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Rational Synthesis and Characterization of Two Three-Dimensional Metal-Organic Frameworks Incorporating Silver Chains and 1,2,3,4,5,6-Cyclohexanehexacarboxylate

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Two new silver polycarboxylate coordination polymers, $[Ag_3(H_3L)(H_2O)_2]_n \cdot 2nH_2O$ (**1**) and $[Ag_6L(NH_3)(H_2O)_3]_n \cdot nH_2O$ (**2**), have been obtained from the reaction of $[Ag(NH_3)_2](OH)$ (freshly synthesized from Ag_2O and aqueous ammonia) with *cis,cis,cis,cis,cis*-1,2,3,4,5,6-cyclohexanehexacarboxylic acid (H_6L) by control of the molar ratio of starting materials. The X-ray crystal structure analysis reveals that both of them crystallize in the triclinic space group $P\bar{1}$ with $a = 6.375(4)$, $b = 9.505(6)$, $c = 15.097(8)$ Å, $\alpha = 93.249(14)$, $\beta = 100.364(15)$, $\gamma = 96.453(15)°$, $V = 891.4(9)$ Å^3, $Z = 2$ for **1**, and $a = 8.0380(7)$, $b = 10.1220(9)$, $c = 13.8458(12)$ Å, $\alpha = 76.3450(10)$, $\beta = 80.9370(10)$, $\gamma = 68.7230(10)°$, $V = 1016.83(15)$ Å^3, $Z = 2$ for **2**. Complex **1** features a three-dimensional (3D) metal-organic framework (MOF) with one-dimensional (1D) rectangular channels surrounded by carboxylato-supported Ag–Ag dimers, Ag–Ag chains, and half deprotonated $[H_3L]^{3-}$ ligands. Each $[H_3L]^{3-}$ ligand connects eight Ag^I atoms. The weakly coordinated water ligands and lattice water molecules are located at the channels and form interesting 1D hydrogen-bonded T4(2)8(2) water tapes with cyclic $R_8^6(16)$ $(H_2O)_8$ and $R_4^4(8)$ $(H_2O)_4$ units. Complex **2** is also a 3D MOF structure constructed by two types of Ag–Ag chains with Ag8 cluster units and linear Ag4 units, respectively, and fully deprotonated L^{6-} ligands. The silver(I) atoms in **2** exhibit linear, T-shaped, Y-shaped, and tetrahedral coordination geometries. Each L^{6-} ligand connects thirteen Ag^I atoms. The intrachain robust argentophilic interactions play a vital role in the formation of the structure.

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Introduction

The design and synthesis of metal-organic frameworks (MOFs) are of great interest because of their intriguing structural topologies and novel properties for potential applications.[1–3] In the past few decades, the development of supramolecular assembled chemistry has allowed the possibility to rationally design and prepare supramolecular architectures through noncovalent interactions, in which it is crucial to meet both geometric as well as energetic considerations.[4] Recent advances in this field have led to many periodic MOFs formed through the deliberate selection of functionalized organic ligands and coordination geometries of transition-metal ions.[5] A successful strategy in building such networks is to employ appropriate bridging ligands that can bind metal ions in different modes and provide a possible way to achieve more robust MOF structures.[6] Moreover, the recent development of self-assembled supramolecular chemistry has made it possible to rationally design and synthesize MOFs depending on the ligand geometry and coordination propensity of the metal ion, which has been proved by the reports of a large number of silver MOFs.[7]

Silver(I) ion principally exhibits linear, trigonal, and tetrahedral coordination and has high affinity for hard donor atoms such as nitrogen or oxygen atoms and soft donor atoms such as sulfur atoms, being a favorable and fashionable building block for MOFs.[8] Furthermore, silver ion is apt to form short Ag···Ag contacts as well as ligand unsupported interactions, which have been proved to be two of the most important factors contributing to the formation of such complexes and special properties.[9–11] Previous works[12,13] have proved rigid benzene-multicarboxylic acids, such as 1,4-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid, and 1,2,4,5-benzenetetracarboxylic acid, are a good choice for the construction of MOFs owing to their versatile coordination modes. However, although many benzene multicarboxylate-bridged MOFs have been reported, those on a silver(I) ion are relatively rare, probably because of their low solubility, which makes structural analyses difficult.[14–16] Compared with benzene multicarboxylic acid, cyclohexane multicarboxylic acid not only has advantages over the former such as having rich coordination modes, being the hydrogen-bond donors and acceptors as well as possessing potential high symmetries, but also

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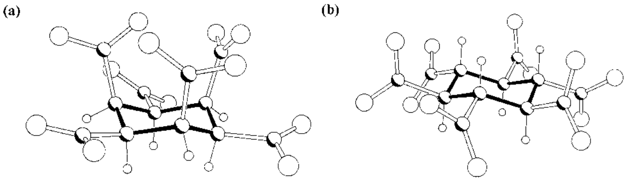
has more conformations and flexibility, which remain largely unexplored for constructing 3D MOFs. Cyclohexanedicarboxylates and cyclohexanetricarboxylates are therefore regarded as excellent candidates for the construction of multidimensional MOFs.[17] Although one could anticipate that 1,2,3,4,5,6-cyclohexanehexacarboxylic acid (H_6L) will be applied as a more flexible ligand than cyclohexanedicarboxylates and cyclohexanetricarboxylates in the construction of functional MOFs (Scheme 1), its coordination chemistry has not been explored until now. Herein, we report the creation of two interesting silver(I) complexes with robust argentophilic interactions by the self-assembled reaction of *cis,cis,cis,cis,cis*-1,2,3,4,5,6-cyclohexanehexacarboxylic acid (H_6L) with freshly synthesized $[Ag(NH_3)_2](OH)$, $[Ag_3(H_3L)(H_2O)_2]_n{\cdot}2nH_2O$ (**1**), and $[Ag_6L(NH_3)(H_2O)_3]_n{\cdot}nH_2O$ (**2**). Complex **1** is a 3D MOF with 1D rectangular channels surrounded by carboxylato-supported Ag–Ag dimers, Ag–Ag chains and half deprotonated μ_8-$[H_3L]^{3-}$ bridges, and water molecules in the channels forming interesting hydrogen-bonded water tapes of eight- and four-membered rings; while **2** is a 3D MOF constructed with two types of Ag–Ag chains with Ag8 cluster units and linear Ag4 units, respectively, and fully deprotonated μ_{13}-L^{6-} bridges.



Scheme 1. Schematic presentation of the L ligand in *cis,cis,cis,cis,cis* (a) and *trans,trans,trans,trans,trans* conformations (b).

