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Use of the macrocyclic ligand cucurbit[6]uril for isolation of tetranuclear lanthanide aquahydroxo-carboxylate complexes from aqueous solutions*

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The tetranuclear lanthanide complexes $\{[Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4(C_{36}H_{36}N_{24}O_{12})_2][Ln(H_2O)_8]_{1.5}[Ln(H_2O)_6(NO_3)_2]_{0.5}\}(NO_3)_9 \cdot nH_2O$ (Ln = Ho, Gd, or Er) were prepared by heating (130 °C) aqueous solutions of lanthanide nitrates, cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$), and 4-cyanopyridine. The tetradentate coordination of the macrocyclic cucurbit[6]uril ligands through the portals leads to the formation of sandwich compounds, in which the tetranuclear hydroxo complex is located between two macrocyclic molecules. The polynuclear complexes are additionally stabilized by the chelating effect of the isonicotinate ligands generated by hydrolysis of 4-cyanopyridine. In the complexes, the aromatic moiety of the isonicotinate ion is encapsulated into the hydrophobic inner cavity of cucurbit[6]uril. In the absence of cucurbit[6]uril, the reaction with 4-cyanopyridine produces only the polymeric complexes $[Nd(C_5NH_4COO)_3(H_2O)_2]$ and $[Ln(C_5NH_4COO)_2(H_2O)_4]NO_3$ (Ln = Pr, Sm, or Gd), whose structures were established by X-ray diffraction. In water and aqueous solutions of nonionic and cationic surfactants, irreversible changes of the tetranuclear fragment of the complex (Ln = Gd) were observed after storage for two days, whereas the anionic surfactant stabilizes the complexes.

Key words: lanthanides, aqua complexes, cucurbit[6]uril, crystal structure.

There are many fields of application of mononuclear lanthanide complexes.[1,2] Methods for the synthesis of such complexes are rather well developed and enable the preparation of both molecular complexes and coordination polymers.[3,4] In recent years, polynuclear lanthanide complexes have attracted increasing interest.[5—10] Polynuclear/cluster lanthanide complexes hold promise as precursors in the sol—gel technology[11,12] and as model compounds in chemistry of metalloenzymes.[13,14] Considerable efforts are made to design luminescent nanodevices based on europium(III) clusters.[15] Gadolinium(III) clusters have attracted attention because of their use in NMR tomography.[16] In spite of the fact that these compounds hold considerable promise, procedures for the synthesis of polynuclear lanthanide complexes are of limited use. The process of their formation is generally difficult to control, and these complexes are often accidentally produced.[5]

Polynuclear lanthanide complexes are formed in aqueous solutions due to hydrolysis of their salts. An increase in pH upon the addition of, for example, an alkali leads to H^+ abstraction from coordinated water molecules and polymerization of aqua ions through bridging hydroxo ligands.[17] However, a high tendency to form insoluble polymeric hydroxo and oxo compounds makes it difficult to isolate intermediate certain-nuclearity polynuclear complexes from aqueous solutions.

One way of controlling the degree of hydrolysis is based on binding by chelating ligands, for example, by polyketonates, polyamines, carboxylates, or alkoxides. The hydrophilic groups of these ligands act as bridges between the metal ions to form a cluster core, whereas the hydrophobic groups are at the periphery, thus hindering further aggregation with the resulting formation of complexes of certain dimensions. For example, the reactions of lanthanide perchlorates (Ln = Pr, Nd, Sm, Eu, Gd, Dy, Er, or Yb) with sodium hydroxide in the presence of amino acids (Gly, Ala, Val, or Tyr)[6,7,18—22] or EDTA[23] produced polynuclear complexes containing up to fifteen lan-

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thanide atoms. The distorted $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ cube, whose vertices are occupied by the metal atoms and oxygen atoms of the μ_3-bridging hydroxo groups, is the main structural fragment of these complexes. Another approach to the synthesis of polynuclear lanthanide complexes in aqueous solutions without the use of polydentate organic ligands and with the use of lanthanide nitrates as the starting salts enables the preparation of the hexanuclear octahedral complexes $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_6(H_2O)_{12}]^{2+}$ (Ln = Gd—Yb).[10,24,25]

In the present study, we used the organic macrocyclic cavitand cucurbit[6]uril for isolation of new lanthanide complexes containing the tetranuclear cation $[Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4(C_{36}H_{36}N_{24}O_{12})_2]^{4+}$ from aqueous solutions.

Results and Discussion

The molecule of the organic macrocyclic cavitand cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$, CB[6]) consists of six methylene-bridged glycoluril fragments and has a barrel-like shape.[26,27] Due to the presence of polar carbonyl groups (portals), cucurbit[6]uril can form complexes with oxophilic metals serving as a polydentate ligand and be involved in hydrogen bonding with metal aqua complexes.[28—30] Earlier, we have demonstrated that cucurbit[6]uril can be used for isolation of polymeric aqua complexes of some metals (Zr, Hf, Sr, U, Mo, Ga, and Al) in the solid phase from aqueous solutions.[31—33] The reactions of CB[6] with aqueous solutions of lanthanide salts, which we have performed earlier by varying such conditions as the total metal concentration, pH (by the addition of NaOH, KOH, or ammonia), and the temperature, produced only mononuclear lanthanide aqua complexes with cucurbit[6]uril.[34—37] In these complexes, the cucurbit[6]uril molecule acts as a bi- or tetradentate ligand and is linked to the aqua complex through hydrogen bonds between the portal oxygen atoms and the aqua ligands coordinated to metal. In the present study, CB[6] was used for the first time for isolation polynuclear lanthanide complexes from aqueous solutions.

Heating of 0.5 *M* aqueous solutions of $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = La, Pr, Nd, Sm, Gd, Ho, or Er), cucurbit[6]uril, and 4-cyanopyridine in a sealed tube at 130 °C afforded plate-like colorless or pale-colored crystals. Before achieving the thermostatically controlled conditions, pH of the solution in the tube was ~4.0. After heating and separation of the crystals, pH was 4.5—5.5. The resulting complexes are soluble in water. However, a prolonged storage (for more than one week) of these aqueous solutions gave rise to insoluble polymeric compounds due to slow hydrolysis.

