INTRODUCTION

Complexes of nitrates of various elements with urea are attracting attention in the context of the development of self-propagating high-temperature synthesis (SHS) methods, in particular, the solution combustion synthesis (SCS) method. The SCS method has been successfully used to obtain a wide range of functional materials, whose components or precursors are oxides, sulfides, nitrides, and silicates of metals [1–6] in nanosized states.

According to this method, nitrates serve as oxidizing agents, while urea (Ur , $\text{CH}_4\text{N}_2\text{O}$) is a fuel. Under conditions of synthesis from solution, complex compounds of the corresponding metal cations with urea should be formed as intermediate compounds, whose compositions should vary according to the nitrate/urea ratio. A study of rare earth element (REE) nitrate–urea–water ternary systems showed that, in

most cases, several compounds with REE nitrate/urea ratios from 1:1 to 1:7 crystallize in each system [7]. In particular, in systems involving gadolinium and erbium compounds at 30°C , compounds $\text{Gd}(\text{NO}_3)_3 \cdot 4\text{Ur}$, $\text{Gd}(\text{NO}_3)_2 \cdot 2\text{Ur}$ [8], $\text{Er}(\text{NO}_3)_3 \cdot 4\text{Ur}$, $\text{Er}(\text{NO}_3)_3 \cdot 3\text{Ur} \cdot 2\text{H}_2\text{O}$ were reported to be formed [9]. Compounds with a REE nitrate/urea ratio of 1:4 for these elements, as well as those for the entire series of REEs, were isolated and structurally characterized [10–12]. Their compositions, which turned out to include water, have the coordination formula $[\text{Ln}(\text{H}_2\text{O})_2(\text{Ur})_4(\text{NO}_3)_2]\text{NO}_3$ ($\text{Ln} = \text{Gd}, \text{Er}$). For indium, an 1:6 complex $[\text{In}(\text{Ur})_6](\text{NO}_3)_3$ was described, which was used as a precursor for the SHS preparation of gallium indium zinc oxide [13]. When using complexes with a high urea content under SCS conditions, complete oxidation of all urea by the reduction of nitrate ions may not be achieved [14]. In this regard, a question arose

concerning the possibility of forming complexes containing a lower urea content. The aim of this work was to continue the search for patterns of formation and structure of metal complexes with urea, namely, the isolation and structural study of complexes of indium-, gadolinium-, and erbium nitrates having a low urea content.

EXPERIMENTAL

In the work, we used urea (special purity grade, *REAKHIM*, Russia), as well as $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and $\text{Er}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, which were obtained by dissolving the corresponding carbonates (reagent grade, *REAKHIM*) in concentrated nitric acid (special purity grade), followed by concentrating the solution until the formation of crystals.

Compounds $[\text{Gd}(\text{H}_2\text{O})_2(\text{Ur})_2(\text{NO}_3)_3]$ (**I**), $[\text{Er}(\text{H}_2\text{O})_2(\text{Ur})(\text{NO}_3)_3]$ (**II**), and $[\text{In}(\text{Ur})_4(\text{NO}_3)_2]\text{NO}_3$ (**III**) were synthesized by reacting the corresponding nitrates with urea in ratios from 1:1 to 1:3 in acetonitrile at 30–40°C. After 6 days, crystals formed, which were separated from the mother liquor and dried. The yield was 65–70%.

The contents of C, H, and N in the produced compounds were determined with a CHNS Flash EA 1112 elemental analyzer (*Thermo Finnigan*, Italy) at the Center for Shared Use,

MIREA – Russian Technological University, Moscow, Russia. The indium content in compound **III** was determined by inductively coupled plasma atomic emission spectroscopy (ICP-MS) with an iCAP 6300 Duo spectrometer (*Thermo Fisher Scientific*, USA) at the Center for Shared Use, Kurchatov Institute National Research Center—IREA, Moscow, Russia. The gadolinium and erbium contents were determined by complexometric titration.

