Discrete and Infinite Cage-Like Frameworks with Inclusion of Anionic and Neutral Species and with Interpenetration Phenomena

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Abstract: Complex [Ag(tpba)N$_3$] (**1**) was obtained by reaction of novel tripodal ligand *N,N′,N″*-tris(pyrid-3-ylmethyl)-1,3,5-benzenetricarboxamide (TPBA) with [Ag(NH$_3$)$_2$]N$_3$. While the reactions between 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (TITMB) and silver(I) salts with different anions and solvent systems give six complexes: [Ag$_3$(titmb)$_2$](N$_3$)$_3$·CH$_3$OH·4H$_2$O (**2**), [Ag$_3$(titmb)$_2$](CF$_3$SO$_3$)$_2$(OH)·5H$_2$O (**3**), [Ag$_3$(titmb)$_2$][Ag(NO$_3$)$_3$]NO$_3$·H$_2$O (**4**), [Ag$_3$(titmb)$_2$(py)](NO$_3$)$_3$·H$_2$O (py = pyridine) (**5**), [Ag$_3$(titmb)$_2$(py)](ClO$_4$)$_3$ (**6**), and [Ag$_3$(titmb)$_2$](ClO$_4$)$_3$·CHCl$_3$ (**7**). The structures of these complexes were determined by X-ray crystallography. The results of structural analysis of complexes **1** and **2**, with the same azide anion but different ligands, revealed that **1** is a twofold interpenetrated 3D framework with interlocked cage-like moieties, while **2** is a M$_3$L$_2$ type cage-like complex with a methanol molecule inside the cage. Entirely different structure and topology between **1** and **2** indicates that the nature of organic ligands affected the structures of assemblies greatly. While in the cases of complexes **2**–**7** with flexible tripodal ligand TITMB, they are all discrete M$_3$L$_2$ type cages. The results indicate that the framework of these complexes is predominated by the nature of the organic ligand and geometric need of the metal ions, but not influenced greatly by the anions and solvents. It is interesting that there is a divalent anion [Ag(NO$_3$)$_3$]$^{2-}$ inside the cage **4** and an anion of ClO$_4^-$ or NO$_3^-$ spontaneously encapsulated within the cage of complexes **5**, **6** and **7**.

Keywords: cage compounds · inclusion compounds · interpenetration · silver(I) complexes · tripodal ligands

Introduction

In recent years, construction of discrete supramolecular frameworks, especially with hollow structures (cages, polyhedra, capsules etc.) has attracted much attention owing to their ability of encapsulating guest molecules or molecular aggregates.[1–3] And some spectacular architectures, termed as "encapsulating complexes", were designed and synthesized by using three-connecting organic ligands.[4, 5] Furthermore, the constrained environments of the hollow structures may provide the encapsulated guests with special chemical and physical properties which are different from those in bulk phase. On the other hand, some hollow frameworks may be apt to be "self-recognition" (interpenetration) rather than "hetero-recognition" (encapsulation).[5c] For example, catenanes, composed of interlocked independent molecules, have received considerable attention currently due to their intrinsic properties.[6] During the past decade, the interpenetrations of the honeycomb- and diamondoid-like structure are well documented. However, to the best of our knowledge, only one example of interlocked cages by the self-assembly process through the formation of the quadruple aromatic stacking was reported.[6a]

We focus our attention on design and synthesis metal-organic frameworks with specific topologies and properties by using flexible tripodal ligands such as 1,3,5-tris(imidazol-1-ylmethyl)benzene (TIB), 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (TITMB).[7] For example, M$_3$L$_2$ type cage-like complex [Zn$_3$(tib)$_2$(OAc)$_6$]·4H$_2$O, obtained by reaction of zinc(II) acetate with the tripodal ligand TIB, exhibits guest-inclusion properties of small molecule such as synthetic camphor in aqueous solution.[7a] Anion-exchange properties were investigated for cylindrical cages obtained from TITMB and silver(I) salts.[7b] For further studies on assembly of flexible tripodal ligand with transition metal salts and on inclusion properties of metal-organic frameworks, we designed and synthesized a novel tripodal ligand *N,N′,N″*-tris(pyrid-3-

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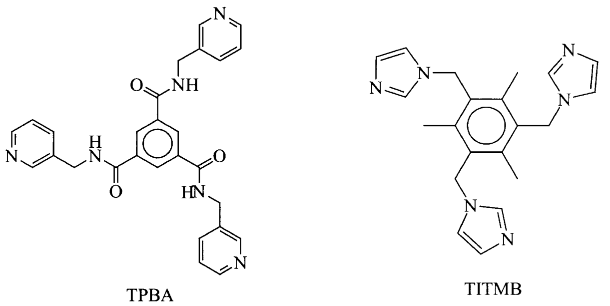
ylmethyl)-1,3,5-benzenetricarboxamide (TPBA). A twofold interpenetrated complex $[Ag(tpba)N_3]$ (**1**) and six cage-like frameworks, $[Ag_3(titmb)_2](N_3)_3 \cdot CH_3OH \cdot 4H_2O$ (**2**), $[Ag_3(titmb)_2](CF_3SO_3)_2(OH) \cdot 5H_2O$ (**3**), $[Ag_3(titmb)_2][Ag(NO_3)_3]NO_3 \cdot H_2O$ (**4**), $[Ag_3(titmb)_2(py)](NO_3)_3 \cdot H_2O$ (**5**), $[Ag_3(titmb)_2(py)](ClO_4)_3$ (**6**) and $[Ag_3(titmb)_2](ClO_4)_3 \cdot CHCl_3$ (**7**) were obtained by assembly reactions between TPBA or TITMB and silver(I) salts with different anions and solvent systems. In this paper we report the crystal structures and inclusion properties of these complexes.

