Self-Assembly of Novel Silver Polymers Based on Flexible Sulfonate Ligands

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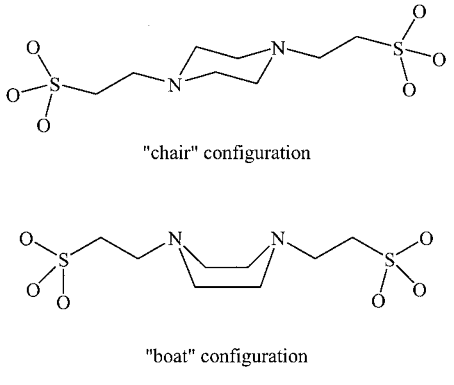
Self-assembly reactions of sulfonates with $AgNO_3$ in the presence of secondary N- or P-containing ligands result in the formation of four new silver-sulfonate polymers, $[Ag(PIP)]_n\cdot[Ag(pesp)]_n\cdot 2nH_2O$ (**1**), $[Ag_2(pesp)(dabco)]_n\cdot 5nH_2O$ (**2**), $[\{Ag(pesp)_{1/2}(hmt)_{1/4}\}\cdot 0.5H_2O]_n$ (**3**) and $[Ag(PPh_3)(pesp)_{1/2}]_n\cdot n$MeOH (**4**), whose structures change from one-dimensional chains to three-dimensional open frameworks based on the secondary ligands.

Introduction

In the past decades, much attention has been focused on the design and synthesis of metal-organic coordination networks (MOCNs)[1−3] based on coordination bonds and non-covalent interactions (such as hydrogen bonding, π-π−stacking and/or weak interactions between molecules),[4] due to their interesting molecular topologies and crystal-packing motifs, along with potential applications as functional materials.[5] In the construction of MOCNs, the stereo and interactive information stored in the ligand, as well as the coordination geometry of the metal ions, should be taken into account.[6] Previous studies have proved that careful selection of a suitable, polyfunctional, organic ligand containing certain features, such as, flexibility, versatile binding modes, and the ability to undergo hydrogen bonding, is helpful for constructing and tailoring the architectures of MOCNs.[7]

Recently, much effort has been devoted to the investigation of new synthetic strategies for constructing MOCNs possessing special architectures, such as, 1D helical-chain and 3D channel-like structures, with the use of rigid or flexible ligands containing oxygen or hybrid oxygen/nitrogen atoms, namely, multi-carboxylate, 4,4′-bipy or their derivatives.[8−12] Surprisingly, fewer examples containing sulfonate ligands have been reported, probably due to their weak coordination ability compared to N- or O-containing ligands.[13] However, the recent development of supramolecular chemistry has made it possible to rationally design and synthesize MOCNs by using ligands that in the past have been regarded as poorly coordinating anions, such as sulfonate ligands. Almost no systematic study in the field of sulfonate ligands has been reported. Only recently, the diversity of complexes, particularly transition-metal complexes, constructed by sulfonates has attracted much interest, not only because of the value of these compounds as inorganic synthons,[14] but also because of their important role in proteins.[13b] However, most of the studies reported are focused on aromatic sulfonates, for example when $-SO_3$ is directly connected to the aromatic ring,[15,16] and the studies on non-aromatic flexible sulfonates are almost neglected[17] because the coordination ability of the latter is much weaker than that of the former.

We have begun to study the reactions of flexible sulfonate ligands with silver(I) salts[18] by self-assembly with twofold aims: one is to obtain coordination information on such ligands and the other is to construct novel coordination polymers. Our strategy, in order to overcome the weak coordination ability of flexible sulfonate ligands, is to employ additional coordination sites in the ligand other than the $-SO_3$ group. Thus, we selected the dipotassium salt of piperazine-1,4-bis(2-ethanesulfonic acid) (K_2pesp) (see Scheme 1) as assembly ligand in view of the following characteristics: a) it contains a piperazine ring and the additional coordi-



Scheme 1. The possible configuration of the piperazine ring in $pesp^{2-}$

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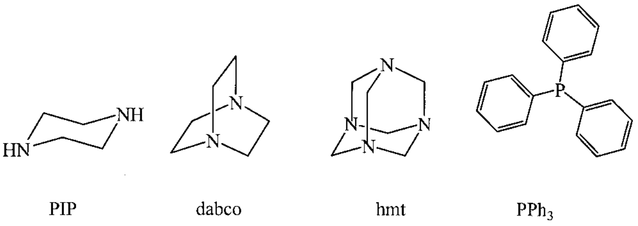
nation from the piperazine nitrogen may be useful for improving the coordination ability; b) it contains the flexible ethyl group that may allow the ligand to adapt to the geometric requirements of the metal ions;[19] c) it can act as a hydrogen-bond acceptor due to the sulfonate oxygen atoms and the nitrogen atoms of the piperazine ring, which may allow the formation of a high-dimensional supramolecular architecture.

