

Mono- and polynuclear aqua complexes and cucurbit[6]uril: Versatile building blocks for supramolecular chemistry*

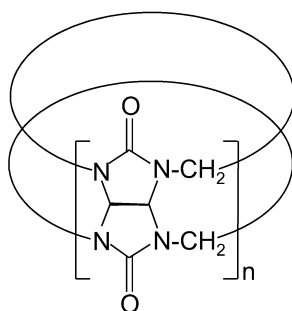
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Abstract: The review surveys new data on the directed construction of supramolecular organic–inorganic compounds from macrocyclic cavitand cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$) and mono- and polynuclear aqua complexes. Due to the presence of polarized carbonyl groups, cucurbit[6]uril forms strong complexes with alkali, alkaline earth and rare-earth metal ions, and hydrogen-bonded supramolecular adducts with cluster and polynuclear aqua complexes of transitional metals. A wide variety of supramolecular compounds and their unique structures are described.

CUCURBIT[M]URILS

Cucurbit[n]urils are organic macrocyclic cavitands synthesized by condensation of formaldehyde with glycoluril [1–6]. The cucurbit[n]uril molecules resemble in shape a barrel containing two identical carbonyl fringed portals (Chart 1). Having a large inner cavity, cucurbit[n]urils can serve as hosts to form inclusion compounds with guest molecules of suitable size [3,4,7–9]. Due to the presence of polarized carbonyl groups, cucurbit[n]urils can also form complexes and hydrogen-bonded supramolecular adducts with mono- and polynuclear aqua complexes.



cucurbit[n]uril

Chart 1

Cucurbituril with composition $C_{36}H_{36}N_{24}O_{12}$ (cucurbit[6]uril, Q6) consisting of six methylene-linked glycoluril fragments has been studied the most. This compound is the first example of cucurbiturils, and almost a century has passed since its first synthesis by Behrend [1]. The chemical nature and structure of cucurbit[6]uril had been unknown until 1981, when full characterization was reported by Freeman [2]. The dimensions of the inner cavity of Q6 (the height is 6 Å and the inner diameter is 5.5

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Å) allow the molecule to accommodate small guest organic molecules or ions, and inclusion of organic molecules and their reactivity inside the cavity have been studied. Cucurbit[6]uril, whose cavity is similar in size to those of α -cyclodextrin and 18-crown-6, has higher negative charges on the donor oxygen atoms of portals, resulting in the enhancement of stability of its adducts with positively charged ions [3,10]. Its easy synthesis, rigid structure, and chemical and thermal stability (it does not decompose upon heating to 400 °C [11]) make cucurbituril very attractive for complexation of cations in aqueous solution and for preparation of various supramolecular compounds.

The results of studies devoted to synthesis, examination of structure and properties of supramolecular compounds of cucurbit[*n*]urils, and investigations of thermodynamic and kinetic aspects of formation of these systems are summarized in reviews [3,4,12–16]. This article is a documentation of the recent advances in the chemistry of supramolecular compounds of cucurbit[6]uril with metal/cluster aqua complexes, mainly based on the work performed in our laboratory. Considerable attention is given to the studies aimed at the directed construction of supramolecular organic–inorganic hybrid materials, which have been performed in the last five years.

SUPRAMOLECULAR COMPOUNDS OF CUCURBITURIL WITH METAL AQUA COMPLEXES

The ability of cucurbit[6]uril to bind metal ions in aqueous solutions was discovered by Behrend and coworkers already in 1905 [1], and the first example of the structurally characterized cucurbituril compound was complex of Q6 with Ca^{2+} cation $\{[\text{Ca}(\text{HSO}_4)_2]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\} \cdot 13\text{H}_2\text{O}$ [2]. By the late 1990s, Freeman and Mock, Kim and coworkers explored and structurally characterized a number of adducts of cucurbituril and s-metals (Na^+ , K^+ , Rb^+ , Cs^+ , Ca^{2+}) with their quite unique structures [17–21]. Due to the strong interactions of carbonyl oxygen donor atoms with the cations, stable complexes are formed, and metal atom and their coordinated water molecules cover each portal of cucurbituril like a “lid” on a “barrel”. Thus, the cavity inside the cucurbituril molecule is isolated to form a supramolecular container in which small molecules like THF or ethylenediamine can be enclosed [18,21]. Small ligands, coordinated to the metal, can also be included into the cavity of Q6, like CH_3OH molecule in the calcium complex $\{[\text{Ca}(\text{H}_2\text{O})_3(\text{HSO}_4)(\text{CH}_3\text{OH})]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}(\text{HSO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Fig. 1) [22].

