ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 10, pp. 723–737. © Pleiades Publishing, Ltd., 2013.
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Synthesis and Molecular and Crystal Structures of Binuclear Complexes of Sm(III), Eu(III), Gd(III), Tb(III), and Dy(III) Nitrates with 4,4,10,10-Tetramethyl-1,3,7,9-Tetraazospiro[5.5]undecane-2,8-Dione

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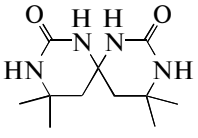
Received February 22, 2013

Abstract—Binuclear complexes of Sm(III), Eu(III), Gd(III), Tb(III), and Dy(III) nitrates with 4,4,10,10-tetramethyl-1,3,7,9-tetraazospiro[5.5]undecane-2,8-dione ($C_{11}H_{20}N_4O_2$, SC)—$[Sm(NO_3)_3(SC)(H_2O)]_2$ (**I**), $[Eu(NO_3)_3(SC)(H_2O)]_2$ (**II**), $[Gd(NO_3)_2(SC)(H_2O)_3)]_2(NO_3)_2$ (**III**), $[Tb(NO_3)_3(SC)(H_2O)]_2$ (**IV**), $[Dy(NO_3)_3(SC)(H_2O)]_2$ (**V**), are synthesized, and their X-ray diffraction analyses are carried out. The crystals of complexes **I**–**V** are monoclinic: space group $P2_1/n$ for **III** and $P2_1/c$ for **I**, **II**, **IV**, and **V**. In centrosymmetric coordination complexes **II**, **III**, **IV**, and **V**, the Ln atoms are coordinated by two O(1) and O(2) atoms of two molecules of the SC ligands bound by a symmetry procedure $(1 - x, -y, 1 - z)$, three bidentate nitrate anions, and a water molecule. The coordination numbers of the metal atoms are equal to 9, and the coordination polyhedra are considerably distorted three-capped trigonal prisms, whose bases include the O(1), O(2), O(12) and O(3), O(7), O(9) atoms. The dihedral angle between the bases of the prism is 18°, and that between the mean planes of the side faces is 55°–71° for **I**, 17° and 55°–71° for **II**, 16° and 55°–70° for **IV**, and 16° and 55°–70° for **V**. The Sm...Sm distance in complex **I** is 9.44 Å, Eu...Eu in **II** is 9.42 Å, Tb...Tb in **IV** is 9.36 Å, and Dy...Dy in **V** is 9.36 Å. The gadolinium atom in complex **III** is coordinated by two oxygen atoms of two ligand molecules bound by a symmetry procedure $(-x, -y + 1, -z + 1)$, two bidentate nitrate anions, and three water molecules. One of the nitro groups in compound **III** is localized in the external coordination sphere of the metal. The coordination number of gadolinium is 9, and the coordination polyhedron is a significantly distorted three-capped trigonal prism, whose base includes the O(1), O(2), O(7) and O(4), O(5), O(9) atoms. The dihedral angle between the bases of the prism is 22.8°, and that between the mean planes of the side faces is 53°–72°. The Gd...Gd distance in complex **III** is 9.17 Å.

DOI: 10.1134/S1070328413100047

INTRODUCTION

Coordination compounds of rare-earth metals with ligands of the class of cyclic spirobisureas remain almost unstudied to date. One of these ligands is 4,4,10,10-tetramethyl-1,3,7,9-tetraazospiro[5.5]undecane-2,8-dione, or spirocarbone ($C_{11}H_{20}N_4O_2$, **SC**).



This ligand as a urea precursor has a series of valuable biological properties: a low toxicity level, LD_{50} = 3000 mg/kg of the weight of white mice [1], membranotropism [2], and the ability to penetrate through and to be accumulated in mice and human cytoplasm of leucosis L1210 and CEM-T4 cell lines, respectively [3]. This ligand also favors an increase in the amount of protein and a decrease in starchiness in oats grains [4]. The efficiency of application of spirocarbone as a stimulator of callus formation in *Forsythia europaea* and root formation in *Philadelphus coronaries* [5] was proved, and the efficiency of using spirocarbon as a stimulator of growth and development in sheep breeding was shown [6]. Therefore, the synthesis and study of coordination compounds of this ligand as a hard Lewis base will clarify the chemistry of the interaction of Sk with rare-earth metal atoms in more detail.

The purpose of this work is to synthesize coordination compounds of Sm(III), Eu(III), Gd(III), Tb(III), and Dy(III) nitrates, being hard Lewis acids, with spirocarbone and water molecules, namely, $[Sm(NO_3)_3(SC)(H_2O)]_2$ (**I**), $[Eu(NO_3)_3(SC)(H_2O)]_2$ (**II**), $[Gd(NO_3)_2(SC)(H_2O)_3)]_2(NO_3)_2$ (**III**), $[Tb(NO_3)_3(SC)(H_2O)]_2$ (**IV**), and

Table 1. Elemental analysis results for complexes **I**–**V**

Compound (empirical formula)	Content (found/calculated), %		
	C	H	N
I ($C_{22}H_{44}N_{14}O_{24}Sm_2$)	22.19/22.22	3.71/3.73	16.48/16.49
II ($C_{22}H_{44}N_{14}O_{24}Eu_2$)	22.11/22.16	3.67/3.72	16.41/16.44
III ($C_{22}H_{52}N_{14}O_{28}Gd_2$)	20.52/20.72	4.09/4.11	15.36/15.38
IV ($C_{22}H_{44}N_{14}O_{24}Tb_2$)	21.89/21.90	3.66/3.68	16.24/16.25
V ($C_{22}H_{44}N_{14}O_{24}Dy_2$)	21.59/21.77	3.58/3.65	16.13/16.16

$[Dy(NO_3)_3(SC)(H_2O)]_2$ (**V**), and to determine their structures.

EXPERIMENTAL

Synthesis of I. The reagents were $Sm(NO_3)_3 \cdot 6H_2O$ (reagent grade), SC obtained according to a described procedure [7], and acetone (special purity grade). A weighed sample of samarium nitrate (1.72 g, 3.8 mmol) was dissolved in acetone (20 mL), spirocarbon (0.82 g, 3.1 mmol) was introduced, and the mixture was magnetically stirred for 5–10 min. The obtained solution was filtered and left to stand in a closed vessel for several days to form crystals. Isolated pale orange crystals were filtered off, washed with acetone, and dried in air. The yield was ~62% (based on the ligand).

Synthesis of II. The reagents were $Eu(NO_3)_3 \cdot 6H_2O$ (reagent grade), SC obtained using a described procedure [7], and acetone (special purity grade). A weighed sample of europium nitrate (3.17 g, 7.1 mmol) was dissolved in acetone (20 mL), and spirocarbon (1.8 g, 7 mmol) was added. The reaction mixture was magnetically stirred for 5–10 min. The obtained solution was filtered and left to stand in an open vessel for several days to form crystals. Isolated pale yellow crystals were filtered off, washed with acetone, and dried in air. The yield was ~87% (based on the ligand).

Synthesis of III. The reagents were $Gd(NO_3)_3 \cdot 6H_2O$ (reagent grade), SC obtained according to a described procedure [7], and acetone (special purity grade). A weighed sample of gadolinium nitrate (2.21 g, 4.9 mmol) was dissolved in acetone (20 mL), and then spirocarbon (1.10 g, 4.3 mmol) was added. The reaction mixture was magnetically stirred for 5–10 min. The obtained solution was filtered and left to stand in an open vessel for several days to form crystals. Isolated white crystals were filtered off, washed with acetone, and dried in air. The yield was ~79% (based on the ligand).

Synthesis of IV. The reagents were $Tb(NO_3)_3 \cdot 5H_2O$ (reagent grade), SC obtained according to a described procedure [7], and acetone (special purity grade). A weighed sample of terbium nitrate (3.04 g, 6.9 mmol) was dissolved in acetone (20 mL), and then spirocarbon (1.45 g, 5.6 mmol) was added. The reaction mixture was magnetically stirred for 5–10 min. The obtained solution was filtered and left to stand in an open vessel for several days to form crystals. Isolated pale pinkish crystals were filtered off, washed with acetone, and dried in air. The yield was ~98% (based on the ligand).

Synthesis of V. The reagents were $Dy(NO_3)_3 \cdot 5H_2O$ (reagent grade), SC obtained according to a described procedure [7], and acetone (special purity grade). A weighed sample of dysprosium nitrate (2.37 g, 5.4 mmol) was dissolved in acetone (20 mL), and then spirocarbon (1.06 g, 4.1 mmol) was added. The reaction mixture was magnetically stirred for 5–10 min. The obtained solution was filtered and left to stand in an open vessel for several days to form crystals. Isolated pale greenish crystals were filtered off, washed with acetone, and dried in air. The yield was ~64% (based on the ligand).

The elemental analysis results for complexes **I**–**V** are presented in Table 1. Analyses to C, H, and N in complexes **I**–**V** were performed on an EA-3000 elemental analyzer (EuroVector, Italy).

The IR spectra of SC and synthesized binuclear complexes **I**–**V** were recorded on a Spectrum ONE FT-IR spectrometer (PerkinElmer) in a range of 400–4000 cm^{-1} (KBr pellets).

