

Chapter 2

Simple Coordination Complexes of Cucurbit[n]urils with Metal Ions

Abstract Generally, the noncovalent interaction of Q[n]s with various guest molecules has led to the development of Q[n]-based host–guest chemistry, which has become the mainstream in Q[n] chemistry. In fact, the establishment of Q[n] chemistry started with Q[n]-based coordination chemistry because the structural characteristics of the first characterized member of the Q[n] family, Q[6], was based on the determination of the complex of Q[6] molecules with Ca^{2+} cations. From a structural viewpoint, the two preorganized (identical) carbonyl fringed portals in Q[n]s are ideal for acting as a rigid platform for developing a variety of Q[n]-metal derived coordination structures. In this chapter, a number of Q[n]-based metallo-supramolecular coordination fashions and examples are reviewed in detail. Overall, molecular bowls, molecular capsules, sandwich pairs, and heterometallic complexes are the general structures in the solid state. We therefore describe them in this chapter as simple coordination complexes of Q[n]s with metal ions.

Keywords Cucurbit[n]urils • Coordination complexes • Metal ions, molecular bowls • Molecular capsules • Sandwich pairs • Heterometallic complexes

It is well known that Q[n]s [1–5] readily coordinate with metal ions because of their two open polar portals rimmed with carbonyl groups (referring to Scheme 1.2). However, Q[n]s of various portal sizes appear to have different coordination abilities with metal ions, and various metal ions seem to show different affinities for a specific Q[n]. Moreover, environmental factors, such as coordination geometry or radius of metal ions, temperature, counter-anions, steric bulk, solvent, metal-to-ligand ratio, and pH of the system, influence the coordination and supramolecular assemblies of a Q[n] with a certain metal ion.

2.1 Simple Coordination of Cucurbit[5]urils with Metal Ions

The unsubstituted or substituted cucurbit[5]urils (Q[5] and SQ[5]s, respectively) are the smallest members or homologs in the Q[n] family. The first known Q[5] is decamethylcucurbit[5]uril ($\text{Me}_{10}\text{Q}[5]$), which was reported in 1992 [6]. The host–guest chemistry of the Q[5]s has received less attention than their larger homologs because of the limited size of the portals and the capacity of their cavities [7–10]. To the best of our knowledge, the first reported crystal structure is a Q[5]-based coordination complex with a molecular bowl confirmation by covering a barium ion on one portal of a decamethylcucurbit[5]uril molecule, and the “bowls” further construct a honeycomb-like supramolecular assembly through hydrogen bonding and ion-dipole interactions (Fig. 2.1) [11].

Unsubstituted Q[5] and its substituted derivatives SQ[5]s are the smallest members of their respective homologous families. Although the smaller portal size of Q[5]s inhibits the entry of most organic molecules into the central cavity, and hence reduces the possible range of Q[5]-based host–guest inclusion complexes, it offers a “concentrated” set of five portal carbonyl oxygens so that larger metal ions are able to fully cover the portal and bind to all five oxygens to yield a stable metal-Q[5] complex. Recent studies reveal that Q[5]s have a strong tendency to coordinate with metal ions and form metal-ion-lidded molecular capsules or molecular bowls because Q[5]s have the smaller portal size and more concentrated portal carbonyl oxygens at portals, which could directly coordinate with metal ions, including alkali, alkaline earth, transition, and lanthanide or uranium [12–16]. Moreover, different Q[5]s, such as the unsubstituted Q[5], and some representative alkyl-substituted Q[5]s, like $\text{Me}_{10}\text{Q}[5]$, dimethylcucurbit[5]uril (DMeQ[5]), 1,2,4-hexamethylcucurbit[5]uril

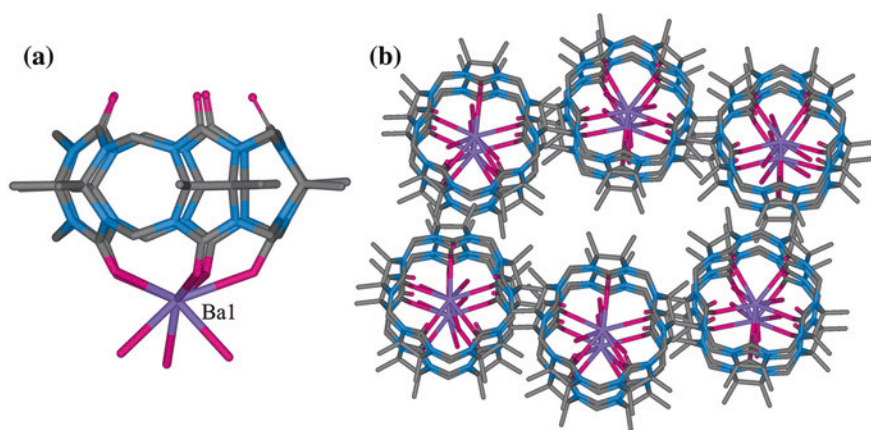


Fig. 2.1 **a** Complex cation of $[\text{Me}_{10}\text{Q}[5](\text{H}_2\text{O})_3\text{Ba}]^{2+}$. **b** Stacking of the complexes in the crystals

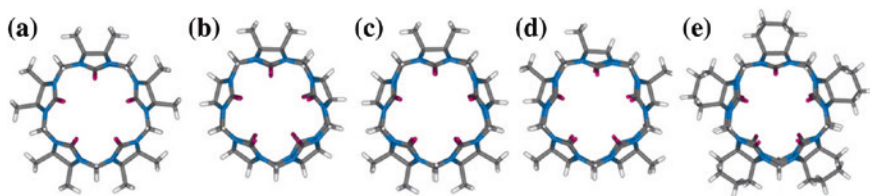


Fig. 2.2 Structures of five representative alkyl-substituted Q[5]s: **a** Me₁₀Q[5]; **b** DMeQ[5]; **c** 1,2,4-HMeQ[5]; **d** PMeQ[5] and **e** CyH₅Q[5]

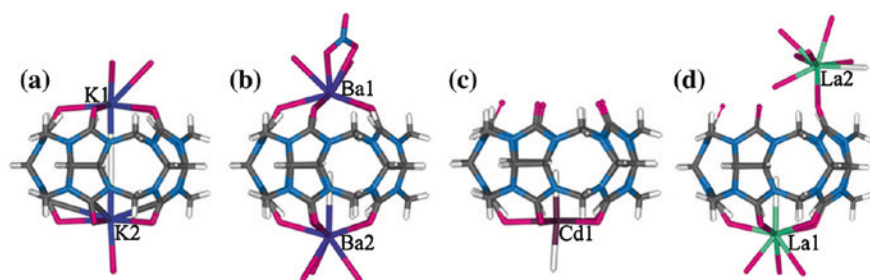


Fig. 2.3 X-ray crystal structures of molecular capsules and molecular bowls of Q[5] with various metal ions: **a** alkali (K⁺); **b** alkaline earth (Ba²⁺); **c** transition (Cd²⁺); and **d** lanthanide (La³⁺) metal ions

(1,2,4-HMeQ[5]), pentamethylcucurbit[5]uril (PMeQ[5]), pentacyclopentanocucurbit[5]uril (CyH₅Q[5]), and so on show no obvious difference in affinity to the metal ions (Fig. 2.2).

For example, a series of molecular capsules or molecular bowls of Q[5] with various metal ions, including alkali (K⁺), alkaline earth (Ba²⁺), transition (Cd²⁺), and lanthanide (La³⁺) metal ions (Fig. 2.3) [17, 18]. Moreover, these Q[5]-based complexes exhibited the remarkable property of encapsulating a negatively charged ion. Its easy synthesis, rigid structure, and chemical and thermal stability could make Q[5] very attractive for complexation of anions in aqueous solution [18]. Further experiments reveal that Q[5] shows special selectivity for including “naked” chloride anion or nitrate anion under certain conditions. The metal-free host has been demonstrated to selectively include nitrate ion, whereas the lanthanide-capped molecular capsule showed preference toward the inclusion of chloride ion (Fig. 2.4) [19].

Our group synthesized complexes of alkyl-substituted Q[5]s (referring to Fig. 2.2) with various metal ions. Most of them were molecular bowls or molecular capsules. The metal ions included alkali [12, 13], alkaline earth [14], transition [15], and lanthanide [16] metal ions. For example, we evaluated the effect of a series of alkaline earth metal ions (Ca²⁺, Sr²⁺, and Ba²⁺) on their complexes with CyH₅Q[5] by mixing their chloride salts with CyH₅Q[5] [20]. The experimental results revealed that coordination of CyH₅Q[5]-based molecular capsules

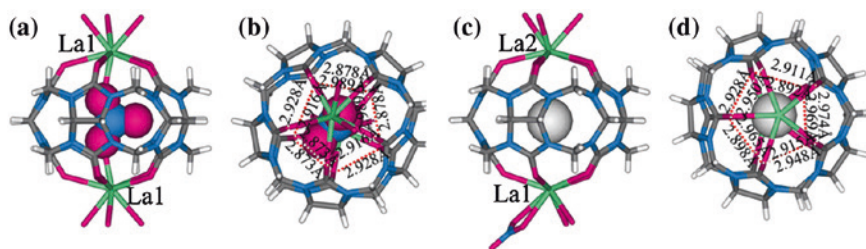


Fig. 2.4 X-ray structures of dinuclear capsule-like complexes of La^{3+} -Q[5]: **a** complex with an included nitrate anion; **b** the corresponding portal sizes; **c** complex with an included chloride ion; **d** the corresponding portal sizes

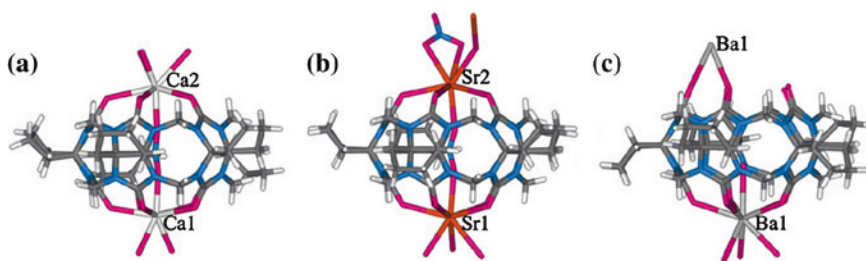


Fig. 2.5 X-ray crystal structures of molecular capsules and molecular bowls of $\text{CyH}_5\text{Q}[5]$ with alkaline earth metal ions: **a** Ca^{2+} ; **b** Sr^{2+} ; and **c** Ba^{2+}

and molecular bowls depended on the ionic radius of the metal cation (Fig. 2.5). In the $\text{CyH}_5\text{Q}[5]/\text{Ca}^{2+}$ complex, the $\text{CyH}_5\text{Q}[5]$ portal is larger than the calcium cation. Thus, the $\text{CyH}_5\text{Q}[5]$ -based molecular capsule is not completely closed, and the $\text{CyH}_5\text{Q}[5]$ molecule even experiences some deformation. In the $\text{CyH}_5\text{Q}[5]/\text{Sr}^{2+}$ complex, the radius of the strontium cation is slightly larger than the $\text{CyH}_5\text{Q}[5]$ portal, and thus they form a completely closed molecular capsule. In the $\text{CyH}_5\text{Q}[5]/\text{Ba}^{2+}$ complex, the barium ion can only cover one portal of the $\text{CyH}_5\text{Q}[5]$ molecule and juxtaposes itself near the portal of other $\text{CyH}_5\text{Q}[5]$ molecule, generating an opened molecular capsule. Based on the radii of these three metal ions, which are 0.99, 1.12, and 1.34 Å, the radius of the metal ion is the underlying reason behind these differences.

