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## ARTICLE

# SO<sub>4</sub><sup>2-</sup> Anions Directed Hexagonal-Prismatic Cages *via* Cooperative C-H...O Hydrogen Bonds

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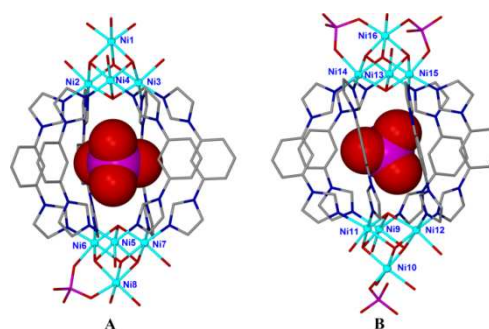
Hexagonal-prismatic cages are constructed by cubane-like Ni<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub> clusters generated *in situ* and clip-like organic ligands. The SO<sub>4</sub><sup>2-</sup> anions template the formation of the above cages *via* weak cooperative C-H...O hydrogen bonds. Further research shows that three internal hydrogen atoms of the bib ligand or its derivatives are necessary because they are all involved in the cooperative C-H...O hydrogen bonding with the captured SO<sub>4</sub><sup>2-</sup> anions. More importantly, not only the size and shape but also the charge of SO<sub>4</sub><sup>2-</sup> anions dominates the formation of the cages.

## Introduction

Self-assembly of metal-coordination cages has attracted much attention in the past two decades because of their fascinating structures,<sup>1</sup> interesting host-guest chemistry<sup>2</sup> and potential properties in catalyses<sup>3</sup> and separation.<sup>4</sup> Generally, the shape and size of the cages are controlled by the symmetry and shape of the ligands as well as the coordination geometry of the metal ions. However, the anions are also extremely important and sometimes play a decisive role since they act as not only the balance charges but also the structure-directing templates.<sup>5</sup> Due to suitable sizes and complementary shapes, the templating anions usually interact with the cage hosts through the coordination bonds,<sup>6</sup> hydrogen bonds,<sup>7</sup> anion...π interactions<sup>8</sup> or simply electrostatic attractions,<sup>9</sup> which can direct the process of the self-assembly of the coordination cages. In some cases, the interactions between the captured anions and the cage hosts are very strong. Therefore, in other words, these coordination cages can serve as the anions receptors. As reported, various mono-charged anions such as halide anions,<sup>10</sup> NO<sub>3</sub><sup>-</sup>,<sup>11</sup> BF<sub>4</sub><sup>-</sup>,<sup>6b, 12</sup> ClO<sub>4</sub><sup>-</sup>,<sup>9</sup> PF<sub>6</sub><sup>-</sup>,<sup>13</sup> and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>,<sup>14</sup> are found as the templates owing to the low free energies of solvation. However, the examples for more hydrophilic and multi-charged anions such as SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> are rare. To effectively encapsulate these multi-charged anions, the introduction of strong and cooperative interactions such as N-H...O hydrogen bonding by the functionalization of the cavities of the cages,<sup>7</sup> which can overcome the anions' high free energies of dehydration, is necessarily required. On the other side, the multigonal prismatic cages such as pentagonal and hexagonal cages are rarely reported.<sup>15</sup> One reason is that multipodal ligands with the C<sub>n</sub> (n ≥ 5) symmetry are difficultly synthesized and could hardly maintain the high symmetry during the process of self-

assembly. Another reason is that for a single metal ion it is impossible to offer the C<sub>n</sub> (n ≥ 5) symmetry coordination sites limited by the coordination number and coordination geometry.<sup>16</sup> However, as for the poly-metal units, this is not necessarily the case. As we all know, polynuclear clusters may endow high-symmetry coordination sites.<sup>17</sup> Therefore, an alternate method of obtaining the high-symmetry coordination sites may be the usage of a metal cluster instead of a metal ion. Herein, we report the self-assembly of the hexagonal-prismatic cages constructed by Ni<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub> cubanes generated *in situ* and clip-like organic ligands. More importantly, the SO<sub>4</sub><sup>2-</sup> anions template the formation of hexagonal-prismatic cages *via* cooperative weak C-H...O hydrogen bonding.

## Results and discussion



**Figure 1.** Two kinds of hexagonal prismatic cages (**A** and **B**) are found in **1**. The encapsulated SO<sub>4</sub><sup>2-</sup> anion is in space filling mode (one set of the disordered oxygen atoms are omitted for clarity). C, gray; N, blue; O, red; S, purple; Ni, sky blue.