Results and Discussion

Synthesis and Characterization

As is well known, the reactions of silver(I) ion with multicarboxylates in aqueous solution often result in the formation of insoluble ‘silver salts’, presumably because of the fast coordination of the carboxylates to silver ion to form polymer structures. Mak and co-workers pioneered the generation of polymeric structures in silver(I)-carboxylate-like complexes by using various zwitterionic betaine ligands.[18] Smith and co-workers[19] obtained a series of Ag–multicarboxylate complexes by using ammoniacal conditions to enhance the solubility of the silver carboxylates. Michaelides and co-workers[14b] reported a novel succinatodisilver(I) complex that was synthesized by gel permeation. Hence, properly tuning the reaction conditions may result in the formation of appropriate crystalline products for X-ray structural analysis. Considering this, we tried reactions of freshly synthesized $[Ag(NH_3)_2](OH)$ and the H_6L ligand in various molar ratios [Equations (1), (2), and (3)].

$$Ag_2O + 4NH_3 + 2H_2O = 2[Ag(NH_3)_2](OH) \quad (1)$$

$$3n[Ag(NH_3)_2](OH) + nH_6L + nH_2O = [Ag_3(H_3L)(H_2O)_2]_n{\cdot}2nH_2O + 6nNH_3 \quad (2)$$

$$6n[Ag(NH_3)_2](OH) + nH_6L = [Ag_6L(NH_3)(H_2O)_3]_n{\cdot}nH_2O + 2nH_2O + 11nNH_3 \quad (3)$$

We first selected the molar ratio of $[Ag(NH_3)_2](OH)/H_6L$ = 3:1, resulting in the formation of complex **1**, which possesses a 3D microporous MOF structure filled with water molecules. As anticipated, only half of the carboxylate groups are deprotonated and the others form intra- or intermolecular hydrogen-bond interactions with the deprotonated ones, which may be attributed to the *cis* conformation of the ligand. The carboxylate groups lie alternately on the axial position and on the equatorial position, which is useful for the formation of intramolecular hydrogen-bonded interactions.

As the self-assembly of the frameworks is greatly influenced by factors such as the solvent system,[3a,20a] the template,[16] the pH value of the solution,[20b,20c] and the steric requirement of the counterion,[21] some changes in the reaction conditions may result in significantly different final reaction products. The successful isolation of **1**, in which not all the carboxylate groups are deprotonated, prompted us to extend our study to change the molar ratio of $[Ag(NH_3)_2](OH)/H_6L$. As expected, when the molar ratio of $[Ag(NH_3)_2](OH)/H_6L$ was increased to 6:1, all the carboxylate groups were deprotonated and then complex **2** was obtained. Furthermore, we attempted to change the silver(I) salts and solvents such as MeOH or EtOH, and raise the pH values in order to prepare different silver MOFs. However, the same product as **2** was obtained, although the yields were somewhat different or precipitates were obtained when treated by other silver(I) salts at higher pH values, suggesting that the proper pH value and molar ratio of the reactants play a vital role in the formation of the products. It should be noted that, in our recently synthesized 3D MOFs $[M_3(trans\text{-}L)(H_2O)_6]_n$ (M = Co^{2+}, Mn^{2+}, and Fe^{2+}; $[trans\text{-}L]^{6-}$ = *trans,trans,trans,trans,trans*-1,2,3,4,5,6-cyclohexanehexacarboxylate),[22] the fully deprotonated L^{6-} ligand changed its *cis* conformation to *trans* conformation under hydrothermal conditions, while in **1** and **2**, the half and fully deprotonated L ligands keep their *cis,cis,cis,cis,cis* conformation, which may be ascribed to the cooperative effect of the intraligand hydrogen-bonding interaction and the metal coordination.

Crystal Structure

X-ray crystallography has established that **1** is a 3D MOF structure with 1D rectangular channels along the *a* axis. As illustrated in part (a) of Figure 1, each asymmetric unit in **1** contains three crystallographically unique silver(I) atoms, one $[H_3L]^{3-}$ ligand, two coordinated water molecules, and two lattice water molecules, all of which lie on general positions. The selected bond lengths and angles are listed in Table 1. Noticeably, the three deprotonated carboxylate groups of each $[H_3L]^{3-}$ ligand are located at the equatorial positions and the rest at the axial positions, in agreement with the IR spectrum, where the absorption peak is at around 1720 cm^{-1} for the protonated carboxylic groups. Ag1 is coordinated in a greatly irregular geometry, by three oxygen atoms from three $[H_3L]^{3-}$ ligands [Ag1–O = 2.256(4)–2.584(4) Å, O–Ag1–O = 82.5(2)–162.4(2)°], an aqua ligand [Ag1–O1w = 2.457(5) Å, O–Ag1–O1w = 80.0(2)–116.1(2)°], as well as a Ag···Ag contact [2.916(1) Å]. The Ag1–Ag1*a* distance is significantly shorter than the van der Waals contact distance 3.40 Å,[23a] is comparable to the Ag···Ag separation (2.89 Å) in metallic silver, and twice the covalent radius of silver (1.455 Å for four-coordinate silver),[24] which provides supporting evidence for the significance of argentophilicity.[25] Similar Ag···Ag distances were found in silver benzenesulfonate (2.915 Å)[23b] and in the

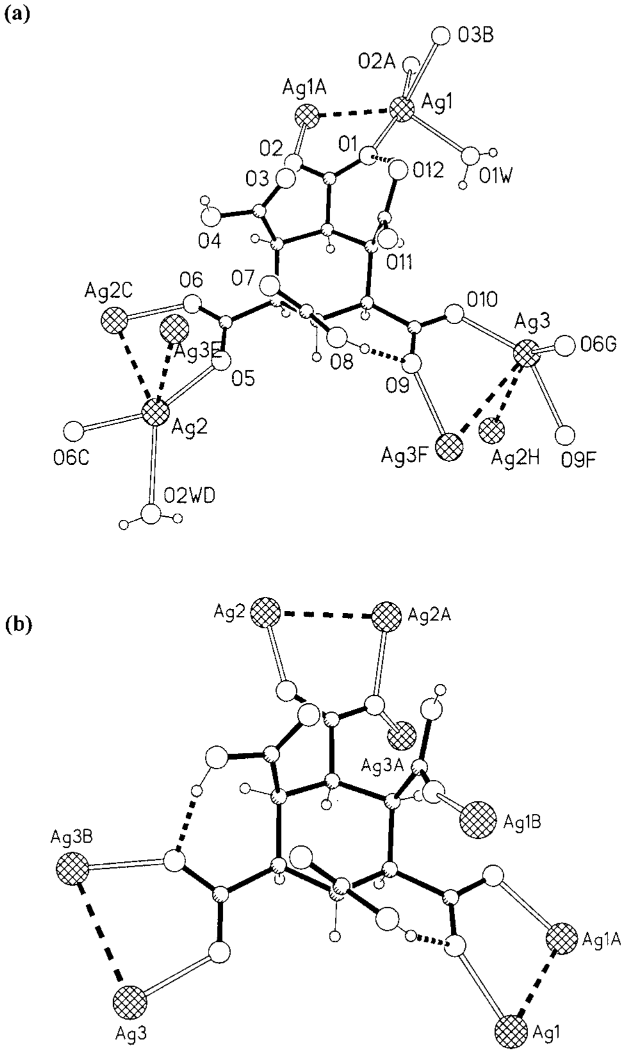


Figure 1. Perspective views showing the coordination environments of silver atoms (a) and the bridging mode of the $[H_3L]^{3-}$ ligand (b) in **1**.