Generally, metal ions that can cover the portals of a Q[5] molecule have a radius larger than 0.84 Å, which is the radius of the Cd^{2+} cation. Nevertheless, there are other factors that could lead to the formation of Q[5]s with metal ions with a smaller radius, such as Hg^{2+} (0.69 Å) [21]. In recent years, there has been a trend toward the use of third species as structure directing agents in Q[n]-metal systems, and the driving forces could be the so-called outer surface interactions of Q[n]s [22]. These species produce Q[n]-based supramolecular assemblies whose properties, structural novelties, and functionalities exceed those

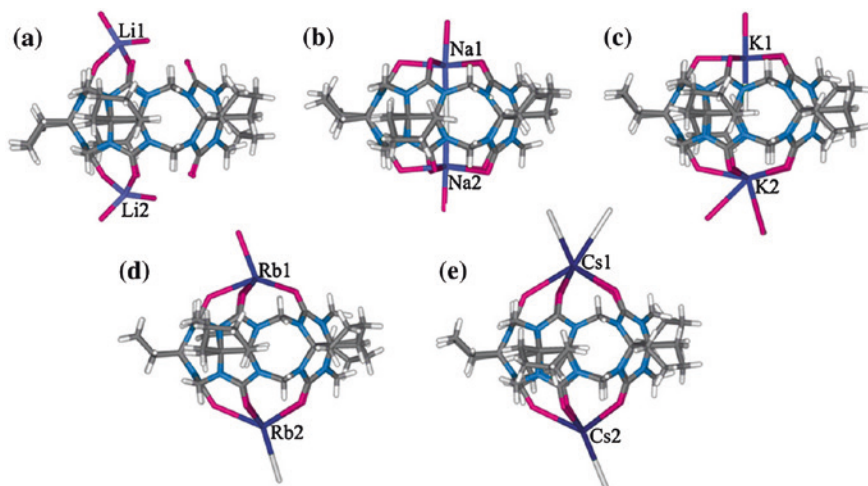


Fig. 2.6 X-ray crystal structures of molecular capsules of CyH₅Q[5] with alkali metal ions: **a** Li⁺; **b** Na⁺; **c** K⁺; **d** Rb⁺; and **e** Cs⁺

of assemblies obtained in the absence of such agents. For example, we cannot obtain all complexes of CyH₅Q[5] with all alkali metal ions by simple combination of CyH₅Q[5] with alkali metal salts. However, in the presence of ZnCl₂ in an acidic medium (HCl), the formed [ZnCl₄]²⁻ anions behave as “structure directing agent”, and facilitate the formation of all five CyH₅Q[5]/M_{alkali} complexes (Fig. 2.6a–e). Among these complexes are those with the smallest (Li⁺, 0.59 Å) and largest (Cs⁺, 1.67 Å) metal radii (except Fr⁺, 1.80 Å) [23]. All four alkali metal ions, Na⁺ (0.97 Å), K⁺ (1.33 Å), Rb⁺ (1.43 Å), and Cs⁺ (1.67 Å) which have larger metal radii, coordinate to the five carbonyl oxygen atoms and fully cover the portals of the CyH₅Q[5] molecules. An exception to this trend is the Li⁺ cation, which has the smallest metal radius and can only coordinate to two portal carbonyl oxygen atoms. The CyH₅Q[5]-based complexes with the fully capped portals initially appear to crystallize with similar molecular structures, such as opened molecular capsules or molecular capsules. The distances of the capped metal ions to the mean planes of the five portal carbonyl oxygens appear to increase with increasing atomic numbers of the alkali metals. But a close inspection shows that the capsules contain different core molecules: a chloride anion for the CyH₅Q[5]/Na⁺ and CyH₅Q[5]/K⁺ complexes, a water molecule for the CyH₅Q[5]/Rb⁺ complex, and none for the CyH₅Q[5]/Cs⁺ complex. Additionally, the interaction between the capped alkali metal ions and the included ion or molecule could affect the distances of the capped metal ions from the portal plane.

An example of the Me₁₀Q[5]–M_{alkali} system can show this trend better [24]. Figure 2.7 shows four Me₁₀Q[5]/M_{alkali} molecular bowls or capsules obtained by reactions of Me₁₀Q[5] with the corresponding alkali metal salts (NaCl, KCl, RbCl, and CsCl) in the presence of hydroquinone (Hyq) as a structure directing agent.

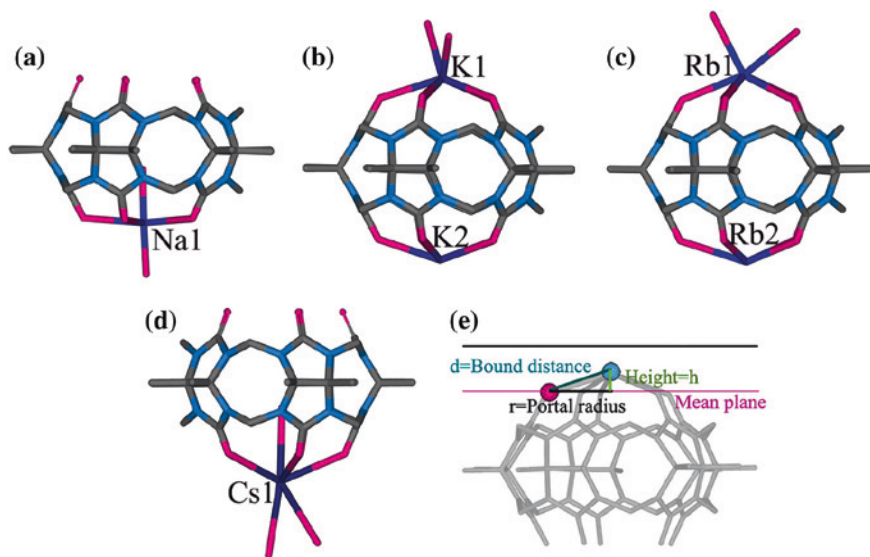


Fig. 2.7 X-ray crystal structures of molecular capsules and molecular bowls of $\text{Me}_{10}\text{Q}[5]$ with alkali metal ions **a** Na^+ ; **b** K^+ ; **c** Rb^+ ; and **d** Cs^+ ; **e** representation of bonding distance of $\text{Me}_{10}\text{Q}[5]$ with metal ions

Table 2.1 Comparison of the structural parameters of four $(\text{Me}_{10}\text{Q}[5])/\text{M}_{\text{alkali}}$ complexes

Parameters	$\text{Me}_{10}\text{Q}[5]/\text{Na}^+$	$\text{Me}_{10}\text{Q}[5]/\text{K}^+$	$\text{Me}_{10}\text{Q}[5]/\text{Rb}^+$	$\text{Me}_{10}\text{Q}[5]/\text{Cs}^+$
d (Å)	2.627	2.775	2.870	3.009
h (Å)	~0	0.832	1.028	1.175
r (Å)	2.627	2.647	2.680	2.770

A careful comparison reveals that a structural trend holds for the four $\text{Me}_{10}\text{Q}[5]$ complexes. These four complexes were all isolated as the sole products of seemingly straightforward reactions of the relevant alkali metal salt with the $\text{Me}_{10}\text{Q}[5]$ ligand. It should be interesting and essential to compare the related structural data of the four complexes. As shown in Fig. 2.7e and Table 2.1, the average metal–carbonyl oxygen bond lengths (d ; $\text{O}_{\text{Me}_{10}\text{Q}[5]}-\text{M}_{\text{alkali}}$) vary from complex to complex. It is well known that the radius of alkali metal ions increases with increasing atomic number. As a result, the metal–carbonyl oxygen bond lengths in the four complexes follow the order $\text{Me}_{10}\text{Q}[5]/\text{Na}^+ < \text{Me}_{10}\text{Q}[5]/\text{K}^+ < \text{Me}_{10}\text{Q}[5]/\text{Rb}^+ < \text{Me}_{10}\text{Q}[5]/\text{Cs}^+$ (Table 2.1). Their crystal data suggest that the height of the alkali cation out-of-portal plane (h) of the four complexes follows the same order (Table 2.1). According to the Pythagorean theorem, the portal radius of the $\text{Me}_{10}\text{Q}[5]$ ligand (r) for the four compounds has the same order. Obviously, all these structural trends can be attributed to the fact that the radii of alkali cations are of the order $\text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$, and this suggests that the portal size of a $\text{Q}[n]$ could be transformed in a certain range. Unexpectedly, all

four complexes include a water molecule instead of an anion in the cavity of the $\text{Me}_{10}\text{Q}[5]$ molecule. In other words, the opened or closed molecular capsules in the four compounds could not recognize or encapsulate the chloride anion. A similar structural feature can be observed in the complexes of $\text{SQ}[5]$ s with alkaline earth metal ions [25].

Although the first reported Ln^{3+} - $\text{Q}[5]$ complex of this type was $\{(\text{LaCl}@\text{Q}[5])\text{LaCl}(\text{H}_2\text{O})_9\}\text{Cl}_4 \cdot \text{HCl} \cdot 7\text{H}_2\text{O}$, obtained from an HCl solution ($\sim 3\text{ M}$) containing $\text{La}(\text{NO}_3)_3$ and $\text{Q}[5]$, La^{3+} cation has 14 lanthanide group members, which could show similar interaction properties with $\text{Q}[5]$ s due to the so-called lanthanide contraction. The La^{3+} cation fully caps one portal of the $\text{Q}[5]$ molecule, while a second La^{3+} partially caps the second portal via coordination to two carbonyl oxygens and a chloride ion is included in the $\text{Q}[5]$ cavity (Fig. 2.3d) [18]. A similar arrangement occurs in the product obtained from the coordination of Pr^{3+} to $\text{Q}[5]$ [26]. The coordination of Gd^{3+} to the dimethyl-substituted derivative ($\text{Me}_2\text{Q}[5]$), or Nd^{3+} to the decamethyl $\text{Me}_{10}\text{Q}[5]$ derivative, once again results in products exhibiting similar structural arrangements (Fig. 2.8b and c respectively) [16].