X-ray diffraction study of the complex with Ln = Ho revealed the following composition: $\{[Ho_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4(CB[6])_2][Ho(H_2O)_8]_{1.5}[Ho(H_2O)_6(NO_3)_2]_{0.5}\}(NO_3)_9 \cdot 31H_2O$ (**1**). The X-ray data statistics are given in Table 1. The space group and the crystals system for the complexes with Ln = Gd (**2**) and Er (**3**) are identical to those for complex **1**, and the corresponding unit cell parameters are similar, which indicates that these complexes are isostructural. Powder X-ray diffraction data show that the reactions with praseodymium(III) and neodymium(III) nitrates produced analogous isostructural compounds. The reactions with lanthanum(III) and samarium(III) nitrates afforded single crystals with different crystallographic parameters. For Ln = La, the crystal system is triclinic, the space group is $P\bar{1}$, a = 15.8721(5) Å, b = 25.2210(8) Å, c = 44.1997(14) Å, α = 78.121(1)°, β = 80.376(1)°, γ = 84.676(1)°. For Ln = Sm, the crystal system is monoclinic, the space group is $P2(1)/c$, a = 16.0535(19) Å, b = 34.200(4) Å, c = 29.396(4) Å, β = 101.299(2)°. Unfortunately, the structures of the latter two compounds were solved only to $R_1 \approx 20\%$. Analysis of the X-ray data demonstrated that the crystals also contain the tetranuclear cation $[Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4(CB[6])_2]^{4+}$.

In the structure of **1**, the coordination environment of the holmium atoms in the tetranuclear cationic complex $[Ho_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4(CB[6])_2]^{4+}$ is shown in Fig. 1. Four metal atoms form a distorted Ho_4 tetrahedron (Ho...Ho, 3.6080(4), 3.7444(6), 3.7444(6), and 3.7878(4) Å). The μ_3-bridging

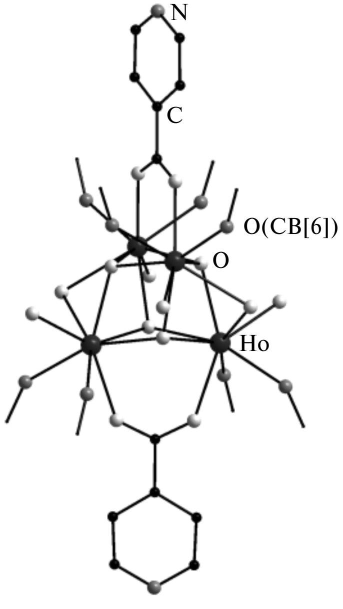


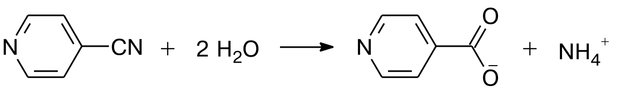
Fig. 1. Coordination environment of the holmium atoms in the tetranuclear complex $[Ho_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4(CB[6])_2]^{4+}$ in the crystal structure of **1**. For the CB[6] molecules, only the oxygen atoms involved in coordination to the holmium atoms are shown. The hydrogen atoms are omitted.

Table 1. Crystallographic data and the X-ray diffraction data collection and refinement statistics

Parameter	**1**	**5**	**6**	**7**
Molecular formula	$C_{84}H_{204}Ho_6N_{60}O_{114}$	$C_{12}H_{16}N_3O_{11}Pr$	$C_{12}H_{16}N_3O_{11}Sm$	$C_{12}H_{16}GdN_3O_{11}$
Molecular weight/g mol^{-1}	4868.65	519.19	528.63	535.53
T/K	150(2)	150(2)	150(2)	150(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbam*	*C*2/*c*	*C*2/*c*	*C*2/*c*
Unit cell parameters				
a/Å	15.0730(5)	9.1109(5)	9.0913(9)	9.0744(5)
b/Å	25.1365(8)	19.9089(13)	19.850(2)	19.8203(13)
c/Å	43.5401(14)	10.1368(6)	10.0693(11)	10.0259(6)
β/deg		108.678(2)	108.626(2)	108.541(2)
V/Å^3	16496.6(9)	1741.86(18)	1721.9(3)	1709.64(18)
Z	4	4	4	4
d/g cm^{-3}	1.960	1.98	2.039	2.081
μ/mm^{-1}	2.982	2.862	3.476	3.946
Transmission, max/min	0.4890/0.3472	0.5683/0.2601	0.8735/0.4769	0.3389/0.1444
F(000)	9768	1024	1036	1044
Crystal dimensions/mm	0.45×0.38×0.28	0.50×0.40×0.20	0.25×0.04×0.04	0.80×0.40×0.35
Scan range, θ/deg	1.40—25.68	2.81—28.28	2.05—25.68	2.58—28.28
Ranges of h, k, l indices	$0 \le h \le 18$ $0 \le k \le 30$ $0 \le l \le 53$	$-12 \le h \le 8$ $-26 \le k \le 6$ $-9 \le l \le 13$	$-7 \le h \le 11$ $-24 \le k \le 24$ $-12 \le l \le 12$	$-12 \le h \le 8$ $-26 \le k \le 26$ $-9 \le l \le 13$
Number of measured reflections	126758	6624	5719	6906
Number of independent reflections (R_{int})	15883 (0.0288)	2084 (0.0182)	1631 (0.0142)	2115 (0.0205)
Number of reflections with $I > 2\sigma(I)$	13257	2061	1596	2091
Number of parameters	1416	141	140	141
S factor based on F^2	1.096	1.162	1.123	1.110
R factors for reflections with $I > 2\sigma(I)$				
R_1	0.0599	0.0133	0.0106	0.0114
wR_2	0.1075	0.0334	0.0279	0.0290
R factors (for all reflections)				
R_1	0.0709	0.0136	0.0110	0.0116
wR_2	0.1117	0.0335	0.0280	0.0290
Residual electron density (max/min)/e Å^{-3}	4.030/–1.481	0.428/–0.541	0.366/–0.359	0.503/–0.573

hydroxo ligand (Ho—(μ_3-O), 2.282(5)—2.367(5) Å) is coordinated at each face of the tetrahedron. The metal atoms and the oxygen atoms of the μ_3-OH groups form the cubane fragment $[Ho_4(\mu_3\text{-}OH)_4]^{8+}$, which is structurally similar to the tetranuclear lanthanide cations in the above-mentioned complexes with amino acids.[6,7,18—22]

Under the conditions of hydrothermal synthesis, 4-cyanopyridine undergoes slow hydrolysis to form isonicotinic acid; hydrolysis leads also to an increase in pH of the solution.