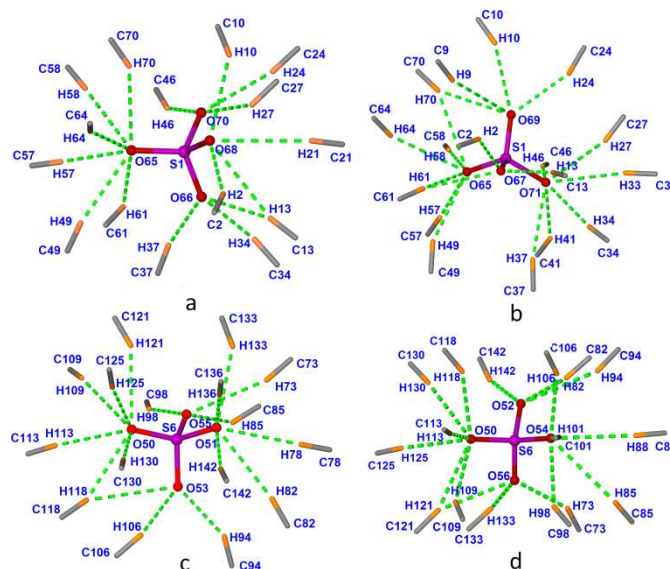
## Syntheses and structures of Hexagonal-prismatic cages

In the presence of 2,4,6-trimethylpyridine (tmp), slow diffusion of 1,3-bis(1-imidazolyl)benzene (bib) into an aqueous of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  results in the complex  $\{ \{ \text{SO}_4 \subset \{ [\text{Ni}_4(\mu_3\text{-OH})_4]_2(\text{bib})_6(\mu_2\text{-SO}_4)(\text{H}_2\text{O})_{10} \} \} (\text{SO}_4)_2 \} \{ \text{SO}_4 \subset \{ [\text{Ni}_4(\mu_3\text{-OH})_4]_2(\text{bib})_6(\mu_2\text{-SO}_4)_2(\text{SO}_4)(\text{H}_2\text{O})_7 \} \} \cdot 30\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$  (**1**). The tmp is necessary because it can provide the basic condition, which is favourable for the formation of the  $\text{Ni}_4(\mu_3\text{-OH})_4$  clusters.<sup>18</sup> In the asymmetric unit, there are two mutually independent hexagonal-prismatic cages (**A** and **B**) (Figure 1). On the whole, the backbones of cage **A** and **B** are similar. Each of them is constructed from two distorted  $\text{Ni}_4(\mu_3\text{-OH})_4$  clusters and six bib ligands. In each  $\text{Ni}_4(\mu_3\text{-OH})_4$  cluster, four Ni(II) ions and four  $\mu_3\text{-OH}^-$  groups occupy eight corners of the cube alternately.<sup>18b</sup><sup>19</sup> Though each Ni(II) cation is in a slightly distorted octahedral environment, the coordination sphere is different. Of four Ni(II) cations, one is in an  $\text{O}_6$  environment, which is completed by three  $\mu_3\text{-OH}^-$  groups and three oxygen atoms from the aqueous ligands and/or the  $\text{SO}_4^{2-}$  anions. The other three Ni(II) cations are all in the  $\text{O}_4\text{N}_2$  environment, which is fulfilled by three  $\mu_3\text{-OH}^-$  groups, one oxygen atom from the aqueous ligand or the  $\text{SO}_4^{2-}$  anion and two nitrogen atoms from two bib ligands. Thus, two adjacent  $\text{Ni}_4(\mu_3\text{-OH})_4$  cubanes are connected by six bib ligands to form a hexagonal-prismatic coordination cage. In each bib ligand, two imidazole rings and the central benzene ring are not coplanar, with the dihedral angles of  $5.45 - 34.91^\circ$ . The centroid  $\cdots$  centroid separations between the adjacent imidazole rings  $\cdots$  benzene rings range from 3.39 to 3.68 Å, suggesting strong  $\pi$ - $\pi$  interactions (see Figure S1). Theoretically, the cage has the  $C_6$  symmetry. In fact, the cage is not perfect owing to strong  $\pi$ - $\pi$  stacking interactions between the bib ligands. The slight deviation from the  $C_6$  symmetry can be estimated by N-Ni-N angles, which is in the range of  $90.56 - 94.20^\circ$  (theoretically  $90^\circ$ ). Though very similar in the backbone, it should be noticed that **A** and **B** have a little difference. In **A**, one  $\text{SO}_4^{2-}$  anion chelates two Ni(II) cations (Ni6, Ni8) in the  $\eta^1, \eta^1\text{-}\mu_2$  mode. In **B**, two  $\text{SO}_4^{2-}$  anions ligate to Ni14, Ni16 and Ni15, respectively, in the  $\eta^1, \eta^1\text{-}\mu_2$  mode. Additionally, one  $\text{SO}_4^{2-}$  anion coordinates to Ni10 in the mono-dentate mode. On the other hand, considering the encapsulated  $\text{SO}_4^{2-}$  anion cage **B** is electroneutral. However, **A** is positively charged and balanced by two external free  $\text{SO}_4^{2-}$  anions.