In recent years, Thuéry focused on the coordination of $\text{Q}[n]$ s with lanthanide and actinide cations and synthesized two $\text{Q}[5]/\text{UO}_2$ complexes. One of these complexes, which has a stoichiometry of $\{\text{UO}_2\text{Q}[5]\}(\text{ReO}_4)_2 \cdot 2\text{H}_2\text{O}$, was prepared

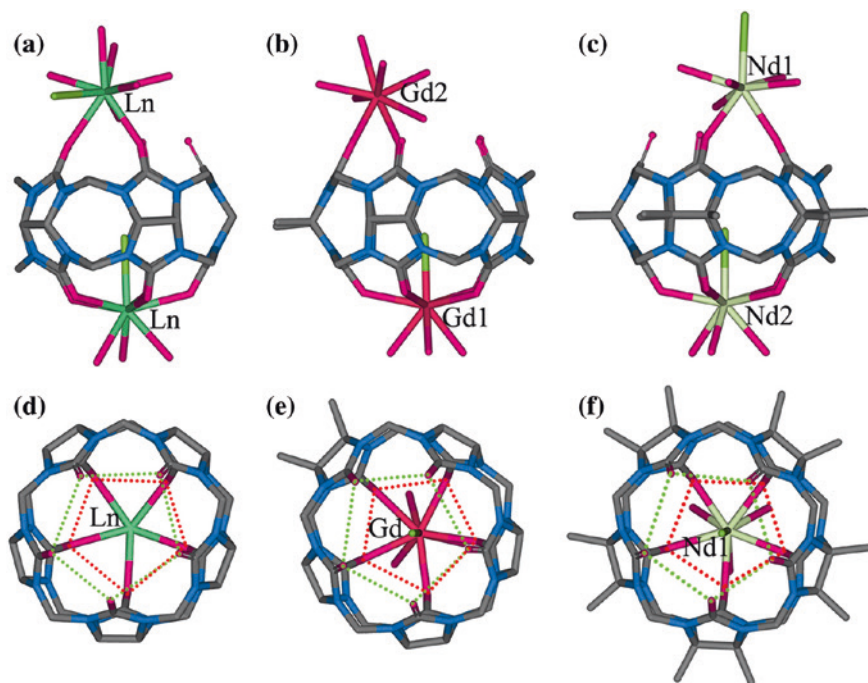


Fig. 2.8 X-ray crystal structures of the complexes of selected Ln^{3+} cations with $\text{Q}[5]$ and its $\text{Me}_2\text{Q}[5]$ and $\text{Me}_{10}\text{Q}[5]$ substituted derivatives: **a** Ln^{3+} - $\text{Q}[5]$ ($\text{Ln} = \text{La}, \text{Pr}$); **b** Gd^{3+} - $\text{Me}_2\text{Q}[5]$; **c** Nd^{3+} - $\text{Me}_{10}\text{Q}[5]$; **d–f** the portal sizes of the corresponding complexes

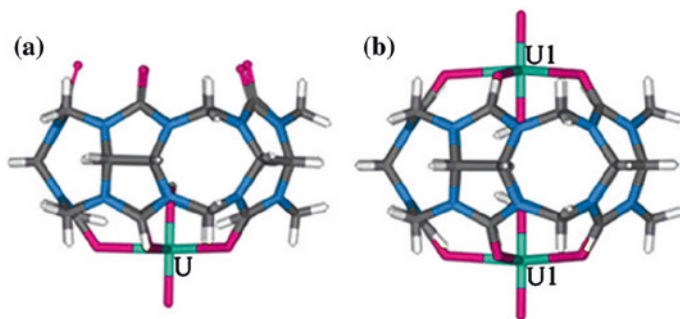


Fig. 2.9 X-ray crystal structures of Q[5] with uranyl ions: **a** molecular bowl; **b** molecular capsule

by mixing Q[5] with excess UO_3 in an aqueous HReO_4 solution. The other, with a stoichiometry of $\{(\text{UO}_2)_2\text{Q}[5]\}(\text{NO}_3)_4 \cdot 4\text{HNO}_3 \cdot 3\text{H}_2\text{O}$, was prepared by mixing Q[5] with excess of $(\text{UO}_2)_2\text{NO}_3$ in an aqueous HNO_3 solution. The Q[5]/ UO_2 complexes had characteristic features of the molecular bowl [27] and molecular capsule [28] respectively (Fig. 2.9).

On the other hand, addition of the second metal ion as a structure directing agent could also result in the formation of unusual complexes or novel Q[n]-based supramolecular assemblies. For example, when Thuéry investigated the inclusion properties of Q[n]/ Ln^{3+} complexes for the perrhenate anion, he introduced potassium cation (KNO_3) into the Q[n]- Ln^{3+} - ReO_4^- system. A series of $\text{Ln}^{3+}/\text{K}^+$ heterometallic capped Q[5]-based capsules were formed ($\text{Ln} = \text{Ce}, \text{Sm}, \text{Gd}$), but no suitable crystal could be obtained in the absence of the KNO_3 reactant in this series (Fig. 2.10a) [27]. In his previous work, U^{6+}/K^+ or Cs^+ heterometallic capped Q[5]-based capsules were obtained by introducing alkali metal ions in the form of their salts, such as KNO_3 or CsNO_3 , into a Q[5]- $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ system (Fig. 2.10b) [28]. Our group also discovered some heterometallic capped Q[5]-based capsules, for example, a $\text{Zn}^{2+}/\text{K}^+$ Q[5]-based capsule that could be

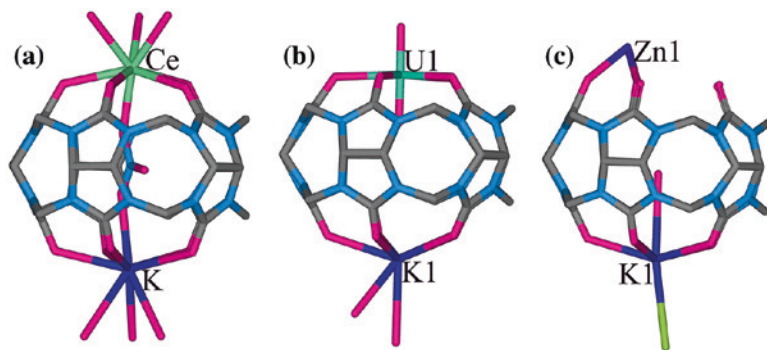


Fig. 2.10 X-ray crystal structures of heterometallic capped molecular capsules: **a** $\text{K}^+/\text{Ce}^{3+}$ complex and **b** K^+/U^{6+} complex; and molecular bowl **c** $\text{K}^+/\text{Zn}^{2+}$ complex

obtained by introducing KCl into a Q[5]–ZnCl₂ system (Fig. 2.10c) [14]. The Zn²⁺ cation coordinates to the two carbonyl oxygens of a Q[5] portal because of its shorter ionic radius.

When a second larger metal ion is introduced to the singularly capped mononuclear Ln³⁺–Q[5] system, such as K⁺, then in particular cases fully doubly capped heterometallic molecular capsules form. Thuéry [27] first reported a series of heterometallic K⁺/Ce³⁺, K⁺/Sm³⁺ (2 complexes) and K⁺/Gd³⁺ Q[5] capsules of this type which were obtained under hydrothermal conditions in the presence of perhenic acid. Five complexes were isolated with all but the fifth, a Yb³⁺ complex (see below), containing K⁺. Each capsule included a bound nitrate ion in its cavity (the cavity of Q[5] is too small to include an [ReO₄][−] anion, contrasting with Q[6] which is able to include this anion—see discussion in Sect. 2.2). In the first four complexes the lanthanide ion is nine-coordinate with a capped square antiprismatic geometry. The [ReO₄][−] anions are present as hydrogen bonded counter ions, although in the case of the Sm³⁺ complex this anion is also present as a monodentate ligand. The Ce³⁺/K⁺ complex forms linear columns along the *c*-crystallographic axis in which the cerium and potassium metal centers from adjacent capsules are bridged by two water molecules and a nitrate ion. The Sm³⁺/K⁺ and Gd³⁺/K⁺ complexes are effectively isomorphous and differ from the Ce³⁺/K⁺ complex in that zigzag columns are present (involving one carbonyl and one water bridge between hetero-metal centers), with the K⁺ and Ln³⁺ ions also bound to one and two terminal water ligands, respectively. A corresponding K⁺/Nd³⁺ capsule was subsequently reported by our group [29] and this product was also found to include a nitrate ion.

The general arrangement of the metal centers in the heterometallic Ln³⁺–K⁺–Q[5] (Ln = Ce, Nd, Sm, Gd) capsule motifs just discussed is represented schematically in Fig. 2.11a [27, 29], with, for comparison, that for a related Gd³⁺/K⁺ complex of dimethyl-substituted Q[5], Me₂Q[5], given in Fig. 2.11b [30]. Comparison of the two portals in each of these doubly capped species reveals that the portals capped by a K⁺ ion are larger than those capped by an Ln³⁺ ion. Reflecting this, there is a difference of ~0.3 Å in the average separation between adjacent carbonyl oxygens rimming the pair of portals in the respective capsules (Fig. 2.11d, e). Our group has demonstrated that reaction of PrCl₃ with Q[5] in the presence of CaCl₂ (Ca²⁺ has a comparable ionic radius to the lanthanides) leads to a heterometallic (Ca²⁺/Pr³⁺) *dinuclear* Ca²⁺-bridged complex with the structure shown in Fig. 2.11c [29]. In this complex two Pr³⁺ ions fully cap the respective outer portals of the dimer while two Ca²⁺ ions link and partially cap each of the “inner” portals. As might be anticipated, in this arrangement the difference in the respective (“outer” vs. “inner”) portal sizes (as expressed by the adjacent carbonyl oxygen internuclear distances—see Fig. 2.11f) show a similar trend to that for the homo-dinuclear Ln³⁺–Q[5] complexes (see Fig. 2.8a) containing both a fully capped and a partially capped portal [18, 26].

In summary, the smaller portal size of Q[5]s offers related concentrated bonding sites so that a metal ion can coordinate with more portal carbonyl oxygens and form a stable Q[5]/metal complex. Therefore, metal ions suitable for coordination to Q[5] molecules have a wider distribution.

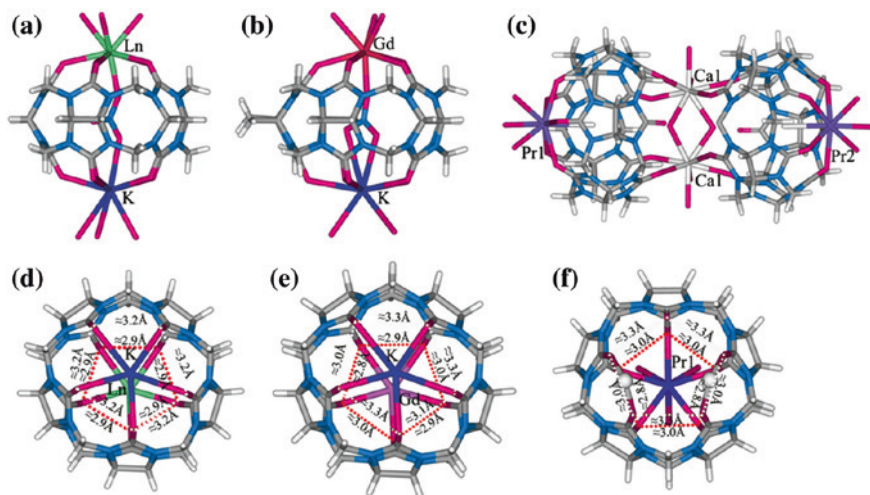


Fig. 2.11 X-ray crystal structures of heterometallic Ln^{3+} and K^+ Q[5] complexes: **a** $\text{Ln}^{3+}/\text{K}^+$ -Q[5] ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}, \text{Gd}$); **b** $\text{Gd}^{3+}/\text{K}^+$ -DMeQ[5]; **c** $(\text{Pr}^{2+})_2/(\text{Ca}^{2+})_2$ -2Q[5]; **d-f** comparison of the portal sizes in the complexes **a-c**, respectively

