

Self-Assembly of Frameworks with Specific Topologies: Construction and Anion Exchange Properties of M_3L_2 Architectures by Tripodal Ligands and Silver(I) Salts

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Abstract: Three five-component architectures, compounds **3**, **4**, and **5** were obtained by self-assembly of tripodal 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (**6**) and 1,3,5-tris(benzimidazol-2-ylmethyl)benzene (**7**) ligands with silver(I) salts. The structures of these novel complexes have been determined by X-ray crystallography. The results of structural analysis indicate that these frameworks have same M_3L_2

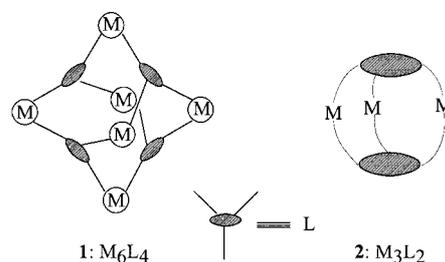
components, but different structures. Compounds **3** and **4** are both M_3L_2 type cage-like complexes, while the **5** is an open trinuclear complex. The complex **3** is a cylindrical cage with simultaneous

inclusion of a perchlorate anion inside of the cage as a guest molecule. Such guests can be exchanged for other anions through the open edge of the cage as evidenced by crystal structure of **4**. The results demonstrate that the molecular M_3L_2 type cage can act as a host for anions and provide a nice example of supramolecular architectures with interesting properties and possible applications.

Keywords: inorganic architectures • ion exchange • self-assembly • silver • supramolecular chemistry • tripodal ligands

Introduction

Supramolecular frameworks with specific topologies, such as closed three-dimensional molecular cages, present a large range of applications in material science, medicine, and chemical technology.^[1] In the past decades, a number of such molecules have been synthesized by assembly of organic ligands and transitional metal salts.^[2–6] For example, tripodal ligands with arene cores were designed and employed for construction of cage-like architectures.^[2–5] Ten-components M_6L_4 cage-like complexes **1** were obtained by assembly of 2,4,6-tris(4-pyridyl)-1,3,5-triazine and 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene ligands with $[Pd(en)(NO_3)_2]$ (*en* = ethylenediamine) and $PdCl_2$.^[2] Many large molecular cages, such as $[Cu^{III}_8(dtc)_4]^{8+}$ (*dtc* = derivative of dithiocarba-

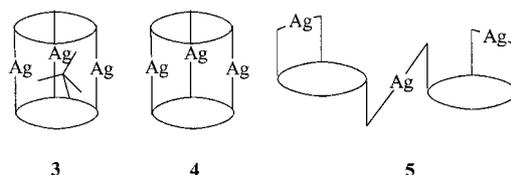


mate), $[Cu^{II}_{12}(tapp)_8]$ (H_3tapp = 2,4,6-triazophenyl-1,3,5-trihydroxybenzene) and $[Pd_{18}(tpb)_6]$ (*tpb* = 1,3,5-tris(3,5-pyrimidyl)benzene) have also been reported most recently.^[3] However, the M_3L_2 type cage-like complexes of type **2** are not well known up to now.^[4] We herein describe the generation of M_3L_2 type cages **3** and **4** constructed from the two tripodal

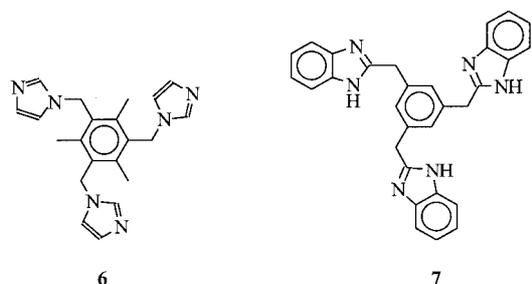
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ligands **6** and three two-coordinate silver(I) atoms. Furthermore, in order to investigate the influence of organic bridging ligand on the formation of supramolecular architectures,



reaction between the designed tripodal ligand **7** and silver(I) perchlorate was also examined; an open trinuclear complex **5** was obtained.

