Syntheses, Crystal Structures and Electrospray Mass Spectra of Coordination Polymers of an *N*,*N*′-Bis(3-pyridylmethyl)-1,4-benzenebis(methylamine) Ligand and Silver(I) Salts

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Four new coordination frameworks $\{[Ag_2(L1)](NO_3)_2\cdot 2H_2O\}_n$ (**1**), $\{[Ag(L1)](CF_3COO)\cdot 2.5H_2O\}_n$ (**2**), $\{[Ag_2(L1)_2][1,4\text{-}C_6H_4(COO)_2]\cdot 7H_2O\}_n$ (**3**) and $\{[Ag(L1)]ClO_4\}_n$ (**4**) were obtained by the reaction of *N*,*N*′-bis(3-pyridylmethyl)-1,4-benzenebis(methylamine) (L1) with the corresponding silver(I) salts. X-ray diffraction analyses reveal that complex **1** has an infinite 1D chain structure, in which L1 acts as a tetradentate ligand. Complexes **2**, **3** and **4** have 2D network structures, and the L1 ligands in these complexes adopt two different coordination modes: one kind of ligand coordinates four silver(I) atoms using its four N atoms, and the other kind of ligand connects only two silver(I) atoms with the two N atoms of the benzenebis(methylamine) unit, while the pyridine units remain free of coordination. Complex $\{[Ag(L2)]ClO_4\}_n$ (**5**) was synthesized by reaction of *N*,*N*′-bis(3-pyridylmethyl)-1,4-benzenebis(methyleneamine) (L2) with silver(I) perchlorate. It has a novel 1D chain structure, which is different from that of **4** due to the different flexibility of the ligands L1 and L2. All of these complexes form 2D or 3D structures stabilized by hydrogen bonding, C–H···π and π-π interactions. The results revealed that the nature of the counteranions and the flexibility of the ligand have an impact on the structure of the supramolecular architectures. The complexes were also characterized by electrospray mass spectrometry.

Introduction

The crystal engineering of coordination polymeric networks based on multidentate ligands is a growing area of coordination and supramolecular chemistry. Many efforts have been devoted to the use of flexible ligands to achieve supramolecular arrays, due to the unpredictable nature of such systems.[1] A variety of networks can be expected since the flexible ligands can adopt different conformations according to the different geometry requirements of the metal ions.[2] It has been reported that chain-like bidentate ligands have the ability to form unique interwoven extended structural motifs such as polycatenanes, polyrotaxanes and helices.[3] Compared with bidentate ligands, long chain-like multidentate ligands are less documented. The silver(I) ion exhibits a diverse coordination geometry due to its variable coordination number. When flexible ligands react with silver(I) salts, interesting and unusual structures are often generated, such as helices, boxes, and brick walls.[4]

In our laboratory, we focus our attentions on the reactions of silver(I) salts with flexible multidentate ligands based on (pyridylmethyl)amine or (pyridylmethylene)amine groups linked by an ethylene spacer (e.g. L3−L6 in Scheme 1), and have obtained various frameworks with interesting structures.[5] For example, 1,2-bis(4′-pyridylmethyleneamino)ethane (L5) reacts with AgOTf or $AgNO_3$ to give a double-stranded helix chain and a 2D network, respectively.[5a] In order to further study the influence of multidentate organic ligands on the formation of the resultant structures, we use two multidentate ligands *N*,*N*′-bis(3-pyridylmethyl)-1,4-benzenebis(methylamine) (L1) and *N*,*N*′-bis(3-pyridylmethyl)-1,4-benzenebis(methylene)amine (L2) (Scheme 1) in this study. In these two ligands, a 1,4-benzenedimethyl or 1,4-benzenedimethylene group was employed, instead of the ethylene group of L3−L6, to examine the influence of the size and flexibility of the spacer group on the structure of the frameworks. Five non-interpenetrated complexes, $\{[Ag_2(L1)](NO_3)_2\cdot 2H_2O\}_n$ (**1**), $\{[Ag(L1)](CF_3COO)\cdot 2.5H_2O\}_n$ (**2**), $\{[Ag_2(L1)_2][1,4\text{-}C_6H_4(COO)_2]\cdot 7H_2O\}_n$ (**3**), $\{[Ag(L1)]ClO_4\}_n$ (**4**) and $\{[Ag(L2)]ClO_4\}_n$ (**5**) were synthesized by reactions of L1 and L2 with the corresponding silver(I) salts. The complexes

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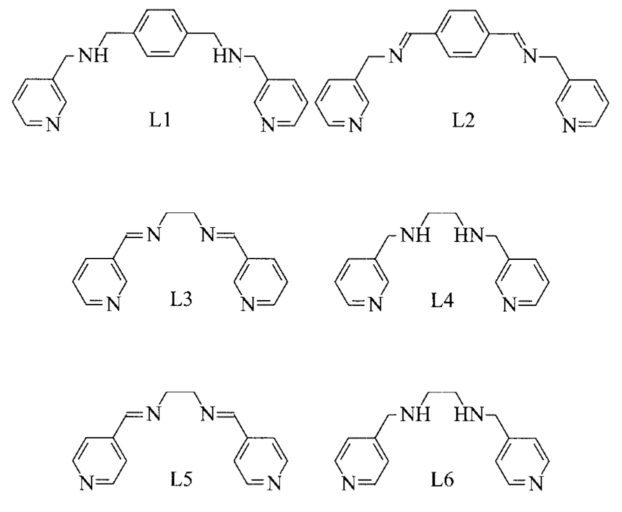
were also characterized by crystal structure and electrospray mass spectrometry.