The phase purity of compounds **I–III** was confirmed by X-ray powder diffraction analysis. X-ray powder diffraction patterns were recorded with a Bruker D8 ADVANCE X-ray diffractometer (*Bruker*, Germany: radiation — CuK_α ; filter — Ni; detector — LYNXEYE; reflection geometry — $2\theta = 5^\circ\text{--}50^\circ$; scan step size — 0.01125° ; signal accumulation time — 0.25 s) at the Research Equipment Sharing Center of Physical Methods for Studying Substances and Materials, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences (IGIC RAS), Moscow, Russia. Since the prepared complexes are sensitive to air components, the diffraction patterns were recorded using fluoroplastic cells with clamp rings for holding a 7.6- μm -thick Capton protective polyimide film for X-ray studies (*Safetystep*, Russia). Sample preparation was carried out in a SPEKS GB22M sealed glove box (*Spektroskopicheskie sistemy*, Russia) with a residual water vapor content of no more than 10 ppm.

Table 1. Elemental analysis of complexes **I**, **II**, and **III**

Complex	Elemental content, %			
	C	H	N	Gd
I				
Found	5.00	2.35	19.80	31.66
Calculated	4.81	2.20	19.62	31.48
II				
Found	2.93	2.01	15.73	37.43
Calculated	2.67	1.79	15.59	37.22
III				
Found	8.65	3.16	26.14	21.33
Calculated	8.87	2.96	25.87	21.23

Infrared (IR) spectroscopic studies were performed with an FSM 2201 FTIR spectrometer (*Infraspek*, Russia; 4000–500 cm^{-1} , KBr pellets, 25°C). The error in measuring the frequencies of absorption bands was no more than 3–4 cm^{-1} .

Single-crystal X-ray diffraction analysis of the complexes **I**, **II**, and **III** was performed with a Bruker SMART APEX II diffractometer (*Bruker*, Germany; graphite monochromator, MoK_α radiation) at IGIC RAS. The unit cell parameters were refined over the whole dataset. The experimental intensities were corrected for absorption using SADABS program [Sheldrick G.M., *SADABS*, Madison, Wisconsin, USA: Bruker AXS, 2008]. The structure was solved by a direct method (SHELXS97) and refined by the full-matrix least squares method (SHELXL-2018/3) using all data in the anisotropic approximation for all non-hydrogen atoms. The H atoms of the water molecule were localized by difference Fourier synthesis and refined without any constraints. The H atoms of NH_2 groups were introduced in geometrically calculated positions with thermal parameters $U_{\text{H}} = 1.2U_{\text{eq}}(\text{N})$, where $U_{\text{eq}}(\text{N})$ are the equivalent isotropic thermal parameters of nitrogen atoms.

RESULTS AND DISCUSSION

The coordination compounds of indium, gadolinium, and erbium nitrates with urea were synthesized at metal/ligand molar ratios from 1:1 to 1:3. These ratios were chosen from the data of the solubility diagrams of the $\text{M}(\text{NO}_3)_3\text{-Ur-H}_2\text{O}$ systems [7–9]. Compounds having metal/ligand ratios of 1:4, 1:2, and 1:1 for indium, gadolinium, and erbium, respectively, were isolated from saturated aqueous solutions. The complex compounds of gadolinium and erbium, which additionally included water, had the coordination formulas $[\text{Gd}(\text{H}_2\text{O})_2(\text{Ur})_2(\text{NO}_3)_3]$ (**I**) and $[\text{Er}(\text{H}_2\text{O})_2(\text{Ur})(\text{NO}_3)_3]$ (**II**). The indium complex was anhydrous: $[\text{In}(\text{Ur})_4(\text{NO}_3)_2]\text{NO}_3$ (**III**).