The holmium atoms of the opposite edges of the Ho_4 tetrahedron are linked in pairs as a result of bidentate coordination of the carboxy groups of the isonicotonate anions (Ho—O, 2.349(5) and 2.348(5) Å). At two other edges, the holmium atoms are coordinated by the μ_2-bridging hydroxo groups (Ho—(μ_2-O), 2.528(6) and 2.565(5) Å). Each metal atom is additionally coordinated by one water molecule (Ho—O, 2.371(6) and 2.376(6) Å).

The tetranuclear aquahydroxo complex forms the sandwich compound $[Ho_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4(CB[6])_2]^{4+}$ with two cucurbit[6]uril molecules through coordination of four oxygen atoms of the CB[6] portals to two holmium atoms of the opposite edges of the Ho_4 tetrahedron (two O atoms per each Ho atom) (Fig. 2). The Ho—O(CB[6]) distances are in the range of 2.315(5)—2.405(5) Å. The aromatic moiety of the isonicotinate anion coordinated to the same two holmium atoms is encapsulated into the cavitand. Two uncoordinated oxygen atoms of the carbonyl groups of the CB[6] portal form hydrogen bonds with the μ_3- and μ_2-bridging hydroxo ligands of the tetranuclear complex

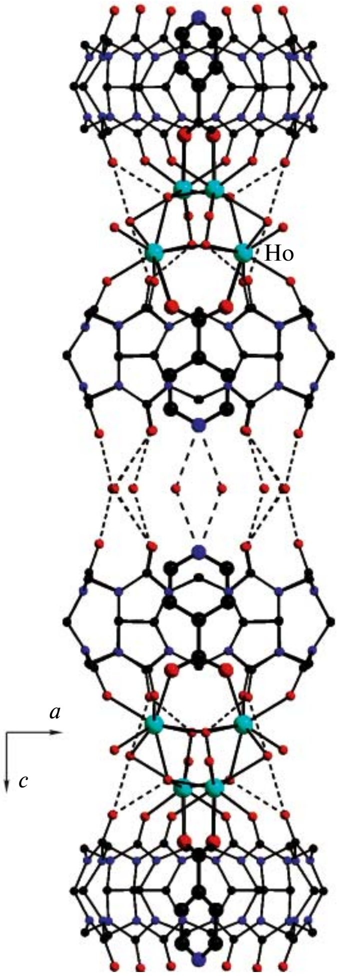


Fig. 2. Fragment of the $\{[Ho_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4(CB[6])_2]^{4+}(H_2O)_7\}_\infty$ chain in the structure of **1**. The holmium, oxygen, nitrogen, and carbon atoms are pale-blue, red, dark-blue, and black, respectively. The atoms of the isonicotinate ion encapsulated into the cavity of cucurbit[6]uril are represented by larger spheres. The hydrogen atoms are indicated by dashed lines. Fig. 2 is available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

(O...O, 2.72—2.89 Å). The coordination number of the holmium atoms is eight.

Encapsulation of the isonicotinate ion into the cavity of cucurbit[6]uril, along with coordination of the tetranuclear holmium complex by the oxygen atoms of the CB[6] portals, leads to a substantial ellipsoidal distortion of the cavitand. The longest and shortest distances between the opposite carbon atoms of the CH groups of the cucurbit[6]uril molecule in compound **1** are 1.55 and 1.27 Å, respectively. This distortion is typical of CB[6] (see Ref. 38) in the case of encapsulation of guests or coordination of the portal oxygen atoms to the metal cations.

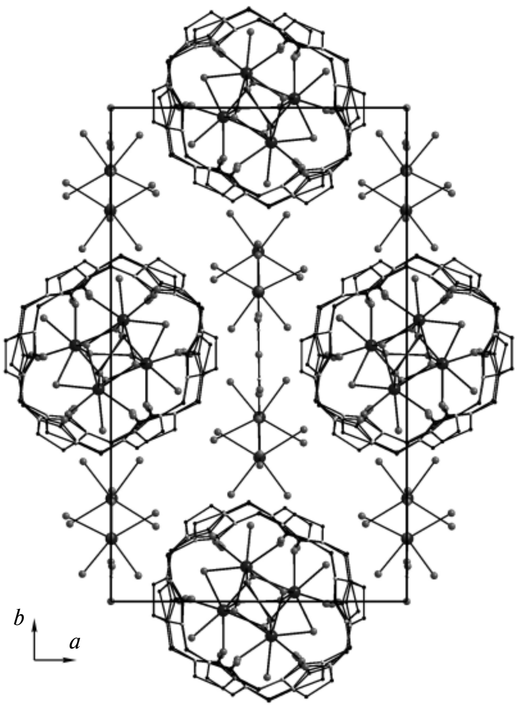


Fig. 3. Crystal packing in the structure of **1** projected onto the *ab* plane. The hydrogen atoms, the water molecules of crystallization, the uncoordinated nitrate anions, and the $[Ho(H_2O)_8]^{3+}$ cations, which are not involved in hydrogen bonding with $[Ho(H_2O)_6(NO_3)_2]^+$, are omitted.

In the crystal structure of **1**, the sandwich complexes are linked to each other through hydrogen bonds between the oxygen atoms of the uncoordinated CB[6] portal and the water molecules of crystallization (O...O, 2.66—2.99 Å) and between the nitrogen atom of the pyridine ring and the water molecule (N...O, 2.76 Å) disordered over two positions (both positions are shown in Fig. 2). This leads to the formation of supramolecular chains, which are arranged in the crystal structure of **1** along the *c* axis to form a pseudohexagonal packing (Fig. 3). The water molecules of crystallization, the nitrate anions, and the $[Ho(H_2O)_8]^{3+}$ cations, as well as the $[Ho(H_2O)_8]^{3+}$ and $[Ho(H_2O)_6(NO_3)_2]^+$ cations, which are linked to each other by hydrogen bonds and disordered about an inversion center (the Ho atoms are on the plane *m* ($z = 0.5$)), are located between the chains.