Scheme 1. Schematic drawing of pyridine-containing ligands L1−L6

Results and Discussion

Preparation of Compounds

The title complexes were readily prepared by reaction of L1 or L2 with silver(I) salts in the dark by layering (**1** and **3**), slow evaporation (**2** and **4**) and diffusion (**5**) methods at room temperature. The elemental analyses and X-ray crystal structure analyses confirmed the chemical formulation of these complexes. The complexes of L1 with different anions were found to show remarkable differences in solubility. Complex **2**, with the CF_3COO^- anion, is soluble in organic solvents such as methanol, ethanol, acetonitrile and has moderate solubility in water, while **1**, **3** and **4** are almost insoluble in water and have low solubility in organic solvents. Complex **5**, with L2, has almost no solubility in water and methanol but reasonable solubility in acetonitrile.

Crystal Structure Description

$\{[Ag_2(L1)](NO_3)_2{\cdot}2H_2O\}_n$ (1)

When the flexible ligand L1 reacts with silver(I) nitrate, a new coordination polymer **1** is obtained and its structure was determined by X-ray crystallography. As shown in Figure 1a, the asymmetric unit of **1** consists of half a molecule of $[Ag_2(L1)](NO_3)_2]{\cdot}2H_2O$. Each silver(I) atom is coordinated by two N atoms with an almost linear coordination geometry [N−Ag−N bond angle is 156.97(9)°, Table 1], one of which is from the benzenedimethylamine unit and the other one is from the pyridine unit of another L1 ligand. Each L1 ligand, in turn, coordinates four silver(I) atoms to generate an infinite 1D chain structure. It is noteworthy that C−H···π interactions[6] associate the 1D chains into a 2D network structure as illustrated in Figure 1b. Such an interaction occurs between the hydrogen atom (H5) bound to C10 (methylene directly attached to the benzene ring) and the pyridine group of a neighboring chain. The C10−H5−X (X refers to the centroid of the pyridine group) angle is 117° and the H···X distance is 2.88 Å. From the crystal-packing diagram of **1** (Figure S1 in the Supporting Information), it can be seen that the nitrate anions are connecting 2D cationic sheets through four C−H···O hydrogen bonds to form a 3D framework. The solvated water molecules are located in the 3D structure by forming one N−H···O(water) hydrogen bond with a cationic chain and three (water)O−H···O(nitrate anion) hydrogen bonds. The hydrogen bonding data are summarized in Table 2.

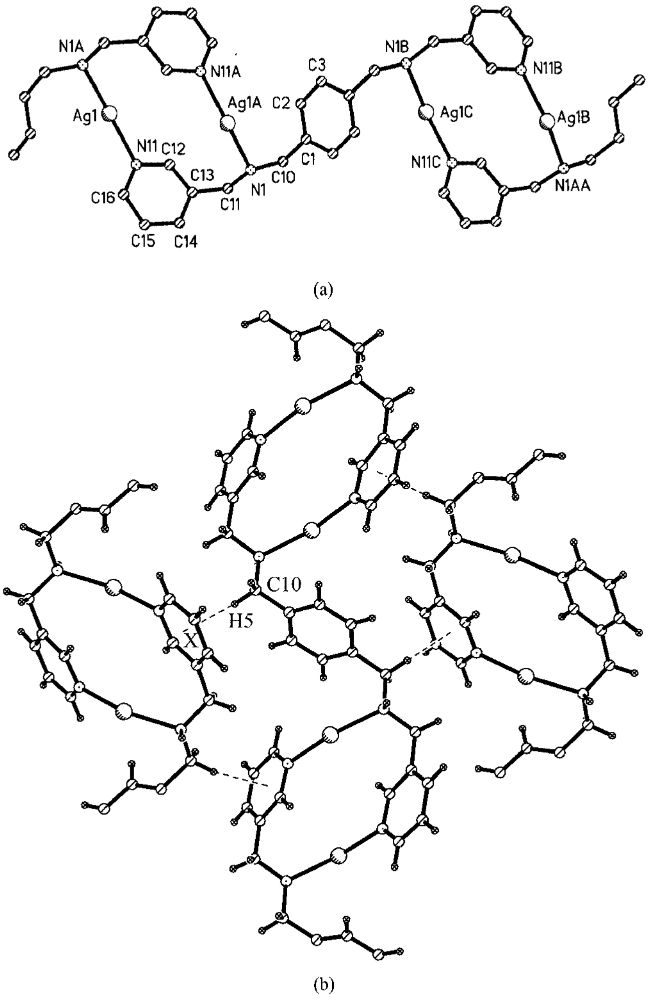


Figure 1. (a) One-dimensional chain structure of complex **1**; water molecules, hydrogen atoms and anions are omitted for clarity; (b) view of 2D cationic sheet of **1** with the C−H···π interactions indicated by dashed lines

In **1** two N atoms of each benzenebis(methylamine) unit in the L1 ligand coordinate to two Ag^I atoms, respectively, while in the reported metal complexes with ligands L3−L6 (Scheme 1) the two N atoms of each ethylenediamine or ethylenediimine unit coordinate to one metal atom in a chelate fashion.[5] This is due to the bulky and rigid 1,4-benzenedimethyl spacer in L1.

Table 1. Selected bond lengths (Å) and angles (°) for complexes **1**−**5**[a]

$\{[Ag_2(L1)](NO_3)_2\cdot 2H_2O\}_n$ (**1**)			
Ag1−N11	2.201(3)	Ag1−N1#1	2.211(3)
N11−Ag1−N1#1	156.97(9)		
$\{[Ag(L1)](CF_3COO)\cdot 2.5H_2O\}_n$ (**2**)			
Ag1−N11	2.218(3)	Ag1−N1	2.281(3)
Ag1−N101	2.314(3)		
N11−Ag1−N1	134.30(10)	N11−Ag1−N101	122.88(9)
N1−Ag1−N101	102.81(9)		
$\{[Ag_2(L1)_2][1,4\text{-}C_6H_4(COO)_2]\cdot 7H_2O\}_n$ (**3**)			
Ag1−N111	2.222(2)	Ag1−N101	2.290(2)
Ag1−N1	2.322(2)		
N111−Ag1−N101	137.67(9)	N111−Ag1−N1	122.00(9)
N101−Ag1−N1	100.33(9)		
$\{[Ag(L1)]ClO_4\}_n$ (**4**)			
Ag1−N2	2.222(2)	Ag1−N1	2.258(2)
Ag1−N11	2.436(2)		
N2−Ag1−N1	157.98(7)	N2−Ag1−N11	109.65(8)
N1−Ag1−N11	89.69(8)		
$\{[Ag(L2)]ClO_4\}_n$ (**5**)			
Ag1−N11	2.272(3)	Ag1−N2#2	2.295(3)
Ag1−N21#3	2.320(2)		
N11−Ag1−N2#2	120.34(9)	N11−Ag1−N21#3	115.84(9)
N2#2−Ag1−N21#3	116.90(9)		