The IR spectroscopy study confirmed the presence of coordinated water molecules in the gadolinium and erbium complexes: broad bands are observed in the range of 3500–3200 cm^{-1} . The broadening of these absorption bands was explained by the formation of a developed system of hydrogen bonds. It was shown that, in complexes **I–III**, the urea molecule is coordinated through the donor oxygen atom of the carbonyl group, as evidenced by the shift of the amide I stretching vibrations ($\nu(\text{CO})$ 1641–1654 cm^{-1}) toward longer wavelengths in comparison with free urea (1675 cm^{-1}). The coordination of nitrate ions

as bidentate cyclic ligands in complexes **I** and **II** was confirmed by the absorption bands at 1490 ($\nu(\text{N-O})$), 1353 ($\nu_{\text{as}}(\text{NO}_2)$), 1041 ($\nu_{\text{s}}(\text{NO}_2)$), and 805 ($\pi(\text{NO}_3)$) cm^{-1} [15]. Complex **III** contains both monodentate coordinated and non-coordinated nitrate ions, which results in the splitting of the absorption bands of nitrate groups: 1498 and 1453 ($\nu(\text{N-O})$), 1389 and 1287 ($\nu_{\text{as}}(\text{NO}_2)$), 1151 and 1033 ($\nu_{\text{s}}(\text{NO}_2)$), and 824 and 800 ($\pi(\text{NO}_3)$) cm^{-1} .

The X-ray powder diffraction analysis confirmed the formation of new compounds in the $\text{M}(\text{NO}_3)_3\text{-Ur-H}_2\text{O}$ systems, where $\text{M} = \text{Er, Gd, In}$ (Fig. 1). Reflections of the initial compounds are not found in the presented diffraction patterns of complex compounds. In addition, the X-ray powder diffraction analysis confirmed that the obtained compounds are not isostructural to each other.

The crystal and molecular structures of the obtained compounds were determined by the single-crystal X-ray diffraction analysis. Table 2 presents the crystallographic characteristics of the complexes.

Table 3 summarizes the bond lengths and bond angles in the presented complexes.

The gadolinium complex $[\text{Gd}(\text{H}_2\text{O})_2(\text{Ur})_2(\text{NO}_3)_3]$ (**I**) is isostructural to the previously described praseodymium compound $[\text{Pr}(\text{H}_2\text{O})_2(\text{Ur})_2(\text{NO}_3)_3]$ [12]. It has a molecular structure; two water molecules, two urea molecules, and three nitrate ions are bound to the central ion. Water molecules and urea molecules in this compound are monodentate ligands and are coordinated to the central atom through donor oxygen atoms, and nitrate groups are bidentate

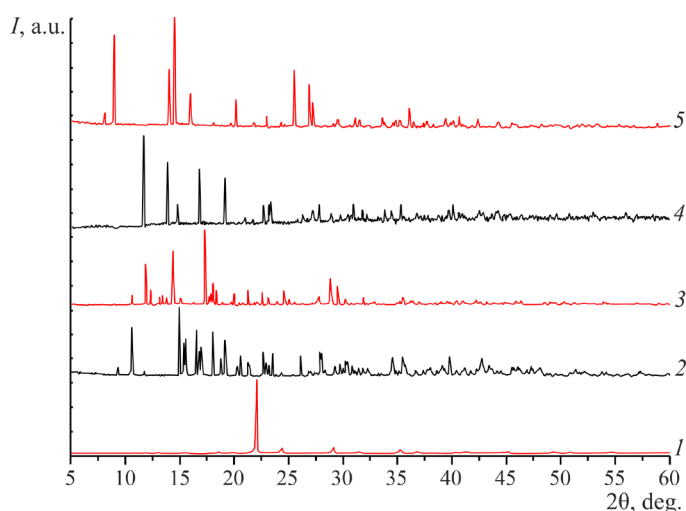


Fig. 1. X-ray powder diffraction patterns of (1) Ur , (2) $\text{Er}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, (3) $[\text{Er}(\text{H}_2\text{O})_2(\text{Ur})(\text{NO}_3)_3]$, (4) $[\text{Gd}(\text{H}_2\text{O})_2(\text{Ur})_2(\text{NO}_3)_3]$, and (5) $[\text{In}(\text{Ur})_4(\text{NO}_3)_2]\text{NO}_3$.

