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Structural Study of Silver(I) Sulfonate Complexes with Pyrazine Derivatives

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In this Article, 11 silver complexes, namely, [Ag(L1)(2-Pyr)(H_2O)] (**1**), Ag(L1)(2,3-Pyr) (**2**), [$Ag_2(L1)_2$(2Et,3Me-Pyr)$_2$(H_2O)] (**3**), [Ag(2,6-Pyr)](L1)•1.5H_2O (**4**), Ag(L1)(2,5-Pyr) (**5**), [Ag(H_2O)$_2$](L2)•H_2O (**6**), [Ag(L2)(2-Pyr)] (**7**), [Ag(L2)(2,3-Pyr)]•1.5H_2O (**8**), [Ag(L2)(2Et,3Me-Pyr)]•2H_2O (**9**), [Ag_2(L2)(2,6-Pyr)(H_2O)$_2$](L2)•H_2O (**10**) and [Ag(L2)(2,5-Pyr)]•H_2O (**11**) (2-Pyr = 2-methylpyrazine; 2,3-Pyr = 2,3-dimethylpyrazine; 2Et,3Me-Pyr = 2-ethyl-3-methylpyrazine; 2,6-Pyr = 2,6-dimethylpyrazine; 2,5-Pyr = 2,5-dimethylpyrazine; L1 = *p*-aminobenzenesulfonate anion and L2 = 6-amino-1-naphthalenesulfonate anion), have been synthesized and characterized by elemental analyses, IR spectroscopy, and X-ray crystallography. In **1**, **3**, and **4**, Ag(I) centers are linked by bridging pyrazine ligands to form one-dimensional chains, whereas compound **2** shows a double-chain structure through weak Ag–C interactions. The structure analyses show that both **5** and **11** form two-dimensional networks composed of 26-membered metallocycles. Unexpectedly, compounds **6** and **10** show discrete structures. In compound **7**, silver(I) centers are bridged by sulfonate anions to form a polymeric helical structure, and the 2-Pyr molecule acts as a monodentate ligand. Compounds **8** and **9** show hinged chain structures containing 14-membered rings, and these chains interlace with each other to generate unique three-dimensional structures. These results indicate that the substituting groups and the substituting sites of pyrazine derivatives play an important role in the framework formation of silver complexes. Additionally, the luminescent properties of these compounds are also discussed.

Introduction

Over the past decades, the design and synthesis of Ag(I) compounds have attracted great attention because of the versatility of their coordination geometries.[1] In recent years, coordination chemists have focused on silver−sulfonate compounds by reason of their alterable coordination modes, intriguing inorganic−organic lamellar structures, selective and reversible guest inclusion properties, and intercalation of guest molecules. Some studies on the interesting coordination of silver sulfonates and their solid-state properties have been reported.[2] Many silver sulfonate compounds have a layered "inorgano−organic" structure where the inorganic component is composed of sulfonate-bridged silver(I) centers and the organic moiety is substituted phenyl groups.[2a−d] Currently, people are enthusiastically investigating the effects of organic groups and secondary ligands on the structures of silver(I) sulfonates.[2b,g,3] In our previous reports, we have studied the structures of silver(I) sulfonate complexes containing monodentate, divergent bidentate, and tetradentate neutral ligands.[3a,b] Herein, we report a series of silver(I) sulfonates complexes containing pyrazine derivatives to probe the influence of neutral ligands on the structures of the complexes.

In this Article, we chose two sulfonate anions containing $-NH_2$ groups (L1 = *p*-aminobenzenesulfonate anion, L2 = 6-amino-1-naphthalenesulfonate anion). The $-NH_2$ groups have potential for the formation of hydrogen bonds and the coordination tendency to silver ions. Pyrazine is a divergent bidentate ligand and commonly acts as a bridging ligand. Some silver coordination polymers containing pyrazine ligands with different topologies have been reported.[4a,e] In this work, pyrazine derivatives were selected as neutral ligands to construct novel silver sulfonate coordination