[a] Symmetry transformations used to generate equivalent atoms: #1: 1 − *x*, −*y*, 1 − *z*; #2: *x*, 1 + *y*, *z*; #3: −*x*, −1 − *y*, 1 − *z*.

Table 2. Hydrogen bonding data for complexes **1**−**5**

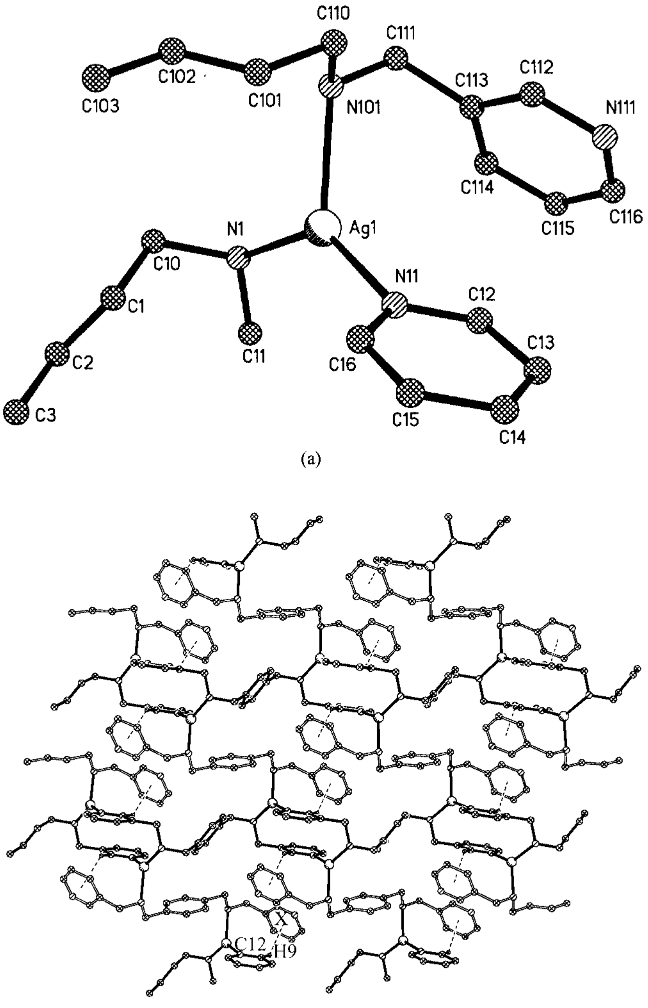
D−H···A[a]	Distance of D···A (Å)	Angle of D−H−A (°)
$\{[Ag_2(L1)](NO_3)_2\cdot 2H_2O\}_n$ (**1**)		
N1−H1···O4#1	3.030(4)	158
O4−H12···O1#2	3.108(4)	161
O4−H12···O3#2	3.015(4)	138
O4−H13···O2	2.969(4)	154
C3−H3···O3#3	3.422(5)	167
C11−H6···O1#4	3.560(5)	169
C11−H7···O3#5	3.330(5)	161
C12−H8···O2#6	3.358(4)	140
$\{[Ag(L1)](CF_3COO)\cdot 2.5H_2O\}_n$ (**2**)		
N1−H1···O3	3.036(4)	173
N101−H2···O1#7	3.096(4)	168
O3−H24···O2#5	2.851(8)	145
C14−H10···F1#8	3.349(6)	142
$\{[Ag_2(L1)_2][1,4\text{-}C_6H_4(COO)_2]\cdot 7H_2O\}_n$ (**3**)		
N1−H1···O12#9	3.141(5)	173
N101−H2···O1	3.104(5)	174
C11−H7···O2#9	3.332(6)	145
C11−H8···O2	3.438(6)	147
C110−H15···O3#7	3.245(9)	126
C110−H16···O12#9	3.349(6)	141
C111−H17···O2#7	3.377(6)	172
$\{[Ag(L1)]ClO_4\}_n$ (**4**)		
N1−H1···O2#10	2.987(9)	133
N2−H2···O3	3.122(12)	174
C3−H4···O1#11	3.386(4)	152
$\{[Ag(L2)]ClO_4\}_n$ (**5**)		
C5−H3···O2	3.359(4)	159
C6−H4···O3	3.241(4)	125
C11−H7···O4#12	3.418(4)	156
C14−H9···O1#12	3.341(4)	140
C15−H10···O4#6	3.512(4)	173

[a] Equivalent atoms generated by #1: 3/2 − *x*, −1/2 + *y*, 3/2 − *z*; #2: 2 − *x*, −*y*, 1 − *z*; #3: −1/2 + *x*, −1/2 − *y*, −1/2 + *z*; #4: −1/2 + *x*, −1/2 − *y*, 1/2 + *z*; #5: −1 + *x*, *y*, *z*; #6: 1 − *x*, −*y*, 1 − *z*; #7: 1 − *x*, −*y*, 2 − *z*; #8: 1 − *x*, 1 − *y*, 1 − *z*; #9: −*x*, −*y*, 2 − *z*; #10: −*x*, −*y*, 1 − *z*; #11: 1 + *x*, *y*, *z*; #12: 1/2 + *x*, −1/2 − *y*, 1/2 + *z*.