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

Compound **1**			
Ag(1)–O(2*a*)	2.256(4)	Ag(3)–O(9*f*)	2.356(4)
Ag(1)–O(1)	2.267(4)	Ag(3)–O(6*g*)	2.542(5)
Ag(1)–O(1w)	2.457(5)	Ag(1)···Ag(1*a*)	2.916(1)
Ag(1)–O(3*b*)	2.584(4)	Ag(2)···Ag(2*c*)	2.916(1)
Ag(2)–O(6*c*)	2.187(4)	Ag(2)···Ag(3*e*)	3.162(1)
Ag(2)–O(5)	2.191(4)	Ag(3)···Ag(2*h*)	3.162(1)
Ag(2)–O(2w*d*)	2.632(6)	Ag(3)···Ag(3*f*)	3.329(2)
Ag(3)–O(10)	2.235(4)		
O(2*a*)–Ag(1)–O(1)	162.4(2)	O(5)–Ag(2)–O(2w*d*)	130.2(2)
O(2*a*)–Ag(1)–O(1w)	116.1(2)	O(10)–Ag(3)–O(9*f*)	142.3(2)
O(1)–Ag(1)–O(1w)	80.0(2)	O(10)–Ag(3)–O(6*g*)	115.3(2)
O(2*a*)–Ag(1)–O(3*b*)	82.5(2)	O(9*f*)–Ag(3)–O(6*g*)	85.0(2)
O(1)–Ag(1)–O(3*b*)	106.5(2)	Ag(2*c*)–O(6)···Ag(3*i*)	91.2(2)
O(1w)–Ag(1)–O(3*b*)	87.5(2)	Ag(2*c*)···Ag(2)···Ag(3*e*)	77.56(3)
O(6*c*)–Ag(2)–O(5)	153.8(2)	Ag(2*h*)···Ag(3)···Ag(3*f*)	62.89(2)
O(6*c*)–Ag(2)–O(2w*d*)	74.5(2)		
Compound **2**			
Ag(1)–O(1*a*)	2.213(3)	Ag(5)–O(4*g*)	2.193(3)
Ag(1)–O(1w)	2.340(4)	Ag(6)–N(1)	2.125(4)
Ag(1)–O(3)	2.397(3)	Ag(6)–O(11)	2.135(3)
Ag(1)–O(1)	2.587(3)	Ag(6)–O(10*i*)	2.528(3)
Ag(2)–O(2*c*)	2.196(3)	Ag(1)···Ag(2*b*)	3.0938(6)
Ag(2)–O(2w)	2.320(4)	Ag(1)···Ag(1*a*)	3.3396(8)
Ag(2)–O(5)	2.335(3)	Ag(2)···Ag(2*d*)	3.336(1)
Ag(3)–O(3*e*)	2.229(3)	Ag(3)···Ag(5*f*)	2.9040(6)
Ag(3)–O(3w)	2.344(4)	Ag(3)···Ag(4)	3.1645(6)
Ag(3)–O(7)	2.354(3)	Ag(4)···Ag(6*e*)	2.9438(5)
Ag(3)–O(6)	2.400(3)	Ag(4)···Ag(5*f*)	3.1282(6)
Ag(4)–O(12*e*)	2.166(3)	Ag(4)···Ag(5*e*)	3.3159(6)
Ag(4)–O(7*f*)	2.204(3)	Ag(5)···Ag(5*g*)	3.1160(8)
Ag(4)–O(9)	2.502(3)	Ag(5)···Ag(6)	3.1310(6)
Ag(5)–O(8)	2.176(3)	Ag(6)···Ag(6*j*)	3.2021(8)
O(1*a*)–Ag(1)–O(1w)	132.8(1)	Ag(4*f*)–O(7)–Ag(3)	125.9(1)
O(1*a*)–Ag(1)–O(3)	134.0(1)	Ag(2*b*)···Ag(1)···Ag(1*a*)	125.76(2)
O(1w)–Ag(1)–O(3)	93.2(1)	Ag(1*b*)···Ag(2)···Ag(2*d*)	106.84(2)
O(1*a*)–Ag(1)–O(1)	92.2(1)	Ag(5*f*)···Ag(3)···Ag(4)	61.88(1)
O(1w)–Ag(1)–O(1)	100.8(1)	Ag(6*e*)···Ag(4)···Ag(5*f*)	116.21(2)
O(3)–Ag(1)–O(1)	75.6(1)	Ag(6*e*)···Ag(4)···Ag(3)	160.47(2)
O(2*c*)–Ag(2)–O(2w)	135.3(1)	Ag(5*f*)···Ag(4)···Ag(3)	54.96(1)
O(2*c*)–Ag(2)–O(5)	136.0(1)	Ag(6*e*)···Ag(4)···Ag(5*e*)	59.67(1)
O(2w)–Ag(2)–O(5)	87.7(1)	Ag(5*f*)···Ag(4)···Ag(5*e*)	57.75(2)
O(3*e*)–Ag(3)–O(3w)	126.7(1)	Ag(3)···Ag(4)···Ag(5*e*)	112.31(1)
O(3*e*)–Ag(3)–O(7)	139.1(1)	Ag(3*f*)···Ag(5)···Ag(5*g*)	126.77(2)
O(3w)–Ag(3)–O(7)	93.9(1)	Ag(3*f*)···Ag(5)···Ag(4*f*)	63.15(1)
O(3*e*)–Ag(3)–O(6)	92.9(1)	Ag(5*g*)···Ag(5)···Ag(4*f*)	64.15(2)
O(3w)–Ag(3)–O(6)	104.6(1)	Ag(3*f*)···Ag(5)···Ag(6)	121.92(2)
O(7)–Ag(3)–O(6)	79.0(1)	Ag(5*g*)···Ag(5)···Ag(6)	111.25(2)
O(12*e*)–Ag(4)–O(7*f*)	161.7(1)	Ag(4*f*)···Ag(5)···Ag(6)	168.66(2)
O(12*e*)–Ag(4)–O(9)	97.7(1)	Ag(3*f*)···Ag(5)···Ag(4*h*)	171.34(2)
O(7*f*)–Ag(4)–O(9)	100.6(1)	Ag(5*g*)···Ag(5)···Ag(4*h*)	58.10(1)
O(8)–Ag(5)–O(4*g*)	166.5(1)	Ag(4*f*)···Ag(5)···Ag(4*h*)	122.25(2)
N(1)–Ag(6)–O(11)	170.1(2)	Ag(6)···Ag(5)···Ag(4*h*)	54.25(1)
N(1)–Ag(6)–O(10*i*)	93.5(1)	Ag(4*h*)···Ag(6)···Ag(5)	66.08(1)
O(11)–Ag(6)–O(10*i*)	94.9(1)	Ag(4*h*)···Ag(6)···Ag(6*j*)	89.51(2)
Ag(1*a*)–O(1)–Ag(1)	87.8(1)	Ag(5)···Ag(6)···Ag(6*j*)	154.36(2)
Ag(3*h*)–O(3)–Ag(1)	114.0(1)		