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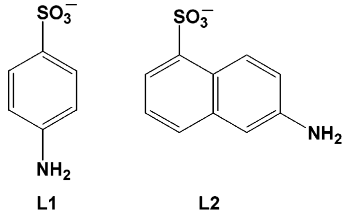
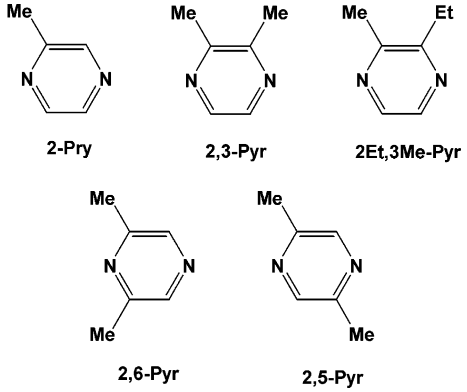
Scheme 1. Structures of the Sulfonate Anions in This Work



Scheme 2. Structures of the Pyrazine Derivatives in This Work



polymers and explore their effect on the structures of complexes. Five pyrazine derivatives incorporating different substitutions were used as neutral ligands (2-methylpyrazine, 2,3-dimethylpyrazine, 2-ethyl-3-methylpyrazine, 2,6-dimethylpyrazine, and 2,5-dimethylpyrazine). The structures of the sulfonate anions and the pyrazine derivatives used in this work are shown in Schemes 1 and 2. Eleven compounds, namely, [Ag(L1)(2-Pyr)(H_2O)] (**1**), Ag(L1)(2,3-Pyr) (**2**), [Ag_2($L1)_2$(2Et,3Me-$Pyr)_2$(H_2O)] (**3**), [Ag(2,6-Pyr)](L1)·1.5H_2O (**4**), Ag(L1)(2,5-Pyr) (**5**), [Ag($H_2O)_2$](L2)·H_2O (**6**), [Ag(L2)(2-Pyr)] (**7**), [Ag(L2)(2,3-Pyr)]·1.5H_2O (**8**), [Ag(L2)(2Et,3Me-Pyr)]·2H_2O (**9**), [Ag_2(L2)(2,6-Pyr)($H_2O)_2$] (L2)·H_2O (**10**), and [Ag(L2)(2,5-Pyr)]·H_2O (**11**), have been synthesized. The crystal structures of these compounds have been determined by single-crystal X-ray diffraction, and the compounds have been characterized by IR and elemental analyses.

Experimental Section

General Procedures. Chemicals were purchased from commercial sources and used without further purification. AgL1 was prepared according to the literature method.[2y]

Physical Measurements. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer, and the FT-IR spectra were recorded from KBr pellets in the range of 4000−400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. The solid-state emission/excitation spectra were recorded on a Varian Cary Eclipse spectrometer at room temperature.

Synthesis of [Ag(L1)(2-Pyr)(H_2O)] (1). An aqueous solution (10 mL) of *p*-aminobenzenesulfonic acid (0.087 g, 0.5 mmol) was added to solid Ag_2CO_3 (0.069 g, 0.25 mmol) and stirred for several minutes until no further CO_2 was given off; then 2-methylpyrazine (0.047 g, 0.5 mmol) was added, and a white precipitate formed. The precipitate was dissolved by dropwise addition of an aqueous solution of NH_3 (14 M). Colorless crystals of **1** were obtained by evaporation of the solution for 5 days at room temperature (68% yield). Anal. Calcd for $C_{11}H_{14}AgN_3O_4S$: C, 33.69; H, 3.60; N, 10.71. Found: C, 34.41; H, 3.49; N, 10.36. IR (cm^{-1}) 3413 (s), 3345 (s), 3201 (w), 3034 (w), 1637 (vs), 1601 (s), 1450 (vs), 1201 (w), 1175 (w), 1030 (w), 1006 (w), 834 (s), 695 (w), 569 (w), 480 (s), 425 (s), 405 (vs).