2.2 Simple Coordination Complexes of Cucurbit[6]urils with Metal Ions

Compared with Q[5]s, Q[6]s have a larger portal size. The portal (r) radius of Q[6] molecules is within 3.3–3.4 Å, similar to the longest $\text{M}_{\text{Cs}}-\text{O}_{\text{carbonyl}}$ bond lengths (3.0–3.3 Å) observed in $\text{CyH}_5\text{Q}[5]/\text{Cs}^+$ or $\text{Me}_{10}\text{Q}[5]/\text{Cs}^+$ complexes. Thus, it is believed that no other single metal ion can fully cover the portal of the Q[6] molecule except the Cs^+ cation, which has the second longest ionic radius. For example, we reported a simple complex of methyl-substituted Q[6], namely symmetrical $\alpha, \alpha', \delta, \delta'$ -tetramethylcucurbit[6]uril (TMeQ[6]) with a Cs^+ cation (Fig. 2.12) [31]. The Cs1 atom seems to cover a portal of the TMeQ[6] molecule, and coordinates to five portal carbonyl oxygens. The length of the bond between

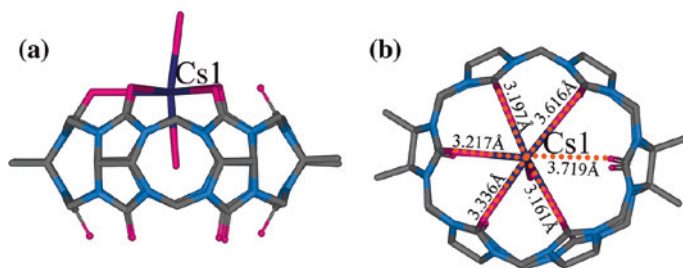


Fig. 2.12 X-ray crystal structures of the TMeQ[6]/ Cs^+ complex: **a** side view; **b** top view

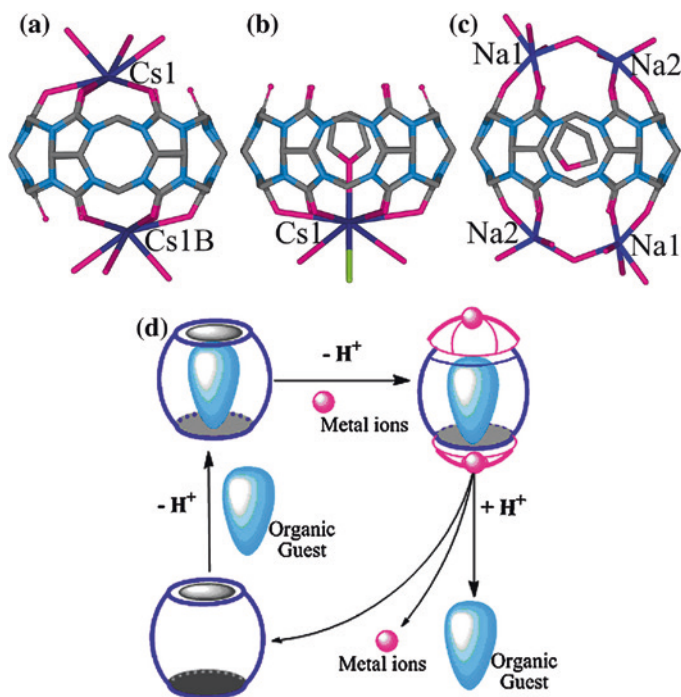


Fig. 2.13 X-ray crystal structures of Q[6] with the alkali metal ion: **a** molecular capsule with Cs^+ ; **b** molecular bowl with Cs^+ ; **c** molecular capsule with Na^+ ; and **d** the representation of molecular capsule and molecular bowl built by Q[n]s

Cs1 and the portal carbonyl oxygens is 3.305 Å on average, and can reach a maximum of 3.616 Å.

Kim and coworkers first reported a simple Q[6]/ Cs^+ complex in 1998 [32], in which the Cs^+ cation can effectively coordinate only four of six carbonyl oxygens of a portal of a Q[6] molecule. The lengths of the $\text{Cs}-\text{O}_{\text{carbonyl}}$ bonds are in the range 3.100–3.378 Å (Fig. 2.13a). However, with the aid of an organic guest (tetrahydrofuran, THF), the Cs^+ cation fully covers the portal of the Q[6] molecule, and forms a typical molecular bowl. The resulting $\text{Cs}-\text{O}_{\text{carbonyl}}$ bond lengths are in the range 3.144–3.584 Å. In particular, the bond length of $\text{Cs}-\text{O}_{\text{THF}}$ is only 2.934 Å, suggesting that the strong bonding between the Cs^+ cation and the included THF further draws the Cs^+ cation toward the portal of the Q[6] molecule, resulting in the formation of the fully covered Q[6]/THF/ Cs^+ molecular bowl (Fig. 2.13b). Such phenomenon exemplifies a typical instance involving Q[n]-based host–guest/coordination chemistry. An earlier case involving Q[n]-based host–guest/coordination chemistry is the Q[6]/THF/ Na^+ molecular capsule also reported by Kim and coworkers in 1996 [33]. In this complex, two Na^+ cations are capped at each of the two portals of the Q[6] molecule, and a THF molecule is included in the cavity of the Q[6] molecule; thus, a sealed molecular capsule is formed (Fig. 2.13c). The bonding and release of the included THF can

be controlled by pH-dependent complexation and decomplexation of metal ions at the portals of the Q[6] molecule (Fig. 2.13d). Their observations suggest that the sodium ion “lids” are removed in strongly acidic solution because of the protonation of the carbonyl groups at the cucurbituril portals; consequently, the encapsulated THF molecule can readily escape from the cavity (Fig. 2.13). Raising the pH of the solution restores the sodium ion “lids” of cucurbituril and, therefore, the capability for encapsulating THF. Interestingly, similar supramolecular interaction behaviors may be observed with other guest molecules such as benzene, cyclopentanone, and furan, as well as with other metal ions such as cesium. Knoche and Buschmann first introduced metal ions into a Q[6]–G_{organic molecule} system to determine the stability constants and the mechanism of formation of association and inclusion complexes of cucurbituril with the 4-methylbenzylammonium ion [34]. Although they only focused on the solution structure of the Q[6]–G_{organic molecule}–M_{alkali} systems, their seminal work on Q[*n*]-based host–guest/coordination chemistry is a significant contribution. We will further demonstrate more cases in the succeeding parts of this chapter.

Returning to the coordination features of Q[6]/metal complexes, we note that they are clearly different from those of Q[5] complexes because of their larger portal size. In typical Q[6]-based complexes, a metal ion with a smaller ionic radius can only coordinate to a limited number of portal carbonyl oxygens (one to three). This restriction results in the formation of Q[6]-based capsules or bowls in which a portal of the Q[6] molecule could be coordinated with multiple metal ions. The aforementioned Q[6]/THF/Na⁺ molecular capsule is a typical instance, in which two coordinated Na⁺ cations at each of the two portals of Q[6] coordinates to two portal carbonyl oxygens. Fedin and coworkers made the greatest contribution to Q[6]-based coordination chemistry; they studied almost all alkaline earth, transition, lanthanide, actinide metal ions, as well as their aqueous complexes, clusters, and so on. For example, they demonstrated that Q[6]/Sr²⁺ capsules may be obtained by slow concentration of an aqueous solution of Sr(NO₃)₂ and Q[6] (Fig. 2.14a) [35]. Each Q[6] molecule is bound to four strontium cations (two cations per portal), forming a molecular capsule that includes a nitrate anion. The coordination of the four Sr²⁺ ions in the Q[6] molecular capsule is different, in that they coordinate two or three portal carbonyl oxygens by sharing a nitrate anion (N31). This sharing results in the formation of infinite 1D supramolecular chains through electrostatic interaction. Furthermore, Fedin and coworkers recently discovered a Q[6]/Mg²⁺ complex that involves the interaction between Q[6] with the amino acid tryptophan and its decarboxylation product tryptamine in the solid state [36]. This complex is the first known supramolecular assembly of cucurbituril with magnesium ion, which has the smallest ionic radius (0.49 and 0.72 Å for hexacoordinated Mg²⁺) among metals studied for their coordination to unsubstituted cucurbituril ligands (Fig. 2.14b). Generally, Q[6] molecules show affinity to alkali and alkaline earth metal ions, and form molecular bowls or capsules [37–39]. However, their interaction with metal ions in the presence of a third species could result in the formation of novel coordination polymers and supramolecular assemblies, which will be described in detail later.

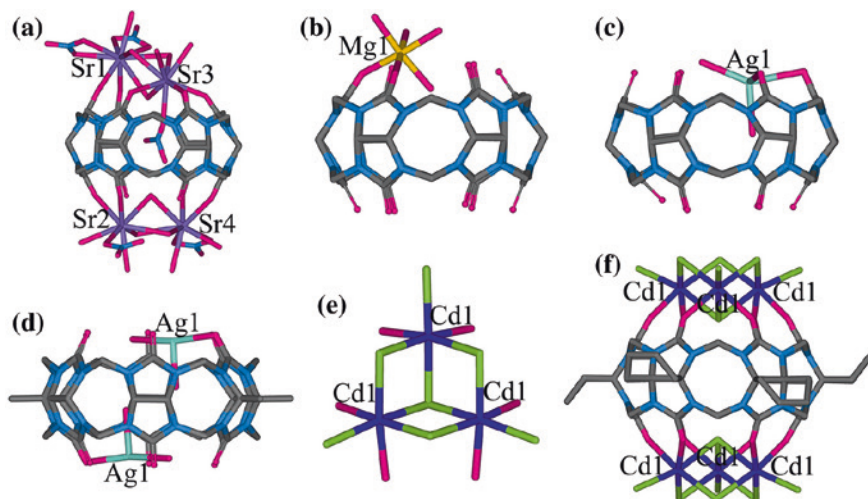


Fig. 2.14 X-ray crystal structures of **a** a Q[6]/ Sr^{2+} complex; **b** a Q[6]/ Mg^{2+} complex; **c** a Q[6]/ Ag^+ complex; **d** a TMeQ[6]/ Ag^+ complex; **e** a $[\text{Cd}_3\text{Cl}_3(\mu_2\text{-Cl})_3(\mu_3\text{-Cl})]^-$ cluster; and **f** a $\text{CyH}_6\text{Q}[6]/\text{Cd}^{2+}$ complex

In aqueous solution, the interaction of Q[6] with transition metal salts prefer to form adducts of Q[6] with metal aqua complexes through hydrogen bonding. There are a few exceptions to the usual products, such as Q[6]/ Ag^+ complexes from a solution containing a Q[6]/isonicotinic acid/ La^{3+} host–guest complex in the presence of AgNO_3 , as shown in Fig. 2.14c [39]. Another is the complex formed by tetramethyl-substituted Q[6] (TMeQ[6]) and AgNO_3 [40, 41]. In the resulting Q[6]/ Ag^+ complex, only one Ag^+ cation coordinates to two carbonyl oxygens of a Q[6] portal, whereas in the TMeQ[6]/ Ag^+ complex, both portals of TMeQ[6] are coordinated to an Ag^+ cation and form a molecular capsule feature (Fig. 2.14d). Another example is the complex of cyclohexanocucurbit[6]uril ($\text{CyH}_6\text{Q}[6]$) with Cd^{2+} cations [42]. Interestingly, two $[\text{Cd}_3\text{Cl}_3(\mu_2\text{-Cl})_3(\mu_3\text{-Cl})]^-$ cluster anions effectively cover each portal of $\text{CyH}_6\text{Q}[6]$, forming one sealed molecular capsule (Fig. 2.14e, f).

