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Synthesis and research of new complex compounds of rare earth element nitrates with N-methylglycolurils

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Abstract. A series of new complex compounds of nitrates of trivalent rare earth elements (lanthanum, cerium, praseodymium, neodymium, samarium, terbium, dysprosium, erbium, ytterbium) with bicyclic bisureas – N-methylglycolurils (N-monomethylglycoluril, 2,4-N-dimethylglycoluril, 2,6-N-dimethylglycoluril, 2,4,6,8-N-tetramethylglycoluril) as ligands were obtained. IR spectroscopy showed that the rare earth elements (REE) ions are coordinated by two oxygen atoms of two N-methylglycoluril molecules, three bidentate nitrate anions, and water molecules. N-methylglycolurils realize bidentate, chelating, and bridging functions and tend to form binuclear complexes with rare earth elements. Mass spectrometry with an inductively coupled plasma of synthesized complexes was carried out, and the metal:ligand ratio was ~1:1, respectively. Powder X-ray diffraction allowed us to establish the structures of complex compounds of 2,4,6,8-N-tetramethylglycoluril with cerium, neodymium, terbium, and dysprosium nitrates. NMR spectroscopy of the obtained complexes was also performed in DMSO-*d*₆ to detect a complex particle in the solution. The resulting complexes are stable in air, however, they are sensitive to trace amounts of water in the solution and are prone to degradation into their original substances.

Keywords: methylglycoluril, rare-earth elements, complex compound, bicyclic bisurea, X-ray diffraction, IR

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Научная статья

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Синтез и исследование новых комплексных соединений нитратов редкоземельных элементов с N-метилгликолурилами

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Аннотация. Получен ряд новых комплексных соединений нитратов трехвалентных редкоземельных элементов (лантана, церия, празеодима, неодима, самария, тербия, диспрозия, эрбия, иттербия) с бициклическими бимочевинами – N-метилгликолурилами в качестве лигандов (N-монометилгликолурил, 2,4-N-диметилгликолурил, 2,6-N-диметилгликолурил, 2,4,6,8-N-тетраметилгликолурил). ИК-спектроскопия показала, что ионы редкоземельных элементов (РЗЭ) координируются двумя атомами кислорода двух молекул N-метилгликолурила, трех бидентатных нитрат-анионов и молекулами воды. N-метилгликолурилы реализуют бидентатную, хелатирующую и мостиковую функции и склонны к образованию биядерных комплексов с редкоземельными элементами. Проведена масс-спектрометрия с индуктивно-связанной плазмой синтезированных комплексов, соотношение металл:лиганд составило ~ 1:1. Методом порошковой рентгеновской дифракции установлено строение комплексных соединений 2,4,6,8-N-тетраметилгликолурила с нитратами церия, неодима, тербия и диспрозия. ЯМР-спектроскопию полученных комплексов проводили в ДМСО-d₆ для обнаружения комплексной частицы в растворе. Образующиеся комплексы устойчивы на воздухе, однако чувствительны к следовым количествам воды в растворе и склонны к распаду до исходных веществ.

Ключевые слова: метилгликолурил, редкоземельные элементы, комплексное соединение, бициклическая бимочевина, рентгеноструктурный анализ, ИК

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Introduction

Bicyclic bisureas, particularly glycolurils, due to the polyfunctionality of their structure, have found a wide range of applications in various spheres of human activity. Currently, there are several important substances and materials are manufactured based on glycoluril and its derivatives on an industrial scale, including medicines [1], crosslinking agents for the production of special-purpose polymers [2, 3], activators of peroxide compounds for bleaching [4], disinfectants [5, 6], independent explosives or their components [7, 8], etc.

However, the coordination compounds of bicyclic bisureas have not been practically studied. This is explained by the fact that only those compounds in which bicyclic bisurea has a set of valuable biological properties are of interest [9]. Additionally, structural N-methyl homologues of glycoluril lack specific biological activity, further limiting the research focus in this area.

Among the ligands containing the glycoluril fragment, 2,4,6,8-tetramethyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione, also known as mebikar (Mb) (Fig. 1e) ($C_8H_{14}N_4O_2$), has been extensively studied. The particular interest in mebikar is primarily due to its valuable physiological properties [10–13].