### Cooperative C-H $\cdots$ O hydrogen bonds

In each cage, one  $\text{SO}_4^{2-}$  anion resides in the cavity as template. The  $\text{SO}_4^{2-}$  anion is disordered and three oxygen atoms are distributed at six sites with the occupancy of 0.5 respectively (in **A** O66, O67, O68, O69, O70 and O71; in **B** O51, O52, O53, O54, O55 and O56). The  $\text{SO}_4^{2-}$  anion is found hydrogen bonding with eighteen C-H groups from six bib ligands (Figure 2). Namely, three hydrogen atoms of each bib ligand, which point inside the cavity of the cage (the internal hydrogen atoms), are all involved in C-H $\cdots$ O hydrogen bonding with the  $\text{SO}_4^{2-}$  anion. According to the literature, a C-H $\cdots$ O hydrogen bond is acknowledged if the distance between a hydrogen atom of the aromatic C-H group and an oxygen atom ( $d$ ) is less than 2.9 Å and the C-H $\cdots$ O angle is larger than  $110^\circ$ .<sup>20</sup> On the whole, in **A**

there are twenty-nine sets of C-H $\cdots$ O hydrogen bonds and in **B** twenty-eight. The undistorted oxygen atom of the  $\text{SO}_4^{2-}$  anion (in **A** O65; in **B** O50) is anchored by six C-H $\cdots$ O hydrogen bonds, with the  $d$  values of 2.33 – 2.88 Å and the C-H $\cdots$ O angles of  $145.71 - 176.13^\circ$ . For the disordered oxygen atoms, they are also involved in hydrogen bonding with the aromatic hydrogen atoms. The numbers of the C-H $\cdots$ O hydrogen bonds are in the range of 3-6 (see Table S2). Additionally, the  $d$  values are in the range of 2.20 – 2.89 Å and the C-H $\cdots$ O angles of  $121.55 - 172.40^\circ$ . Through these cooperative C-H $\cdots$ O hydrogen bonds, the cages capture the  $\text{SO}_4^{2-}$  anions into their cavities. According to the literature, the  $\text{SO}_4^{2-}$  anion can also be captured in the urea-functionalized tetrahedral metal-coordination cage *via* twelve strong N-H $\cdots$ O hydrogen bonds. However, this is the first example of encapsulating  $\text{SO}_4^{2-}$  anion into metal-coordination cage mainly *via* weak C-H $\cdots$ O hydrogen bonding. However, compared with classical N-H $\cdots$ O hydrogen bonds, the unconventional C-H $\cdots$ O hydrogen bonds are much weaker. Therefore, the disorder of  $\text{SO}_4^{2-}$  anions may be attributed to the relatively weak cooperative hydrogen bond interactions, which could not restrict the rotation of  $\text{SO}_4^{2-}$  anion.

