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Tetranuclear Lanthanide Aqua Hydroxo Complexes with Macrocyclic Ligand Cucurbit[6]uril

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Tetranuclear lanthanide aqua hydroxo complexes with two structural types of core – $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4\}^{4+}$ [Ln = Pr (**1**), Nd (**2**), Eu (**3**), Gd (**4**), Tb (**5**)] and $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2\}^{6+}$ [Ln = Er (**6**), Yb (**7**)] – were prepared by heating (130 °C) of aqueous solutions of lanthanide(III) chlorides, cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$, CB[6]), and 4-cyanopyridine. The formation of Ln_4 complexes results from the combined influence of the tetradentate coordination of the polycation by the portals of the macrocyclic ligand CB[6] and the chelating effect of the carboxylate ligands of isonicotinic acid generated as a result of hydrolysis of 4-cyanopyridine. X-ray diffraction analysis of **1**–**7** revealed the sandwich structure with the tetranuclear lanthanide complex situated between two macrocyclic molecules. The compounds were characterized by elemental analysis, IR, and electrospray ionization (ESI) mass spectrometry. Luminescence spectra of **3** and **5** and magnetic properties of **4** were also studied.

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Introduction

The wide variety of applications that lanthanide complexes have in many fields is well known.[1–5] The synthetic procedures are well-mastered and many lanthanide-containing compounds can be designed with required physicochemical properties, both as molecular compounds or coordination polymers. In recent years, special attention has been focused on the polynuclear lanthanide complexes due to their fascinating structures and potential applications, which may ultimately lead to new materials.[6–17] Some of these compounds hold promise as precursors in metalorganic chemical vapor deposition and sol-gel technology.[18–20] Interest in gadolinium(III) nanoclusters with tunable electron relaxation behavior can be conceived for magnetic resonance imaging applications.[21–23] Great efforts have been focused on the europium(III) nanoclusters to construct luminescent nanodevices.[24,25] The sharpness of the intra-f-shell emission lines in lanthanide luminescence spectra makes them interesting candidates for phosphors, optical sensors, and probes in biochemistry. Although the polynuclear lanthanide complexes are very promising, the examples of well-characterized finite-size lanthanide clusters stable in aqueous solutions are limited and the syntheses are still characterized by random self-organization.[6] A high tendency to form insoluble polymeric hydroxo and oxo compounds makes difficult isolation of intermediate complexes of certain-nuclearity from aqueous solutions. The commonly employed strategy is to control the hydrolysis of metal ions with the aid of supporting ligands: polyketonates, polyamines, carboxylates, or alkoxides. For example, the reactions of lanthanide perchlorate salts with sodium hydroxide in the presence of the bifunctional amino acids or EDTA produced polynuclear complexes containing up to 15 lanthanide atoms.[9–17] The main structural fragment of these complexes is the distorted $\{Ln_4(\mu_3\text{-}OH)_4\}^{8+}$ cube, where alternate vertices are occupied by constituent lanthanide ions and the triply bridging μ_3-OH ligands.

In the present study, we report on the use of the organic macrocyclic ligand cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$, CB[6]) as a supporting ligand for the isolation of tetranuclear lanthanide complexes from aqueous solutions. The cucurbit[6]uril molecule resembles in shape a barrel containing oxygen atoms of carbonyl groups (portals) on the planes of the top and the bottom.[26,27]

Because of the presence of polar carbonyl groups, CB[6] can form complexes with oxophilic metals serving as a polydentate ligand and be involved in hydrogen bonding with metal aqua complexes.[28–31] Previous studies in our group have evidenced the potential of using CB[6] for isolation of polynuclear Zr, Hf, Sr, U, Mo, Al, Ga, and In aqua complexes.[32–35] As a rule, polynuclear cationic metal aqua complexes are highly charged, and coordinated water mole-

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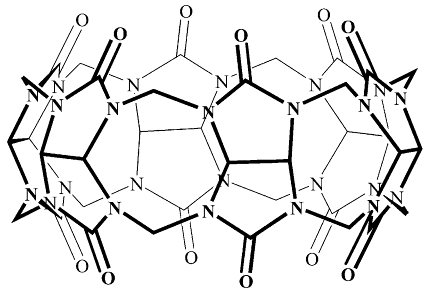


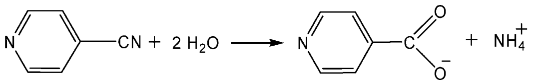
cucurbit[6]uril

cules in these complexes possess rather strong acidic properties, which favor the formation of hydrogen bonds with the carbonyl oxygen atoms of cucurbit[6]uril. Last year we managed to isolate and structurally characterize a tetranuclear lanthanide complex with CB[6] from aqueous solutions of holmium(III) nitrate for the first time.[23] Here we report the synthesis of a series of lanthanide(III) hydroxo complexes from aqueous solutions of CB[6], lanthanide chlorides, and 4-cyanopyridine. Two types of lanthanide complexes were obtained, in which metal atoms form a cubane-like fragment $\{Ln_4(\mu_3\text{-}OH)_4\}^{8+}$ and are coordinated additionally by two or four μ_2-hydroxo bridges with formation of $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2\}^{6+}$ and $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4\}^{4+}$ cores, correspondingly. Compounds of both structural types were characterized by single crystal X-ray analysis.

