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# Influence of Neutral Ligands on the Structures of Silver(I) Sulfonates

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This article represents a systematical examination of the structures of silver(I) sulfonates incorporating neutral ligands. To survey the influence of the properties of neutral ligands on the structures of silver(I) sulfonates, three kinds of sulfonate anions (L1 = 1-naphthalenesulfonate, L2 = *p*-toluenesulfonate, and L3 = 1, 3, 6, 8-pyrenetetrasulfonate) and three kinds of neutral ligands (pyrazine, Pyr, a divergent bidentate ligand; hexamethylenetetramine, hmt, a divergent tetradentate ligand; and $\beta$-picoline, Pic, a monodentate ligand) were selected for study, and five novel silver(I) sulfonates containing neutral ligands have been synthesized: [Ag(L1)(Pyr)]·$H_2O$ (**1**), Ag(L2)(Pyr) (**2**), $Ag_4(L3)(Pyr)_4(H_2O)_2$ (**3**), [Ag(L1)(hmt)]·$H_2O$ (**4**), and $Ag(L1)(Pic)_2$ (**5**). The crystal structures have been determined by single-crystal X-ray diffraction, and these compounds show a variety of structures with different dimensionalities. Moreover, the luminescent properties of compounds **2**, **4**, and **5** are also discussed.

## Introduction

In the past, sulfonates were a relatively unexplored class of ligands because the sulfonate group is a poor ligand that is incapable of forming stable coordinate bonds with transition metal ions.[1] However, silver(I) sulfonates are an exception.[2] In recent years, the design and synthesis of silver(I) sulfonates have attracted great attention because of their flexible coordination modes, interesting inorganic−organic lamellar structures, selective and reversible guest inclusion properties,[2l] and their ability to intercalate guest molecules.[2m,2t] In light of previous reports, the structural motif observed for most silver(I) sulfonates is a two-dimensional sheet with each sulfonate group coordinating to several silver ions (a structure analogous to that of metal phosphonates).[3] In these two-dimensional networks, the inorganic component serves as a rigid structure for the pendent or organic groups. In addition, further study on the effect of the organic group on the structures of silver(I) sulfonates has been discussed in detail.[2b] Until now, some coordination polymers from Ag($CF_3SO_3$) and O- or N-containing ligands have been synthesized.[4] These studies are mainly focused on supramolecular chemistry and crystal engineering on the basis of

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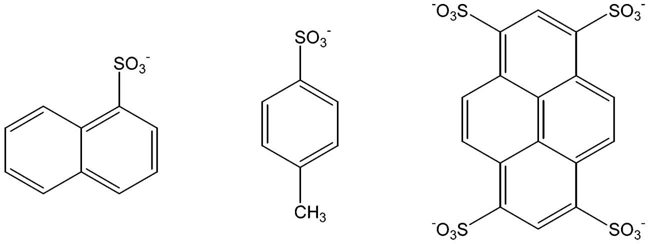
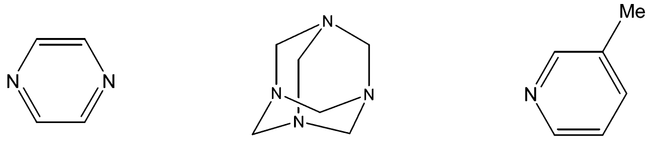
**Scheme 1.** Structures of the Sulfonate Ligands in This Work



L1 L2 L3

**Scheme 2.** Structures of Three Neutral Ligands



Pyrazine (Pyr) hexamethylenetetramine (hmt) β-picoline (Pic)

polymeric coordination with the use of novel polydentate ligands, where the role of $CF_3SO_3^-$ was not discussed in detai ( it was only discussed as a counteranion). It is noteworthy that some silver(I) sulfonate complexes with nitrogen-based secondary ligands exhibiting different bonding modes dependent on the presence of secondary ligands have been reported. It has also been demonstrated that existence and changes of the secondary ligands can have a great effect on the structures of silver(I) sulfonates, often with surprising results.[2e−2j,2s] However, systematic studies to probe the influence of neutral ligands on the structures of silver(I) sulfonates are still scarce.

With the aim of obtaining information on the structures of the silver compounds with chosen sulfonates (see Scheme 1) on the basis of different secondary ligands, pyrazine (Pyr), hexamethylenetetramine (hmt), and $\beta$-picoline (Pic) (see Scheme 2) are employed in this study. The current work extends the previous work on silver(I) sulfonate coordination chemistry by examining the structural diversity of the three different silver(I) sulfonates in the presence of the same secondary ligand and the structures of the same silver(I) sulfonate based on different secondary ligands. As expected, adaptations in the secondary ligand structure can result in remarkable alterations to the structures of silver(I) sulfonates, yielding new frameworks rather than modified parent networks. In this paper, we describe the details of the preparation of five novel silver(I) sulfonate compounds containing pyrazine (Pyr), hexamethylenetetramine (hmt), and $\beta$-picoline (Pic) as secondary ligands, namely, $[Ag(L1)(Pyr)]\cdot H_2O$ (**1**), $Ag(L2)(Pyr)$ (**2**), $Ag_4(L3)(Pyr)_4(H_2O)_2$ (**3**), $[Ag(L1)(hmt)]\cdot H_2O$(**4**) and $Ag(L1)(Pic)_2$ (**5**), of which compounds **2**, **4**, and **5** exhibit photoluminescent properties at room temperature. All crystal structures have been determined by single-crystal X-ray diffraction, and the compounds are also characterized by IR and elemental analyses.

## Experimental Section

**General Procedures.** Chemicals were purchased from commercial sources and used without further purification.

**Physical Measurements.** The FTIR spectra were recorded from KBr pellets in the range of 4000−400 $cm^{-1}$ on a Mattson Alpha-Centauri spectrometer. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer. The emission/excitation spectra were recorded on a Varian Cary Eclipse spectrometer. TGA was performed from room temperature to 500 °C using a Perkin-Elmer TG-7 analyzer in nitrogen. X-ray powder diffraction data were obtained on a Rigaku D/max 2500v PC X-ray diffractometer using Cu K$\alpha$ radiation.

**Synthesis of Compound 1.** A mixture of sodium 1-naphthalenesulfonate (0.115 g, 0.5 mmol) and $AgNO_3$ (0.085 g, 0.5 mmol) in water (5 mL) was stirred for 5 min, then filtered. Pyrazine (0.040 g, 0.5 mmol) in ethanol (5 mL) was added to the filtrate, and a white precipitate formed immediately. The pH value of the mixture was 8. Then it was transferred to a Teflon-lined stainless steel autoclave and heated at 140 °C for 1 day prior to being cooled to room temperature at 10 °C/h. Colorless needle crystals were obtained (0.175 g). Yield: 85%. Elemental analysis calcd (%) for $[Ag(L1)(Pyr)]\cdot H_2O$: C, 40.70; H, 3.17; N, 6.78. Found: C, 40.79; H, 3.21; N, 6.85. IR (KBr, $cm^{-1}$): 3525(ms), 3054(w), 2360(ms), 2339(ms), 1646(w), 1384(s), 1206(vs), 1151(ms), 1057(s), 1024(w), 973(w), 827(ms), 802(ms), 771(s), 692(ms), 620(s), 568(w), 522(ms), 421(w).