X-ray diffraction analysis. An experimental material for crystals **I**–**V** was obtained on an Xcalibur-3 automated four-circle diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å) at 293(2) K. The structures were solved by a direct method using the SHELX-97 program package [8]. Positions of hydrogen atoms were calculated geometrically and refined by the riding model with $U_{iso} = nU_{equiv}$ of the bearing atom ($n = 1.5$ for water and methyl groups, $n = 1.2$ for other hydrogen atoms). The structures were refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms for F^2.

The main experimental characteristics and unit cell parameters are given in Table 2.

The coordinates of atoms and other parameters of structures **I**–**V** were deposited with the Cambridge Crystallographic Data Centre (nos. 924470 (**I**), 924469 (**II**), 924472 (**III**), 924473 (**IV**), and 924474 (**V**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DICUSSION

The IR spectra of compounds **I**–**V** and spirocarbone are presented in Table 3. All synthesized compounds are characterized by the shift of the band corresponding to the ν(C=O) stretching vibrations (amide I) by 7–12 cm^{-1} to the far range because of the coordination of SC molecules and the shift of the bands corresponding to the ν_s(N–H) and ν_{as}(N–H) and vibrations to the short range, which is typical of the amino groups at coordinated carbonyl [9]. The IR spectra of complexes **I**–**V** contain the ν_{s+as}(HOH) absorption bands of water and a set of absorption bands of the coordinated Sk ligand. The free nitrate anion, being planar and related to the D_{3h} point group, has four different ground vibrational frequencies: from symmetrical stretching vibrations ν_s(NO) ≈ 1050–1060 cm^{-1}, unsymmetrical doubly degenerate stretching vibrations ν_e(NO) ≈ 1350–1400 cm^{-1}, and two frequencies of bending vibrations $\delta(NO_3)$ ≈ 810–840 and ~710–730 cm^{-1}. Only three frequencies are usually active in the IR spectrum: ν_e(NO) and two $\delta(NO_3)$ [10]. For the coordination of the nitrate ion, its symmetry can decrease to C_s and C_{2v}. As a result, six intense lines appear in the IR spectrum [11]: the full symmetrical vibration at 970–1040 cm^{-1}, stretching antisymmetrical vibration split into two intense lines at 1550–1410 and 1290–1250 cm^{-1}, nonplanar vibration at 830–800 cm^{-1}, and planar bending vibration appeared as two bands at 780–700 and ~680 cm^{-1} [10]. The IR spectrum of compound **III** contains bands at 1386 and 1056 cm^{-1}. This asserts that some nitrate anions are not coordinated and are localized in the external sphere of the complex. These bands are absent from the spectra of compounds **I**, **II**, **IV**, and **V** and, hence, in these compounds the nitrate anions are coordinated according to the bidentate-chelating mode and are localized in the internal sphere of the complexes.

In centrosymmetric complexes **I**, **II**, **IV**, and **V**, the lanthanide atoms are coordinated by two O(1) and O(2) atoms of two spirocarbone molecules bound by the symmetry procedure ($1 - x$, $-y$, $1 - z$), three bidentate nitrate anions, and one water molecule. The coordination numbers of the metal atoms are 9, and the coordination polyhedra are significantly distorted three-capped trigonal prisms, whose bases include the O(1), O(2), O(12) and O(3), O(7), O(9) atoms. For compound **I**, the dihedral angle between the bases of the prism is 18°, that between the mean planes of the side faces is 55°–71°, and the Sm...Sm 9.44 Å distance is 9.44 Å. The six-membered heterocycles of compound **I** are in the half-chair conformation with the deviation of the C(3) and C(9) atoms from the planes of other atoms of the cycle by –0.544(16) and –0.507(16) Å, respectively. The shortened intramolecular contacts H(3b)...H(10a) 2.24 and H(5a)...H(9a) 2.29 Å (doubled van der Waals radius is 2.32 Å [12]) appear in this conformation (Table 4, Fig. 1). For complex **II**, the dihedral angle between the bases of the prism is 17°, that between the mean planes of the side faces is 55°–71°, and the Eu...Eu 9.42 Å distance is 9.42 Å. The six-membered heterocycles in complex **II** exist in the half-chair conformation with the deviation of the C(3) and C(9) atoms from the planes of other atoms of the cycle by –0.513(4) and –0.510(4) Å, respectively. The shortened intramolecular contacts are H(3b)...H(10a) 2.22 and H(5a)...H(9a) 2.17 Å (Table 5, Fig. 1). For complex **IV**, the dihedral angle between the bases of the prism is 16°, that between the mean planes of the side faces is 55°–70°, and the Tb...Tb distance is 9.36 Å. The six-membered heterocycles in compound **IV** are in the half-chair conformation with the deviation of the C(3) and C(9) atoms from the planes of other atoms of the cycle by –0.510(8) and –0.507(9) Å, respectively. The shortened intramolecular contacts are H(3b)...H(10a) 2.18 and H(5a)...H(9a) 2.20 Å (Table 6, Fig. 1). For complex **V**, the dihedral angle between the bases of the prism is 16°, that between the mean planes of the side faces is 55°–70°, and the Dy...Dy distance is 9.36 Å The six-membered heterocycles in complex **V** are in the half-chair conformation with the deviation of the C(3) and C(9) atoms from the planes of other atoms of the cycle by –0.49(2) and –0.52(2) Å, respectively. The shortened intramolecular contacts are H(3b)...H(10a) 2.03 and H(5a)...H(9a) 2.16 Å (Table 7, Fig. 1).

Table 2. Main crystallographic experimental data for structures **I**–**V**

Parameter	Values				
Empirical formula	$C_{22}H_{44}N_{14}O_{24}Sm_2$	$C_{22}H_{44}N_{14}O_{24}Eu_2$	$C_{22}H_{52}N_{14}O_{28}Gd_2$	$C_{22}H_{44}N_{14}O_{24}Tb_2$	$C_{22}H_{44}N_{14}O_{24}Dy_2$
Molecular weight	1189.41	1192.63	1275.28	1206.55	1213.71
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
Cell parameters:					
a, Å	6.5018(7)	6.48805(16)	6.4705(7)	6.4688(3)	6.4519(8)
b, Å	23.265(2)	23.2586(4)	15.6158(17)	23.2498(10)	23.255(2)
c, Å	13.9162(16)	13.8726(2)	21.737(2)	13.8122(5)	13.7905(15)
β, deg	98.976(11)	98.8220(19)	94.697(10)	98.583(4)	98.481(11)
V, Å^3	2079.2(4)	2068.65(7)	2189.0(4)	2054.08(16)	2046.5(4)
Z	2	2	2	2	2
ρ_{calcd}, g/cm^3	1.90	1.92	1.94	1.951	1.970
$\mu(MoK_\alpha)$, mm^{-1}	2.90	3.107	3.11	3.518	3.727
$F(000)$	1180	1184	1268	1192	1196
Crystal size, mm	0.04 × 0.06 × 0.24	0.03 × 0.05 × 0.31	0.03 × 0.05 × 0.20	0.03 × 0.04 × 0.19	0.15 × 0.22 × 0.35
θ Range, deg	2.96–5.00	2.97–32.53	3.11–28.45	2.98–29.00	3.02–25.00
$2\theta_{max}$, deg	50.00	65.06	56.90	58.00	50.00
Reflection index ranges	$-7 \le h \le 7$, $-27 \le k \le 15$, $-12 \le l \le 16$	$-9 \le h \le 9$, $-34 \le k \le 34$, $-20 \le l \le 20$	$-8 \le h \le 8$, $-20 \le k \le 20$, $-27 \le l \le 28$	$-8 \le h \le 8$, $-31 \le k \le 29$, $-18 \le l \le 18$	$-7 \le h \le 7$, $-27 \le k \le 27$, $-15 \le l \le 16$
Number of measured reflections	6800	44024	27758	19305	15517
Number of independent reflections (R_{int})	3672 (0.0943)	7072 (0.0629)	5052 (0.2168)	4865 (0.0847)	3587 (0.1273)
Number of reflections with $I > 2\sigma(I)$	2010	5044	2581	3040	2273
Number of refined variables	284	285	302	285	285
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0656$, $wR_2 = 0.1227$	$R_1 = 0.0330$, $wR_2 = 0.0505$	$R_1 = 0.0657$, $wR_2 = 0.0704$	$R_1 = 0.0462$, $wR_2 = 0.0588$	$R_1 = 0.0660$, $wR_2 = 0.1309$
R factor for all reflections	$R_1 = 0.1456$, $wR_2 = 0.1467$	$R_1 = 0.0654$, $wR_2 = 0.0568$	$R_1 = 0.1722$, $wR_2 = 0.0921$	$R_1 = 0.1033$, $wR_2 = 0.0706$	$R_1 = 0.1204$, $wR_2 = 0.1491$
Goodness-of-fit for F^2	0.952	0.975	0.969	0.998	1.066
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e Å^{-3}	1.446 and −0.807	1.044 and −0.580	2.096 and −1.327	0.951 and −1.060	1.617 and −1.287

