Cucurbituril as a New Macrocyclic Ligand for Complexation of Lanthanide Cations in Aqueous Solutions

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Dedicated to Professor F. A. Kuznetsov on the occasion of his 70th birthday

Keywords: Lanthanides / Solid-state structures / Supramolecular chemistry / Aqua complexes / Cucurbituril

(Aqua)lanthanide complexes with cucurbituril $\{[Gd(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2\cdot 7H_2O$ (**1**), $\{[Gd(NO_3)(C_2H_5OH)(H_2O)_3](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2\cdot 5.5H_2O$ (**2**), $\{[Ho(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2\cdot 7H_2O$ (**3**), $\{[Yb(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2\cdot 6H_2O$ (**4**), $\{[La(H_2O)_6(SO_4)](C_{36}H_{36}N_{24}O_{12})\}(NO_3)\cdot 12H_2O$ (**5**), $\{[Gd(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})_3\}Br_6\cdot 45H_2O$ (**6**), and $\{[Ce(H_2O)_5]_2(C_{36}H_{36}N_{24}O_{12})_2\}Br_6\cdot 26H_2O$ (**7**) were obtained in high yield by reaction of cucurbituril with aqueous solutions of lanthanide(III) species. The crystal structures of the compounds show a packing of 1:1, 2:2, and 2:3 in the (cucurbituril)lanthanide complexes in which cucurbituril plays a bidentate ligand role, and water molecules of the (aqua)lanthanide complexes form hydrogen bonds with carbonyl groups of the cucurbituril molecule. The guest water molecule is situated in the cucurbituril molecule cavity of **2** and **5**. The crystal structure of **6** is a packing of three-deck sandwiches, built from alternating cucurbituril molecules and $Gd(H_2O)_4{}^{3+}$ ions. The largest distance between outermost oxygen atoms in the sandwiches is 30.04 Å.
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Introduction

Lanthanide(III) species exhibit rich and unique spectroscopic and magnetic properties, and rare-earth compounds are used for numerous applications, as relaxation agents in nuclear magnetic resonance imaging,[1] as luminescent probes in biology and medicine,[2] or as catalysts for the cleavage of RNA and DNA.[3]

In aqueous solution, large f-element ions form high-coordination number aqua complexes with various, often unique, coordination environments. The extremely high rates of exchange of ligands at f-element centers make the isolation of their coordination complexes difficult, particularly from aqueous solutions. A successful method of overcoming this kinetic instability is to increase the thermodynamic stability of the complexes by exploring the chelate and macrocyclic effects.[4]

There is a considerable body of information concerning macrocyclic ligand complexes of the lanthanides, where a metal atom is coordinated in a multidentate manner with nitrogen- or oxygen-donor ligands: crown ethers, calixarenes, etc.[5,6] The coordination selectivity exhibited by these ligands towards rare-earth cations has been widely investigated, in particular because of its role in processes of separation of f-elements in acidic aqueous solution, which is an important step in strategies for management and storage of high-level radioactive waste and clean-up of decommissioned nuclear facilities.[7]

However, the scope of neutral macrocyclic ligand systems studied for f-elements is limited, as the complexation with most of them occurs in organic solvents and not in aqueous solutions, where water acts as a very strong competitor. Introduction of the sulfonate group in the *para* position to the phenolic group of calixarenes made it possible to prepare (calixarene)lanthanide complexes in aqueous solution, but the metal ion coordinates to the ligand through the sulfonate functionalities, and in no case was evidence obtained

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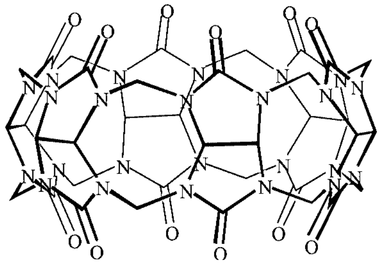
for a multidentate mode of lanthanide complexation by the calixarene involving the phenolic oxygen atoms.[6a−6d]

In the present work, we report the synthesis and crystallization of lanthanide (La, Ce, Gd, Ho, Yb) complexes in aqueous media with the macrocyclic ligand cucurbituril. Using lanthanide nitrates or bromides, the following compounds were obtained: $\{[Gd(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2{\cdot}7H_2O$ (**1**), $\{[Gd(NO_3)(C_2H_5OH)(H_2O)_3](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2{\cdot}5.5H_2O$ (**2**), $\{[Ho(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2{\cdot}7H_2O$ (**3**), $\{[Yb(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2{\cdot}6H_2O$ (**4**), $\{[La(H_2O)_6(SO_4)](C_{36}H_{36}N_{24}O_{12})\}(NO_3){\cdot}12H_2O$ (**5**), $\{[Gd(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})_3\}Br_6{\cdot}45H_2O$ (**6**), and $\{[Ce(H_2O)_5]_2(C_{36}H_{36}N_{24}O_{12})_2\}Br_6{\cdot}26H_2O$ (**7**) and characterized by single-crystal X-ray analysis.

Results and Discussion

Cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) is a barrel-shaped macrocyclic cavitand with an internal cavity having a ca. 5.5 Å diameter and two identical carbonyl-fringed portals on each side.[8] Each portal of this molecule has six carbonyl oxygen atoms located in a plane which can interact with metal cations in such a way that cucurbituril behaves like a macrocyclic ligand. These portal atoms have a higher electric charge compared with crown ether oxygen atoms and consequently stronger interactions between carbonyl groups and positively charged ions take place.[9] Its easy synthesis, rigid structure, and chemical and thermal stability make cucurbituril very attractive for complexation of cations in aqueous solution.