Supramolecular architectures have attracted much attention over the last few years, not only due to their interesting structures but also because of their fascinating properties and possible applications, such as ion and molecular recognition, ion-exchange, selective guest inclusion, and catalysis for specific reactions.^[7–9] For example, Lehn and co-workers have reported that multicomponent cylindrical nanoarchitectures, obtained by self-assembly of Cu^I or Ag^I with polytopic linear and circular ligands, showed anion inclusion and exchange both in and out of the inner cavities.^[7] Reaction of 1,4-bis(3-pyridyloxy)benzene with Pd^{II} generated a quadruply stranded helicate with spontaneous encapsulation of a hexafluorophosphate anion.^[8] The above-mentioned M₆L₄ and M₃L₂ type cage-like architectures have been proved to have ability to encapsulate guest molecules.^[2, 4a] However, no anion inclusion and exchange was reported for these M₆L₄ and M₃L₂ type cage-like complexes, although the guest-induced formation of M₃L₂ cage has been reported by Fujita et al.^[5a] We present herein the anion encapsulation and exchange properties of the architecture **3**.

Results and Discussion

Self-assembly of the cage-like complexes [Ag₃(6**)₂][ClO₄]₃ (**3**) and [Ag₃(**6**)₂][ClO₄]₃ · 4CH₃CN (**4**):** When the tripodal ligand **6** is mixed with silver(I) perchlorate or tetrafluoroborate salt in ethanol in the dark, a colorless precipitate appears immediately, which is insoluble in water and common organic solvents (methanol, ethanol, acetonitrile, etc.). Single crystals suitable for X-ray crystallographic analysis were obtained by a layering method.^[10] Compound **3** was obtained as colorless needle by slow diffusion between two layers of aqueous solution of AgClO₄ · H₂O and a solution of **6**, in a molar ratio 1.5:1, in ethanol at room temperature. The complex is stable in both solid and solution states in the dark. The structure of **3** was determined by X-ray crystallography. It provides unambiguous evidence for the cage-like architecture. The BF₄[−] analogue obtained by reaction of **6** with AgBF₄ has space group of *C2/c* and cell parameters of *a* = 21.794(3), *b* = 20.201(4), *c* = 14.813(2) Å, β = 128.600(10)°; these are similar to those of **3** as listed in Table 1. This indicates that the BF₄[−] analogue is isomorphous and isostructural with **3**. The complex was found to have high thermal stability. The TGA data of [Ag₃(**6**)₂][BF₄]₃ indicate that the framework is stable

Table 1. Summary of crystal data and refinement results for complexes **3**, **4**, and **5**.

	3	4	5
formula	C ₄₂ H ₃₈ Ag ₃ Cl ₃ N ₁₂ O ₁₂	C ₅₀ H ₆₀ Ag ₃ Cl ₃ N ₁₆ O ₁₂	C ₆₀ H ₄₈ Ag ₃ Cl ₃ N ₁₂ O ₁₂
<i>M_r</i>	1342.88	1507.10	1559.06
crystal size [mm]	0.40 × 0.30 × 0.05	0.56 × 0.40 × 0.32	0.40 × 0.40 × 0.36
crystal system	monoclinic	monoclinic	triclinic
space group	<i>C2/c</i>	<i>C2/c</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	21.829(1)	19.897(3)	14.135(2)
<i>b</i> [Å]	20.6742(8)	10.4280(10)	14.564(2)
<i>c</i> [Å]	14.8822(6)	29.010(3)	15.451(2)
α [°]			69.420(10)
β [°]	129.072(1)	92.540(10)	84.040(10)
γ [°]			79.150(10)
<i>V</i> [Å ³]	5214.3(4)	6013.3(12)	2922.1(7)
<i>Z</i>	4	4	2
ρ_{calcd} [g cm ^{−3}]	1.710	1.665	1.772
μ [mm ^{−1}]	1.335	1.173	1.209
<i>T</i> [K]	200(1)	297(2)	297(2)
reflections collected	14 720	5995	10 848
unique reflections	5982	5260	10 046
observed reflections	2400	3022	7505
parameters	326	421	828
<i>S</i> on <i>F</i> ²	1.142	0.855	1.040
<i>R</i> ₁	0.0548		
<i>R</i> _w	0.1231		
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]		0.0346	0.0341
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]		0.0780	0.0870
$\Delta\rho_{\text{min/max}}$ [e Å ^{−3}]	1.98/−2.04	0.699/−0.353	0.536/−0.852