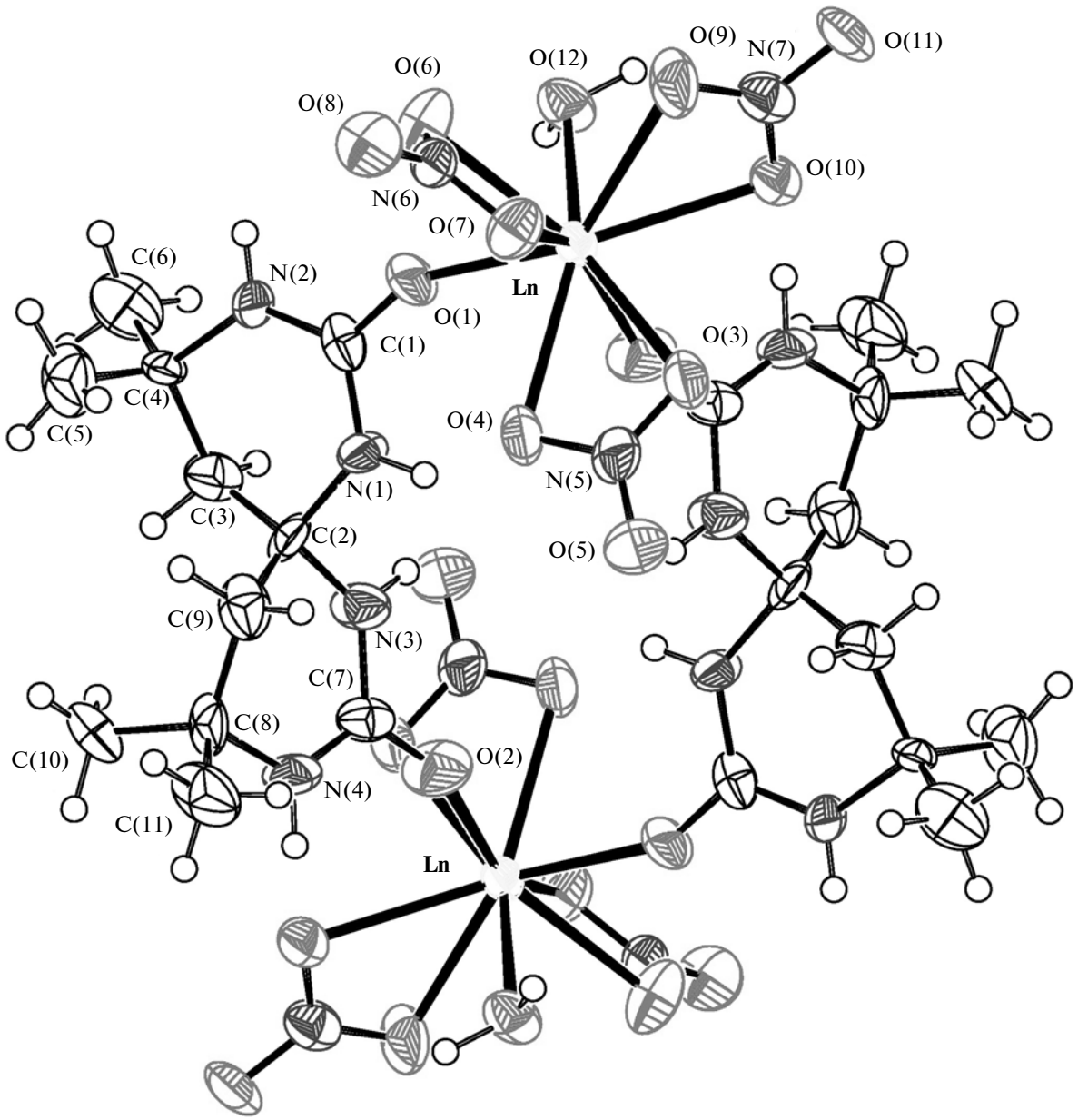


Fig. 1. Structures of compounds **I**, **II**, **IV**, and **V**.

Complexes **I**, **II**, **IV**, and **V** include intermolecular hydrogen bonds N(1)–H(1)...O(4). The complexes and coordinated nitrate anions are bound into layers parallel to the (0 1 0) plane by multiple intermolecular hydrogen bonds (Table 8, Fig. 2).

The crystals of compound **III** are isostructural to the earlier studied neodymium [13] and yttrium [14] crystals. The complex exists in the partial position in the inversion center. The gadolinium ion is coordinated by two oxygen atoms of two spirocarbone molecules bound by the symmetry procedure ($-x$, $-y + 1$, $-z + 1$), two bidentate nitrate anions, and three water molecules. One of the nitro groups of the compound exists in the external coordination sphere of the metal. The coordination number of gadolinium is 9, and the coordination polyhedron is a significantly distorted three-capped trigonal prism, whose base is formed by the O(1), O(2), O(7) and O(4), O(5), O(9) atoms. The dihedral angle between the bases of the prism is 22.8°, that between the mean planes of the side faces is 53°–72°, and the Gd...Gd distance is 9.17 Å.

Two six-memebered cycles of spirocarbone **III** have different conformations. The cycle containing the N(1) atom exists in the half-chair conformation

Table 3. Band assignment in the IR spectra of complexes **I**–**V** and spirocarbon

Assignment	SC	I	II	III	IV	V
	ν, cm^{-1}					
ν_{s+as}(HOH)	3416	3929, 3466	3930, 3467	3927, 3471	3931, 3472	3933, 3465
ν_{s+as}(NH)	3335, 3293, 3218	3392, 3358, 3180	3392, 3357, 3171	3392, 3357, 3170	3392, 3356, 3172	3393, 3356
$\nu_s(-CH_2-)$	3075	3007, 3015	3015, 3007	3015, 3007	3014, 3008	3009
ν_{s+as}(Me)	2991, 2978	2976	2976	2976	2976	2976
$\nu_{as}(-CH_2-)$	2932	2937	2937	2938	2938	2933
ν(C=O, amide I)	1653	1642	1646	1644	1645	1641
$\nu_3(E', NO_3^-)$		1516	1516	1516	1519	1517
δ(NH)	1487	1483	1484	1485	1486	1486
$\delta_s(-CH_2-)$	1447	1449	1448	1449, 1435	1448	1449
ν(C–N)	1418	1403	1403	1403	1403	1404
ν_{as}(N=O)				1386		
$\delta_s(CMe_2)$	1385, 1367, 1335	1372, 1356, 1345	1372, 1357, 1346	1373, 1357, 1347	1373, 1358, 1348	1373, 1359, 1349
ν(CO) + ν(NH) + δ(NH) (amide III)	1288	1304, 1276	1305, 1276	1306, 1276	1307, 1276	1308, 1276
$\omega(-CH_2-) + \tau(-CH_2-)$	1254	1256, 1222	1257, 1222	1257, 1222	1257, 1222	1257, 1222
$\delta(C_{spiro} + C_{quatern})$	1209, 1192	1203, 1189	1203, 1189	1203, 1190	1203, 1190	1203, 1190
δ_s(CCH)		1162, 1141	1162, 1141	1162, 1141	1162, 1141	1163, 1141
δ(NH)	1118	1110	1110	1110	1110	1111
δ(rings)	1093	1098	1098	1098	1098	1098
ν_s(NO)				1056		
$\nu_1(A_1', NO_3)$		1039	1040	1041	1041	1041
δ(NH)	1015	1017	1017	1017	1017	1018
γ(rings) + out-of-plane vibrations						
δ(CH)rings + $\rho(CH_2)$	978, 955, 928, 908	993, 984, 943, 913	993, 983, 943, 913	993, 983, 943, 913	993, 984, 943, 913	994, 985, 944, 914
ρ(Me)	824	821	821	822	822	822
$\nu_2(NO_3)$		814	814	813	813	813
ω(NH)	764	750	750	751	751	751
$\omega(Met \leftarrow OH_2)$		732	732	732	733	733
$\nu_4(NO_3)$		705	706	706	706	706
$\rho(Met \leftarrow OH_2)$		646	667, 649	667, 649	651	652
δ(amide III)	593	613, 592	613, 592	614, 592	614, 593	615, 593
$\nu_{s+as}(Met \leftarrow O{=}C)$		543, 564[13]	564, 545	564, 545	564, 546	564, 547
δ(C–N–C)	491	500	500	500	500	501
δ_γ(skeletal vibrations of rings)	467, 457	466, 456	468, 456	469, 456	469, 456, 421, 411	457