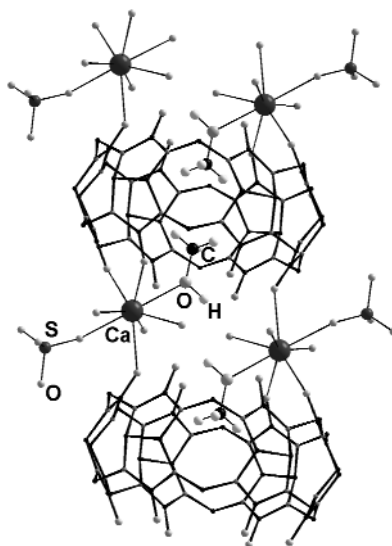


Fig. 1 Fragment of the chain in $\{[\text{Ca}(\text{H}_2\text{O})_3(\text{HSO}_4)(\text{CH}_3\text{OH})]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}(\text{HSO}_4)_2 \cdot 4\text{H}_2\text{O}$. The cavity of Q6 encapsulates the methyl groups of two coordinated to the calcium ions CH_3OH molecules.

The presence of more polar oxygen atoms in Q6 as compared to those in crown ethers or cryptands is responsible for the formation of stronger interactions between these oxygen atoms and metal cations. The formation constants of metal complexes with Q6 are much higher than the formation constants of complexes with the above-mentioned organic macrocycles [10]. Besides, the rigidity of Q6 hinders its conformational changes upon complex formation, in contrast, for example, to metal complexes with crown ethers. The metal cations are coordinated by the oxygen atoms located in the planes of the portals of Q6 rather than are included into the cavity of the cavitand.

In the structures of compounds of cucurbit[6]uril with K^+ [19], Rb^+ [20], and Ca^{2+} [17,22] each metal atom is coordinated by oxygen atoms at the portals of two Q6 molecules (one or two oxygen atoms from each molecule). This leads to the formation of hybrid organic–inorganic polymers consisting of alternating $[M(H_2O)_x]^{n+}$ units and cucurbit[6]uril. In the crystals, the polymer molecules form molecular cylinders linked to each other through hydrogen bonds, and the channels are occupied by the water molecules of crystallization and anions (Fig. 2). The supramolecular chains in the structure with rubidium form honeycomb-like packing containing large channels (the diameter of the channels filled with water molecules is ~ 10 Å, and the volume of these channels comprises 23 % of the total volume of the structure). Such compounds are promising for the design of porous materials, which find use in separation processes, supramolecular catalysis, and optoelectronics.

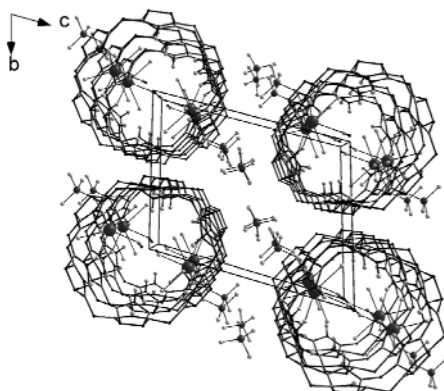


Fig. 2 Molecular cylinders in $\{[Ca(H_2O)_3(HSO_4)(CH_3OH)]_2(C_{36}H_{36}N_{24}O_{12})\}(HSO_4)_2 \cdot 4H_2O$ (view along the *a* axis).

Our recent studies show that cucurbit[*n*]urils are excellent ligands for oxophilic metal cations with much structural diversity to be expected. The reactions of Ln^{3+} with Q6 in aqueous solutions afforded supramolecular compounds in which (according to the X-ray diffraction data) the Ln^{3+} is bound to the macrocycle through both the direct coordination of the metal atom by portal oxygen atoms and hydrogen bonding between the coordinated water molecules and oxygen atoms of cucurbit[6]uril [23–25]. In the resulting compounds, the aqua complex:cucurbit[6]uril ratio is 1:1, 2:2, or 2:3. In 1:1 complexes, the metal atom together with its ligand environment forms the lid that closes the Q6 molecule from one side ($Ln = La, Gd, Ho, Yb$). The compounds with ratio 2:2 and 2:3 have the most interesting structure—they are the nanosized double- and triple-decker sandwich complexes. In the $\{[Ce(H_2O)_5]_2(C_{36}H_{36}N_{24}O_{12})_2\}Br_6 \cdot 26H_2O$ complex, two cerium aqua ions are coordinated by two Q6 molecules to form sandwich-type compound (Fig. 3). The crystal structure of $\{[Sm(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})_3\}Br_6 \cdot 44H_2O$ (Fig. 4) and $\{[Gd(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})_3\}Br_6 \cdot 45H_2O$ can be described as packing of nanosized triple-decker sandwiches built from alternating Q6 molecules and aqua complexes. The shape of this supramolecule can be approximated by an oblique cylinder whose largest van der Waals size is 33 Å.

