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Anion encapsulation by Ln(III)/K(I) heterobismetal-capped cucurbit[5]uril

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Three Ln(III)/K(I) (Ln = La, Ce and Nd) heterobismetal-capped cucurbit[5]uril molecular capsules, $\{[LaK(C_{30}H_{30}N_{20}O_{10})Cl]Cl(H_2O)_3\}Cl_2 \cdot 8H_2O$ (**1**), $\{[CeK(C_{30}H_{30}N_{20}O_{10})Cl]Cl(H_2O)_3\}Cl_4(H_3O)_2^{2+} \cdot 8H_2O$ (**2**) and $\{[NdK(C_{30}H_{30}N_{20}O_{10})Cl]Cl(H_2O)_3\}Cl_2 \cdot 12.5H_2O$ (**3**), were synthesised by self-assembly in aqueous solution, and their anion encapsulation property was confirmed by X-ray crystallography. The effect of the lanthanide cation radius on the structure of the heterobismetal-capped cucurbit[5]uril molecular capsules has been investigated.

Keywords: cucurbit[5]uril; anion encapsulation; heterobismetal complexes; X-ray crystallography

Introduction

The design and synthesis of anion receptors for host–guest chemistry has been one of the most attractive areas in contemporary supramolecular chemistry (*1–5*), due to the importance of anions in biochemical systems (*6*), synthesis (*7*), catalysis (*8*), recycling and environmental processes (*9*). However, design of artificial anion cage for the encapsulation or sensing of anions is still challenging in practice. This is because anions possess a wide range of different geometries, such as spherical, linear, trigonal, tetrahedral, octahedral, and have a lower charge-to-radius ratio that results in their less effective electrostatic binding interactions than isoelectronic cations (*2a*). Cryptands are unique among synthetic molecular receptors because of their intramolecular cavities that are available for the encapsulation of anion guests (*1*, *2*). Cucurbit[*n*]uril ($n = 5-8$, 10, hereafter abbreviated as Q[*n*]), as one kind of cryptands (Figure 1), represents a relatively new family of molecular hosts (*10*). Its intrinsic capacity and two identical carbonyl-fringed portals on each side make it capable of encapsulating many kinds of guests (*11–13*). However, the number of reported examples of Q[*n*] encapsulate anions is quite limited (*14*, *15*). Recently, Thuéry synthesised a series of uranyl heterobismetal complexes with Q[5] under hydrothermal conditions (*16*). In order to understand whether heterobismetal-capped Q[5] molecular capsules can encapsulate anions and whether such encapsulation is selective, we try to use Q[5] to chelate different metal cations in different solutions and report here the design, synthesis and crystal structures of a series of Ln(III)/K(I) (Ln = La, Ce and Nd) heterobismetal-capped Q[5] molecular capsules.

Experimental section

General

Hydrochloric acid, potassium chloride, lanthanide chloride, cerium nitrate and neodymium nitrate were of commercial origin and used without further purification. Q[5] was synthesised by published procedures (*17*). The C, H and N microanalyses were carried out with a CE instruments EA 1110 elemental analyser.

Crystal structure determination

Preliminary examination and data collection were performed with Mo Kα radiation on the Bruker Smart Apex 2000 diffractometer equipped with a graphite crystal incident beam monochromator ($\lambda = 0.71073$ Å) in $\omega/2\theta$ scan mode. Absorption corrections were applied by using the multiscan program SADABS. Structural solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program package (*18*), respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. The carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.

Although presenting an approximate mirror plane, complex **2** could not be solved in a high symmetry space group. It was solved in a lower symmetry space group, and then transformed to a higher symmetry space group with

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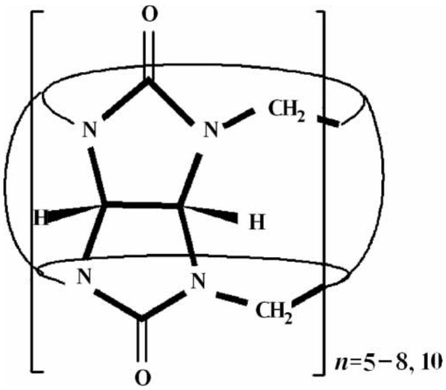

Figure 1. Molecular structure of cucurbit[$n = 5$–8, 10]uril.