Table 4. Bond lengths and bond angles in structure **I***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Sm(1)–O(1)	2.283(8)	O(2)–Sm(1)[1]	2.274(9)	O(11)–N(7)	1.249(13)
Sm(1)–O(2)[1]	2.274(9)	O(2)–C(7)	1.271(15)	N(1)–C(1)	1.344(16)
Sm(1)–O(3)	2.479(9)	O(3)–N(5)	1.254(13)	N(1)–C(2)	1.473(16)
Sm(1)–O(4)	2.524(9)	O(4)–N(5)	1.267(13)	N(2)–C(1)	1.314(15)
Sm(1)–O(6)	2.563(9)	O(5)–N(5)	1.237(13)	N(2)–C(4)	1.471(14)
Sm(1)–O(7)	2.526(8)	O(6)–N(6)	1.240(13)	N(3)–C(2)	1.406(14)
Sm(1)–O(9)	2.532(10)	O(7)–N(6)	1.280(13)	N(3)–C(7)	1.370(15)
Sm(1)–O(10)	2.535(8)	O(8)–N(6)	1.212(12)	N(4)–C(7)	1.334(16)
Sm(1)–O(12)	2.416(7)	O(9)–N(7)	1.243(14)	N(4)–C(8)	1.432(15)
O(1)–C(1)	1.259(14)	O(10)–N(7)	1.279(12)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Sm(1)O(3)	125.6(3)	O(7)Sm(1)O(10)	109.7(3)	O(8)N(6)O(6)	122.7(12)
O(1)Sm(1)O(4)	75.2(3)	O(9)Sm(1)O(6)	73.4(3)	O(8)N(6)O(7)	118.1(13)
O(1)Sm(1)O(6)	71.7(3)	O(9)Sm(1)O(10)	50.8(3)	O(9)N(7)O(10)	119.9(12)
O(1)Sm(1)O(7)	102.1(3)	O(10)Sm(1)O(6)	123.2(3)	O(9)N(7)O(11)	121.3(13)
O(1)Sm(1)O(9)	138.5(3)	O(12)Sm(1)O(3)	149.2(3)	O(11)N(7)O(10)	118.8(12)
O(1)Sm(1)O(10)	146.6(3)	O(12)Sm(1)O(4)	148.1(3)	O(1)C(1)N(1)	106.1(11)
O(1)Sm(1)O(12)	76.2(3)	O(12)Sm(1)O(6)	83.7(3)	O(1)C(1)N(2)	109.0(12)
O(2)[i]Sm(1)O(1)	81.5(3)	O(12)Sm(1)O(7)	128.7(3)	N(2)C(1)N(1)	105.7(10)
O(2)[i]Sm(1)O(3)	78.7(3)	O(12)Sm(1)O(9)	78.3(3)	N(1)C(2)C(3)	103.3(11)
O(2)[i]Sm(1)O(4)	77.7(3)	O(12)Sm(1)O(10)	76.3(3)	N(1)C(2)C(9)	108.1(12)
O(2)[i]Sm(1)O(6)	152.6(3)	C(1)O(1)Sm(1)	153.0(9)	N(3)C(2)N(1)	107.3(10)
O(2)[i]Sm(1)O(7)	146.8(3)	C(7)O(2)Sm(1)[i]	156.6(9)	N(3)C(2)C(3)	108.3(11)
O(2)[i]Sm(1)O(9)	127.8(3)	N(5)O(3)Sm(1)	96.4(8)	N(3)C(2)C(9)	109.0(11)
O(2)[i]Sm(1)O(10)	77.3(3)	N(5)O(4)Sm(1)	93.9(7)	N(2)C(4)C(3)	120.1(14)
O(2)[i]Sm(1)O(12)	84.4(3)	N(6)O(6)Sm(1)	97.2(8)	N(2)C(4)C(5)	122.4(13)
O(3)Sm(1)O(4)	51.2(3)	N(6)O(7)Sm(1)	97.9(7)	N(2)C(4)C(6)	117.4(14)
O(3)Sm(1)O(6)	121.7(3)	N(7)O(9)Sm(1)	127.4(11)	O(2)C(7)N(3)	108.2(11)
O(3)Sm(1)O(7)	72.4(3)	N(7)O(10)Sm(1)	127.7(12)	O(2)C(7)N(4)	108.6(12)
O(3)Sm(1)O(9)	91.9(3)	C(1)N(1)C(2)	125.7(12)	N(4)C(7)N(3)	105.9(12)
O(3)Sm(1)O(10)	75.0(3)	C(1)N(2)C(4)	118.2(12)	N(4)C(8)C(9)	114.8(12)
O(4)Sm(1)O(6)	100.3(3)	C(7)N(3)C(2)	120.3(13)	N(4)C(8)C(10)	109.6(12)
O(4)Sm(1)O(7)	71.6(3)	C(7)N(4)C(8)	121.5(13)	N(4)C(8)C(11)	109.4(12)
O(4)Sm(1)O(9)	133.3(3)	O(3)N(5)O(4)	115.1(11)		
O(4)Sm(1)O(10)	123.9(3)	O(5)N(5)O(3)	124.5(12)		
O(7)Sm(1)O(6)	49.4(3)	O(5)N(5)O(4)	120.3(12)		
O(7)Sm(1)O(9)	70.1(3)	O(6)N(6)O(7)	119.2(12)		

* Symmetry procedure: [i] $1-x, 1-y, 1-z$.

Table 5. Bond lengths and bond angles in structure **II***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Eu(1)–O(1)	2.2911(19)	O(2)–Eu(1)^{i}	2.2641(19)	O(11)–N(7)	1.234(3)
Eu(1)–O(2)^{i}	2.2641(19)	O(2)–C(7)	1.264(3)	N(1)–C(1)	1.333(3)
Eu(1)–O(3)	2.476(2)	O(3)–N(5)	1.266(3)	N(1)–C(2)	1.462(3)
Eu(1)–O(4)	2.525(2)	O(4)–N(5)	1.266(3)	N(2)–C(1)	1.315(3)
Eu(1)–O(6)	2.562(2)	O(5)–N(5)	1.217(3)	N(2)–C(4)	1.466(3)
Eu(1)–O(7)	2.510(2)	O(6)–N(6)	1.232(3)	N(3)–C(2)	1.451(3)
Eu(1)–O(9)	2.515(2)	O(7)–N(6)	1.267(3)	N(3)–C(7)	1.333(3)
Eu(1)–O(10)	2.525(2)	O(8)–N(6)	1.225(3)	N(4)–C(7)	1.316(3)
Eu(1)–O(12)	2.419(2)	O(9)–N(7)	1.258(3)	N(4)–C(8)	1.464(4)
O(1)–C(1)	1.261(3)	O(10)–N(7)	1.245(3)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Eu(1)O(3)	126.28(7)	O(9)Eu(1)O(6)	74.34(8)	O(1)C(1)N(2)	120.2(3)
O(1)Eu(1)O(4)	76.10(7)	O(9)Eu(1)O(10)	50.17(7)	N(2)C(1)N(1)	119.6(2)
O(1)Eu(1)O(6)	71.08(8)	O(10)Eu(1)O(4)	123.62(7)	N(1)C(2)C(3)	107.1(2)
O(1)Eu(1)O(7)	101.70(8)	O(10)Eu(1)O(6)	123.37(8)	N(1)C(2)C(9)	107.0(2)
O(1)Eu(1)O(9)	138.62(8)	O(12)Eu(1)O(3)	149.28(7)	N(3)C(2)N(1)	107.5(2)
O(1)Eu(1)O(10)	146.29(7)	C(7)O(2)Eu(1)^{1}	156.9(2)	N(3)C(2)C(3)	106.5(2)
O(1)Eu(1)O(12)	75.63(7)	N(5)O(3)Eu(1)	97.23(17)	N(3)C(2)C(9)	107.6(2)
O(2)^{1}Eu(1)O(1)	81.88(8)	N(5)O(4)Eu(1)	94.86(16)	N(2)C(4)C(3)	107.5(2)
O(2)^{1}Eu(1)O(3)	78.51(8)	N(6)O(6)Eu(1)	96.24(17)	O(12)Eu(1)O(4)	148.38(7)
O(2)^{1}Eu(1)O(4)	77.49(7)	N(6)O(7)Eu(1)	97.85(16)	O(12)Eu(1)O(6)	83.20(7)
O(2)^{1}Eu(1)O(6)	152.38(8)	N(7)O(9)Eu(1)	96.37(16)	O(12)Eu(1)O(7)	128.34(7)
O(2)^{1}Eu(1)O(7)	146.74(7)	N(7)O(10)Eu(1)	96.24(16)	O(12)Eu(1)O(9)	78.41(8)
O(2)^{1}Eu(1)O(9)	127.11(7)	C(1)N(1)C(2)	126.9(2)	O(12)Eu(1)O(10)	76.35(7)
O(2)^{1}Eu(1)O(10)	77.25(7)	C(1)N(2)C(4)	126.2(2)	C(1)O(1)Eu(1)	151.76(19)
O(2)^{1}Eu(1)O(12)	84.78(7)	C(7)N(3)C(2)	126.5(3)	N(2)C(4)C(5)	109.1(2)
O(3)Eu(1)O(4)	51.03(7)	C(7)N(4)C(8)	125.7(2)	N(2)C(4)C(6)	108.0(2)
O(3)Eu(1)O(6)	122.13(8)	O(3)N(5)O(4)	116.7(2)	O(2)C(7)N(3)	118.4(3)
O(3)Eu(1)O(7)	72.83(7)	O(5)N(5)O(3)	121.5(3)	O(2)C(7)N(4)	121.4(3)
O(3)Eu(1)O(9)	91.34(8)	O(5)N(5)O(4)	121.8(3)	N(4)C(7)N(3)	120.3(3)
O(3)Eu(1)O(10)	74.92(7)	O(6)N(6)O(7)	116.0(2)	N(4)C(8)C(9)	107.3(2)
O(4)Eu(1)O(6)	100.70(7)	O(8)N(6)O(6)	123.0(3)	N(4)C(8)C(10)	109.6(3)
O(7)Eu(1)O(4)	71.52(7)	O(8)N(6)O(7)	121.0(3)	N(4)C(8)C(11)	107.1(3)
O(7)Eu(1)O(6)	49.38(7)	O(10)N(7)O(9)	117.2(2)		
O(7)Eu(1)O(9)	70.78(8)	O(11)N(7)O(9)	120.9(3)		
O(7)Eu(1)O(10)	110.30(7)	O(11)N(7)O(10)	121.9(3)		
O(9)Eu(1)O(4)	133.04(8)	O(1)C(1)N(1)	120.1(3)		

* Symmetry procedure: ^{i} $1-x, 1-y, 1-z$.

