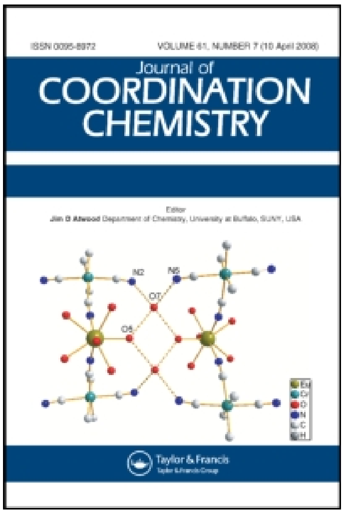

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Coordination sphere geometry changes of lanthanoid(III) nitrate complexes with hexamethylenetetramine

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The 1 : 2 adducts of lanthanoid nitrate complexes with hexamethylenetetramine (hmta) have been synthesized and characterized by X-ray crystallography, IR spectroscopy, and bond valence calculations. The effect of lanthanoid contraction is observed. The lanthanoids create three isostructural groups: La–Nd (group **I**), Sm–Gd (group **II**), and Dy–Lu (group **III**). As an example, one structure for each group is presented in detail. There is a change in the composition of the lanthanoid coordination sphere, geometry, and coordination number with changing size of the lanthanoid. As the ionic radii decrease, the number of water molecules increases, whereas the nitrate ions move outside the inner coordination shell forming three isostructural groups. The hmta molecules are not coordinated to the central atom. Group **I** is formed by 10-coordinate complexes with the nitrate ions and water molecules in the inner and outer coordination sphere ($[Ln(NO_3)_2(H_2O)_6]^+ \cdot NO_3^- \cdot 2hmta \cdot 2H_2O$). Group **II** includes the adducts of general formula ($[Ln(NO_3)(H_2O)_7]^{2+} \cdot 2NO_3^- \cdot 2hmta \cdot 3H_2O$) with nine-coordinate lanthanoid. Group **III** consists of eight-coordinate lanthanoid with general formula $[Ln(H_2O)_8]^{3+} \cdot 3NO_3^- \cdot 2hmta \cdot 2H_2O$].

Keywords: Lanthanoids; Lanthanoid contraction; Hexamethylenetetramine; Coordination sphere geometry

1. Introduction

Lanthanoids (rare earth elements, Ln) and their complexes attract continuing interest with the applications in diagnostic medicine (e.g. contrast agents for magnetic resonance imaging [1, 2], radiotherapeutic drugs [3], and fluoroimmunoassay [4]), as catalysts [5, 6], as the components of permanent magnetic materials [7], and in some other small volume applications but of high value; rare earth sulfides are used as nontoxic alternatives to cadmium and lead in inorganic pigments for plastics.

Lanthanoids interact with ligands almost exclusively electrostatically. This results in a high degree of lability in most lanthanoid complexes. Lanthanoids are kinetically stable only in the compounds containing chelating ligands. In metal-to-ligand bonding, d-orbitals are mostly involved (f-orbitals do not participate in the bond formation) and the coordination geometry of lanthanoid complexes is dominated mainly by steric effects.

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The ligand geometry around the lanthanoid minimizes interligand repulsions, and the coordination number (CN) is limited by the bulk of the ligands. CNs of lanthanoids mostly achieve values from 8 to 12 and coordination geometries are often irregular. Lower CNs can be achieved only with very bulky ligands and the highest CNs are usually achieved with chelating ligands, which have small bite-angles such as nitrates [8]. The lanthanoids, as typical hard Lewis acids, display strong affinity for O-donor ligands. Both the large CNs and oxygen ligand preference cause water molecules to be in the lanthanoid inner coordination sphere. Lanthanoids exist in different stable oxidation states, but +3 dominates due to energetic effects.

In lanthanoid chemistry, the geometry of the inner coordination sphere is important for the application in ion extraction, in separation processes [9], and in magnetic resonance imaging [10–15]. As an example, the number of coordinating water molecules in gadolinium complex accompanying the ligand [DOTA [16] (1,4,7,10-tetrazacyclododecane-N,N′,N″,N″-tetraacetic acid), DTPA [17] (diethylenetriamine-N,N′,N′,N″,N″-pentaacetic acid) or EDTA [18] (ethylenediamine-N,N,N′,N′-tetraacetic acid)] enhances the relaxation times of water protons and improves the contrast of the image [19]. The inner coordination sphere can be controlled *via* the supramolecular assembly and the importance of the outer sphere contribution cannot be neglected. Maximizing the number of outer sphere water molecules influences the relaxivity effectiveness [20]. The fluorescence lifetime of lanthanoid compounds used as biological probes [21, 22] also depends on the inner sphere interactions with water. Introducing uncharged ligands to the outer coordination sphere can influence the inner coordination sphere and also, in case of ligands possessing lone electron pairs, stabilize the compound in solution *via* hydrogen bonds. Therefore the agent chosen is hexamethylenetetramine (hmta), $C_6H_{12}N_4$ (synonyms: 1,3,5,7-tetraazaadamantane, methenamine, hexamine, urotropine), which has been known for more than 140 years [23]. Rather unusual is one of its properties – decreasing solubility in water with increasing temperature (which is connected with the increase in water association accompanying temperature lowering) can be supportive in supramolecular engineering. Hmta as a potential tetradentate ligand or as a hydrogen-bond acceptor, suitable for the self-assembly of supramolecular architectures has attracted scientists' interest for many years [24–30]. Renewed interest has led to numerous reports on the crystal and molecular structures [31–36].

In this article, we report the changes in the geometry and arrangement of lanthanoid(III) nitrate hydrates induced by introducing hmta to the outer coordination sphere. There is only one structure of this type reported in the literature, $[Nd(NO_3)_2(H_2O)_6]^+ \cdot (NO_3)^- \cdot 2N_4(CH_2)_6 \cdot 3H_2O$ [37] and thus we extended the synthesis and structural studies to the whole lanthanoid series (from La to Lu) with two exceptions: (a) promethium because of its radioactivity (the most stable nuclide ^{145}Pm with half-life time $t_{1/2} = 17.7$ years) and (b) terbium because its oxide exists only as Tb_4O_7 and the synthesis gave only mixed oxidation state complexes; as a consequence, the coordination sphere was multipositionally disordered.