[a] Symmetry codes for **1**: *a*) –*x* + 1, –*y* + 2, –*z*; *b*) –*x*, –*y* + 2, –*z*; *c*) –*x*, –*y* + 3, –*z* – 1; *d*) *x*, *y* + 1, *z*; *e*) –*x*, –*y* + 1, –*z*; *f*) –*x* – 1, –*y* + 1, –*z* – 1; *g*) *x* – 1, *y* – 1, *z*; *h*) *x*, *y* – 1, *z*; *i*) *x* + 1, *y* + 1, *z*. For **2**: *a*) –*x* + 2, –*y* + 3, –*z*; *b*) –*x* + 3, –*y* + 2, –*z*; *c*) *x* + 1, *y* – 1, *z*; *d*) –*x* + 4, –*y* + 2, –*z*; *e*) *x* + 1, *y*, *z*; *f*) –*x* + 4, –*y* + 3, –*z* – 1; *g*) –*x* + 3, –*y* + 3, –*z* – 1; *h*) *x* – 1, *y*, *z*; *i*) –*x* + 3, –*y* + 4, –*z* – 1; *j*) –*x* + 2, –*y* + 4, –*z* – 1; *k*) *x* – 1, *y* + 1, *z*.

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succinatodisilver complex (2.938 and 3.104 Å).[14b] Ag2 adopts a slightly distorted Y-shaped geometry, coordinated by two oxygen atoms from two $[H_3L]^{3-}$ ligands [Ag2–O = 2.187(4) and 2.191(4) Å, O–Ag2–O = 153.8(2)°] and a weakly coordinated aqua ligand [Ag2–O2w = 2.632(6) Å, O–Ag2–O2w = 74.5(2) and 130.2(2)°] as well as two Ag···Ag contacts [2.916(1) and 3.162(1) Å]. Similarly, Ag3 also has a distorted Y-shaped geometry, surrounded by three oxygen atoms from three $[H_3L]^{3-}$ ligands [Ag3–O = 2.235(4)–2.542(5) Å, O–Ag3–O = 85.0(2)–142.3(2)°] as well as by two Ag···Ag contacts [3.162(1) and 3.329(2) Å]. Each $[H_3L]^{3-}$ ligand connects eight Ag^{I} atoms through one protonated carboxylic group and three deprotonated carboxylato groups with μ_2:η^1:η^1, μ_2:η^1:η^1, and μ_3:η^2:η^1 coordination modes, respectively (Figure 1, b). Two of the three protonated carboxylic groups of each $[H_3L]^{3-}$ ligand donate two strong intraligand hydrogen bonds to the deprotonated carboxylato groups, further stabilizing their *cis* conformation [O8···O9 = 2.564(6) Å, O8–H8O···O9 = 164(9)°; O12···O1 = 2.582(6) Å, O12–H12O···O1 = 160(9)°]. Moreover, there are rich intermolecular hydrogen-bond interactions between the protonated or deprotonated carboxylate groups with water molecules (Table 2). Two types of cluster units of Ag···Ag interactions exist: the carboxylato-supported Ag1···Ag1 dimer and the 1D carboxylato-supported Ag2···Ag3···Ag3···Ag2 chain unit (Figure 2, a and b). The distances of Ag2···Ag2*a*, Ag2···Ag3*a*, and Ag3···Ag3*d* are 2.916(1), 3.162(1), and 3.329(2) Å, respectively. Such robust Ag···Ag interactions make the silver(I) atoms form a silver chain running along the *a* axis direction supported by the μ_2- and μ_3-carboxylate bridges. These dimeric motifs and 1D Ag···Ag chains are connected by the $[H_3L]^{3-}$ ligands into an open MOF having a rectangular channel along the *a* axis direction (Figure 2, c). Water molecules are located at these channels and form 1D hydrogen-bonded water tapes[26] (Figure 3, a, b). There are cyclic $R^{6}_{8}(16)$ $(H_2O)_8$ and $R^{4}_{4}(8)$ $(H_2O)_4$ units with two water molecules shared between the adjacent circles, leading to a T4(2)8(2) water tape. The water tapes further donate hydrogen bonds to the deprotonated carboxylate groups of the host [O···O 2.738(7)–3.161(8) Å] (Table 2). Each water molecule is tetrahedrally surrounded by four hydrogen bonds or three hydrogen bonds and one Ag–H_2O coordination bond (Figure 3, b). Other interesting water chains and tapes have been observed in MOF structures of $[(H_2O)_2\subset\{Ni(Hsglu)(H_2O)_2\}]\cdot H_2O$ [Hsglu = *N*-(2-hydroxybenzyl)-l-glutamic acid],[27a] apdo·$4H_2O$ (apdo = *trans*-4,4′-azopyridine dioxine),[27b] [Co(tartarate)(2,2′-bipy)·$5H_2O$],[27c] [Cu(DPA)(CO_3)]·$3H_2O$ (DPA = 2,2′-dipyridylamine),[27d] $[Fe(2,2'\text{-bipy})_2(CN)_2]\cdot$

Table 2. Geometrical parameters of hydrogen bonds for **1** and **2**.[a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
Compound **1**				
O(4)–H(4O)···O(4w*b*)	0.85(1)	1.89(3)	2.731(6)	168(13)
O(8)–H(8O)···O(9)	0.85(1)	1.74(3)	2.564(6)	164(9)
O(12)–H(12O)···O(1)	0.85(1)	1.77(3)	2.582(6)	160(9)
O(1w)–H(1wa)···O(2w)	0.85(1)	2.08(3)	2.905(9)	163(8)
O(1w)–H(1wb)···O(3w)	0.85(1)	1.99(4)	2.775(7)	154(9)
O(2w)–H(2wa)···O(11*d*)	0.85(1)	1.90(3)	2.738(7)	168(13)
O(2w)–H(2wb)···O(4w*e*)	0.85(1)	2.34(3)	3.161(8)	162(8)
O(3w)–H(3wa)···O(2*c*)	0.85	2.12	2.923(6)	157.9
O(3w)–H(3wb)···O(1w*f*)	0.85	2.02	2.790(7)	151.7
O(4w)–H(4wa)···O(3w)	0.85	2.01	2.817	159.1
O(4w)–H(4wb)···O(2*a*)	0.85	2.17	3.008(6)	170.7
Compound **2**				
O(1w)–H(1wa)···O(4w)	0.85(1)	1.94(1)	2.772(5)	166(5)
O(1w)–H(1wb)···O(5)	0.85(1)	1.90(2)	2.734(5)	168(7)
O(2w)–H(2wa)···O(6*c*)	0.85(1)	1.82(2)	2.644(5)	162(6)
O(2w)–H(2wb)···O(4w)	0.85(1)	1.98(2)	2.811(6)	165(8)
O(3w)–H(3wa)···O(9*d*)	0.85(1)	1.84(1)	2.675(5)	171(4)
O(3w)–H(3wb)···O(10*b*)	0.85(1)	1.93(2)	2.727(5)	157(5)
O(4w)–H(4wa)···O(4*a*)	0.85(1)	2.31(4)	3.039(5)	144(6)
O(4w)–H(4wa)···O(5*a*)	0.85(1)	2.33(4)	2.970(6)	133(5)
O(4w)–H(4wb)···O(10*g*)	0.85(1)	1.82(2)	2.650(5)	167(6)
N(1)–H(1Na)···O(2*f*)	0.89(1)	2.24(2)	3.048(5)	151(4)
N(1)–H(1Nb)···O(3w*e*)	0.90(1)	2.26(2)	3.134(6)	165(4)
N(1)–H(1Nc)···O(6*e*)	0.89(1)	2.36(3)	3.109(6)	142(4)