**Synthesis of Compound 2.** $Ag_2CO_3$ (0.166 g, 0.6 mmol) was added to an aqueous solution (10 mL) of *p*-toluenesulfonic acid (0.172 g, 1 mmol) and stirred for several minutes until no $CO_2$ was given off; then the mixture was filtered. Pyrazine (0.160 g, 2 mmol) in methanol was added to the filtrate, and a white precipitate formed immediately. The pH value of the mixture was 8.5. Then, the precipitate was dissolved by the dropwise addition of an aqueous solution of $NH_3$. Colorless crystals grew out of the filtrate by slow evaporation in a dark room for several days (0.251 g). Yield: 70%. Elemental analysis calcd (%) for $Ag(L2)(Pyr)$: C, 36.79; H, 3.09; N, 7.80. Found: C, 36.84; H, 3.01; N, 7.91. IR (KBr, $cm^{-1}$): 3447(w), 3044(w), 2922(w), 2360(s), 2339(s), 1700(w), 1493(w), 1431(w), 1129(vs), 1130(s), 1042(s), 816(ms), 692(s), 568(s).

**Synthesis of Compound 3.** After a mixture of sodium 1,3,6,8-pyrenetetrasulfonate ($Na_4L3$) (0.061 g, 0.1 mmol) and $AgNO_3$ (0.068 g, 0.4 mmol) in water (5 mL) was stirred for 5 min, pyrazine (0.096 g, 1.2 mmol) in methanol (5 mL) was added, and a yellow precipitate formed immediately. The pH value of the mixture was 8.5. The precipitate was dissolved by the dropwise addition of an aqueous solution of $NH_3$. After filtration, brown crystals grew out of the filtrate, after it stood in a dark room for several days (0.065 g). Yield: 50%. Elemental analysis calcd (%) for $Ag_4(L3)(Pyr)_4(H_2O)_2$: C, 29.42; H, 2.01; N, 8.58. Found: C, 29.51; H, 2.09; N 8.65. IR (KBr, $cm^{-1}$): 3446(ms), 2361(vs), 2336(vs), 1700(vw), 1652(ms), 1455(ms), 1420(w), 1181(w), 672(ms), 590(w), 521(w), 440(ms).

**Synthesis of Compound 4.** An aqueous solution (5 mL) of hmt (0.070 g, 0.5 mmol) was added dropwise to a stirred $MeCN/H_2O$ (1:1 (v/v), 10 mL) solution containing $AgNO_3$ (0.085, 0.5 mmol) and sodium 1-naphthalenesulfonate (0.115 g, 0.5 mmol) for 10 min.

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**Table 1.** Crystal Data and Structure Refinements for Compounds **1**−**5**

| | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| empirical formula | $C_{14}H_{13}O_4N_2SAg$ | $C_{11}H_{11}O_3N_2Sag$ | $C_{32}H_{26}O_{14}N_8S_4Ag_4$ | $C_{16}H_{21}N_4O_4SAg$ | $C_{22}H_{21}AgN_2O_3S$ |
| fw | 413.19 | 359.15 | 1306.33 | 473.30 | 501.34 |
| cryst size (mm) | 0.178 × 0.108 × 0.031 | 0.325 × 0.178 × 0.114 | 0.271 × 0.185 × 0.082 | 0.168 × 0.154 × 0.040 | 0.305 × 0.128 × 0.095 |
| cryst syst | trigonal | triclinic | orthorhombic | orthorhombic | monoclinic |
| space group | $R\bar{3}$ | $P\bar{1}$ | *Fddd* | *Pbca* | $P2_1/c$ |
| *a* (Å) | 33.263(1) | 7.167(2) | 14.486(5) | 11.5004(8) | 7.3225(4) |
| *b* (Å) | 33.263(1) | 8.205(3) | 21.824(5) | 10.8436(7) | 27.847(1) |
| *c* (Å) | 7.2940(6) | 11.531(4) | 24.041(5) | 27.674(2) | 10.3597(5) |
| α (deg) | 90 | 83.527(6) | 90 | 90 | 90.00 |
| *β* (deg) | 90 | 74.274(5) | 90 | 90 | 100.697(1) |
| *γ* (deg) | 120 | 67.555(5) | 90 | 90 | 90.00 |
| vol ($Å^3$) | 6988.9(7) | 603.3(3) | 7600(4) | 3451.1(4) | 2075.7(2) |
| *Z* | 18 | 2 | 8 | 8 | 4 |
| $R_{int}$ | 0.0529 | 0.0781 | 0.0260 | 0.0524 | 0.0374 |
| R1 [$I > 2\sigma(I)$] | 0.0426 | 0.0475 | 0.0398 | 0.0315 | 0.0554 |
| wR2 (all data) | 0.1204 | 0.1144 | 0.1300 | 0.0759 | 0.1288 |

The pH value of the mixture was 8.5. The mixture was dissolved by the dropwise addition of an aqueous solution of $NH_3$. The resulting colorless solution was allowed to stand in a dark room for several days, yielding brown lamellar crystals (0.166 g). Yield: 70%. Elemental analysis calcd (%) for $[Ag(L1)(hmt)]\cdot H_2O$: C, 40.60; H, 4.47; N, 11.84. Found: C, 40.53; H, 4.44; N, 11.82. IR (KBr, $cm^{-1}$): 3737(ms), 3673(ms), 3424(ms), 2944(w), 2361(vs), 2339(vs), 1829(vw), 1773(w), 1735(ms), 1504(ms), 1459(ms), 1393(w), 1338(vw), 1239(s), 1185(s), 1048(s), 1008(s), 809(ms), 767(ms), 689(s), 616(ms), 503(ms), 409(ms).

**Synthesis of Compound 5.** A mixture of sodium 1-naphthalenesulfonate (0.115 g, 0.5 mmol) and $AgNO_3$ (0.085 g, 0.5 mmol) in water (5 mL) was stirred for 5 min and then filtered; Pic(0.186 g, 2.0 mmol) was added to the filtrate, and a white precipitate formed immediately. The pH value of the mixture was 8. Finally, the mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 140 °C for 1 day prior to being cooled to room temperature at 10 °C/h. Colorless needle crystals were obtained (0.175 g). Yield: 70%. Elemental analysis calcd (%) for $[Ag(L1)(Pic)_2]$: C, 52.71; H, 4.22; N, 5.59. Found: C, 52.61; H, 4.24; N, 5.51. IR (KBr, $cm^{-1}$): 3844(vw), 3745(vw), 3521(w), 3051(vw), 2923(vw), 1647(vw), 1596(vw), 1452(w), 1025(vs), 1064(s), 800(ms), 770(ms), 696(ms), 619(ms), 568(ms), 518(ms).