Table 6. Bond lengths and bond angles in structure **IV***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Tb(1)–O(1)	2.267(4)	O(2)–Tb(1)^{i}	2.240(4)	O(11)–N(7)	1.234(5)
Tb(1)–O(2)^{i}	2.240(4)	O(2)–C(7)	1.248(7)	N(1)–C(1)	1.334(6)
Tb(1)–O(3)	2.442(4)	O(3)–N(5)	1.259(5)	N(1)–C(2)	1.455(6)
Tb(1)–O(4)	2.498(4)	O(4)–N(5)	1.262(6)	N(2)–C(1)	1.305(7)
Tb(1)–O(6)	2.531(4)	O(5)–N(5)	1.215(5)	N(2)–C(4)	1.457(6)
Tb(1)–O(7)	2.477(4)	O(6)–N(6)	1.239(6)	N(3)–C(2)	1.454(7)
Tb(1)–O(9)	2.480(4)	O(7)–N(6)	1.253(6)	N(3)–C(7)	1.329(6)
Tb(1)–O(10)	2.505(4)	O(8)–N(6)	1.224(6)	N(4)–C(7)	1.328(6)
Tb(1)–O(12)	2.384(3)	O(9)–N(7)	1.250(6)	N(4)–C(8)	1.457(7)
O(1)–C(1)	1.262(6)	O(10)–N(7)	1.251(6)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Tb(1)O(3)	127.13(13)	O(9)Tb(1)O(4)	132.49(15)	O(8)N(6)O(6)	122.4(6)
O(1)Tb(1)O(4)	76.47(13)	O(9)Tb(1)O(6)	73.83(15)	O(8)N(6)O(7)	121.9(6)
O(1)Tb(1)O(6)	71.01(15)	O(9)Tb(1)O(10)	50.72(14)	O(9)N(7)O(10)	117.2(5)
O(1)Tb(1)O(7)	101.17(15)	O(10)Tb(1)O(6)	123.18(14)	O(11)N(7)O(9)	121.3(5)
O(1)Tb(1)O(9)	138.57(15)	O(12)Tb(1)O(3)	149.47(14)	O(11)N(7)O(10)	121.5(5)
O(1)Tb(1)O(10)	146.10(15)	O(12)Tb(1)O(4)	148.60(13)	O(1)C(1)N(1)	120.0(6)
O(1)Tb(1)O(12)	75.40(14)	O(12)Tb(1)O(6)	82.07(14)	O(1)C(1)N(2)	121.1(5)
O(2)^{1}Tb(1)O(1)	81.95(15)	O(12)Tb(1)O(7)	128.06(14)	N(2)C(1)N(1)	118.9(5)
O(2)^{1}Tb(1)O(3)	79.08(15)	O(12)Tb(1)O(9)	78.72(15)	N(1)C(2)C(3)	106.9(4)
O(2)^{1}Tb(1)O(4)	77.28(14)	O(12)Tb(1)O(10)	76.60(13)	N(1)C(2)C(9)	107.7(5)
O(2)^{1}Tb(1)O(6)	152.24(16)	C(1)O(1)Tb(1)	151.6(4)	N(3)C(2)N(1)	107.7(5)
O(2)^{1}Tb(1)O(7)	146.51(14)	C(7)O(2)Tb(1)^{1}	156.2(4)	N(3)C(2)C(3)	106.5(5)
O(2)^{1}Tb(1)O(9)	127.49(15)	N(5)O(3)Tb(1)	97.4(3)	N(3)C(2)C(9)	107.4(5)
O(2)^{1}Tb(1)O(10)	77.03(14)	N(5)O(4)Tb(1)	94.7(3)	N(2)C(4)C(3)	107.0(5)
O(2)^{1}Tb(1)O(12)	85.22(14)	N(6)O(6)Tb(1)	95.9(4)	N(2)C(4)C(5)	109.4(5)
O(3)Tb(1)O(4)	51.37(13)	N(6)O(7)Tb(1)	98.1(4)	N(2)C(4)C(6)	108.0(5)
O(3)Tb(1)O(6)	122.34(15)	N(7)O(9)Tb(1)	96.6(3)	O(2)C(7)N(3)	119.8(6)
O(3)Tb(1)O(7)	72.54(14)	N(7)O(10)Tb(1)	95.4(3)	O(2)C(7)N(4)	121.2(5)
O(3)Tb(1)O(9)	90.27(15)	C(1)N(1)C(2)	127.2(5)	N(4)C(7)N(3)	119.0(6)
O(3)Tb(1)O(10)	74.46(13)	C(1)N(2)C(4)	127.3(5)	N(4)C(8)C(9)	107.6(5)
O(4)Tb(1)O(6)	101.65(14)	C(7)N(3)C(2)	127.6(5)	N(4)C(8)C(10)	110.1(6)
O(4)Tb(1)O(10)	123.21(14)	C(7)N(4)C(8)	125.9(5)	N(4)C(8)C(11)	107.5(5)
O(7)Tb(1)O(4)	71.25(13)	O(3)N(5)O(4)	116.4(5)		
O(7)Tb(1)O(6)	49.81(14)	O(5)N(5)O(3)	122.0(6)		
O(7)Tb(1)O(9)	70.83(14)	O(5)N(5)O(4)	121.7(5)		
O(7)Tb(1)O(10)	111.07(14)	O(6)N(6)O(7)	115.7(5)		

* Symmetry procedure: ^{i} $1-x, 1-y, 1-z$.

Table 7. Bond lengths and bond angles in structure **V***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Dy(1)–O(1)	2.261(8)	O(2)–Dy(1)[1]	2.214(8)	O(11)–N(7)	1.218(12)
Dy(1)–O(2)[1]	2.214(8)	O(2)–C(7)	1.267(13)	N(1)–C(1)	1.359(15)
Dy(1)–O(3)	2.432(9)	O(3)–N(5)	1.283(13)	N(1)–C(2)	1.457(15)
Dy(1)–O(4)	2.513(9)	O(4)–N(5)	1.302(13)	N(2)–C(1)	1.279(15)
Dy(1)–O(6)	2.537(9)	O(5)–N(5)	1.199(13)	N(2)–C(4)	1.464(15)
Dy(1)–O(7)	2.471(9)	O(6)–N(6)	1.198(13)	N(3)–C(2)	1.442(14)
Dy(1)–O(9)	2.488(9)	O(7)–N(6)	1.274(13)	N(3)–C(7)	1.365(15)
Dy(1)–O(10)	2.488(8)	O(8)–N(6)	1.233(13)	N(4)–C(7)	1.309(15)
Dy(1)–O(12)	2.375(9)	O(9)–N(7)	1.268(13)	N(4)–C(8)	1.468(15)
O(1)–C(1)	1.274(13)	O(10)–N(7)	1.251(12)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Dy(1)O(3)	128.4(3)	O(9)Dy(1)O(6)	73.4(3)	O(6)N(6)O(8)	123.1(12)
O(1)Dy(1)O(4)	76.5(3)	O(10)Dy(1)O(4)	123.6(3)	O(8)N(6)O(7)	119.9(12)
O(1)Dy(1)O(6)	70.6(3)	O(10)Dy(1)O(6)	123.2(3)	O(10)N(7)O(9)	117.1(10)
O(1)Dy(1)O(7)	100.9(3)	O(10)Dy(1)O(9)	51.2(3)	O(11)N(7)O(9)	122.4(11)
O(1)Dy(1)O(9)	137.9(3)	O(12)Dy(1)O(3)	148.8(3)	O(11)N(7)O(10)	120.5(11)
O(1)Dy(1)O(10)	146.2(3)	O(12)Dy(1)O(4)	147.9(3)	O(1)C(1)N(1)	119.3(11)
O(1)Dy(1)O(12)	74.8(3)	O(12)Dy(1)O(6)	82.4(3)	O(1)C(1)N(2)	120.9(11)
O(2)[1]Dy(1)O(1)	82.0(3)	O(12)Dy(1)O(7)	128.5(3)	N(2)C(1)N(1)	119.8(11)
O(2)[1]Dy(1)O(3)	79.0(3)	O(12)Dy(1)O(9)	79.6(4)	N(1)C(2)C(3)	110.0(10)
O(2)[1]Dy(1)O(4)	76.9(3)	O(12)Dy(1)O(10)	76.9(3)	N(1)C(2)C(9)	105.9(10)
O(2)[1]Dy(1)O(6)	152.0(3)	C(1)O(1)Dy(1)	150.4(8)	N(3)C(2)N(1)	106.6(9)
O(2)[1]Dy(1)O(7)	146.0(3)	C(7)O(2)Dy(1)[1]	155.2(9)	N(3)C(2)C(3)	109.5(10)
O(2)[1]Dy(1)O(9)	128.6(3)	N(5)O(3)Dy(1)	97.8(7)	N(3)C(2)C(9)	105.1(10)
O(2)[1]Dy(1)O(10)	77.6(3)	N(5)O(4)Dy(1)	93.4(7)	N(2)C(4)C(3)	107.7(10)
O(2)[1]Dy(1)O(12)	85.2(3)	N(6)O(6)Dy(1)	95.6(7)	N(2)C(4)C(5)	108.2(12)
O(3)Dy(1)O(4)	52.6(3)	N(6)O(7)Dy(1)	96.8(7)	N(2)C(4)C(6)	108.6(11)
O(3)Dy(1)O(6)	122.5(3)	N(7)O(9)Dy(1)	95.6(7)	O(2)C(7)N(3)	117.9(12)
O(3)Dy(1)O(7)	72.7(3)	N(7)O(10)Dy(1)	96.1(7)	O(2)C(7)N(4)	124.2(12)
O(3)Dy(1)O(9)	89.4(4)	C(1)N(1)C(2)	124.8(10)	N(4)C(7)N(3)	117.9(12)
O(3)Dy(1)O(10)	73.6(3)	C(1)N(2)C(4)	127.8(11)	N(4)C(8)C(9)	106.7(11)
O(4)Dy(1)O(6)	101.3(3)	C(7)N(3)C(2)	127.9(11)	N(4)C(8)C(10)	108.7(12)
O(7)Dy(1)O(4)	71.1(3)	C(7)N(4)C(8)	127.5(11)	N(4)C(8)C(11)	107.8(11)
O(7)Dy(1)O(6)	49.8(3)	O(3)N(5)O(4)	116.0(10)		
O(7)Dy(1)O(9)	70.3(3)	O(5)N(5)O(3)	123.0(11)		
O(7)Dy(1)O(10)	111.1(3)	O(5)N(5)O(4)	120.9(11)		
O(9)Dy(1)O(4)	132.3(4)	O(6)N(6)O(7)	117.0(11)		