Results and Discussion

Self-assembly of $[Ag(tpba)N_3]$ (1) and $[Ag_3(titmb)_2](N_3)_3 \cdot CH_3OH \cdot 4H_2O$ (2): Compared with TITMB, the new TPBA ligand (Scheme 1), prepared by reaction of 3-aminomethylpyridine with 1,3,5-benzenetricarbonyl trichloride, abounds with acceptors and donors for hydrogen bonding since an amide group was introduced in each arm of TPBA. The hydrogen bonds have been intensively examined in crystal engineering as a directional interactions.[8] Due to presence of the amide and methylene groups, TPBA is also a flexible tripodal ligand and can have *cis,cis,cis*- and *cis,trans,trans*-conformations like those observed for TITMB.[7e]



Scheme 1. Schematic drawing for tripodal ligands TPBA and TITMB.

Complex **1** was readily prepared by reaction of TPBA with $[Ag(NH_3)_2]N_3$ in the dark. The structure of complex **1** was revealed by X-ray crystallography. The compound crystallizes in a chiral space group of $P6_3$ (Table 1). As illustrated in Figure 1, azide anions in **1** serve as end-to-end bridging ligands to link two silver(I) atoms and each TPBA ligand connects three silver(I) atoms to result the formation of a eleven-component cage-like framework: six metal ions, three linear N_3^- anions and two TPBA ligands. The three silver(I) atoms joined by the one TPBA ligand form an equilateral triangle with an edge length (Ag1···Ag1A separation) of 13.90 Å. It is noteworthy that the two TPBA ligands having *cis,cis,cis*-conformations are in a face-to-back orientation, so that the cage is concave at the bottom. While in the previous reported M_3L_2 cages, the TIB or TITMB ligands with *cis,cis,cis*-conformations are all in the face-to-face orientation.[7a–d] Furthermore, the three pyridyl groups of each TPBA ligand in complex **1** exhibit a propeller-type arrangement (Figure 2a) in generation of molecular chirality from the reaction of achiral components.[9]

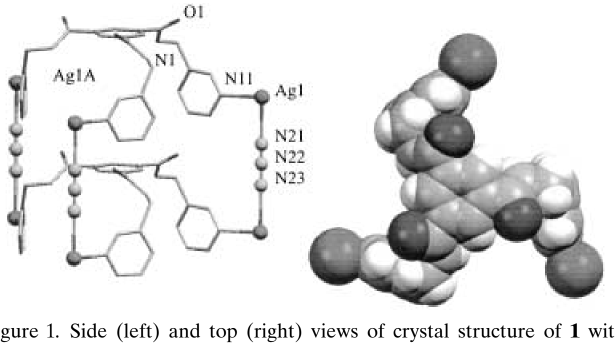


Figure 1. Side (left) and top (right) views of crystal structure of **1** with cage-like moiety.

In complex **1**, each silver(I) center is coordinated by five nitrogen atoms from three TPBA ligands and two azide anions in trigonal bipyramidal geometry. Such connection mode makes the complex **1** a three-dimensional network structure as shown in Figure 2. The 3D structure can be considered as 2D layers (Figure 2a) composed of TPBA and silver(I) atoms pillared by azide anions, with a distance of 7.53 Å between two adjacent layers (Figure 2b). Such separation between two adjacent layers is a suitable distance for passing through an aromatic ring. The remarkable feature of complex **1** is that the whole crystal packing is a twofold interpenetrated 3D structure (Figure 3a) with interlocked cage-like moieties (Figure S1, Supporting Information). The topology of **1** can be expressed as $(6^3)(6^9,8)$ which is similar to that present in the previously reported twofold interpenetrated complexes [Ag(tricyanomethanide)(L)] (L = 1,4-diazobicyclo-[2.2.2]octane, pyrazine, 4,4′-bipy) and $[Ag(hexanedinitrile)]SO_3CF_3$.[10] The fully eclipsed stacking of the central benzene rings with the centroid–centroid distance of 3.76 Å indicates the presence of face-to-face $\pi-\pi$ repulsive interactions in **1** (Figure 3b).[11] However, there are hydrogen-bonding interactions between the amide groups with a N1···O1A distance of 3.063(8) Å to give a triple helix (Figure 3b), which are favorable the crystal packing in an interpenetrating mode. The data of hydrogen bonds are summarized in Table 3. It has been reported that frameworks with amide-containing ligands and metal ions prefer to interpenetrated structure due to the possible strong intermolecular interactions among the amide groups.[5b]

When $[Ag(NH_3)_2]N_3$ reacted with TITMB, instead of TPBA, in methanol solution, a discrete 3D cage-like framework **2** is generated with spontaneously encapsulation of one methanol molecule inside the cage (Figure 4a). However, when the same reaction was carried out in acetonitrile solution by same layering method, a 2D polycatenated honeycomb network was obtained.[12] The results provide nice examples that the solvent medium predominated the topology and structure of assemblies. It is noticeable that two azide anions in **2** are weakly bound to two silver(I) atoms, respectively, with a Ag···N distance of 2.64 Å, and the additional azide anion is free of interaction with the metal atom. There are five hydrogen bonds formed between the cage framework and methanol molecule: three C(2-position of imidazolyl group)-H···O(methanol) hydrogen bonds and

Table 1. Summary of crystal data and refinement results for complexes **1**–**7**.