**X-ray Data Collection and Structure Refinement.** Experimental data for the X-ray analyses are provided in Table 1. Diffraction intensities for **1**−**5** were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$Å). The structures were solved with the direct methods using SHELXS-97[5] and refined with full-matrix least-squares techniques using the SHELXL-97 program[6] within WINGX.[7] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbons were generated geometrically; the aqua hydrogen atoms were located from difference Fourier maps and refined with isotropic displacement parameters. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[8]

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **1**−**5**[a]

| | | | |
|---|---|---|---|
| compound **1** | | | |
| Ag(1)−N(2)#1 | 2.243(4) | Ag(1)−N(1) | 2.269(4) |
| Ag(1)−O(2)#2 | 2.567(3) | Ag(1)−O(1)#3 | 2.568(3) |
| N(2)#1−Ag(1)−N(1) | 175.1(1) | | |
| compound **2** | | | |
| Ag(1)−N(1) | 2.197(3) | Ag(1)−N(2)#1 | 2.203(4) |
| Ag(1)−O(1)#2 | 2.675 (3) | Ag(1)−O(3)#3 | 2.707 (3) |
| N(1)−Ag(1)−N(2)#1 | 177.3(1) | | |
| compound **3** | | | |
| Ag(1)−N(1)#1 | 2.202(4) | Ag(2)−N(2)#2 | 2.256(4) |
| Ag(2)−OW | 2.494(7) | | |
| N(1)−Ag(1)−N(1)#1 | 172.1(1) | N(2)#2−Ag(2)−N(2) | 179.3(2) |
| compound **4** | | | |
| Ag(1)−N(4)#1 | 2.334(2) | Ag(1)−N(2)#2 | 2.339(2) |
| Ag(1)−N(1) | 2.363(2) | Ag(1)−O(3) | 2.594(2) |
| N(4)#1−Ag(1)−N(2)#2 | 117.88(8) | N(2)#2−Ag(1)−N(1) | 119.26(7) |
| N(4)#1−Ag(1)−O(3) | 92.26(8) | N(1)−Ag(1)−O(3) | 94.44(7) |
| compound **5** | | | |
| Ag(1)−N(1) | 2.134(3) | Ag(1)−N(2) | 2.143(3) |
| Ag(1)−Ag(1)#1 | 3.2808(7) | Ag(1)−O(3) #1 | 2.612(3) |
| N(1)−Ag(1)−N(2) | 164.0(1) | N(1)−Ag(1)−Ag(1)#1 | 97.45(9) |
| N(2)−Ag(1)−Ag(1)#1 | 85.97(8) | | |

[a] Symmetry operations. For **1**: #1 *x*, *y*, *z* − 1; #2 −*x* + *y* + 2/3, −*x* + 1/3, *z* − 2/3; #3 *x* − *y* + 1/3, *x* − 1/3, −*z* − 1/3. For **2**: #1 *x* + 1, *y*, *z*; #2 *x*, 1 + *y*, *z*; #3 1 − *x*, −*y*, 1 − *z*. For **3**: #1 −*x* + 3/4, *y*, −*z* + 3/4; #2 −*x* + 7/4, *y*, −*z* + 3/4. For **4**: #1 −*x* + 1, *y* + 1/2,−*z* + 1/2; #2 *x* + 1/2, *y*, −*z* + 1/2. For **5**: #1 −*x* + 2, −*y*, −*z*.

## Results and Discussion

Previous studies have established the role of the secondary ligands in silver carboxylate networks, for example, the silver carboxylate coordination networks in the presence of hexamethylenetetramine (hmt).[9] However, the studies on silver(I) sulfonates have received considerably less attention. In this work, a series of silver(I) sulfonate complexes with

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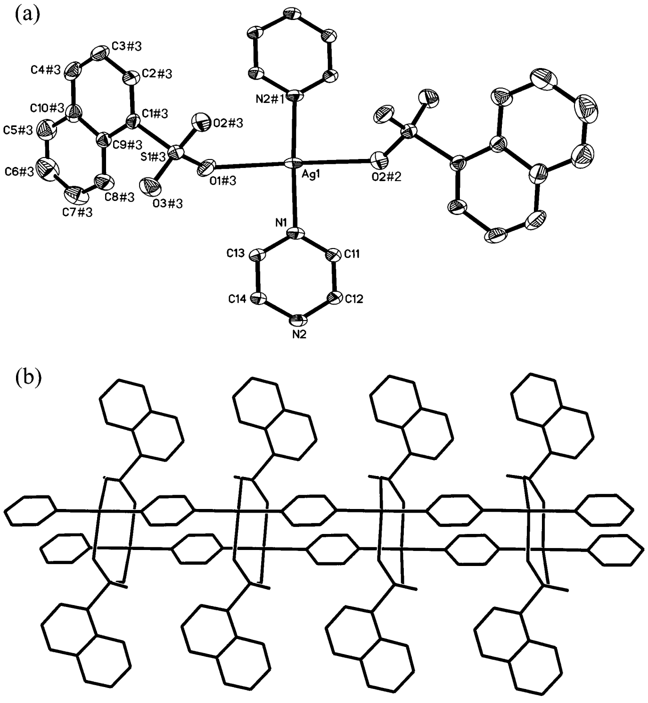

**Figure 1.** (a) Coordination environment of silver cation and the (b) double-chain structure with eight-membered rings in **1**.

neutral ligands have been synthesized. Selected metric parameters for all of the structures are listed in Table 2.

$[Ag(L1)(Pyr)]\cdot H_2O$ (**1**) was prepared using a solvothermal method. Single-crystal X-ray analysis revealed that compound **1** has a double-chain structure (Figure 1b). As shown in Figure 1a, there is one crystallographically unique silver ion which is coordinated by two oxygen atoms from two different sulfonate groups with Ag(1)−O(1)#3 and Ag(1)−O(2)#2 distances being longer than those observed in [AgL1][2b] and two nitrogen atoms from two pyrazine ligands; they complete a flattened tetrahedral coordination geometry. Furthermore, as illustrated in Figure 1b, pairs of sulfonate groups bridge pairs of silver atoms through their sulfonate oxygen atoms to give centrosymmetric dimeric units with eight-membered rings. Each $[Ag_2(L1)_2]$ unit is linked through four pyrazine ligands to two neighboring symmetry equivalent units, resulting in a one-dimensional double-chain structure in which there are $\pi-\pi$ interactions between pyrazine rings with the distance of 3.50 Å.

It is interesting to note that a closer examination of the packing diagram reveals the presence of two kinds of channels (Figure 2). The $\pi$-face and -edge contacts of the naphthalene rings result in channels with a diameter of 8.3 Å (defined by the distance between the two 7-position carbon atoms of two opposite naphthyl rings). When the van der Waals radii of the atoms are taken into account, the effective diameter of the channel is about 5.0 Å, which is a void space. Meanwhile, there are other small pores which are surrounded by sulfonate groups with water clusters residing in them. The guest water molecules, which do not show any covalent interactions, are hydrogen bonded to the uncoordinated oxygen atoms from the sulfonate groups, and the sulfonate groups act as anchors for holding the water clusters.