A novel, one-dimensional silver polymer containing two different helical chains, $[Ag(PIP)]_n\cdot[Ag(pesp)]_n\cdot 2n$H2O (**1**),[20] was obtained by the self-assembly reaction of the dipotassium salt of piperazine-1,4-bis(2-ethanesulfonic acid) (K_2pesp) with $AgNO_3$, in the presence of piperazine (PIP) in a mixed water/MeOH solution. To extend our work, we carried out systematic studies by introducing other secondary ligands, such as 1,4-diazabicyclo[2.2.2]octane (dabco), hexamethylenetetramine (hmt) and PPh_3, and three other interesting polymers were successfully synthesized. Herein, we describe the details of the preparation and characterization of the four novel silver(I) polymers: $[Ag(PIP)]_n\cdot[Ag(pesp)]_n\cdot 2nH_2O$ (**1**), $[Ag_2(pesp)(dabco)]_n\cdot 5nH_2O$ (**2**), $[\{Ag(pesp)_{1/2}(hmt)_{1/4}\}\cdot 0.5H_2O]_n$ (**3**) and $[Ag(PPh_3)(pesp)_{1/2}]_n\cdot n$MeOH (**4**), based on mixed sulfonate and N- or P-containing ligands.

Results and Discussions

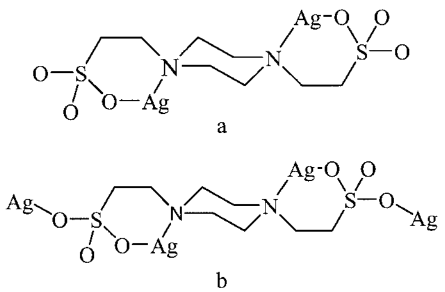
Syntheses

Previous studies have established the role of the secondary ligand in mixed ligand systems, for example, a bridging secondary ligand, such as 4,4′-bipy, generates extended frameworks,[21] whereas a terminal ligand, such as phen, often yields low-dimensional structures.[22] In order to obtain novel structural topologies based on secondary ligands, different N-containing secondary ligands, such as piperazine (PIP), 1,4-diazabicyclo[2.2.2]octane (dabco), hexamethylenetetramine (hmt) (see Scheme 2), were introduced in our study. It was found that increasing the coordination sites of the secondary ligand increased the dimensionality of the complex thus formed. When a terminal PPh_3 ligand was employed as a secondary ligand, complex **4**, which possesses a one-dimensional branch-like chain structure, was successfully isolated. The result is similar to previous observations.[21,22] Unfortunately, the effort to extend the study to diphosphane-bridging ligands, such as dppe [ethylenebis(diphenylphosphane)], failed and only a one-dimensional helical chain constructed by dppe was obtained,[23] indicating that the diphosphane-bridging ligands have higher coordination ability than $pesp^{2-}$.



Scheme 2. The secondary ligands introduced in our work

An interesting reaction was observed during the preparation of complexes **1** and **2**. When the pH value was adjusted to 7 or 8 by $HClO_4$, a previously reported complex, $[Ag_2(\mu_2\text{-}OH_2)(pesp)]_n$, was obtained.[18] This result may arise from partial protonation of piperazine or 1,4-diazabicyclo[2.2.2]octane and then loss of their coordination ability. In complexes **1**−**4**, all the piperazine rings in $pesp^{2-}$, as well as in the PIP ligands, adopt the most stable "chair" configuration (see Scheme 1), as found in other Ag-PIP complexes.[24] The strong peaks at 1250−1150 cm^{-1} in the IR spectra correspond to the sulfonate groups in **1**−**4**.[13c] Complexes **1**−**4** are insoluble in water and other organic solutions such as MeOH, EtOH, and DMF. The coordination modes of $pesp^{2-}$ in **1**−**4** are given in Scheme 3.