Scheme 1. Cucurbituril

A number of adducts of cucurbituril and s-metals (Na^+, K^+, Rb^+, Cs^+, Ca^{2+}) have been prepared with their quite unique structures and reactivities.[10] Due to the strong interactions of carbonyl oxygen donor atoms with cations, stable complexes are formed, and the metal ions and their coordinated water molecules cover each portal of cucurbituril like a "lid" on a "barrel". Also aliphatic and aromatic ammonium ions show a high affinity toward cucurbituril to form host−guest complexes.[11]

We have recently shown that the macrocyclic cavitand cucurbituril is by its geometry almost ideally suited for design of supramolecular adducts with triangular cluster aqua ions $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se), as well as their heterometal cuboidal derivatives.[12] Six water molecules, coordinated to the cluster core, form hydrogen bonds with the six carbonyl oxygen atoms of cucurbituril leading to the formation of nanosized molecules with the ratio of cluster/cucurbituril of 1:1 or 2:1. In the latter case the cavity in the cavitand molecule is effectively closed by cluster "lids" and small molecules or ions can be trapped inside. We have also shown that cucurbituril molecules are associated with (aqua)indium and -aluminum cations by hydrogen bonds with the portal oxygen atoms and also coordinate to the cluster water molecules.[13] An attractive point here is that, since cucurbituril usually belongs to the second coordination sphere, the aqua complexes will be much less perturbed by the adduct formation with cucurbituril than by introducing other ligands in the first coordination sphere. This enhances the relevance of the structural information obtained from cucurbituril adducts to the hydrolytic species actually present in solution. However, as we found in the present study cucurbituril can coordinate directly to Ln^{3+}.

The synthesis of the compounds **1**−**7** is straightforward. They were obtained by reaction of cucurbituril with aqueous solutions of lanthanide(III) species. Cucurbituril is not soluble in water, but it is well soluble in hot saturated aqueous solutions of Ln^{III} salts. Within a week or even overnight well-shaped colorless crystals suitable for X−ray studies separate in high yields. When taken out of the mother liquor, the crystals of compounds **6** and **7** lose water of crystallization and crystallinity. This fact explains the difference between the analytically deduced formulae and the stoichiometry found by X-ray analysis, performed at a low temperature with crystals sealed inside quartz capillaries.

The gadolinium complex **1** was obtained from solutions containing gadolinium nitrate and cucurbituril. The elemental analysis gives the formula $\{[Gd(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2{\cdot}7H_2O$ (**1**). The crystals suitable for the X-ray experiment were obtained by diffusion of ethanol into the solution used to prepare **1**, and have the composition $\{[Gd(NO_3)(C_2H_5OH)(H_2O)_3](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2{\cdot}5.5H_2O$ (**2**).

The crystal structure of compound **2** shows a 1:1 packing of (cucurbituril)gadolinium complexes in which cucurbituril plays the role of the bidentate ligand (Figure 1). One guest water molecule is situated inside the cucurbituril molecule cavity. In addition to the two oxygen atoms of the two cucurbituril carbonyl groups, the gadolinium cation has one ethanol molecule, one bidentate nitrate and three aqua ligands in its coordination environment. The coordination number of gadolinium is eight and its coordination polyhedron is a distorted triangulated dodecahedron in which the nitrate anion occupies the shortest edge.

Isostructural complexes of holmium, $\{[Ho(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2{\cdot}7H_2O$ (**3**), and ytterbium, $\{[Yb(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2{\cdot}6H_2O$ (**4**), were obtained under the same conditions, but in contrast to the gadolinium complex **2**, holmium and ytterbium cations have no ethanol molecules in their coordination environment (Figure 2). The space vacated by ethanol is occupied with water molecules forming hydrogen bonds with one another and the carbonyl groups of the cucurbituril molecule.

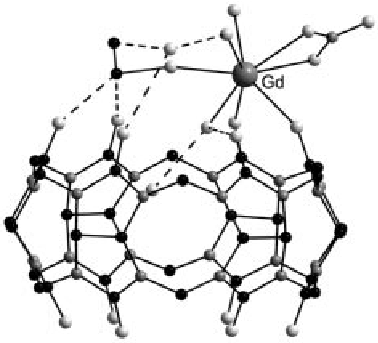


Figure 1. Structure of $\{[Gd(H_2O)_3(C_2H_5OH)(NO_3)](1/2\text{-}H_2O\subset C_{36}H_{36}N_{24}O_{12})\}^{2+}$ complex in **2**; dashed lines show hydrogen bonds

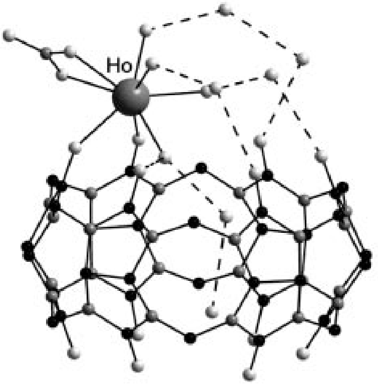


Figure 2. Structure of $\{[Ho(H_2O)_4(NO_3)](H_2O\subset C_{36}H_{36}N_{24}O_{12})\}^{2+}$ complex in **3**; dashed lines show hydrogen bonds

The crystal packing of compound **3** is shown in Figure 3. The cationic complexes form polar, i.e. having a preferential direction, hydrogen-bonded chains running along the *c* axis and the centers of the supermolecules form a body-centered motif. The chains are shifted from each other by one-half of a crystallographic translation along the axis of their expansion. The space between the polar chains is filled with solvate water molecules and nitrate anions. The ytterbium compound **4** has the same crystal structure, but complex **3** has one more solvate water molecule.