Results and Discussion

Syntheses

The reaction of lanthanide(III) chlorides (Ln = Pr, Nd, Eu, Gd, Tb, Er, Yb), cucurbit[6]uril, and 4-cyanopyridine were carried out in sealed tubes at 130 °C. Cucurbit[6]uril is water insoluble, but it is well soluble in hot saturated aqueous solutions of Ln^{III} salts and for this reason a great excess of metal salt to CB[6] was used in the reactions. These experimental conditions, namely concentrated metal solutions and high reaction temperatures promote polymerization of aqua ions.[36] At the same time, 4-cyanopyridine undergoes hydrolysis under hydrothermal reaction conditions to form isonicotinic acid, leading also to an increase in pH of the solution [Equation (1)]. As we have shown earlier, slow hydrolysis of 4-cyanopyridine is necessary for the isolation of tetranuclear complexes from lanthanide nitrate aqueous solutions.[23]



(1)

Slow cooling of the sealed reaction tubes and allowing them to stand at room temperature for several days, produces high yields of well-shaped pale colored or colorless crystals of complexes **1**–**7**.

After separation of the crystals, the pH of the solutions was 5–6. The resulting complexes **1**–**7** are soluble in water; however the storage of the solutions for more than three–four days gave rise to insoluble polymeric compounds due to slow hydrolysis. For the complexes, water of crystallization is often lost during storage (compared to the X-ray diffraction data collected at low temperature from a crystal immediately after withdrawal from the solution).

Structures

The structures of **1**–**7** have been determined by single crystal X-ray diffraction. All the compounds have a sandwich structure with the tetranuclear lanthanide complex situated between two cucurbit[6]uril molecules. Four lanthanide atoms and four bridging μ_3-OH groups form a distorted cubane-like $\{Ln_4(\mu_3\text{-}OH)_4\}^{8+}$ core, which is structurally similar to the tetranuclear lanthanide cation in the above-mentioned complexes with amino acids.[9–17] In compounds **1**–**7** the metal atoms of the cubane-like core are coordinated additionally by four (**1**–**5**) or two (**6**, **7**) μ_2-hydroxo ligands, which results in two different structural types for these complexes.

In the first type, complexes (**1**–**5**), four μ_2-OH groups bridge the lanthanide atoms of the cubane-like core with formation of $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4\}^{4+}$ (Figure 1, a). The structure may be regarded as the cubane core capped by four μ_2-hydroxo ligands on each side plane of the cube. In compounds **6** and **7**, only two opposite side planes of the cubane core are capped by two μ_2-OH ligands, and the polynuclear core of the second type, $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2\}^{6+}$, is formed (Figure 1, b).

In both structural types, Ln atoms are linked in pairs by carboxy groups of two bidentate isonicotinate anions situated over cubane planes that are not capped by μ_2-OH ligands. Each of two cucurbit[6]uril molecules acts as a tetradentate ligand bonding to the Ln_4 core through coordination of four oxygen atoms of its portal to the lanthanide atoms (two O atoms per Ln atom). The cavity of CB[6]

$(H_3O)_3\{[Pr_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2][Pr(H_2O)_7(C_5NH_4COOH)]_2\}Cl_{11}\cdot 29H_2O$ (**1**)

$(H_3O)_3\{[Nd_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2][Nd(H_2O)_7(C_5NH_4COOH)]_2\}Cl_{11}\cdot 29H_2O$ (**2**)

$(H_3O)_5[Eu_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]Cl_7\cdot 38H_2O$ (**3**)

$(H_3O)_6[Gd_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]Cl_8\cdot 36H_2O$ (**4**)

$(H_3O)_4[Tb_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]Cl_6\cdot 40H_2O$ (**5**)

$(H_3O)_5[Er_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]Cl_9\cdot 35H_2O$ (**6**)

$(H_3O)_3[Yb_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]Cl_7\cdot 38H_2O$ (**7**)

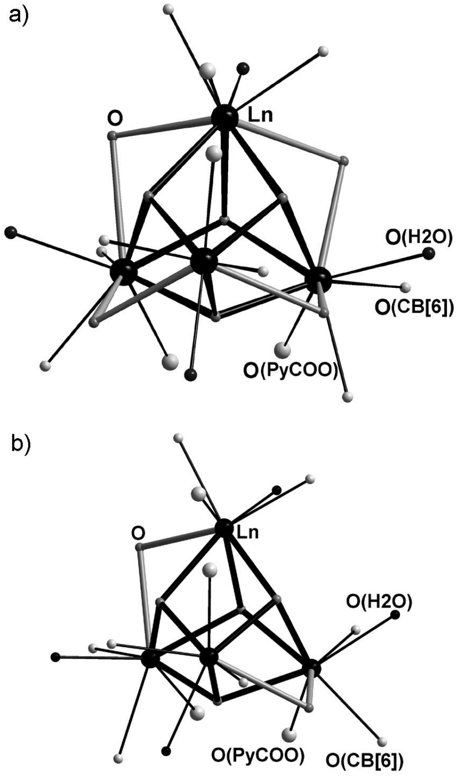


Figure 1. The coordination environments of lanthanide atoms in two types of tetranuclear hydroxo complexes: a) $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4\}^{4+}$ [Ln = Pr (**1**), Nd (**2**), Eu (**3**), Gd (**4**), Tb (**5**)]; b) $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2\}^{2+}$ [Ln = Er (**6**), Yb (**7**)]. The cubane-like core is shown by thick black lines and Ln–μ_2-O hydroxo bridges by thick gray lines. Hydrogen atoms are omitted for clarity.