Previously, A. Y. Tsvadze and his colleagues reported a number of complex compounds based on mebikar, including $[Co(Mb)_2(H_2O)_2Br_2] \cdot 2H_2O$, $[Ni(Mb)_2(H_2O)_2Br_2]$, $[NiMb(H_2O)_4](NO_3)_2$, and $[Cu_2(Mb)_3Br_4] \cdot 2H_2O$, $CdCl_2 \cdot Mb \cdot 3H_2O$, $CaCl_2 \cdot 2Mb \cdot H_2O$, $Co(NO_3)_2 \cdot 2Mb \cdot 4H_2O$, $Ni(NO_3)_2 \cdot Mb \cdot 4H_2O$, $CdX_2 \cdot Mb$ ($X = Br, I, N, C, S$), $Cd(NO_3)_2 \cdot 1.5Mb \cdot H_2O$, $ZnCl_2 \cdot Mb$, $ZnI_2 \cdot Mb$, $Ca(NO_3)_2 \cdot 2Mb$, $Cu(NO_3)_2 \cdot 0.5Mb$, $[Li_2(Mb)_2(H_2O)_4]Br_2$ [14, 15]. These compounds were characterized by elemental analysis, IR and RAMAN spectroscopy, and in some cases, X-ray diffraction. The studies showed that Mb is coordinated to the metals through oxygen atoms of urea fragments, which was confirmed by a decrease in the frequency of oscillation of amide-I and an increase in the frequency of deformation vibrations of methylamine groups. Later, E. E. Natreba obtained and characterized complexes with mebicar composition: $[MnMb(NO_3)_2]_2$, $[SmMb(H_2O)_2(NO_3)_3]_2$, $[GdMb(H_2O)(NO_3)_3]_2 \cdot H_2O$, $[Eu(Mb)_2(NO_3)_3]_2$, $[PrmB(H_2O)_2(NO_3)_3]_2$ using data from elemental analysis, IR spectroscopy, X-ray diffraction [16–20].

However, there is no information in the literature about the existence of complex compounds of other N-methylglycolurils such as N-monomethylglycoluril ($C_5H_8N_4O_2$, 2-methyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione, MeGl) (Fig. 1b), 2,4-N-dimethylglycoluril (2,4-dimethyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione, $C_6H_{10}N_4O_2$, 2,4-Me₂Gl) (Fig. 1c), 2,6-N-dimethylglycoluril (2,6-dimethyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione, $C_6H_{10}N_4O_2$, 2,6-Me₂Gl) (Fig. 1d), as well as their coordinating ability with nitrates of rare earth elements.

Due to the non-planar spatial structure of N-methylglycolurils in the form of a half-open book, they can act as bidentate ligands with a bridging function.

N-methylglycolurils display ambidentate ligand behavior, acting as a rigid Lewis base. This characteristic provides motivation to investigate their complexing properties, which allows us to get a complete understanding of the chemistry of the interaction of bicyclic bisureas with lanthanide ions, and to find out the denticity of ligands.

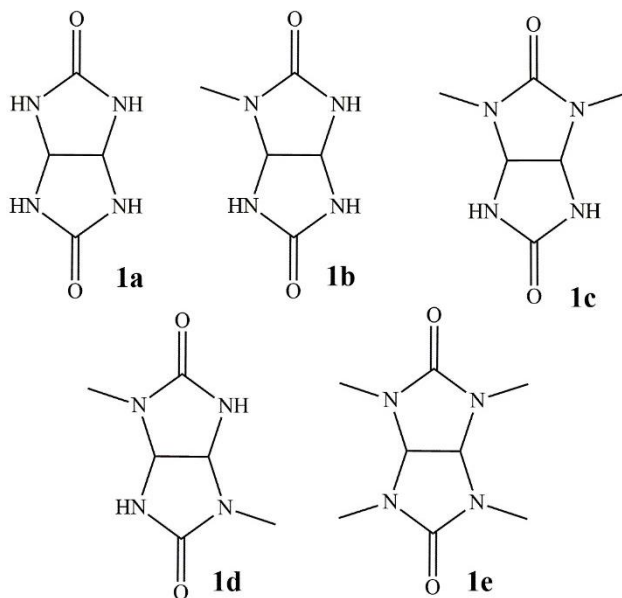


Fig. 1. Structural formulas of glycoluril (1a), monomethylglycoluril (1b), 2,4-dimethylglycoluril (1c), 2,6-dimethylglycoluril (1d), mebicar (1e)