2. Results and discussion

Lanthanoids have large ionic radii which decrease continually with increasing atomic number (lanthanoid contraction) due to the imperfect nucleus screening by the f-electrons. According to the recent relativistic calculations [8], 10–30% of lanthanoid contraction is caused by the relativistic effects. However, the rare earth elements have similar chemical and physical properties due to the same electronic structure of the outer shells. The small differences in ionic radii and comparable properties allow lanthanoid complexes to be isostructural across the whole series. As an example, the lanthanoid nitrate salts with 4,4′-bipyridine [38] or with crown ether [39, 40] can be given. In the present lanthanoid nitrates with hmta, the effect of contraction is also observed. There is change in composition of lanthanoid coordination sphere, geometry, and CN with changing size of Ln. As the ionic radii decrease, the number of water molecules increases, and nitrate ions move outside the inner coordination sphere forming three isostructural groups (figure 1). The Ln–O_{water} and Ln–$O_{nitrate}$ bond distances diminish with decreasing ionic radii [2.548(2)–2.313(4) Å and 2.689(3)–2.572(9) Å, respectively]. The lanthanoids as typical hard acids display strong affinity for O-donor ligands and therefore water offers competition to other ligands in aqueous solutions. The hmta molecules are not coordinated to the central atom.

The crystal structures of 1 : 2 adducts of lanthanoid(III) nitrates with hmta can be assembled into three groups. Isostructural group **I** is formed by 10-coordinate complexes of lanthanum, cerium, praseodymium, and neodymium [37] (table 1), in which the nitrate groups and water molecules are in the inner and outer coordination spheres ($[Ln(NO_3)_2(H_2O)_6]^+ \cdot NO_3^- \cdot 2hmta \cdot 2H_2O$). In published data [37], the number of outer coordination sphere water molecules was wrongly interpreted (one disordered molecule was refined as two separate fully ordered molecules, which cause abnormality of displacement ellipsoids) and thus the neodymium complex compound also fits the series. Isostructural group **II** includes the nitrate salts of samarium, europium, and gadolinium with hmta ($[Ln(NO_3)(H_2O)_7]^{2+} \cdot 2NO_3^- \cdot 2hmta \cdot 3H_2O$), and in this group the lanthanoid is nine-coordinate (table 1). The crystal structure of terbium complex has not been reported herein, because the water molecules coordinated to Tb are disordered due to the mixed (III, IV) valence. Isostructural group **III** consists of eight-coordinate dysprosium, holmium, erbium, thulium, ytterbium, and lutetium compounds with general formula $[Ln(H_2O)_8]^{3+} \cdot 3NO_3^- \cdot 2hmta \cdot 2H_2O$ (table 1). The complexes obtained are isostructural within the reported groups (table 1) and thus only one compound is presented in detail, as a representative for each particular coordination group (table 2).

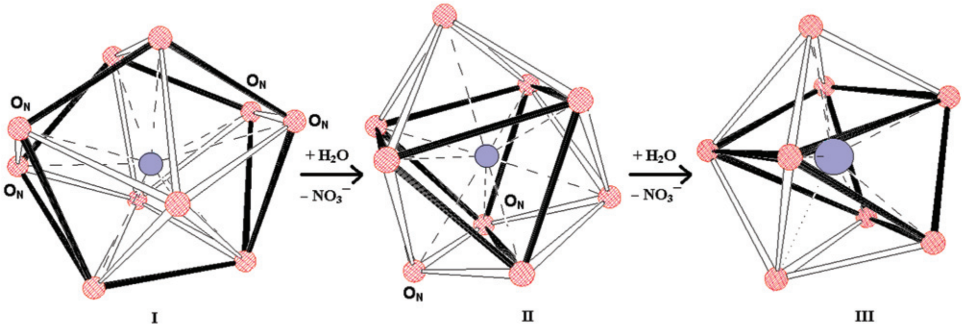

Figure 1. The coordination sphere geometry changes occurring across the series of coordinated aqua lanthanoid nitrate hydrate compounds with hmta.

Table 1. Details concerning crystal data of all lanthanoid compounds.

Group **I** Empirical formula $C_{12}H_{40}N_{11}O_{17}Ln$

Ln	**La**	**Ce**	**Pr**	**Nd**[a]
Formula weight	749.46	750.67	751.46	772.72
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions (Å, °)				
a	18.0172(9)	17.9728(9)	17.9085(7)	17.902(4)
b	9.3737(4)	9.4013(5)	9.4162(4)	9.335(2)
c	18.6719(8)	18.5960(10)	18.5339(9)	18.489(4)
β	112.382(4)	112.061(5)	111.853(3)	112.07(2)
Volume (Å^3), Z	2915.9(2), 4	2912.1(3), 4	2900.8(2), 4	2864.54, 4
Calculated density (g cm^{-3})	1.707	1.712	1.721	1.793
F(000)	1528	1532	1536	1580
Absorption coefficient (mm^{-1})	1.554	1.653	1.769	1.910

Group **II** Empirical formula $C_{12}H_{44}N_{11}O_{19}Ln$

Ln	**Sm**	**Eu**	**Gd**
Formula weight	796.93	798.54	803.83
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)			
a	10.800(2)	10.794(2)	10.7911(4)
b	10.133(2)	10.098(2)	10.0979(4)
c	28.009(6)	27.918(4)	27.9404(12)
β	90.50(3)	90.500(10)	90.627(4)
Volume (Å^3), Z	3065.1(11), 4	3042.9(9), 4	3044.4(2), 4
Calculated density (g cm^{-3})	1.730	1.740	1.75
F(000)	1628	1632	1636
Absorption coefficient (mm^{-1})	2.010	2.156	2.273

Group **III** Empirical formula $C_{12}H_{44}N_{11}O_{19}Ln$

Ln	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Formula weight	809.08	811.51	813.84	815.51	819.62	821.55
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)						
a	10.1835(5)	10.180(3)	10.1560(10)	10.1504(9)	10.1251(6)	10.1341(7)
b	10.9144(5)	10.904(4)	10.8900(10)	10.9046(9)	10.8798(6)	10.8710(8)
c	14.8210(8)	14.792(6)	14.760(2)	14.7918(13)	14.7553(8)	14.7602(8)
α	83.103(4)	83.10(3)	83.110(10)	83.033(7)	83.072(4)	82.982(5)
β	77.058(4)	77.01(3)	77.070(10)	77.067(8)	77.152(5)	77.110(5)
γ	72.687(4)	72.69(2)	72.690(10)	72.665(8)	72.770(5)	72.625(6)
Volume (Å^3), Z	1530.19(13), 2	1525.1(9), 2	1516.6(3), 2	1520.6(2), 2	1511.00(15), 2	1510.09(17), 2
Calculated density (g cm^{-3})	1.756	1.767	1.782	1.781	1.801	1.807
F(000)	822	824	826	828	830	832
Absorption coefficient (mm^{-1})	2.535	2.688	2.862	3.012	3.190	3.364

[a] Literature data [37].