encapsulates the aromatic part of the isonicotinate anion. The structure of the resulting $[Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]^{2+}$ cation, where the tetranuclear lanthanide hydroxo complex of the first type is sandwiched between two CB[6] molecules, is shown in Figure 2 (for compound **4** as an example). The formation of Ln_4 complexes results from the combined influence of the chelating effect of the carboxylate ligands of isonicotinic acid and the tetradentate coordination of the polycation by the portals of the macrocyclic ligand cucurbit[6]uril. The lanthanide complex is connected with the CB[6] molecules also by numerous hydrogen bonds between oxygen atoms of the carbonyl groups of the portals and the μ_3- and μ_2-bridging hydroxo ligands of the complex [O···O, 2.71–2.98 Å (in **4** as an example)]. The shape of the sandwich complex can be approximated by a cylinder with van der Waals dimensions of about 13 × 20 Å. The sandwich cation with lanthanide complexes of the second type **6** and **7** (with the cubane core capped by two μ_2-OH ligands) has the same structure as $[Ho_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]^{4+}$, which we presented previously for the compound isolated from the aqueous solution of holmium(III) nitrate.[23]

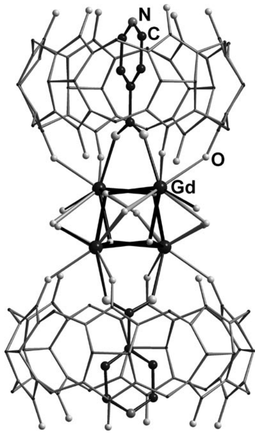


Figure 2. The structure of $[Gd_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4(C_5NH_4COO)_2(H_2O)_4(CB[6])_2]^{2+}$ complex in **4**. Hydrogen atoms are omitted for clarity.

Thus, each metal atom in the cubane core of complexes of the first type (Ln = Pr, Nd, Eu, Gd, Tb) is coordinated by three μ_3-hydroxo ligands, by two μ_2-hydroxo ligands, by one oxygen atom of the isonicotinate anion, by two oxygen atoms of the CB[6] molecule, and one coordination position is occupied by a water molecule, so the coordination number for the Ln atoms is nine (Figure 1, a). The coordination number of the Ln atoms in complexes of the second type (Ln = Er and Yb) is eight since only one coordination position (instead of two in **1**–**5**) is occupied by a μ_2-OH ligand. This fact is in good agreement with the lanthanide contraction. The bond lengths in both types of lanthanide cores are presented in Table 1. The distances Ln–O agree well with the average bond lengths in Ln_4 hydroxo complexes[9–17,23] and decrease from **1** to **7** in accordance with the decrease of the lanthanide radius (1.13 Å for Pr^{3+} and 1.01 Å for Yb^{3+}[37]).

The sandwich cation is a common fragment for **1**–**7** but there are some differences in the structures and crystal packing of the compounds. Compounds **1** and **2** are isostructural. In these compounds the external CB[6] portals

Table 1. The bond lengths in the lanthanide core of the complexes **1**–**7**.

Ln	Pr (**1**)	Nd (**2**)	Eu (**3**)	Gd (**4**)	Tb (**5**)	Er (**6**)	Yb (**7**)
Ln–(μ_3-O)	2.406(4)–2.450(4)	2.392(3)–2.438(4)	2.326(5)–2.436(5)	2.315(5)–2.428(5)	2.291(4)–2.412(4)	2.284(4)–2.333(4)	2.266(3)–2.315(4)
Ln–(μ_2-O)	2.672(4)–2.781(4)	2.649(4)–2.768(4)	2.577(5)–2.778(5)	2.564(5)–2.762(6)	2.549(4)–2.753(5)	2.529(4)–2.550(4)	2.532(4)–2.535(4)
Ln–O(CB[6])	2.453(4)–2.558(4)	2.440(4)–2.546(4)	2.422(5)–2.462(5)	2.411(5)–2.444(5)	2.390(4)–2.428(4)	2.304(4)–2.377(4)	2.285(3)–2.375(4)
Ln–O(PyCOO)	2.428(4), 2.429(4)	2.410(4), 2.421(4)	2.414(5)–2.436(5)	2.401(5)–2.422(5)	2.390(4), 2.404(4)	2.326(4), 2.329(4)	2.297(4), 2.301(4)
Ln–O(H_2O)	2.507(5), 2.519(4)	2.493(5), 2.508(4)	2.424(5)–2.460(5)	2.408(5)–2.452(5)	2.388(4)–2.427(4)	2.355(5), 2.369(4)	2.322(4), 2.326(4)
Ln···Ln	3.7832(6)–3.9787(4)	3.7532(5)–3.9571(4)	3.7453(5)–3.9223(5)	3.7238(5)–3.9078(5)	3.6953(4)–3.8805(4)	3.5901(4)–3.7790(5)	3.5640(3)–3.7258(4)

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of the sandwich cation are coordinated by mononuclear lanthanide complex $[Ln(H_2O)_7(C_5NH_4COOH)]^{3+}$ (Ln = Pr and Nd). Only one oxygen portal atom is involved in the coordination with the mononuclear complex [Ln–O(CB[6]) 2.482(4) Å (**1**), 2.465(4) Å (**2**)], which is not usual for lanthanide complexes with macrocyclic ligand CB[6].[31] The coordination environment of the Ln atom consists also of seven aqua ligands and a monodentate isonicotinic acid. This type of coordination of isonicotinic acid is known for lanthanide complexes,[38] though the bidentate type is more common. The bond length $Ln–O(C_5NH_4COOH)$ is 2.402(4) Å and 2.389(4) Å for **1** and **2**, respectively. Two aqua ligands of $[Ln(H_2O)_7(C_5NH_4COOH)]^{3+}$ form hydrogen bonds with oxygen portal atoms coordinated to this complex CB[6] molecule, three other aqua ligands form hydrogen bonds with the portal of the CB[6] molecule of the neighboring sandwich cation, resulting in a chain structure of the complexes **1** and **2** (Figure 3).