$\{[Ag(L1)](CF_3COO)\cdot 2.5H_2O\}_n$ (2) and $\{[Ag_2(L1)_2][1,4\text{-}C_6H_4(COO)_2]\cdot 7H_2O\}_n$ (3)

The same space group and the similar cell parameters (see Exp. Sect.) indicate that complexes **2** and **3** are isomorphous and isostructural. As a typical example, the structure of complex **2** is described here in detail. In complex **2**, the amount of disordered water molecules was confirmed by elemental analysis and thermogravimetric analysis. The TGA data of **2** show an initial weight loss of 7.6% (calcd. 7.7%) from 20 to 80 °C, representing the loss of uncoordinated water molecules; no further weight loss was observed over the temperature range 80−170 °C. The crystal structure of complex **2** (cationic part) is shown in Figure 2a with the atom numbering scheme. Each silver(I) atom is coordinated by two N atoms of the benzenebis(methylamine) units from two different L1 ligands, and one N atom of the pyridine unit of the third L1 ligand. The coordination environment of the silver(I) atom can be described as a triangle, with the N−Ag−N coordination angles varying from 102.81(9)° to 134.30(10)° (Table 1). The average Ag−N bond length of 2.271(3) Å in **2** is similar to those of reported silver(I) complexes with the same AgN_3 binding site, for example $[Ag_3(\text{py-hep})_2](ClO_4)_3\cdot 0.5CH_3CN$ [py-hep = 1,6-bis(4'-pyridyl)-2,5-diazahexane] exhibits an average Ag−N bond length of 2.297(5) and 2.314(5) Å for the two crystallographically independent silver atoms.[7] The remarkable structural feature of **2** is that the flexible ligand L1 adopts two different coordination modes at the Ag^I atoms: one kind of ligand coordinates four silver(I) atoms as a tetradentate ligand, and the other kind coordinates only two silver(I) atoms with the N atom of the benzenebis(methylamine) unit as a bidentate ligand, while the pyridine units remain free of coordination. In the reported metal complexes with L4 and L6 the ligands are all tetradentate and each ligand coordinates three different metal atoms.[5b,5d−5f] The whole structure of **2** can be described as the silver(I) atoms being bridged by the tetradentate L1 ligands to form 1D chains, which are further linked by the bidentate L1 ligands to generate a wavelike 2D network structure (Figure 2b). In each 2D sheet, there are two kinds of macrometallacyclic rings: the smaller, 12-membered one contains two Ag^I atoms and two L1 ligands and the larger, 44-membered one is made up of two bidentate L1 ligands, two tetradentate L1 ligands and four three-coordinate silver(I) atoms. In addition, the large ring adopts a "chair" conformation to make the uncoordinated pyridine groups point inside of the ring; the large void space of the 44-membered ring is filled by uncoordinated pyridine groups, which may prevent the occurrence of interpenetration. Furthermore, these uncoordinated pyridine groups are stabilized in the large ring by C−H···π interactions.[8] For example as exhibited in Figure 2b, the C12−H9−X (X refers to the centroid of the uncoordinated pyridine group) angle is 142° and the H···X distance is 2.88 Å. The wavelike 2D networks are held together by hydrogen bonds to form a 3D structure (Figure S2). The trifluoroacetate anions and water molecules are sandwiched between the cationic 2D layers and are held there by two N−H···O, one O−H···O and one C−H···F hydrogen bonds (Table 2).

Similar C−H···π interactions (the C112−H19-centroid angle is 137° and the H···centroid distance is 2.88 Å) and crystal packing were found for complex **3**. The uncoordinated 1,4-benzenedicarboxylate anions and water molecules are also located in the voids between the 2D cationic layers and 3D structure is formed by two N−H···O and five C−H···O hydrogen bonds (Figure S3, Table 2).



(a)

(b)

Figure 2. (a) Molecular structure of the asymmetric unit of complex **2**; (b) 2D cationic network structure of complex **2** with the C−H···π interactions indicated by dashed lines; the 1D chain substructure of complex **2** is indicated by solid lines, and the bidentate L1 ligands connecting the 1D chains are indicated by open lines.

{[Ag(L1)]ClO$_4$}$_n$ (4) and {[Ag(L2)]ClO$_4$}$_n$ (5)

As described above, the complex with a nitrate anion has a 1D chain structure while those with trifluoroacetate or 1,4-benzenedicarboxylate anions show a 2D network structure. To further investigate the influence of the anion on the structure of Ag^I complexes of L1, the reaction of silver(I) perchlorate with ligand L1 was carried out and complex **4** was isolated and characterized by X-ray crystallography. As shown in Figure 3a, the asymmetric unit of **4** consists of one molecule of $[Ag(L1)]ClO_4$. Each silver(I) atom is coordinated by two N atoms from the benzenebis(methylamine) units of two different L1 ligands, with an N−Ag−N angle of 157.98(7)°. In addition, an Ag−N distance of 2.436(2) Å indicates the occurrence of a weak interaction between the silver(I) atom and the N atom of the pyridine unit. Thus, the coordination environment of the silver(I) atom in **4** can be regarded as a T-shaped coordination mode, while the Ag^I atoms in **2** and **3** have a triangular coordination geometry. Similar T-shaped silver(I) atoms have been observed in Ag^I complexes with flexible bis(thioether) ligands.[4e] The L1 ligand in **4** adopts the same kind as in **2** and **3**, and in the 2D network structure of complex **4**, 12- and 44-membered macrometallacyclic rings similar to those observed in complexes **2** and **3** were also found. However, there is an obvious difference between the structures of **4** and **2** (**3**): the perchlorate anions are located in the voids of the 44-membered rings and held there through N−H···O and C−H···O hydrogen bonds (Table 2), while in the case of complexes **2** and **3**, the anions occupy the void between the 2D cationic layers. This difference in the location of the anions in **4** and **2** (**3**) is caused by the different size of the anions. $CF_3CO_2^-$ and $1,4\text{-}C_6H_4(COO)_2^{2-}$ in **2** and **3** are too large to fit in the void of the 44-membered ring, while the smaller perchlorate anion in **4** can. In addition, C−H···π interactions[9] in **4** occur between the benzene ring groups, rather than the pyridine groups observed in **2** and **3**. For example, the distance between the hydrogen atom (H5) bound to C5 (located at the benzene group of the bidentate ligand) and the centroid of the benzene group of the adjacent tetradentate ligand is 2.55 Å and the C5−H5−centroid angle is 155°. The uncoordinated pyridine rings of the bidentate ligand are parallel to each other and located above and below the 12-membered ring of the 2D network (Figure 3, b and c). The centroid-centroid separation of 3.66 Å between the uncoordinated and adjacent coordinated pyridine groups indicates the presence of π-π interactions.