Rare earth metal salts and their complex compounds are used as effective catalysts for dienes polymerization and copolymerization. 2-Ethylhexyl neodymium phosphate is used for the polymerization of isoprene [21].

In connection with the above, this work aims to synthesize and determine the structure of previously unknown complex compounds of rare earth element nitrates with N-methylglycoluril and water molecules.

Materials and methods

Crystallohydrates of REE nitrates were obtained by the method [22]. Suspension of oxides (PrO_2 , Nd_2O_3 , SmO , Tb_4O_7 , Dy_2O_3 , Er_2O_3 , Yb_2O_3) or lanthanum carbonate ($\text{La}_2(\text{CO}_3)_3$) introduced into nitric acid, heated to dissolution, evaporated the solution to a syrupy state, and the crystals are formed by cooling. The crystals were filtered using a Buchner funnel and then dissolved in distilled water for recrystallization. Recrystallization was carried out twice, resulting in newly obtained crystals which were filtered and dried in air.

N-monomethylglycoluril (MeGl) was obtained by condensation of 4,5-dihydroxyimidazolidinone-2 with methyl urea pH=1-2 at 90°C with a yield of 36.3% [23]. The NMR ^1H spectra (DMSO- d_6 , TMS) δ showed the following signals, ppm: 2.60 3H (c, CH_3), 5.14 1H (d, CH), 5.19 1H (d, CH), 7.20 1H (c, NH), 7.30 2H (c, NH). The NMR ^{13}C spectra (DMSO- d_6 , TMS) δ showed signals at ppm: CH_3^- , C-H, and C=O 27.56 ppm, 62.54 and 69.89 ppm, 159.75 and 161.79 ppm, respectively.

2,4-N-dimethylglycoluril (2,4-Me $_2$ Gl) was obtained by condensation of 4,5-dihydroxyimidazolidinone-2 with dimethyl urea pH=1-2 at 90°C with a yield of

46.8% [24]. The NMR ¹H spectra (DMSO-d₆, TMS) δ showed signals at ppm: 2.64 6H (c, CH₃), 5.12 2H (c, CH), 7.54 2H (c, NH). The NMR ¹³C spectra (DMSO-d₆, TMS) δ showed signals at ppm: CH₃-, C-H, and C=O 28.22 ppm, 76.67 ppm, and 158.22 and 160.20 ppm, respectively.

2,6-N-dimethylglycoluril (2,6-Me₂Gl) was obtained by condensation of methyl urea with glyoxal pH=1-2 at 90°C with a yield of 44%. NMR ¹H spectra (DMSO-d₆, TMS) δ showed signals at ppm: 2.78 6H (c, CH₃), 5.17 1H (d, CH), 5.19 1H (d, CH), 7.40 2H (c, NH) (cis isomer); 2.61 6H (c, CH₃), 5.10 2H (c, CH), 7.56 2H (c, NH) (trans-isomer), whereas NMR ¹³C spectra (DMSO-d₆, TMS) δ, showed signals at ppm: CH₃-, C-H and C=O cis isomers (26.69 ppm; 60.63 and 75.63 ppm; 160.19 ppm, respectively) and trans-isomers (27.44 ppm, 67.37 ppm, and 159.61 ppm) [24].

2,4,6,8-N-tetramethylglycoluril (Mb) was obtained by condensation of dimethyl urea with glyoxal pH=1-2 at 90°C with a yield of 57.3%. The product was identified by the melting temperature (T_{pl} = 226-228°C). The NMR ¹H spectra (DMSO-d₆, TMS) δ showed peaks at ppm: 2.82 12H (s, CH₃), 5.06 2H (s, CH). And the NMR ¹³C spectra (DMSO-d₆, TMS) δ showed signals at ppm: CH₃-, C-H, and C=O 30.44 ppm, 71.92 ppm, and 159.05 ppm, respectively. The data obtained are consistent with the literature [25].