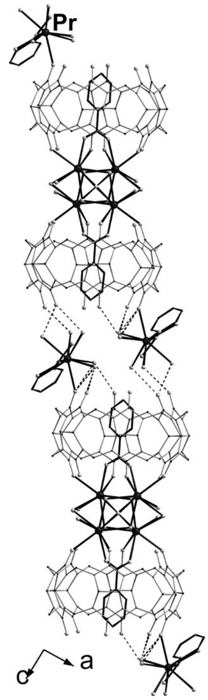

Figure 3. Fragment of the $\{[Pr(H_2O)_7(C_5NH_4COOH)](CB[6])[Pr_4(OH)_8(H_2O)_4(C_5NH_4COO)_2](CB[6])[Pr(H_2O)_7(C_5NH_4COOH)]^{8+}\}_\infty$ chain in the structure of **1**. Dashed lines show hydrogen bonds.

According to the X-ray data the crystal structure of the isotypical compounds **3**–**5** has a clear layered motive along the *c* direction. The parquet-like layer consists of $[Ln_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]^{2+}$ (Ln = Eu, Gd, Tb) sandwich cations, the angle between sandwiches belonging to neighboring rows is about 50°. As an example, the parquet-like layer of gadolinium sandwich cations in **4** is represented in Figure 4. Sandwiches of the neighboring rows are located close enough to each other and connected by hydrogen bonds between CB[6] carbonyl portals of one sandwich and CH and CH_2 groups of CB[6] of another one [$d_{av.}$(O···H–C) = 2.57 Å]. Formation of the system of hydrogen bonds O···H–C between the neighboring CB[*n*] (*n* = 6, 7) molecules is known for some cucurbit[*n*]turil compounds.[31,39]

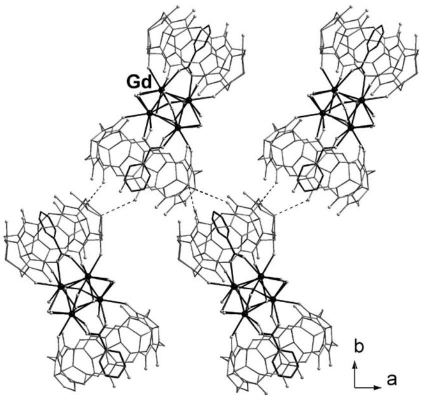

Figure 4. Parquet-like layer of $[Gd_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]^{2+}$ sandwich cations in the crystal structure of **4** (projection on the *ab* plane). Dashed lines show hydrogen bonds.

In the isotypical compounds **6** and **7**, the sandwich complexes of the second structural type $[Ln_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]^{4+}$ (Ln = Er, Yb) are linked to each other through hydrogen bonds between the water molecules of crystallization and the nitrogen atom of the pyridine ring and the oxygen atoms of the uncoordinated CB[6] portal (O···O, 2.79–2.93 Å and 2.85–2.97 Å for **6** and **7**, respectively). This leads to the formation of supramolecular chains (Figure 5). The chain packing of sandwiches is like that in holmium(III) complex,[23] the difference is a moderate shift (about 3.7 and 3.8 Å in **6** and **7**) of sandwiches across the direction of their expansion, whereas in the nitrate compound sandwiches arrange exactly one under another.

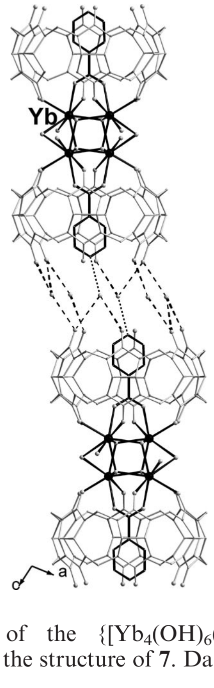

Figure 5. Fragment of the $\{[Yb_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]^{4+}\}_\infty$ chain in the structure of **7**. Dashed lines show hydrogen bonds.

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In the crystal structures of all **1**–**7** complexes the water molecules of crystallization and the chloride anions are located between the sandwich complexes and linked to each other and to sandwiches by a complex network of hydrogen bonds.

IR Spectroscopy

The IR spectra of complexes **1**–**7** 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, as usual.[23,34] The shift of the ν(C=O) intense band from 1734 cm^{-1} in the spectrum of cucurbit[6]uril to 1722–1726 cm^{-1} in the spectra of complexes **1**–**7** 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. A comparison of the spectra of 4-pyridinecarboxylic acid with the spectra of the complexes identifies the absorption bands of the carboxylate group of the isonicotinate ion coordinated to the metal atoms: the asymmetric vibrations are observed at 1610–1614 cm^{-1}; the symmetric vibrations, at 1416–1423 cm^{-1}.

Electrospray Ionization Mass Spectrometry

Freshly prepared aqueous solutions of representative complexes belonging to both structural types, namely **4** (Ln = Gd) for the first structural type and **6** (Ln = Er) for the second one, were investigated by electrospray mass spectrometry (ESI-MS). In general, the ESI-MS allow identification of the intact sandwich complexes $[Gd_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]^{2+}$ and $[Er_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]^{4+}$. These species are typically observed to different extents as proton, HCl and/or H_2O adducts and in consequence appear as 3+, 4+, and 5+ charged cations. The ESI-MS spectrum of aqueous solutions of **6** is shown in Figure 6. A prominent peak centered at *m*/*z* = 770.4 Th is assigned to the $\{Er_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2\}^{4+}$ tetracation (see inset in Figure 6). Two partially overlapped peaks in the *m*/*z* = 1045–1060 range correspond to 3+ charged species of formula $\{Er_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2 + Cl + HCl + H_2O\}^{3+}$ (*m*/*z* = 1056.8 Th) and $\{Er_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2 + Cl + HCl\}^{3+}$ (*m*/*z* = 1050.5 Th) whereas ions observed at lower mass-to-charge ratios correspond to species of general formula $\{Er_4(OH)_6(H_2O)_{4-n}(C_5NH_4COO)_2(CB[6])_2 + H\}^{5+}$ (five peaks at 616.5, 612.4, 609.1, 605.8, and 602.0 Th for *n* = 0–4, respectively). Additional doubly charged cations are observed in the *m*/*z* = 775–790 range which might come from fragmentation processes occurring during the ionization process.