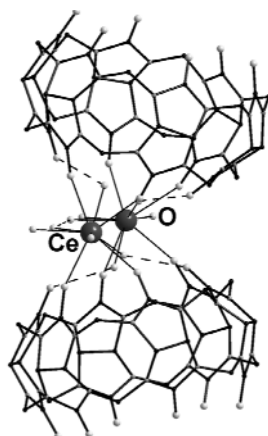


Fig. 3 The double-decker sandwich complex: fragment of $\{[\text{Ce}(\text{H}_2\text{O})_5]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})_2\}\text{Br}_6 \cdot 26\text{H}_2\text{O}$.

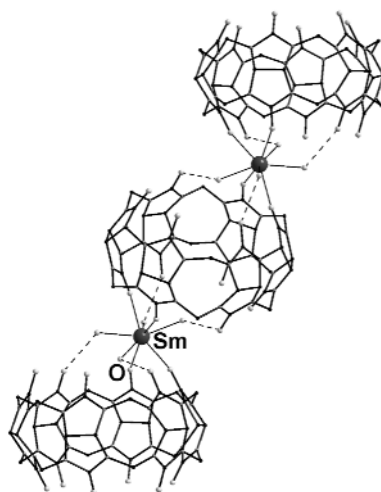


Fig. 4 The triple-decker sandwich complex: fragment of $\{[\text{Sm}(\text{H}_2\text{O})_4]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})_3\}\text{Br}_6 \cdot 44\text{H}_2\text{O}$.

Unlike the complexes of cucurbit[6]uril with *s*- and *f*-metal ions in which there are direct interactions between the metal atoms and oxygen atoms at the portals of Q6, coordination of transition and post-transition metals by the macrocycle occurs through hydrogen bonding between the portal oxygen atoms and coordinated water molecules of the aqua complexes. In this type of compound, cucurbit[6]uril acts as an outer-sphere ligand.

In the supramolecular compounds with $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, $\{[\text{Cr}(\text{H}_2\text{O})_6](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}(\text{NO}_3)_3 \cdot 13(\text{H}_2\text{O})$ and $\{[\text{Ni}(\text{H}_2\text{O})_6]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}(\text{SO}_4)_2 \cdot 16\text{H}_2\text{O}$, the cucurbituril molecule is closed from both sides by the aqua complexes due to the formation of hydrogen-bonding system between the cucurbituril C=O groups and aqua ligands [26]. In the adducts of cucurbit[6]uril with $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{In}(\text{H}_2\text{O})_6]^{3+}$, the metal complexes are located between the Q6 molecules and are linked to each other through a complex network of hydrogen bonds involving the portal oxygen atoms and water molecules [27]. In $\{[\text{InCl}_2(\text{H}_2\text{O})_4]_3(\text{Cl} \cdot \text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, the macrocyclic molecules form a hexagonal one-layer packing (Fig. 5), the crystallographic positions occupied by the macrocycles in this structure having the highest symmetry D_{6h} possible for cucurbit[6]uril. The cavity of Q6 contains the Cl^- anion disordered over 12 positions. Crystallization

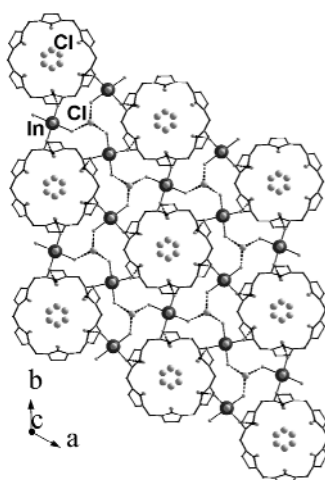


Fig. 5 The hexagonal one-layer packing in $\{[\text{InCl}_2(\text{H}_2\text{O})_4]_3(\text{Cl}-\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$.

with cucurbit[6]uril allowed characterization of *trans*- $[\text{In}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ and *trans*- $[\text{In}(\text{H}_2\text{O})_2\text{Cl}_4]^-$ for the first time.

Recently, the suitability of cucurbituril for isolation of polynuclear complexes from aqueous solutions has been shown for polynuclear aqua complexes of strontium [28], molybdenum [29], uranium [30], zirconium, and hafnium [31]. In the structure of tetranuclear strontium aqua nitrate complex with cucurbit[6]uril $\{[\text{Sr}_4(\text{H}_2\text{O})_{12}(\text{NO}_3)_4](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$, each Q6 molecule is bound to four strontium cations (two cations per each portal) (Fig. 6). Four Sr^{2+} form two pairs, which are linked to each other through the bridging nitrate anion. In these pairs, the Sr atoms are linked through three bridging aqua ligands. The nitrate anion coordinated to the strontium atom is located in the plane of the cucurbit[6]uril molecule. The tetranuclear metal aqua complexes in $\{[(\text{UO}_2)_4\text{O}_2\text{Cl}_4(\text{H}_2\text{O})_6](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\} \cdot 5\text{H}_2\text{O}$ and $\{[\text{M}_4(\text{OH})_8(\text{H}_2\text{O})_{16}](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_8 \cdot 16\text{H}_2\text{O}$ [$\text{M} = \text{Zr}, \text{Hf}$ (Fig. 7)] are linked with cucurbit[6]uril through hydrogen bonding between the coordinated water molecules and carbonyl oxygen atoms of the Q6 portal.