Syntheses of Ag(L1)(2,3-Pyr) (2), [Ag_2($L1)_2$(2Et,3Me-$Pyr)_2$(H_2O)] (3), [Ag(2,6-Pyr)] (L1)·1.5(H_2O) (4), and Ag(L1)(2,5-Pyr) (5). A procedure similar to that used for compound **1**, with corresponding pyrazine derivatives instead of 2-methylpyrazine, was used to prepare compounds **2**−**5**. Compound **2** (70% yield). Anal. Calcd for $C_{12}H_{14}AgN_3O_3S$: C, 37.12; H, 3.63; N, 10.82. Found: C, 37.88; H, 3.61; N, 11.02. IR (cm^{-1}): 3389 (w), 3336 (w), 3231 (s), 3095 (vs), 2361 (w), 2339 (s), 1594 (vs), 1207 (s), 1172 (w), 1115 (s), 1024 (w), 692 (w), 570 (w). Compound **3** (69% yield). Anal. Calcd for $C_{26}H_{34}Ag_2N_6O_7S_2$: C, 37.98; H, 4.17; N, 10.22. Found: C, 38.13; H, 3.98; N, 10.31. IR (cm^{-1}): 3369 (vs), 2360 (s), 2338 (vs), 1599 (s), 1459 (vs), 1414 (vs), 1207 (w), 1169 (w), 1120 (w), 1030 (w), 1005 (w), 824 (s), 692 (w), 567 (w), 478 (s). Compound **4** (62% yield). Anal. Calcd for $C_{12}H_{17}AgN_3O_{4.5}S$: C, 34.71; H, 4.13; N, 10.12. Found: C, 34.64; H, 4.09; N 10.22. IR (cm^{-1}): 3420 (vs), 3339 (s), 3230 (vs), 2360 (vs), 1594 (w), 1497 (vs), 1208 (w), 1159 (w), 1114 (w), 1023 (w), 999 (s), 842 (vs), 694 (w), 669 (vs), 569 (w), 471 (s), 420 (s). Compound **5** (65% yield). Anal. Calcd for $C_{12}H_{14}AgN_3O_3S$: C, 37.13; H, 3.63; N, 10.82. Found: C, 36.89; H, 3.58; N, 10.90. IR (cm^{-1}): 3422 (s),

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3338 (s), 3209 (w), 2362 (vs), 1599 (w), 1207 (vs), 1154 (s), 1024 (w), 694 (w), 569 (w), 476 (s).

Synthesis of [Ag(H_2O)$_2$](L2)·H_2O] (6). Ag_2CO_3 (0.069 g, 0.25 mmol) was added to an aqueous solution (10 mL) of 6-amino-1-naphthalenesulfonic acid (0.112 g, 0.5 mmol) and stirred for several minutes until no CO_2 was given off; then the precipitate was dissolved by dropwise addition of aqueous solution of NH_3 (14 M). Colorless block crystals were obtained by evaporation of the solution for 7 days at room temperature (59% yield). Anal. Calcd for $C_{10}H_{14}AgNO_6S$: C, 31.27; H, 3.67; N, 3.65. Found: C, 31.87; H, 3.59; N, 3.90. IR (cm^{-1}): 3732 (vs), 3414 (w), 3335 (w), 2360 (s), 2339 (vs), 1634 (s), 1616 (s), 1510 (s), 1219 (w), 1196 (w), 1178 (w), 1146 (w), 1041 (w), 693 (vs), 612 (s), 511 (vs).

Synthesis of [Ag(L2)(2-Pyr)] (7). Ag_2CO_3 (0.069 g, 0.25 mmol) was added to an aqueous solution (10 mL) of 6-amino-1-naphthalenesulfonic acid (0.112 g, 0.5 mmol) and stirred for several minutes until no CO_2 was given off; then 2-methylpyrazine (0.047 g, 0.5 mmol) was added. After the mixture was stirred for 15 min, the precipitate was dissolved by dropwise addition of aqueous solution of NH_3 (14 M). Brown block crystals were obtained by evaporation of the solution for 6 days at room temperature (77% yield). Anal. Calcd for $C_{15}H_{14}AgN_3O_3S$: C, 42.47; H, 3.33; N, 9.91. Found: C, 41.96; H, 3.42; N, 10.05. IR (cm^{-1}): 3418 (s), 3325 (s), 2359 (vs), 1626 (vs), 1511 (vs), 1212 (w), 1184 (w), 1041 (w), 614 (s).