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_{27}H_{24}AgN_9O_3$	$C_{43}H_{60}Ag_3N_{21}O_5$	$C_{44}H_{59}Ag_3F_6N_{12}O_{12}S_2$	$C_{42}H_{50}Ag_4N_{16}O_{13}$	$C_{47}H_{55}Ag_3N_{16}O_{10}$	$C_{47}H_{53}Ag_3Cl_3N_{13}O_{12}$	$C_{43}H_{49}Ag_3Cl_6N_{12}O_{12}$
F_w	630.42	1274.73	1449.76	1418.46	1327.68	1421.98	1462.25
crystal system	hexagonal	orthorhombic	trigonal	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P6_3$	$P2_12_12_1$	$P321$	$Cmcm$	$Pna2_1$	$C2/c$	$P2_1/c$
Flack parameter	0.43(10)	0.48(3)	0.03(6)		0.119(9)		
a [Å]	13.895(3)	14.7673(6)	11.227(2)	14.5770(18)	16.809(4)	22.694(2)	14.9487(5)
b [Å]	13.895(3)	15.9120(5)	11.227(2)	28.480(4)	20.492(6)	20.814(2)	20.7327(7)
c [Å]	7.528(3)	21.2314(9)	14.439(3)	12.2056(16)	14.953(4)	14.930(1)	17.3551(5)
γ [°]	120.00		120.00			130.40(1)	90.8886(9)
V [Å^3]	1258.7(6)	4988.9(3)	1576.0(6)	5067.1(11)	5151(2)	5370.5(8)	5378.2(3)
Z	2	4	1	4	4	4	4
μ [mm^{-1}]	0.852	1.234	1.067	1.602	1.203	1.306	1.450
refls coll	12508	46103	14461	15082	48456	16067	49279
obs refls	1388	5247	1959	1131	8606	3825	7588
$R1$ [$I > 2\sigma(I)$]	0.0551	0.0522	0.0634	0.0722	0.0374	0.0624	0.0512
$wR2$ [$I > 2\sigma(I)$]	0.1434	0.0501	0.1817	0.1738	0.0701	0.1704	0.1373

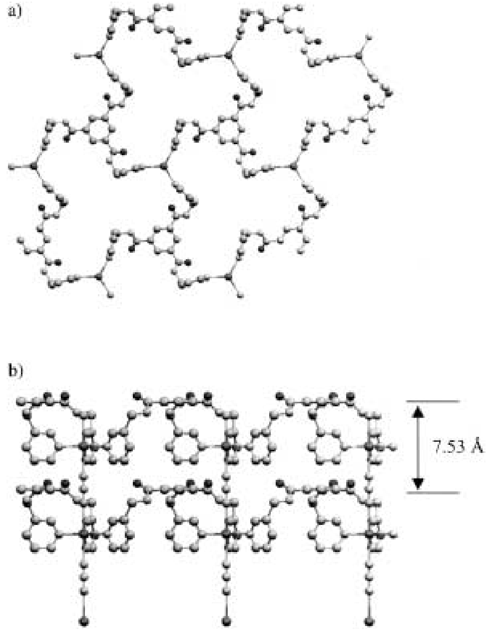


Figure 2. a) 2D layer and b) 3D structure of **1**.

two C(methanol)-H···N(azide anion) hydrogen bonds (Table 3). Interestingly, the discrete cages are further linked by hydrogen bonds (Table 3) between the azide anions and water molecules to form a 1D cage-chain as exhibited Figure 4b.

Self-assembly of cage-like complexes $Ag_3(titmb)_2](CF_3SO_3)_2(OH)\cdot 5H_2O$ (3), $[Ag_3(titmb)_2][Ag(NO_3)_3]NO_3\cdot H_2O$ (4), $[Ag_3(titmb)_2(py)](NO_3)_3\cdot H_2O$ (5), $[Ag_3(titmb)_2(py)](ClO_4)_3$ (6) and $[Ag_3(titmb)_2](ClO_4)_3\cdot CHCl_3$ (7): Previous studies showed that when ligand TITMB reacted with silver salts with perchlorate, nitrate or terephthalate anion in methanol or ethanol solution, similar cage-like architectures were obtained.[7a–d] The results suggest that the anions do not influence the structures greatly in this system, which is further evidenced by the reaction of $AgCF_3SO_3$ with TITMB in methanol solution to give cage-like compound **3** (Figure S2, Supporting Information), although the size and shape of $CF_3SO_3^-$ is different from those of ClO_4^- or NO_3^-. In complex **3**, two TITMB ligands, with *cis,cis,cis*-conformation and face-to-face orientation, are held together by three silver(I) atoms through Ag–N coordination bonds to generate the cage-like structure with the height of 10.56 Å and intermetallic Ag···Ag distance of 7.15 Å.

It is interesting to note that the solubility of the cage-like complexes with different anions varied significantly, although they have the same M_3L_2 framework structures. In contrast to the very poor solubility of cage-like complexes $[Ag_3(titmb)_2]X_3$, where $X = ClO_4^-$ or NO_3^-, in water and common organic solvents such as methanol, acetonitrile, etc.,[7b] complex **3** is soluble in methanol aqueous solution. Therefore, to investigate the reaction details of TITMB with $AgCF_3SO_3$ and the solution behavior of the complex, ^1H NMR titration experiments and electrospray mass spectral (ES-MS) measurements were carried out. When the D_2O (0.016 mL each time) solution of $AgCF_3SO_3$ (0.169 mmol mL^{-1}) was added to the CD_3OD solution (0.5 mL) of TITMB (2.6 mg, 7.2 µmol) in batches, the ^1H NMR spectrum of the mixture displayed only one set of signals with variation of metal-to-ligand molar ratio from 0 to 3.0; this indicates the rapid chemical exchange between the free ligand and the complex. The most remarkable finding is that the proton signals of TITMB, especially the one of 4-H of imidazolyl group, continuously down-field shifted until the metal-to-ligand molar ratio reaches a value of 3:2, and excess addition of metal salt has no further influence on the ^1H NMR spectra (Figure S3, Supprtong Information), which shows the quantitatively self-assembly of the M_3L_2 cage **3** in solution. The NMR results suggest that the reaction of TITMB with $AgCF_3SO_3$ is thermodynamically controlled.[2c] Moreover, species of $[Ag_3(titmb)_2(CF_3SO_3)_2]^+$ and $[Ag_3(titmb)_2(CF_3SO_3)]^{2+}$ were observed in the ES-MS of **3** in methanol solution, which confirm the existence of M_3L_2 under the ES-MS experiment conditions. It should be mentioned that the M_3L_2 cage is a pure product from the reaction of TITMB with $AgCF_3SO_3$ in methanol aqueous solution even in absence of any guest molecules as evidenced by above ^1H NMR results, while for the reported Pd^{II}-linked cages, the self-assembly process is guest-controlled.[4d]