Professor Zhang in our laboratory investigated coordination assemblies by reactions between alkali metal salts and a *meta*-hexanomethyl-substituted cucurbit[6]uril (*m*-HMeQ[6]) in aqueous solutions. X-ray diffraction analysis revealed that each *m*-HMeQ[6] coordinates with three alkali metal ions, K^+ , Rb^+ , or Cs^+ and forms a 1:2, *m*-HMeQ[6]: $\text{M}_{\text{alkali}}^+$ complex (Fig. 2.15) [43].

In 2002 Fedin and coworkers reported the first lanthanide complex of Q[6] (a Sm^{3+} species) [44]. The product formed on slow evaporation of an aqueous solution of SmBr_3 and Q[6] and had an Sm^{3+} :Q[6] stoichiometry of 2:3. The X-ray structure shows a triple-decker sandwich arrangement (height: ~ 33 Å) of type $\{(\text{Q}[6])[\text{Sm}(\text{H}_2\text{O})_4](\text{Q}[6])[\text{Sm}(\text{H}_2\text{O})_4](\text{Q}[6])\}^{6+}$ (Fig. 2.16). Each Sm^{3+} is coordinated by four waters and two Q[6] units. Relative to Q[5], Q[6] has a larger

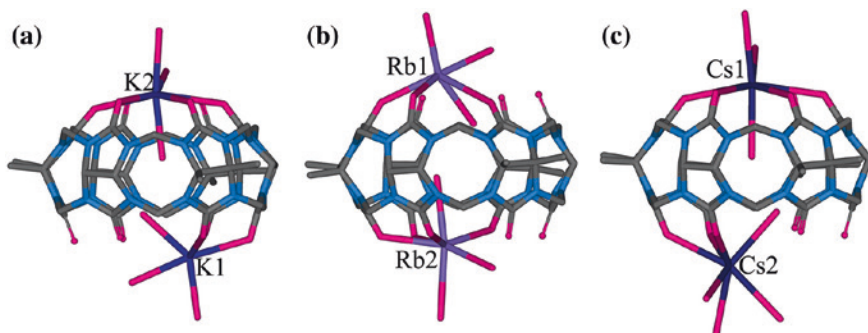


Fig. 2.15 X-ray crystal structures of molecular capsules of *m*-HMeQ[6] with metal ions: **a** K^+ ; **b** Rb^+ ; **c** Cs^+

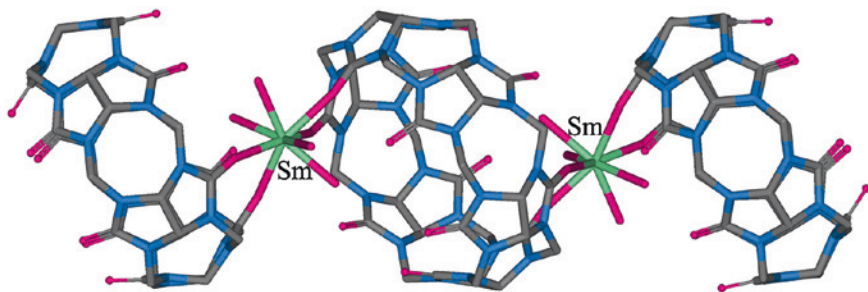


Fig. 2.16 X-ray crystal structure of the Sm^{3+} -Q[6] triple-decker sandwich

portal size with a portal radius of 3.3–3.4 Å. This radius is substantially longer than the bond length range observed for Ln^{3+} -O_{carbonyl} bonds: 2.223–2.478 Å. As a consequence a single lanthanide cation is unable to coordinate simultaneously to all six carbonyl oxygens lining a Q[6] portal; generally only one to three portal carbonyl oxygens have been found to bind. In the above complex, each Sm^{3+} cation ion coordinates to two portal carbonyl oxygens from each of two Q[6]s, with the average bond length being 2.401 Å; each metal center achieves 8-coordination.

In a further paper Fedin reported a systematic study of Q[6] coordination with La^{3+} , Ce^{3+} , Gd^{3+} , Ho^{3+} , and Yb^{3+} nitrates or bromides in aqueous solution [45]. While Q[6] is not soluble in water, it readily dissolves on heating with a saturated solution of the above Ln^{3+} salts. Seven complexes were isolated—the first five were obtained from the corresponding Ln^{3+} nitrate salt while the remaining two were from the corresponding bromide salt: (i) $[Gd(NO_3)(H_2O)_4(Q[6])](NO_3)_2 \cdot 7H_2O$, (ii) $[Ho(NO_3)(H_2O)_4(Q[6])](NO_3)_2 \cdot 7H_2O$, (iii) $[Yb(NO_3)(H_2O)_4(Q[6])](NO_3)_2 \cdot 6H_2O$, (iv) $[La(H_2O)_6(SO_4)(Q[6])](NO_3)_2 \cdot 12H_2O$, (v) $[Gd(NO_3)(C_2H_5OH)(H_2O)_2(H_2O@Q[6])](NO_3)_2 \cdot 5.5H_2O$. Two additional complexes $\{[Gd(H_2O)_4]_2(Q[6])_3\}Br_6 \cdot 45H_2O$ and $\{[Ce(H_2O)_5]_2(Q[6])_2\}Br_6 \cdot 26H_2O$, obtained employing the corresponding La^{3+} bromide salts, were also isolated (see later). With the exception of $[La(H_2O)_6(SO_4)(Q[6])](NO_3)_2 \cdot 12H_2O$ (iv), all of

these products were isolated either directly from water or following diffusion of ethanol into their aqueous solution. While the X-ray structure of (i) was not determined, the 1:1 ($\text{Ln}^{3+}:\text{Q}[6]$) complexes (ii) and (iii) were shown to be isostructural (Fig. 2.17a). In the case of (iv), the reaction solution contained lanthanum nitrate, Q[6], and copper sulfate. The X-ray structure of the latter product showed that the complex consists of an La^{3+} bound to a portal of Q[6] via two oxygens, with the nine-coordinate coordination sphere of the metal center being completed by six water molecules and a monodentate sulfate ligand (Fig. 2.17b). The X-ray structure of $[\text{Gd}(\text{NO}_3)(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})_2(\text{H}_2\text{O}@\text{Q}[6])](\text{NO}_3)_2 \cdot 5.5\text{H}_2\text{O}$ (v), which crystallized from the reaction solution following the slow diffusion of alcohol, showed that the Gd^{3+} is eight-coordinate with the coordination sphere consisting of a bidentate Q[6] unit, an ethanol molecule, a bidentate nitrate, and three aqua ligands (Fig. 2.17c) [45]. This product incorporates one water molecule in the Q[6] cavity (not shown in Fig. 2.17c). In a related study, it was shown that Gd^{3+} chloride reacts with Q[6] to yield $\{[\text{Gd}(\text{H}_2\text{O})_6]_2(\text{H}_2\text{O}@\text{Q}[6])\}\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ in which Q[6] acts as a bis-bidentate ligand such that a pair of carbonyl oxygens

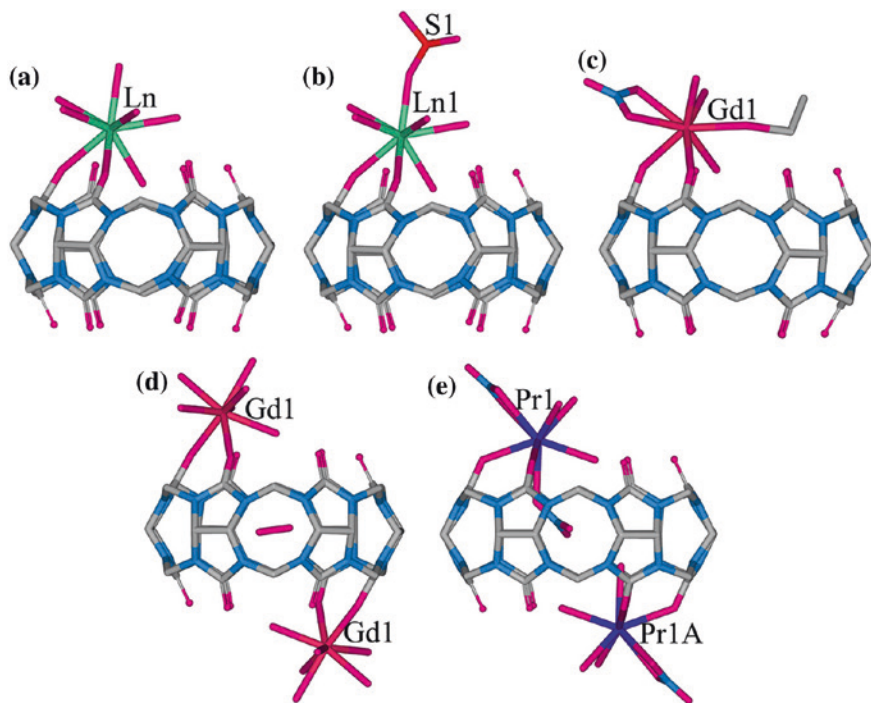


Fig. 2.17 X-ray crystal structures of selected Ln^{3+} -Q[6] complexes prepared from La^{3+} nitrate salts: **a** the isostructural complexes $[\text{Ho}(\text{NO}_3)(\text{H}_2\text{O})_4(\text{Q}[6])]^{2+}$ and $[\text{Yb}(\text{NO}_3)(\text{H}_2\text{O})_4(\text{Q}[6])]^{2+}$; **b** $[\text{La}(\text{H}_2\text{O})_6(\text{SO}_4)(\text{Q}[6])]^{2+}$ with bound sulfate group; **c** $[\text{Gd}(\text{NO}_3)(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})_2(\text{H}_2\text{O}@\text{Q}[6])]^{2+}$ with coordinated ethanol molecule, the included water molecule is not shown; **d** $\{[\text{Gd}(\text{H}_2\text{O})_6]_2[(\text{H}_2\text{O}@\text{Q}[6])]\}^{6+}$, included water molecule not shown; **e** $\{[\text{Pr}(\text{NO}_3)_2(\text{H}_2\text{O})_3]\{\text{Pr}(\text{NO}_3)(\text{H}_2\text{O})_3(\text{H}_2\text{O}@\text{Q}[6])\}\}^{3+}$, the included (bound) nitrate ion and water molecule not shown

at each portal coordinate to a Gd^{3+} cation along with six water molecules [46]. A guest water molecule resides in the cavity of the Q6 and is disordered between two positions (Fig. 2.17d). Under hydrothermal conditions (at 120 °C) $\text{Pr}(\text{NO}_3)_3$ reacts with Q[6] in water to yield $[\{\text{Pr}(\text{NO}_3)_2(\text{H}_2\text{O})_3\}\{\text{Pr}(\text{NO}_3)(\text{H}_2\text{O})_3(\text{H}_2\text{O}@Q[6])\}](\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ [47]. An X-ray diffraction study (Fig. 2.17e) demonstrated that the two metal centers in this complex are each linked to the Q[6] through tridentate coordination of three portal oxygens from the respective portals. Each metal center is also bound to a bidentate nitrate ligand and three water molecules located exo to the central cavity. The cavity encapsulates both a nitrate ion and a water ligand (both disordered over two positions) which are each bound in a monodentate fashion to the respective metal centers, each of which achieves a coordination number of nine.