Syntheses of [Ag(L2)(2,3-Pyr)]·1.5H_2O (8), [Ag(L2)(2Et,3Me-Pyr)]·2H_2O (9), [Ag_2(L2)(2,6-Pyr) (H_2O)$_2$](L2)·H_2O (10), and [Ag(L2)(2,5-Pyr)]·H_2O (11). A procedure similar to that used for compound **7**, with corresponding pyrazine derivatives instead of 2-methylpyrazine, was used to prepare compounds **8**−**11**. Compound **8** (78% yield). Anal. Calcd for $C_{16}H_{19}AgN_3O_{4.5}S$: C, 41.30; H, 4.12; N, 9.03. Found: C, 40.97; H, 3.98; N, 9.53. IR (cm^{-1}): 3410 (s), 3345 (s), 3199 (vs), 1601 (s), 1202 (w), 1175 (w), 1123 (w), 1030 (w), 1006 (w), 695 (s), 569 (w), 423 (vs). Compound **9** (59% yield). Anal. Calcd for $C_{17}H_{22}AgN_3O_5S$: C, 41.82; H, 4.54; N, 8.61. Found: C, 40.99; H, 4.52; N, 8.67. IR (cm^{-1}): 3426 (s), 2977 (vs), 2360 (w), 2339 (w), 1629 (s), 1512 (s), 1409 (vs) 1185 (w), 1045 (w), 971 (s), 922 (s), 851 (s), 793 (s), 717 (vs), 692 (w), 614 (w), 560 (s), 508 (w), 467 (w), 404 (w). Compound **10** (76% yield). Anal. Calcd for $C_{26}H_{30}Ag_2N_4O_9S_2$: C, 37.97; H, 3.68; N, 6.81. Found: C, 37.35; H, 3.61; N, 6.76. IR (cm^{-1}): 3434 (vs), 3331 (w), 1624 (s), 1510 (vs), 1190 (w), 1044 (w), 828 (vs), 691 (w), 614 (w), 555 (s), 511 (s), 464 (s), 422 (vs). Compound **11** (79% yield). Anal. Calcd for $C_{16}H_{18}AgN_3O_4S$: C, 42.12; H, 3.98; N, 9.21. Found: C, 41.98; H, 3.91; N, 9.63. IR (cm^{-1}): 3445 (s), 3339 (s), 3039 (vs), 1623 (s), 1512 (s), 1499 (s), 1207 (w), 1184 (w), 1150 (s), 795 (vs), 693 (w), 614 (w), 509 (vs).

X-ray Crystallography. Experimental details of the X-ray analyses are provided in Table 1. Diffraction intensities for compounds **6** and **10** were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 293 K. Diffraction intensities for other compounds were collected on a Rigaku RAXIS-RAPID diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 293 K. The structures were solved with the direct method of 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] Further details are provided in the Supporting Information.

Results and Discussion

Descriptions of Crystal Structures. Selected bond distances and angles for compounds **1**−**11** are listed in Table 2. Pyrazine derivatives prefer to coordinate to silver ion in a linear mode to form an infinite polymeric chain structure, and such chain structures are retained in the structures of **1**−**5**. Pyrazine derivatives having different substituting groups can produce a variety of electronically and sterically different pyrazine-related coordination environments (Scheme 3) which induce L1 anions to adopt different coordination modes, and this finally results in the structural changes of **1**−**5** (Scheme 4).

Compound **1** possesses one crystallographically unique silver ion in the structure (Figure 1). Each silver cation is four-coordinated by two nitrogen atoms from two 2-Pyr ligands, one amino nitrogen atom, and one aqua ligand. The Ag−N_{amino} bond distance is considerably longer than the Ag−N_{2-Pyr} lengths, but all Ag−N bond distances found in **1** are within the normal range observed in N-containing Ag(I) complexes.[2g,9,10] The silver cations are bridged by 2-Pyr ligands to form a one-dimensional (1D) infinite polymeric chain structure as shown in Figure 2a, and these 1D polymeric chains stack to form the overall structure of **1** (Figure 2b). Adjacent pyrazine rings in the chain have a dihedral angle of 23.1°. In a previous report,[11] compound [Ag($C_2F_3O_2$)(2-Pyr)] (**12**) shows a three-dimensional (3D) network structure, in which both trifluoroacetate anion and 2-methylpyrazine act as bidentate bridging ligands. The synthesis and structure of the binary complex AgL1 (**13**) have been reported.[2y] Compound **13** shows a 3D polymeric structure where the Ag(I) center is four-coordinated by three oxygen atoms from three different L1 ligands and one nitrogen atom from another L1 ligand.