The IR spectra of the initial substances and the obtained complexes were recorded using a Nicolet 6700 IR Fourier spectrometer with the prefix NPVO on a diamond crystal with a resolution of 4 cm⁻¹, 64 scans, a range of 350-4500 cm⁻¹.

Powder X-ray diffraction (XRD) analysis was performed on an XRD-7000 X-ray diffractometer (Shimadzu, Japan) with CuKα radiation, λ = 1.54073 Å, range 3-50 2θ, measurement speed 3°/min.

Inductively coupled plasma mass spectrometry (ICP-MS) was performed on a Nexion 300 Series ICP Ms device.

NMR analysis was performed using a Bruker AVANCE 400 III HD NMR spectrometer (Bruker, Billerica, MA, USA). One-dimensional spectra were taken on the nuclei of atoms ¹H (frequency 400.17 MHz) and ¹³C (frequency 100.63 MHz) to confirm the structure. DMSO-d₆ was used as a solvent.

Results and discussion

The general method of synthesis of complex compounds I-XXXIV

A sample of nitrate hexahydrate of the corresponding rare earth element (0.8 mmol) was dissolved in a glass containing 5 mL of acetone. Then, a portion of the corresponding N-methylglycoluril (0.001 mol) was added and mixture was stirred on a magnetic stirrer for 10 minutes. The resulting solution was filtered, the glass was covered, and left for a day for the precipitate to settle. The resulting precipitates were filtered out, washed three times with 5 ml portions of acetone, and dried in air. The yields (based on ligand) are presented in Tables 1-4. The I-XXXIX complexes are stable in air, limitedly soluble in most organic solvents, and decompose into original substances in water, DMSO, and alcohol. In solution, the synthesized complexes are sensitive to the presence of trace amounts of water.

Table 1

Characteristic data for complexes I – IX with monomethylglycoluryl

№	Metal	CC Output %	MeGl				ICP-MS REE/MeGl
			O=C<, cm ⁻¹				
			Urea, 1 743 cm ⁻¹	Δ, cm ⁻¹	MeUrea, 1 685 cm ⁻¹	Δ, cm ⁻¹	
I	La	29	1 701	42	1 671	14	0.97:1
II	Ce	30	1 698	45	1 668	17	0.89:1
III	Pr	25	1 688	55	1 652	33	0.94:1
IV	Nd	27	1 687	56	1 651	34	0.93:1
V	Sm	26	1 689	54	1 646	39	0.95:1
VI	Tb	23	1 700	43	1 650	35	0.99:1
VII	Dy	16	1 685	58	1 656	29	0.92:1
VIII	Er	24	1 670	73	1 646	39	0.91:1
IX	Yb	20	1 618	25	1 673	12	0.90:1

In the IR spectra of synthesized complexes I-IX, in comparison with MeGl, there is a shift of the absorption bands corresponding to the valence vibrations of both carbonyl groups (O=C<) to the long-wavelength region, which indicates the coordination of MeGl molecules through the oxygen atoms of urea fragments. Additionally, wide absorption bands ν_{s+as} (HOH) 3550-3300 cm⁻¹ and groups of absorption bands of MeGl rings are observed in the spectrum.

ICP-MS of the synthesized complexes revealed the content of the rare earth element in the samples, tables 1-4 present the molar ratios of the rare earth metal to the ligand. The data obtained are consistent with the literature reports indicating that the ratio of mebikar to rare earth metal is 1:1 [17-21].