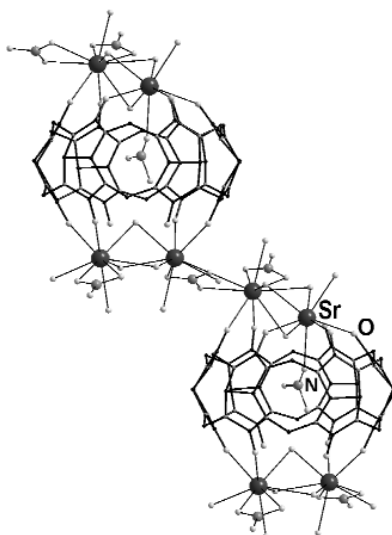


Fig. 6 Fragment of the chain in $\{[\text{Sr}_4(\text{H}_2\text{O})_{12}(\text{NO}_3)_4](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$.

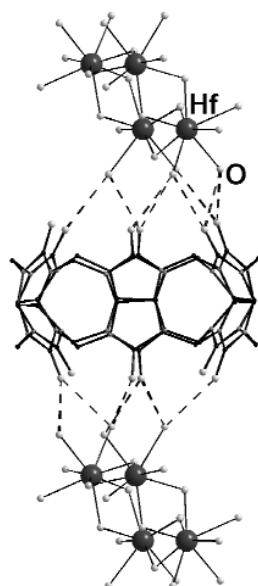


Fig. 7 Fragment of the chain in $\{[\text{Hf}_4(\text{OH})_8(\text{H}_2\text{O})_{16}](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_8 \cdot 16\text{H}_2\text{O}$.

By comparing the modes of binding of cucurbit[6]uril to different metals, several conclusions can be drawn. In the case of alkali, alkaline earth and rare-earth metals (groups 1–3), metal ions are coordinated directly with carbonyl oxygen atoms of cucurbituril portals. These are the most electropositive metals, forming hard and large ions (e.g., ionic radius of Na^+ 0.97, Cs^+ 1.73, Ca^{2+} 1.03, La^{3+} 1.14 Å [32]), whose bonding to ligands can be accounted for in terms of electrostatic (ion–dipole) interactions. Only in these conditions can cucurbituril, being a weak donor, but possessing polar C=O groups, compete with water for the first coordination sphere. Transition metals (and of group 13) form smaller ions (In^{3+} 0.76, Al^{3+} 0.50, Ni^{2+} 0.67, Cr^{3+} 0.58 Å [32]), which prefer covalent bonding. Higher charge and smaller size of the metal cation enhance the acidity of coordinated water in the aqua-ions, so that, e.g., $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{In}(\text{H}_2\text{O})_6]^{3+}$ are by 4–5 order of magnitude more acidic than any $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$, ($n = 8, 9$) [33]. This acidity allows to form strong hydrogen bonds between the polar C=O groups of cucurbituril and the coordinated water molecules, thus increasing energy gain of keeping cucurbituril in the second coordination sphere instead of substituting it for coordinated water.

SUPRAMOLECULAR COMPOUNDS OF CUCURBITURIL WITH CLUSTER AQUA COMPLEXES

Studies of interactions of cucurbit[6]uril with cluster aqua complexes of molybdenum and tungsten and their heterometallic derivatives not only made it possible for the first time to isolate a series of new cluster aqua complexes from solutions and structurally characterize them, but also led to discovery of a new class of supramolecular compounds. In aqueous solution, trinuclear thio- and seleno-complexes of molybdenum and tungsten produce oxydatively and hydrolytically stable aqua ions $[\text{M}_3(\mu_3\text{-Y})(\mu_2\text{-Y})_3(\text{H}_2\text{O})_9]^{4+}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{Y} = \text{S}, \text{Se}$) of C_{3v} symmetry (Fig. 8a) [34–37]. The coordinatively unsaturated μ_2 -bridging chalcogen atoms are readily coordinated to transition and post-transition metal atoms resulting in heterometallic mono- and bis-cuboidal derivatives $[\text{M}_3\text{M}'\text{Y}_4(\text{H}_2\text{O})_9]^{n+}$ and $[\text{M}_6\text{M}'\text{Y}_8(\text{H}_2\text{O})_{18}]^{8+}$ (Figs. 8b,c) [38]. Six coordinated H_2O molecules located in *cis* positions with respect to the μ_3 -bridging chalcogen atom of these clusters are virtually in a single plane and are well suited in size and symmetry to six carbonyl groups at each portal of Q6. Triangular and cuboidal aqua complexes have rather high positive charges, exhibit pronounced acidic properties, and can serve as

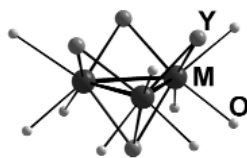


Fig. 8a Cluster aqua complex $[M_3Y_4(H_2O)_9]^{4+}$.