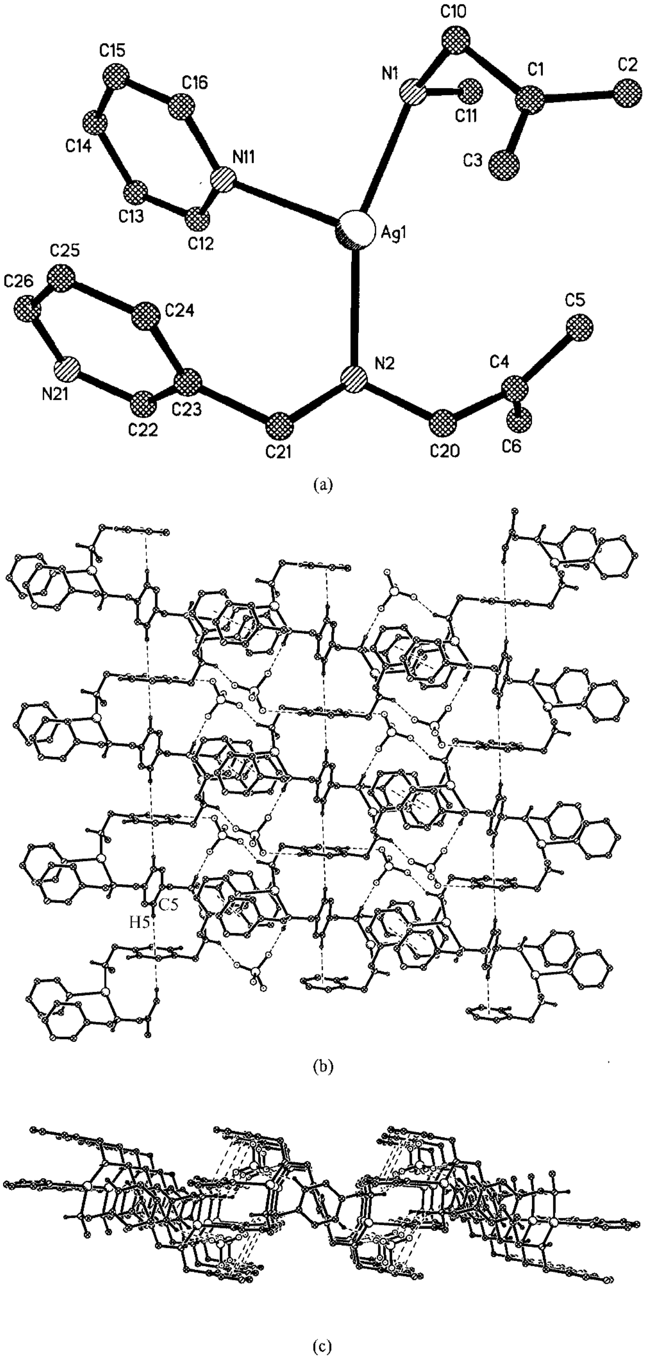


Figure 3. (a) Molecular structure of the asymmetric unit of complex **4**; (b) top and (c) side views of the 2D structure of **4** with the hydrogen bonds, π···π and C−H···π interactions indicated by dashed lines

In order to investigate the effect of the nature of the organic ligand on the structure of the complex, we prepared a Schiff-base ligand L2 by reducing the flexibility of the ligand L1. Reaction of L2 with silver(I) perchlorate gave an unexpected coordination polymer $\{[Ag(L2)]ClO_4\}_n$ (**5**) with a 1D chain structure. The coordination environment of the silver(I) atom is shown in Figure 4a with the atom numbering scheme. Each silver(I) atom in complex **5** is threefold coordinated by two pyridine N atoms from two different L2 ligands and one imine N atom of the other ligand, with Ag···N distances ranging from 2.272(3) to 2.320(2) Å and N−Ag−N bond angles in the range 115.84(9)−120.34(9)° (Table 1). There is only one kind of coordination mode for the L2 ligand in **5** as opposed to the two kinds of coordination modes for the L1 ligand in **2**, **3** and **4** as mentioned above. In addition to the 12-membered macrometallacyclic rings in **5**, which are the same as those in complexes **2**−**4**, there are also 34-membered rings formed by two L2 ligands bridging two silver(I) atoms, with an intra-ring Ag···Ag distance of 16.74 Å. These large 34-membered rings are linked by two Ag−N coordination bonds (N atom of imine group of other rings) to give the 12-membered ring and form a cationic 1D chain. It is interesting to note that three of the four N atoms of each L2 ligand participate in the coordination with three Ag^I atoms; the remaining imine N atom remains uncoordinated. In the reported metal complexes of L3 and L5, each ligand coordinates to two or three different metal atoms as bidentate, tridentate or tetradentate ligands, and the two imine N atoms in one ligand either both participate in coordination or both remain uncoordinated.[5a,5c,5e] For example, each L5 ligand in $[Cu(L5)(CH_3CN)]NO_3$ connects two Cu^I atoms using its two imine N and one pyridine N atoms, another pyridine