[a] Symmetry codes for **1**: *a*) –*x* + 1, –*y* + 2, –*z*; *b*) –*x*, –*y* + 2, –*z*; *c*) *x*, *y* – 1, *z*; *d*) *x* + 1, *y*, *z*; *c*) –*x* + 1, –*y* + 1, –*z*; *f*) –*x*, –*y* + 1, –*z*. For **2**: *a*) –*x* + 3, –*y* + 2, –*z*; *b*) *x* + 1, *y* – 1, *z*; *c*) –*x* + 4, –*y* + 2, –*z*; *d*) –*x* + 4, –*y* + 3, –*z* – 1; *e*) –*x* + 3, –*y* + 3, –*z* – 1; *f*) –*x* + 2, –*y* + 4, –*z* – 1; *g*) –*x* + 3, –*y* + 3, –*z*.

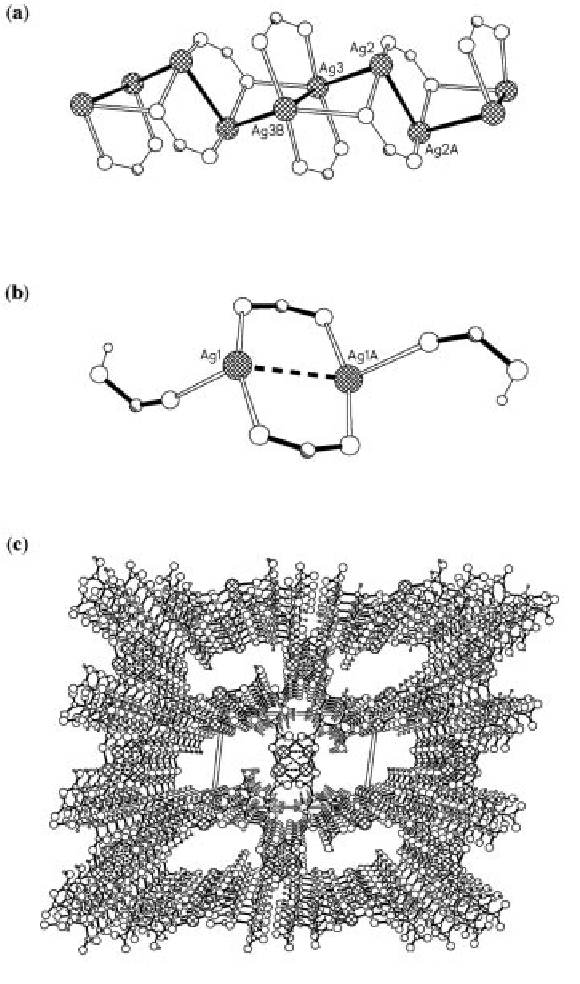

Figure 2. (a) The silver chain along the *a* axis, (b) the binuclear motif of silver atom, and (c) perspective view of the 1D channels along the *a* axis direction in **1**.

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$2.5H_2O$,[27e] and $[Co_2(ptc)(py)_2(H_2O)_4]\cdot 4H_2O$ (ptc = pyrazine-2,3,5,6-tetracarboxylate).[27f]

Complex **2** is also a 3D MOF structure with more complicated Ag···Ag interactions. As illustrated in Figure 4 (a), each asymmetric unit in **2** contains one formula unit, and therefore there are six crystallographically unique silver(I) atoms, one L^{6-} ligand, one ammonia ligand, three aqua ligands, and one lattice water molecule, all of which lie in general positions. Compared with **1**, all the carboxylate groups are deprotonated, which is in agreement with the IR spectrum with no absorption peak around 1720 cm^{-1}. Ag1 and Ag3 have similar greatly distorted tetrahedral coordination geometries. They are coordinated by three carboxylato oxygen atoms from two L^{6-} ligands [Ag1–O = 2.213(3)–2.587(3) Å, O–Ag1–O = 75.6(1)–134.0(1)°; Ag3–O = 2.229(3)–2.400(3) Å, O–Ag3–O = 79.0(1)–139.1(1)°] and an aqua ligand [Ag1–O1w = 2.340(4) Å, O–Ag1–O1w = 93.2(1)–132.8(1)°; Ag3–O3w = 2.340(4) Å, O–Ag3–O3w = 93.9(1)–126.7(1)°] as well as surrounded by two Ag···Ag contacts [3.0938(6) and 3.3396(8) Å for Ag1 and 2.9040(6) and 3.1645(6) Å for Ag3]. Ag2 is coordinated in a Y-shaped coordination geometry by two carboxylato oxygen atoms from different L^{6-} ligands [Ag2–O = 2.196(3) and 2.335(3) Å; O–Ag2–O = 136.0(1)°] and an aqua molecule [Ag2–O2w = 2.320(4), O–Ag2–O2w = 87.7(1) and 135.3(1)°] as well as two relatively weak Ag···Ag contacts