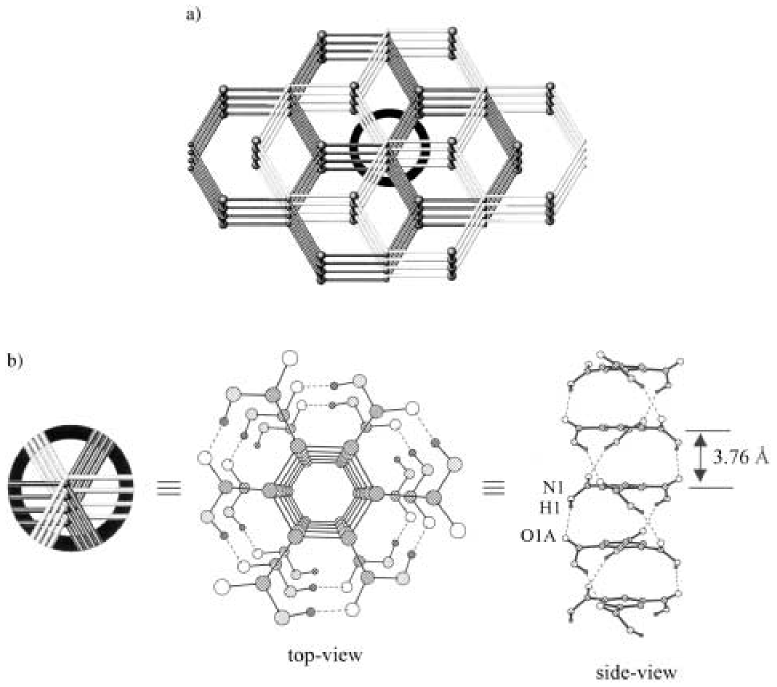


Figure 3. a) Schematic drawing of twofold interpenetrated 3D structure of complex **1** in which the TPBA units are presented by three spokes radiating from a point and silver atoms by dark spheres. b) Stacking of the TPBA ligands held through N-H ··· O hydrogen bonds with the pyridyl groups omitted for clarity.

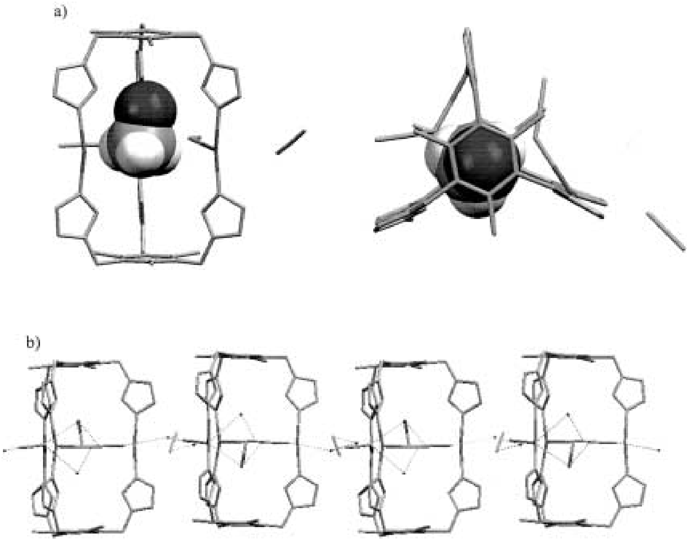


Figure 4. a) Side (left) and top (right) views of cage structure of **2**. Water molecules were omitted for clarity. b) 1D cage-chain formed by hydrogen bonds.

On the other hand, as reported previously,[7b] when the tripodal ligand TITMB is treated with silver(I) perchlorate in ethanol in the dark, a M_3L_2 type cage-like architecture $[Ag_3(titmb)_2](ClO_4)_3$ was obtained with simultaneous inclusion of a perchlorate anion inside of the cage. However, when TITMB and silver(I) perchlorate reacted in acetonitrile and dimethylformamide solution, a different species $[Ag_3(titmb)_2](ClO_4)_3 \cdot 4\,CH_3CN$ was generated with four acetonitrile solvent molecules per formula unit and inside of the cage is empty. Furthermore, two different structures were obtained when TITMB reacted with $[Ag(NH_3)_2]N_3$ in different solvents as mentioned above. This means that the reaction solvents have subtle influence on the formation of inorganic–organic hybrid architectures, which promoted us to make further investigations about the impact of reaction medium on the structure of assemblies. Four complexes were successfully isolated with the presence of chloroform, or pyridine (py) molecules in the reaction medium, namely $[Ag_3(titmb)_2][Ag(NO_3)_3]NO_3 \cdot H_2O$ (**4**), $[Ag_3(titmb)_2(Py)](NO_3)_3 \cdot H_2O$ (**5**), $[Ag_3(titmb)_2(Py)](ClO_4)_3$ (**6**), $[Ag_3(titmb)_2](ClO_4)_3 \cdot CHCl_3$ (**7**).

Complex **4** was synthesized in chloroform. The crystallographic analysis of **4** showed that a divalent anion $[Ag(NO_3)_3]^{2-}$ was accommodated in the cationic cage $[Ag_3(titmb)_2]^{3+}$ (Figure 5). Only one example has been reported on such an inclusion of an anionic metal complex into a discrete cationic metallocage.[2c] Obviously the Ag3 atom within the cationic cage is six-coordinate in trigonal-prismatic coordination geometry. The dihedral angles between the planes of the three nitrate anions are 119.4, 119.4 and 121.2°, respectively. Each nitrate anion was nearly perpendicular to the central benzene ring planes with the free N–O bond extending outwards through the open "windows" of the cage (Figure 5). While the same reaction was carried out in absence of chloroform, cage complex $[Ag_3(titmb)_2][NO_3]_3 \cdot 5\,H_2O$ with encapsulation of two water molecules inside the cage was obtained.[7d]