Table 2. Crystallographic data for **1**–**3**.

	La (**1**)	Eu (**2**)	Dy (**3**)
Empirical formula	$C_{12}H_{40}N_{11}O_{17}La$	$C_{12}H_{44}N_{11}O_{19}Eu$	$C_{12}H_{44}N_{11}O_{19}Dy$
Formula weight	749.46	798.54	809.08
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	18.0172(9)	10.794(2)	10.1835(5)
b	9.3737(4)	10.098(2)	10.9144(5)
c	18.6719(8)	27.918(4)	14.8210(8)
α			83.103(4)
β	112.382(4)	90.500(10)	77.058(4)
γ			72.687(4)
Volume (Å^3), Z	2915.9(2), 4	3042.9(9), 4	1530.19(13), 2
Calculated density (g cm^{-3})	1.707	1.740	1.756
F(000)	1528	1632	822
Max 2θ (°)	50.21	54.99	50.20
Absorption coefficient (mm^{-1})	1.554	2.156	2.535
Max. and min. transmission	0.593 and 0.486	0.378 and 0.268	0.473 and 0.381
Diffractometer used	Kuma KM-4-CCD	Siemens P3	Kuma KM-4-CCD
Reflections collected	31,912	4812	16,479
Independent reflection	5172 [R(int) = 0. 0275]	4399 [R(int) = 0.0336]	5427 [R(int) = 0.0347]
Completeness (%)	93.4	65.3	99.7
Data/restraints/parameters	5172/0/408	4399/0/388	5427/0/424
Goodness-of-fit on F^2	1.177	1.151	1.137
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0307$,	$R_1 = 0.0333$,	$R_1 = 0.0287$,
R indices (all data)	$wR_2 = 0.0634$	$wR_2 = 0.0879$	$wR_2 = 0.0754$
Largest difference peak and	$R_1 = 0.0314$,	$R_1 = 0.0366$,	$R_1 = 0.0299$,
hole (e Å^{-3})	$wR_2 = 0.0638$	$wR_2 = 0.0895$	$wR_2 = 0.0762$
	0.923 and −0.535	0.68 and −1.32	1.351 and −1.216

2.1. *Structural aspects common for all compounds*

The noncoordinating nitrate groups are planar and the O–N–O angles are close to 120°. The average N–O distance is 1.24 Å [41]. The C–N bond lengths in the hmta molecules lie in the range 1.44(1)–1.48(1) Å. The average values of the C–N–C and N–C–N angles are equal to 108.1(1)° and 112.0(1)°, respectively, which are in good agreement with those found by Terpstra and Craven [42]. The arrangement of cations, anions, and neutral hmta molecules in the structures is determined by a complex 3-D network of O–H $\cdots$ O hydrogen bonds (figure 2) between the water molecules coordinating to Ln and both the inner and outer NO_3^- anions; the O–H $\cdots$ N hydrogen bonds between the water molecules of complex cation and the N atoms of the hmta molecules are given in table 3. Apart from the water molecules coordinating to Ln, there are additional ones in the outer coordination sphere. These water molecules are involved in intermolecular O–H $\cdots$ O hydrogen bonds with oxygen atoms of water bonded to Ln. The intermolecular interactions exist between the hmta molecules and the oxygen atoms of both the inner and outer coordination sphere nitrate ions, which can be classified as weak C–H $\cdots$ O hydrogen bonds according to Desiraju and Steiner [43].

The coordination sphere structure solution was confirmed by bond-valence sum calculations [44]. A total valence of 2.98, 2.94, 3.02 v.u. (valence units) for lanthanum, europium, dysprosium, respectively, were calculated on the basis of the following equation: $\Sigma v_{ij} = \exp[(R_{ij} - d_{ij})/b]$ [45, 46], in which v_{ij} is the bond valence, R_{ij} is the bond-valence parameter, d_{ij} is the bond length, and b is the constant equal to 0.37 Å [47].