Table 2. Crystallographic characteristics, details of the X-ray diffraction experiment, and refinement of structures I–III

Parameters	I	II	III
Empirical formula	C ₂ H ₁₂ GdN ₇ O ₁₃	CH ₈ ErN ₅ O ₁₂	C ₄ H ₁₆ InN ₁₁ O ₁₃
<i>M</i>	499.44	449.38	541.10
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>C2/c</i>	<i>P2₁/n</i>	<i>C2/c</i>
Unit cell parameters:			
<i>a</i> , Å	10.685(6)	7.756(4)	11.232(2)
<i>b</i> , Å	8.756(4)	10.265(5)	21.869(4)
<i>c</i> , Å	15.367(8)	14.449(7)	7.341(2)
β, °	97.34(3)	98.33(3)	99.44(3)
<i>V</i> , Å ³	1425.8(13)	1138.2(9)	1778.7(7)
<i>Z</i>	4	4	4
Temperature <i>T</i> , K	150	150	100
Density ρ, g/cm ³	2.327	2.622	2.021
Number of independent reflections	2073	3304	1864
Goodness of fit	1.131	1.087	1.235
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0544/0.0553	0.0492/0.0517	0.1012/0.0995

Note: *a*, *b*, *c* are the lengths of the edges of the unit cell; β is the angle between the edges of the unit cell; *V* is the volume of the unit cell; *Z* is the number of formula units per unit cell; and *R* is the reliability factor.

chelating ligands. Thus, the coordination number of the central ion is 10. If all nitrate ions are represented as points, then the coordination polyhedron can be described as a distorted pentagonal bipyramid with water molecules in the axial position (Fig. 2). The gadolinium atom lies in the plane of the internal polygonal base formed by the nitrogen atoms of the nitrate ligands. The planar nitrate groups are oriented perpendicular to the polygon base. The almost planar urea molecules are turned about the polygon base at an angle of 44.60°, while the angle between their planes is 86.06°.

The somewhat shorter metal–oxygen bonds in **I** than those in the similar praseodymium compound are due to the decrease in the radius of the central atom.

In the erbium complex [Er(H₂O)₂(Ur)(NO₃)₃] (**II**), the erbium/urea ratio is 1:1. This is the first example of a structurally characterized complex compound of rare earth nitrate with urea of such composition. This complex, as complex **I**, has a molecular structure.

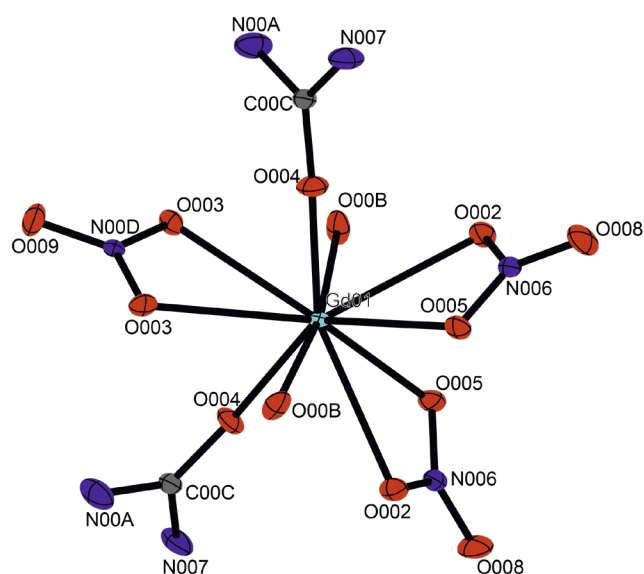

Fig. 2. Structure of [Gd(H₂O)₂(Ur)₂(NO₃)₃] (**I**).