The comparison of calculated and experimental X-ray powder diffraction data for compounds **1** and **3** shows that complex **1** is isostructural with **3** (see figure in the Supporting Information).

Another example of 1:1 stoichiometry is given by an adduct with hexaaqualanthanum(III) sulfate, $\{[La(H_2O)_6(SO_4)](C_{36}H_{36}N_{24}O_{12})\}(NO_3)\cdot 12H_2O$ (**5**). It was isolated from an aqueous solution containing lanthanum nitrate, copper(II) sulfate and cucurbituril. The crystal structure of compound **5** is a packing of supermolecules, which consist of a cucurbituril molecule capped by a cationic (aqua)lanthanum complex on one side (Figure 4). Cucurbituril is bound to the lanthanum cation via two carbonyl groups and the coordination polyhedron of La^{3+} (CN = 9, mono-capped square antiprism) is completed by six water molecules and one monodentate sulfate anion. The sulfate is disordered over two orientations around the S(1)−O(1S) bond with relative weights of 0.60 and 0.40 for O(2S1), O(3S1), O(4S1) and O(2S2), O(3S2), O(4S2), respectively. Three aqua ligands participate in hydrogen bonding with four carbonyl groups and another one does the same with a guest water molecule disordered over two positions (Figure 4). There is one water molecule in the open portal of the cucurbituril molecule, which is hydrogen-bound with the guest water molecule.

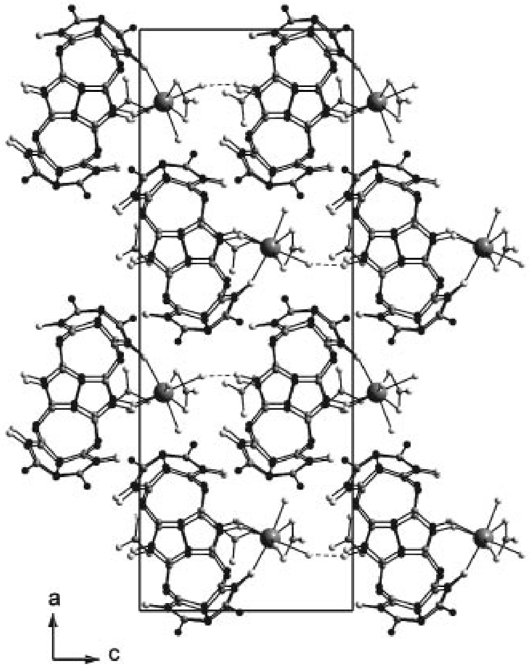


Figure 3. Crystal packing in **3** (projection on the *ac* plane); solvate water molecules and nitrate anions omitted for clarity

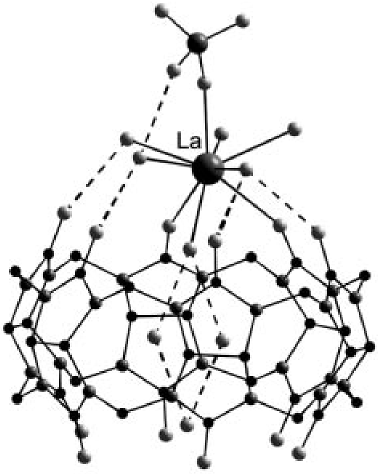


Figure 4. Structure of $\{[La(H_2O)_6(SO_4)](2H_2O\subset C_{36}H_{36}N_{24}O_{12})\}^{2+}$ complex in **5**; dashed lines show hydrogen bonds

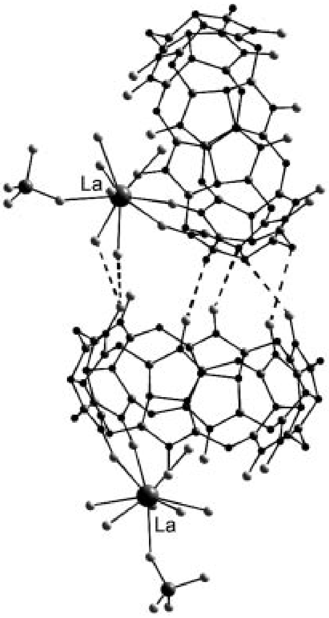


Figure 5. Two supermolecules in **5**; dashed lines show hydrogen bonds

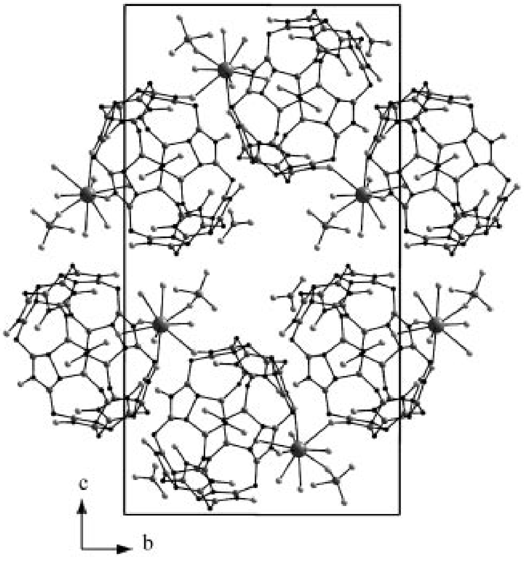


Figure 6. Crystal packing in **5** (projection on the *bc* plane); solvate water molecules and nitrate anions are omitted for clarity