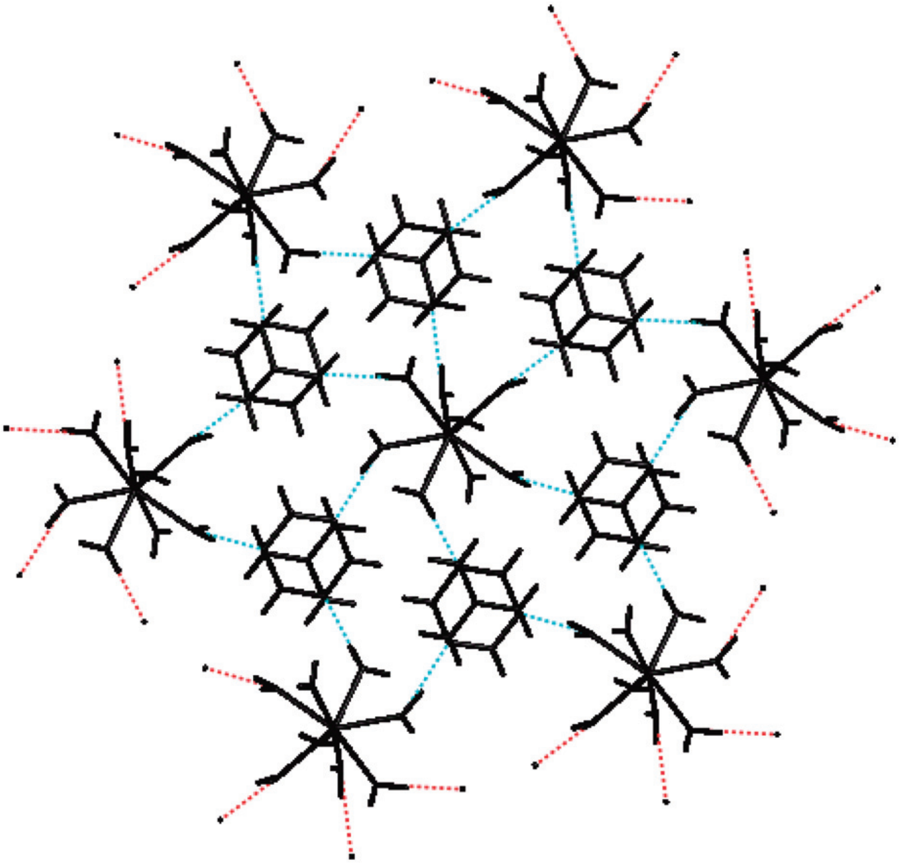

Figure 2. The hydrogen bond network in **3**.

The values of $R_{\mathrm{Ln–O}}$ bond-valence parameters were 2.148, 2.038, and 2.005 Å, respectively, for La, Eu, and Dy [48]. According to Palenik [49] the difference between observed and expected values larger than 0.25–0.30 v.u. is a reasonable guide to those structural studies that should be examined in more detail, because of possible errors.

2.2. *Hexaaqua-bis(nitrato-O,O′)-lanthanum(III) nitrate bis(1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane) dihydrate (1)*

The asymmetric unit contains $[La(NO_3)_2(H_2O)_6]^+$, two $(NO_3)^-$, two hmta molecules, and two water molecules (figure 3). One water molecule and the nitrate ion from the outer coordination sphere are disordered. The central atom is 10-coordinate as a tetradecahedron distorted toward bicapped square antiprism [50] (figure 1). The La–O (nitrate) bond length vary from 2.619(3) to 2.762(3) Å. Generally, water oxygen atoms are closer to La than nitrate oxygen atoms. The average La–O_{water} distance is 2.548 Å, while the average La–O_{nitrate} is 2.689 Å. According to Addison *et al.* [41], a bidentate nitrate group is unsymmetrically bound to the coordinating atom if the distances between the two oxygen atoms of one nitrate ion differ by more than 0.2 Å. Here the differences are 0.143

Table 3. Selected hydrogen bond parameters.

Donor–H···acceptor	D–H	H···A	D···A	∠DHA
1				
O(1)–H(1B)···N(24)$^{\mathrm{i}}$	1.04	1.97	3.0163	179
O(3)–H(3B)···O(91)$^{\mathrm{ii}}$	0.97	1.79	2.7337	165
O(6)–H(6A)···O(51)$^{\mathrm{iii}}$	0.88	2.15	2.9642	154
O(91)–H(91A)···N(21)$^{\mathrm{iv}}$	0.97	2.03	2.9220	152
O(91)–H(91B)···O(53)	0.98	2.12	3.1024	174
C(11)–H(11B)···O(10)	0.97	2.58	3.3912	141
C(15)–H(15B)···O(52)$^{\mathrm{i}}$	0.97	2.50	3.3663	148
2				
O(1)–H(1B)···N(21)	1.15	1.75	2.9003	179
O(3)–H(3A)···O(92)	0.92	1.87	2.7788	172
O(7)–H(7B)···O(41)	0.98	1.90	2.8625	167
O(91)–H(91A)···O(32)	1.06	1.78	2.8411	174
O(92)–H(92B)···O(93)	0.90	2.52	3.3133	146
O(92)–H(92B)···O(10)$^{\mathrm{i}}$	0.90	2.36	3.0531	134
C(13)–H(13B)···O(42)$^{\mathrm{ii}}$	1.13	2.49	3.5217	152
C(24)–H(24B)···O(8)	1.01	2.53	3.3198	135
3				
O(1)–H(1A)···O(32)$^{\mathrm{i}}$	0.95	1.87	2.8140	174
O(2)–H(2A)···O(92)	0.84	1.92	2.7509	173
O(2)–H(2B)···N(14)	0.94	1.85	2.7766	168
O(91)–H(91A)···O(42)	0.76	2.46	3.0428	135
O(91)–H(91B)···N(13)	0.97	2.06	3.0267	171
C(16)–H(16A)···O(33)$^{\mathrm{ii}}$	0.97	2.51	3.3773	149

Symmetry code: (**1**) (i) $1/2-x$, $-1/2+y$, $1/2-z$; (ii) $1/2+x$, $1/2-y$, $1/2+z$; (iii) $1-x$, $1-y$, $1-z$; (iv) x, $-1+y$, z. (**2**) (i) $1-x$, $1-y$, $-z$; (ii) $1-x$, $1/2+y$, $1/2-z$. (**3**) (i) x, $-1+y$, z; (ii) $1-x$, $1-y$, $-z$.

and 0.047 Å, which implies that the nitrates are symmetrically bound to La. For $[\mathrm{La(NO_3)_3(H_2O)_5}]\cdot\mathrm{H_2O}$ [51] only one nitrate is bound to the central atom, the remaining two are unsymmetrical, probably as the result of large number of coordinated water molecules and three nitrate ions in the inner coordination sphere (CN is 11). There are two distinct mean La–$\mathrm{O_{nitrate}}$ bond lengths (2.619 and 2.655 Å) determined on the basis of 10-coordinate lanthanum structures (containing at least two nitrate ions and O-ligands) included in the Cambridge Structural Database (CSD) [52] (Version 5.26) (figure 4). The large number of constituents may cause the nitrate ions to be connected unsymmetrically to lanthanoid. In the coordinated nitrate the planarity is preserved, but the N–O bond lengths and the O–N–O angles are different. The terminal N–O bonds are shortened (average length of 1.228 Å) and the N–O bonds involving chelating oxygens are lengthened (average distance of 1.256 Å) in comparison to isolated nitrate. The O–N–O interbond angle involving both coordinated oxygen atoms is smaller than 120° (average value is 117°), and the other two angles are correspondingly larger (average value of 121.4°). The sum of all O–N–O interbond angles is 360° and the mean N–O distance is 1.25 Å, like in pentaaquatris(nitrato)lanthanum(III) hydrate [50].