Table 3. Bond lengths and bond angles in complexes I–III

Bond length, Å	Bond angle, °	Torsion angle, °
I		
Gd01 O002 2.6482(19)	O002 Gd01 O002 93.38(9)	Gd01 O002 N006 O005 7.5(2)
Gd01 O003 2.665(2)	O002 Gd01 O003 144.46(6)	Gd01 O002 N006 O008 –171.9(2)
Gd01 O004 2.283(2)	O002 Gd01 O003 116.17(6)	Gd01 O003 N00D O003 –0.002(0)
Gd01 O005 2.513(2)	O003 Gd01 O003 47.72(8)	Gd01 O003 N00D O009 180.000(0)
Gd01 O00B 2.411(2)	O004 Gd01 O002 71.21(7)	Gd01 O004 C00C N007 –151.7(3)
	O004 Gd01 O002 138.39(6)	Gd01 O004 C00C N00A 29.7(5)
	O004 Gd01 O003 73.50(6)	Gd01 O005 N006 O002 –8.0(2)
	O004 Gd01 O003 73.55(6)	Gd01 O005 N006 O008 171.4(2)
	O004 Gd01 O004 143.86(10)	
	O004 Gd01 O005 74.34(7)	
	O004 Gd01 O005 137.95(6)	
	O004 Gd01 O00B 87.42(8)	
	O004 Gd01 O00B 90.07(8)	
	O005 Gd01 O002 49.32(6)	
	O005 Gd01 O002 66.85(7)	
	O005 Gd01 O003 123.17(6)	
	O005 Gd01 O003 147.80(6)	
	O005 Gd01 O005 80.76(9)	
	O00B Gd01 O002 119.66(7)	
	O00B Gd01 O002 66.55(7)	
	O00B Gd01 O003 62.10(6)	
	O00B Gd01 O003 109.81(6)	
	O00B Gd01 O005 115.77(6)	
	O00B Gd01 O005 70.90(7)	
	O00B Gd01 O00B 171.91(9)	
II		
Er01 O003 2.462(3)	O003 Er01 O00A 143.26(8)	Er01 O003 N008 O004 179.1(3)
Er01 O005 2.341(3)	O003 Er01 O00G 106.50(9)	Er01 O003 N008 O007 –1.5(3)
Er01 O006 2.400(3)	O005 Er01 O003 72.67(9)	Er01 O007 N008 O003 1.5(3)
Er01 O007 2.422(3)	O005 Er01 O006 78.83(10)	Er01 O007 N008 O004 –179.1(3)
Er01 O00A 2.478(3)	O005 Er01 O007 125.19(8)	Er01 O00B N00E O009 –169.0(3)
Er01 O00B 2.393(3)	O005 Er01 O00A 79.57(9)	Er01 O00B N00E O00G 10.6(3)
Er01 O00D 2.198(2)	O005 Er01 O00B 76.14(9)	Er01 O00D C00I N00F 8.0(7)
Er01 O00G 2.585(3)	O005 Er01 O00G 121.81(9)	Er01 O00D C00I N00J –172.3(3)