Table 2

Characteristic data for X – XVIII complexes with 2,4-dimethylglycoluryl

№	Metal	CC Output %	2,4-Me ₂ Gl				ICP-MS REE/2,4- Me ₂ Gl
			O=C<, cm ⁻¹				
			Urea 1 735	Δ, cm ⁻¹	Me ₂ Urea 1 710	Δ, cm ⁻¹	
X	La	55	1 672	63	1 640	70	0.92:1
XI	Ce	53	1 678	57	1 648	62	0.96:1
XII	Pr	50	1 673	62	1 649	61	0.98:1
XIII	Nd	60	1 679	56	1 648	62	0.91:1
XIV	Sm	58	1 679	56	1 650	60	0.97:1
XV	Tb	49	1 671	64	1 641	69	0.96:1
XVI	Dy	51	1 679	56	1 649	61	0.97:1
XVII	Er	56	1 680	55	1 650	60	0.94:1
XVIII	Yb	48	1 669	66	1 650	60	0.95:1

According to the results of IR spectroscopy, the absorption bands corresponding to the valence vibrations of the carbonyl groups of both urea fragments (C=O<) are shifted to the long-wavelength region, which indicates the coordination of 2,4-Me₂Gl molecules through oxygen atoms. There are also absorption bands ν_{s+as} (HOH) 3550-3300 cm⁻¹, and a set of absorption bands of 2,4-N-dimethylglycoluryl rings.

Table 3

Characteristic data for complexes XIX – XXVII with 2,6-dimethylglycoluryl

№	Metal	CC Output %	2,6-Me ₂ Gl		ICP-MS REE/2,6-Me ₂ Gl
			O=C<, cm ⁻¹		
			MeUrea 1 694	Δ, cm ⁻¹	
XIX	La	45	1 679	15	0.96:1
XX	Ce	43	1 682	12	0.97:1
XXI	Pr	40	1 672	22	0.98:1
XXII	Nd	50	1 682	12	0.96:1
XXIII	Sm	44	1 668	26	0.91:1
XXIV	Tb	42	1 667	27	0.90:1
XXV	Dy	37	1 666	28	0.89:1
XXVI	Er	50	1 662	32	0.92:1
XXVII	Yb	41	1 681	13	0.94:1

In the IR spectra of the synthesized complex compounds, a shift of the absorption bands corresponding to the valence vibrations of carbonyl groups (O=C<) to the long-wavelength region was observed. The observed experimental effect indicates the coordination of rare-earth element atoms through oxygen atoms of carbonyl groups of 2,6-Me₂Gl methyl-urea fragments. Broad absorption bands of ν_{s+as} (HOH) in the region of 3550-3300 cm⁻¹ and groups of absorption bands of 2,6-Me₂Gl rings were also detected in the spectra.

Table 4

Characteristic data for complexes XXVIII–XXXVI with mebikar

№	Metal	CC Output %	Mb		ICP-MS REE/Mb
			O=C<, cm ⁻¹		
			Me ₂ Urea 1 703	Δ, cm ⁻¹	
XXVIII	La	40	1 673	30	0.93:1
XXIX	Ce	52	1 662	41	0.97:1
XXX	Pr	50	1 663	40	0.98:1
XXXI	Nd	51	1 663	40	0.95:1
XXXII	Sm	70	1 658	45	0.97:1
XXXIII	Tb	55	1 653	50	0.96:1
XXXIV	Dy	46	1 654	49	0.95:1
XXXV	Er	71	1 654	49	0.97:1
XXXVI	Yb	55	1 655	48	0.93:1

In the IR spectra of the synthesized XXVIII–XXXVI complexes, there is a shift of 30-50 cm⁻¹ into the long-wavelength region of the absorption band, relative to the mebikar, corresponding to valence vibrations (C=O<). This shift indicates the coordination of mebikar molecules with rare-earth metal ions through oxygen atoms. In addition, absorption bands ν_{s+as} (HOH) of water and a set of absorption bands of Mb rings were observed.

For all the obtained complex compounds in the IR spectra, a decrease in the symmetry of the nitrate anion was detected, so the free nitrate ion, as a planar ion

(point group D_{3h}) in the IR spectra, manifests itself in the form of characteristic vibrational frequencies: asymmetric doubly degenerate valence vibrations $\nu_e(\text{NO})$, symmetric valence vibrations $\nu_s(\text{NO})$, and two frequencies of deformation vibrations $\delta(\text{NO}_3)$. For coordination compounds, a decrease in the symmetry of the nitrate anion coordinated by the bidentate-chelate type to C_s and C_{2v} is observed [26]. The detection of a set of absorption bands in the IR spectra at 1530, 1252, 1051, 832 cm^{-1} speaks in favor of the formation of complex compounds. This circumstance testifies to the coordination of atoms of rare earth elements with nitrate ions through oxygen atoms according to the bidentate-chelate type.