2.3. *Heptaaqua-(nitrato-O,O′)-europium(III) dinitrate bis(1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane) trihydrate (2)*

Eu is nine-coordinate by one bidentate nitrate ion and seven water molecules. The outer coordination sphere includes two $(\mathrm{NO_3})^-$ anions, two hmta molecules, and three

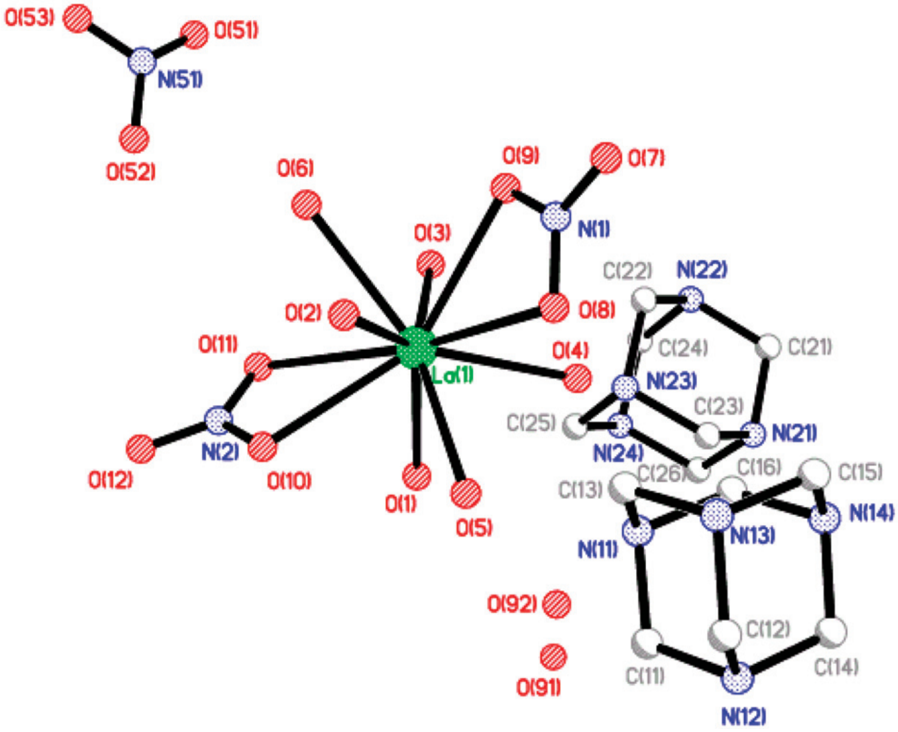

Figure 3. The perspective view of **1** with atom-numbering scheme. The hydrogen atoms and disordered water molecule and nitrate ion were omitted for clarity.

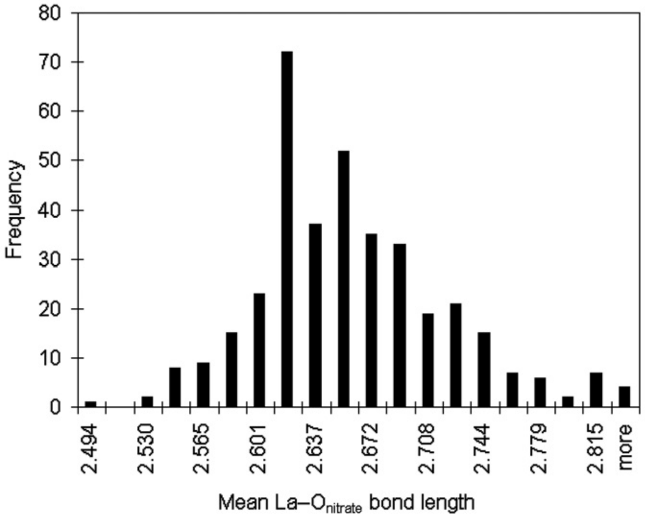

Figure 4. The distribution of La–O$_{\mathrm{nitrate}}$ bond length among structures from CSD.

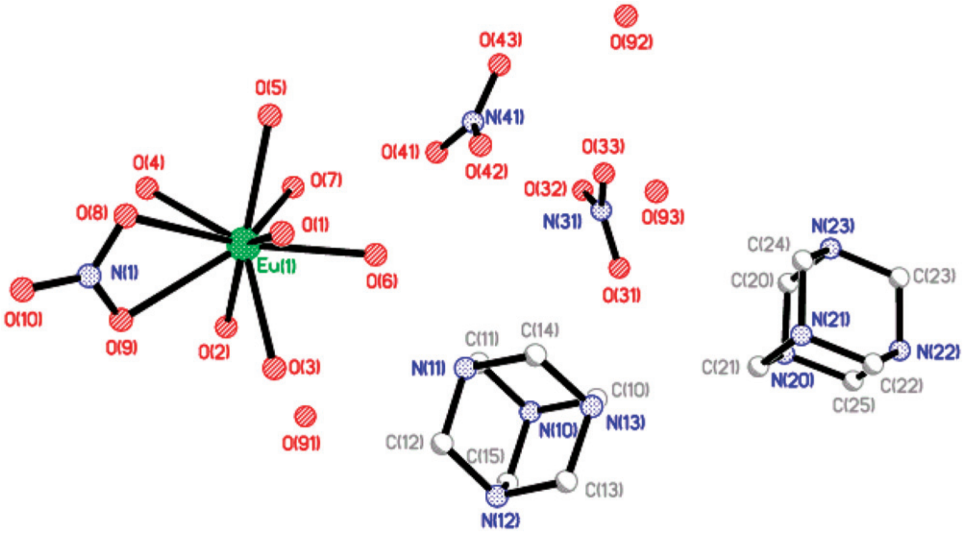

Figure 5. The perspective view of **2** with atom-numbering scheme. The hydrogen atoms were omitted for clarity.

water molecules (figure 5). The coordination polyhedron can be approximated by a tricapped trigonal prism [50] (figure 1). The average Eu–O_{water} distance is 2.427 Å, while Eu–$O_{nitrate}$ bond lengths are 2.589 and 2.548 Å, implying that nitrate ion is symmetrically bound [41]. The mean value of Eu–$O_{nitrate}$ bond lengths (equal to 2.519 Å) was determined on the basis of nine-coordinate lanthanum structures (containing at least one nitrate and O-ligands) included in the CSD [52] (figure 6). There are no deviations from the planarity of nitrates. The sum of all O–N–O interbond angles is 360° and the mean N–O distance is 1.24 Å, like in the isolated ion. However, in the inner coordination sphere the terminal N–O bond is lengthened (1.245(6) Å) and the N–O bonds involving both chelating oxygen atoms are shortened (average 1.238(6) Å) in comparison to tetraaquatrinitratoeuropium(III) dihydrate [53], in which one nitrate ion is asymmetrically bonded to Eu. The O–N–O interbond angle involving both coordinated oxygen atoms is smaller than 120° (average 117°) and the other two angles are correspondingly larger.