Table 3. Continued

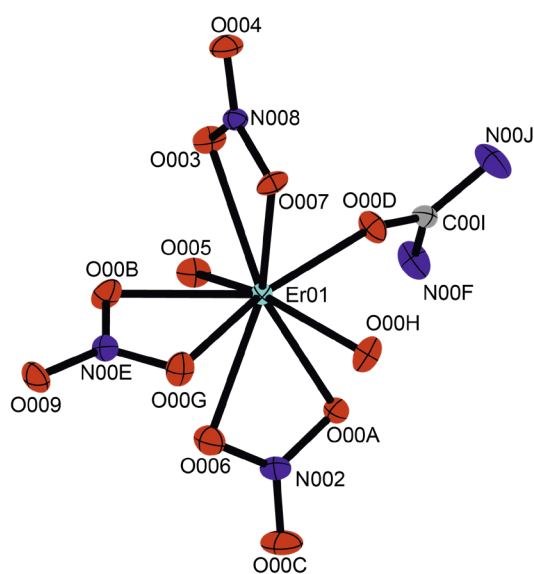
Bond length, Å	Bond angle, °	Torsion angle, °
II		
Er01 O00H 2.293(2)	O006 Er01 O003 139.70(9)	
	O006 Er01 O007 143.24(9)	
	O006 Er01 O00A 52.20(9)	
	O006 Er01 O00G 65.83(9)	
	O007 Er01 O003 52.54(8)	
	O007 Er01 O003 52.54(8)	
	O007 Er01 O00G 77.46(9)	
	O00A Er01 O00G 108.46(8)	
	O00B Er01 O003 72.21(9)	
	O00B Er01 O006 73.73(10)	
	O00B Er01 O007 85.00(10)	
	O00B Er01 O00A 123.89(9)	
	O00B Er01 O00G 50.98(8)	
	O00D Er01 O003 78.22(10)	
	O00D Er01 O005 82.40(10)	
	O00D Er01 O006 125.78(9)	
	O00D Er01 O007 87.76(9)	
	O00D Er01 O00A 74.61(9)	
	O00D Er01 O00B 147.44(9)	
	O00D Er01 O00G 155.77(8)	
	O00D Er01 O00H 85.80(10)	
	O00H Er01 O003 128.16(9)	
	O00H Er01 O005 153.13(9)	
	O00H Er01 O006 88.81(10)	
	O00H Er01 O007 78.13(9)	
	O00H Er01 O00A 74.03(9)	
	O00H Er01 O00B 123.33(8)	
	O00H Er01 O00G 72.54(9)	
III		
In1 O1 2.169(9)	O1 In1 O1 103.6(5)	In1 O1 N1 O2 18.0(14)
In1 O1 2.169(9)	O4 In1 O1 170.9(3)	In1 O1 N1 O3 -164.9(11)
In1 O4 2.127(8)	O4 In1 O1 85.5(3)	In1 O4 C1 N2 -2.4(18)
In1 O4 2.127(8)	O4 In1 O1 85.5(3)	In1 O4 C1 N3 -179.5(8)
In1 O5 2.114(8)	O4 In1 O1 170.9(3)	In1 O5 C2 N4 170.4(9)

Table 3. Continued

Bond length, Å	Bond angle, °	Torsion angle, °
III		
In1 O5 2.114(8)	O4 In1 O4 85.5(5)	In1 O5 C2 N5 -8(2)
	O5 In1 O1 92.4(3)	
	O5 In1 O1 92.4(3)	
	O5 In1 O1 93.2(3)	
	O5 In1 O1 93.2(3)	
	O5 In1 O4 87.3(3)	
	O5 In1 O4 86.1(3)	
	O5 In1 O4 87.3(3)	
	O5 In1 O4 86.1(3)	
	O5 In1 O5 171.0(5)	