Two neighboring supermolecules form hydrogen bonds between carbonyl groups of one supermolecule and aqua ligands (mean O···O distance: 2.861 Å) and the C−H groups (mean O···C distance: 3.050 Å) of another one (Figure 5). The supermolecules are stacked in columns shifted by one half of a crystallographic translation with regards to each other. The columns form corrugated layers parallel to the *ab* plane (Figure 6). There are channels between the layers filled with water of crystallization and nitrate anions. All the moieties of **5** are involved in a complicated network of hydrogen bonds.

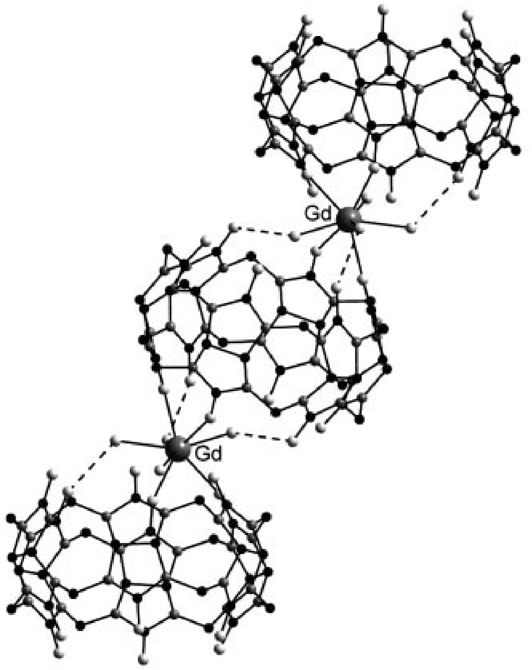


Figure 7. Three-deck sandwich $\{(C_{36}H_{36}N_{24}O_{12})[Gd(H_2O)_4](C_{36}H_{36}N_{24}O_{12})[Gd(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}^{6+}$ complex in **6**; dashed lines show hydrogen bonds

Compound **6**, $\{[Gd(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})_3\}Br_6\cdot 45H_2O$, was obtained from an aqueous solution containing gadolinium bromide and cucurbituril. The crystal structure of **6** reveals a packing of nanosized three-deck sandwiches, $\{(C_{36}H_{36}N_{24}O_{12})[Gd(H_2O)_4](C_{36}H_{36}N_{24}O_{12})[Gd(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}^{6+}$ (Figure 7), built from alternating cucurbituril molecules and Gd^{3+} cations. The shape of the sandwich complex can be approximated by an oblique cylinder with van der Waals dimensions about 15 × 28 Å. The largest distance between the oxygen atoms from the opposite sides is 30.04 Å.

Each Gd^{3+} is octacoordinated by two bidentate cucurbituril molecules, the mean Gd−O distance being 2.375 Å, and by four aqua ligands with a mean Gd−O distance of 2.397 Å. The coordination polyhedron of gadolinium is a slightly distorted square antiprism.

Crystal packing of sandwich complexes in **6** is shown in Figure 8. The centers of sandwiches coincide with centers of inversion in a body-centered motif (crystallographic position *2b* (1/2, 0, 0; 0, 1/2, 1/2) of $P2_1/n$ space group). The complexes are arranged in pillars oriented along the *a* axis. In each pillar, the sandwiches stack parallel to each other, being related by crystallographic translation. Each pillar has four other pillars as neighbors, oriented with respect to the former at angles of ca. 90°. The pillars are shifted by one-half of a crystallographic translation along the axis of their expansion and leaving quadrangular channels between them. The channels are filled with disordered solvate water molecules and bromide anions.