Powder X-ray diffraction analysis of the synthesized complex compounds of mebikar with lanthanum, cerium, neodymium, terbium, dysprosium, erbium, and ytterbium (samples XXVIII-XXIX, XXXI, XXXIII-XXXVI, respectively), allowed the determination of their crystal structure and parameters of the elementary cells. This was achieved by comparing the diffractograms of the studied samples with the diffractograms available in the CCDC database. Complex compounds were used as comparison samples: praseodymium with mebikar, PrMb, CCDC No. 1435137; samaria with mebikar, SmMb, CCDC No. 1451436; europia with mebikar, EuMb, CCDC No. 1451437; gadolinium with mebikar, GdMb CCDC No. 1450653.

For complex compounds of mebikar with cerium and neodymium (XXIX and XXXI, respectively), there was a complete correspondence of the diffraction patterns of the powder diffraction of the tested samples with the one calculated based on the structural model of the sample comparing the complex compound of praseodymium nitrate with the mebikar CCDC No. 1435137 (Fig. 2). Table 5 shows the structural data of the studied compounds and the sample comparisons. Figure 3 shows the structure of the complex compound of mebikar with neodymium nitrate.

Table 5

Parameters of crystal lattices, synthesized complexes XXIX and XXXI and the PrMb comparison sample

Compound	Comparison sample PrMb	Sample NdMb (XXXI)	Sample CeMb (XXIX)
Unit Cell Parameters			
a, Å	9.8967	9.8923	9.9028
b, Å	10.3689	10.3397	10.3995
c, Å	11.0018	10.9857	11.0262
α , °	74.650	74.520	74.780
β , °	68.064	67.984	68.151
γ , °	67.257	67.335	67.117
Spatial group	P	P	P
Syngony	triclinic	triclinic	triclinic

Based on the XRD data, it is possible to judge the identity of their crystal structures. Furthermore, based on the literature data²⁰, it can be concluded that the synthesized compounds XXIX and XXXI are centrosymmetric binuclear complexes of neodymium and cerium cations with two mebikar molecules (connected

by the center of symmetry), bidentate nitrate anions and two water molecules. The general formula of these complexes is $[M(C_8H_{14}N_4O_2)(H_2O)_2(NO_3)_3]_2$, where M represents Ce, Pr, or Nd. The decrease in the parameters of the crystal lattice is associated with a natural decrease in the radii of cations in a number of rare earth metals due to lanthanide compression.

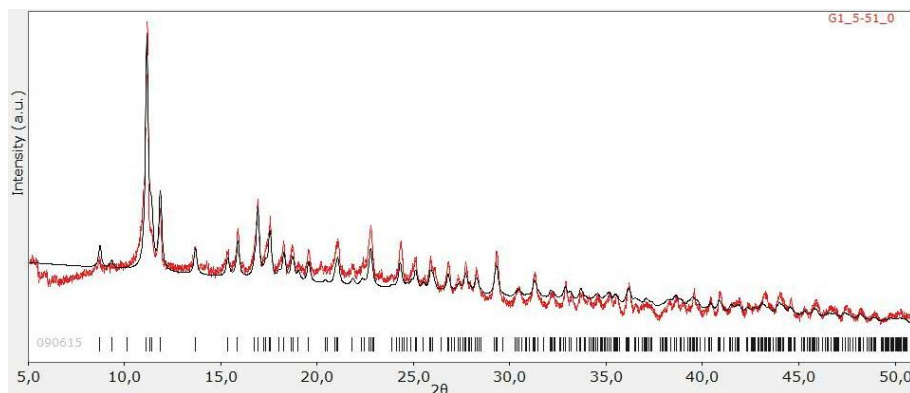


Fig. 2. Diffractogram of the comparison sample PrMb (black); Complex XXXI NdMb (red)

For complex compounds of mebikar with terbium and dysprosium (XXXIII and XXXIV, respectively), a complete correspondence of the diffraction patterns of the powder diffraction of the tested samples was observed with that calculated based on the structural model of the sample comparing the complex compound of gadolinium nitrate with mebikar CCDC No. 1450653.