2.4. *Octaaquadysprosium(III) trinitrate bis(1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane) dihydrate (3)*

The complex is eight-coordinated and the Dy coordination geometry is a bicapped trigonal prism distorted toward a square antiprism [50] (figure 1). Only water exists in the coordination sphere, probably because of steric effects. The decrease of the ionic radius leads to narrowing of the coordination sphere and thus enhancing the interaction of Ln^{3+}–OH_2 bonds. The remaining water molecules, nitrate ions, and hmta molecules are situated in the outer coordination sphere (figure 7). One nitrate ion is disordered. The average Dy–O_{water} distance is 2.367 Å, which is in agreement with that found in the 18-crown-6 octa-aqua-dysprosium trichloride tetrahydrate (mean of 2.387 Å) [54]. This is the only structure of eight-coordinate dysprosium compound with water in the

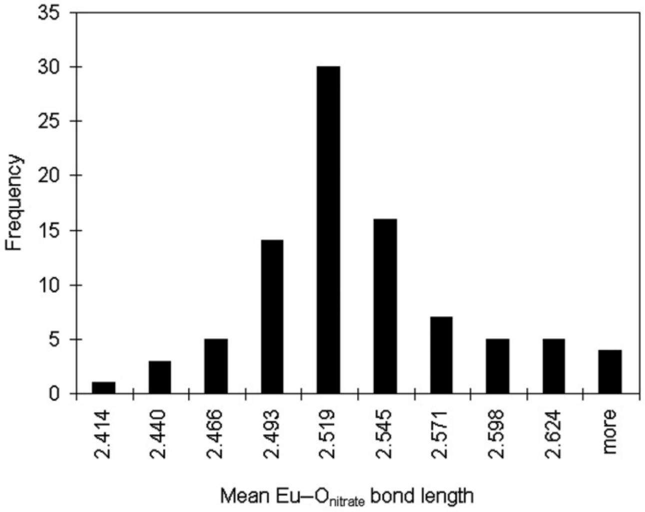

Figure 6. The distribution of Eu–O$_{nitrate}$ bond length among structures from CSD.

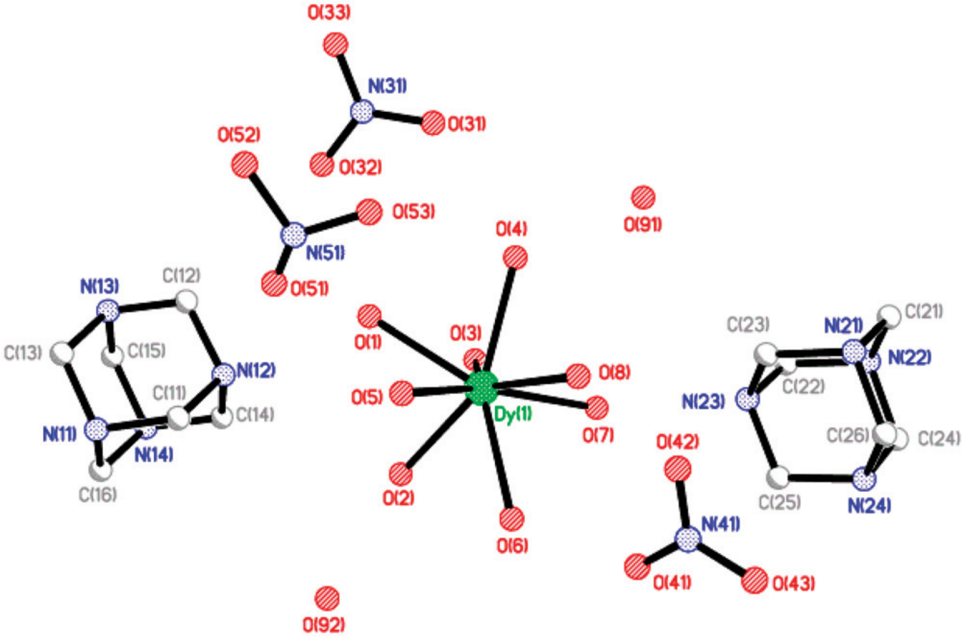

Figure 7. The perspective view of **3** with atom-numbering scheme. The hydrogen atoms and disordered nitrate ion were omitted for clarity.

CSD [52]. In complexes of lighter lanthanoid nitrates with hmta average distance between the Ln and oxygen of water is 2.548 Å. In opposition to groups **I** and **II**, two independent (not coordinated to the central atom) water molecules form additional O–H···O contacts with nitrate ions.

Besides this structure there is no Ln(NO_3) complex with all three NO_3^- ions in the outer coordination sphere [52]. However, some heteroanion compounds contain nitrate ion not coordinated, i.e. (μ_2-tris(2-(3-methoxy-2-oxybenzylideneamino)ethyl)amine)-diaqua-(o-vanillin)-di-dysprosium(III) dinitrate dihydrate [55]. In all other structures, there is always at least one nitrate ion bonded to the metal.