* Symmetry procedure: [i] $1-x, 1-y, 1-z$.

Table 8. Geometric parameters of hydrogen bonds in structures **I**, **II**, **IV**, and **V**

D–H...A	Symmetry procedure	H...A	Angle D–H...A, deg
		I	
N(1)–H(1)...O(4)		2.49	132
O(12)–H(12a)...O(11)	$1-x, 1-y, 2-z$	1.87	171
O(12)–H(12b)...O(7)	$1+x, y, z$	1.96	174
N(2)–H(2)...O(8)	$1+x, y, z$	2.38	151
N(3)–H(3)...O(5)	$1+x, y, z$	2.23	164
N(4)–H(4)...O(11)	$x, y, -1+z$	2.23	173
		II	
N(1)–H(1)...O(4)		2.47	136
O(12)–H(12a)...O(11)	$1-x, 1-y, 2-z$	1.96	171
O(12)–H(12b)...O(7)	$1+x, y, z$	2.02	171
N(2)–H(2)...O(8)	$1+x, y, z$	2.34	154
N(3)–H(3)...O(5)	$1+x, y, z$	2.21	163
N(4)–H(4)...O(11)	$x, y, -1+z$	2.21	172
		IV	
N(1)–H(1)...O(4)		2.45	136
O(12)–H(12a)...O(11)	$1-x, 1-y, 2-z$	1.94	178
O(12)–H(12b)...O(7)	$1+x, y, z$	2.03	170
N(2)–H(2)...O(8)	$1+x, y, z$	2.38	154
N(3)–H(3)...O(5)	$1+x, y, z$	2.23	162
N(4)–H(4)...O(11)	$x, y, -1+z$	2.21	173
		V	
N(1)–H(1)...O(4)		2.42	136
O(12)–H(12a)...O(11)	$1-x, 1-y, 2-z$	2.02	148
O(12)–H(12b)...O(7)	$1+x, y, z$	2.05	154
N(2)–H(2)...O(8)	$1+x, y, z$	2.37	154
N(3)–H(3)...O(5)	$1+x, y, z$	2.21	164
N(4)–H(4)...O(11)	$x, y, -1+z$	2.26	171

Table 9. Bond lengths and bond angles in structure **III***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Gd(1)–O(1)	2.266(6)	O(1)–C(1)	1.279(10)	O(14)–N(7)	1.254(9)
Gd(1)–O(2)[1]	2.329(6)	O(2)–Gd(1)[1]	2.329(6)	N(1)–C(1)	1.322(11)
Gd(1)–O(3)	2.378(5)	O(2)–C(7)	1.277(10)	N(1)–C(4)	1.467(10)
Gd(1)–O(4)	2.479(6)	O(6)–N(5)	1.260(8)	N(2)–C(1)	1.351(10)
Gd(1)–O(5)	2.382(5)	O(7)–N(5)	1.254(9)	N(2)–C(2)	1.455(9)
Gd(1)–O(6)	2.463(6)	O(8)–N(5)	1.208(9)	N(3)–C(7)	1.328(10)
Gd(1)–O(7)	2.606(6)	O(9)–N(6)	1.257(8)	N(3)–C(9)	1.471(9)
Gd(1)–O(9)	2.600(6)	O(10)–N(6)	1.265(8)	N(4)–C(2)	1.466(10)
Gd(1)–O(10)	2.503(6)	O(11)–N(6)	1.241(8)	N(4)–C(7)	1.334(9)
Gd(1)–N(5)	2.972(8)	O(12)–N(7)	1.238(8)		
Gd(1)–N(6)	2.968(7)	O(13)–N(7)	1.241(9)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Gd(1)O(2)[1]	96.6(2)	O(5)Gd(1)O(6)	84.34(19)	O(7)N(5)Gd(1)	61.0(4)
O(1)Gd(1)O(3)	80.0(2)	O(5)Gd(1)O(7)	132.5(2)	O(7)N(5)O(6)	115.3(8)
O(1)Gd(1)O(4)	79.5(2)	O(5)Gd(1)O(9)	65.72(19)	O(8)N(5)Gd(1)	174.5(7)
O(1)Gd(1)O(5)	153.2(2)	O(5)Gd(1)O(10)	115.6(2)	O(8)N(5)O(6)	121.7(9)
O(1)Gd(1)O(6)	121.9(2)	O(5)Gd(1)N(5)	108.2(2)	O(8)N(5)O(7)	123.0(9)
O(1)Gd(1)O(7)	72.7(2)	O(5)Gd(1)N(6)	90.7(2)	O(9)N(6)Gd(1)	60.9(4)
O(1)Gd(1)O(9)	124.6(2)	O(6)Gd(1)O(4)	140.11(19)	O(9)N(6)O(10)	117.3(7)
O(1)Gd(1)O(10)	78.6(2)	O(6)Gd(1)O(7)	49.42(18)	O(10)N(6)Gd(1)	56.5(4)
O(1)Gd(1)N(5)	97.6(2)	O(6)Gd(1)O(9)	70.52(19)	O(11)N(6)Gd(1)	176.1(6)
O(1)Gd(1)N(6)	102.1(2)	O(6)Gd(1)O(10)	77.2(2)	O(11)N(6)O(9)	121.9(8)
O(2)[1]Gd(1)O(3)	73.39(19)	O(6)Gd(1)N(5)	24.58(18)	O(11)N(6)O(10)	120.8(8)
O(2)[1]Gd(1)O(4)	143.86(19)	O(6)Gd(1)N(6)	71.35(19)	O(12)N(7)O(13)	118.6(9)
O(2)[1]Gd(1)O(5)	86.3(2)	O(7)Gd(1)N(5)	24.88(18)	O(12)N(7)O(14)	119.9(8)
O(2)[1]Gd(1)O(6)	71.95(19)	O(7)Gd(1)N(6)	84.6(2)	O(13)N(7)O(14)	121.5(8)
O(2)[1]Gd(1)O(7)	71.14(19)	O(9)Gd(1)O(7)	101.50(19)	O(1)C(1)N(1)	121.0(9)
O(2)[1]Gd(1)O(9)	134.7(2)	O(9)Gd(1)N(5)	86.4(2)	O(1)C(1)N(2)	119.1(9)
O(2)[1]Gd(1)O(10)	140.06(19)	O(9)Gd(1)N(6)	24.97(18)	N(1)C(1)N(2)	119.9(9)
O(2)[1]Gd(1)N(5)	68.6(2)	O(10)Gd(1)O(7)	69.60(19)	N(2)C(2)N(4)	107.4(7)
O(2)[1]Gd(1)N(6)	143.30(19)	O(10)Gd(1)O(9)	49.87(18)	N(2)C(2)C(3)	107.7(7)
O(3)Gd(1)O(4)	70.54(18)	O(10)Gd(1)N(5)	72.8(2)	N(2)C(2)C(8)	108.3(7)
O(3)Gd(1)O(5)	75.38(18)	O(10)Gd(1)N(6)	24.92(18)	N(4)C(2)C(3)	115.3(7)
O(3)Gd(1)O(6)	140.7(2)	N(6)Gd(1)N(5)	77.8(2)	N(4)C(2)C(8)	106.5(7)
O(3)Gd(1)O(7)	131.67(19)	C(1)O(1)Gd(1)	157.8(6)	N(1)C(4)C(3)	108.4(7)
O(3)Gd(1)O(9)	126.81(17)	C(7)O(2)Gd(1)[i]	146.5(6)	N(1)C(4)C(5)	110.0(7)
O(3)Gd(1)O(10)	142.0(2)	N(5)O(6)Gd(1)	101.0(5)	N(1)C(4)C(6)	107.5(7)
O(3)Gd(1)N(5)	141.4(2)	N(5)O(7)Gd(1)	94.1(5)	O(2)C(7)N(3)	121.2(8)
O(3)Gd(1)N(6)	140.71(19)	N(6)O(9)Gd(1)	94.1(5)	O(2)C(7)N(4)	119.5(8)
O(4)Gd(1)O(7)	138.3(2)	N(6)O(10)Gd(1)	98.6(5)	N(3)C(7)N(4)	119.3(9)
O(4)Gd(1)O(9)	69.73(19)	C(1)N(1)C(4)	126.7(8)	N(3)C(9)C(8)	106.6(6)
O(4)Gd(1)O(10)	74.91(19)	C(1)N(2)C(2)	123.6(8)	N(3)C(9)C(10)	108.6(7)
O(4)Gd(1)N(5)	147.4(2)	C(7)N(3)C(9)	126.1(7)	N(3)C(9)C(11)	107.3(7)
O(4)Gd(1)N(6)	71.32(18)	C(7)N(4)C(2)	125.5(7)		
O(5)Gd(1)O(4)	82.5(2)	O(6)N(5)Gd(1)	54.4(4)		