Scheme 3. The coordination modes of $pesp^{2-}$ in **2**−**4**

Structural Description

The structure of complex **1** has already been reported[20] and a detailed discussion will not be carried out here.

X-ray diffraction shows that complex **2** has a pseudo-two-dimensional layer structure, made up of a 1D zigzag chain containing a three-coordinate silver center. As shown in Figure 1(a), each silver ion is coordinated to one oxygen atom from the sulfonate group and to two nitrogen atoms from the $pesp^{2-}$ and dabco ligands, in a trigonal geometry. The coordination mode of $pesp^{2-}$ is similar to that seen in **1** as a μ_2-chelating ligand with the oxygen atom of the sulfonate group and the nitrogen atom of the piperazine ring (see a in Scheme 3). The average $Ag-N_{pesp}$ distance is 2.283(5) Å, which is shorter than that observed in **1** [2.334(9) Å],[20] presumably due to the coordination influence of the secondary ligand. Thus, each $pesp^{2-}$ ligand chelates two silver ions to form an $[Ag_2pesp]$ unit and such units are linked head-to-tail by dabco [the average $Ag-N_{dabco}$ distance is 2.237(6) Å] to form a 1D, infinite, zigzag chain structure (see Figure 1b). Although the coordination mode of $pesp^{2-}$ is the same in complexes **1** and **2**, the structures of the chains are quite different: in **1**, the helical chain is formed only by $pesp^{2-}$ and each $pesp^{2-}$ ligand links two silver ions and vice versa to form the 1D helical chain; whereas in **2**, the 1D polymer is formed by the mixed ligands, $pesp^{2-}$ and dabco, that alternate in the chain. Complex **2** can also be regarded as a variation of complex **1**, in which every second $pesp^{2-}$ ligand is replaced by dabco.

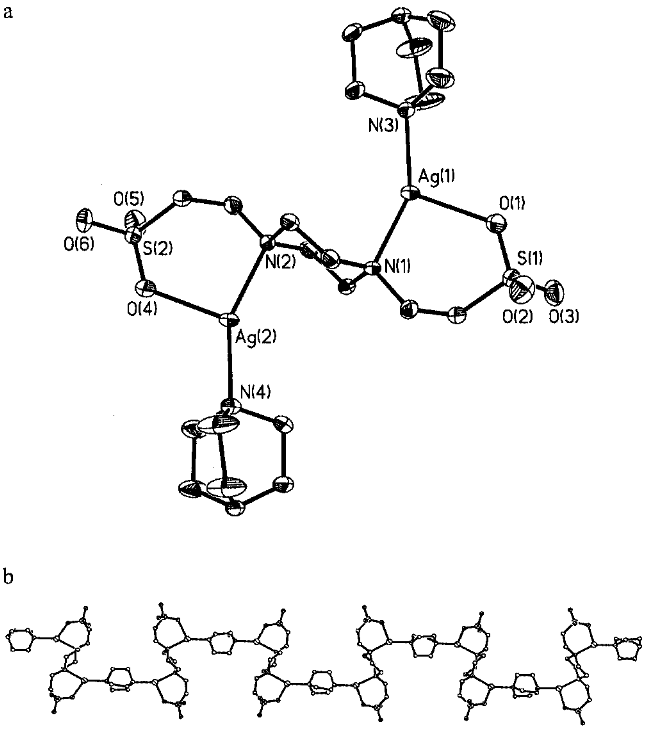


Figure 1. Coordination environment of the silver ion in **2** (a); the 1D chain structure of **2** (b)

There are weak interactions between the chains: the oxygen atom of the sulfonate group is weakly coordinated to the silver ion of the adjacent chain; the Ag−O distance is 2.665 Å (see Figure 2). These weak interactions make the complex a 2D brick-wall-like supramolecular structure [Figure 2 (top)], in which, if considering the weak Ag−O bond, the silver ion is four-coordinate, in a tetrahedral geometry, as in **1**. The free water molecules reside in the grids and form hydrogen bonds with the uncoordinated sulfonate oxygen atoms (O···O distances 2.790−2.987 Å). It should be noted that the 2D brick wall is one of the supramolecular isomers found in the self-assembly of T-shape modules.[25] Meanwhile, a 1D helical chain, [Ag$_2$pesp]$_n$, is generated by the weak Ag−O bonds [Figure 2 (bottom)]. Thus, the 2D layer can also be viewed as consisting of ladders sharing side pieces, which are formed by [Ag$_2$pesp]$_n$ helical chains and the rungs by dabco ligands, and **2** can be described as a pseudo-two-dimensional supramolecular architecture formed by weak coordinate bonds.