up to 297 °C. The measurements for the complex **3** was not carried out for safety reasons, since it is a perchlorate salt. It is believed that the **3** also has high thermal stability as its tetrafluoroborate analogue.

The crystal structure of complex **3** is shown in Figure 1 (top) with the atom numbering scheme. The two **6** ligands have a *cis,cis,cis*-conformation and a face-to-face orientation; they are joined together by three silver(I) atoms through coordination bonds to nitrogen to give a three-dimensional individual M₃L₂ type cage. The N–Ag–N angles of 168.0(4) and 169.1(2)° (Table 2) indicate that the silver(I) atoms are two-coordinate with near linear geometry.^[11] The distance between two central benzene rings is 10.99 Å with a dihedral angle of 0.6° and the intermetallic Ag–Ag distances are 6.09 (Ag1–Ag2, Ag1A–Ag2) and 6.68 Å (Ag1–Ag1A). Thus the complex is a cylindrical cage, while the previously reported M₃L₂ type cage-like complex [Zn₃(tib)₂(OAc)₆] (tib = 1,3,5-tris(imidazol-1-ylmethyl)benzene; OAc = acetate anion) is close to a spherical cage.^[4a] In addition, two benzene rings of **3** have an eclipsed conformation with staggered angles of 10.1 and 12.0° between each two methyl groups (see Newman projection shown in Figure 1 bottom). The corresponding angle in [Zn₃(tib)₂(OAc)₆] is 44.5° and implies a gauche conformation.

An important structural feature of complex **3** is its spontaneous encapsulation of a perchlorate anion as illustrated in Figure 1. External to the cage are two other ClO₄[−] anions. The internal ClO₄[−] anion positioned at the center of the cage, since the distances between the Cl2 and each centroid of the benzene ring are equivalent (Cl2–X1A = Cl2–X1B = 5.49 Å) and the angle of X1A–Cl2–X1B is 177.3° (X1A and X1B refer to the centroids of the two benzene rings, respectively). There is one C–H⋯O hydrogen bond for the

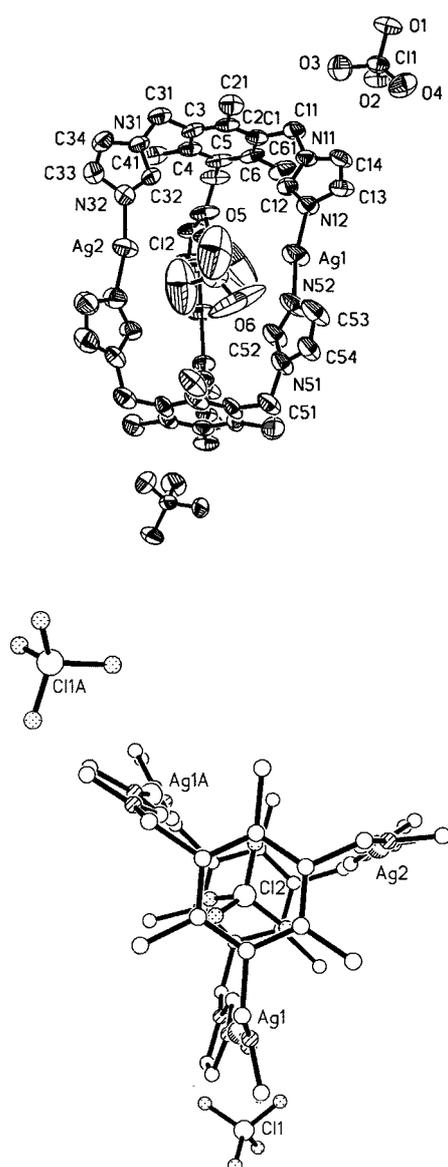


Figure 1. Crystal structure of the cylindrical cage complex **3** with thermal ellipsoids drawn at 50% probability: side view with atom numbering scheme (top) and view along the axis of the cylinder (bottom).