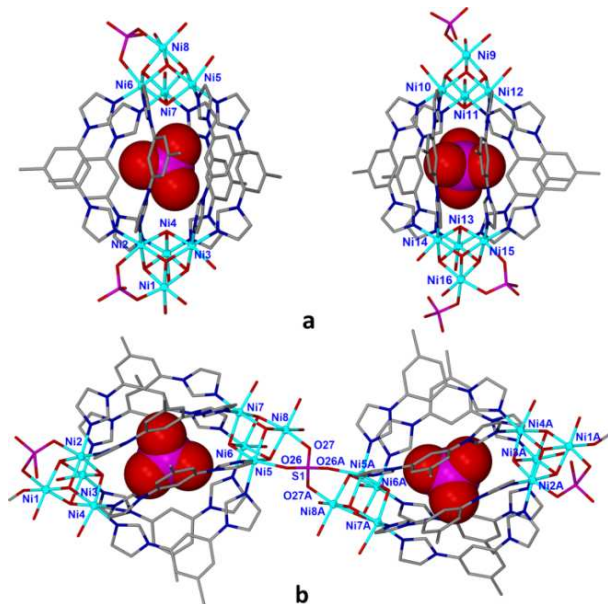


**Figure 2.** To clearly present the hydrogen bonds, the disordered  $\text{SO}_4^{2-}$  anion in cage **A** is divided into two sets, which are drawn respectively in Figure 2a and 2b. Similarly, the hydrogen bonds for the disordered  $\text{SO}_4^{2-}$  anion in cage **B** are drawn in Figure 2c and 2d respectively. C, gray; N, blue; O, red; S, purple; Ni, sky blue. The hydrogen bonds are in green.

### Influences of internal hydrogen atoms of di-imidazole ligands

As the above discussion, the encapsulation of  $\text{SO}_4^{2-}$  anion into hexagonal-prismatic cage is elaborately realized *via* the C-H $\cdots$ O hydrogen bonding. We think that the three internal hydrogen atoms of the bib ligand are necessary because they are all involved in the cooperative C-H $\cdots$ O hydrogen bonding with the captured  $\text{SO}_4^{2-}$  anion. To verify this suggestion, we use the 2,6-di(1H-imidazol-1-yl)pyridine (dip) instead of bib. Compared with the bib, dip has two internal imidazole H atoms due to the substitution of the central phenyl ring with the pyridine ring. Though the difference between bib and dip is

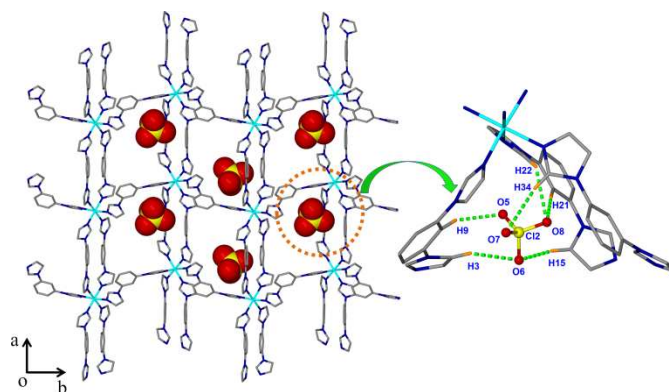
slight, under the same condition no hexagonal-prismatic cage can be obtained. However, when we use the external  $\text{CH}_3$ -substituted bib ligand 1,1'-(5-methyl-1,3-phenylene)bis(1H-imidazole) (5- $\text{CH}_3$ -bib), which retains three internal hydrogen atoms and bears an additional external  $\text{CH}_3$ - group, this is not necessarily the case. Under similar condition,  $\{\{\text{SO}_4\left\{[\text{Ni}_4(\mu_3\text{-OH})_4]_2(5\text{-CH}_3\text{-bib})_6(\mu_2\text{-SO}_4)_2(\text{H}_2\text{O})_8\right\}\}(\text{SO}_4)\}\{\text{SO}_4\left\{[\text{Ni}_4(\mu_3\text{-OH})_4]_2(5\text{-CH}_3\text{-bib})_6(\mu_2\text{-SO}_4)(\text{SO}_4)_2(\text{H}_2\text{O})_8\right\}\}\cdot 77\text{H}_2\text{O}\cdot 5\text{CH}_3\text{OH}$  (**2**) and  $\{\{\text{SO}_4\left\{[\text{Ni}_4(\mu_3\text{-OH})_4]_2(5\text{-CH}_3\text{-bib})_6(\mu_2\text{-SO}_4)(\text{CH}_3\text{O})(\text{H}_2\text{O})_7\right\}\}_2(\mu_4\text{-SO}_4)\}(\text{SO}_4)_2\cdot x\text{H}_2\text{O}\cdot y\text{CH}_3\text{OH}$  (**3**) can be obtained simultaneously. Though they crystallize in different space groups and have different arrangements, they both have the analogous hexagonal-prismatic cage units (Figure 3). Similar to **1**, in **2** there are two kinds of hexagonal-prismatic cages. In **3**, a hexagonal-prismatic cage dimer, which is bridged by a  $\text{SO}_4^{2-}$  group, can be obtained. Certainly, a  $\text{SO}_4^{2-}$  anion is captured in the cavity of the cage through the  $\text{C-H}\cdots\text{O}$  hydrogen bonding with the internal hydrogen atoms of  $\text{CH}_3$ -bib ligands. Furthermore, if we replace the external  $\text{CH}_3$ - group of 5- $\text{CH}_3$ -bib with  $\text{CH}_3\text{O}$ - group, we will obtain a new ligand 1,1'-(5-methoxy-1,3-phenylene)bis(1H-imidazole) (5- $\text{CH}_3\text{O}$ -bib). Under the same condition, similar cage-like complex (**4**) can also be obtained. Different to **1**, **2** and **3**, in **4** there are four discrete  $\text{SO}_4^{2-}$  anion templated hexagonal-prismatic cages. In conclusion, the above result indicates that the internal hydrogen atoms of the bib ligand are extremely important since they may afford the  $\text{C-H}\cdots\text{O}$  hydrogen bonding with the captured  $\text{SO}_4^{2-}$  anion.