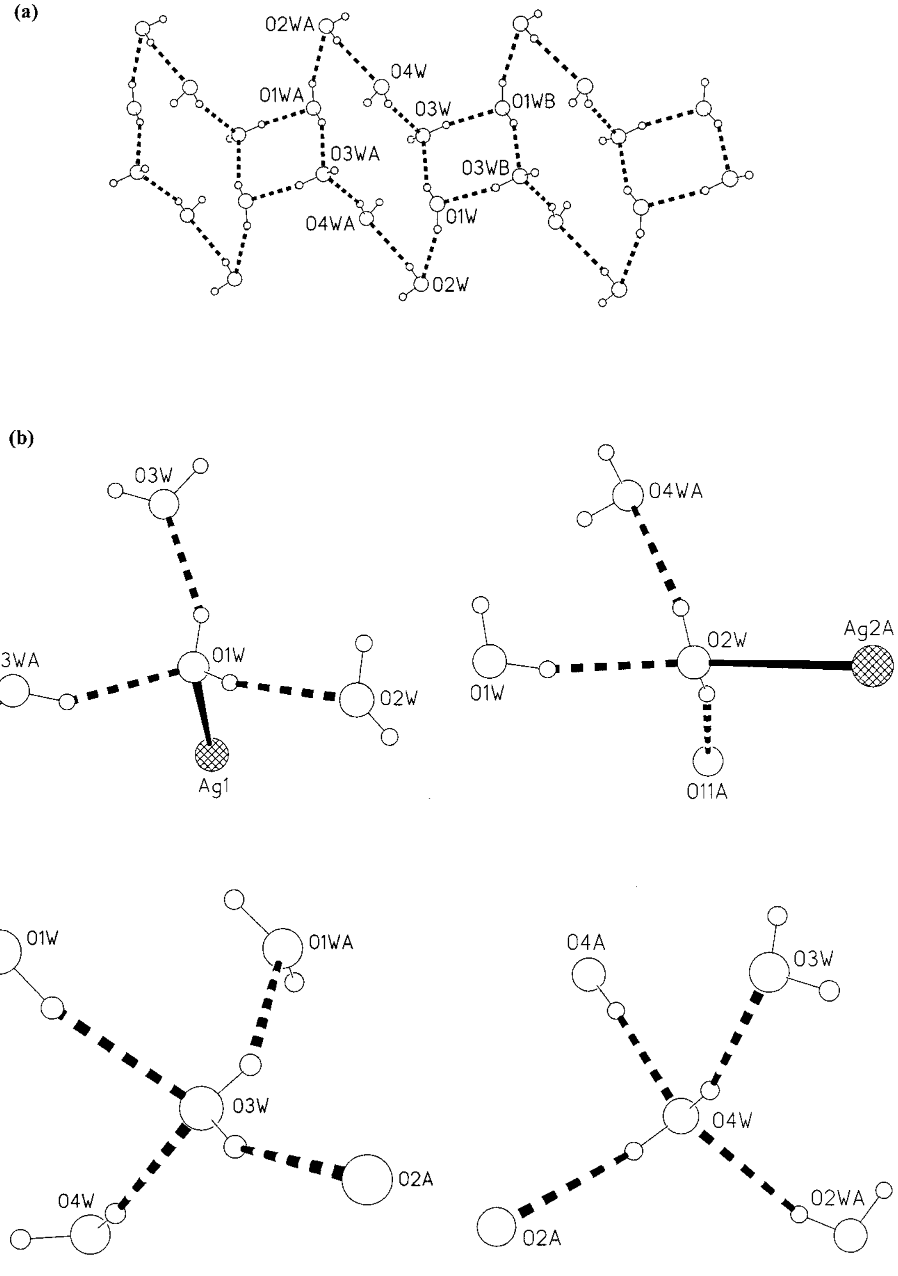

Figure 3. Perspective views showing 1D water tape (a) and the hydrogen-bonding modes of each water molecule (b) in **1**.

[Ag2···Ag1*b* = 3.0938(6) Å, Ag2···Ag2*d* = 3.336(1) Å]. Ag4 and Ag6 have similar slightly distorted T-shaped coordination geometries. Ag4 is coordinated by three carboxylato oxygen atoms from three L^{6-} ligands [Ag4–O = 2.166(3), 2.204(3), and 2.502(3) Å, O–Ag4–O = 97.7(1), 100.6(1), and 161.7(1)°], while Ag6 is coordinated by two carboxylato oxygen atoms from two L^{6-} ligands and an ammonia ligand [Ag6–O/N = 2.125(4), 2.135(3), and 2.528(3) Å, O/N–Ag6–O = 93.5(1), 94.9(1), and 170.1(2)°]. Moreover, Ag4 and Ag6 are further surrounded by four and three Ag···Ag contacts, respectively [Ag···Ag = 2.9438(6)–3.3159(6) Å for Ag4 and 2.9438(6)–3.2021(8) Å for Ag6]. Ag5 adopts a nearly linear geometry, coordinated by two oxygen atoms from different L^{6-} ligands [Ag5–O = 2.176(3) and 2.193(3) Å, O–Ag5–O = 166.5(1)°]. Interestingly, Ag5 is surrounded by five strong or weak Ag···Ag contacts [Ag···Ag = 2.9040(6)–3.3159(6) Å]. Most of these Ag···Ag interactions are slightly longer than that found in ternary silver-hexamethylenetetramine-carboxylato compounds (2.8154–2.9144 Å).[9b] Each L^{6-} ligand connects 13 silver atoms (Figure 4, b) to generate a complicated 3D MOF structure.

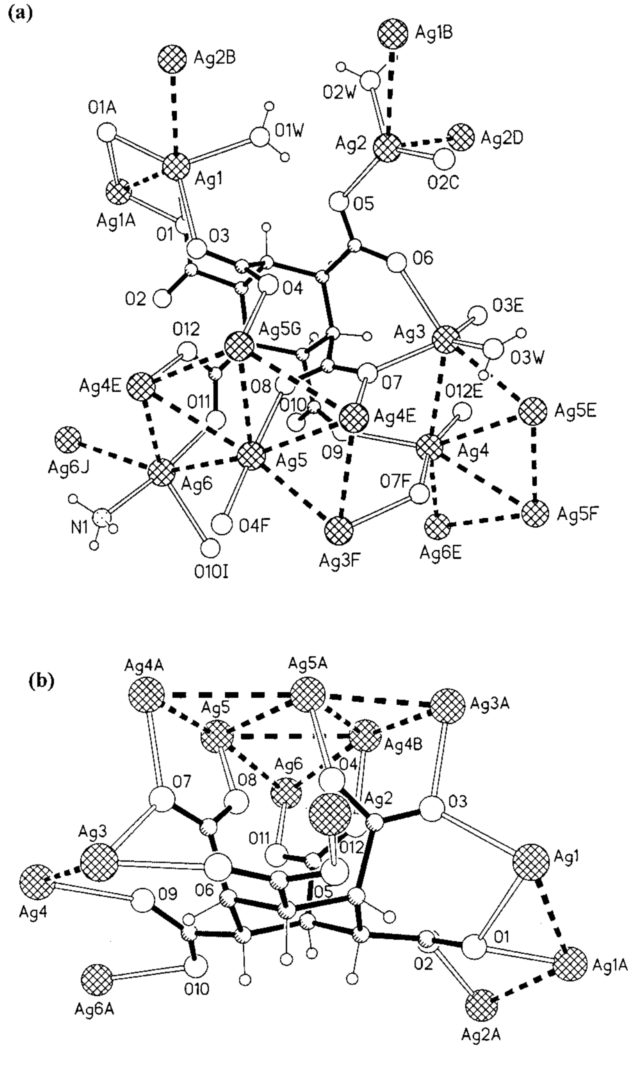

Figure 4. Perspective views showing the coordination environment of silver atoms (a) and the bridging mode of the L^{6-} ligand (b) in **2**.