ADDSYM SHELX (PLATON) (*19*), which led to the second parameter on the SHELXL weighting line having an exceptionally large value. For complex **2**, no hydrogen atoms are given for all isolated water molecules and for complex **3**, no hydrogen atoms are given for all disordered water molecules since it is difficult and unnecessary.

CCDC 700843, 717052 and 706232 contain the three supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

A summary of the crystallographic data, data collection and refinement parameter for complexes **1**–**3** is given in Table 1.

Synthesis

$\{[LaK(C_{30}H_{30}N_{20}O_{10})Cl]Cl(H_2O)_3\}Cl_2{\cdot}8H_2O$ (**1**)

Q[5] (1.66 g, 2.0 mmol) was first dissolved in 3.0 mol l^{-1} hydrochloric acid (100 ml). To this solution (10 ml, 0.02 mol l^{-1}) was added $LaCl_3$ (2 ml, 0.2 mol l^{-1}) and KCl (1 ml, 0.2 mol l^{-1}). The mixed solution was stirred thoroughly and then left in an open beaker. One week later, colourless crystals of **1** were separated and dried on a filter paper. Anal. calcd for **1**: C, 26.72; H, 3.89; N, 20.77. Found: C, 26.47; H, 4.01; N, 20.57.

$\{[CeK(C_{30}H_{30}N_{20}O_{10})Cl]Cl(H_2O)_3\}Cl_4(H_3O)_2^{2+}{\cdot}8H_2O$ (**2**)

A solution of Q[5] (10 ml, 0.02 mol l^{-1}) in HCl (3 mol l^{-1}), $Ce(NO_3)_3{\cdot}6H_2O$ (2 ml, 0.2 mol l^{-1}) and KCl (1 ml, 0.2 mol l^{-1}) was added. The mixture was set aside for two months to allow colourless crystals to deposit. Anal. calcd for **2**: C, 25.96; H, 4.21; N, 20.18. Found: C, 25.83; H, 4.12; N, 20.26.

$\{[NdK(C_{30}H_{30}N_{20}O_{10})Cl]Cl(H_2O)_3\}Cl_2{\cdot}12.5H_2O$ (**3**)

$Nd(NO_3)_2$ (2 ml, 0.2 mol l^{-1}), KCl (1 ml, 0.2 mol l^{-1}) and distilled water (10 ml) were added to a solution of Q[5] (10 ml, 0.02 mol l^{-1}) in 3.0 mol l^{-1} hydrochloric acid and kept at room temperature in an open beaker. Colourless crystals of **3** were separated after two weeks. Anal. calcd for **3**: C, 25.11; H, 4.28; N, 19.52. Found: C, 25.07; H, 4.37; N, 19.38.

Results and discussion

Slow evaporation of hydrochloric acid aqueous solution containing KCl, $LaCl_3$ and Q[5], whose molar ratio is 1:2:1, results in the formation of complex **1**. Single-crystal structural analysis (Figure 2) reveals that one lanthanum cation and one potassium cation are coordinated to each portal of the Q[5] molecule. Three water molecules (O1W,

Table 1. Summary of the crystallographic data for **1**, **2** and **3**.

	1	**2**	**3**
Empirical formula	$C_{30}H_{52}Cl_4KLaN_{20}O_{21}$	$C_{60}H_{116}K_2Ce_2Cl_8N_{40}O_{46}$	$C_{60}H_{122}K_2Nd_2Cl_8N_{40}O_{51}$
Formula weight	1384.18	2917.77	2870.26
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnnm*	*Pnnm*	*Pnnm*
a (Å)	14.796	23.993(6)	24.006(4)
b (Å)	24.092(4)	14.776(4)	14.791(3)
c (Å)	14.796(3)	14.776	14.791
Volume (Å^3)	5274.2(13)	5238.3(19)	5252.1(13)
Z	4	2	2
Crystal size	0.45 × 0.32 × 0.27	0.35 × 0.29 × 0.27	0.47 × 0.35 × 0.31
D_{calcd} (mg/m^3)	1.744	1.850	1.815
Temperature (K)	123(2)	123(2)	123(2)
Reflns measured	19,601	26,308	39,030
Unique reflns	5276	5168	5314
R(int)	0.0426	0.0495	0.0377
$R1/wR2[I > 2\sigma(I)]$	0.0758/0.1783	0.1087/0.2339	0.0539/0.1338
$R1/wR2$ (all data)	0.0790/0.1804	0.1099/0.2344	0.0560/0.1353
Goodness of fit on F^2	1.159	1.160	1.165