Complex **5** was afforded by reaction in pyridine, instead of chloroform. The structure of **5** was determined by X-ray crystallography, which provides unambiguous evidence for the same cage-like framework (Figure 6). It is interesting that

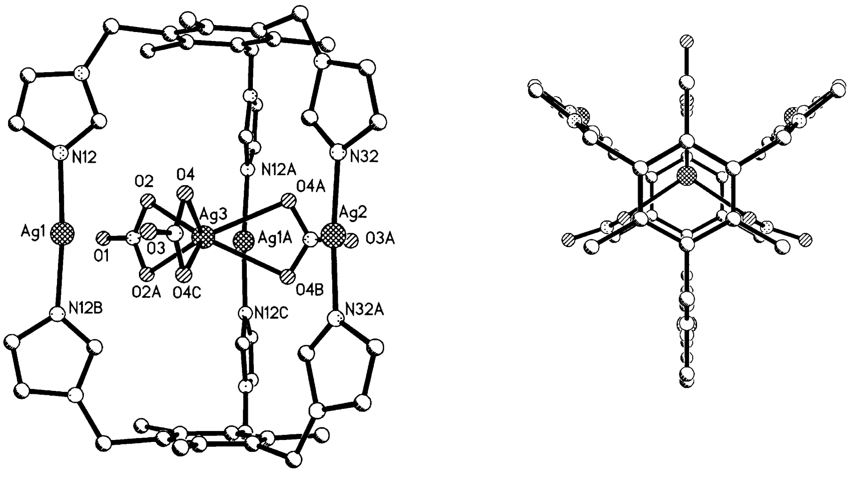


Figure 5. Side (left) and top (right) views of cage structure of **4** with one $[Ag(NO_3)_3]^{2-}$ anion encapsulated inside the cage.

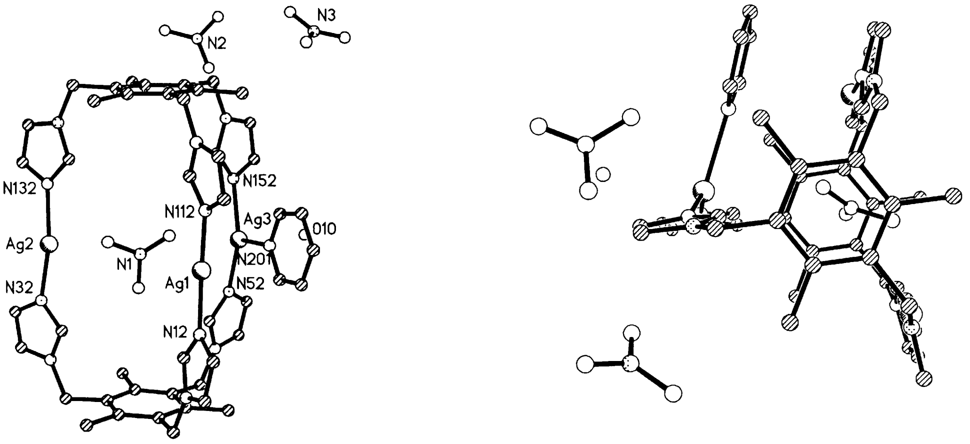


Figure 6. Side (left) and top (right) views of cage structure of **5** with one nitrate anion encapsulated inside the cage.

there is one pyridine molecule per cage coordinated to Ag3 atom. Thus Ag3 atom is three-coordinate with the N-Ag-N angles of 141.91(15), 114.63(17) and 103.41(17)° (Table 2). While the Ag1 and Ag2 are two-coordinate with near linear geometry since the N-Ag-N angles are 160.39(14) and 165.46(14)°, respectively (Table 2).[13] Furthermore, one of the three nitrate anions was located inside the cage in **5** through C(2-position of imidazolyl group)-H···O(nitrate anion) and C(methyl group of neighboring cage)-H···O(nitrate anion) hydrogen bonds (Table 3). While in the above-mentioned complex $[Ag_3(titmb)_2][NO_3]_3 \cdot 5H_2O$, three nitrate anions are all outside the cage.[7d]

Complex **6** was prepared by the reaction of silver(I) perchlorate with TITMB under the same conditions for preparation of **5**. The structure of **6** is similar with that of **5** with one perchlorate anion located inside the cage; however, the pyridine did not coordinate with silver(I) atom (Figure S4, Supporting Information). When silver perchlorate reacted with TITMB in the presence of chloroform, complex **7** was obtained. As shown in Figure 7, the backbone of **7** is also a M_3L_2 cage. One ClO_4^- anion is inside the cage while the other two stay outside together with one chloroform molecule.

The crystallographic studies showed that the reactions between the TITMB ligand and silver(I) salts with different anions and/or reaction medium provide M_3L_2 type cage-like frameworks **2**–**7** having inclusion properties for solvent molecules and various anions including $[Ag(NO_3)_3]^{2-}$ complex anion. There is subtle difference between these cage-like structures. For example, the heights of the cages in **2**, **5**, **6** and **7**, namely the centroid–centroid distance between the two almost parallel (dihedral angles are less than 2.6°) benzene ring planes within the cage, are ranging from 11.01 to 11.11 Å, while the corresponding distances in **3** and **4** are 10.56 and 10.64 Å, respectively. Accordingly, the intramolecular metal–metal distances in the range of 6.51 to 7.16 Å between each two silver(I) atoms within the cages **3** and **4** are longer than those (from 4.94 to 6.84 Å) in complexes **2**, **5**, **6** and **7**. Such difference may probably be caused by the different shape and size of the solvent molecules and the anions, and as a result, different hydrogen bonds (Table 3) were formed between the

Table 2. Selected bond lengths [Å] and angles [°] for complexes **1**–**7**.[a]