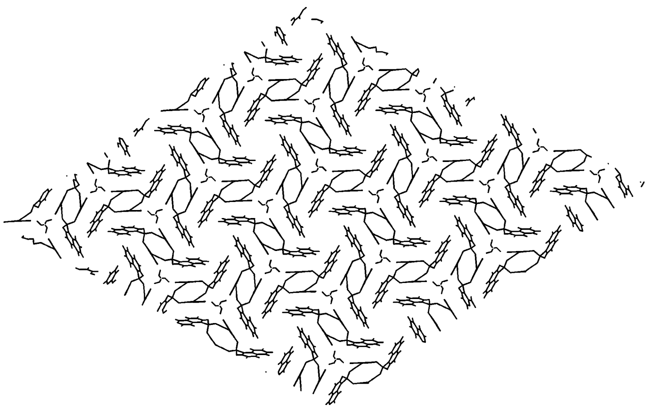

**Figure 2.** Packing diagram of compound **1**.

**Table 3.** Hydrogen-bond Geometries for Compounds **1**, **3**, and **4** (Å, deg)[a]

| D−H···A | D−H | H···A | D···A | ∠D−H···A |
|---|---|---|---|---|
| compound **1** | | | | |
| OW(1)−H(1A)···O2 | 0.91(2) | 1.91(2) | 2.807(7) | 169(5) |
| OW(1)−H(1B)···OW(1)#1 | 0.89(2) | 1.85(3) | 2.685(5) | 156(5) |
| compound **3** | | | | |
| OW−H(12)···O(3)#1 | 0.97(2) | 1.84(7) | 2.721(7) | 150(11) |
| OW−H(11)···O(3)#2 | 0.97(2) | 2.13(11) | 2.709(7) | 117(9) |
| compound **4** | | | | |
| OW1−H(11)···O(1)#1 | 0.825(19) | 2.17(2) | 2.954(3) | 159(4) |
| OW1−H(12)···O(2)#2 | 0.834(18) | 2.00(2) | 2.787(3) | 158(4) |

[a] Symmetry operations. For **1**: #1 $-x + y + 2/3, -x + 1/3, z + 1/3$. For **3**: #1 $x, -y - 1/4, -z + 3/4$; #2 $-x + 7/4, y, -z + 3/4$. For **4**: #1 $x + 1/2, y, -z + 1/2$. #2 $-x + 1, y - 1/2, -z + 1/2$.

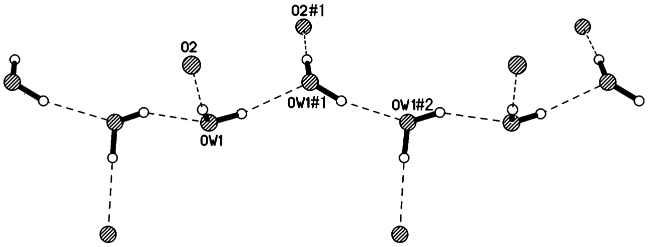

**Figure 3.** Hydrogen-bonding motif of the self-assembled chain of water molecules in **1**. The hydrogen bonds are represented by dashed lines.

Water clusters have been extensively studied both theoretically and experimentally.[10] A variety of water clusters $[(H_2O)_n, n = 2-10]$ found in a number of crystal hosts have been characterized and display different configurations. However, water clusters in silver(I) sulfonate frameworks have never been reported. The geometric parameters of the water clusters are summarized in Table 3. In the case of compound **1**, the water clusters which are associated by strong O−H···O hydrogen bonds arrange themselves to form a 1D helical chain structure (Figure 3). This supramolecular water chain is associated with the host by hydrogen bonds between uncoordinated sulfonate oxygen atoms and water molecules. As shown in Figure 3, OW1 donates hydrogen bonds to O(2) and OW1#1 which in turn donates to O2#1 and OW1#2. The water molecule behaves as an acceptor as well as a donor, while the uncoordinated sulfonate oxygen

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(10) (a) Liu, K.; Cruzan, J. D.; Saykally, R. J. *Science* **1996**, *271*, 929. (b) Ugald, J. M.; Alkorta, I.; Elguero, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 717. (c) Ludwig, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1808.

atom behaves completely as an acceptor. The OW···OW distance is 2.685(5) Å, while these distances in regular ice, liquid water, and water vapor are 2.74, 2.85, and 2.98 Å, respectively.[6c] The shorter OW···OW distance in compound **1** comes from the overall compactness of the metal−organic framework (MOF). As well-known water molecule has two hydrogen atoms and two lone-electron pairs which enable it to participate in four hydrogen bonds in a tetrahedral configuration, but it also frequently shows a 3-coordinate configuration.[11] The water molecules in compound **1** also show a 3-coordinate mode. The polymeric double chains are bridged through the hydrogen-bonding interactions between the water molecules and the sufonate oxygen atoms to form an overall three-dimensional supramolecular structure. The presence of water molecules in the structure can play an important role in stabilizing the supramolecular structure because of the formation of hydrogen bonds. In addition, water molecules could be viewed as playing a space-filling role in cases where there are cavities of a suitable size as a result of the close packing of the molecules.[12] The XRPD pattern taken on the single-crystalline sample (Figure S1b in Supporting Information) indicates that the structure of the sample at room temperature is consistent with crystal structure of **1** (the calculated XRPD pattern of complex **1** according to the single-crystal diffraction data is shown in Figure S1a). According to the TGA result (Figure S2 in Supporting Information), water molecules have been removed after heating at 120 °C. The characteristic peaks of **1** disappeared after heating at 120 °C (Figure S1c). This indicates that the crystal lattice collapses after the guest water molecules have been removed.

The network of silver 1-naphthalenesulfonate, which is the parent of compound **1**, was studied in a previous report.[2b] The overall structure was maintained as a two-dimensional solid, but the polymeric layers are not formed exclusively by Ag−$SO_3$ interactions. In each layer, the parallel ribbons of sulfonate-bridged Ag centers are connected through the organometallic bonds between the silver centers and the naphthyl groups from the neighboring ribbons. There were two distinct silver centers and two unique L1 ligands: Ag1 and Ag2 were all 6-coordinate with Ag1 coordinating to six sulfonate oxygen atoms and Ag2 forming organometallic bonds to naphthyl groups in an $\eta^2\pi$ mode, as well as coordinating to four sulfonate oxygen atoms. As could be expected, the presence of Pyr does have a great influence. Compound **1** shows a lower dimensionality than the parent compound. Since the introduction of secondary ligands, the number of the coordination sites for the sulfonate groups decreases, and structural changes occur. As a result of the presence of Pyr, in compound **1** each silver center provides two coordination sites for sulfonate oxygen atoms, and there are no $\pi$ interactions between the silver center and the naphthyl ring. It is noteworthy that the formation of hydrogen bonds between uncoordinated sulfonate oxygen atoms and water molecules results in a 3D supermolecular structure for **1**.

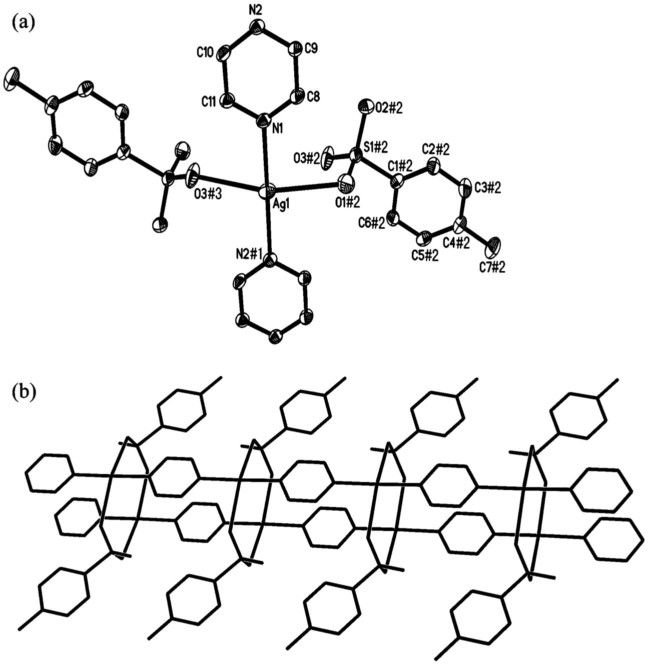

**Figure 4.** (a) Coordination environment of the silver cation and the (b) double-chain structure with eight-membered rings in **2**.