Table 2. Selected bond lengths [Å] and angles [°] for complexes **3**, **4**, and **5**.^[a]

[Ag ₃ (6) ₂](ClO ₄) ₃ (3)			
Ag1–N12	2.098(4)	Ag1–N52	2.094(4)
Ag2–N32	2.084(5)	Ag–N _{av}	2.092(4)
N12–Ag1–N52	169.1(2)	N32–Ag2–N32a	168.0(4)
[Ag ₃ (6) ₂](ClO ₄) ₃ ·4CH ₃ CN (4)			
Ag1–N1	2.109(4)	Ag2–N3	2.117(3)
Ag2–N6b	2.116(3)	Ag–N _{av}	2.113(3)
N1–Ag1–N1b	175.3(2)	N6b–Ag2–N3	172.92(14)
[Ag ₃ (7) ₂](ClO ₄) ₃ (5)			
Ag1–N1	2.086(3)	Ag1–N3	2.090(3)
Ag2–N7	2.076(3)	Ag2–N5	2.089(3)
Ag3–N11	2.112(3)	Ag3–N9	2.112(3)
Ag–N _{av}	2.093(3)		
N1–Ag1–N3	174.91(12)	N7–Ag2–N5	178.87(13)
N11–Ag3–N9	175.75(12)		

[a] Symmetry transformations used to generate equivalent atoms: a: $-x + 1, -y, -z + 1$; b: $x + 1.5, y + 0.5, z$.

internal ClO₄[−] anion and seven for the external ClO₄[−] anions (Table 3). Both internal and external ClO₄[−] anions can be exchanged by other anions, such as tetrafluoroborate anion (see below).

Table 3. Distances [Å] and angles [°] of hydrogen bonding for complexes **3**, **4**, and **5**.^[a]

D–H...A ^[b]	Distance (D...A)	D–H–A	Angle (D–H–A)
[Ag ₃ (6) ₂](ClO ₄) ₃ (3)			
C14–H3...O2	3.346(9)	C14–H3–O2	147.2
C33–H5...O1a	3.432(10)	C33–H5–O1a	153.0
C34–H6...O4b	3.419(8)	C34–H6–O4b	148.0
C52–H7...O6	3.260(11)	C52–H7–O6	136.4
C54–H9...O1c	3.187(7)	C54–H9–O1c	146.3
C31–H13...O1d	3.321(9)	C31–H13–O1d	132.6
C51–H14...O2c	3.300(7)	C51–H14–O2c	132.7
C41–H21...O3b	3.413(9)	C41–H21–O3b	169.7
[Ag ₃ (6) ₂](ClO ₄) ₃ ·4CH ₃ CN (4)			
C3–H3...N7e	3.160(10)	C3–H3–N7e	148.5
C15–H15...O3f	3.384(8)	C15–H15–O3f	161.1
C20–H20...O2e	3.129(6)	C20–H20–O2e	129.5
C21–H21B...O4g	3.349(7)	C21–H21–O4g	158.4
C24–H24C...O5	2.894(7)	C24–H24–O5	109.3
[Ag ₃ (7) ₂](ClO ₄) ₃ (5)			
N2–H2...O6	3.047(6)	N2–H2–O6	145.6
N2–H2...O7	3.223(6)	N2–H2–O7	156.0
N4–H4...O8 h	2.949(6)	N4–H4–O8 h	163.5
N6–H6...O9 h	2.956(11)	N6–H6–O9 h	154.3
N8–H8...O11	3.064(9)	N8–H8–O11	162.0
N10–H10...O2i	3.051(5)	N10–H10–O2i	163.7
N12–H12...O3j	2.987(5)	N12–H12–O3j	177.2
C28–H28...O9 h	3.416(8)	C28–H28–O9 h	152.1
C38–H38B...O5k	3.358(6)	C38–H38B–O5k	146.6
C46–H46B...O1i	3.3408(6)	C46–H46B–O1i	144.0