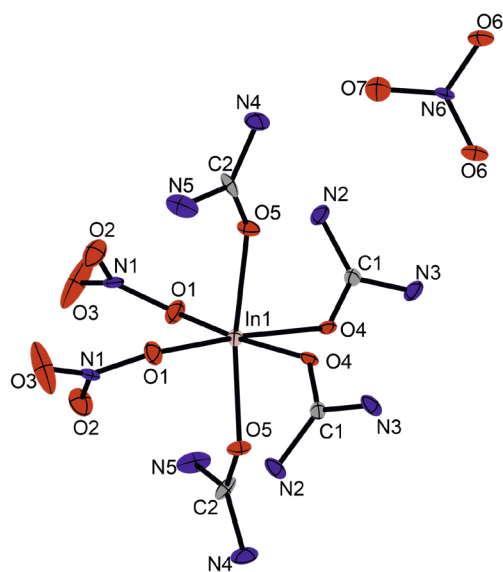
Two water molecules, one urea molecule, and three bidentate chelating nitrate ions are bound to the central ion. The coordination number of the central ion is 9. The coordination polyhedron is a tricapped trigonal prism (Fig. 3). The planar nitrate ligands are located in three mutually perpendicular planes (the angles between them are 72.33°, 85.82°, and 89.36°). The almost planar urea molecule is located at angles of 40.89°, 67.48°, and 79.43° with respect to these planes.

In erbium complex **II** in comparison with gadolinium complex **I**, the radius of the central atom is much smaller resulting in the shorter lengths of metal–oxygen bonds, as well as the number of

Fig. 3. Structure of $[\text{Er}(\text{H}_2\text{O})_2(\text{Ur})(\text{NO}_3)_3]$ (**II**).

coordinated urea molecules (one instead of two). In complexes **I** and **II**, there are no intramolecular hydrogen bonds, but numerous intermolecular hydrogen bonds between coordinated urea molecules, nitrate ions and water molecules of neighboring molecular complexes.

In indium complex *cis*- $[\text{In}(\text{Ur})_4(\text{NO}_3)_2]\text{NO}_3$ (**III**), the indium/urea ratio is 1:4. The complex has an ionic structure. Four urea molecules and two monodentate nitrate ions occupying *cis* positions are bound to the central atom. One nitrate ion is located in the outer sphere. The coordination number of the central ion is 6. The coordination polyhedron is a distorted octahedron (Fig. 4). The structure is stabilized by hydrogen bonds. Each urea molecule

Fig. 4. Structure of $[\text{In}(\text{Ur})_4(\text{NO}_3)_2]\text{NO}_3$ (**III**).

forms hydrogen bonds of the N–H...O type with the neighboring urea molecule and with inner-sphere or outer-sphere nitrate ions.

CONCLUSIONS

The analysis of the structures of the complexes of gadolinium and erbium nitrates with urea demonstrated, that they are molecular with monodentate water and urea molecules and bidentate chelating nitrate groups in the inner sphere. The decrease in the radius of the central atom leads to a decrease in the number of ligands in the inner sphere of the erbium complex in comparison with the gadolinium complex. Although both complexes contain two water molecules and three nitrate groups, the gadolinium complex contains two coordinated urea molecules, whereas the erbium complex contains one. This leads to a decrease in the coordination number from 10 to 9 and a significant change in the coordination polyhedron. Thus, complex compounds of gadolinium and erbium with a low urea content differ in composition and structure, in contrast to the isostructural compounds $[\text{Ln}(\text{Ur})_4(\text{H}_2\text{O})(\text{NO}_3)_2]\text{NO}_3$ (Ln = Gd, Er) containing four urea molecules. This may be due to the fact that urea loses its structure-forming role with a decrease in the number of coordinated urea molecules. In this case, steric factors determined primarily by the size of the central REE ion become more important.

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Complex **III** differs from $[\text{In}(\text{Ur})_6](\text{NO}_3)_3$ by the smaller number of coordinated urea molecules. The typical coordination number 6 for indium is achieved by additional coordination of nitrate ions, rather than water molecules, as is usually observed in urea complexes. In this case, a *cis* isomer is formed, and nitrate ions are coordinated as monodentate ligands, which is quite rare.

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Authors' contributions

- E.K. Bettels** – synthesis;
I.A. Karavaev – IR spectroscopy;
G.A. Buzanov – X-ray powder diffraction;
A.S. Kubasov – X-ray single-crystal diffraction;
E.V. Savinkina – overall supervision, literature review, analysis of results, and writing the text of the article.

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