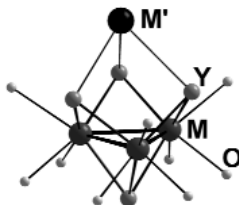


Fig. 8b Cluster aqua complex $[M_3M'Y_4(H_2O)_9]^{n+}$.

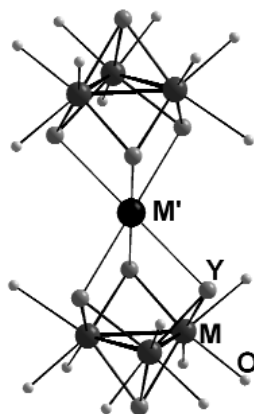


Fig. 8c Cluster aqua complex $[M_6M'Y_8(H_2O)_{18}]^{8+}$.

good hydrogen bond donors. In contrast, the O atoms of the polarized carbonyl groups of cucurbituril are potential hydrogen bond acceptors. The geometric and functional complementarity gives rise to extensive hydrogen bond networks involving cucurbituril molecules and triangular/cuboidal aqua complexes resulting in the formation of very stable hybrid organic–inorganic supramolecular compounds. In spite of the fact that the energy of each individual hydrogen bond is low, extensive complementary hydrogen bond networks (in the examples under consideration, up to 12 hydrogen bonds can be formed between the Q6 molecule and aqua complexes) provide the formation of very stable supramolecular compounds. The compounds are insoluble in aqueous solutions of hydrochloric acid in which the starting reagents are readily soluble.

The cluster:cucurbituril ratio in the resulting supramolecules can be either 1:1 or 2:1; in the latter case, the cavity in the cucurbit[6]uril molecule is effectively closed by cluster “lids” and small molecules or ions can be trapped inside. The sizes of supramolecules closed by two lids are 25–30 Å.

Over the past five years, we synthesized a wide variety of supramolecular adducts whose structures depend on the nature of the cluster, the presence of guest molecules in solution, the reagent ratio (cluster:cucurbituril), and the concentration of hydrochloric acid in the aqueous solutions in which the reactions proceed.

The reaction of Q6 with the tungsten sulfide aqua complex $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ in 2 M HCl afforded three products with different compositions and structures depending on the presence or absence of pyridine in the system. Without pyridine, $\{[\text{W}_3\text{S}_4(\text{H}_2\text{O})_7\text{Cl}_2](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ is formed in which only one portal of Q6 is closed by the cluster through a network of complementary hydrogen bonds involving six carbonyl groups of the portal and six aqua ligands [39]. In the crystal, supramolecular cations are linked in zigzag chains (Fig. 9). The same reaction in the presence of pyridine led to destruction of the chain structure to form a layered compound with layers composed of 2:1 supramolecules (both portals are closed by the cluster complexes $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_8\text{Cl}]^{3+}$ as lids), and the pyridinium cation is included into the cucurbituril molecule [40].

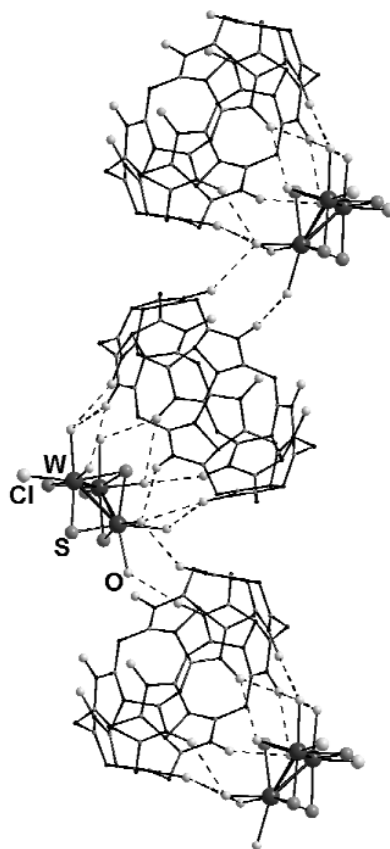


Fig. 9 Fragment of the chain in $\{[\text{W}_3\text{S}_4(\text{H}_2\text{O})_7\text{Cl}_2](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_2 \cdot 10\text{H}_2\text{O}$.