$[Ag(tpba)N_3]$ (**1**)			
Ag1−N11	2.348(4)	Ag1−N21	2.63(2)
Ag1−N23[a]	2.64(4)		
N11-Ag1-N11[b]	119.98(2)	N11-Ag1-N21	89.1(3)
N11-Ag1-N23[a]	90.9(3)	N21-Ag1-N23[a]	180.0
$[Ag_3(titmb)_2](N_3)_3 \cdot CH_3OH \cdot 4H_2O$ (**2**)			
Ag1−N112	2.132(5)	Ag1−N12	2.133(5)
Ag2−N132	2.133(5)	Ag2−N32	2.166(5)
Ag3−N152	2.114(5)	Ag3−N52	2.160(5)
N112-Ag1-N12	159.4(2)	N132-Ag2-N32	167.2(2)
N152-Ag3-N52	164.6(2)		
$[Ag_3(titmb)_2](CF_3SO_3)_2(OH) \cdot 5H_2O$ (**3**)			
Ag1-N12	2.099(5)	N12-Ag1-N12[c]	177.2(3)
$[Ag_3(titmb)_2][Ag(NO_3)_3]NO_3 \cdot H_2O$ (**4**)			
Ag1−N12	2.104(7)	Ag2−N32	2.026(14)
Ag3−O2	2.458(13)	Ag3−O4	2.484(11)
N12-Ag1-N12[d]	173.8(4)	N32-Ag2-N32[e]	173.8(8)
O2-Ag3-O2[e]	48.9(6)	O2[e]-Ag3-O4[f]	130.4(3)
O2-Ag3-O4[f]	107.9(3)	O4-Ag3-O4[f]	96.4(6)
O4[f]-Ag3-O4[e]	48.5(5)	O4-Ag3-O4[e]	116.7(6)
$[Ag_3(titmb)_2(Py)](NO_3)_3 \cdot H_2O$ (**5**)			
Ag1−N12	2.094(4)	Ag1−N112	2.100(4)
Ag2−N32	2.105(4)	Ag2−N132	2.125(5)
Ag3−N152	2.222(4)	Ag3−N201	2.429(4)
Ag3−N52	2.209(4)	N32-Ag2-N132	165.46(14)
N52-Ag3-N152	141.91(15)	N52-Ag3-N201	114.63(17)
N152-Ag3-N201	103.41(17)	N12-Ag1-N112	160.39(14)
$[Ag_3(titmb)_2(Py)](ClO_4)_3$ (**6**)			
Ag1−N12	2.112(5)	Ag1−N52	2.134(4)
Ag2−N32	2.150(5)	Ag2[g]−N32	2.158(6)
N12-Ag1-N52	171.55(18)	N32-Ag2-N32[g]	140.2(2)
$[Ag_3(titmb)_2](ClO_4)_3 \cdot CHCl_3$ (**7**)			
Ag1−N112	2.121(4)	Ag1−N12	2.126(4)
Ag2−N32	2.093(4)	Ag2−N132	2.098(4)
Ag3−N52	2.076(4)	Ag3−N152	2.080(4)
N112-Ag1-N12	168.76(15)	N32-Ag2-N132	168.52(18)
N52-Ag3-N152	165.11(17)		

[a] Symmetry transformations used to generate equivalent atoms: [a] $x, y, z-1$; [b] $-y+1, x-y+1, z$; [c] $y, x, -z$; [d] $-x, y, z$; [e] $-x, y, -z+½$; [f] $x, y, -z+½$; [g] $-x, y, -z+3/2$.

framework of the cage and guest solvent molecule or anions. Therefore, the formation of the cage-like structure is mainly depended on the ligand and coordination geometry of the metal center, the anion and reaction medium only have subtle influence on the size and shape of the cages.

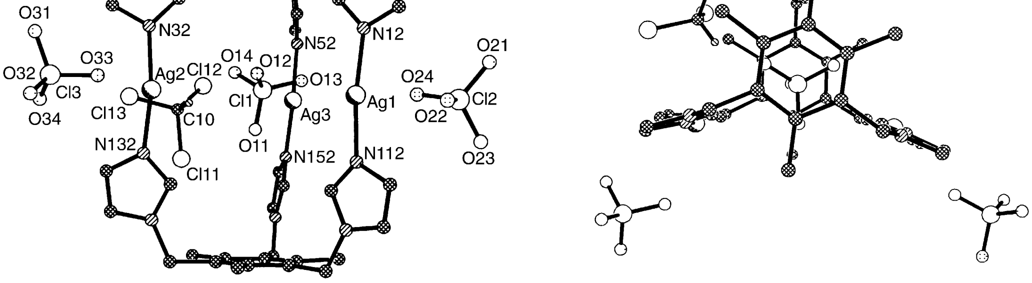


Figure 7. Side (left) and top (right) views of cage structure of **7** with one perchlorate anion encapsulated inside the cage and one chloroform molecule outside the cage.

Experimental Section

Elemental analyses were taken on a Perkin–Elmer 240C elemental analyzer, at the Center of Materials Analysis, Nanjing University. ^1H NMR spectroscopic measurements were performed on a Bruker DRX500 NMR spectrometer. Electrospray mass spectral (ES-MS) measurements were carried out on an LCQ System (Finnigan MAT) using methanol as the mobile phase. All procedures for synthesis and measurements of silver(I) complexes were carried out in the dark. $[Ag(NH_3)_2]N_3$ and $[Ag(Py)_2]NO_3$ (Py = pyridine) were prepared as described previously.[12]

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

Synthesis of $[Ag(tpba)N_3]$ (1): A solution of TPBA (36.0 mg, 0.075mmol) in methanol (15 mL) was added to an aqueous solution of freshly prepared $[Ag(NH_3)_2]N_3$ (0.075 mmol mL^{-1}, 1 mL), and the mixture was stirred for half an hour then filtered. Colorless crystals were obtained after the filtrate was allowed to stand for a few weeks. Yield: 53 %; elemental analysis calcd (%) for $C_{27}H_{24}AgN_9O_3$: C 51.44, H 3.84, N 19.99; found: C 51.36, H 3.83, N 19.97.