The coordinated water molecules, amino groups, and sulfonate groups of L1 ligands in **1** are involved in the formation of complicated hydrogen-bonding interactions. It is interesting to note that four sulfonate groups, two amino groups, and two water molecules compose a large ring which

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Table 1. Crystal Data and Structure Refinements for Compounds **1**−**11**

	1	**2**	**3**
empirical formula	$C_{11}H_{14}AgN_3O_4S$	$C_{12}H_{14}AgN_3O_3S$	$C_{26}H_{34}Ag_2N_6O_7S_2$
fw	392.18	388.19	822.45
cryst size [mm]	0.48 × 0.31 × 0.10	0.36 × 0.30 × 0.22	0.37 × 0.33 × 0.19
cryst syst	orthorthombic	monoclinic	orthorhombic
space group	*Pbca*	$P2_1/n$	$P2_12_12$
a [Å]	13.271(3)	7.078(1)	13.518(3)
b [Å]	14.427(3)	14.533(3)	14.308(3)
c [Å]	14.477(3)	12.958(3)	7.780(2)
α [deg]	90	90	90
β [deg]	90	93.24(3)	90
γ [deg]	90	90	90
V [Å^3]	2772(1)	1330.8(5)	1504.8(5)
Z	8	4	2
R_{int}	0.0381	0.0170	0.0429
R1 [$I > 2\sigma(I)$]	0.0381	0.0279	0.0417
wR2 (all data)	0.1035	0.0706	0.0996
flack x			0.0294

	4	**5**	**6**
empirical formula	$C_{12}H_{17}AgN_3O_{4.5}S$	$C_{12}H_{14}AgN_3O_3S$	$C_{10}H_{14}AgNO_6S$
fw	415.22	388.19	384.15
cryst size [mm]	0.35 × 0.29 × 0.18	0.37 × 0.29 × 0.19	0.11 × 0.10 × 0.10
cryst system	monoclinic	monoclinic	monoclinic
space group	$C2/c$	*Pn*	$P2_1$
a [Å]	13.482(3)	8.640(2)	8.878
b [Å]	14.254(3)	7.446(2)	9.014
c [Å]	16.552(3)	10.576(2)	9.558
α [deg]	90	90	90
β [deg]	107.99(3)	95.90(3)	116.99
γ [deg]	90	90	90
V [Å^3]	3025.5(11)	676.8(2)	681.6
Z	8	2	2
R_{int}	0.0165	0.0176	0.0518
R1 [$I > 2\sigma(I)$]	0.0340	0.0209	0.0330
wR2 (all data)	0.0949	0.0518	0.1411
flack x		−0.0223	−0.0815

	7	**8**	**9**
empirical formula	$C_{15}H_{14}AgN_3O_3S$	$C_{16}H_{19}AgN_3O_{4.5}S$	$C_{17}H_{22}AgN_3O_5S$
fw	424.22	465.27	488.31
cryst size [mm]	0.50 × 0.37 × 0.26	0.63 × 0.43 × 0.39	0.22 × 0.15 × 0.14
cryst syst	monoclinic	trigonal	trigonal
space group	$P2_1/c$	*R*3*c*	*R*3*c*
a [Å]	9.119(2)	21.949(7)	21.902(3)
b [Å]	6.850(1)	21.949(7)	21.902(3)
c [Å]	24.826(5)	20.220(5)	20.776(4)
α [deg]	90	90	90
β [deg]	90.40(3)	90	90
γ [deg]	90	120	120
V [Å^3]	1550.7(5)	8436(3)	8631(2)
Z	4	18	18
R_{int}	0.0283	0.0384	0.0610
R1 [$I > 2\sigma(I)$]	0.0284	0.0312	0.0371
wR2 (all data)	0.0896	0.0888	0.0796
flack x		0.0200	−0.0016