The third compound in the $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}/\text{Q6}$ system, $(\text{H}_9\text{O}_4)\{[\text{W}_3\text{S}_4(\text{H}_2\text{O})_6\text{Cl}_3]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_3 \cdot 16.15\text{H}_2\text{O}$, is formed in a 6–8 M hydrochloric acid solution [41]. The increase in acidity leads to the incorporation of hydroxonium ions into the crystal structure, and the clusters of the adjacent supramolecules (type 2:1) are linked in chains through hydrogen bonds between the $[\text{H}_9\text{O}_4]^+$ cations and the chloride ligands (Fig. 10). The supramolecular chains form a honeycomb-like structure containing channels with the van der Waals diameter of 5.2 Å.

The inclusion of a guest does not necessarily lead to changes in the structure of supramolecules. In the case of the W_3Se_4 complexes $\{[\text{W}_3\text{Se}_4(\text{H}_2\text{O})_8\text{Cl}]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ [42] and $\{[\text{W}_3\text{Se}_4(\text{H}_2\text{O})_6\text{Cl}_3]_2(\text{PyH}^+\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_3 \cdot 18\text{H}_2\text{O}$ [43], both compounds (with PyH^+ encapsulated in the cavity of cucurbituril and without it) have similar chain structures. The supramolecules of

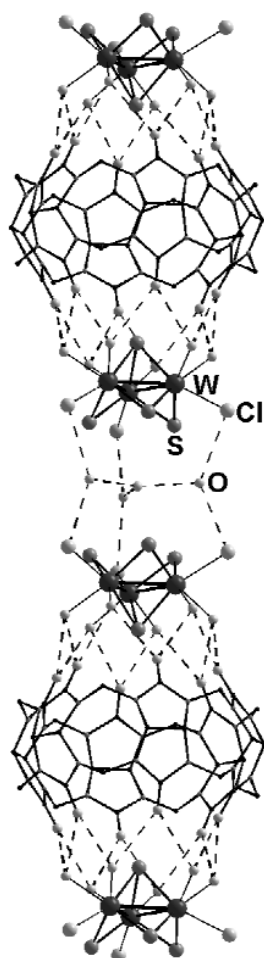


Fig. 10 Fragment of the chain in $(\text{H}_9\text{O}_4)\{[\text{W}_3\text{S}_4(\text{H}_2\text{O})_6\text{Cl}_3]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_3 \cdot 16.15\text{H}_2\text{O}$: bonding of the supramolecules through the $[\text{H}_9\text{O}_4]^+$ cation.

2:1 type are linked to each other through short (compared to the sum of the van der Waals radii of 3.9 Å) nonbonded Se...Se interactions between three μ_2 -Se ligands of W_3Se_4 clusters of the adjacent supramolecules. Such interactions are typical for trinuclear chalcogenide clusters of transition metals [44], and the stronger Se...Se interaction may be the reason of retaining chain structure in the case of selenide compounds.

The chalcogen–chalcogen interactions between the adjacent clusters are analogous to the interactions between the adjacent layers formed by the chalcogen atoms in dichalcogenides of the early transition metals (MY_2) belonging to an important class of inorganic materials [42]. An important property of these compounds is that they can include small molecules or atoms between the layers to form intercalates. A comparison of the structures of $\{[\text{Mo}_3\text{Se}_4(\text{H}_2\text{O})_8\text{Cl}]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_6 \cdot 16\text{H}_2\text{O}$ [45] and $\{[\text{Mo}_6\text{HgSe}_8(\text{H}_2\text{O})_{14}\text{Cl}_4](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_4 \cdot 14\text{H}_2\text{O}$ [42,46], where the Hg atoms are located between the chalcogenide clusters M_3Y_4 , shows that these compounds are related as a matrix and an intercalate from the structural viewpoint (Fig. 11). Therefore, supramolecular chemistry of small chalcogenide clusters unexpectedly intersects with the chemistry of solid-state layered compounds. In both cases, nonbonded Y...Y interactions play an important role in the structural organization.