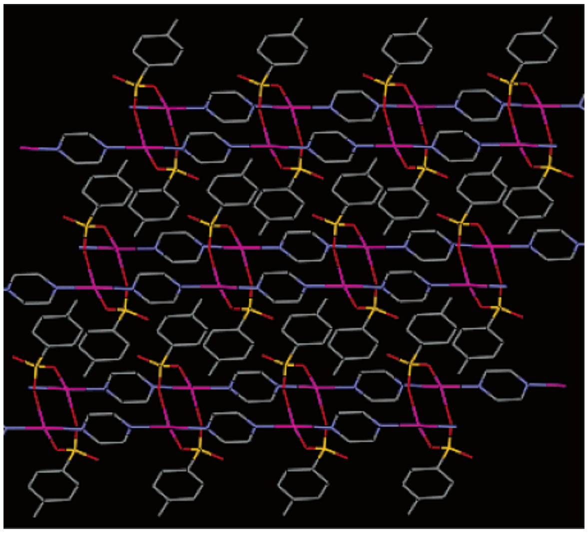

**Figure 5.** Packing diagram of double chains in [Ag(L2)(Pyr)] **2**.

Even as we have imagined, the structure of silver(I) sulfonate really gets drastic changes by employing secondary ligands. According to the above results, other four compounds with L1, L2 ,and L3 sulfonate ligands and Pyr, hmt, and Pic neutral ligands have been prepared, respectively.

X-ray diffraction shows that compound **2** has a one-dimensional double-chain structure analogous to that of compound **1** as illustrated in Figures 4b and 5. As shown in Figure 4a, each silver ion is coordinated by two oxygen atoms from different L2 ligands with Ag(1)−O(1)#2 and Ag(1)−O(3)#3 distances being 2.675 (3) and 2.707 (3) Å, respectively, both of which are longer than the normal Ag−O distances in the parent compound (AgOTs),[2d] and by two

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(11) Jeffrey, G. A.; Maluszynska, H. *Acta Crystallogr.* **1990**, *B46*, 546.
(12) Custelcean, R.; Afloroaei, C.; Vlassa, M.; Polverejan, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3094.

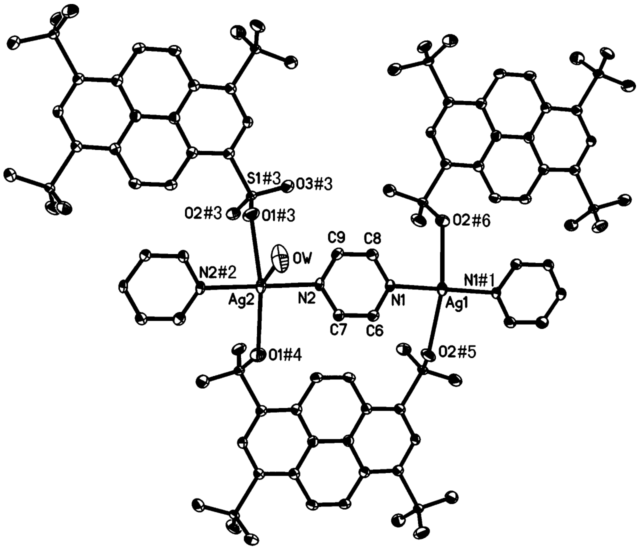

**Figure 6.** Coordination environment of the silver cations in **3**.

nitrogen atoms from different pyrazine ligands, The Ag ion forms the same coordination geometry as that found in compound **1**. The sulfonate group coordinates to the silver ion as a bridging bidentate ligand in compound **2**. A pair of silver ions are bridged by two $\mu_2$-sulfonate groups, and there is no bonding action between silver ions with an Ag−Ag distance of 3.413 Å, which is beyond the van der Waals contact distance for Ag−Ag of 3.40 Å.[2a] Consequently, the dimeric units are generated with eight-membered rings, just like those that appeared in compound **1**. Each dimeric unit is connected to two neighboring units through four pyrazine ligands to form an infinite double-chain structure, as observed in compound **1** (Figure 4b). Within the double-chain structure, there are $\pi-\pi$ interactions between the pyridine rings with a distance of 3.47 Å.

Compared with that of the parent compound (AgOTs),[2d] the sulfonate groups in compound **2** possess a $\mu_2$-coordination mode rather than the $\mu_5$-bridging mode of the parent compound. This consequence may be the result of the Pyr secondary ligands occupying the coordination sites of the Ag ions; thus the sulfonate group can coordinate to fewer Ag ions than the parent compound can. Therefore, the number of Ag ions bonded to one sulfonate group decreased from five in the parent compound to two in compound **2**. The dimensionality of **2** is lower than its parent compound with two-dimensional structure. Undoubtedly this change may be the result of the introduction of the secondary ligand of Pyr.