2.5. *Description of isostructurality*

Both inorganic nitrate salts of Ln and presented coordination compounds form three complementary isostructural groups but the coordination sphere changes occur between different elements. The change of geometry and composition of the central atom coordination sphere across the series of inorganic salts is in agreement with lanthanoid contraction. Lanthanum [51] and cerium [56] nitrates exist as pentaaqua monohydrates, $[Ln(NO_3)_3(H_2O)_5]\cdot H_2O$, in which the metals are 11-coordinate with geometry of strongly distorted icosahedron with two vertices replaced by one. A second isostructural group form 10-coordinate salts of praseodymium [57], neodymium [58], samarium [59], europium [53], gadolinium [60], terbium [61], and dysprosium [62] with general formula $[Ln(NO_3)_3(H_2O)_4]\cdot 2H_2O$. The coordination polyhedron can be described as bicapped dodecahedron. The triaqua ytterbium [63] and lutetium [64] nitrates form compounds without water in the outer coordination sphere, $[Ln(NO_3)_3(H_2O)_3]$. The lanthanoid is nine-coordinate with geometry of a distorted tricapped trigonal prism. Europium, gadolinium, dysprosium, holmium, erbium, thulium, and ytterbium form an isostructural subset [64] of compounds with general formula $[Ln(NO_3)_3(H_2O)_4]\cdot H_2O$, which overlaps with the above-mentioned isostructural groups of hydrated lanthanoid nitrates. There are also polymeric compounds of lanthanum and cerium, $[Ln(NO_3)_3(H_2O)_4]_n$, existing as well-separated monomeric salts of neodymium and lutetium: $[Nd(NO_3)_3(H_2O)_4]$, $[Lu(NO_3)_3(H_2O)_3]\cdot H_2O$ [64]. There are no structures of holmium, erbium, and thulium nitrates [64] in the Inorganic Crystal Structures Database [65] (ICSD). As holmium, erbium, thulium hexahydrates, and trihydrates are unknown, it is difficult to predict whether they will be an independent group or can be included in the groups of hexahydrates and trihydrates, or the gap can be filled only by known pentahydrates.

In agreement with the lanthanoid contraction, the CNs of Ln decrease as the element atomic number increases apart from the type of compound, whether it is lanthanoid nitrate with organic ligand or hydrated lanthanoid inorganic salt. The Ln coordination sphere composition changes but the general trend is distinct for the inorganic and metal-organic compounds due to the intermolecular interactions with hmta in coordination compounds. This means that there is a possibility of controlling the lanthanoid inner coordination sphere by outer, neutral organic ligand possessing lone pair electrons. The number of nitrate ions in the inner coordination sphere decreases and the number of water molecules increases for the lanthanoid nitrate compounds with hmta as the ionic radii decrease; whereas for the hydrated lanthanoid nitrates the number of NO_3^- ions remains constant and the number of H_2O molecules decreases. The lanthanoid ions adopt almost identical coordination polyhedra for the given CN ($CN = 10, 9$) for both compound types (figure 8). After swapping nitrate ions to the water molecules, the positions of oxygen atoms from both water and nitrate in the polyhedron are the same as those in the lanthanoid salt.

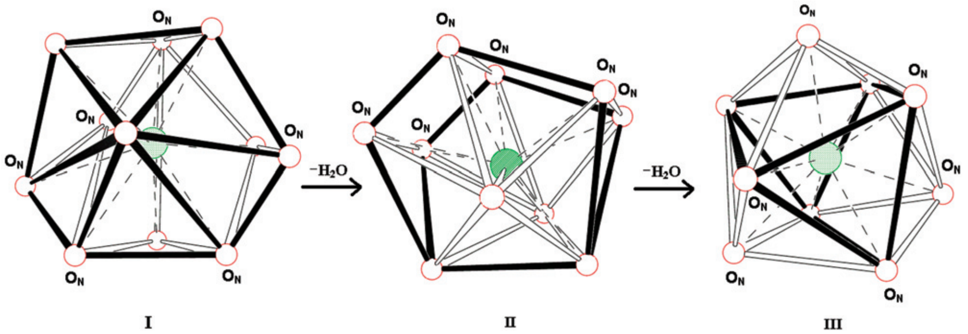

Figure 8. The coordination sphere geometry changes occurring across the series of hydrated lanthanoid nitrates (for complementary isostructural groups).

2.6. *IR spectra*

The IR spectra recorded for complexes of three different structural groups are almost identical due to the similar vibration frequencies of the nitrate and hmta. Although ν_3 mode (NO_3^-) shows degeneracy for **I** and **II**, the ν_1 mode attributed to $\nu(Ln–O_{nitrate})$ [66] is not activated. The split absorption bands attributed to CN ($1260–1200\,cm^{-1}$, $101–0960\,cm^{-1}$, $690–960\,cm^{-1}$, $500–513\,cm^{-1}$) and CH_2 ($2970–2830\,cm^{-1}$) bending and stretching vibrations of hmta and strong band (*ca* $1041\,cm^{-1}$) corresponding to the nitrate group bonded to the metal ion can be observed in the IR spectra of lanthanoid complexes of lower hydration state ($nH_2O = 0.5–3.5$), indicating the existence of Ln–N and $Ln–O_{nitrate}$ bonds. According to the thermal analysis results, hmta molecules and nitrates may migrate from the outer coordination sphere to the inner coordination sphere and bond directly to the Ln ion after dehydration, due to the absence of steric hindrance caused by water [67].

3. Conclusions

Due to the importance of coordination sphere geometry and composition in luminescence [68–71], magnetism [72, 73], thermodynamics [74], and thermochemistry [75, 76] of lanthanoid complexes, as well as in metathesis reactions [77], synthesis of nanoparticles [78] and in structural chemistry [79], the change of coordination sphere geometry and composition have been studied and presented on the basis of lanthanoid(III) nitrate complexes with hmta. According to the lanthanoid contraction, the central atom CNs decrease as the element atomic number increases. As a consequence, waters replace nitrates in the coordination sphere. Different trend can be observed across the series of hydrated lanthanoid(III) nitrates, which means that there is a possibility of controlling the lanthanoid inner coordination sphere by a neutral organic ligand possessing a lone pair electrons, located in the outer coordination sphere. These electrons can act as hydrogen bond acceptors, and in consequence they can influence the supramolecular structure of the compounds. The lone electron pairs of water molecules, nitrate ions, and nitrogen atoms of hmta molecules compete as hydrogen bond acceptors, and the hydrogen bond hierarchy predominates in some point the supramolecular structure. Additionally, nitrogen atoms acting as hydrogen bond donors saturate inner coordination sphere hydrogen bond acceptors and thus, due to both, bulk of the ligand and its electronic properties, nitrate ions cannot access and/or bond to the central atom. It can be supposed that bulk and hydrogen bond multidonor compounds influence the inner coordination sphere and the supramolecular structure more than less functional and smaller ones.