Table 6

Parameters of crystal lattices, synthesized complexes XXXIII and XXXIV, and the GdMb comparison sample

Compound	Comparison sample GdMb	Sample TbMb (XXXIII)	Sample DyMb (XXXIV)
Unit Cell Parameters			
a, Å	10.3861	10.3523	10.3236
b, Å	10.8047	10.7834	10.7495
c, Å	21.2707	21.2502	21.2364
β , °	128.413	128.324	128.256
Spatial group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
Syngony	monoclinic	monoclinic	monoclinic

From the information provided, it appears that Table 6 shows the characteristics of the elementary cells of the synthesized complexes XXXIII and XXXIV and the comparison sample. Comparative analysis of diffractograms of the comparison sample and mebikar complexes with terbium and dysprosium nitrates suggests the identity of their crystal structures. According to literature data¹⁸, it can be concluded that the synthesized compounds are centrosymmetric binuclear complexes of terbium and dysprosium cations with two mebikar molecules (connected by a center of symmetry), bidentate nitrate anions, and two water molecules. The

general formula of these complexes is $[M(C_8H_{14}N_4O_2)(H_2O)(NO_3)_3]_2 \cdot H_2O$, where M represents Gd, Tb, or Dy.

A change in the structure of complex mebikar compounds in a number of rare-earth elements, such as an increase in their symmetry, and a decrease in the parameters of the crystal lattice, may be associated with a decrease in the radius of trivalent REE cations.

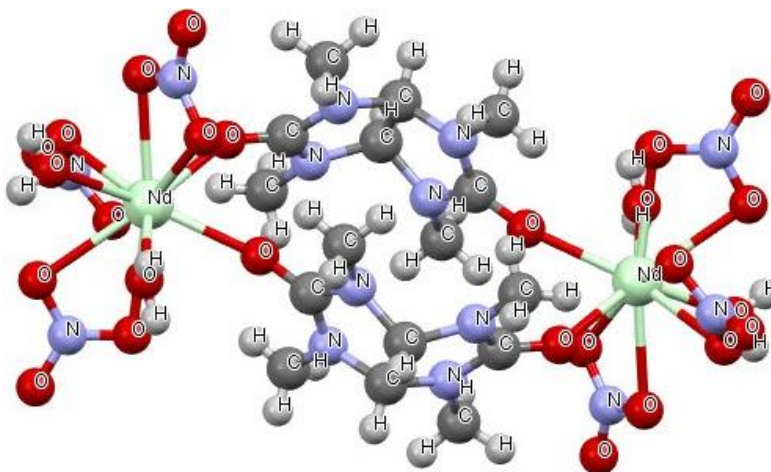


Fig. 3. Structure of the synthesized complex of neodymium nitrate with mebikar

Powder X-ray diffraction was also carried out for complex compounds of lanthanum, erbium and ytterbium with mebikar, however, the diffractograms obtained did not coincide with the diffractograms of compounds already described in the literature, which indicates their different structure from the complexes already described.

Conclusions

As a result of this work, 32 new complex compounds of N-methylglycolurils (N-monomethylglycoluryl, 2,4-N-dimethylglycoluryl, 2,6-N-dimethylglycoluryl, 2,4,6,8-N-tetramethylglycoluryl) were synthesized with hydrates of nitrates of trivalent rare earth elements (lanthanum, cerium, praseodymium, neodymium, samarium, terbium, dysprosium, erbium, ytterbium). The results of IR spectroscopy indicate that the methylglycolurils in these complexes can act as bidentate, chelating, and bridging ligands, coordinating through carbonyl groups of urea fragments. The crystal structures were proved, and the parameters of the elementary cells of complex compounds of mebikar with cerium, neodymium, terbium, and dysprosium were determined. The ratio of metal and ligand in the complexes is ~1:1, respectively. It is established that the obtained complexes are unstable in solution and disintegrate into initial substances.

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