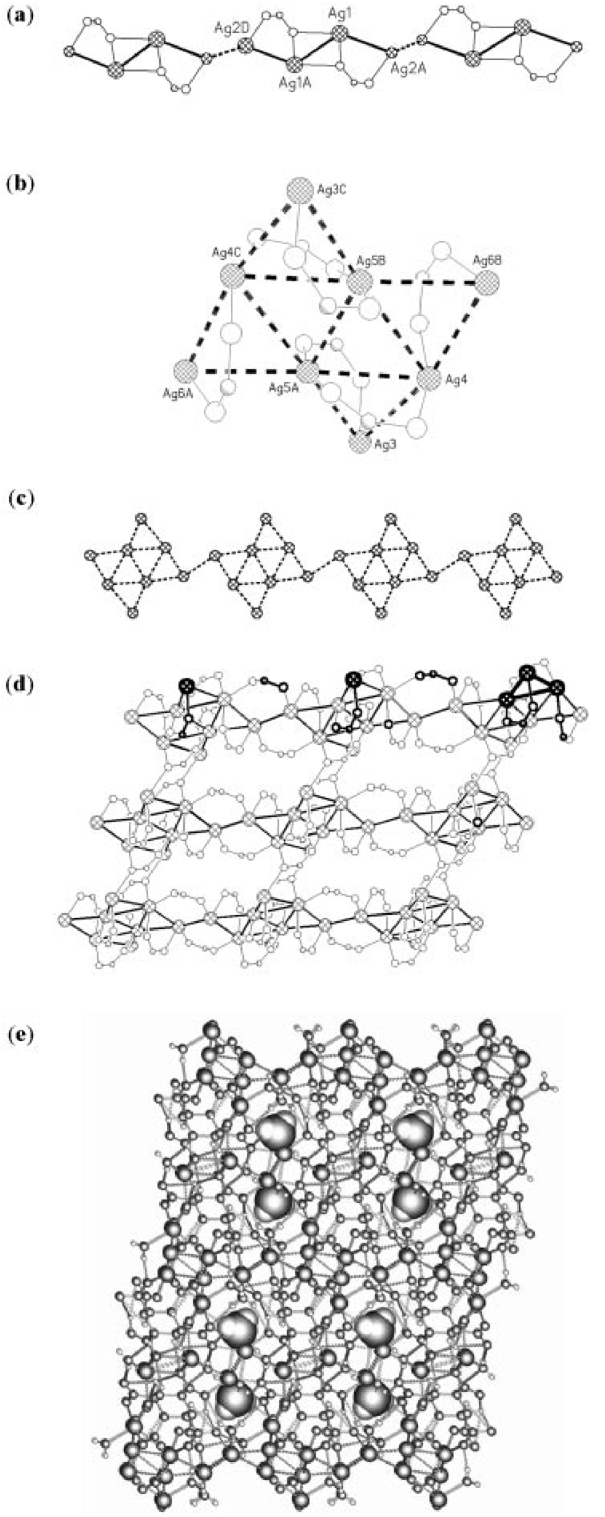

Figure 5. (a) The 1D silver chain constructed from Ag1 and Ag2 atoms by Ag···Ag interactions, (b) the Ag_8 cluster aggregated by Ag···Ag interactions, (c) the 1D silver chain constructed by Ag_8 clusters, (d) the 2D silver layer formed by the 1D silver chains and carboxylates along the *c* axis, and (e) the 3D MOF along the *b* axis direction in **2**.

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The Ag···Ag interactions in **2** are much more complicated and interesting than in compound **1**. As shown in Figure 5, the six crystallographically independent silver(I) atoms can be divided into two groups. Ag1 and Ag2 are connected by Ag···Ag interactions to generate 1D μ_3-carboxylato-supported ···Ag1···Ag1···Ag2···Ag2··· silver(I) chains running along the *b* axis (Figure 5, a), while Ag3, Ag4, Ag5, and Ag6 are aggregated by complicated μ_2-carboxylato-supported Ag···Ag interactions into 1D Ag···Ag tapes with a Ag8 cluster unit with six edge-sharing triangles (Figure 5b, c, d). Two of the six triangles constructed by Ag4, Ag4*a*, Ag5, and Ag5*a* are coplanar but others are somewhat out of the plane. The dihedral angles between this plane and the plane made of Ag3, Ag4, and Ag5*a* as well as the plane of Ag5, Ag6, and Ag4*a* by edge-sharing are 7.8 and 13.0°. Interestingly, the 1D Ag···Ag tapes are further connected by carboxylates into 2D layers along the *bc* plane (Figure 5, c), which are further extended by adjacent ···Ag1···Ag1···Ag2···Ag2··· silver(I) chains into a 3D MOF structure (Figure 5e). The lattice water molecules are located at the cavities of **2** and form rich hydrogen-bonding interactions with the MOF host [O4w···O4*a* = 3.039(5) Å, O4w–H4wa···O4*a* = 144(6)°; O4w···O5*a* = 2.970(6) Å, O4w–H4wb···O5*a* = 133(5)°; O4w···O10*g* = 2.650(5) Å, O4w–H4wb···O10*g* = 167(6)°; O1w···O4w = 2.772(5) Å, O1w–H1wa···O4w = 166(5)°; O2w···O4w = 2.811(6) Å, O2w–H2wb···O4w = 165(8)°].

Thermogravimetric Analysis

In order to examine the thermal stabilities of the porous networks, we carried out thermogravimetric (TG) analyses and measurement of the XPRD patterns to confirm the purity of the two complexes (Figure 6). Samples of the complexes were heated to 600 °C with exposure to air. The TGA curve (Figure 7) of **1** shows that the first weight loss of 5.1% between 20 and 68 °C corresponds to a loss of the included water molecules (calculated: 4.9%), while the second weight loss of 2.4% between 68 and 93 °C is in accordance with the loss of one coordinated water molecule per unit cell (calculated: 2.5%), and the succeeding weight loss of 2.8% corresponds to another coordinated water molecule between 93 and 175 °C (calculated: 2.5%). Complex **1** began to decompose at 190 °C to yield the residue Ag_2O at about 450 °C (found: 43.4%; calculated: 46.9%). The TGA curve of **2** shows that the first weight loss of 4.5% between 50 and 110 °C corresponds to the gradual loss of one included molecule, one coordinated water, and one coordinated ammonia molecule or two coordinated water molecules per unit cell (calculated: 4.8%), while the remaining water molecules were completely removed at 225 °C. Complex **2** began to decompose at 230 °C to yield the residue Ag_2O at about 455 °C (found: 61.3%; calculated: 64.5%). Powder XRD patterns (Figure S2 in the Supporting Information) of the dehydrated samples of **1** and **2** indicate that removal of the guest molecules causes a significant structural change of crystalline to amorphous to the framework of **1** and **2**.

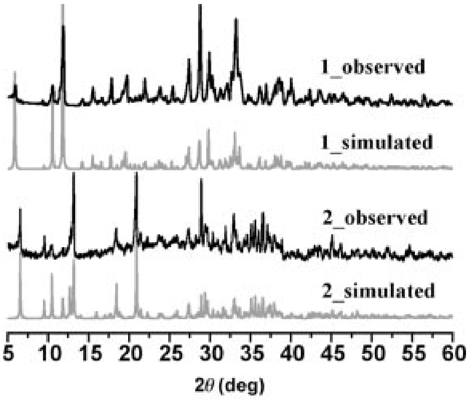

Figure 6. Observed (black) and calculated (gray) powder X-ray diffraction patterns for **1** and **2**.