Synthesis of $[Ag_3(titmb)_2](N_3)_3 \cdot CH_3OH \cdot 4H_2O$ (2): A solution of TITMB (36.0 mg, 0.10 mmol) in methanol (15 mL) was carefully layered over an aqueous solution of freshly prepared $[Ag(NH_3)_2]N_3$ (0.075 mmol mL^{-1}, 2 mL). Colorless crystals were isolated by filtration after several weeks. Yield: 77 %; elemental analysis calcd (%) for $C_{43}H_{60}Ag_3N_{21}O_5$: C 40.52, H 4.74, N 23.08; found: C 40.56, H 4.83, N 22.95.

Synthesis of $[Ag_3(titmb)_2](CF_3SO_3)_2(OH) \cdot 5H_2O$ (3): An aqueous solution (5 mL) of $AgCF_3SO_3$ (19.3 mg, 0.075 mmol) was added slowly with constant stirring to a solution of TITMB (18.0 mg, 0.05 mmol) in methanol (20 mL) to give a clear solution. The reaction mixture was left to stand at room temperature for several weeks. Colorless crystalline was obtained. The crystals were unstable and rapidly lost solvent molecules.

Synthesis of $[Ag_3(titmb)_2][Ag(NO_3)_3]NO_3 \cdot H_2O$ (4): The compound was prepared by layering method described above for complex **2**. A buffer layer of a solution (10 mL) of methanol/chloroform/water 8:2:1 was carefully layered over an aqueous solution of $AgNO_3$ (17.0 mg, 0.1mmol) in water (3 mL). Then a solution of TITMB (18.0 mg, 0.05 mmol) in methanol (3 mL) was layered over the buffer layer. Yield: 36 %; elemental analysis calcd (%) for $C_{42}H_{50}Ag_4N_{16}O_{13}$: C 35.56, H 3.55, N 15.80; found: C 35.70, H 3.58, N 15.90.

Synthesis of $[Ag_3(titmb)_2(Py)](NO_3)_3 \cdot H_2O$ (5): The compound was prepared by layering method. A buffer layer of a solution (10 mL) of methanol/pyridine/water 4:1:1 was carefully layered over an aqueous solution of freshly prepared $[Ag(Py)_2]NO_3$ (0.025 mmol mL^{-1}, 3 mL). Then a solution of TITMB (18.0 mg, 0.05 mmol) in methanol (3 mL) was layered over the buffer layer. Single crystals appeared after several weeks. Yield: 61 %; elemental analysis calcd (%) for $C_{47}H_{55}Ag_3N_{16}O_{10}$: C 42.52, H 4.18, N 16.88; found: C 42.60, H 4.24, N 16.83.

Synthesis of $[Ag_3(titmb)_2(Py)](ClO_4)_3$ (6): The compound was prepared by layering method. A buffer solution (10 mL) of methanol/pyridine/water 4:1:1 was carefully layered over an aqueous solution of freshly prepared $[Ag(py)_2](ClO_4)_2$ (0.025 mmol mL^{-1}, 3 mL). Then a solution of TITMB (18.0 mg, 0.05 mmol) in methanol (3 mL) was layered over the buffer layer. Yield: 67 %; elemental analysis calcd (%) for $C_{47}H_{53}Ag_3Cl_3N_{13}O_{12}$: C 39.70, H 3.76, N 12.81; found: C 39.62, H 3.72, N 12.68.

Synthesis of $[Ag_3(titmb)_2](ClO_4)_3 \cdot CHCl_3$ (7): The compound was prepared by layering method. A buffer layer of a solution (10 mL) of methanol/chloroform/water 8:2:1 was carefully layered over an aqueous solution of $AgClO_4 \cdot H_2O$ (16.9 mg, 0.075mmol) in water (3 mL). Then a solution of

Table 3. Bond lengths [Å] and angles [°] of hydrogen bonding for complexes **1**–**7**[1].