Use of a lanthanide bromide salt rather than a nitrate salt has been shown to result in changes in both the composition and the structure of the corresponding Ln^{3+} -Q[6] complexes—once again emphasizing the difficulties in predicting the nature of the product from a given synthetic procedure [45]. Thus, complex crystallization from an aqueous solution containing cerium bromide and Q[6] results in a 2:2 Ce^{3+} -Q[6] sandwich complex incorporating two cucurbituril ligands linked by two bound $[\text{Ce}(\text{H}_2\text{O})_5]^{3+}$ units (Fig. 2.18a). Each nine-coordinated Ce^{3+} has four carbonyl oxygens and five aqua ligands in its coordination sphere. The 2:2 structure contrasts with the 1:1 arrangements found in the $(\text{Ln}^{3+};\text{Q}[6])$ complexes (a)–(e) discussed above (see Fig. 2.17)—all of which employed the corresponding lanthanide nitrate salt as a precursor [45]. The trigonal crystal packing of the above sandwich complex is shown in Fig. 2.18b. Triangular channels with a van der Waals diameter of ~ 4.3 Å are filled with disordered water molecules and bromide anions (omitted in Fig. 2.18b for clarity). In contrast, the corresponding GdBr_3 -Q[6] system results in a triple-decker sandwich (Fig. 2.18c). The latter is related to that described above for the Sm^{3+} -Q[6] triple-decker sandwich [44] shown in Fig. 2.16.

As discussed already for Q[5]-based complex systems [24], there are also examples of Q[6] systems prepared in the presence of added small organic molecules that appear to play a structure directing role. Thus, Fedin and coworkers showed that the interaction of aqueous Gd^{3+} nitrate with Q[6] in the presence of pyridine yielded a hydrogen-bonded (supramolecular) adduct between the aqua nitrate complex $[\text{Gd}(\text{NO}_3)(\text{H}_2\text{O})_7]^{2+}$ and Q[6] (Fig. 2.19a) [48]. In the above assembly the water molecules coordinated to the Gd^{3+} center are hydrogen bonded to carbonyl groups of Q[6], with the cavity of the Q[6] molecule encapsulating a pyridine molecule. These workers also reported a further La^{3+} -Q[6] capsule-like complex of type $[\text{La}(\text{H}_2\text{O})_6(\text{X}@Q[6])(\text{NO}_3)]^{2+}$ ($\text{X} = 0.5 \text{ C}_5\text{H}_5\text{N} + 0.5 \text{ H}_2\text{O}$) [49] in which a pyridine molecule occupies the internal cavity of one half of the Q[6] molecules (Fig. 2.19b), while a water molecule occupies the other half. The La^{3+} center is bound to two adjacent carbonyl oxygens, a bidentate nitrate ligand and six aqua ligands to yield a coordination number of ten. The metal center is disordered between the two portal faces (with both occupancy positions shown in Fig. 2.19b). In a related study Liu and coworkers [50] crystallized a 1:1

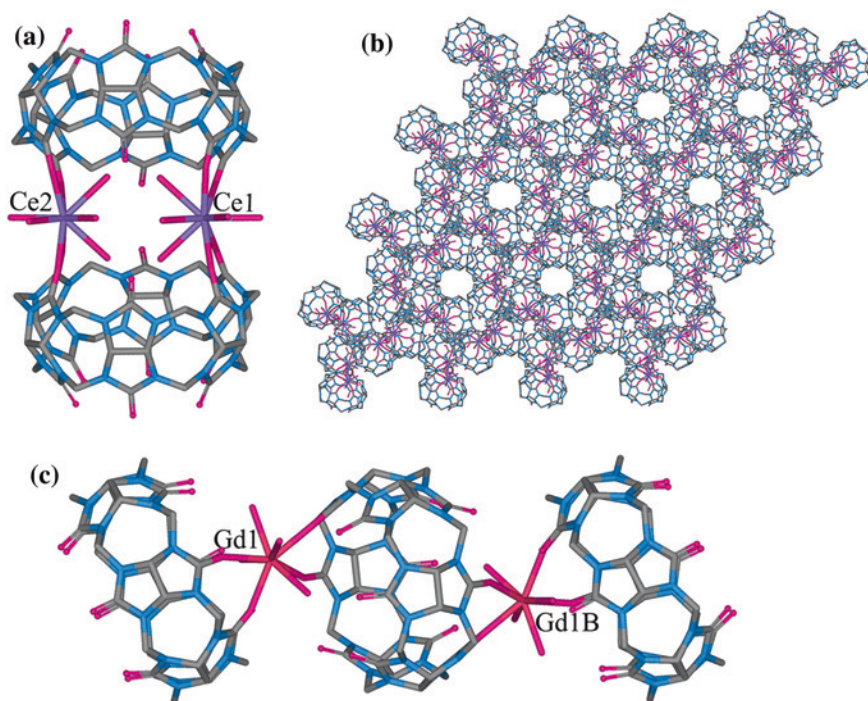


Fig. 2.18 X-ray crystal structures of **a** the Ce^{3+} -Q[6] sandwich complex; **b** the 3D Ce^{3+} -Q[6] packing in **a** showing the presence of nanochannels; **c** the Gd^{3+} -Q[6] triple-decker sandwich complex

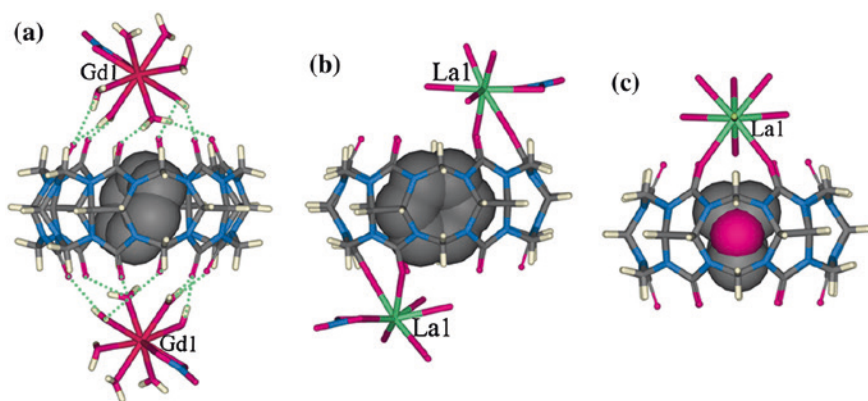


Fig. 2.19 X-ray crystal structures of Ln^{3+} -Q[6] assemblies: **a** hydrogen-bonded host-guest assembly of two $[\text{Gd}(\text{H}_2\text{O})_7\text{NO}_3]^{2+}$ cations with Q[6] which encapsulates a pyridine molecule in its cavity; **b** a La^{3+} -Q[6] complex incorporating an encapsulated pyridine molecule (pyridine encapsulation occurs for half the complexes while the other half encapsulate a water molecule); the La^{3+} site is disordered between each portal (both positions shown); **c** La^{3+} -Q[6] complex incorporating an encapsulated tetrahydrofuran molecule

(La³⁺:Q[6]) cationic inclusion complex of type {[La(H₂O)₆Cl](THF@Q[6])}²⁺ (THF = tetrahydrofuran) through slow diffusion of THF vapor into a solution containing Q[6] and lanthanum nitrate in 3 M HCl (Fig. 2.19c). The La³⁺ coordination sphere in this case consists of two carbonyl oxygens, six water molecules and a chloride ion.

Fedin and coworkers have synthesized a series of polynuclear lanthanide complexes by reacting Q[6] with aqueous solutions of lanthanide(III) nitrates [51], chlorides [52] or bromides [39], Q[6], and 4-cyanopyridine under hydrothermal conditions (130 °C). These μ -hydroxo polynuclear lanthanide complexes are formed in aqueous solution and their formation involves hydrolysis of the corresponding Ln³⁺ salts with, under the conditions employed, the 4-cyanopyridine also being hydrolyzed to isonicotinic acid. Thus, for example, using lanthanide nitrates, a series of tetranuclear aqua-hydroxo-carboxylate complexes of type {[Ln₄(μ_3 -OH)₄(μ_2 -OH)₂(C₅NH₄COO)₂(H₂O)₄(Q[6])₂][Ln(H₂O)₈]_{1.5}[Ln(H₂O)₆(NO₃)₂]_{0.5}}(NO₃)₉ · nH₂O (Ln = Ho, Gd, or Er) was obtained and characterized by X-ray diffraction analysis, elemental analysis, infrared spectrophotometry, and electrospray ionization (ESI) mass spectrometry [51]. The sandwich structure involves coordination of a central tetrahedral lanthanum cluster to two Q[6] via four oxygens (two per Ln³⁺ cent) at each portal (Fig. 2.20a). The presence of bridging bidentate carboxylate groups in the tetranuclear cluster was postulated to stabilize the observed structure by inhibiting formation of infinite polymeric species.

The above products are generally similar to a range of complexes formed from chloride [52] and bromide [39] lanthanide salts (Fig. 2.20b) in that sandwich complexes are generated; although, in particular complexes, some structural differences do occur—reflecting variation in the synthetic conditions and/or due to the intrinsic differences in the properties of the lanthanide cations themselves. Some variations on the basic structure are illustrated in Fig. 2.20c–f. All these complexes incorporate a tetranuclear lanthanide cluster (Ln1–Ln4) core positioned between two neighboring Q[6] molecules. Ln1 and Ln2 each coordinate to two portal carbonyl oxygens of a Q[6] molecule while Ln3 and Ln4 coordinate to two portal carbonyl oxygens of the second Q[6] molecule in the sandwich complex, with the carboxylate groups (O1, O2 and O3, O4) from two isonicotinates coordinating to Ln1, Ln2 and Ln3, Ln4, respectively. The aromatic ring of each bridging bidentate isonicotinate is included in a Q[6] cavity. The four Ln³⁺ cations are linked by four μ_3 -OH groups and from one to four μ_2 -OH groups (depending on the particular lanthanide involved). Thus, for example, there are four μ_3 -OH groups and one μ_2 -OH group in the structure shown in Fig. 2.20c. In particular complexes, one or two additional isonicotinate ligands also bind to particular Ln³⁺ sites (Fig. 2.20c–f) while in other cases the carbonyls from the second (“outside”) portal of each Q[6] also bind to further Ln³⁺ cations (Fig. 2.20d, e). Selected compounds from the above series have been employed as precursors for the synthesis of lanthanide-silver heterometallic coordination polymers [39]. In these heteronuclear compounds the affinity of the isonicotinate pyridyl nitrogen for Ag⁺ has been exploited to produce chain polymers in which La³⁺, Pr³⁺ and Dy³⁺ sandwich complexes are