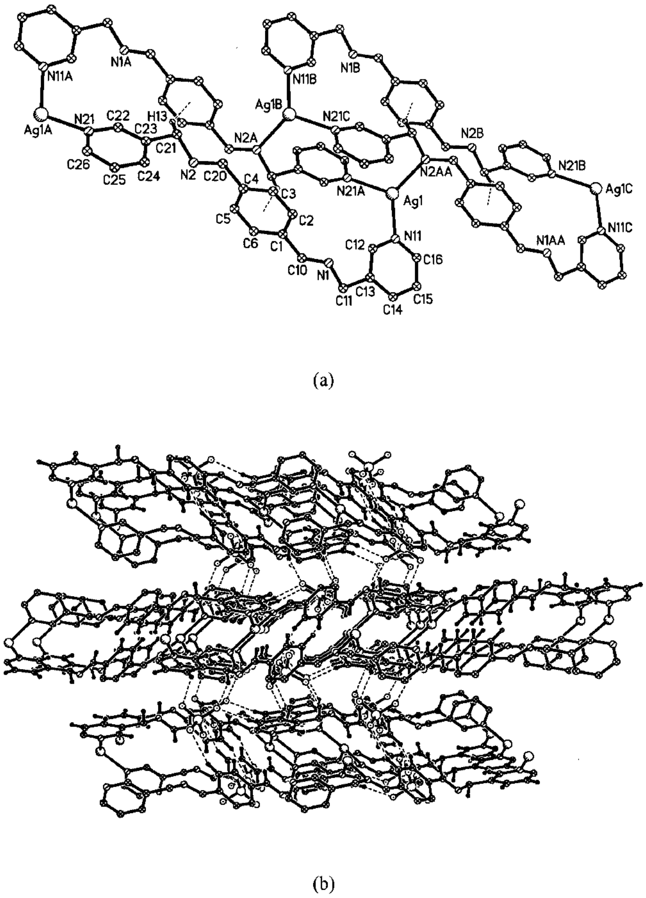


Figure 4. (a) 1D chain structure of complex **5** in which the C−H···π interactions are indicated by dashed lines; (b) crystal packing diagram of **5** with the hydrogen bonds indicated by dashed lines

N atom of L5, rather than one of the imine N like for L2 in **5**, remains uncoordinated.[5e] As reported previously, the imine groups (i.e. -C=N-) in L2 ligand may conjugate with the central benzene ring group thereby decreasing the electron density around the imine N atoms. As a result the electron-donating ability of the imine group is reduced and the N atom of imine group is thus difficult to coordinate to a metal atom.[10] In the case of complex **5**, the imine group containing the N1 atom almost conjugates with the central benzene ring group, since the N1−C10−C1−C2 torsion angle is 0.6(4)°, and therefore the N1 atom does not coordinate to the silver(I) atom, whereas the N2−C20−C4−C5 torsion angle is 16.6(4)°, which means that the imine group containing the N2 atom does not strictly conjugate with the central benzene ring, and, consequently, the N2 atom coordinates to the silver(I) atom. Such a difference between the N1 and N2 imine groups may be caused by the π-π and C−H···π interactions since such interactions are related with the pyridylmethyl group on the N2 side; no such interactions were detected for the pyridylmethyl group on the N1 side. The centroid-centroid distance of 4.17 Å between the two pyridine groups within the 12-membered ring implies the existence of weak π-π interactions. In addition, there are C−H···π interactions[11] in the 34-membered ring, for example between the hydrogen atom (H13) bound to C21 (the methylene directly connecting pyridine group) and the benzene group of another ligand within the same ring (Figure 4, a). The H···centroid distance is 2.96 Å and the C−H−centroid angle is 150°. The Ag−N (N atom of the coordinated imine group) bond length is 2.295(3) Å (Table 1), which is shorter than those observed in the complexes $[Ag_2(L5)_2](CF_3SO_3)_2 \cdot H_2O$ and $[Ag_3(L5)_2](NO_3)_3 \cdot H_2O$ with the corresponding Ag−N bond lengths ranging from 2.328(2) to 2.405(2) Å and from 2.331(4) to 2.407(3) Å, respectively.[5a]

From the crystal-packing diagram of complex **5** shown in Figure 4 (see b) it can be seen that the cationic 1D chains and uncoordinated perchlorate anions are held together by five C−H···O hydrogen bonds (Table 2).