4. Experimental

4.1. *Synthesis and analysis*

The weighed samples of appropriate lanthanoid oxides were dissolved in nitric acid (1 : 1). The obtained solutions were cooled and then mixed with cooled saturated aqueous solution of hmta (molar ratio 1 : 2). The mixtures were stirred vigorously and placed in a refrigerator at 278 K for a few days. The crystals of $Ln(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot nH_2O$ (Ln = La – Lu) were removed from the solutions and sealed in glass capillaries. Elemental analyses were carried out with a EuroVector 3018 analyser. IR spectra were recorded with a Shimadzu DR-8011 spectrophotometer. The compounds of lower hydration state were obtained by heating hydrated salts to the temperatures determined from the thermal curves at the heating rate of 10°C min^{-1}.

4.1.1. $[La(NO_3)_2(H_2O)_6]^+ \cdot NO_3^- \cdot 2hmta \cdot 2H_2O$ (1)

Water was added to the solid La_2O_3 (1.62 g, 0.005 mol) (3 mL) and the mixture was heated to 60°C. To the hot mixture dropwise HNO_3 (5.8 mL) was added up to pH 7. The obtained solution was cooled, mixed with cooled saturated aqueous solution of hmta (2.8 g, 0.02 mol) and then placed in a refrigerator at 278 K for a few days. The resulting colorless, crystalline product was filtered and sealed in glass capillaries. $C_{12}H_{40}N_{11}O_{17}La$: Calcd C 19.23, H 5.39, N 20.55; found C 19.19, H 5.36, N 20.54. IR (KBr, cm^{-1}): 3700–2600br (νOH, νCH_2), 1655w (νOH), 1638w (νOH), 1437m (νCH_2), 1390m ($\nu_3 NO_3$), 1380m ($\nu_3 NO_3$), 1368m ($\nu_3 NO_3$), 1225s (νCN), 1008s (νCN), 819m ($\nu_2 NO_3$, νCH_2), 688s ($\nu_4 NO_3$, νCN), 507s (νCN).

4.1.2. $[Eu(NO_3)(H_2O)_7]^{2+} \cdot 2NO_3^- \cdot 2hmta \cdot 3H_2O$ (2). Using Eu_2O_3 as a starting material (1.76 g, 0.005 mol) and following the same procedure as for **1**, light-pink crystals were obtained. $C_{12}H_{44}N_{11}O_{19}Eu$: Calcd C 18.05, H 5.57, N 19.29; found C 18.00, H 5.55, N 19.25. IR (KBr, cm^{-1}): 3700–2600br (νOH, νCH_2), 1684w (νOH), 1653w (νOH), 1466m (νCH_2), 1375m ($\nu_3 NO_3$), 1296m ($\nu_3 NO_3$), 1240s (νCN), 1009s (νCN), 813m ($\nu_2 NO_3$, νCH_2), 687s ($\nu_4 NO_3$, νCN), 513m (νCN).

4.1.3. $[Dy(H_2O)_8]^{3+} \cdot 3NO_3^- \cdot 2hmta \cdot 2H_2O$ (3). Using Dy_2O_3 as a starting material (1.86 g, 0.005 mol) and following the same procedure as for **1**, light-yellow crystals were obtained. $C_{12}H_{44}N_{11}O_{19}Dy$: Calcd C 17.81, H 5.49, N 19.03; found C 17.80, H 5.52, N

19.00. IR (KBr, cm^{-1}): 3700–2600br (νOH, νCH_2), 1686w (νOH), 1640w (νOH), 1465m (νCH_2), 1394m (ν_3NO_3), 1240s (νCN), 1009s (νCN), 813w (ν_2NO_3, νCH_2), 689s (ν_4NO_3, νCN), 513m (νCN).

4.2. *X-ray crystal structure analysis*

Single crystals of the compounds placed in glass capillaries were mounted on a KM-4-CCD automatic diffractometer equipped with a CCD detector or on a Siemens P3 four circle diffractometer and used for data collection. 3-D X-ray intensity data were collected with graphite monochromated Mo-Kα radiation at room temperature with ω and ω–2θ scan modes, respectively, for KM-4-CCD and Siemens P3 diffractometers. The unit cell parameters were determined from least-squares calculation of the angular settings of reflections in the θ range of 5–20°. Variable scan rates with a maximum scan time 60 s per reflection/frame were applied. Decay corrections were made on the basis of two reference frames or three reference reflections for KM-4-CCD and Siemens P3 diffractometers, respectively. The minimum decay of 48% was observed for Dy compound and the maximum decay of 92% was observed for Sm compound. Transparent crystals used for data collection became opaque. Because of large decomposition it was a try to make measurements of crystals at lower temperature, but during cooling the crystals always broke. Lorentz-polarization correction was applied to the intensity data and the numerical absorption correction was used [80]. The structures were solved by Patterson superposition procedure and subsequently completed by difference Fourier recycling. All nonhydrogen atoms were refined anisotropically using full-matrix, least-squares on F^2. All hydrogens were found from difference Fourier synthesis after four cycles of anisotropic refinement and were refined as "riding" on the adjacent atom with individual isotropic displacement factor 1.2 times the value of equivalent displacement factor of the parent atom. The carbon-bonded hydrogen atoms positions were idealized after each cycle of refinement. The solution and refinements were performed with SHELXS97 [81] and SHELXL97 [81] software. The graphical manipulations were performed using the XP routine of the SHELXTL [81], ORTEP [82], and PLUTON [83]. Atomic scattering factors were those incorporated in the computer programs. Details concerning the crystal data of all lanthanoid compounds are summarized in table 1 and crystallographic data for **1**–**3** are given in table 2. Selected hydrogen bond parameters are listed in table 3.

Supplementary material

CCDC258316 (**1**; La), CCDC258317 (**2**; Eu), CCDC258318 (**3**; Dy), CCDC266389 (Ho), CCDC266390 (Er), CCDC266391 (Tm), CCDC266392 (Yb), CCDC266393 (Lu), CCDC266394 (Ce), CCDC266395 (Pr), CCDC266396 (Sm), and CCDC266397 (Gd) contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/products/csd/request/.

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