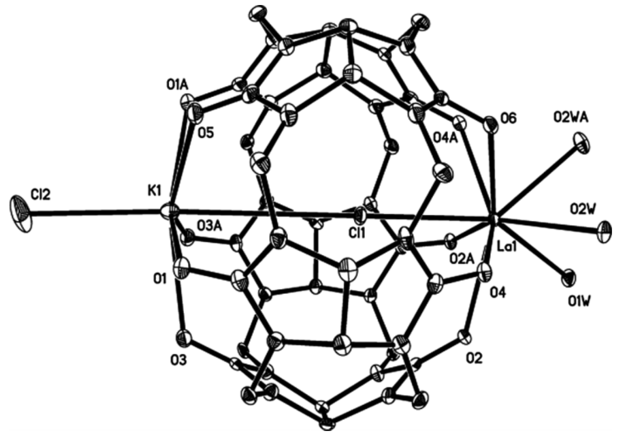

Figure 2. ORTEP diagram of **1**; displacement ellipsoids are drawn at the 50% probability level; solvate water molecules and anions are omitted for clarity.

O2W and O2WA) are coordinated to the lanthanum cation from outside with distances of 2.533(5), 2.608(3) and 2.608(3) Å. One chlorine anion (Cl2) is coordinated to the potassium cation (K1) from outside with a distance of 3.112(3) Å. The other chlorine anion (Cl1) resides in the cavity of Q[5] and coordinated to the potassium cation (K1) and lanthanum cation (La1) from inside. So, the structure of complex **1** can be viewed as a heterobismetal-capped Q[5] molecular capsule, in which a chlorine anion is encapsulated, formed through each portal of the Q[5] sealed by one La(III) cation and one K(I) cation. The remarkable feature in complex **1** is that the Q[5] molecule and the encapsulated chlorine anion, as well as metal cations and the coordinated chlorine anion, two coordinated water molecules lie on special positions of site symmetry *m*. Selected bond lengths (Å) for complex **1** are shown in Table 2. In the crystal structure of complex **1**, the heterobismetal-capped Q[5] molecular capsule is separated and the isolated molecular capsule is surrounded by water molecules and chlorine anions, and they interact to form a hydrogen-bonded layer structure.

At first glance, complex **1** is structurally very similar to its counterpart, $[K_4(C_{30}H_{30}N_{20}O_{10})_2(HCONH_2)_2(H_2O)_2Cl_2]Cl_2(CH_3OH)(H_2O)_{17.5}$, which we previously reported (*15a*). At least two significant differences existed between complex **1** and its counterpart, however. Firstly, the encapsulated chlorine anion is not sited in the centre of the closed molecular capsule of complex **1**, wherein the bond length of La1—Cl1 (2.855 Å) is much shorter than that of K1—Cl1 (4.013 Å). The reason is that the electrostatic interaction between the lanthanum cation and the encapsulated chlorine anion is much stronger than that between the potassium cation and the encapsulated chlorine anion. Secondly, to a certain extent, Q[5] is a rigid cryptand with D_{5h} symmetry, having two mean portal diameters $\sim$2.4 Å (taking into account the van der Waals radii of the relevant atoms) (*10*). However, complex **1** shows two varied portal diameters, of which the portal coordinated to the K(I) cation is bigger (mean value 2.727 Å) than that coordinated to the La(III) cation (mean value 2.518 Å). Obviously, the deformation of the Q[5] molecule in complex **1** is due to the coordination of heterobismetal ions to the portal oxygen atoms. Since each portal of the Q[5] molecule is coordinated by the same metal cations, the latter shows almost two same portal diameters (mean value 2.714 Å).