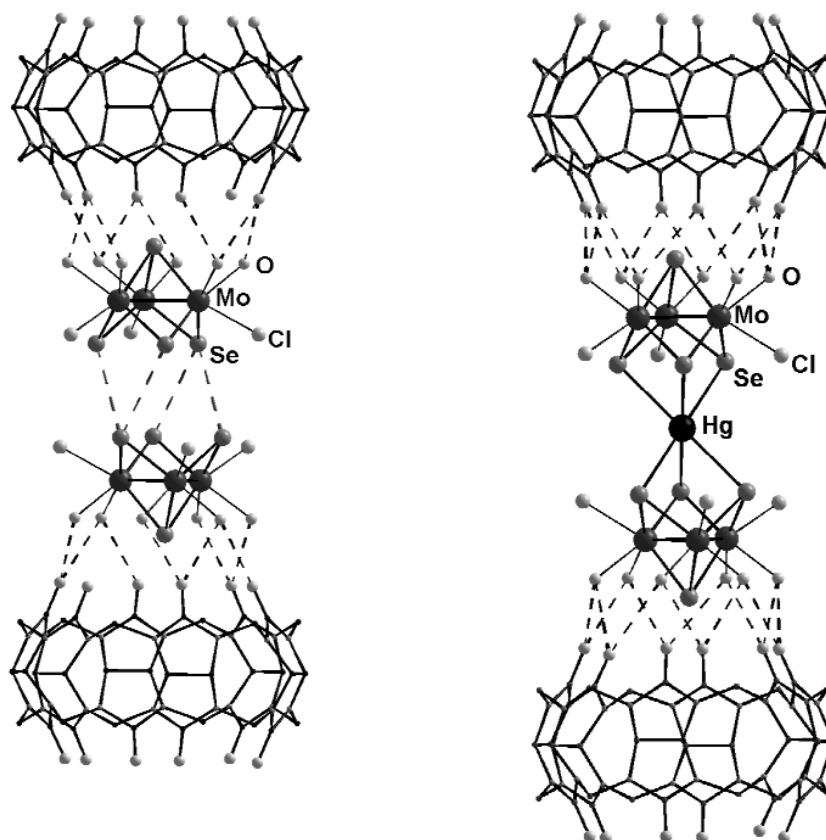


Fig. 11 Comparison of the chain structures in $\{[\text{Mo}_3\text{Se}_4(\text{H}_2\text{O})_8\text{Cl}_2](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_6 \cdot 16\text{H}_2\text{O}$ (matrix) and $\{[\text{Mo}_6\text{HgSe}_8(\text{H}_2\text{O})_{14}\text{Cl}_4](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_4 \cdot 14\text{H}_2\text{O}$ (intercalate).

The concentration of hydrochloric acid in the reaction medium is another important factor to influence the formation of supramolecular compounds. When the concentration of HCl is under 3 M, the number of Cl ligands coordinated to the M_3Y_4 core does not exceed 3. An increase in the concentration of HCl leads to the replacement of the water molecules in $[\text{M}_3\text{Y}_4(\text{H}_2\text{O})_{9-x}\text{Cl}_x]^{(4-x)+}$ presented in solution, by the halide ligands, and resulting in a sharp weakening of the cluster-cucurbit[6]uril interaction. First, the cluster complex loses a positive charge, i.e., its acidity and ability to act as a donor in hydrogen bonding are decreased. Second, coordination of more than three Cl^- ligands to the cluster core requires the replacement of the *cis*-aqua ligands responsible for binding of the cluster complex to the portals of Q6, and the complementarity between Q6 and the cluster is gradually lost. At this stage, another structure building principles based on chalcogen–chalcogen interactions, packing factors, etc. take over.

The structure of $(\text{H}_3\text{O})_2\{[\text{Mo}_3\text{Se}_4(\text{H}_2\text{O})_4\text{Cl}_5](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\} \cdot 15\text{H}_2\text{O}$ [45] prepared from 6 M HCl is a good example for this situation. The Mo atoms are coordinated by four Cl^- ligands in *cis*-positions with respect to the μ_3 -Se atom. As a result, the cucurbituril molecules and the chloro aqua complexes are not involved in the complementary hydrogen bonding. The structure of the compound consists of alternating layers of two types. One layer is composed of the cucurbituril molecules, whereas another layer is built from dimeric cluster aggregates $[\text{Mo}_3\text{Se}_4\text{Cl}_5(\text{H}_2\text{O})_4]_2^{2-}$ held by short, nonbonded Se...Se interactions. It can be compared with the chain structure of $\{[\text{Mo}_3\text{Se}_4(\text{H}_2\text{O})_8\text{Cl}_2](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_6 \cdot 16\text{H}_2\text{O}$ [45] (Fig. 11) prepared from 2 M HCl.

In supramolecular adducts of cucurbit[6]uril with mono- and bis-cuboidal heterometallic molybdenum and tungsten aqua complexes $[\text{M}_3\text{M}'\text{Y}_4(\text{H}_2\text{O})_9]^{n+}$ and $[\text{M}_6\text{M}'\text{Y}_8(\text{H}_2\text{O})_{18}]^{8+}$ (Figs. 8b,c), the

μ_2 -bridging chalcogen atoms are coordinated to the transition or post-transition metal atoms, and non-bonded Y...Y interactions cannot occur. In the crystals, supramolecules are linked through additional hydrogen bonds either in chains ($\{[\text{Mo}_3(\text{NiCl})\text{S}_4(\text{H}_2\text{O})_8\text{Cl}](\text{PyHcC}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_3 \cdot 14.5\text{H}_2\text{O}$ [47], $\{[\text{Mo}_3(\text{PdCl})\text{Se}_4(\text{H}_2\text{O})_7\text{Cl}_2](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl} \cdot 7\text{H}_2\text{O}$ [48]) or in layers ($\{[\text{Mo}_3(\text{PdCl})\text{S}_4(\text{H}_2\text{O})_6\text{Cl}_3](\text{PyHcC}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl} \cdot 14\text{H}_2\text{O}$ [49]).