Thus, the presence of peaks containing sandwich fragments in ESI-MS mass spectra of **4** and **6** is unambiguous evidence of the existence of a sandwich structure in aqueous solutions of tetranuclear lanthanide complexes of both structural types.

Magnetism

Magnetic susceptibility measurements for complex **4** (Ln = Gd) were performed in an applied field of 1000 G between 2 K and 270 K (Figure 7). Data were corrected for both sample diamagnetism (Pascal's constants) and the

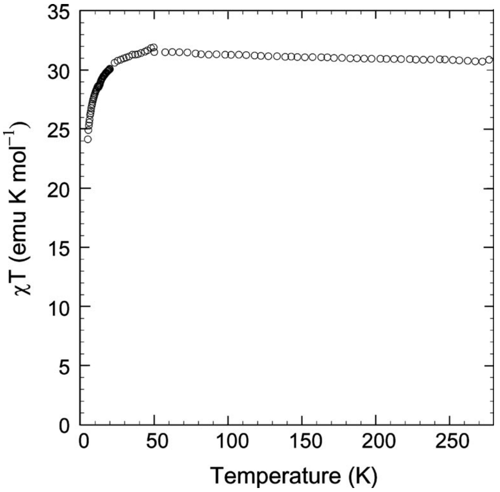

Figure 7. Temperature dependence of the magnetic susceptibility for compound **4**.

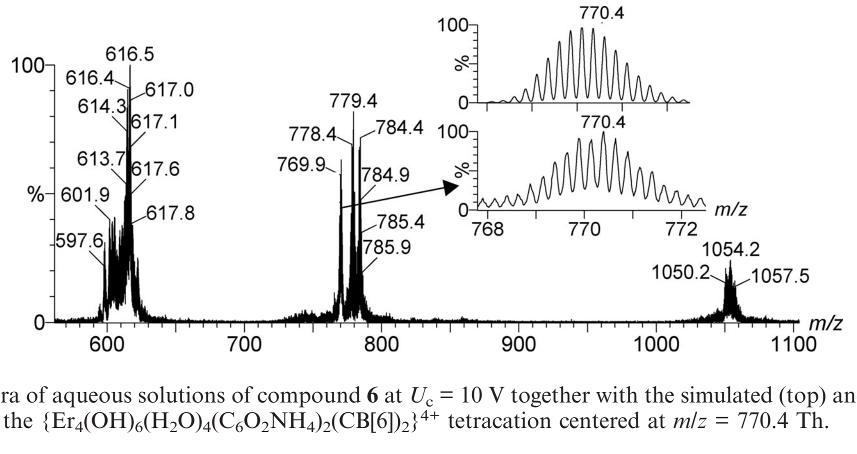

Figure 6. ESI mass spectra of aqueous solutions of compound **6** at U_c = 10 V together with the simulated (top) and experimental (bottom) isotopic distribution for the $\{Er_4(OH)_6(H_2O)_4(C_6O_2NH_4)_2(CB[6])_2\}^{4+}$ tetracation centered at *m*/*z* = 770.4 Th.

sample holder. The susceptibility of the sample rises monotonically as the temperature lowers following a typical Curie–Weiss behavior, from which the Curie constant C could be determined. The presence of four Gd^{III} per molecule is confirmed by a Curie constant of 31.4 emu K mol (31.5 is expected for four $S = 7/2$ and $g = 2$) and an almost negligible value for the Weiss constant (–1 K), as expected for a nearly perfect paramagnetic system with very weak antiferromagnetic interactions between the magnetic centers.

Luminescence Spectroscopy

The luminescence spectra of powder samples of europium **3** and terbium **5** compounds were obtained at room and at liquid nitrogen temperatures. When excited by a 313 nm source, **3** and **5** emit intense red and green light, respectively, and sharpening of the lines is more pronounced at 77 K. As the temperature increases to 300 K the line intensity is reduced by a factor of about two although no variations were observed in the number of levels.

The spectra of **3** and **5** are typical of Eu^{III} and Tb^{III} ions. The spectrum of **3** (Figure 8, a) shows five peaks arising from transitions between the first excited state $^5D_0$ and the ^7F_J levels of the ground states ($J = 0, 1, 2, 3, 4$). The strongest peak at 613 nm is assigned to the $^5D_0 \to {}^7F_2$ transition and is responsible for the red emission color. The presence of the $^5D_0 \to {}^7F_0$ nondegenerate transition, prohibited by the selection rules, and the splitting observed for $^7F_{1-4}$ levels point to a low symmetry local environment for the Eu^{3+} ions in the compound. The spectrum of **5** (Figure 8, b) originates from the $^5D_4 \to {}^7F_J$ transitions ($J = 6, 5, 4, 3$). The most intense peak with its maximum at 543 nm is attributed to the $^5D_4 \to {}^7F_5$ transition. Besides this main emission line, the peak at 491 nm ($J = 6$), and much less intense bands in the spectral range from 575 to 630 nm ($J = 4, 3$) are also observed. As for the Eu^{3+} ion, the splitting of $^5D_4 \to {}^7F_{6-3}$ transitions indicates site symmetry of the terbium ion without a center of inversion. It should be noted, the intensity of the emission of complexes **3** and **5** is much stronger than that of europium(III) and terbium(III) chlorides and also their mononuclear complexes with CB[6] measured at the same conditions.