Symmetry transformations used to generate equivalent atoms: a: $-x, -y, -z$; b: $-x, y, -z - 0.5$; c: $-x, -y, -z - 1$; d: $x, -y, z + 2.5$; e: $x + 0.5, y + 1.5, z$; f: $-x - 1, y, -z + 0.5$; g: $x, y + 1, z$; h: $x, y + 1, z$; i: $-x, -y + 2, -z - 1$; j: $-x, -y + 1, -z - 1$; k: $-x + 1, -y + 1, -z$. [b] D: donor; A: acceptor.

In order to investigate whether the internal ClO₄[−] anion can be replaced by other small neutral molecules, the reaction between **6** and AgClO₄·H₂O was carried out in other solvents. It is surprising that when the acetonitrile and dimethylformamide (DMF) were used as reaction solvents instead of ethanol, a different species **4** was obtained. The crystals of **4** are unstable in isolated solid state and lose solvent molecules very quickly to give colorless powder. The structural analysis of **4** reveals that there are four acetonitrile solvent molecules in **4**, while in the case of **3**, no solvent molecules were found. This means that the reaction solvents have great influence on the formation of inorganic architectures. The size of **4** is different from that of **3**, although the complex **4** is also a M₃L₂ type cylindrical cage (Figure 2 top). The centroids of two benzene rings with a dihedral angle of 1.9° are separated by a distance of 10.63 Å, which is shorter than the corresponding distance of **3** (10.99 Å). The Ag–Ag distances are 7.21 (Ag1–Ag2, Ag1–Ag2A) and 7.04 Å (Ag2–Ag2A); these are longer than those of **3** (6.09 and 6.68 Å). In addition, the most important point is that the locations of perchlorate anion are different between the complexes **3** and **4**. Figure 2 (bottom)

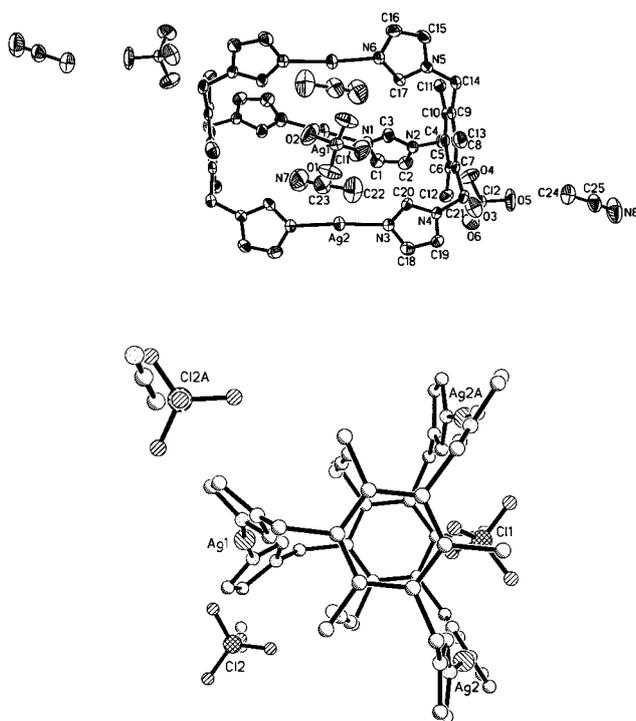


Figure 2. Crystal structure of the cylindrical cage complex **4** with thermal ellipsoids drawn at 50% probability: side view with atom numbering scheme (top) and view along the axis of the cylinder (bottom).

exhibits the cage **4** viewed down the benzene rings to emphasize the location of perchlorate anion and acetonitrile solvate molecules. It is evident that the center of the cage is empty, instead there are one perchlorate anion and two acetonitrile molecules at the edge of the cage (Figure 2 bottom). The Cl1 atom is centered between of two methyl carbons (C23 and C23A) with a distance of 5.26 Å and an angle of 173.3° (C23–Cl1–C23A). Two CH₃CN molecules also

positioned between two methyl groups. The two benzene rings have an eclipsed conformation with a staggered angle of about 11°, which is similar to that of **3**. There is one C–H⋯N hydrogen bond and four C–H⋯O hydrogen bonds as listed in Table 3.