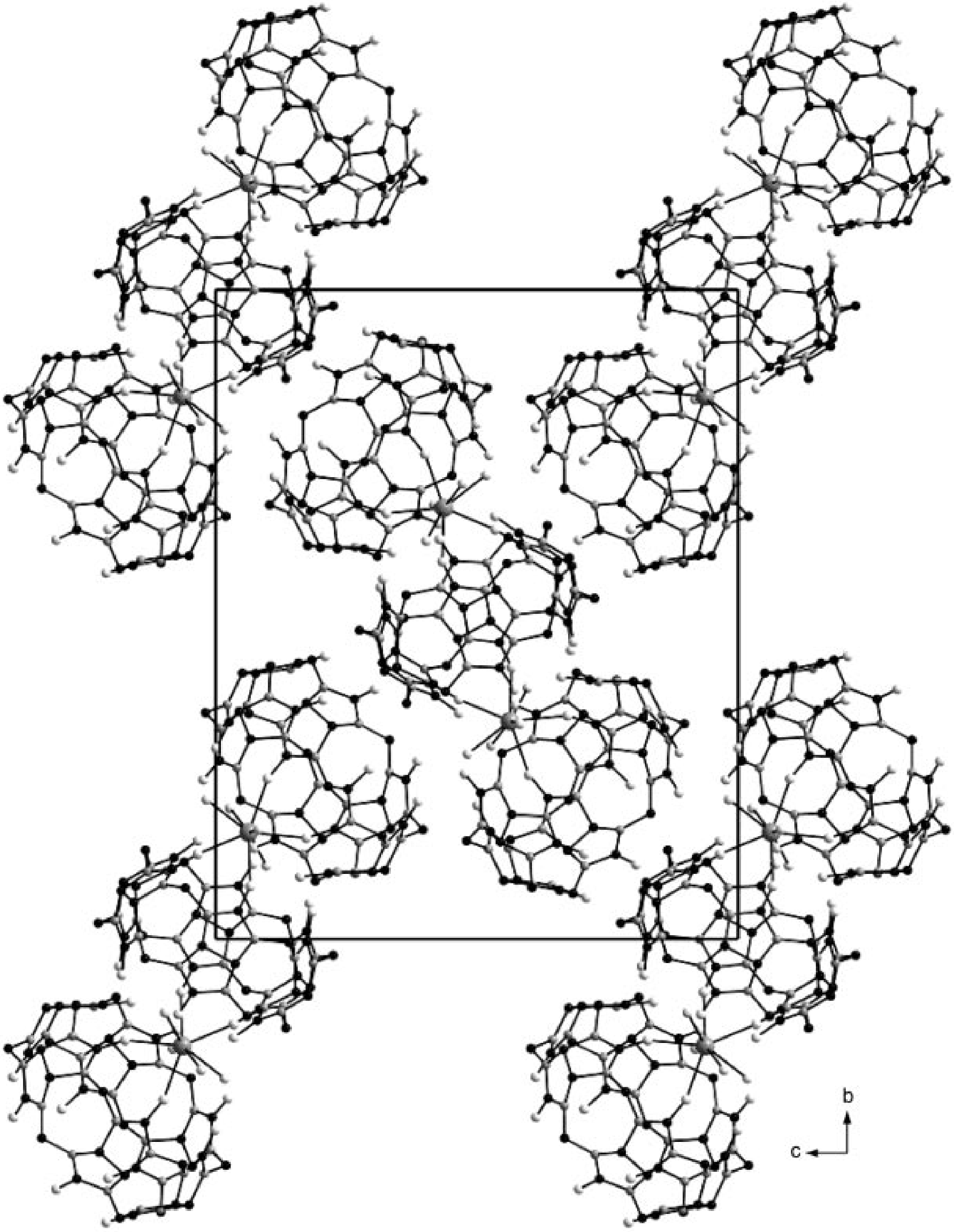


Figure 8. Crystal packing in **6** (projection on the *bc* plane); solvate water molecules and bromide anions are omitted for clarity

As a whole, the structure of **6** can be described as two interpenetrating networks, one of them being built of sandwich complexes and another representing a complicated network of hydrogen bonds formed by solvate water molecules and bromide anions.

Calculations carried out with the KPACK[14] program showed the sandwich complexes occupy 46.0% of the cell volume. The water molecules and bromide anions occupy another 18.0%. The packing coefficient in **6** is thus 0.64. Water molecules coat the sandwiches forming a bulky network of hydrogen bonds.

Another sandwich compound is a 2:2 (cucurbituril)cerium(III) complex, $\{[Ce(H_2O)_5]_2(C_{36}H_{36}N_{24}O_{12})_2\}Br_6\cdot 26H_2O$ (**7**), crystallized from an aqueous solution containing cerium bromide and cucurbituril. The crystal structure of **7** represents a packing of supermolecules built from two cucurbituril molecules and two (aqua)cerium(III) ions sandwiched between them (Figure 9). Nonacoordinated Ce^{3+} has four oxygen atoms of cucurbituril carbonyl groups and five aqua ligands in its coordination environment. Two of the five aqua ligands of each cerium cation are disordered over two positions.

The trigonal crystal packing of sandwich complexes in **7** is shown in Figure 10. Large triangular channels with a van der Waals diameter of about 4.3 Å are filled with disordered water molecules and bromide anions.

To summarize, the cases when cucurbituril directly coordinates to a metal center, seem to be limited by

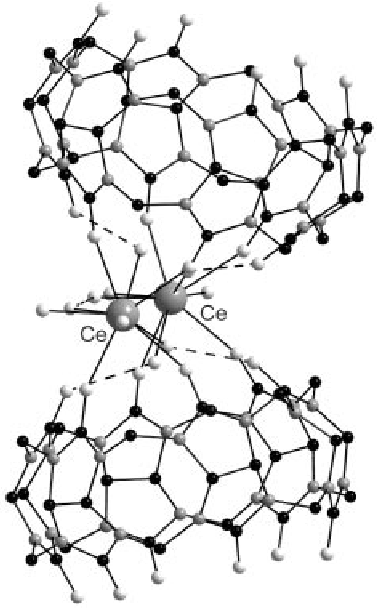


Figure 9. Structure of $\{[Ce(H_2O)_5]_2(C_{36}H_{36}N_{24}O_{12})_2\}^{6+}$ complex in **7**; dashed lines show hydrogen bonds