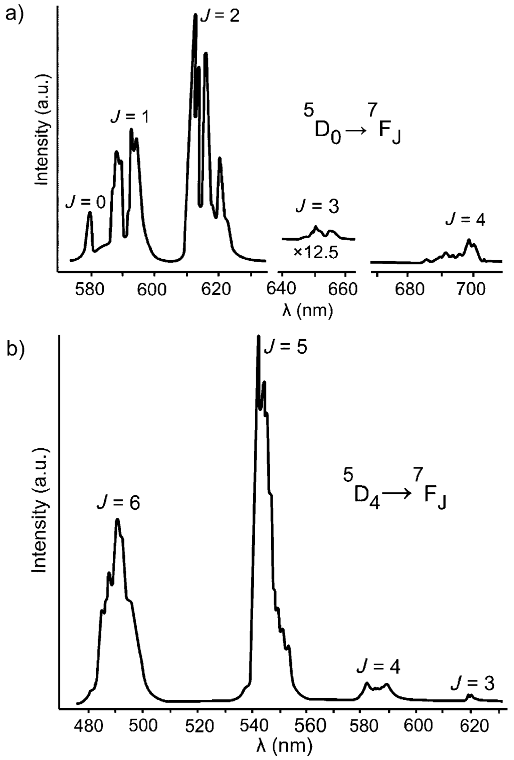

Figure 8. a) Emission spectrum of **3** at 77 K, under Hg 313 nm excitation; b) emission spectrum of **5** at 77 K, under Hg 313 nm excitation.

Conclusions

To summarize, tetranuclear lanthanide complexes were obtained under hydrothermal synthesis from aqueous solutions of lanthanide(III) chlorides, organic macrocyclic cavitand cucurbit[6]uril, and 4-cyanopyridine. Single crystal X-ray analysis revealed two types of lanthanide complexes, in which metal atoms and hydroxo bridges form $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2\}^{6+}$ or $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4\}^{4+}$ cores. The compounds of both structural types have a sandwich structure with the tetranuclear Ln$_4$ complex situated between two cucurbit[6]uril molecules. The compounds are soluble in water and tetranuclear sandwich fragments remain in aqueous solutions (ESI-MS). That makes them interesting as promising starting compounds, for example, for the synthesis of coordination polymers through coordination of metal ions by the nitrogen atoms of isonicotinate encapsulated into the cavity of cucurbit[6]uril.

Experimental Section

General: The starting compounds $LnCl_3 \cdot 6H_2O$ (Ln = Pr, Nd, Eu, Gd, Tb, Er, and Yb) of high purity grade and 4-cyanopyridine (99 %) were used as purchased. Cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12} \cdot 10H_2O$) was synthesized according to a known procedure.[40] 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 IR spectra were recorded with a SCIMITAR FTS 2000 Fourier-transform spectrometer in the 4000–400 cm^{-1} range. Magnetic susceptibility measurements were recorded with a Quantum Design SQUID magnetometer on 18 mg of polycrystalline sample. Electrospray ionization mass spectra were recorded with a Q-TOF I (quadrupole-hexapole-time-of-flight) mass spectrometer with an orthogonal Z-spray electrospray interface (Micromass, Manchester, U.K.) operating at a resolution of approximately 5000 (FWHM). The instrument was calibrated using a solution of NaI in 2-propanol/water from m/z 50 to 2000. Sample solutions (5×10^{-4} M) in water were introduced through a fused-silica capillary to the ESI source via a syringe pump at a flow rate of 10 μL min. The temperature of the source block was set to 120 °C and the desolvation temperature to 150 °C. The cone voltage was set at 10 V (that means mild ionization conditions) to control the extent of fragmentation. Nitrogen was employed as the drying and nebulizing gas. Isotope experimental pat-

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terns were compared with theoretical patterns obtained using the MassLynx 4.0 program. Photoluminescence spectra were obtained with a DFS-24 spectrometer operating in the 400–840 nm range. Solid powder samples were sealed in a suitable tube. Entrance and exit slits were set to give a resolution of 0.4 nm. The UV excitation source was the Hg 313 nm line.

Synthesis of $(H_3O)_3\{[Pr_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2][Pr(H_2O)_7(C_5NH_4COOH)]_2\}Cl_{11}\cdot 29H_2O$ (1): A solution of $PrCl_3\cdot 6H_2O$ (0.30 g, 0.84 mmol) in water (1.5 mL), cucurbit[6]uril (0.010 g, 0.009 mmol), and 4-cyanopyridine (0.045 g, 0.43 mmol) was placed in a glass tube. The sealed tube was treated as follows: (1) heated from 20 °C to 130 °C for 5 h; (2) storage at 130 °C for 12 h; (3) slow cooling to room temperature for 48 h. Pale-green polyhedral-like crystals were filtered off and dried in air for 12 h. Yield 0.011 g (54% based on cucurbit[6]uril). IR (KBr): $\tilde{\nu}$ = 3406 (s), 3005 (w), 2930 (w), 2858 (w), 1726 (s), 1670 (w), 1610 (s), 1564 (s), 1484 (s), 1422 (m), 1374 (m), 1326 (s), 1280 (s), 1239 (s), 1190 (s), 1146 (m), 1067 (w), 1052 (w), 1030 (w), 983 (w), 966 (s), 820 (m), 797 (s), 759 (s), 711 (m), 676 (s), 626 (m), 572 (w), 460 (w) cm^{-1}. $C_{96}H_{201}Cl_{11}N_{52}O_{90}Pr_6$ (4759.50): calcd. C 24.23, H 4.26, N 15.30; found C 24.35, H 4.33, N 15.26.