Therefore, the addition of 4-cyanopyridine to solutions of lanthanide nitrates and cucurbit[6]uril under the conditions of hydrothermal synthesis (130 °C) gave rise to tetranuclear lanthanide complexes. The analogous reactions in the absence of cyanopyridine (thermostatically controlled conditions, 120 °C) produced only mononuclear lanthanide complexes with cucurbit[6]uril.[39] The addition of cyanopyridine not only increases pH of the reaction solution but also gives rise to isonicotinic acid as a result of slow hydrolysis of PyCN. The carboxy group of isonicotinic acid serves as a bridge between the lanthanide atoms, thus stabilizing the polynuclear complex. Under analogous experimental conditions (130 °C), the reactions of lanthanide nitrates and CB[6] were carried out directly with isonicotinic acid, but these reactions did not produce polynuclear complexes even upon an increase of pH of the reaction solution to 5 by adding an alkali. It should be noted that attempts to use the chelating effect of the carboxylate ligands for isolation of polynuclear lanthanide complexes from solutions failed in the case of phenylacetic and adipic acids.[20,40] Apparently, the conditions of slow hydrolysis of cyanopyridine, under which the formation of carboxy groups occurs simultaneously with a gradual increase in pH of the solution, are necessary for the formation of polynuclear complexes.

The involvement of cucurbit[6]uril in the reactions under consideration is of key importance in the formation of tetranuclear lanthanide complexes: a) cucurbit[6]uril acts as a tetradentate ligand and the oxygen atoms of the CB[6] portals coordinate the lanthanide atoms; b) the hydrophobic inner cavity of the macrocyclic cavitand cucurbit[6]uril is occupied by the aromatic moiety of the isonicotinate ion. In the absence of CB[6], the reaction with 4-cyanopyridine under the analogous conditions led to isolation of only polymeric lanthanide complexes. Heating of 0.5 *M* aqueous solutions of $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Pr, Sm, Gd, or Nd) and 4-cyanopyridine in a sealed tube at 130 °C followed by slow cooling did not lead to the formation of a crystalline precipitate. The reaction at 140 °C afforded needle-like crystals. According to the X-ray diffraction data, the complexes have the composition $[Nd(C_5NH_4COO)_3(H_2O)_2]$ (**4**) and $[Ln(C_5NH_4COO)_2(H_2O)_4]NO_3$ (Ln = Pr (**5**), Sm (**6**), or Gd (**7**)). The structures of these complexes consist of polymeric chains, in which the mononuclear aqua complexes are linked to each other through the bidentate bridging carboxylate groups of the isonicotinate anion. Earlier, complex **4** has been synthesized[41] by evaporation of an aqueous solution of neodymium(III) nitrate and sodium isonicotinate; complexes of similar composition are known for Ln = Sm [42] and Eu.[43] The structures of complexes **5**—**7** were established for the first time. The parameters of crystallographic study are given in Table 1. Complexes **5**—**7** are isostructural with the compounds (Ln = La or Eu), which have been prepared earlier by evaporation of aqueous solutions of the corresponding lanthanide nitrates, isonicotinic acid, and ammonia and characterized.[44,45] The metal atom in complexes **5**—**7** is coordinated by four oxygen atoms of four bridging isonicotinate ions and four water molecules. The coordination polyhedron can be described as a distorted square antiprism (Fig. 4). The Ln—O bond lengths in complexes **5**—**7** are listed in Table 2.

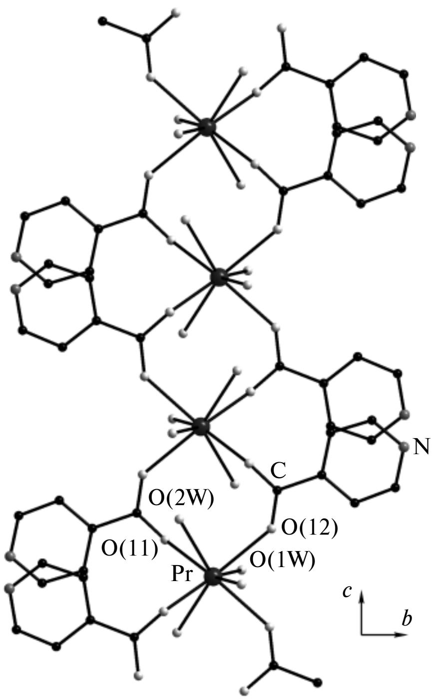


Fig. 4. Fragment of the polymeric chain $[Pr(C_5NH_4COO)_2(H_2O)_4]^+_\infty$ in the structure of **5**.

Table 2. The Ln—O bond lengths in the $[Ln(C_5NH_4COO)_2(H_2O)_4]NO_3$ complexes (Ln = Pr (**5**), Sm (**6**), or Gd (**7**))

Fragment	Bond	5	6	7
Ln—O (PyCOO)	Ln—O(11)	2.3830(11)	2.3409(11)	2.3182(10)
	Ln—O(12)	2.4187(11)	2.3746(11)	2.3510(10)
Ln—O (H_2O)	Ln—O(1W)	2.5516(11)	2.5028(12)	2.4779(10)
	Ln—O(2W)	2.5414(12)	2.4960(12)	2.4735(10)

The IR spectra of complexes **1**—**3** show a broad stretching band in the 3700—2800 cm^{-1} region assigned to different types of water molecules and hydroxy groups involved in hydrogen bonding. Bands corresponding to vibrations in the cucurbit[6]uril molecule are observed in the 1800—400 cm^{-1} region. The shift of the ν(C=O) intense band from 1734 cm^{-1} in the spectrum of cucurbit[6]uril to 1721—1725 cm^{-1} in the spectra of complexes **1**—**3** is attributed to both coordination of the CO groups of the portals to the metal atoms and the involvement of the carbonyl groups in hydrogen bonding. The absorption band of the nitrate anions is observed at 1384 cm^{-1}. A comparison of the spectra of 4-pyridinecarboxylic acid with the spectra of the complexes enabled the identification of the absorption bands of the carboxylate group of the isonicotinate ion coordinated to the metal atoms: the asymmetric vibrations are observed at 1614—1618 cm^{-1}; the symmetric vibrations, at 1422—1423 cm^{-1}. The Ln—O absorption bands are observed in the characteristic 600—200 cm^{-1} region.[46]

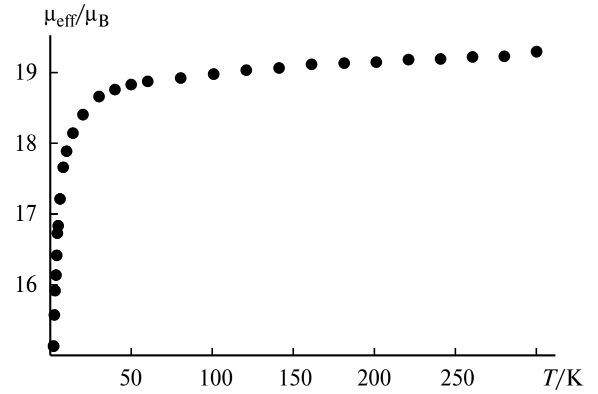


Fig. 5. Temperature dependence of the effective magnetic moment for compound **2**.