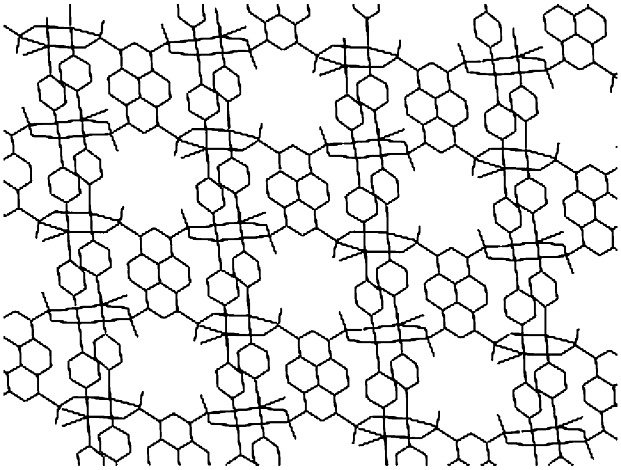

**Figure 7.** Polymeric layer of **3**.

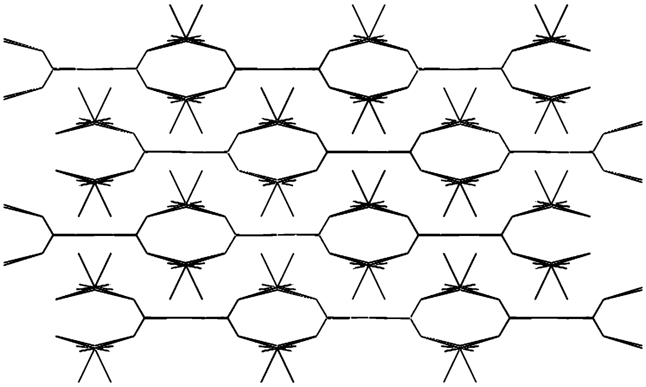

**Figure 8.** Perspective view of the parallel stacking of polymeric layers in **3**.

The monosulfonate, bisulfonate, and trisulfonate ligands[13] have been investigated extensively; the tetrasulfonate ligand has been studied only sparsely,[14] and no study on silver(I) tetrasulfonate has ever been reported. To extend this work, the L3 ligand was selected as a tetrasulfonate ligand. As shown in Figure 6, there are two crystallographically unique silver ions in the structure of **3**. The Ag1 ion has a nearly buckled square-plane geometry consisting of four bonds from two sulfonate oxygen atoms and two nitrogen atoms. The Ag2 ion is five-coordinate with a distorted square-pyramidal geometry composed of bonds from two sulfonate oxygen atoms, two nitrogen atoms, and one water molecule disordered over two sites with occupancies of 0.5 and 0.5. As shown in Figure 7, silver ions are bridged by pyrazine molecules to form an infinite polymeric chain, and two neighboring chains are connected by $\mu_2$-bridging sulfonate groups at 1,8-position or at 3,6-positions to form an infinite double-chain structure, resembling the double-chain structures in compounds **1** and **2**. Each double chain is then connected to the two adjacent double chains through the pyrene parts of the sulfonate anions to form a two-dimensional network. These polymeric sheets stack in a parallel fashion to form the overall structure of **3** (Figure 8). From the data listed in Table 3, it can be seen that there are hydrogen bonds between the adjacent layers, and the hydrogen-bonding data indicate that the coordinated water molecules acting as donors are hydrogen-bonded to the uncoordinated sulfonate oxygen atoms from the adjacent layer.

In this paper, we attempt to gain an insight into the structural diversity of silver sulfonates resulting from the employment of secondary ligands. With this in mind, we have tried our best to determine the structure of silver 1,3,6,8-pyrenetetrasulfonate, the parent compound of **3**. However,

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(13) (a) Dalrymple, S. A.; Shimizu, G. K. H. *Chem.—Eur. J.* **2002**, *8*, 3010. (b) Mahmoudkhani, A. H.; Côté, A. P.; Shimizu, G. K. H. *Chem. Commun.* **2004**, *23*, 2678.

(14) Hoffart, D. J.; Côté, A. P.; Shimizu, G. K. H. *Inorg. Chem.* **2003**, *42*, 8603.

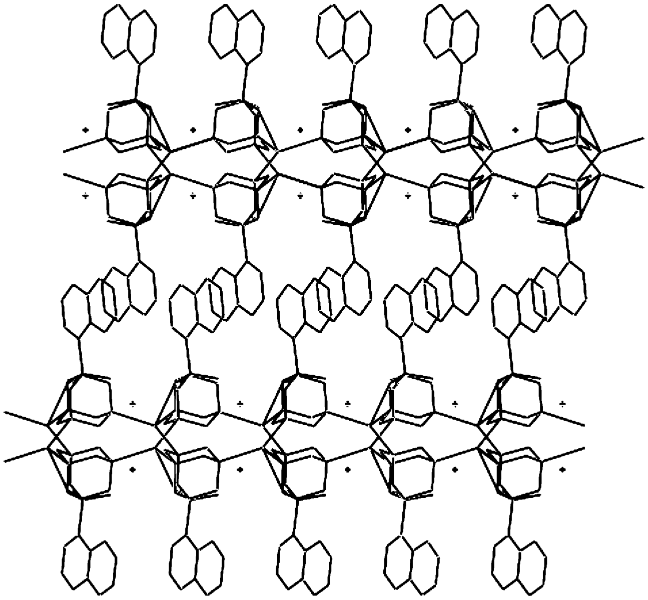

**Figure 9.** Perspective view of compound **4**, showing the infinite lamellar structure and naphthalene groups directed into the interlayer region.

we failed to obtain single crystals suitable for X-ray diffraction. Because L3 has four sulfonate groups, this parent compound is supposed to have a 3D polymeric structure.

With the purpose of investigating whether the same secondary ligand can produce the same effect on different silver(I) sulfonates, we deliberately selected three sulfonate ligands as shown in Scheme 1. L1 and L2 are monosulfonate anions with appendages of different breadths, while L3 is a tetrasulfonate anion which has not been used in the construction of coordination polymers before. Each compound, **1**, **2**, and **3**, contains pyrazine molecules as secondary ligand. Pyrazine is divergent bidentate ligand which is a common ligand used to construct coordination polymers. Pyrazine is a strong ligand for the silver ion and prefers to act as a linear $\mu_2$-ligand to bridge silver ions to form an infinite polymeric chain structure. When pyrazine is introduced, the coordination site of sulfonate group is replaced by pyrazine. Commonly, the $-SO_3^-$ group can coordinate to more silver ions than a pyrazine molecule. Thus the dimensionality of the compound will decrease with the introduction of pyrazine to the parent compound. This phenomenon has happened for each of the compounds. The chain of alternate silver ions and pyrazine molecules is the structural feature of the coordination of silver ions with pyrazine molecules. The intact existence of this kind of chain in **1**, **2**, and **3** indicates that the interaction between the silver ion and pyrazine is much stronger than that between the silver ion and the sulfonate anion. It is very interesting to note that in each of compounds pairs of Ag−pyrazine chains are bridged by $\mu_2$-sulfonate groups to form double chains. The double-chain structures are arranged in different ways through van der Waals forces, hydrogen-bonding interactions, or covalent bonds.

From above discussion, it can be seen that the introduction of the divergent bidentate ligand Pyr does result in great structural changes for each of the three selected silver sulfonates. To survey the structural influence of different neutral ligands on the same silver sulfonate, we selected silver 1-naphthalenesulfonate, synthesized compounds **4** and **5** , and determined their structures.