**Figure 3.** (a) Two kinds of hexagonal prismatic cages are found in **2**. (b) The dimeric hexagonal-prismatic coordination cages in **3**. The encapsulated  $\text{SO}_4^{2-}$  anion is in space filling mode (one set of the disordered oxygen atoms are omitted for clarity). C, gray; N, blue; O, red; S, purple; Ni, sky blue. Symmetry code A,  $1+y, x-1, -z$ .

### Anion templated effects

If we replace  $\text{NiSO}_4$  with other Ni(II) salts such as  $\text{Ni}(\text{NO}_3)_2$  and  $\text{NiCl}_2$ , under the same condition we could not obtain the hexagonal-prismatic coordination cages. The above results indicate that the size and shape match between the cage host and the guest anion may be important for the formation of the cage.<sup>12a</sup> Considering the similarity in the size and shape between  $\text{ClO}_4^-$  and  $\text{SO}_4^{2-}$ , we use  $\text{Ni}(\text{ClO}_4)_2$  instead of  $\text{NiSO}_4$ . However, a 2-D coordination polymer (**5**) rather than the cage can be obtained (Figure 4). In **5**, the Ni(II) cation is in an octahedral  $\text{N}_6$  environment and coordinated by six independent bib ligands. Along the crystallographic  $a$  axis, two adjacent Ni(II) cations are connected by two *syn*-bib ligands to form a double chain. Further, these chains are bridged by *anti*-bib ligands into a corrugated layer along the  $ac$  plane. One  $\text{ClO}_4^-$  anion is between the layers. However, the other  $\text{ClO}_4^-$  anion resides in the cavity enclosed by three bib ligands. As expected, the captured  $\text{ClO}_4^-$  anion is involved in the  $\text{C-H}\cdots\text{O}$  hydrogen bonding. The above results further suggest that in addition to the shape and size match the charge is also important. Compared with univalent  $\text{ClO}_4^-$  anion, divalent  $\text{SO}_4^{2-}$  anion could form stronger hydrogen bonds due to the higher charge. As we know, this kind of anion templated effect dominated by not only the size and shape but also the charge is rarely seen in the coordination molecular cages.<sup>7a</sup>



**Figure 4.** The 2-D coordination polymer constructed by  $\text{Ni}(\text{ClO}_4)_2$  and bib ligands. For clarity, only the  $\text{ClO}_4^-$  anions in the layer are presented. C, gray; N, blue; O, red; S, purple; Ni, sky blue. The hydrogen bonds are in green.

### Conclusions

In summary, hexagonal-prismatic cages are constructed by  $\text{Ni}_4(\mu_3\text{-OH})_4$  cubanes generated *in situ* and clip-like organic ligands. Interestingly, the  $\text{SO}_4^{2-}$  anions template the formation of hexagonal-prismatic cages *via* cooperative weak  $\text{C-H}\cdots\text{O}$  hydrogen bonding, which is the first observation of multi-charged anion templates through these weak interactions in metal-coordination cages. Further research shows that three internal hydrogen atoms of the bib ligand or its derivatives are necessary because they are all involved in the cooperative  $\text{C-H}\cdots\text{O}$  hydrogen bonding with the captured  $\text{SO}_4^{2-}$  anions. More importantly, not only the size and shape but also the charge of  $\text{SO}_4^{2-}$  anions dominates the formation of the cages. The above result indicates that the high  $C_n$  ( $n \geq 5$ ) symmetry coordination

sites can be obtained through the usage of cluster units as the nodes. At the same time, the anion templates play an important role in the formation of the coordination cages. We think this work will throw a light on the research of high-symmetry metal-coordination cages.

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### Notes and references

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