* Symmetry procedure: [i] $-x, 1-y, 1-z$.

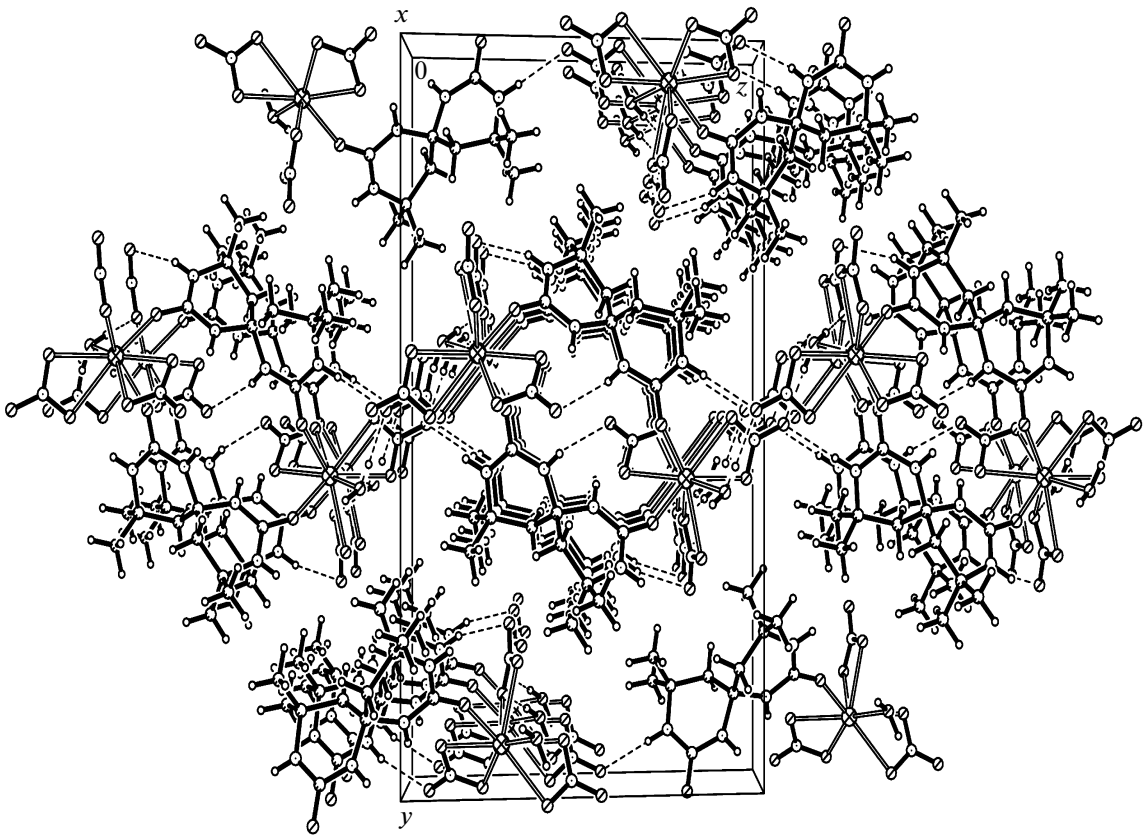


Fig. 2. General view of structures **I**, **II**, **IV**, and **V** along the [010] direction.

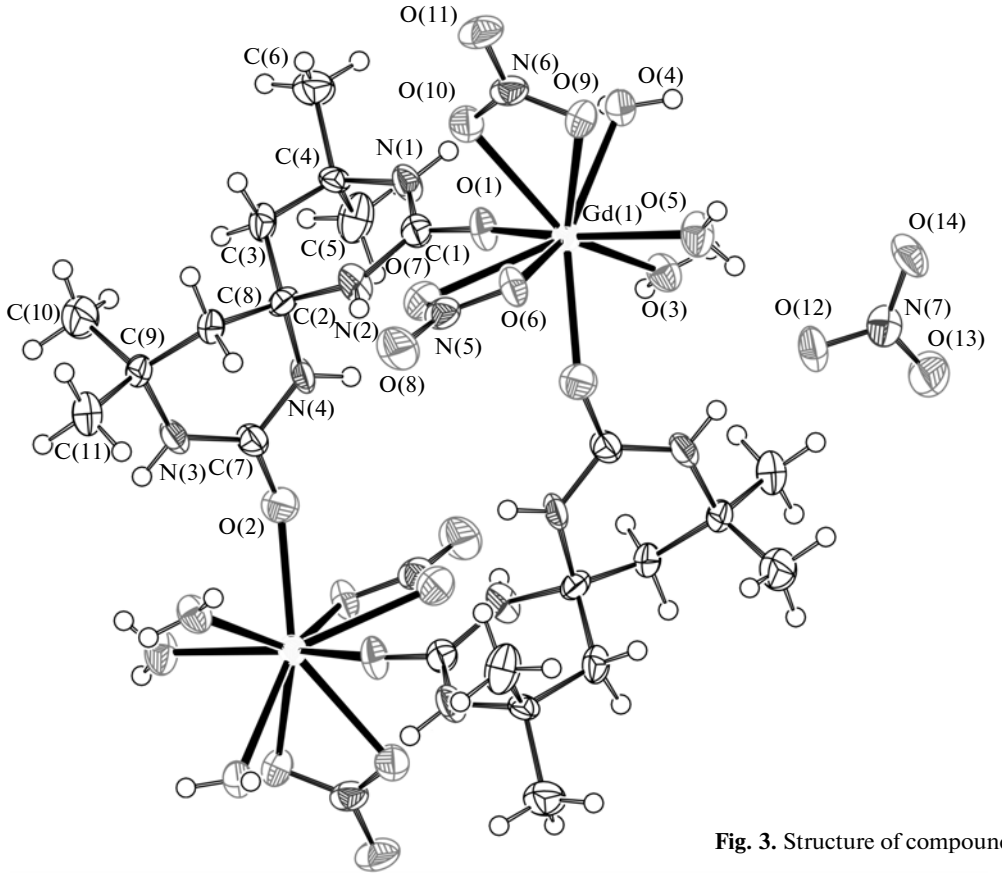


Fig. 3. Structure of compound **III**.

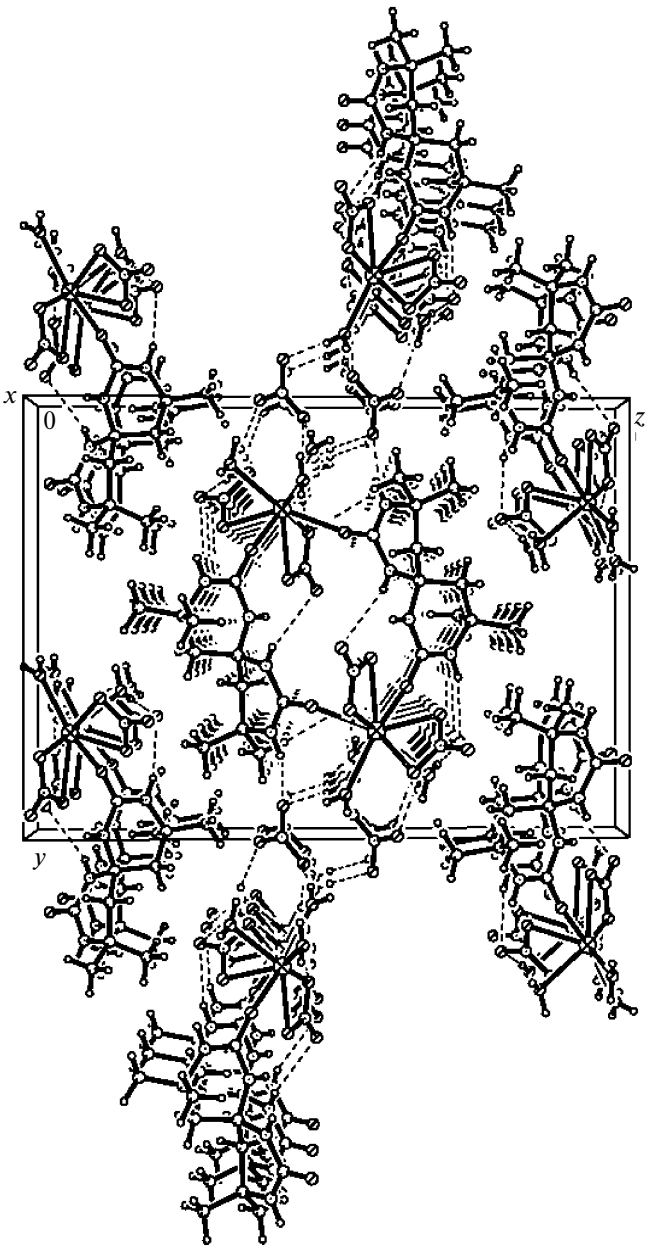


Fig. 4. General view of structure **III** along the [110] direction.