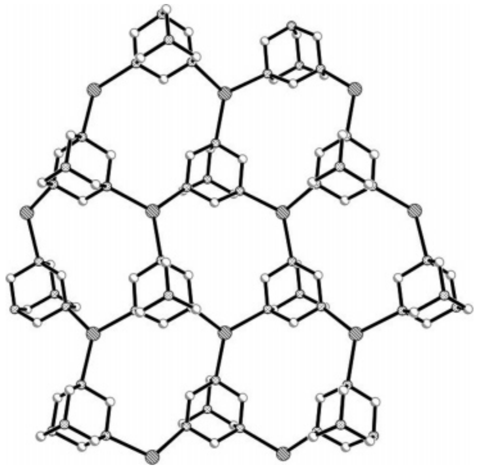

**Figure 10.** View of a single layer of compound **4** composed of Ag ions and hmt ligands.

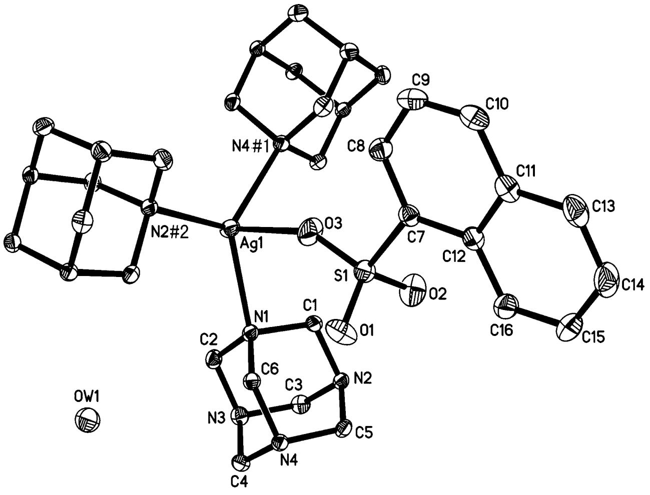

**Figure 11.** Coordination environment of silver cation in **4**.

As shown in Figure 9, compound **4** shows a two-dimensional network from which the naphthalene groups of the sulfonate protrude from both sides. The structure of the compound consists of two-dimensional infinite layers of hexagonal units. As illustrated in Figure 10, each hexagonal unit is organized by three Ag atoms and three $\mu_3$-hmt ligands each at corner. Each Ag ion is coordinated by three nitrogen atoms from three different hmt ligands and one oxygen atom, and they complete a distorted tetrahedral coordination geometry as shown in Figure 11. In addition, there is one lattice water molecule with no coordination to any other atoms in the structure. The guest water molecules are hydrogen bonded to the uncoordinated oxygen atoms from sulfonate groups. The geometric parameters of the hydrogen bonds are summarized in Table 3. OW1 donates hydrogen bonds to uncoordinated sulfonate oxygen atoms. A well-known water molecule often shows a 3-coordinate configuration; however, the water molecule of compound **4** shows a 2-coordinate mode. The sulfonate ligands are bridged by the hydrogen-bonding interactions between the water molecules and the sulfonate oxygen atoms to form one-

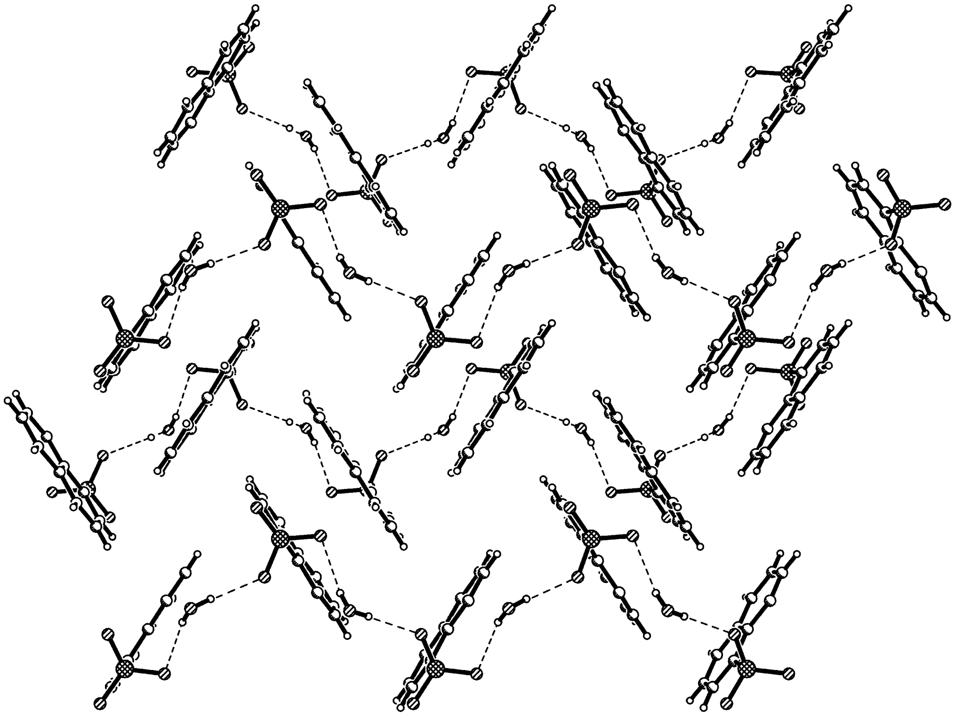

**Figure 12.** Hydrogen-bonding motif of the self-assembled chain of L1 ligands and water molecules in **4**. The hydrogen bonds are represented by dashed lines.

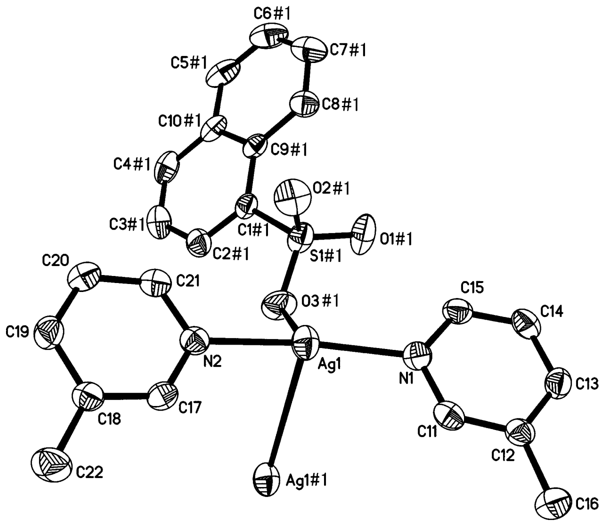

**Figure 13.** Coordination environment of silver cation in **5**.

dimensional zigzag chains as shown in Figure 12. Further study demonstrates that there are $\pi-\pi$ interactions between the naphthyl rings from neighboring layers with a distance of 3.42 Å.

Just like compound **1**, compound **4** shows a totally different structure from its parent compound resulting from the introduction of hmt ligands. The silver ion coordination sites for the sulfonate group and naphthyl ring in the parent compound have been occupied by the hmt ligand in **4**. There is no bonding action between the Ag center and the naphthyl ring, and most coordination sites are occupied by hmt ligands; there is only one coordination site for the sulfonate oxygen atom. Although both **4** and its parent compound show two-dimensional polymeric layered structures, the construction of the layers are greatly different. For the parent compound, the layers are formed through the interaction of Ag$-$SO$_3$ and Ag$-$C bonds; while for **4**, the layers are formed through the Ag$-$N bonds between the Ag centers and the hmt ligands.

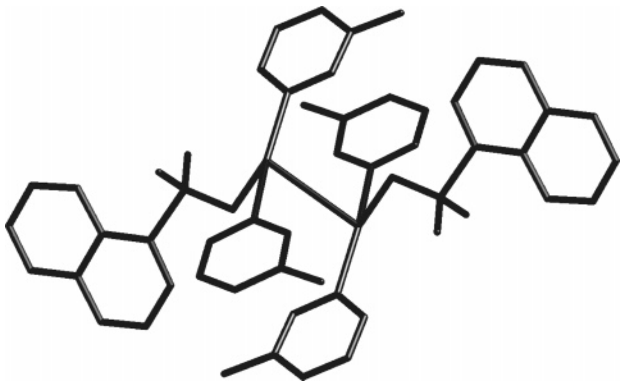

**Figure 14.** Dimeric structure of compound **5**.

X-ray diffraction reveals that compound **5** containing the L1 sulfonate anion and the Pic secondary ligand possesses one crystallographically unique silver ion in the structure (Figure 13). Ag(1) is coordinated by two nitrogen atoms from different $\beta$-picoline ligands and one sulfonate oxygen atom with a long Ag$-$O distance of 2.611 Å, and it has a distorted tetrahedral coordination geometry. As shown in Figure 14, there is a Ag$-$Ag interaction with a Ag(1)$-$Ag(1)#1 distance of 3.2808(7) Å, which is shorter than the van der Waals contact distance for Ag$-$Ag of 3.40 Å. Since Pic is a monodentate terminal ligand, when Pic was introduced into the parent compound of **5**, most Ag center coordination sites were occupied by Pic to generate a discrete dimeric structure. Within the dimeric unit, there are $\pi-\pi$ interactions between pyridine rings with a distance of 3.49 Å.