The magnetic properties of complex **2** (Ln = Gd) were studied in the temperature range of 2—300 K in magnetic field of 5 kOe (Fig. 5). The paramagnetic component of the magnetic susceptibility χ of the complex was calculated taking into account the diamagnetic contribution of the ions ($2100 \cdot 10^{-6}$ cm^3 mol^{-1}) estimated according to the Pascal scheme. The plot of the effective magnetic moment *vs.* the temperature was calculated by the equation

$$\mu_{eff}(T) = [(3k/N\mu_B{}^2)\chi T]^{0.5} \approx (8\chi T)^{0.5},$$

where N is Avogadro's number, k is the Boltzmann constant, and μ_B is the Bohr magneton. The effective magnetic moment μ_{eff} decreases with decreasing temperature from 19.3 μ_B at 300 K, to 15.1 μ_B at 2 K, which is indicative of weak antiferromagnetic interactions between the paramagnetic Gd^{III} ions. The magnetic moment at 300 K (19.3 μ_B) is in good agreement with the magnetic moment of 19.44 μ_B calculated for six weakly interacting Gd^{III} ions (S = 7/2).

Aqueous solutions of the complexes synthesized under the conditions analogous to those used for the synthesis of **1** starting from praseodymium(III) and samarium(III) nitrates were studied by electrospray mass spectrometry. The presence of peaks of the $[Pr_4(OH)_6(C_5NH_4COO)_2(H_2O)_4(CB[6])_2]^{4+}$ and $[Sm_4(OH)_6(C_5NH_4COO)_2(H_2O)_4(CB[6])_2]^{4+}$ ions is unambiguous evidence of the existence of tetranuclear complexes in aqueous solutions.

The state of complex **2** (Ln = Gd) in water was studied by nuclear magnetic relaxation.[47,48] The observed spin-spin relaxation rate ($R_{app(\mathbf{2})} = 1/T_{app(\mathbf{2})}$) is the sum of the proton relaxation contributions in the bulk ($R_{d(\mathbf{2})} = 1/T_{d(\mathbf{2})}$) and the paramagnetic contribution ($R_{p(\mathbf{2})} = 1/T_{p(\mathbf{2})}$):

$$R_{app(\mathbf{2})} = R_{d(\mathbf{2})} + R_{p(\mathbf{2})}.$$

The changes in the paramagnetic contribution are sensitive, in particular, to the number of water molecules in the first coordination sphere of the gadolinium complex or its rotational mobility. The relaxation parameters in an aqueous solution of compound **2** and gadolinium nitrate were compared.

The spin-spin relaxation efficiency coefficient $K_{re(\mathbf{2})}$ [47] of the $[Gd(H_2O)_8]^{3+}$ ions (16.5 L mmol^{-1} s^{-1}) is independent of the acidity in solutions with pH 2—6 and is constant with time ($\geq$14 days). An aqueous solution of compound **2** at a concentration of 0.1 mmol L^{-1} has pH 5.2—5.4, which is similar to the acidity of a solution of gadolinium nitrate and is lower than pH 6.5 corresponding to the start of hydrolysis. Therefore, according to the data from nuclear magnetic relaxation, the tetranuclear gadolinium complexes are stable in freshly prepared solutions, which is in good agreement with the results of electrospray mass spectrometry. Therefore, the relaxivity of this solution is determined by the presence of the following two types of dissociation products: two aqua ions and four hydroxo-bridged gadolinium ions in the complex cation involving isonicotinic acid and cucurbit[6]uril molecules. Taking into account the additive character of the relaxation rates of the aqua ions ($K_{re(\mathbf{2})}{}^{aqua}$) and the complex cation ($K_{re(\mathbf{2})}{}^{tetra}$) in solution

$$R_{app(\mathbf{2})} = 2K_{re(\mathbf{2})}{}^{aqua} + K_{re(\mathbf{2})}{}^{tetra},$$

the relaxivity coefficient per each gadolinium ion ($K_{re(\mathbf{2})}{}^{Gd-OH}$) in the tetranuclear fragment can be estimated

$$K_{re(\mathbf{2})}{}^{tetra} = 4K_{re(\mathbf{2})}{}^{Gd-OH}.$$

Based on $R_{app(\mathbf{2})}$ = 45.4 L mmol^{-1} s^{-1} and $K_{re(\mathbf{2})}{}^{aqua}$ = 16.5 L mmol^{-1} s^{-1}, we obtained $K_{re(\mathbf{2})}{}^{tetra}$ = 22.4 L mmol^{-1} s^{-1} and $K_{re(\mathbf{2})}{}^{Gd-OH}$ = 3.1 L mmol^{-1} s^{-1}. The latter value is substantially lower than that of the aqua ion. Nevertheless, it is sufficiently high from the viewpoint of mononuclear gadolinium hydroxo complexes (0.1—1 L mmol^{-1} s^{-1}) and is comparable with the constants $K_{re(\mathbf{2})}$ for its other complexes, including most of commercial contrast agents for magnetic resonance imaging.[16,49]

Hydrolytic stability of the complex cation containing the tetranuclear cluster is responsible for stability of the

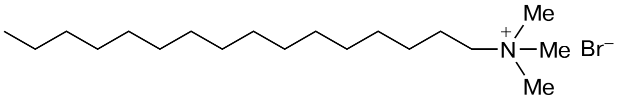
Table 3. Relaxivities of solutions of complex **2** (Ln = Gd) in various media with time

Media	Relaxivity of solution $R_{app(\mathbf{2})}$/L mmol^{-1} s^{-1}		
	I	II	III
Water	45.4	47.0	65.5
CTAB	48.2	50.9	56.8
Brij-35	56.9	59.5	74.5
SDS	61.0	60.8	59.6

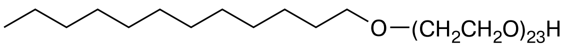
Note. I, immediately after the preparation; II, after storage for one day; III, after storage for 4 days.

relaxivities of a solution of complex **2** for two days (Table 3). An increase in $R_{\mathrm{app}(\mathbf{2})}$ during subsequent storage of the solution occurs apparently due to a change in the state of the complex as a result of deeper hydrolysis.