The syntheses of **2**–**7** were carried out similarly to that of **1**. The number of water molecules of crystallization (*n*) estimated by X-ray diffraction and elemental analysis can vary for different samples depending on the experimental conditions and air humidity during storage.

Synthesis of $(H_3O)_3\{[Nd_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2][Nd(H_2O)_7(C_5NH_4COOH)]_2\}Cl_{11}\cdot 29H_2O$ (2): Pale-vinous polyhedral-like crystals. Yield 0.017 g (84%). IR (KBr): $\tilde{\nu}$ = 3420 (s), 3007 (w), 2928 (m), 2856 (w), 1726 (s), 1665 (m), 1612 (s), 1566 (m), 1483 (s), 1421 (s), 1373 (s), 1325 (s), 1280 (m), 1239 (s), 1189 (s), 1146 (s), 1067 (m), 1032 (w), 982 (w), 965 (s), 821 (m), 797 (s), 759 (s), 710 (w), 675 (m), 652 (w), 624 (m), 566 (w), 479 (w), 404 (m), 379 (s) cm^{-1}. $C_{96}H_{201}Cl_{11}Nd_6N_{52}O_{90}$ (4779.48): calcd. C 24.13, H 4.24, N 15.24; found C 24.25, H 4.34, N 15.21.

Synthesis of $(H_3O)_5[Eu_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]Cl_7\cdot 38H_2O$ (3): Colorless polyhedral-like crystals. Yield 0.010 g (56%). IR (KBr): $\tilde{\nu}$ = 3428 (s), 3117 (w), 2998 (w), 2924 (w), 2853 (w), 1724 (s), 1613 (s), 1560 (m), 1483 (s), 1419 (m), 1373 (m), 1325 (s), 1279 (w), 1238 (s), 1188 (s), 1143 (m), 1030 (m), 1011 (w), 964 (s), 820 (m), 797 (s), 759 (s), 675 (s), 622 (m), 559 (w), 528 (w), 459 (m), 419 (m) cm^{-1}. $C_{84}H_{187}Cl_7Eu_4N_{50}O_{83}$ (4081.83): calcd. C 24.71, H 4.62, N 17.16; found C 24.84, H 4.71, N 17.25.

Synthesis of $(H_3O)_6[Gd_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]Cl_8\cdot 36H_2O$ (4): Colorless polyhedral-like crystals. Yield 0.012 g (68%). IR (KBr): $\tilde{\nu}$ = 3428 (s), 3116 (w), 2978 (w), 2929 (w), 1724 (s), 1671 (w), 1612 (s), 1561 (w), 1483 (s), 1455 (m), 1419 (s), 1373 (s), 1325 (s), 1279 (s), 1238 (s), 1187 (s), 1143 (m), 1050 (w), 1011 (w), 964 (s), 820 (m), 796 (s), 759 (s), 675 (m), 652 (w), 622 (m), 567 (w), 462 (m), 418 (m) cm^{-1}. $C_{84}H_{166}Cl_8Gd_4N_{50}O_{72}$ (3941.16 for *n* = 26): calcd. C 25.60, H 4.25, N 17.77; found C 25.70, H 4.20, N 17.77. ESI-MS: *m*/*z* (%) = 1043.5 (18) $[Gd_4(OH)_8(C_5NH_4COO)_2(H_2O)_4(CB[6])_2 + H + H_2O + HCl]^{3+}$, 773.4 (45) $[Gd_4(OH)_8(C_5NH_4COO)_2(H_2O)_3(C_{36}H_{36}N_{24}O_{12})_2 + 2H + HCl]^{4+}$, 759.9 (32) $[Gd_4(OH)_8(C_5NH_4COO)_2(H_2O)_2(C_{36}H_{36}N_{24}O_{12})_2 + 2H]^{4+}$, 608.8 (100) $[Gd_4(OH)_8(C_5NH_4COO)_2(H_2O)_2(C_{36}H_{36}N_{24}O_{12})_2 + 3H]^{5+}$.

Synthesis of $(H_3O)_4[Tb_4(OH)_8(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]Cl_6\cdot 40H_2O$ (5): Colorless polyhedral-like crystals. Yield 0.013 g (72%). IR (KBr): $\tilde{\nu}$ = 3427 (s), 3116 (w), 3001 (w), 2928 (w), 2859 (w), 1724 (s), 1664 (m), 1611 (s), 1563 (m), 1482 (s), 1453 (m), 1416 (s), 1372 (s), 1324 (s), 1279 (s), 1234 (s), 1185 (s), 1142 (s), 1030 (m), 1011 (m), 963 (s), 897 (w), 821 (m), 795 (s), 759 (s), 675 (s), 621 (m), 560 (w), 459 (w), 422 (m) cm^{-1}. $C_{84}H_{158}Cl_6N_{50}O_{69}Tb_4$ (3820.87 for *n* = 25): calcd. C 26.40, H 4.17, N 18.33; found C 26.37, H 4.06, N 18.36.