In supramolecular compounds $\{[\text{Mo}_3(\text{PdE}(\text{OH})_3)\text{S}_4(\text{H}_2\text{O})_6\text{Cl}_3]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_2 \cdot n\text{H}_2\text{O}$ ($\text{E} = \text{P}, n = 20$; $\text{E} = \text{As}, n = 19$) [50] and $\{[\text{Mo}_3(\text{Pd}(\text{PhSO}_2))\text{S}_4(\text{H}_2\text{O})_8\text{Cl}][\text{Mo}_3(\text{Pd}(\text{PhSO}_2))\text{S}_4(\text{H}_2\text{O})_7\text{Cl}_2](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_3 \cdot 11\text{H}_2\text{O}$ [51], the Q6 molecules are closed by the two cluster lids and the palladium atoms of these clusters are coordinated by the inorganic $\text{P}(\text{OH})_3$ or $\text{As}(\text{OH})_3$ ligands (Fig. 12) or by PhSO_2 ligand. The size of the such supramolecules is more than 30 Å. The compounds with $\text{E}(\text{OH})_3$ ligands are the first examples of the structurally characterized tribasic forms of phosphorus and arsenous acids. The tautomeric form of hypophosphorous acid, bis(hydroxy)phosphine $\text{HP}(\text{OH})_2$, was trapped for the first time by coordination at the Ni site of cluster $[\text{W}_3(\text{NiCl})\text{Se}_4(\text{H}_2\text{O})_9]^{3+}$ and was structurally characterized in a supramolecular adduct $\{[\text{W}_3(\text{Ni}(\text{HP}(\text{OH})_2))\text{Y}_4(\text{H}_2\text{O})_9](\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_4 \cdot 11\text{H}_2\text{O}$ ($\text{Y} = \text{S}, \text{Se}$) [52]. A characteristic feature of the crystal structure of heterometallic indium-containing compound $\{[\text{W}_3(\text{InCl}_3)\text{S}_4(\text{H}_2\text{O})_9]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_4 \cdot 28\text{H}_2\text{O}$ [53] are large channels (~ 7 Å in diameter) occupied by water molecules of solvation and counter ions.

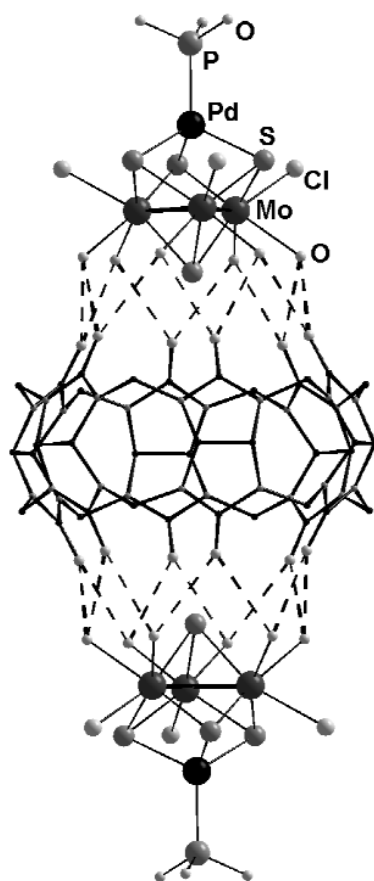


Fig. 12 Structure of the supramolecule in $\{[\text{Mo}_3(\text{PdP}(\text{OH})_3)\text{S}_4(\text{H}_2\text{O})_6\text{Cl}_3]_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\}\text{Cl}_2 \cdot 20\text{H}_2\text{O}$.

In summary, this review illustrates the advances in the chemistry of supramolecular compounds of the macrocyclic organic cavitand cucurbit[6]uril with mono/polynuclear metal aqua complexes and also with cluster aqua complexes of molybdenum and tungsten. Due to the strong interactions of carbonyl oxygen donor atoms of Q6 with metal cations, more stable complexes than other macrocyclic ligands are formed. The geometric and functional complementarity of the portal oxygen atoms of cucurbit[6]uril and water molecules of cluster aqua complexes is responsible for the formation of an extensive hydrogen bond network that leads to very stable hybrid organic–inorganic compounds. It makes Q6 a very attractive molecular building block for the directed construction of nanosized highly ordered supramolecular compounds.

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