	10	**11**
empirical formula	$C_{26}H_{30}Ag_2N_4O_9S_2$	$C_{16}H_{18}AgN_3O_4S$
fw	822.40	456.26
cryst size [mm]	0.44 × 0.10 × 0.10	0.30 × 0.26 × 0.19
cryst syst	orthorhombic	monoclinic
space group	$Pna2_1$	*Cc*
a [Å]	11.931(3)	10.018(2)
b [Å]	18.766(4)	17.175(3)
c [Å]	13.323(3)	10.438(2)
α [deg]	90	90
β [deg]	90	91.28(3)
γ [deg]	90	90
V [Å^3]	2983(2)	1795.5(6)
Z	4	4
R_{int}	0.0933	0.0245
R1 [$I > 2\sigma(I)$]	0.0424	0.0341
wR2 (all data)	0.0788	0.0909
flack x	−0.0457	−0.0407

is parallel to the *ab* plane via hydrogen bonds (Supporting Information Figure S1a). Moreover these rings fuse to form a hydrogen-bonding two-dimensional (2D) sheet (Supporting Information Figure S1b). These 2D sheets and the 1D

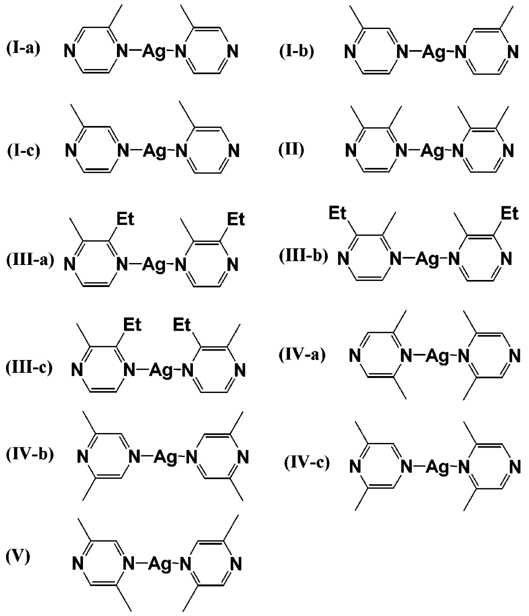
Table 2. Selected Bond Lengths [Å] and Angles [deg] for **1**−**11**[a]