D-H···A[2]	Distance (D···A)	D-H-A	Angle (D-H-A)
$[Ag(tpba)N_3]$ (**1**)			
N1-H1···O1[a]	3.063(8)	N1-H1-O1[a]	148
$[Ag_3(titmb)_2](N_3)_3 \cdot CH_3OH \cdot 4H_2O$ (**2**)			
C12-H3···O5	3.343(8)	C12-H3-O5	159
C13-H4···O1	3.338(8)	C13-H4-O1	145
C32-H11···O5	3.303(8)	C32-H11-O5	160
C33-H12···N208	3.433(9)	C33-H12-N208	153
C52-H19···O5	3.195(8)	C52-H19-O5	150
C112-H27···O4	3.433(8)	C112-H27-O4	155
C113-H28···O1	3.312(7)	C113-H28-O1	143
C132-H35···O4	3.181(8)	C132-H35-O4	157
C133-H36···N207	3.254(9)	C133-H36-N207	137
C152-H43···O4	3.218(9)	C152-H43-O4	151
C201-H49···O3	2.399(7)	C201-H49-O3	148
C201-H50···N205	3.290(9)	C201-H50-N205	141
C201-H50···N206	2.523(8)	C201-H50-N206	132
C31-H9···N204[b]	3.372(8)	C31-H9-N204[b]	158
C31-H10···N203[c]	3.453(9)	C31-H10-N203[c]	166
C114-H29···N209[d]	3.444(9)	C114-H29-N209[d]	152
C131-H33···N204[d]	3.445(8)	C131-H33-N204[d]	146
C131-H34···[e]	3.411(8)	C131-H34-N203[e]	147
O1···N209[f]	2.75		
O1···O2	2.83		
O2···N203[g]	2.90		
$[Ag_3(titmb)_2](CF_3SO_3)_2(OH) \cdot 5H_2O$ (**3**)			
C11-H2···O10[h]	3.353(8)	C11-H2-O10[h]	159
$[Ag_3(titmb)_2][Ag(NO_3)_3]NO_3 \cdot H_2O$ (**4**)			
C12-H12···O4	3.222(15)	C12-H12-O4	130
C31-H31A···O3[i]	3.30(2)	C31-H31A-O3[i]	166
C31-H31B···O3[j]	3.30(2)	C31-H31B-O3[j]	166
$[Ag_3(tiitmb)tmb)_2(Py)](NO_3)_3 \cdot H_2O$ (**5**)			
O10-H54···O1[k]	2.813(5)	O10-H54-O1[k]	154
O10-H54···O2[k]	3.402(5)	O10-H54-O2[k]	148
O10-H55···O5[k]	2.876(5)	O10-H55-O5[k]	168
C11-H2···O3[l]	3.327(6)	C11-H2-O3[l]	139
C12-H3···O7	3.312(9)	C12-H3-O7	139
C32-H11···O7	3.294(9)	C32-H11-O7	137
C41-H15···N31	3.243(7)	C41-H15-N31	132
C61-H24···N11	3.285(7)	C61-H24-N11	126
C141-H39···N131	3.304(7)	C141-H39-N131	133
C151-H41···O2	3.242(6)	C151-H41-O2	135
C14-H5···O1[l]	3.169(6)	C14-H5-O1[l]	170
C31-H9···O4[m]	3.280(6)	C31-H9-O4[m]	151
C33-H12···O10[n]	3.411(6)	C33-H12-O10[n]	151
C34-H13···O5[m]	3.464(6)	C34-H13-O5[m]	161
C51-H17···O5[o]	3.396(6)	C51-H17-O5[o]	151
C51-H18···O3[o]	3.430(6)	C51-H18-O3[o]	157
C111-H25···O3[p]	3.323(6)	C111-H25-O3[p]	166
C114-H29···O2[p]	3.173(6)	C114-H29-O2[p]	139
C134-H37···O4[n]	3.306(6)	C134-H37-O4[n]	137
$[Ag_3(titmb)_2(Py)](ClO_4)_3$ (**6**)			
C52-H52···O5	3.306(19)	C52-H52-O5	135
C34-H34···O2[q]	3.288(9)	C34-H34-O2[q]	139
C31-H31A···O4[q]	3.555(9)	C31-H31A-O4[q]	173
C14-H14···O3[r]	3.338(10)	C14-H14-O3[r]	153
$[Ag_3(titmb)_2](ClO_4)_3 \cdot CHCl_3$ (**7**)			
C10-H49···O14	3.030(10)	C10-H49-O14	148
C151-H42···[s]	3.425(8)	C151-H42-O32[s]	153
C151-H41···O22[t]	3.412(6)	C151-H41-O22[t]	164
C134-H37···O23[u]	3.418(7)	C134-H37-O23[u]	145
C53-H20···O21[v]	3.294(6)	C53-H20-O21[v]	143
C34-H13···O21[w]	3.298(6)	C34-H13-O21[w]	156
C14-H5···O33[w]	3.348(6)	C14-H5-O33[w]	148
C141-H39···N131	3.259(7)	C141-H39-N131	132
C61-H23···N11	3.292(7)	C61-H23-N11	127
C41-H16···N51	3.320(7)	C41-H16-N51	131

[1] Symmetry transformation used to generate equivalent atoms: [a] $1+x-y$, $1+x$, $-½+z$; [b] $-½+x$, $³⁄₂-y$, $1-z$; [c] $-x$, $½+y$, $³⁄₂-z$; [d] $½+x$, $³⁄₂-y$, $1-z$; [e] $1-x$, $½+y$, $³⁄₂-z$; [f] x, $-1+y$, z; [g] $½-x$, $1-y$, $-½+z$; [h] $1-x$, $-x+y$, $1-z$; [i] $½+x$, $½-y$, $-z$; [j] $½-x$, $½-y$, $½+z$; [k] $1-x$, $-y$, $½+z$; [l] $½+x$, $½-y$, $1+z$; [m] $-½+x$, $½-y$, $1+z$; [n] $-½+x$, $½-y$, z; [o] x, y, $1+z$; [p] $½+x$, $½-y$, z; [q] x, y, $1+z$; [r] $½-x$, $³⁄₂-y$, $2-z$; [s] $1-x$, $½+y$, $-½-z$; [t] $1-x$, $½+y$, $½-z$; [u] $1-x$, $1-y$, $-z$; [v] x, $³⁄₂-y$, $-½+z$; [w] $-x$, $1-y$, $-z$; [2] D: donor; A: acceptor.

TITMB (18.0 mg, 0.05 mmol) in methanol (3 mL) was layered over the buffer layer. Yield: 60%; elemental analysis calcd (%) for $C_{43}H_{49}Ag_3Cl_6N_{12}O_{12}$: C 35.32, H 3.38, N 11.50; found: C 35.37, H 3.52, N 11.54.

Crystallography: The X-ray diffraction measurements for complexes **1**, **2**, **3**, **5** and **7** were carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer at 200 K for **2**, **3**, **5** and **7** and at 100 K for **1** using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å). The structures were solved by direct methods using SIR92[14] and expanded using Fourier techniques.[15] One of nitrate ion in **5** is disordered: oxygen atoms O7, O8, and O9 have two positions with the site occupancy factors of 0.73 and 0.27, respectively. All calculations were carried out on an SGI workstation using the teXsan crystallographic software package.[16]

The data collection for complexes **4** and **6** were recorded on a Bruker Smart Apex CCD with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structures was solved by direct methods using SHELX-97[17] and refined by full-matrix least-square method anisotropically for non-hydrogen atoms except the atoms O5 and O6 in **4**. Atoms O5 and O6 in **4** have two positions with the site occupancy factors of 0.364(15) and 0.136(15), respectively. Atom Ag2 in **6** has two positions with the site occupancy factors of 0.5 and 0.5, respectively. Calculations were performed on a PC-586 computer with the Siemens SHELXTL program package.[18]

The crystal parameters, data collection and refinement results for the compounds **1**–**7** are summarized in Table 1. Selected bond length and angles are listed in Table 2. Further details are provided in the Supporting Information.

CCDC-209336–209342 (**1**–**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

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