alkali,[10a−10c] alkali earth[10d,10e] and rare earth metal cations (groups 1−3). These are the most electropositive metals, forming hard and large (e.g., ionic radius of Na^+ 0.97 Å, Ca^{2+} 1.03 Å, Gd^{3+} 0.94 Å, Lu^{3+} 0.86 Å[12i]) ions, whose bonding to ligands can be accounted for in terms of electrostatic (ion−dipole) interactions. Only under these conditions can cucurbituril, being a weak donor, but possessing polar C=O groups, compete with other ligands for the first coordination sphere. Transition metals (and metals of group 13) form smaller ions (In^{3+} 0.76 Å, Al^{3+} 0.50 Å, Ni^{2+} 0.67 Å[12i]) which prefer covalent bonding. The higher charge and smaller size of the metal cation enhance the acidity of the coordinated water in the aqua-coordinated ions, so that, e.g., $[Al(H_2O)_6]^{3+}$ and $[In(H_2O)_6]^{3+}$ are by 4−5 orders of magnitude more acidic than any $[Ln(H_2O)_n]^{3+}$, (n = 8, 9).[15] This acidity allows for the formation of strong hydrogen bonds between the polar C=O groups of cucurbituril and the coordinated water molecules, thus increasing the energy gain of keeping cucurbituril in the second coordination sphere instead of substituting it for coordinated water.

Experimental Section

General: The lanthanide nitrates and bromides were of commercial quality and used without further purification. Cucurbituril was synthesized by published procedures.[8] Elemental analyses were carried out in the Laboratory of Microanalysis, Institute of Organic Chemistry SB RAS, Novosibirsk. The IR spectra were recorded on KBr pellets with an IFS-85 spectrometer (Bruker). X-ray powder patterns were recorded with a Philips APD diffractometer (Cu-K_α radiation).

X-ray Structure Determination: A summary of the crystallographic data, data collection and refinement parameters for compounds **2**−**7** is given in Table 1. For **2**, **4** and **5**, data were reduced in the usual way and absorption correction from ψ-scans was applied using the HELENA[16] program. For crystals **3**, **6** and **7**, data reduction and cell refinement were carried out using the Denzo,[17] Scalepak[17] and maXus[18] packages. The structures were solved by direct methods using SIR97[19] (for **2**) and SHELXS-97[20] (for **3**−**7**) programs and refined anisotropically for non-hydrogen atoms (except for some disordered atoms) by full-matrix least squares on F_o^2 using the SHELXL-97[20] program. In the case of **3**, **4** and **7** a racemic merohedral twinning was found with the twinning law of $\{-1, 0, 0, 0, -1, 0, 0, 0, -1\}$ and relative component weights of 0.66(1)/0.34(1) for **3**, 0.53(5)/0.47(5) for **4** and 0.45(2)/0.55(2) for **7**. The hydrogen atoms of cucurbituril molecules were refined in the rigid-body approximation. The positions of hydrogen atoms of the coordinated water molecules in the structure of **2** were calculated using the CALC-OH[21] program. In the case of **7** only 15 bromide ions out of a total of 18 per unit cell could be found, but the chemical analysis confirmed the formula with 18 Br^-. Figures showing the coordination environment of lanthanide cations and tables with selected bond lengths and valence angles for compounds **2**−**7** are given in the Supporting Information. CCDC-177555 (**2**), -177556 (**3**), -177557 (**4**), -177558 (**5**), -177559 (**6**) and -177560 (**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: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Syntheses

$\{[Gd(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2\cdot 7H_2O$ (1): In a solution of $Gd(NO_3)_3\cdot 5H_2O$ (0.24 g, 0.54 mmol) in water (5 mL), cucurbituril (0.025 g, 0.021 mmol) was dissolved after heating for 15 min on a hot plate. The solution was filtered and the filtrate was left in an open beaker for 1 d. Colorless crystals of **1** were separated and dried on a filter paper. Yield: 0.028 g (86%). IR (KBr): $\tilde{\nu}$ = 634 (m), 676 (m), 757 (m), 801 (s), 966 (s), 1149 (s), 1191 (s), 1235 (s), 1326 (s), 1381 (s), 1487 (s), 1735 (s), 3362 cm^{-1} (s). μ_{eff} (298 K) = 7.81 μ_B. $C_{36}H_{58}GdN_{27}O_{32}$ (1538.27): calcd. C 28.11, H 3.80, N 24.58; found C 28.57, H 3.81, N 24.56. Crystals of $\{[Gd(NO_3)(C_2H_5OH)(H_2O)_3](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2\cdot 5.5H_2O$ (**2**) for X-ray experiments were obtained by diffusion of ethanol into an aqueous solution of **1**.

$\{[Ho(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2\cdot 7H_2O$ (3): In a solution of $Ho(NO_3)_3\cdot 5H_2O$ (0.23 g, 0.52 mmol) in water (5 mL), cucurbituril (0.022 g, 0.019 mmol) was dissolved after heating for 10 min on a hot plate. The solution was left in an open beaker for 1 d. Pale crystals of **3** were separated and dried on a filter paper. Yield: 0.022 g (76%). $C_{36}H_{58}HoN_{27}O_{32}$ (1545.95): calcd. C 27.97, H 3.78, N 24.46; found C 27.81, H 3.35, N 24.10.