In addition, there are weak interionic contacts in these cage-like complexes. The shortest distance of 2.81 Å between the silver atom (Ag2, Ag2A in Figure 2 bottom) and the oxygen atom of the perchlorate anion containing Cl1 indicates the existence of Ag⋯O contacts in the compound **4**.^[12] Such an Ag⋯O interaction in the **3** is somewhat weaker than that in the **4**, since the shortest Ag–O distance between the silver atom and oxygen atom of central perchlorate anion (Figure 1 bottom) is 3.01 Å in the **3**.

Self-assembly of the trinuclear open complex [Ag₃(7**)₂][ClO₄]₃ (**5**):** When the connection mode of pendant groups of the tripodal ligand changed from the 1-position of imidazole (**6**) to the 2-position of benzimidazole (**7**), it was found that the precipitate formed from reaction of AgClO₄·H₂O with **7** in methanol and water solution is soluble in acetonitrile. Hence the single crystals of **5** were obtained by slow evaporation of the reaction mixture.

The results of elemental and structural analyses indicate that the complex **5** has same compositions of M₃L₂ as **3**, but they have different structures. As shown in Figure 3, the complex **5** is an open trinuclear complex although it also contains two tripodal ligands **7** and three silver(I) atoms. Each silver(I) atom is two-coordinate with N–Ag–N angles ranging from 174.91(12) to 178.87(13)° (Table 2) and Ag2 links the two tripodal ligands **7**. It is interesting that the conformations of ligand **6** in architectures **3** and **4** are all *cis,cis,cis*. However, in complex **5**, the ligand **7** that contains N1, N3, and N5 has a *cis,cis,cis* conformation, while that with N7, N9, and N11 has a *cis,trans,trans* conformation. A plane formed by N1, N3, and N5 is almost parallel to the benzene ring plane of C25, C26,