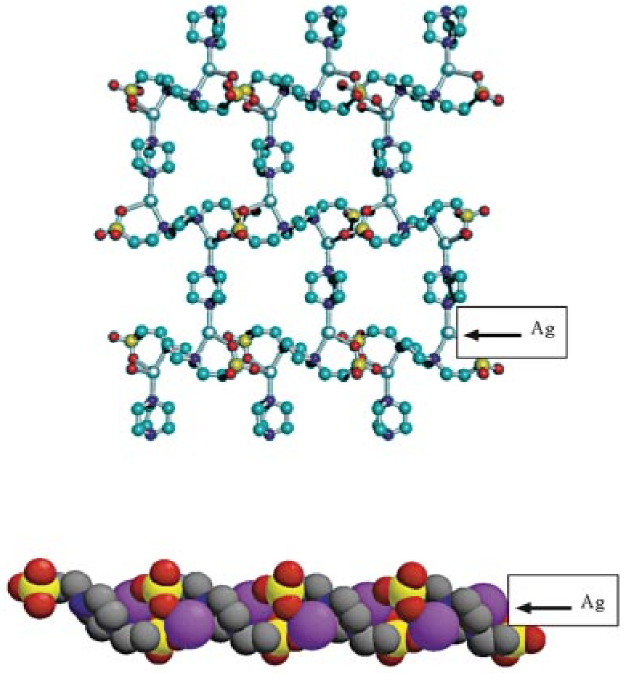


Figure 2. Two-dimensional layer structure (top) and one-dimensional helical chain (bottom) generated by the weak Ag−O bonds in **2**

In contrast with complexes **1** and **2**, X-ray diffraction shows that **3** is a three-dimensional polymer with open-square channels. The central silver ion is coordinated to two oxygen atoms from two different pesp^{2-} ligands and to two nitrogen atoms from hmt and pesp^{2-} in a tetrahedral geometry (see Figure 3); the average Ag−O and Ag−N distances are 2.395(9) and 2.346(7) Å, respectively. The Ag−N distance is longer than that observed in **1** and **2**, probably due to the influence of the secondary ligand. Each pesp^{2-} adopts a chelating-bridging coordination mode to link four silver ions (see b in Scheme 3), which is not observed in **1** and **2**. The hmt ligand acts as a μ$_4$-bridge, which links four silver ions to four nitrogen atoms, as observed in [Ag$_2$(μ$_4$-hmt)(SO$_4$)(H$_2$O)]·4H$_2$O,[26] to form an [Ag$_4$(hmt)] tetrahedral core, in which the four silver ions occupy the vertexes and hmt stands at the center (average Ag−Ag distance and Ag−Ag−Ag angle 6.262 Å and 60°, respectively). Each silver ion in the Ag$_4$ core is chelated by one oxygen of the -SO$_3$ group and the adjacent nitrogen of the piperazine ring of pesp^{2-} (see b in Scheme 3) to form an [Ag$_4$(hmt)(pesp)$_4$] unit that may be viewed as the basic building unit of the entire structure. The Ag$_4$ units are joined together by pesp^{2-} ligands to form a 2D layer structure along the *ab*