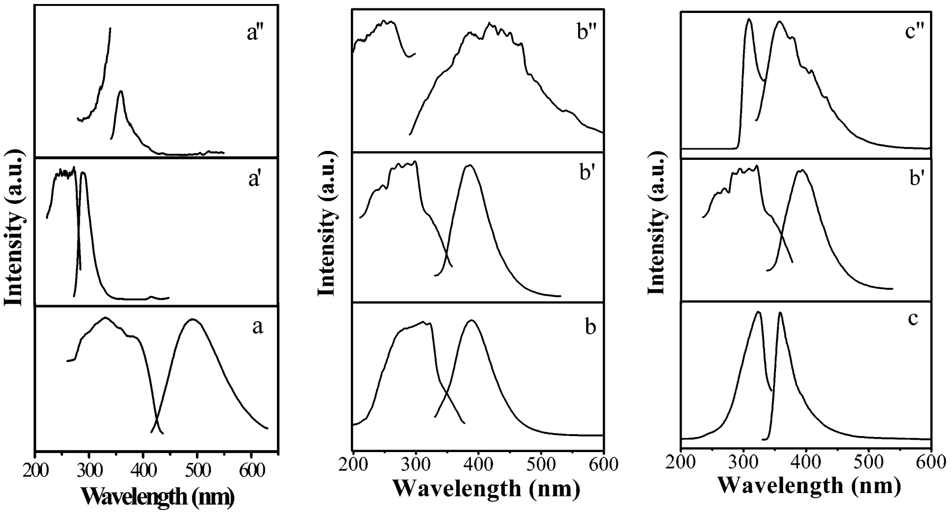

**Figure 15.** Solid-state photoluminescent spectra of (a) **2**, (b) **4**, and (c) **5** and free ligands (a′) HL2, (b′) HL1, (a″) Pyr, (b″) hmt, and (c″) Pic at room temperature.

Compounds **1**, **4** ,and **5** have the same parent compound. From their structures, it can be seen that the introduction of secondary ligands results in drastic structural changes. Since the coordination ability of the secondary ligand is stronger than the sulfonate anion, the Ag ion coordination sites in the parent compound are replaced by the secondary ligand. Although compounds **1**, **4**, and **5** have the same sulfonate anion, their structures are greatly different from each other. The structures of the ternary complexes are mainly determined by the nature of the secondary ligands because of their strong coordination ability for the silver ion. Pyr prefers to coordinate to the silver ion in a linear mode to form an infinite polymeric chain structure; such chain structures are retained in the structure of **1**. The hmt ligand can coordinate to silver ion in $\mu_2$-, $\mu_3$-, and $\mu_4$-modes to form a variety of polymeric structures. In compound **4**, hmt coordinates to the silver ion in a $\mu_3$-mode to form a two-dimensional structure. Since Pic is a terminal strong ligand for the silver ion, the coordination sites of the sulfonate groups in the parent compounds are occupied by Pic molecules, the number of silver ions bonded to each sulfonate group decreases, the dimensionality of the complex decreases to zero, and a discrete structure is formed.

On the basis of above results, the secondary ligand not only leads to structural changes but also sometimes is the dominant factor determining the structural features of the complex, even if there are great structural differences among the sulfonate ligands. The structural units formed by the coordination of the silver ion and secondary ligand are assembled together through the weak coordination interaction between silver ions and sulfonate groups. On the basis of this idea, the ternary system of silver ion, sulfonate ions, and N-containing neutral ligand has both strong coordination action and weak coordination action and can be used to design and construct materials with specific structural features and functionality. In the first step, a neutral ligand is selected to form a tight subunit through coordination with silver ion, and in the second step, a sulfonate anion is selected to assemble the subunits in specific way through the weak coordination interaction between the silver ion and the sulfonate anion.

**Luminescent Properties.** Luminescent compounds are of great current interest because of their various applications in chemical sensors, photochemistry, and electroluminescent (EL) displays.[15] The luminescent properties of silver carboxylate compounds have been investigated extensively;[9b,16] however, studies concerning silver sulfonates are limited.[2o,17] In this paper, the luminescent properties of compounds **2**, **4**, and **5** were investigated in the solid state. The solid-state photoluminescent spectra of **2**, **4**, **5**, and the free ligands are depicted in Figure 15. Compound **2** exhibits both blue photoluminescence with an emission maximum at 493 nm upon excitation at 330 nm and the strongest excitation peak at 333 nm upon emission at 490 nm. The main emission peaks of HL2 and pyrazine are at 289 and 359 nm, respectively. The removal of a proton from HL2 and the coordination of the $L2^-$ anion and pyrazine to the silver(I) centers play important roles in the red shift of the emission. Compound **4** exhibits an emission maximum at 393 nm upon excitation at 323 nm. For hmt, the emission band maximum at 420 nm is much broader than that of **4**. The emission spectrum of HL1 shows both a similar shape and maximum (394 nm) to that of **4**. The resemblance of the emission spectrum of compound **4** with that of the free HL1 indicates that the luminescence of compound **4** is HL1-based emission. Compound **5** shows an emission with a maximum at 359 nm upon excitation at 323 nm. Free ligands HL1 and Pic show emission with maxima at 394 nm and 358 nm,

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respectively. In comparison to complex **4**, a blue shift of 34 nm has been observed in compound **5** because of the replacement of hmt with Pic. The resemblance of the emission spectra of **5** to that of the free Pic indicates that the luminescence of compound **5** is Pic-based emission. The luminescence of compounds **2**, **4**, and **5** should originate from the transitions between the energy levels of sulfonate anion, neutral ligand, or both. The shifts of the emission bands are attributed to both the deprotonation of the sulfonic acid and the coordination action of the sulfonate anion and neutral ligand to silver ions.[18]

## Conclusion

In summary, a series of silver(I) sulfonate complexes, **1**−**5**, with pyrazine, hexamethylenetetramine, and $\beta$-picoline have been synthesized and characterized. The structures of these compounds have been determined by single-crystal X-ray analysis. As a consequence, remarkable structural changes in the silver(I) sulfonate compounds were observed by introducing neutral ligands. Compounds **1**−**4**, containing pyrazine or hexamethylenetetramine ligands, possess polymeric structures, while compound **5**, containing $\beta$-picoline, shows a discrete structure. These results indicate that the structures of the compounds reported here may be controlled by the secondary ligands, and the dimensionalities of the compounds increase when the coordination sites of the secondary ligands are increased. Because of the strong coordination effect of the neutral ligand on the silver ion, the structural features formed by silver ions and neutral ligands are retained in the overall structures, but they are arranged in different ways through the coordination interaction between silver ion and sulfonate anion and the hydrogen-bonding interactions. Therefore new silver(I) sulfonates with higher dimensionality can be obtained by using other polydentate neutral ligands. Further studies involving other silver(I) sulfonates and other secondary ligands are in progress in our laboratory.

**Acknowledgment.** We thank the National Natural Science Foundation of China (No. 20471014), the Fok Ying Tung Education Foundation, and the Natural Science Foundation of Jilin province (China) for support.

**Supporting Information Available:** XRPD patterns, a TGA curve for compound **1**, and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Valeur, B. *Molecular fluorescence: Principles and Applications*; Wiley-VCH: Weinheim, Germany, 2002.