Complexes $\{[CeK(C_{30}H_{30}N_{20}O_{10})Cl]Cl(H_2O)_3\}Cl_4(H_3O)_2^{2+}\cdot 8H_2O$ (**2**) and $\{[NdK(C_{30}H_{30}N_{20}O_{10})Cl]Cl(H_2O)_3\}Cl_2\cdot 12.5H_2O$ (**3**) were prepared by the same method as illustrated for complex **1**. Their X-ray crystallographies reveal that these three complexes are all isomorphous. As a result, the host structure of the molecular capsule in complexes **2** and **3** is very similar to that in complex **1**. They have the same Q[5] crust and encapsulated the same chlorine anion. The only difference is that the lanthanum cation is replaced by the cerium or neodymium cation. It must be mentioned that there are two kinds of anion, chlorine anion

Table 2. Selected bond lengths (Å) for **1**, **2** and **3**.

1	La(1)—O(1W)	2.533(5)	La(1)—O(2)#1	2.600(3)
	La(1)—O(4)	2.551(3)	La(1)—O(2W)	2.608(3)
	La(1)—O(4)#1	2.551(3)	La(1)—O(2W)#1	2.608(3)
	La(1)—O(6)	2.562(4)	La(1)—Cl(1)	2.8553(15)
	La(1)—O(2)	2.600(3)		
2	Ce(1)—O(1W)	2.503(8)	Ce(1)—O(3)#1	2.566(5)
	Ce(1)—O(1)#1	2.512(5)	Ce(1)—O(3)	2.566(5)
	Ce(1)—O(1)	2.512(5)	Ce(1)—O(2W)	2.595(6)
	Ce(1)—O(2)	2.528(7)	Ce(1)—O(2W)#1	2.595(6)
	Ce(1)—Cl(1)	2.838(3)		
3	Nd(1)—O(1W)	2.471(3)	Nd(1)—O(3)	2.554(2)
	Nd(1)—O(5)	2.511(2)	Nd(1)—O(3)#1	2.554(2)
	Nd(1)—O(5)#1	2.511(2)	Nd(1)—O(6)	2.527(3)
	Nd(1)—O(2W)	2.539(2)	Nd(1)—Cl(1)	2.7906(13)
	Nd(1)—O(2W)#1	2.539(2)		

Symmetry transformations used to generate equivalent atoms: #1 *x*, *y*, $-z$.

and nitrate anion, in the reaction solution of complexes **2** and **3**. However, their crystal structures show that the chlorine anion, instead of the nitrate anion, is encapsulated in the heterobismetal-capped Q[5] molecular capsule. These structure features indicate that the heterobismetal-capped Q[5] molecular capsule has the ability to selectively encapsulate the chlorine anion in the presence of the nitrate anion, which further confirmed the conclusion we previously reported that the chlorine anion is more suitable than the nitrate anion to metal-coordinated Q[5]. Obviously, the major formation reason of these molecular capsules is electrostatic interactions.