Electrospray (ES) Mass Spectra

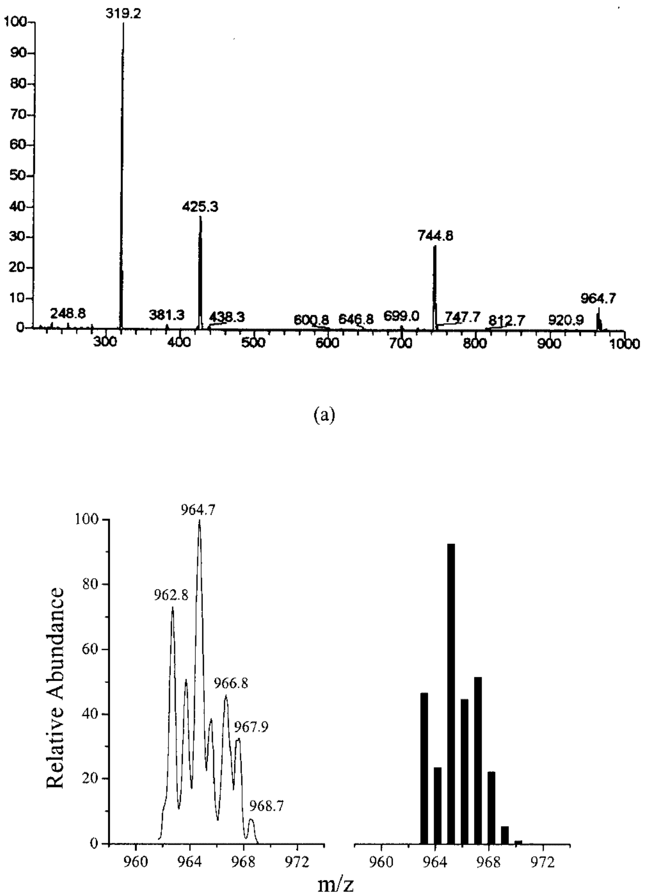
Complexes **1**−**5** were further characterized by ES mass spectrometry and the spectroscopic data are summarized in Table 3. As revealed by X-ray analysis, complexes **1**−**4** are composed of the same ligand and metal atom, and each Ag^I atom is coordinated by at least two L1 ligands. Hence it is reasonable that the same three peaks at *m*/*z* = 319.2, 425.3, 744.8, corresponding to $[HL1]^+$, $[AgL1]^+$ and $[Ag(L1)_2]^+$ species, respectively, appear in the ES mass spectra of these complexes. In addition, there are peaks at *m*/*z* = 913.9, 964.7 and 950.8 corresponding to $[Ag_2(L1)_2(NO_3)]^+$, $[Ag_2(L1)_2(CF_3CO_2)]^+$ and $[Ag_2(L1)_2(ClO_4)]^+$ species in the ES mass spectra of **1**, **2** and **4**, respectively. As an example, the ES mass spectrum of complex **2** is shown in Figure 5. All the assignments are ensured by good agreement between the observed and calculated isotopic distributions. Figure 5 (see b) shows a typical example of a comparison between the experimental and calculated isotopic distributions for the peak at *m*/*z* = 964.7. The observation of mono- and dinuclear cationic species in the ES-MS spectra of complexes **1**−**5** (Table 3) confirms the coordination of the ligand to the Ag^I atom and suggests the presence of polymeric species in solution under the ES mass experimental conditions.

Conclusion

The present study shows that the reactions of the multidentate ligand L1 with various silver(I) salts can afford a variety of polymeric frameworks and that C−H···π interactions play an important role in the crystal structures. Furthermore, the results of the present study show that the nature of the counteranions has a great impact in determining the structure of the coordination polymers in this system.[12] Complex **1** contains two-coordinate silver(I) and a tetradentate L1 ligand, which may be responsible for the formation of the 1D chain structure. The 2D structures of complexes **2**, **3** and **4** all contain 12- and 44-membered macrometalla-

Table 3. ES mass spectroscopic data for complexes **1**−**5**

1		**2**		**3**	
m/*z*	Assignment	*m*/*z*	Assignment	*m*/*z*	Assignment
319.2	$[HL1]^+$	319.2	$[HL1]^+$	319.2	$[HL1]^+$
425.3	$[AgL1]^+$	425.3	$[AgL1]^+$	425.3	$[AgL1]^+$
744.8	$[Ag(L1)_2]^+$	744.8	$[Ag(L1)_2]^+$	744.8	$[Ag(L1)_2]^+$
913.9	$[Ag_2(L1)_2(NO_3)]^+$	964.7	$[Ag_2(L1)_2(CF_3CO_2)]^+$		
4		**5**			
m/*z*	Assignment	*m*/*z*	Assignment		
319.2	$[HL1]^+$	315.3	$[HL2]^+$		
425.3	$[AgL1]^+$	421.2	$[AgL2]^+$		
744.8	$[Ag(L1)_2]^+$	579.8	$[Ag_2(L2)_3]^{2+}$		
950.8	$[Ag_2(L1)_2(ClO_4)]^+$	736.7	$[Ag(L2)_2]^+$		
		1050.6	$[Ag(L2)_3]^+$		



(a)

(b)

Figure 5. (a) The ES mass spectrum of complex **2**; (b) the observed (traces) and calculated (bars) isotopic distributions for the peak at *m*/*z* = 964.7

cyclic rings, although the structure of complex **4** is different from that of complex **2** or **3**. In **2** and **3**, the anions [$CF_3CO_2^-$ in **2** and 1,4-$C_6H_4(COO)_2^{2-}$ in **3**] are too large to fill the void of the 44-membered macrometallacyclic rings, whereas in **4**, the size of the perchlorate anion allows it to be accommodated in the void of the 44-membered ring by forming N−H···O and C−H···O hydrogen bonds. These results show that the size of the counteranions plays a key role in the construction of such coordination polymers. In complex **5**, due to the presence of the −C=N− imine group in the L2 ligand, a 1D chain structure is formed rather than a 2D network like **4**. The results show that the nature of ligand has a remarkable impact on the structure of the frameworks in this system.

Experimental Section

General: All commercially available chemicals were of reagent grade and used as received without further purification. Elemental analyses for C, H and N were carried out on a Perkin−Elmer 240C elemental analyzer at the Analysis Center of Nanjing University. Thermogravimetric and differential thermal analyses were taken on a simultaneous SDT 2960 thermal analyzer under N_2 with a heating rate of 10 °C/min. The electrospray mass spectral (ES-MS) measurements of the complexes were carried out on an LCQ System (Finnegan MAT, USA) using a mixing solution of methanol and water (1:1) as mobile phase. The samples for ES-MS measurements were prepared by redissolving the final isolated compounds in methanol (**1**−**4**) or in methanol and acetonitrile (1:1; for **5**). Ligands L1 and L2 were prepared by procedures reported previously.[10] All procedures for the synthesis and measurement of the silver(I) complexes were carried out in the dark.

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

Synthesis of {[Ag_2(L1)](NO_3)$_2$·2H_2O}$_n$ (1): Complex **1** was synthesized by the layering method. A solution of L1 (31.8 mg, 0.1 mmol) in ethanol (5 mL) was carefully layered over a solution of $AgNO_3$ (17.0 mg, 0.1 mmol) in water (10 mL). Colorless crystals were isolated in 61% yield by filtration after two weeks at room temperature. $C_{20}H_{26}Ag_2N_6O_8$: calcd. C 34.60, H 3.78, N 12.11; found C 34.63, H 3.76, N 11.94.