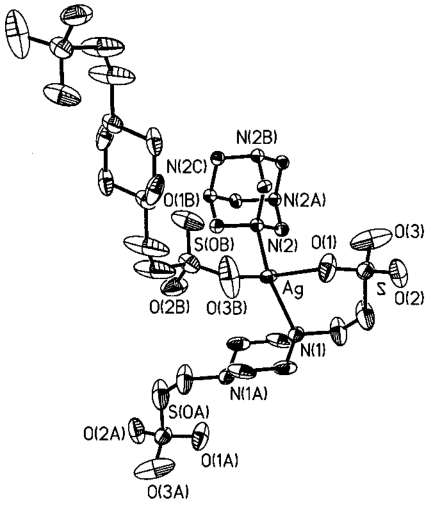


Figure 3. Coordination environment of the silver ion in **3**

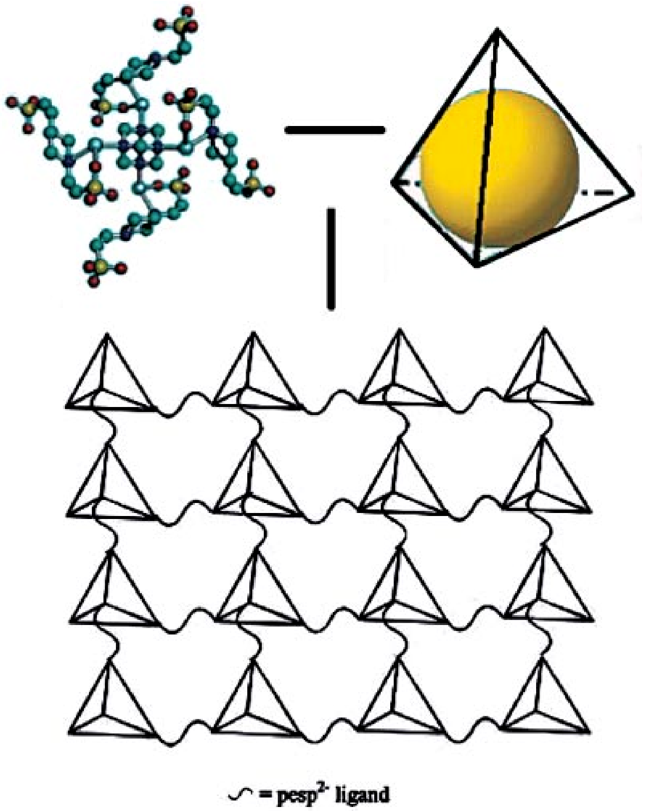


Figure 4. Two-dimensional diagram showing the connections between the Ag_4 cores that form the 2D layer in **3**

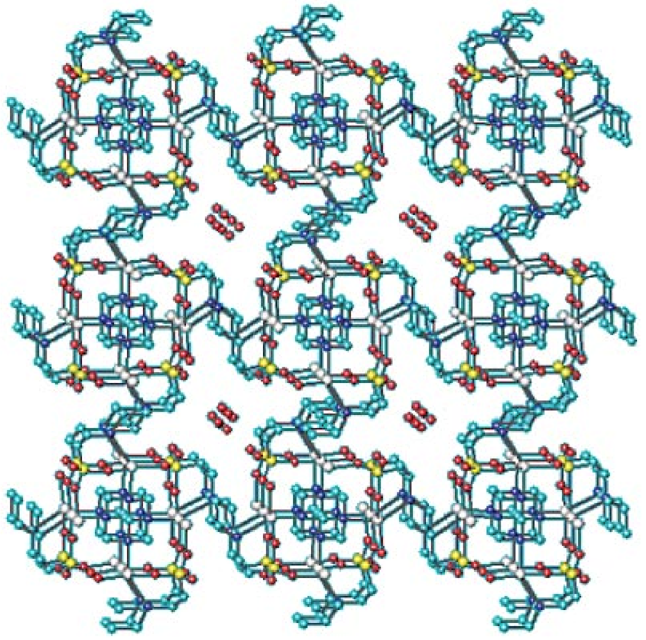


Figure 5. Three-dimensional open framework of **3** with square channels

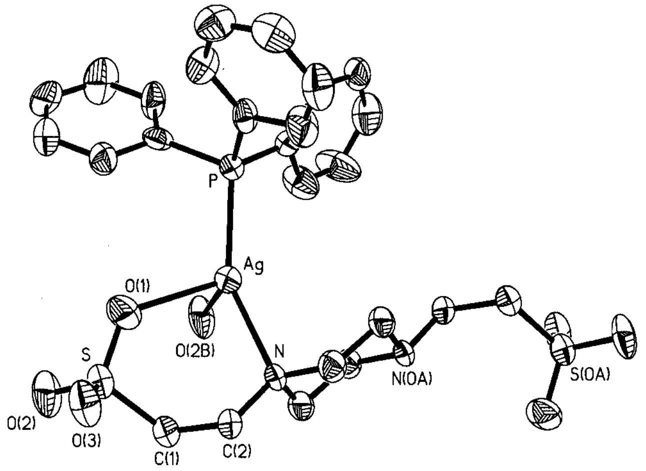


Figure 6. Coordination environment of the silver ion in **4**

plane (see Figure 4). The adjacent layers are further connected by Ag−O bonds, provided by the remaining oxygen atoms of the sulfonate groups, to complete the tetrahedral coordination environments of the AgI ions, thereby generating a 3D open framework with square channels along the *a* axis, in which the free water molecules reside (see Figure 5). Hydrogen-bonding interactions between the uncoordinated sulfonate oxygen atoms and the free water molecules are present; the O···O distance is 2.965 Å.