Although they crystallise with the same orthorhombic *Pnnm* space group and with a very similar molecular structure, a careful comparison reveals that significant dissimilarity still existed in these three complexes. For example, the metal–carbonyl oxygen bond distances ($\mathrm{Ln(III)—O_{Q[5]}}$) for these three complexes are observed to vary from complex to complex (Table 3). The $\mathrm{La(III)—O_{Q[5]}}$ bond lengths (mean value 2.573 Å) in complex **1** are slightly longer than the $\mathrm{Ce(III)—O_{Q[5]}}$ bond lengths (mean value 2.532 Å) in complex **2**, while the $\mathrm{Ce(III)—O_{Q[5]}}$ bond lengths in complex **2** are almost equal to the $\mathrm{Nd(III)—O_{Q[5]}}$ bond lengths (mean value 2.531 Å) in complex **3**. According to the lanthanide contraction, the radius of the Ln(III) cation decreases with the increasing atomic number. Visibly, tendency of bond lengths is consistent with the decreasing order of the Ln(III) cation radius. Another remarkable feature of the three heterobismetal-capped Q[5] molecular capsules is that the Ln(III) cations are all out of the mean plane of the five carbonyl oxygen atoms of the Q[5] portal (Figure 3). The cerium ion is 0.511 Å above the mean plane of the five carbonyl oxygen atoms of the Q[5] portal in complex **2**. This value is slightly smaller than that (0.528 Å) in complex **1** and is slightly larger than that (0.506 Å) in complex **3**. In consequence, the Q[5] portal, coordinated to the Ln(III) cation, mean semidiameter for the three complexes is in the order **1** > **2** ≈ **3** (see Table 3). Portal semidiameter of Q[5] should decrease with a decrease in the ionic radius of the coordinated metal. However, in order to avoid too much distortion of Q[5], the self-assembly process puts the Ln(III) cations at different site out-of-plane spontaneously. The modulation mechanism lead to that Q[5] can coordinate many kinds of metal ions whereas these metal ions have dissimilar ionic radius.

Table 3. Comparison of complexes **1**, **2** and **3**.

	1	**2**	**3**
$\mathrm{Ln(III)—O_{Q[5]}}$ mean bond length (Å)	2.573	2.532	2.531
Ln(III) out-of-plane height (Å)	0.528	0.511	0.506
Q[5] mean portal semidiameter (Å)	2.518	2.480	2.480

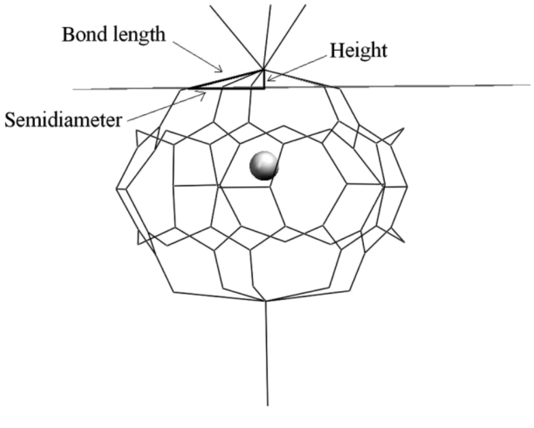

Figure 3. Ln(III) cations are out of the mean plane of the Q[5] portal.

When preparing complex **1**, we found that the amount of potassium chloride must be substantially less than that of the lanthanum reagent, as more would have led to the formation of a potassium product in which Q[5] coordinated only to potassium ion without any lanthanum component. This suggests that the reactant proportion plays a key role and the lanthanide ion can be replaced by the potassium ion. The syntheses of complexes **2** and **3** have the same phenomena. Apparently, potassium ion is the most suitable metal ion to coordinate to the portal of Q[5]. This can be further confirmed by the fact that the addition of potassium ion to the reaction mixture of synthesis Q[*n*] leads to an increase in the proportion of Q[5] (*20*). There are two main reasons for this. First, the ionic radius of potassium ion is more close to the semidiameter of the Q[5] portal than the other three lanthanide cations. Second, potassium ion has a lower charge than the other three lanthanide cations, which means that the formed molecular capsule has higher stabilisation.

Conclusion and perspectives

It is well known that precisely controlling the solid structures of the target products remains to be a great challenge, since the self-assembly reaction is highly influenced by all kinds of factors. However, three heterobismetal-capped Q[5] molecular capsules, in which chlorine anion can be encapsulated selectively, have been self-assembled in aqua medium from Q[5] and two different metal ions successfully. We also demonstrated that their structural behaviour was consistent with the ionic radius of the coordinated metal ions. This structural behaviour of these complexes of Q[5] and other complexes of Q[5] previously reported (*14–16*) owe to the complexation mechanism, adjusting the portal semidiameter of Q[5] and putting metal ions at different site out-of-plane. Obviously, Q[5] can chelate some other metal ions and some other anions can be encapsulated in Q[5]-based molecular capsules in a similar way, which means Q[5] can be used as a ‘catch-all’ complexing agent.

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