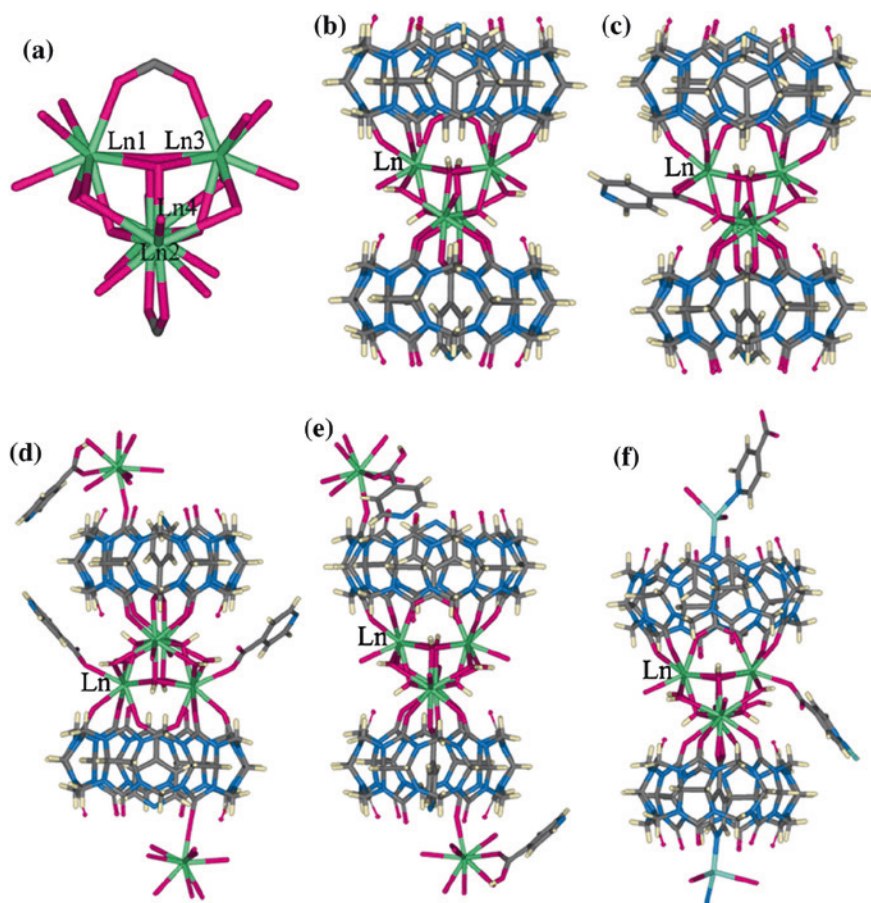


Fig. 2.20 X-ray crystal structures of tetranuclear lanthanide aqua hydroxo-Q[6] sandwich complexes: **a** representative tetranuclear lanthanide aqua hydroxo core; typical sandwich complexes in which **b** Ln = Gd [55], Ho [55], Er [55, 56], Yb [56]; **c** Ln = Dy [57], Ho [57], Er [57]; **d** Ln = La [57]; **e** Ln = Pr [56, 57], Nd [56]; and **f** Ln = La [57], Pr [57], Dy [57]; the tetrahedral Ag^+ centers are shown above and below the *top* and *bottom* portals of the Q[6] sandwich structure

linked via coordination of their nitrogen atoms to Ag^+ ions to yield repeating units of the type shown in Fig. 2.20f.

Although Fedin et al. originally focused on the preparation of polynuclear lanthanide complexes, the approaches that they adopted greatly aided the developments in Q[n]-based host–guest coordination chemistry.

Since 2008, Thuéry have synthesized numerous Q[6]-based complexes with lanthanides and actinides in various media, such as neutral aqueous solution, nitric acid, sulfuric acid, formic acid, and perrenic acid. These reactions have been carried out in the presence of various species, which could behave as structural inducers: examples include sebacic acid, L-(+)-tartaric acid, citric acid, and

second metal salts. For example, Thuéry characterized a series of Q[6]/Ln³⁺-based molecular capsules (Ln = Ce³⁺, Pr³⁺) and molecular bowls (Ln = Yb³⁺, Lu³⁺) including a perrhenate anion in perrhenic acid (Fig. 2.21a, b). Only the coordination of Sm³⁺ cations with Q[6] form a molecular pair in which two Sm³⁺ cations link two neighboring Q[6] molecules (Fig. 2.21c) [53]. In the presence of the α -amino acid L-cysteine (L-cys), the reaction of Nd(NO₃)₃, Eu(NO₃)₃, or Tb(NO₃)₃ salts with Q[6] gives simple complexes that belong to Q[n]-based host–guest/coordination chemistry, as shown in Scheme 1.1. In all three cases, each metal cation is bound to the bidentate Q[6] and the monodentate L-cys molecules, with the latter in the zwitterionic form, and the ammonium group of L-cys is directed away from Q[6] (Fig. 2.21d) [27]. In the presence of *p*-sulfobenzoic acid (4-SB), combination of Q[6] with Nd(NO₃)₃ seems to give a molecular pair in which two Q[6]-based capsules are close to each other (the two Nd³⁺ cations between the two capsules have 50 % occupancy). However, the Nd³⁺ cation at the other portal of Q[6] coordinates to both the Q[6] molecule and 4-SB (Fig. 2.21e) [53]. It is interesting to compare the former two Q[6]/Ln³⁺/guest complexes

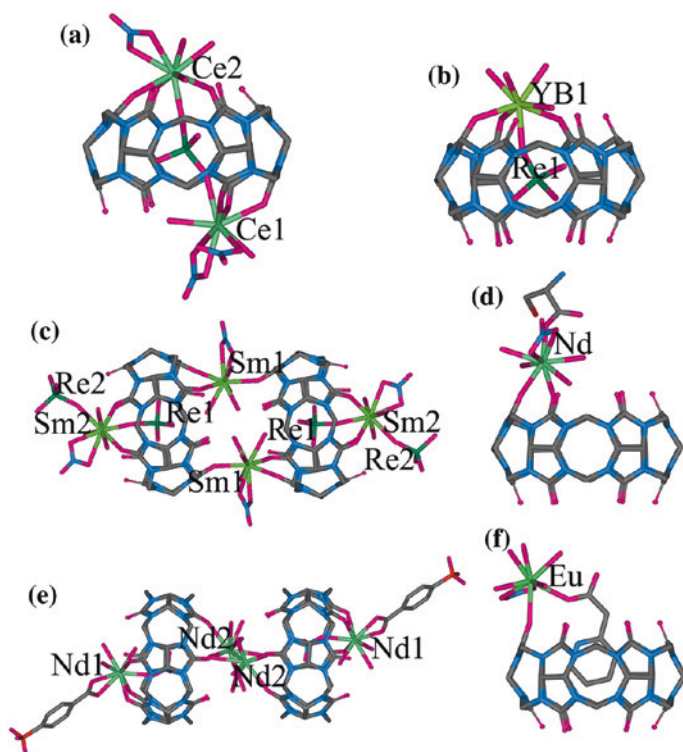


Fig. 2.21 X-ray crystal structures of simple complexes of Q[6]/Ln³⁺ cations and the corresponding supramolecular assemblies: **a** a molecular capsule of Q[6]/Ln³⁺ (Ln = Ce, Pr); **b** a molecular bowl of Q[6]/Ln³⁺ (Ln = Yb, Lu), **c** a molecular pair of Q[6]/Sm³⁺; **d** a Q[6]/Ln³⁺/L-cys complex (Ln = Nd, Eu, Tb); **e** a Q[6]/Nd³⁺/4-SB complex pair; and **f** a Q[6]/Eu³⁺/HPA complex

with that obtained from the anion derived from 2-pyridylacetic acid (HPA). The crystal structure of the $\text{Q}[6]/\text{Eu}^{3+}/\text{AP}^-$ complex shows that the $\text{Q}[6]$ molecule coordinates with a Eu^{3+} cation, and includes the aromatic moiety of the organic guest. Moreover, the anion moiety (COO^-) of the guest further coordinates to the capped Eu^{3+} cation, resulting in the formation of the typical organic-guest-induced $\text{Q}[6]/\text{metal}$ complex (Fig. 2.21f) [54].

Using a hydrothermal method, Thuéry obtained some simple $\text{Q}[6]/\text{UO}_2^{2+}$ complexes by combination of $\text{Q}[6]$ and UO_3 or $\text{UO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the presence of perrhenic acid and formic acid, respectively [55]. The crystal structure of the complex with perrhenic acid shows a dinuclear species in which one uranyl ion is bound to each $\text{Q}[6]$ portal through bidentate coordination, to one perrhenate ion located *trans* with respect to the macrocycle, and to half a perrhenate ion, which occupies the same coordination site as an aqua ligand. Both are given occupancy parameters of 0.5 (Fig. 2.22a) [55]. The crystal structure of the complex with sebacic acid shows uranyl coordination by $\text{Q}[6]$. Each U1 atom is bound to two carbonyl atoms from two $\text{Q}[6]$ molecules, which are adjacent in its equatorial plane. The average length of such bond is $2.38(4) \text{ \AA}$, in agreement with the average value of $2.36(4) \text{ \AA}$ for urea derivatives reported in the Cambridge Structural Database (CSD) (Fig. 2.22b) [56]. Heterometallic $\text{Q}[n]$ -based complexes commonly feature coordination of two different metal ions at both portals of the $\text{Q}[n]$ molecule. Thuéry demonstrated an unusual case in which a series of novel heterometallic uranyl–lanthanide molecular complexes ($\text{Q}[6]/\text{UO}_2^{2+}/\text{Ln}^{3+}$, $\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Lu}$) are obtained from the reaction of uranyl and lanthanide nitrates with $\text{Q}[6]$ in the presence of perrhenic acid under hydrothermal conditions. Both metal cations of UO_2^{2+} and Ln^{3+} are bound to carbonyl groups of the same $\text{Q}[6]$ portal (Fig. 2.22c) [57].