X-ray diffraction analysis shows that **4** is a one-dimensional branch-like polymer containing a 1D helical backbone made up of an $[Ag_2(pesp)]$ unit and PPh_3 "leaves". As shown in Figure 6, the central silver ion is coordinated to two oxygen atoms and one nitrogen atom from two $pesp^{2-}$ ligands, and the remaining coordination site is occupied by the phosphorous atom of PPh_3 [the Ag−O, Ag−N and Ag−P distances are 2.431(8), 2.317(9) and 2.371(3) Å, respectively], in a tetrahedral geometry. The $pesp^{2-}$ ligand adopts the same coordination mode as in **3** (see b in Scheme 3), linking four silver ions. The dinuclear unit $[Ag_2(pesp)]$, formed by one chelating $pesp^{2-}$ ligand and two silver ions, may be viewed as the basic building block of the whole structure. Each Ag_2 unit is connected to another Ag_2 unit through Ag-O bonding to generate a one-dimensional branch-like chain structure (see Figure 7), in which every silver is coordinated to a PPh_3 "leaf" to prevent the framework from extending to a two- or three-dimensional architecture. It should be noted that the backbone of the polymer possesses a one-dimensional helical chain, namely $[Ag_2(pesp)]_n$, which is similar to that found in **2** except that the Ag-O interactions between the chains in **2** are weak. When considering the weak Ag−O bond in **2**, the coordination environments of the metal ion and $pesp^{2-}$ are the same in **2** and **4**. The solvent molecules are located at the two sides of the chain.

Thermogravimetric Analysis for 3

Thermogravimetric analysis (TGA) for complex **3** shows that there is a weight loss of 2.85 % from 42 °C to 140 °C, which is equivalent to the loss of 0.5 uncoordinated water molecules (calcd. 2.97 %). At temperatures above 150 °C, complex **3** starts to decompose and the decomposition ends above 800 °C. In order to determine whether the backbone can be retained after removal of the guest water molecules,

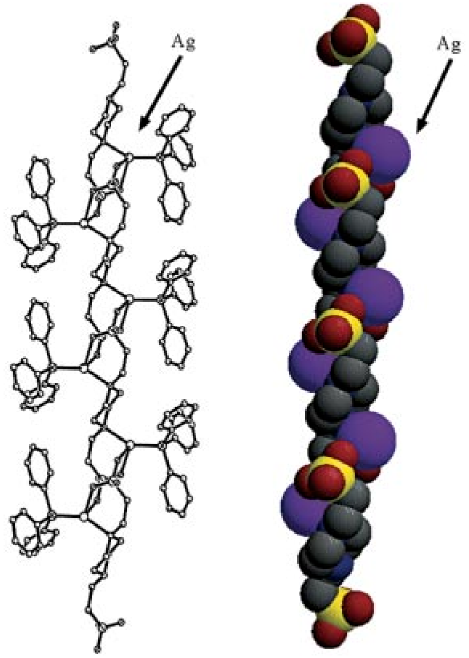


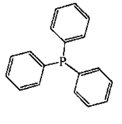
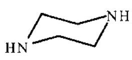
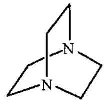
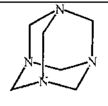
Figure 7. One-dimensional chain structure of **4**

heating-cooling and dehydrate-hydrate experiments were carried out according to the TGA results and monitored by X-ray powder diffraction (XRPD). When **3** was heated to 140 °C, part of the guest water molecules evolved from the sample and the samples were changed into powders; XRPD determination showed that most of the characteristic XRPD peaks had disappeared. After rehydrating the sample for 24 hours, the XRPD pattern showed that hardly any characteristic XRPD peaks were recovered. These results illustrate that the backbone collapses after removal of the water molecules, indicating that complex **3** possesses low thermal stability.