$\{[Yb(NO_3)(H_2O)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_2\cdot 6H_2O$ (4): In a solution of $Yb(NO_3)_3\cdot 5H_2O$ (0.21 g, 0.47 mmol) in water (5 mL), cucurbituril (0.021 g, 0.018 mmol) was dissolved after heating for 10 min on a hot plate. The solution was left in an open beaker for 1 d. Colorless crystals of **4** were separated and dried on a filter paper. Yield: 0.020 g (73%). $C_{36}H_{56}N_{27}O_{31}Yb$ (1536.04): calcd. C 28.15, H 3.67, N 24.62; found C 28.13, H 3.70, N 24.51.

$\{[La(H_2O)_6(SO_4)](C_{36}H_{36}N_{24}O_{12})\}(NO_3)\cdot 12H_2O$ (5): In a solution of $La(NO_3)_3\cdot 5H_2O$ (0.13 g, 0.31 mmol) and $CuSO_4\cdot 5H_2O$ (0.18 g, 0.72 mmol) in water (10 mL), cucurbituril (0.030 g, 0.026 mmol) was dissolved after heating for 15 min on a hot plate. The solution was left in an open beaker for about 7 d. Colorless crystals of **5** were separated and dried on a filter paper. Yield: 0.027 g (68%).

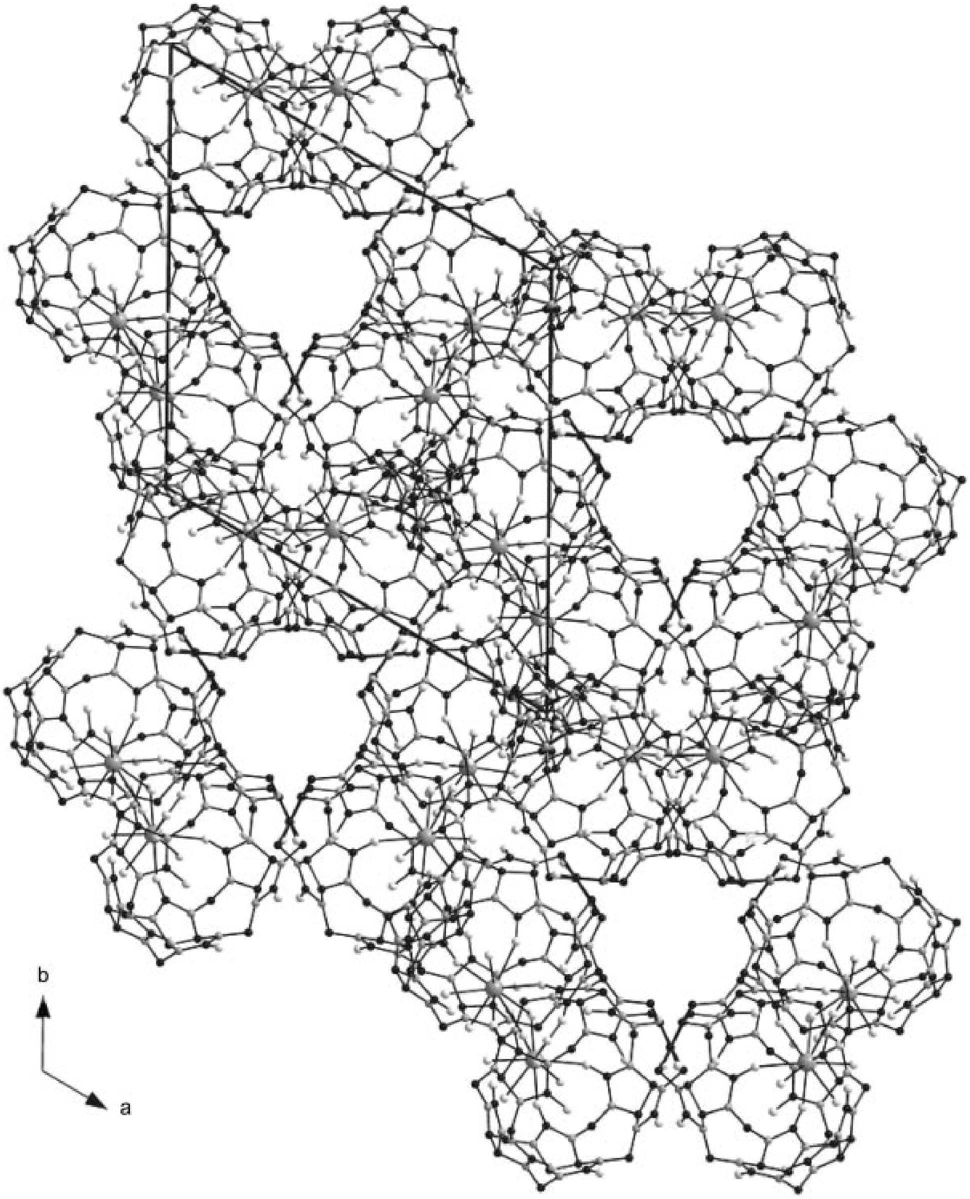


Figure 10. Crystal packing in **7** (projection on the *ab* plane); solvate water molecules and bromide anions are omitted for clarity

$C_{36}H_{72}LaN_{25}O_{37}S$ (1618.09): calcd. C 26.72, H 4.49, N 21.64, S 1.98; found C 27.01, H 4.56, N 21.78, S 2.02.