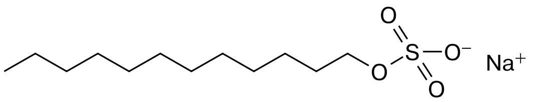
Aqueous solutions of surfactants are of considerable interest as highly organized media for various reactions, including those with complexes.[49] Table 3 presents the results of measurements of the relaxivity in solutions of complex **2** at a concentration of 0.1 mmol L^{-1} against 10 mmol L^{-1} of selected surfactants, such as cetyltrimethylammonium bromide (CTAB), oxyethylated (23 OEt units) dodecanol (Brij-35), and sodium dodecylsulfate (SDS).



CTAB



Brij35



SDS

In the case of the cationic and nonionic surfactants, a gradual increase in the relaxivity with time is consistent with that observed for an aqueous solution. Both the aqua ions $[Gd(H_2O)_8]^{3+}$ and the complex cation containing the tetranuclear fragment would not interact with the positively charged CTAB micelles, which is consistent with rather large $R_{\mathrm{app}(\mathbf{2})}$ for water and a solution of this cationic surfactant. Nonionic micelles have no effect on the relaxivity in solutions of gadolinium nitrate, which is attributed to the absence of interactions between these species. However, the presence of the nonionic surfactant Brij-35 in a solution of complex **2** leads to a higher value of $R_{\mathrm{app}(\mathbf{2})}$ immediately after the preparation of the sample. Since $K_{\mathrm{re}(\mathbf{2})}{}^{\mathrm{aqua}}$ (16.5 L mmol^{-1} s^{-1}) of the gadolinium aqua ion is equal in both water and a solution of Brij-35, the relaxation efficiency coefficient for the tetranuclear cationic complex $K_{\mathrm{re}(\mathbf{2})}{}^{\mathrm{tetra}} = (56.9{-}33.0) = 23.9$ L mmol^{-1} s^{-1}. In this case, the relaxivity coefficient per gadolinium ion is twice as large as that in water: $K_{\mathrm{re}(\mathbf{2})}{}^{\mathrm{Gd-OH}} = 23.9/4 \approx 6.0$ L mmol^{-1} s^{-1}. This effect can be attributed to solubilization of the cucurbituril ligands by nonionic micelles, thus increasing the size of the complex, which hinders its rotation, and, consequently,[16] increases $K_{\mathrm{re}(\mathbf{2})}{}^{\mathrm{Gd-OH}}$.

A special case was observed in a solution of the anionic surfactant. The relaxivity of a freshly prepared solution remains virtually unchanged after storage for three days. It should be noted that opalescence of a solution of complex **2** observed in the presence of SDS does not hinder magnetic relaxation measurements.[48] When analyzing $R_{\mathrm{app}(\mathbf{2})}$ in a medium of the anionic surfactant, it should be taken into account that the gadolinium aqua ions are bound to micelles and are characterized by a higher relaxivity ($K_{\mathrm{re}(\mathbf{2})}{}^{\mathrm{mic}} = 18.5$ L mmol^{-1} s^{-1})[49] compared to water. Based on this fact, we obtain $K_{\mathrm{re}(\mathbf{2})}{}^{\mathrm{tetra}} = 61.0 - 37.0 = 24.0$ L mmol^{-1} s^{-1} and $K_{\mathrm{re}(\mathbf{2})}{}^{\mathrm{Gd-OH}} = 24.0/4 = 6.0$ L mmol^{-1} s^{-1}. As can be seen from a comparison with the data for the nonionic surfactant, the electrostatic binding of the complex cation with the diphilic dodecylsulfate cation leads to stabilization of its state in solution.

The values of $R_{\mathrm{app}(\mathbf{2})}$ for the complex cation in solutions of Brij-35 and SDS are substantially larger than the relaxivities of commercial contrast agents for magnetic resonance imaging and are similar to those of many compounds tested in clinical practice.[49] Taking into account the revealed hydrolytic stability of the cation containing the tetranuclear fragment, the results of our study demonstrate that such complexes hold promise as potential contrast agents for magnetic resonance imaging.

To summarize, tetranuclear lanthanide complexes were synthesized under thermostatically controlled conditions from aqueous solutions of lanthanide nitrates, cucurbit[6]uril, and 4-cyanopyridine at 130 °C. Slow hydrolysis of 4-cyanopyridine affords sandwich complexes in which the $[Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4]^{4+}$ cation is coordinated by two CB[6] molecules. The formation of polynuclear Ln_4 complexes results from the combined influence of the chelating effect of the carboxylate ligands of isonicotinic acid generated as a result of hydrolysis of 4-cyanopyridine and the tetradentate coordination of the polycation by the portals of the macrocyclic ligand cucurbit[6]uril. Since the resulting complexes are soluble in water, they can be considered as promising starting compounds, for example, for the synthesis of coordination polymers through coordination of metal ions (Ag^+ or Pd^{2+}) by the nitrogen atoms encapsulated into the cavity of pyridine-4-carboxylic acid. In addition, the study of the magnetic relaxation characteristics of gadolinium complex **2** demonstrated that further investigation on the synthesis of polynuclear hydroxo-bridged complexes, which are stabilized by macrocycles and can be used as contrast agents for magnetic resonance imaging, holds promise.

Experimental

The starting compounds $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = La, Pr, Nd, Sm, Gd, Ho, and Er) of high purity grade and 4-cyanopyridine (99%) were used without additional purification. Cucurbit[6]uril was synthesized according to a known procedure.[26] The IR spectra were recorded on SCIMITAR FTS 2000 and BOMEM MB-102 Fourier-transform spectrometers in the 4000—200 cm^{-1} range. Elemental analysis was carried out in the Laboratory of Microanalysis of the Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The X-ray diffraction patterns of polycrystalline samples were measured on a Philips APD1700 diffractometer using Cu radiation (λ(Cu-Kα_1) = 1.54060; λ(Cu-Kα_2) = 1.54439). The X-ray diffraction study was performed on a Bruker Nonius X8Apex single-crystal diffractometer equipped with a 4K-CCD detector.[50] The magnetic properties of the complex were measured on a SQUID Quantum Design magnetometer. The electrospray mass spectra (ESI-MS) were recorded on a Micromass Q-TOF mass spectrometer (Manchester, UK). Solutions for measurements of the magnetic relaxation characteristics were prepared in water twice distilled in glassware. The acidity of solutions was monitored on an Orion 420A+ instrument (USA) equipped with a combined electrode. The spin-spin relaxation times T_2 at 298 K were measured on a multinuclear pulse relaxometer produced at the Kazan State University (operating frequency was 15.006 MHz for ^{1}H) using the Carr—Purcell—Meiboom—Gill (CPMG) imaging sequence (relative measurement error was at most 3%).