Conclusions

Four novel silver polymers possessing different architectures were synthesized by self-assembly reactions of flexible sulfonate ligands with silver salts, in the presence of secondary ligands, at room temperature, in mixed solvents (H_2O/DMF or H_2O/MeOH). Contrary to our previously reported complex, $[Ag_2(\mu_2\text{-}OH_2)(pesp)]_n$,[18] the flexible ligand $pesp^{2-}$ adopts bent configurations in the four complexes, acting as a μ_2-bridge in **1** and μ_4-bridges in **2**, **3** and **4** through bridging and/or chelating modes. The formation of the four complexes may be controlled by the secondary ligands,[27] and the dimensionality of the complexes increases when increasing the coordination sites of the secondary ligands (see Table 1). Our results indicate that the flexible ligand is more adjustable than the rigid one and can adopt various configurations and coordination modes to meet the different geometric requirements of the metal ions.[19] The architecture of the MOCNs can be tailored by changing the secondary ligands.

Table 1. Comparison of bond lengths and dimensionality in **1**, **2**, **3** and **4**

	 4	 1	 2	 3
Ag-N/$P_{secondary}$	2.371 Å	2.197, 2.203 Å	2.222, 2.251 Å	2.335 Å
Dimensionality	1D branch-like chain	1D helical chain	2D layer	3D open framework

Experimental Section

Materials and Analyses: All chemicals were used are as purchased without further purification. IR spectra were recorded on a Magna 750 FT-IR spectrophotometer as KBr pellets. Elementary analyses were carried out in the elementary analysis group of this institute.

Synthesis of $[Ag_2(pesp)(dabco)]_n \cdot 5nH_2O$ (2): K_2pesp (0.045 g, 0.125 mmol) and dabco (0.015 g, 0.125 mmol) were dissolved in water (5 mL) and placed on the bottom of a glass tube. A solution of $AgNO_3$ (0.043 g, 0.25 mmol) in MeOH (5 mL) was carefully layered on it through an H_2O/MeOH (5 mL) buffer. The tube was left standing in the dark for about two weeks and colorless prism-like crystals were obtained (0.054 g). Yield 30 %. $C_{14}H_{38}Ag_2N_4O_{11}S_2$ (718.33): calcd. C 23.41, H 5.33, N 7.80; found C $_2$3.25, H 5.25, N 7.85. IR (KBr, cm^{-1}): 3450 (vs), 2966 (m), 2949 (m), 2825 (s), 1655 (m), 1462 (s), 1356 (s), 1315 (s), 1250 (s), 1213 (vs), 1196 (vs), 1167 (vs), 1055 (vs), 1039 (vs), 1009 (s), 781 (m), 652 (s), 586 (vs), 526 (s).

Synthesis of $[\{Ag(pesp)_{1/2}(hmt)_{1/4}\} \cdot 0.5H_2O]_n$ (3): K_2pesp (0.045 g, 0.125 mmol) and hmt (0.035 g, 0.25 mmol) were dissolved in water (5 mL) and placed on the bottom of a glass tube. A solution of $AgNO_3$ (0.043 g, 0.25 mmol) in DMF (5 mL) was carefully layered on it through an H_2O/DMF (5 mL) buffer. The tube was left standing in the dark for about two weeks and colorless, large prism-like crystals were obtained (0.042 g). Yield 55 %. $C_{5.5}H_{12}AgN_2O_{3.5}S$ (302.09): calcd. C 21.87, H 4.00, N 9.27; found C 21.88, H 4.10, N 9.25. IR (KBr, cm^{-1}): 3448 (vs), 2949 (s), 1655 (m), 1462 (m), 1356 (m), 1315 (s), 1248 (s), 1215 (vs), 1200 (vs), 1167 (vs), 1039 (vs), 1007 (vs), 816 (s), 688 (s), 588 (vs).