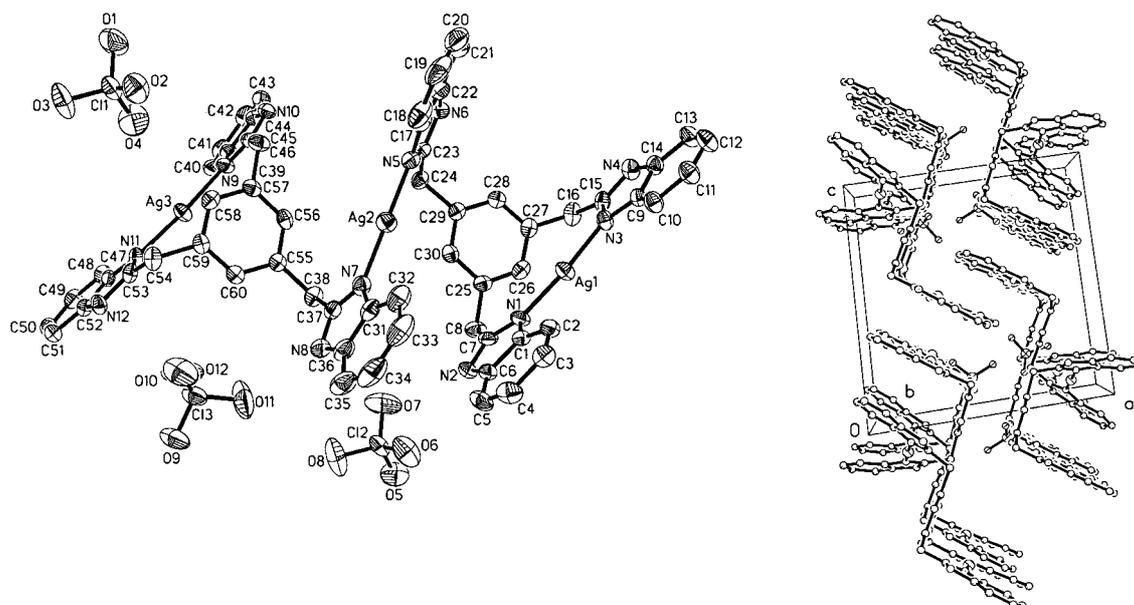


Figure 3. Crystal structure of the cationic moiety of **5** with the ellipsoids drawn at the 50% probability level (left) and crystal packing diagram along the *b* axis (right).

C27, C28, C29, and C30 with a dihedral angle of 4.2° between these two planes, while the dihedral angle between the planes N7, N9, N11 and C55, C56, C57, C58, C59, C60 is 44.8° . The results demonstrate that the nature of the organic ligand has a great influence on the formation of supramolecular architectures.

In addition to the coordination bonds, which were considered to be the determinant force for the formation of **5**, there are weak interactions. The Ag1–C26 and Ag3–C58 distances are 2.676(3), 2.724(3) Å, respectively. Normal Ag–C bond lengths have been reported to be in range of 2.01 to 2.20 Å.^[13] Relatively long distances between Ag and C indicate the existence of weak Ag–C interactions in **5**. Furthermore, there are N–H⋯O and C–H⋯O hydrogen bonds, as summarized in Table 3, and π – π interactions. The crystal packing diagram for **5** along the *b* axis is exhibited in Figure 3 (right); the centroid-to-centroid distance between two nearest benzimidazole rings is 3.47 Å, with a dihedral angle of 3.1° .

Anion exchange properties of cage-like complexes: We have begun to study the anion exchange properties of these cage-like architectures. As revealed by the crystal structure of **3**, the cavity of the cage included one perchlorate anion that is only loosely bound to the framework. On the other hand, there are three large open windows of approximately 6×11 Å (Ag–Ag and two benzene rings separations, respectively) and these windows may facilitate the exchange of guest anion in and out of the cavity. Such consideration is demonstrated by the crystal structure of complex **4**. When the CH₃CN and DMF solvents were used, the perchlorate anion moved from the center to edge of the cavity as mentioned above. It means that the windows are large enough to allow the ClO₄[−] anion in and out of the cage. Therefore such a cage-like complex is expected to have anion exchange property. The powdered complex [Ag₃(**6**)₂][BF₄]₃ was suspended in aqueous solution of NaClO₄ and stirred to allow anion exchange; this procedure was repeated three times (see Experimental Section). The elemental microanalysis and infrared spectral data confirmed that the product is **3**, that is, [Ag₃(**6**)₂][ClO₄]₃. Namely the BF₄[−] anion was completely exchanged by ClO₄[−] anion. The FT-IR spectrum of exchanged product showed characteristic bands at 1084 and 1121 cm^{−1}, which are different from those of the original [Ag₃(**6**)₂][BF₄]₃ (at 1053, 1083, 1098 and 1120 cm^{−1}). Further studies on anion exchange with other anions such as nitrate are underway to determine whether the perchlorate anion can be exchanged selectively.

Experimental Section

The elemental analysis of C, H, and N were performed on a Perkin–Elmer 240C elemental analyzer at the analysis center of Nanjing University. Infrared (IR) spectra were recorded on a Bruker IFS66V vacuum-type FT-IR spectrophotometer by using KBr discs. Reagents of silver(I) salts were commercially available and used as received without further purification. The tripodal ligands **6** and **7** were prepared by procedures reported previously.^[14, 15] All procedures for synthesis and measurements were carried out in dark.

Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Synthesis of [Ag₃(6**)₂][ClO₄]₃ (**3**):** The compound was prepared by layering method. An solution of **6** (18.0 mg, 0.05 mmol) in ethanol (3 mL) was added slowly and carefully to a layer of a solution of AgClO₄·H₂O (16.9 mg, 0.075 mmol) in water (3 mL) in a tube. Single needle crystals suitable for X-ray diffraction analysis were obtained with yield of 63% in several days by standing. Elemental analysis calcd (%) for C₄₂H₄₈Ag₃Cl₃N₁₂O₁₂ (1342.88): C 37.57, H 3.60, N 12.52; found C 37.35, H 3.33, N 12.45.

The analogue with the BF₄[−] anion, [Ag₃(**6**)₂][BF₄]₃, was prepared by the same procedures by using AgBF₄ instead of AgClO₄·H₂O. Elemental analysis calcd (%) for C₄₂H₄₈Ag₃B₃N₁₂F₁₂ (1304.94): C 38.66, H 3.71, N 12.88; found C 38.60, H 3.88, N 12.98.

Synthesis of [Ag₃(6**)₂][ClO₄]₃·4CH₃CN (**4**):** AgClO₄·H₂O (16.9 mg, 0.075 mmol) and ligand **6** (18.0 mg, 0.05 mmol) were dissolved in CH₃CN (5 mL) and DMF (5 mL), respectively. They were then placed in a tube as two layers. The complex **4** was obtained by slow diffusion between these layers. Single crystals appeared after several days. The crystals were unstable and lost solvent very quickly.

Synthesis of [Ag₃(7**)₂][ClO₄]₃ (**5**):** A solution of ligand **7** (23.4 mg, 0.05 mmol) in methanol (5 mL) was added to a solution of AgClO₄·H₂O (16.9 mg, 0.075 mmol) in water (1 mL) and the mixture was stirred. A pale yellow precipitate appeared immediately. Then acetonitrile (ca. 6 mL) was added until the precipitate disappeared. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of reaction mixture in several days. Yield 54%. Elemental analysis calcd (%) for C₆₀H₄₈Ag₃Cl₃N₁₂O₁₂ (1559.06): C 46.22, H 3.10, N 10.78; found C 46.42, H 3.33, N 10.66.

Anion exchange reaction: Well-ground powder of [Ag₃(**6**)₂][BF₄]₃ (20.0 mg) was suspended in a solution of NaClO₄ (2.0 g) in water (20 mL), and the mixture was stirred for one day at room temperature, then filtrated, washed with water, and dried in vacuum to give colorless powder. This procedure was repeated at least three times. Elemental analysis calcd (%) for [Ag₃(**6**)₂][ClO₄]₃ (C₄₂H₄₈Ag₃Cl₃N₁₂O₁₂): C 37.57, H 3.60, N 12.52; found C 37.73, H 3.83, N 12.33.

Crystallography: A colorless needle crystal of **3** was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.7107$ Å) at 200 K. Calculations were carried out on an SGI workstation with the teXsan software package.^[16] An empirical absorption correction based on ψ scans was applied for **3** with transmission factors 0.768–0.935. The structures were solved by direct method using SHELXS-86 and refined by the full-matrix least-square method anisotropically for non-hydrogen atoms. The hydrogen atoms were generated geometrically.

The X-ray diffraction measurements for complexes **4** and **5** were performed on a Siemens P4 automatic four-circle diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) at room temperature. Intensity data were collected in the variable ω scan mode. The structures were solved by direct methods by using SHELXS-97 and refined by full-matrix least-square calculation on F^2 with SHELXL-97.^[17] One of perchlorate anion in each complex is disordered. Oxygen atoms O3, O4, O5, and O6 of complex **4** have two positions with the site occupancy factors (s.o.f) of 0.75 and 0.25, respectively. Atoms Cl3, O9, O10, O11, and O12 of complex **5** have two positions with the site occupancy factors (s.o.f) of 0.76 and 0.24, respectively. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically. Calculations were performed on a PC-586 computer with the Siemens SHELXTL program package.^[18] Details of the crystal parameters, data collection and refinement for complexes **3**, **4** and **5** are summarized in Table 1, and selected bond lengths and angles are given in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152696 (**3**), CCDC-152697 (**4**) and CCDC-152698 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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