{Bis(cucurbit[6]uril)bis(μ_2-pyridine-4-carboxylato-*O,O´*)-tetra(μ_3-hydroxo)di(μ_2-hydroxo)tetraaquatetraholmium(III)}-sesqui{octaaquaholmium(III)}semi{hexaaquadinitratoholmium(III)} nonanitrate hentricontahydrate, $\{[Ho_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4(CB[6])_2][Ho(H_2O)_8]_{1.5}[Ho(H_2O)_6(NO_3)_2]_{0.5}\}(NO_3)_9\cdot 31H_2O$ (1). Cucurbit[6]uril (0.010 g, 0.009 mmol), $Ho(NO_3)_3\cdot 6H_2O$ (0.40 g, 0.88 mmol), 4-cyanopyridine (0.050 g, 0.48 mmol), and H_2O (1.5 mL) were placed in a tube. The sealed tube was treated as follows: 1) heated from 20 °C to 130 °C for 5 h; 2) kept at 130 °C for 5 h; 3) cooled to 20 °C for 48 h. Pale-orange plate-like crystals of **1** were filtered off, washed with ethanol and diethyl ether, and dried in air for 1 day. The yield was 0.025 g (30% based on consumed cucurbit[6]uril). Found (%): C, 20.20; H, 3.20; N, 17.06. $C_{84}H_{186}Ho_6N_{60}O_{114}$. Calculated (%): C, 20.80; H, 3.87; N, 17.33. IR (KBr), ν/cm^{-1}: 3415 s, 3123 w, 3012 w, 2941 w, 2854 w, 2400 w, 1723 s, 1655 w, 1618 s, 1562 m, 1489 s, 1458 w, 1422 m, 1384 m, 1354 w, 1326 s, 1294 w, 1237 s, 1190 s, 1146 m, 1033 m, 984 w, 967 s, 893 w, 834 w, 820 m, 799 s, 761 s, 749 w, 678 s, 651 m, 632 m, 564 w, 472 m, 464 m, 427 m, 373 s.

Complexes **2** and **3** were prepared analogously.

{Bis(cucurbit[6]uril)bis(μ_2-pyridine-4-carboxylato-*O,O´*)-tetra(μ_3-hydroxo)di(μ_2-hydroxo)tetraaquatetragadolinium(III)}-sesqui{octaaquagadolinium(III)}semi{hexaaquadinitratogadolinium(III)} nonanitrate tritetracontahydrate, $\{[Gd_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4(CB[6])_2][Gd(H_2O)_8]_{1.5}[Gd(H_2O)_6(NO_3)_2]_{0.5}\}(NO_3)_9\cdot 43H_2O$ (2), colorless plate-like crystals, the yield was 0.027 g (32% based on consumed cucurbit[6]uril). Found (%): C, 19.76; H, 4.17; N, 17.09. $C_{84}H_{210}Gd_6N_{60}O_{126}$ (per n = 43). Calculated (%): C, 20.09; H, 4.21; N, 16.74. IR (KBr), ν/cm^{-1}: 3411 s, 3281 w, 3126 w, 2935 w, 2857 w, 2400 w, 1722 s, 1656 w, 1615 s, 1562 m, 1487 s, 1460 w, 1422 m, 1385 s, 1375 w, 1356 w, 1326 s, 1293 w, 1261 w, 1237 s, 1190 s, 1145 s, 1032 m, 984 m, 968 s, 897 w, 835 w, 820 m, 799 s, 761 s, 748 w, 677 s, 651 w, 632 m, 563 w, 469 w, 464 m, 420 m, 371 s. The crystals belong to the orthorhombic system, space group *Pbam*, a = 15.1454(8) Å, b = 24.9664(12) Å, c = 44.1327(22) Å.

{Bis(cucurbit[6]uril)bis(μ_2-pyridine-4-carboxylato-*O,O´*)-tetra(μ_3-hydroxo)di(μ_2-hydroxo)tetraaquatetraerbium(III)}-sesqui{octaaquaerbium(III)}semi{hexaaquadinitratoerbium(III)} nonanitrate nonatricontahydrate, $\{[Er_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(C_5NH_4COO)_2(H_2O)_4(CB[6])_2][Er(H_2O)_8]_{1.5}[Er(H_2O)_6(NO_3)_2]_{0.5}\}(NO_3)_9\cdot 39H_2O$ (3). Pale-pink plate-like crystals, the yield was 0.037 g (43% based on consumed cucurbit[6]uril). Found (%): C, 19.90; H, 3.64; N, 17.08. $C_{84}H_{202}Er_6N_{60}O_{122}$ (per n = 39). Calculated (%): C, 20.14; H, 4.16; N, 16.78. IR (KBr), ν/cm^{-1}: 3416 s, 3122 w, 3010 w, 2937 w, 2855 w, 2400 w, 1721 s, 1654 m, 1614 s, 1562 w, 1489 s, 1457 w, 1423 m, 1384 m, 1353 m, 1326 s, 1293 w, 1237 s, 1191 s, 1146 m, 1035 m, 984 m, 967 s, 834 w, 820 m, 799 s, 761 s, 749 w, 679 s, 652 m, 632 m, 564 m, 470 m, 442 w, 428 m, 381 s. The crystals belong to the orthorhombic system, space group *Pbam*, a = 15.0708(7) Å, b = 25.1423(11) Å, c = 43.5181(19) Å.

The number of water molecules of crystallization estimated by X-ray diffraction (for complex **1**) and elemental analysis (for complexes **1—3**) can vary for different samples depending on the experimental conditions and air humidity during storage. For compound **1**, the X-ray diffraction data are in agreement with the elemental analysis data. For these complexes, water of crystallization is often lost during storage (compared to the X-ray diffraction data collected from a crystal immediately after withdrawing from the solution).