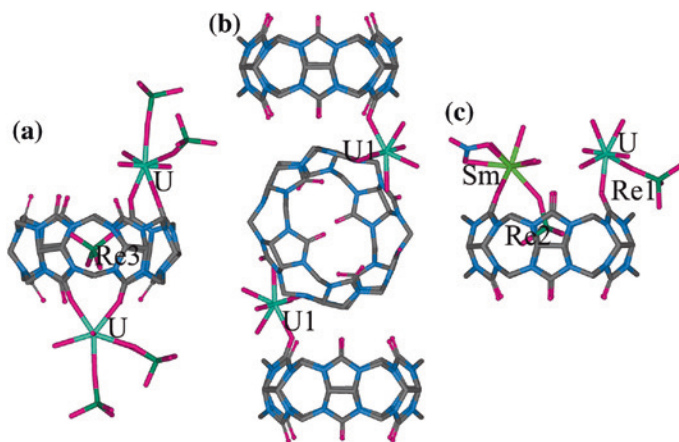
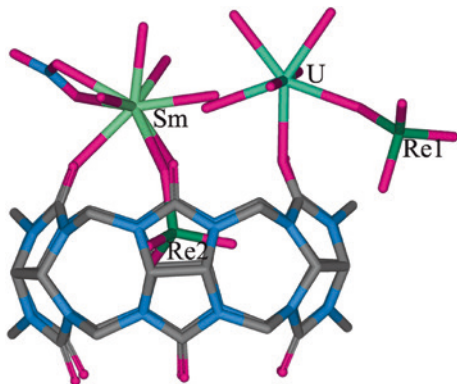


Fig. 2.22 X-ray crystal structures of two $\text{Q}[6]/\text{UO}_2^{2+}$ complexes formed in the presence of **a** perrhenic acid; **b** formic acid; and **c** the heterometallic $\text{Q}[6]/\text{UO}_2^{2+}/\text{Ln}^{3+}$ complexes ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Lu}$)

Fig. 2.23 X-ray structure of the isomorphous heterometallic complexes of type $[\text{UO}_2\text{Ln}(\text{Q}[6])(\text{ReO}_4)_2(\text{NO}_3)(\text{H}_2\text{O})_7]$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Lu}$), shown for $\text{Ln} = \text{Sm}$



Initial attempts by Thuéry to prepare heteronuclear uranyl-lanthanide Q[6] complexes were unsuccessful [27]. However, four such species of type $[\text{UO}_2\text{Ln}(\text{Q}[6])(\text{ReO}_4)_2(\text{NO}_3)(\text{H}_2\text{O})_7](\text{ReO}_4)_2$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Lu}$) were subsequently isolated following reaction of a mixture of uranyl nitrate and lanthanide nitrate with Q[6] in the presence of $[\text{ReO}_4]^-$ under hydrothermal conditions [57]. In an unusual arrangement both the UO_2^{2+} and Ln^{3+} cations bind to carbonyl groups on the *same* Q[6] portal (Fig. 2.23). The UO_2^{2+} also binds to a monodentate $[\text{ReO}_4]^-$ group as well as to three waters while the Ln^{3+} binds to a monodentate $[\text{ReO}_4]^-$ and a nitrate ligand together with four waters, with the latter $[\text{ReO}_4]^-$ included in the Q[6] cavity. This was the first reported example of the inclusion of a tetrahedral oxoanion in Q[6].

In a subsequent study it was shown that UO_2^{2+} combined with Nd^{3+} , Dy^{3+} , Er^{3+} , or Yb^{3+} nitrate in each case reacts with Q[6] and 1,2-ethanedisulfonate (EDS^{2-}) under hydrothermal conditions to yield heterometallic complexes of type $[(\text{UO}_2)_4\text{Nd}_2(\text{EDS})_4(\text{OH})_4(\text{Q}[6])(\text{H}_2\text{O})_{16}](\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$, and $[(\text{UO}_2)_2\text{Ln}_{1.5}(\text{EDS})_2(\text{OH})_2(\text{NO}_3)_{1.5}(\text{Q}[6])(\text{H}_2\text{O})_{7.5}][(\text{UO}_2)_2(\text{EDS})-(\text{OH})_2(\text{H}_2\text{O})_4]\text{NO}_3 \cdot 5.5\text{H}_2\text{O}$ (where $\text{Ln} = \text{Dy}, \text{Er}$ and Yb) [58]. In each complex the Ln^{3+} ion is bound to a Q[6] and partially caps a portal. Each EDS^{2-} co-ligand binds to a UO_2^{2+} and an Ln^{3+} ion via its two sulfonate groups in a bis-monodentate manner, with the UO_2^{2+} ion also being part of a bis(hydroxide)-bridged dinuclear unit that forms part of a link between adjacent Q[6] units such that each complex adopts a ribbon-like 1D assembly.

In summary, unlike in the coordination of Q[5] with the metal ions, a wider bonding site distribution is available because of the larger portal size of Q[6]s. With such distribution, the metal ion can generally coordinate to one to three portal carbonyl oxygens, and more than one metal ion may be located at the same portal of a Q[6] molecule.

2.3 Simple Coordination Complexes of Cucurbit[n, n ≥ 7]urils with Metal Ions

A comparison of complexes of Q[n, n ≥ 7]s and Q[5 or 6]s shows that the coordination of Q[n, n ≥ 7]s with metal ions is more difficult than that of Q[5 or 6] with metal ions. Few of the simple complexes involving with Q[n, n ≥ 7]s have been reported in Q[n]-based coordination chemistry. The larger portal size of Q[n, n ≥ 7]s result in an even wider distribution of the carbonyl oxygens, which may be a reason for the difficulty in the coordination of Q[n, n ≥ 7] with metal ions. The first crystal structures of Q[7]/metal-based coordination complexes were obtained by Thuéry. He investigated the influence of perrhenate ions on the structure of lanthanide complexes with Q[n]s to further probe the properties of Q[n]s in perrhenate encapsulation [27]. The compound has a very large assembly uniting two different Q[7]/Yb³⁺ complexes: The first comprises two Q[7] molecules bridged by one Yb³⁺ cation, with two partially included (but not coordinated) [Yb(ReO₄)(NO₃)(H₂O)₅]⁺ cations (Fig. 2.24a). The second is built from one bidentate Q[7], one coordinated cation that is disordered over two positions related by a mirror plane, and one coordinated and included ReO₄[−] anion (Fig. 2.24b). However, in the presence of CsNO₃ or aqueous formic acid, combination of Q[7] with UO₂(NO₃)₂ or UO₃ can yield simple Q[7]/UO₂²⁺ complexes, as shown in Fig. 2.24c, d, respectively [59]. In both Q[7]/UO₂²⁺ complexes, the UO₂²⁺ cation coordinates one portal carbonyl oxygen, and a pair of OH[−] anions link two UO₂²⁺ cations.

Even though more Q[8]/metal-based simple complexes have been reported, only two typical Q[8]/metal-based coordination complexes have been synthesized

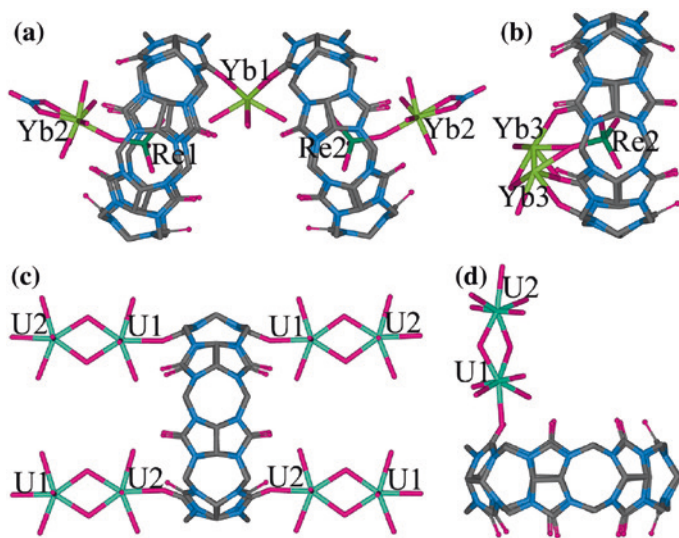


Fig. 2.24 X-ray crystal structures of **a** and **b** two different Q[7]/Yb³⁺ complexes and two different Q[7]/UO₂²⁺ complexes in the presence of **c** CsNO₃ and **d** formic acid

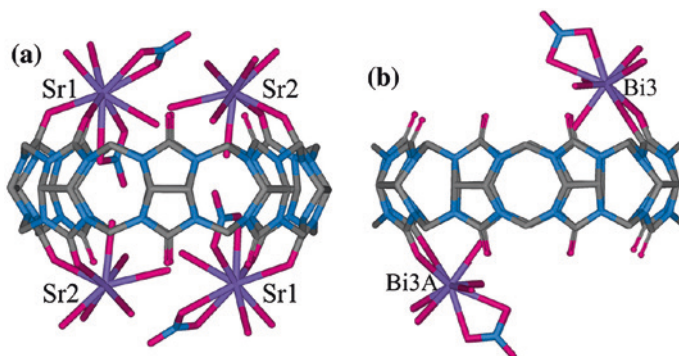


Fig. 2.25 X-ray crystal structures of two different Q[8]/Metal complexes **a** Q[8]/Sr²⁺ complex and **b** Q[8]/Bi³⁺ complex

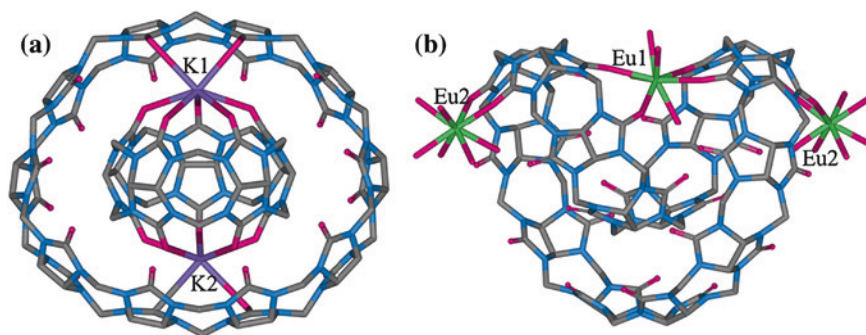


Fig. 2.26 X-ray crystal structures of **a** the Q[5]@Q[10]/K⁺ complex and **b** tQ[14]/Eu³⁺

and characterized by X-ray diffraction in the early development of cucurbituril chemistry. One was obtained by slow concentration of aqueous solutions containing strontium nitrate and Q[8]. The crystal structure of this Q[8]/Sr²⁺ complex shows that each Q[8] molecule is bound to four strontium cations (two cations per each portal), and the strontium atoms linked to the portal of the larger macrocycle are remote from each other and are not linked to each other through the bridging ligands (Fig. 2.25a) [60]. The other Q[8]/metal-based coordination complex was obtained by reacting Bi(NO₃)₃ with Q[8] in 3M HNO₃. This complex has a Q[8] molecule coordinated by two [Bi(NO₃)(H₂O)₅]²⁺ fragments (Fig. 2.25b) [61].

Cucurbit[10]uril (Q[10]), which was discovered by Day in 2002, used to be the largest member in the Q[n] family. However, it is rare to see a simple complex of Q[10] or its derivatives [4, 62, 63] with metal ions not only because Q[10] itself is rare, but also because of the wider carbonyl oxygen distribution. A host-guest/Mⁿ⁺ complex, Q[5]@Q[10]/K⁺ was synthesized by Liu and coworkers (Fig. 2.26a) [64]. A Q[5] molecule is included in the cavity of Q[10], and two K⁺ cations, each of which does not fully cover portal of Q[5] molecule, coordinates

two portal carbonyl oxygens of the Q[10] molecule. As mentioned previously, we recently reported the new largest member of the Q[n] family, namely tQ[14]. In fact, determination of the structural characteristics of tQ[14] was also first based on the determination of the complex of tQ[14] molecules with the aid of Eu^{3+} cations (Fig. 2.26b) [5]. This was accomplished because the tQ[14]/ Eu^{3+} structures belong to coordination polymers, which will be presented in detail later.

Based on the above results, we summarized the main simple Q[n]-based complexes, in which Q[n]s play the role of poly-dentate ligands and interact with metals through direct coordination to the portal carbonyl oxygens. These simple complexes could be applied to selective inclusion of anions, absorption of molecules, drug delivery, and so forth.

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Metal Ions

Coordination, Structures and Properties

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