Synthesis of $[Ag(PPh_3)(pesp)_{1/2}]_n \cdot n$MeOH (4): K_2pesp (0.045 g, 0.125 mmol) was dissolved in a mixed H_2O/MeOH solution (v/v = 1:1; 4 mL) and placed on the bottom of a glass tube. A solution of $AgNO_3$ (0.043 g, 0.25 mmol) and PPh_3 (0.065 g, 0.25 mmol) in a mixed MeOH/EtOH solution (v/v = 1:1; 4 mL) was carefully layered on it through an H_2O/MeOH (5 mL) buffer. The tube was left standing in the dark for about three weeks and colorless well-formed prism-like crystals were obtained (0.055 g). Yield 40 %. $C_{23}H_{27}AgNO_4PS$ (552.37): calcd. C 50.01, H 4.93, N 2.54; found C 50.15, H 4.80, N 2.45. IR (KBr, cm^{-1}): 3450 (s), 3055 (s), 1585 (m), 1479 (s), 1437 (vs), 1398 (vs), 1385 (vs), 1296 (vs), 1095 (s), 1028 (m), 744 (vs), 694 (vs), 515 (vs).

Crystallographic Analyses: The intensity data of **1**−**4** were collected on a SIEMENTS SMART CCD diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation at room tem-

Table 2. Crystallographic data for complexes **2**−**4**

Complex	**2**	**3**	**4**
Empirical formula	$C_{14}H_{38}Ag_2N_4O_{11}S_2$	$C_{5.5}H_{13}AgN_2O_4S$	$C_{23}H_{27}AgNO_4PS$
Formula mass	718.26	311.11	552.36
Space group	*Pna*2(1)	*I*4(1)/*a*	*P*21/*n*
T (°C)	293	293	293
a (Å)	20.5479(4)	23.1184(5)	9.4059(10)
b (Å)	9.34230(10)	23.1184(5)	17.3134(17)
c (Å)	12.8479(3)	6.7338(2)	15.1957(16)
β (deg)	90	90	104.316(2)
V (Å^3)	2466.34(8)	3598.95(15)	2397.7(4)
Z	4	16	4
$\rho_{calcd.}$ (g cm^{-3})	1.935	2.297	1.530
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	1.817	2.460	1.023
Reflections collected	7677	5412	7908
Independent reflections	3586 [R(int) = 0.0206]	1574 [R(int) = 0.0399]	4213[R(int) = 0.0992]
Data/restraints/parameters	3586/1/298	1574/0/127	4213/0/289
Goodness of fit	1.094	1.079	1.205
$R_1[I > 2\sigma(I)]$	0.0330	0.0496	0.0914
wR_2	0.0768	0.1185	0.1392

Table 3. Selected bond lengths [Å] and angles [°] for **2**−**4**

2			
Ag(1)−N(3)	2.222(6)	Ag(2)−N(4)	2.251(6)
Ag(1)−N(1)	2.274(5)	Ag(2)−N(2)	2.291(5)
Ag(1)−O(1)	2.425(5)	Ag(2)−O(4)	2.482(5)
N(3)−Ag(1)−N(1)	150.41(18)	N(4)−Ag(2)−N(2)	52.13(18)
N(3)−Ag(1)−O(1)	114.04(18)	N(4)−Ag(2)−O(4)	113.58(18)
N(1)−Ag(1)−O(1)	92.08(18)	N(2)−Ag(2)−O(4)	93.19(17)
3			
Ag−N(2)	2.335(6)	Ag−O(1)	2.358(7)
Ag−N(1)	2.356(7)	Ag−O(3)[a]	2.431(9)
N(2)−Ag−N(1)	121.4(3)	N(2)−Ag−O(3)[a]	115.0(3)
N(2)−Ag−O(1)	112.7(3)	N(1)−Ag−O(3)[a]	120.2(4)
N(1)−Ag−O(1)	86.9(3)	O(1)−Ag−O(3)[a]	89.3(3)
4			
N−Ag	2.317(9)	Ag−O(1)	2.431(8)
P−Ag	2.371(3)	Ag−O(2)[b]	2.514(8)
N−Ag−P	150.2(2)	N−Ag−O(2)[b]	94.4(3)
N−Ag−O(1)	91.5(3)	P−Ag−O(2)[b]	104.2(2)
P−Ag−O(1)	109.7(2)		

[a] Symmetry transformations used to generate equivalent atoms: $y - 1/4, -x + 5/4, -z + 5/4$. [b] $-x + 2, -y - 1, -z$.

perature. All absorption corrections were performed with the SADABS program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package on a legend computer. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically (C−H 0.96 Å). The crystallographic data of complexes **1**−**4** are listed in Table 2, selected bond lengths and angles in Table 3. Additional crystallographic details have been deposited at the Cambridge Crystallographic Data Center. CCDC-188274 (for **1***) and -200970 to -200972 (for **2**−**4**) 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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