Synthesis of {[Ag(L1)](CF_3COO)·2.5H_2O}$_n$ (2): An aqueous (5 mL) solution of L1 (31.8 mg, 0.1 mmol) and a solution of CF_3COOAg (22.1 mg, 0.1 mmol) in water (5 mL) were mixed and allowed to stand in air at room temperature for about fifteen days. Light-brown crystals were obtained in 76% yield. $C_{22}H_{27}AgF_3N_4O_{4.5}$: calcd. C 45.22, H 4.66, N 9.59; found C 45.35, H 4.65, N 9.50.

Synthesis of {[Ag_2(L1)$_2$][1,4-$C_6H_4(COO)_2$]·7H_2O}$_n$ (3): A solution of L1 (31.8 mg, 0.1 mmol) in methanol (5 mL) was carefully layered over an aqueous solution of freshly prepared [Ag(Py)$_2$]$_2$[1,4-$C_6H_4(COO)_2$] (Py = pyridine; 0.025 mmol mL^{-1}, 2 mL). Colorless crystals appeared within two weeks at room temperature in 43% yield. $C_{48}H_{62}Ag_2N_8O_{11}$: calcd. C 50.45, H 5.47, N 9.81; found C 50.48, H 5.51, N 9.73.

Synthesis of {[Ag(L1)]ClO_4}$_n$ (4): A methanol (5 mL) solution of L1 (31.8 mg, 0.1 mmol) and an acetonitrile (5 mL) solution of $AgClO_4$·H_2O (22.5 mg, 0.1 mmol) were mixed and allowed to stand at room temperature for ten days. Light-brown crystals were obtained in 63% yield. $C_{20}H_{22}AgClN_4O_4$: calcd. C 45.69, H 4.22, N 10.66; found C 45.60, H 4.30, N 10.58.

Synthesis of {[Ag(L2)]ClO_4}$_n$ (5): An aqueous (3 mL) solution of $AgClO_4$·H_2O (22.5 mg, 0.1 mmol) was added dropwise to a solution of L2 (31.4 mg, 0.1 mmol) in CH_3OH (6 mL) with stirring. The resulting precipitate was isolated and then dissolved in CH_3CN (8 mL) to give a clear solution. Crystals were obtained in 46% yield by slow diffusion of diethyl ether into the clear solution at room temperature for about two days. $C_{20}H_{18}AgClN_4O_4$: calcd. C 46.04, H 3.48, N 10.74; found C 46.24, H 3.68, N 10.75.

X-ray Crystal Structure Determination: The intensity data for complexes **1**−**5** (Table 4) were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). The structures were solved by direct methods with SIR92,[13] and expanded using Fourier techniques.[14] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2. The hydrogen atoms, except those from water molecules, were generated geometrically. The F1, F2 and F3 atoms in **2** have two positions with site occupation factors of 0.815(8) and 0.185(8), respectively. The O4, O5 and O6 atoms in **2** have site occupation factors of 0.429(13), 0.571(13) and 0.571(13), and the O2, O3 and O4 atoms in **4** are disordered over two positions with site occupation factors of

Table 4. Crystallographic data for complexes **1**−**5**

Complex	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{20}H_{26}Ag_2N_6O_8$	$C_{22}H_{27}AgF_3N_4O_{4.5}$	$C_{48}H_{62}Ag_2N_8O_{11}$	$C_{20}H_{22}AgClN_4O_4$	$C_{20}H_{18}AgClN_4O_4$
Molecular mass	694.21	584.35	1142.80	525.74	521.70
Crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	8.625(8)	9.6191(15)	9.662(3)	9.503(4)	11.032(9)
b (Å)	12.192(12)	11.3789(15)	11.431(4)	19.101(8)	11.262(8)
c (Å)	11.590(11)	12.1015(14)	12.719(4)	11.675(4)	16.086(12)
α (°)		72.260(5)	64.93(2)		
β (°)	94.69(9)	83.813(7)	84.17(2)	100.66(3)	93.63(6)
γ (°)		71.706(9)	72.58(3)		
V (Å^3)	1215(2)	1197.7(3)	1213.7(7)	2082.5(14)	1995(3)
Z	2	2	1	4	4
$D_{calcd.}$ (g·cm^{-3})	1.898	1.620	1.564	1.677	1.737
μ [mm^{-1}]	1.670	0.903	0.875	1.131	1.181
Reflections collected	11227	11089	11868	20335	19762
Independent reflections	2709	5402	5477	4753	4569
R_{int}	0.0544	0.0385	0.0372	0.0780	0.0673
Obsd. reflections [$I > 2\sigma(I)$]	2008	4267	4410	3120	2955
Parameters refined	163	354	334	299	271
R (obsd. data)	0.0289	0.0412	0.0361	0.0322	0.0307
wR (obsd. data)	0.0486[a]	0.0928[b]	0.0814[c]	0.0455[d]	0.0522[e]
Goodness of fit	0.896	1.041	1.003	0.848	0.819
Residuals [e·Å^{-3}]	0.430; −0.400	0.726; −0.697	0.682; −0.574	0.570; −0.552	0.676; −0.455

[a] $w = 1/[\sigma^2(F_o)^2 + (0.0198P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $w = 1/[\sigma^2(F_o)^2 + (0.0550P)^2 + 0.0824P]$, where $P = (F_o^2 + 2F_c^2)/3$. [c] $w = 1/[\sigma^2(F_o)^2 + (0.0450P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. [d] $w = 1/\sigma^2(F_o)^2$. [e] $w = 1/[\sigma^2(F_o)^2 + (0.0214P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

0.523(7) and 0.477(7), respectively. All calculations were carried out on an SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation.[15]

CCDC-218881 (**1**), -218882 (**2**), -218883 (**3**), -218884 (**4**) and -218885 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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