Compound **1**			
Ag(1)−N(2)	2.248(3)	Ag(1)−N(3)#1	2.257(3)
Ag(1)−N(1)	2.604(3)	Ag(1)−OW(1)	2.632(3)
N(2)−Ag(1)−N(3)#1	165(1)	N(2)−Ag(1)−N(1)	100.7(1)
N(3)#1−Ag(1)−N(1)	91.22(9)		
Compound **2**			
Ag(1)−N(2)	2.171(2)	Ag(1)−N(3)#3	2.182(2)
Ag(1)−O(1)#2	2.532(2)		
N(2)−Ag(1)−N(3)#3	170.52(7)	N(2)−Ag(1)−O(1)#2	95.14(6)
N(3)#3−Ag(1)−O(1)# 2	93.63(6)		
Compound **3**			
Ag(1)−N(3)	2.234(3)	Ag(2)−N(2)	2.292(4)
Ag(1)−N(3)#1	2.234(3)	Ag(2)−N(2)#2	2.292(4)
Ag(1)−O(2)	2.591(4)	Ag(2)−OW1	2.409(5)
Ag(1)−O(2)#1	2.591(4)		
N(3)−Ag(1)−N(3)#1	164.0(2)	N(3)−Ag(1)−O(2)	97.0(1)
N(3)#1−Ag(1)−O(2)	93.6(1)	O(2)−Ag(1)−O(2)#1	97.1(2)
N(2)−Ag(2)−N(2)#2	164.3(2)	N(2)−Ag(2)−OW1	97.9(1)
Compound **4**			
Ag(1)−N(1)	2.167(3)	Ag(1)−N(4)	2.171(3)
Ag(2)−N(3)	2.183(3)	Ag(2)−N(2)	2.191(3)
Compound **5**			
Ag(1)−N(2)	2.233(2)	Ag(1)−N(3)#1	2.247(2)
Ag(1)−N(1)	2.488(2)	Ag(1)−O(2)#2	2.518(2)
N(2)−Ag(1)−N(3)#1	159.51(8)	N(2)−Ag(1)−N(1)	101.67(9)
N(3)#1−Ag(1)−N(1)	93.85(8)	N(2)−Ag(1)−O(2)#2	96.29(8)
N(3)#1−Ag(1)−O(2)# 2	91.44(9)	N(1)−Ag(1)−O(2)#2	108.10(7)
Compound **6**			
Ag(1)−OW1	2.142(8)	Ag(1)−OW2	2.141(7)
OW1−Ag(1)−OW2	176.2(7)		
Compound **7**			
Ag(1)−N(2)	2.196(2)	Ag(1)−N(1)	2.210(2)
Ag(1)−O(1)#1	2.564(2)		
N(2)−Ag(1)−N(1)	151.80(9)	N(2)−Ag(1)−O(1)#1	88.09(8)
N(1)−Ag(1)−O(1)#1	119.93(8)		
Compound **8**			
Ag(1)−N(1)	2.479(4)	Ag(1)−N(2)	2.253(3)
Ag(1)−N(3)#1	2.234(3)	Ag(1)−O(3)#1	2.649(4)
N(3)#1−Ag(1)−N(1)	102.0(1)	N(2)−Ag(1)−N(1)	95.9(1)
N(3)#1−Ag(1)−O(3)# 1	90.5(1)	N(2)−Ag(1)−O(3)#1	101.1(1)
N(3)#1−Ag(1)−N(2)	160.3(1)		
Compound **9**			
Ag(1)−N(2)#1	2.239(4)	Ag(1)−N(1)	2.257(3)
Ag(1)−N(3)	2.481(4)	Ag(1)−O(3)#1	2.634(4)
N(1)−Ag(1)−N(3)	93.1(1)	N(2)#1−Ag(1)−N(3)	102.5(1)
N(1)−Ag(1)−O(3)#1	96.5(1)	N(2)#1−Ag(1)−O(3)# 1	94.9(1)
N(2)#1−Ag(1)−N(1)	162.1(1)		
Compound **10**			
Ag(1)−OW1	2.115(4)	Ag(1)−N(2)	2.140(3)
Ag(2)−OW2	2.241(5)	Ag(2)−N(1)	2.375(4)
Ag(2)−N3	2.386(5)		
OW1−Ag(1)−N(2)	177.0(2)	OW2−Ag(2)−N(1)	125.7(2)
Compound **11**			
Ag(1)−N(1)	2.219(5)	Ag(1)−N(2)#1	2.228(5)
Ag(1)−N(3)#1	2.540(4)	Ag(1)−O(1)#3	2.725(4)
N(1)−Ag(1)−N(2)#1	165.1(1)	N(1)−Ag(1)−N(3)#1	100.3(2)
N(2)#1−Ag(1)−N(3)# 1	91.5(2)	N(1)−Ag(1)−O(1)#3	77.7(1)
N(2)#1−Ag(1)−O(1)# 3	109.6(2)		

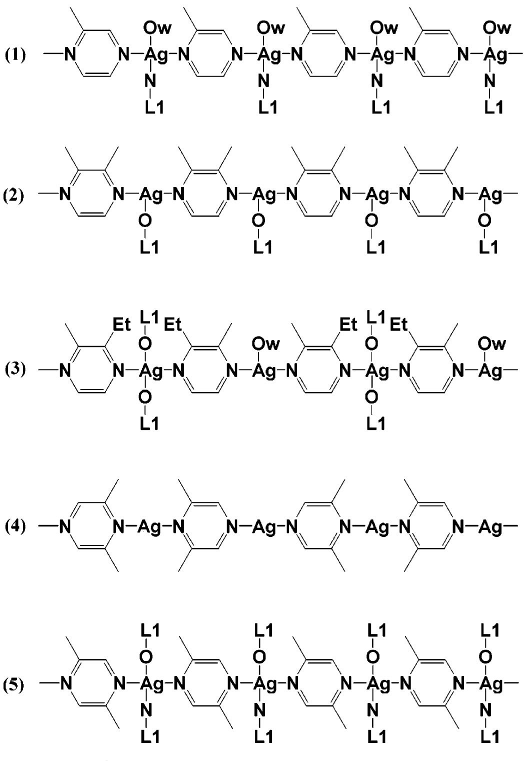
[a] Symmetry operations. For **1**: #1 $x, -y + {}^{3}/_{2}, z - {}^{1}/_{2}$. For **2**: #2 $-x + 2, -y, -z$; #3 $x - 1, y, z$. For **3**: #1 $-x, -y, z$; #2 $-x, -y - 1, z$. For **5**: #1 $x + {}^{1}/_{2}, -y, z - {}^{1}/_{2}$; #2 $x - 1, y, z$. For **7**: #1 $-x + 1, y - {}^{1}/_{2}, -z + {}^{1}/_{2}$. For **8**: #1 $-y + {}^{1}/_{3}, -x + {}^{2}/_{3}, z + {}^{1}/_{6}$. For **9**: #1 $x + {}^{1}/_{3}, x - y + {}^{5}/_{3}, z + {}^{1}/_{6}$. For **11**: #1 $x + {}^{1}/_{2}, -y + {}^{1}/_{2}, z + {}^{1}/_{2}$; #3 $x - {}^{1}/_{2}, -y + {}^{1}/_{2}, z + {}^{1}/_{2}$.