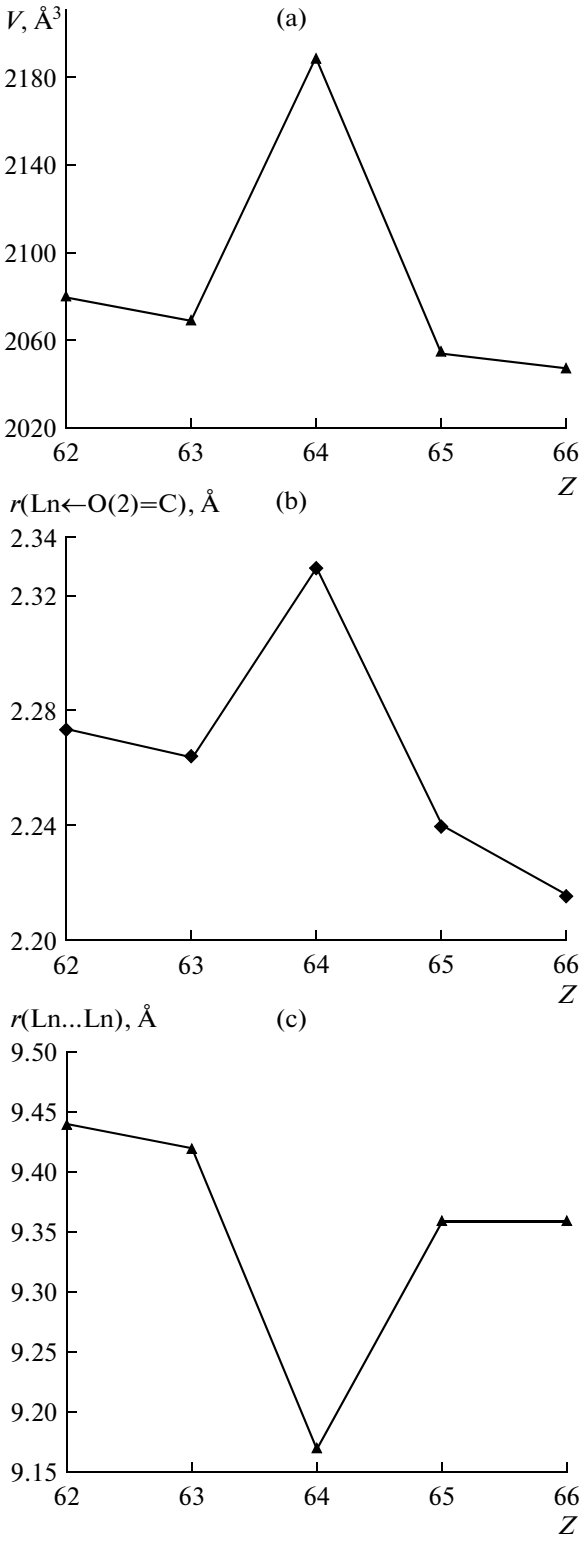


Fig. 5. Plots of the (a) unit cell volume ($V = f(Z)$), (b) Ln←O(2)=C bond length ($r = f(Z)$), and (c) Ln...Ln distance ($r = f(Z)$) on the number of lanthanide in complexes **I–V**.

with the N–C(=O)–N–C(Me)$_2$ planar fragment, and the C(2) and C(3) atoms deviate from this plane by –0.211(15) and 0.378(16) Å, respectively. The cycle containing the N(3) atom exists in the sofa conformation with the deviation of the C(8) atom from the mean plane of other atoms of the cycle by –0.556(13) Å. The dihedral angle between the mean planes of the cycle is 87.4(2)°. This conformation of the cycle includes shortened intramolecular H...H contacts involving the hydrogen atoms of the axial methyl groups H(4)...H(5e) 2.29 and H(3c)...H(10a) 2.07 Å (Table 9, Fig. 3).

The intramolecular hydrogen bond N(2)–H(2)...O(7) (H...O 2.28 is formed inside the complex. The complexes and uncoordinated nitrate anions are bound into layers parallel to the (1 1 0) plane by multiple intermolecular hydrogen bonds N(1)–H(1)O(11)^{i} (^{i} –1 + x, y, z) (H...O 2.29 Å, angle N–H...O 164°), N(3)–H(3)...O(12)^{ii} (^{ii} –x, 1 – y, 1 – z) (H...O 2.14 Å, angle N–H...O 157°), N(4)–H(4)...O(8)^{i} (H...O 2.42 Å, N–H...O 139°), O(3)–H(3a)...O(6)^{i} (H...O 1.94 Å, O–H...O 169°), O(3)–H(3b)...O(14)^{iii} (^{iii} –x, 2 – y, 1 – z) (H...O 2.87 Å, O–H...O 166°), O(4)–H(4a)...O(13)^{iii} (H···O 2.05 Å, O–H...O 162°), O(4)–H(4b)...O(11)^{i} (H···O 2.15 Å, O–H···O 176°), O(5)–H(5a)...O(12 (H...O 1.89 Å, O–H...O 180°), O(5)–H(5b)...O(14)^{iv} (^{iv} 1 – x, 2 – y, 1 – z) (H...O 2.08 Å, O–H...O 158°) (Fig. 4).

For the synthesized compounds, the nonmonotonic changes in the unit cell volume, distance between the lanthanide atoms Ln...Ln, and bond lengths between the Ln atoms and carbonyl oxygen of spirocarbone are worth of mentioning (Fig. 5).

The observed violation of the monotonic character for the gadolinium atom is a consequence of the secondary periodicity named the tetrad effect [15]. The reasons for this effect are considered to be the nonuniform rate of deepening of the 4*f* orbitals in the series of lanthanides leading to the "gadolinium break," the spin-orbital interaction dividing the whole series of lanthanides into four segments, and an additional stabilization by the crystalline field, which is maximum at the beginning and at the end of two subgroups of the lanthanide family.

REFERENCES

1. Mahbub, A., Fazal, H., and Khalid, L., *Indian J. Exp. Biol.*, 1992, vol. 30, p. 1181.
2. Starikovich, L.S., Dudok, E.P., Sibirnaya, N.A., et al., *Medichna Khimiya,* 2009, vol. 11, vol. 1, p. 57.
3. Starikovich, L.S., Starikovich, M.A., Rechitskii, A.N., et al., *Studiabiologica,* 2009, vol. 3, no. 2, p. 93.
4. Musatov A.G., Semyashkina A.A., and Dashevskii, R.F., *Khranenie i pererabotka zerna*, 2007, no. 7, p. 38.
5. Gurevich, A.S., Titov, V.A., Babaeva, E.V., et al., *Introduktsiya, akklimatizatsiya i kul'tivatsiya rastenii: Sb. nauch. tr.*, Kaliningrad: Kaliningr. univ., 1998, p. 30.
6. Kozichar, M.V., *Cand. Sci. (Agric) Dissertation*, Kherson, 1998.
7. Netreba, E.E., Fedorenko, A.M., and Pavlov, A.A., *Nauch. Visnik Uzhgorod. Un-tu, Ser. Khim.*, 2011, no. 1(25), p. 107
8. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
9. Grigor'ev, A.I., *Vvedenie v kolebatel'nuyu spektroskopiyu neorganicheskikh soedinenii* (Introduction to Vibrational Spectroscopy of Inorganic Compounds), Moscow: MGU, 1977.
10. Kharitonov, Yu.Ya., *Analiticheskaya khimiya (analitika). Kn. 1* (Analytical Chemistry (Analytics). Book 1), Moscow: Vyssh. shkola, 2003.
11. Nakamoto, K., Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds, New York: Wiley, 1986.
12. Zefirov, Yu.V. and Zorkii, P.M., *Usp. Khim.*, 1989, vol. 58, no. 5, p. 713.
13. Netreba, E.E., *Visnik Kharkiv. Nats. Un-tu*, 2012, no. 10(26), p. 320.
14. Netreba, E.E., *Nauch. Visnik Uzhgorod. Un-tu, Ser. Khim.*, 2012, no. 2(28), p. 40
15. Bandurkin, G.A., Dzhurinskii, B.F., and Tananaev, I.V., *Osobennosti kristallokhimii soedinenii redkozemel'nykh elementov* (Characteristic Features of the Crystal Chemistry of Lanthanide Compounds), Moscow: Nauka, 1984.

Translated by E. Yablonskaya