Synthesis of $(H_3O)_5[Er_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]Cl_9\cdot 35H_2O$ (6): Pale-pink polyhedral-like crystals. Yield 0.016 g (89%). IR (KBr): $\tilde{\nu}$ = 3424 (s), 3120 (w), 2954 (w), 2925 (s), 2854 (m), 1725 (s), 1657 (w), 1614 (s), 1564 (w), 1489 (s), 1457 (m), 1422 (s), 1375 (s), 1327 (s), 1279 (m), 1241 (s), 1187 (s), 1144 (m), 1051 (w), 983 (w), 965 (s), 898 (w), 820 (m), 797 (s), 760 (s), 678 (s), 652 (m), 627 (m), 561 (w), 522 (w), 463 (m), 430 (m). $C_{84}H_{179}Cl_9Er_4N_{50}O_{78}$ (4125.86): calcd. C 24.45, H 4.37, N 16.97; found C 24.39, H 4.46, N 16.73. ESI-MS: *m*/*z* (%) = 1056.8 (17) $[Er_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2 + Cl + HCl + H_2O]^{3+}$, 1050.5 (20) $[Er_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2 + Cl + HCl]^{3+}$, 770.4 (62) $[Er_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]^{4+}$, 616.5 (88) $[Er_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2 + H]^{5+}$, 612.4 (40) $[Er_4(OH)_6(H_2O)_3(C_5NH_4COO)_2(CB[6])_2 + H]^{5+}$, 609.1 (30) $[Er_4(OH)_6(H_2O)_2(C_5NH_4COO)_2(CB[6])_2 + H]^{5+}$, 605.8 (30) $[Er_4(OH)_6(H_2O)(C_5NH_4COO)_2(CB[6])_2 + H]^{5+}$, 602.0 (30) $[Er_4(OH)_6(C_5NH_4COO)_2(CB[6])_2 + H]^{5+}$.

Synthesis of $(H_3O)_3[Yb_4(OH)_6(H_2O)_4(C_5NH_4COO)_2(CB[6])_2]Cl_7\cdot 38H_2O$ (7): Colorless polyhedral-like crystals. Yield 0.017 g (94%). IR (KBr): $\tilde{\nu}$ = 3402 (s), 3121 (w), 3006 (w), 2926 (m), 2854 (w), 1722 (s), 1655 (w), 1613 (s), 1565 (w), 1491 (s), 1456 (w), 1423 (s), 1374 (s), 1327 (s), 1279 (m), 1241 (s), 1189 (s), 1145 (s), 1030 (w), 1011 (w), 983 (w), 966 (s), 820 (m), 796 (s), 760 (s), 679 (s), 653 (m), 627 (m), 568 (w), 472 (m), 432 (m). $C_{84}H_{179}Cl_7N_{50}O_{79}Yb_4$ (4094.08): calcd. C 24.64, H 4.41, N 17.11; found C 24.54, H 4.37, N 17.10.

Table 2. Crystal data and structure refinement details for **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{96}H_{201}Cl_{11}N_{52}O_{90}Pr_6$	$C_{96}H_{201}Cl_{11}N_{52}O_{90}Nd_6$	$C_{84}H_{187}Cl_7Eu_4N_{50}O_{83}$	$C_{84}H_{186}Cl_8Gd_4N_{50}O_{82}$
Formula mass [g mol]	4759.50	4779.48	4081.83	4121.43
a [Å]	28.1330(10)	28.1098(8)	16.0366(6)	15.9642(3)
b [Å]	14.5378(5)	14.5225(4)	33.8771(12)	33.7242(6)
c [Å]	40.9798(14)	40.8623(12)	29.4760(11)	29.4218(6)
β	92.736(1)	92.913(1)	100.667(1)	100.611(1)
V [Å^3]	16741.3(10)	16659.4(8)	15736.8(10)	15569.2(5)
$\rho_{(calcd.)}$ [g cm^3]	1.888	1.906	1.725	1.758
Space group	*C*2/*c*	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*c*
Z	4	4	4	4
μ [cm^{-1}]	2.008	2.113	1.807	1.906
T [K]	100(2)	100(2)	150(2)	100(2)
$R_1(F)[F_o^2>2\sigma(F_o^2)]$	0.0418	0.0485	0.0513	0.0584

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Table 3. Crystal data and structure refinement details for **5**–**7**.

	5	**6**	**7**
Empirical formula	$C_{84}H_{188}Cl_6N_{50}O_{84}Tb_4$	$C_{84}H_{179}Cl_9Er_4N_{50}O_{78}$	$C_{84}H_{179}Cl_7N_{50}O_{79}Yb_4$
Formula mass [g mol]	4091.22	4125.86	4094.08
a [Å]	15.9016(5)	28.6320(10)	28.7453(10)
b [Å]	33.5874(10)	13.8116(5)	13.9283(5)
c [Å]	29.3337(9)	38.9602(13)	38.8743(14)
β	100.729(2)	101.135(1)	100.946(1)
V [Å^3]	15393.1(8)	15116.9(9)	15281.1(9)
$\rho_{(calcd.)}$ [g cm^3]	1.765	1.813	1.780
Space group	$P2_1/c$	$C2/c$	$C2/c$
Z	4	4	4
μ [cm^{-1}]	2.078	2.474	2.664
T [K]	100(2)	100(2)	100(2)
$R_1(F)[F_o^2>2\sigma(F_o^2)]$	0.0469	0.0441	0.0400

X-ray Crystallography: The X-ray diffraction data were collected with the use of graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) at 100 and 150 K (Tables 2 and 3) with a Bruker Nonius X8Apex single-crystal diffractometer equipped with a 4K-CCD detector. 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 non-hydrogen atoms using the SHELXTL program package.[41] The hydrogen atoms of cucurbit[6]uril and the isonicotinate ion were calculated geometrically and refined using a riding model. The hydrogen atoms of the water molecules were not revealed.

CCDC-656569 (for **1**), -656571 (for **2**), -656572 (for **3**), -656573 (for **4**), -656574 (for **5**), -656575 (for **6**), -656575 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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