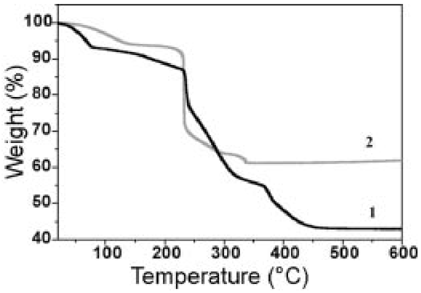

Figure 7. TG analyses for **1** (black) and **2** (gray).

Conclusion

Two new silver(I) compounds incorporating *cis*,*cis*,*cis*,*cis*,*cis*,*cis*-1,2,3,4,5,6-cyclohexanehexacarboxylic acid (H_6L) have been successfully obtained, by controlling the molar ratio of the self-assembled reactions, and crystallographically characterized. Rich Ag···Ag interactions and versatile coordination modes of the half or fully deprotonated ligands ($[H_3L]^{3-}$ or L^{6-}) lead to two interesting microporous MOFs. Our work is the first to reveal that the H_6L ligand is characteristic of multifunctional coordination sites and pH-dependent coordination fashions and has a much more important effect on the structures of MOFs.

Experimental Section

General Remarks: The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} with a Bio-Rad FTS-7 spectrometer. Powder X-ray diffraction (PXRD) intensities for **1** and **2** were measured at 293 K on a Rigaku D/max-IIIA diffractometer (Cu-K_α, λ = 1.54056 Å). The crushed single-crystalline powder samples were prepared by crushing the crystals and scanned from 5 to 60° with a step of 0.1°/s.

Table 3. Crystal and structure refinement for compounds **1** and **2**.[a]

Compound	**1**	**2**
Empirical formula	$C_{12}Ag_3H_{17}O_{16}$	$C_{12}H_{17}Ag_6NO_{16}$
Formula weight	740.87	1078.49
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	triclinic (no. 2)	triclinic (no. 2)
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	6.375(4)	8.038(1)
b [Å]	9.505(6)	10.122(1)
c [Å]	15.097(8)	13.846(1)
α [°]	96.453(15)	80.937(1)
β [°]	93.249(14)	76.345(1)
γ [°]	100.364(15)	68.723(1)
V [Å^3]	891.4(9)	1016.8(2)
Z	2	2
Calculated density [g/cm^3]	2.768	3.522
Absorption coefficient [mm^{-1}]	3.363	5.753
$F(000)$	716	1012
Crystal size [mm]	0.17 × 0.17 × 0.14	0.18 × 0.12 × 0.05
θ range for data collection [°]	2.2–27.0	2.2–26.0
Limiting indices	$-8 \le h \le 7$, $-11 \le k \le 12$, $-19 \le l \le 16$	$-9 \le h \le 9$, $-12 \le k \le 12$, $-16 \le l \le 17$
Reflections collected/unique	6378/3635	7866/3894
Completeness	93.9% (θ_{max} = 27.0°)	97.4% (θ_{max} = 26.0°)
Absorption correction	multiscan (SADABS; Bruker, 2002)	multiscan (SADABS; Bruker, 2002)
Max. and min. transmission	0.6521/0.5922	0.7619/0.4241
Refinement method	full-matrix least-square on F^2	full-matrix least-square on F^2
Data/restraints/parameters	3635/16/321	3894/18/359
Goodness-of-fit on F^2	1.026	1.064
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0454$, $wR_2 = 0.1132$	$R_1 = 0.0270$, $wR_2 = 0.0599$
R indices (all data)	$R_1 = 0.0494$, $wR_2 = 0.1165$	$R_1 = 0.0315$, $wR_2 = 0.0618$
Largest diff. peak and hole [e/Å^3]	2.803/–1.661	0.820/–0.751

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Synthesis of 1: Excess aqueous NH_3 solution was dropped slowly into a suspension of Ag_2O (0.087 g, 0.375 mmol) in $MeCN/H_2O$ (30 mL, v/v = 2:1) with magnetic stirring for 15 min. Then the powder of the ligand *cis,cis,cis,cis,cis*-1,2,3,4,5,6-cyclohexanehexacarboxylic acid (0.092 g, 0.25 mmol) was slowly added to the former solution and stirred for 30 min after being dissolved. The resultant solution was allowed to slowly diffuse in darkness at room temperature for several weeks to give colorless needle-like crystals. The crystals were isolated by deionized water and dried in air (yield 0.112 g, about 60% based on Ag). $C_{12}H_{17}Ag_3O_{16}$ (740.87): calcd. C 19.45, H 2.31; found C 19.69, H 2.34. IR (KBr) (400–4000 cm^{-1}): $\tilde{\nu}$ = 3430 m, 2903 w, 2563 w, 1916 vw, 1717 vs, 1557 vs, 1460 vs, 1385 vs, 1316 s, 1240 s, 1206 s, 1160 m, 1028 m, 994 m, 894 m, 803 m, 760 m 687 m, 618 w, 495 w cm^{-1}.

Synthesis of 2: Complex **2** was prepared as described for **1** by only changing the molar ratio of Ag_2O to H_6L ligand from 1.5:1 to 3:1. Colorless prism-like crystals were isolated by deionized water and dried in air (yield 0.135 g, about 80% based on Ag). $C_{12}H_{17}Ag_6NO_{16}$ (1078.49): calcd. C 13.36, H 1.59, N 1.30; found C 13.47, H 1.58, N 1.22. IR (KBr) (400–4000 cm^{-1}): $\tilde{\nu}$ = 3354 m, 3320 m, 3259 m, 3181 m, 1545 vs, 1386 vs, 1319 s, 1203 m, 1166 m, 1032 w, 994 w, 916 w, 844 m, 767 m, 692 m, 591 m, 523 w cm^{-1}.

X-ray Crystallographic Study: Single crystals of complexes **1** and **2** with approximate dimensions 0.21 × 0.20 × 0.14 mm^3 (**1**) and 0.20 × 0.30 × 0.26 mm^3 (**2**) were used for X-ray diffraction analyses. The crystals were mounted on the end of a thin glass fiber using an inert epoxy gel. Data collection of **1** and **2** was performed with Mo-K_α radiation (λ = 0.71073 Å) with a Bruker Apex CCD diffractometer at 123(2) K. The raw data frames were integrated with SAINT$^+$, which also applied corrections for Lorentz and polarization effects. Absorption corrections were applied by using the multiscan program SADABS.[28] The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program.[29] Hydrogen atoms on organic ligands were generated by the riding mode (C–H bond length: 0.98 Å); the water, hydroxy, and ammonia hydrogen atoms were located from difference maps, and refined with nominal geometric restraints [O–H 0.85(1), N–H 0.90 Å]. Selected bond lengths and bond angles are listed in Table 1. A summary of the crystal data is given in Table 3.

CCDC-291579 (for **1**) and -291580 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (for details see the footnote on the first page of this article): The supporting information contains the IR spectra for compounds **1** and **2**, and the powder XRD of the dehydrated samples of **1** and **2**.

Acknowledgments

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