$\{[Gd(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})_3\}Br_6\cdot45H_2O$ (6): In a solution of $GdBr_3$ (0.15 g, 0.38 mmol) in water (13 mL), cucurbituril (0.052 g, 0.044 mmol) was dissolved after heating for 15 min on a hot plate. The solution was left in an open beaker for about 7 d. Colorless crystals of **6** were separated and dried on a filter paper. Yield: 0.050 g (77%). $C_{108}H_{180}Br_6Gd_2N_{72}O_{72}$ ($\{[Gd(H_2O)_4]_2$-$(C_{36}H_{36}N_{24}O_{12})_3\}Br_6\cdot28H_2O$) (4432.98): calcd. C 29.26, H 4.06, Br 10.81, N 22.75; found C 29.00, H 3.87, Br 10.86, N 23.25.

$\{[Ce(H_2O)_5]_2(C_{36}H_{36}N_{24}O_{12})_2\}Br_6\cdot26H_2O$ (7): In a solution of $CeBr_3$ (0.11 g, 0.30 mmol) in water (5 mL), cucurbituril (0.022 g, 0.020 mmol) was dissolved after heating for 15 min on a hot plate. The solution was left in an open beaker for about 7 d. Colorless crystals of **7** were separated and dried on a filter paper. Yield: 0.020 g (63%). $C_{72}H_{144}Br_6Ce_2N_{48}O_{60}$ (3401.88): calcd. C 25.42, H 4.27, N 19.76; Br 14.09. found C 25.25, H 4.34, N 19.46, Br 14.29.

Acknowledgments

The Spanish team thanks the University of La Laguna for financial support. The Russian team is grateful to the Russian Foundation for Basic Research (grants 01-03-32789 and 01-03-06274) and INTAS (grant 2002-2346) for supporting this work. V. P. F. thanks the University of La Laguna for a Visiting Professor position.

Table 1. Crystal data and structure refinement for **2−7**

	2	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{38}H_{59}GdN_{27}O_{30.50}$	$C_{36}H_{58}N_{27}O_{32}Ho$	$C_{36}H_{56}N_{27}O_{31}Yb$	$C_{36}H_{72}LaN_{25}O_{37}S$	$C_{108}H_{214}Br_6Gd_2N_{72}O_{89}$	$C_{72}H_{144}Br_6Ce_2N_{48}O_{60}$
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic	trigonal
Space group	$Pna2_1$	$Pna2_1$	$Pna2_1$	$P2_1/c$	$P2_1/n$	$P3_2$
Unit cell dimensions [Å, °]	a = 31.976(3), b = 14.727(2) c = 11.808(1)	a = 32.0840(1) b = 14.7160(1) c = 11.7250(1)	a = 31.946(5) b = 14.794(2) c = 11.8048(8)	a = 12.603(1) b = 16.225(2) c = 30.244(4) β = 97.047(8)	a = 16.5490(1) b = 26.9470(2) c = 21.9000(2) β = 100.3160(5)	a = 20.7418(2), c = 29.3987(3)
Volume [Å^3]	5560.5(10)	5535.94(15)	5579.1(12)	6137.7(12)	9608.34(13)	10953.46(19)
Z	4	4	4	4	2	3
$D_{calcd.}$ [Mg/m^3]	1.839	1.855	1.829	1.751	1.638	1.547
Temperature [K]	200(2)	150(2)	296(2)	293(2)	150(2)	150(2)
Diffractometer	Enraf−Nonius MACH-3	Nonius Kappa CCD	Enraf−Nonius CAD4	Bruker	Nonius Kappa CCD	Nonius Kappa CCD
Radiation [Å]	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)
Data collection method	ω-scans	CCD technique	ω-scans	2θ/ω-scans	CCD technique	CCD technique
$2\theta_{max}$ [°]	59.94	54.88	59.88	50.00	66.04	43.92
Crystal size [mm]	0.27 × 0.15 × 0.10	0.18 × 0.15 × 0.12	0.75 × 0.43 × 0.35	0.48 × 0.43 × 0.30	0.44 × 0.36 × 0.28	0.28 × 0.25 × 0.18
μ(Mo-K_α) [mm^{-1}]	1.316	1.555	1.799	0.853	2.046	2.356
Absorption correction	ψ-scans	none	ψ-scans	ψ-scans	none	none
Reflns. collected	8461	48262	6445	11607	95034	26529
Unique reflns.	8461	12620	6445	10482	35921	17777
R_{int}	0	0.0721	0	0.0520	0.0695	0.0345
Observed reflns.	5890	10479	4719	6236	22384	15871
Final R indices [$F \geq 4\sigma(F)$][a]	$R1$ = 0.0478, $wR2$ = 0.1201	$R1$ = 0.0577, $wR2$ = 0.1366	$R1$ = 0.0576, $wR2$ = 0.1600	$R1$ = 0.0616, $wR2$ = 0.1487	$R1$ = 0.0697, $wR2$ = 0.2061	$R1$ = 0.0797, $wR2$ = 0.2113
R indices (all data)	$R1$ = 0.1055, $wR2$ = 0.1390	$R1$ = 0.0741, $wR2$ = 0.1435	$R1$ = 0.0730, $wR2$ = 0.1644	$R1$ = 0.1181, $wR2$ = 0.1780	$R1$ = 0.1240, $wR2$ = 0.2266	$R1$ = 0.0910, $wR2$ = 0.2183
GooF on F^2	1.070	1.032	1.014	1.021	1.096	1.078

[a] Definitions: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, GooF $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

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Received January 22, 2002
[I02036]