Bis(μ_2-pyridine-4-carboxylato-*O,O´*)-diaqua(pyridine-4-carboxylato-*O,O´*)-neodymium(III), $[Nd(C_5NH_4COO)_3(H_2O)_2]$ (4). Cucurbit[6]uril (0.010 g, 0.009 mmol), $Nd(NO_3)_3\cdot 6H_2O$ (0.40 g, 0.92 mmol), 4-cyanopyridine (0.135 g, 1.30 mmol), and H_2O (1.5 mL) were placed in a tube. The sealed tube was treated as follows: 1) heated from 20 °C to 140 °C for 5 h; 2) stored at 140 °C for 5 h; 3) cooled to 20 °C for 48 h. Pale-lilac needle-like crystals were filtered off and dried in air for 1 day. The yield was 0.274 g (55% based on consumed neodymium nitrate). Found (%): C, 39.74; H, 2.90; N, 7.61. $C_{18}H_{16}N_3NdO_8$. Calculated (%): C, 39.55; H, 2.95; N, 7.69. IR (KBr), ν/cm^{-1}: 3449 s, 3352 s, 3076 w, 3042 w, 2812 w, 2259 w, 1902 w, 1637 m, 1590 s, 1546 s, 1498 s, 1437 s, 1411 s, 1385 s, 1319 m, 1282 s, 1233 m, 1086 w, 1062 s, 1036 s, 1014 s, 977 w, 951 w, 867 s, 851 s, 775 s, 712 s, 683 s, 615 m, 547 s, 452 m, 417 m.

Complexes **5—7** were prepared according to an analogous procedure.

[Bis(μ_2-pyridine-4-carboxylato-*O,O´*)-tetraaqua]praseodymium(III) nitrate, $[Pr(C_5NH_4COO)_2(H_2O)_4]NO_3$ (5). Pale-green needle-like crystals, the yield was 0.210 g (41% based on consumed praseodymium nitrate). Found (%): C, 27.81; H, 2.97; N, 8.03. $C_{12}H_{16}N_3O_{11}Pr$. Calculated (%):C, 27.76; H, 3.11; N, 8.09. IR (KBr), ν/cm^{-1}: 3447 s, 3114 w, 3042 m, 2922 w, 2853 w, 2747 w, 1635 m, 1589 s, 1545 s, 1498 m, 1439 s, 1410 s, 1282 s, 1233 m, 1086 w, 1061 s, 1014 s, 954 w, 850 s, 775 s, 712 s, 683 s, 611 m, 545 s, 452 m, 416 m.

[Bis(μ_2-pyridine-4-carboxylato-*O,O´*)-tetraaqua]samarium(III)] nitrate, $[Sm(C_5NH_4COO)_2(H_2O)_4]NO_3$ (6). Pale-yellow needle-like crystals, the yield was 0.237 g (50% based on consumed samarium nitrate). Found (%): C, 27.08; H, 3.00; N, 7.91. $C_{12}H_{16}N_3O_{11}Sm$. Calculated (%): C, 27.26; H, 3.01; N, 7.95. IR (KBr), ν/cm^{-1}: 3402 s, 3076 w, 3043 m, 2812 w, 2763 w, 2311 w, 1638 m, 1592 s, 1548 s, 1498 m, 1438 s, 1411 s, 1385 m, 1319 m, 1281 s, 1233 s, 1087 w, 1062 s, 1036 s, 1014 s, 950 w, 868 s, 851 s, 776 s, 712 s, 683 s, 613 m, 549 s, 453 m, 418 m.

[Bis(μ_2-pyridine-4-carboxylato-*O,O´*)-tetraaqua]gadolinium(III)] nitrate, $[Gd(C_5NH_4COO)_2(H_2O)_4]NO_3$ (7). Colorless needle-like crystals, the yield was 0.236 g (50% based on consumed gadolinium nitrate). Found (%): C, 26.52; H, 3.03; N, 7.73. $C_{12}H_{16}N_3O_{11}Gd$. Calculated (%): C, 26.91; H, 3.01; N, 7.85. IR (KBr), ν/cm^{-1}: 3455 s, 3399 s, 3114 w, 3077 w, 3043 m, 2813 w, 2763 w, 2309 w, 1889 w, 1641 m, 1593 s, 1549 s, 1498 m, 1438 s, 1413 s, 1386 w, 1319 m, 1280 s, 1233 s, 1087 w, 1062 s, 1036 s, 1014 s, 944 w, 868 s, 852 s, 776 s, 713 s, 683 s, 617 m, 551 s, 453 s, 418 s.

Electrospray mass-spectrometric study. Aqueous solutions of the tetranuclear complexes prepared from praseodymium(III) and samarium(III) nitrates were studied by electrospray mass spectrometry.

Electrospray mass spectrum for $\{Pr_4\}$, *m/z* (*I* (%)): 598.9 $[Pr_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H + H_2O]^{5+}$ (17), 611.4 $[Pr_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H + H_2O + HNO_3]^{5+}$ (17), 743.8 $[Pr_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2]^{4+}$ (71), 759.6 $[Pr_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + HNO_3]^{4+}$ (63), 764.1 $[Pr_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H_2O + HNO_3]^{4+}$ (29), 1012.5 $[Pr_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + NO_3]^{3+}$ (23), 1018.5 $[Pr_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H_2O + NO_3]^{3+}$ (20), 1039.5 $[Pr_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H_2O + H + 2\ NO_3]^{3+}$ (63), 1060.5 $[Pr_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H_2O + 2\ H + 3\ NO_3]^{3+}$ (100).

Electrospray mass spectrum for $\{Sm_4\}$, *m/z* (*I* (%)): 606.5 $[Sm_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H + H_2O]^{5+}$ (17), 619.1 $[Sm_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H + H_2O + HNO_3]^{5+}$ (17), 757.7 $[Sm_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H_2O]^{4+}$ (100), 773.6 $[Sm_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H_2O + HNO_3]^{4+}$ (50), 1030.9 $[Sm_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H_2O + NO_3]^{3+}$ (12), 1052.2 $[Sm_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H_2O + NO_3 + HNO_3]^{3+}$ (35), 1072.9 $[Sm_4(OH)_6(C_6O_2NH_4)_2(H_2O)_4(CB[6])_2 + H_2O + NO_3 + 2\ HNO_3]^{3+}$ (44).

X-ray diffraction study. The crystallographic characteristics and the X-ray data collection and refinement statistics for compounds **1** and **5—7** are given in Table 1. The X-ray data sets were collected according to a standard procedure at 150 K (Mo-Kα-radiation, λ = 0.71073 Å, graphite monochromator). Semiempirical absorption corrections were applied based on the intensities of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters for nonhydrogen atoms using the SHELXTL program package.[50] The hydrogen atoms of cucurbit[6]uril and the isonicotinate ion in **1** were calculated geometrically and refined using a riding model. The hydrogen atoms of the water molecules in **1** were not revealed. The atomic coordinates of compounds **1** and **5—7** were deposited with the Cambridge Structural Database and can be obtained from the authors.

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