cationic Ag−Pyr chains are linked by hydrogen bonds to form a 3D supramolecular structure.

Scheme 3 Pyrazine-Related Environments of Silver Ions in the Polymeric Chain of Silver Ions and Pyrazine Derivatives



Scheme 4 Arrangements of the Pyrazine Derivatives in Compounds **1**−**5**



Structure of Ag(L1)(2,3-Pyr) (2). There exists one kind of crystallographically unique silver ion in the structure of **2** (Figure 3a). The Ag(I) center shows an approximate "T"-shaped coordination environment consisting of two N atoms from two different 2,3-Pyr molecules and one sulfonate O atom. Ag(I) centers are connected by 2,3-Pyr ligands through the nitrogen atoms into a 1D chain (Figure 3b). There are weak interactions between silver ions of one chain and benzene rings of the adjacent chain with the Ag−C distance of 3.01 Å, which is close to the sum of van der Waals radii of Ag(I) ion and the carbon atom. So **2** can be viewed as a

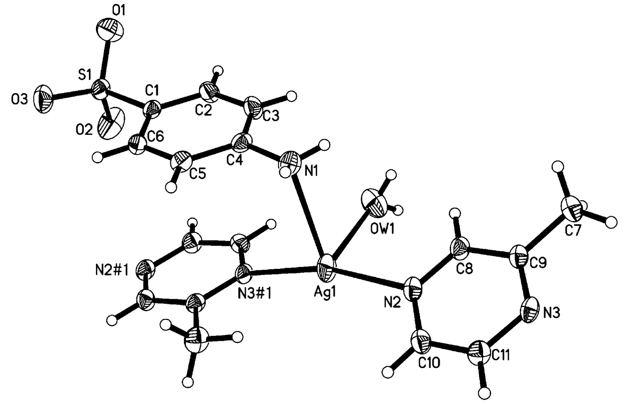


Figure 1. Coordination environment of the silver ion in compound **1**.

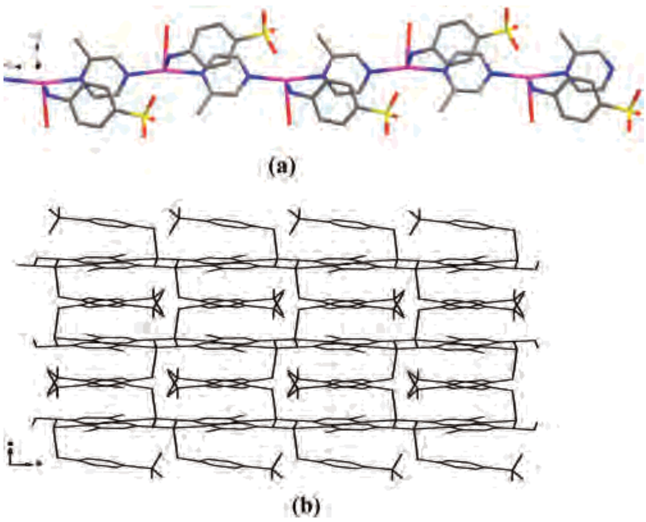


Figure 2. (a) Polymeric chain structure in **1**. (b) Packing diagram of compound **1**.

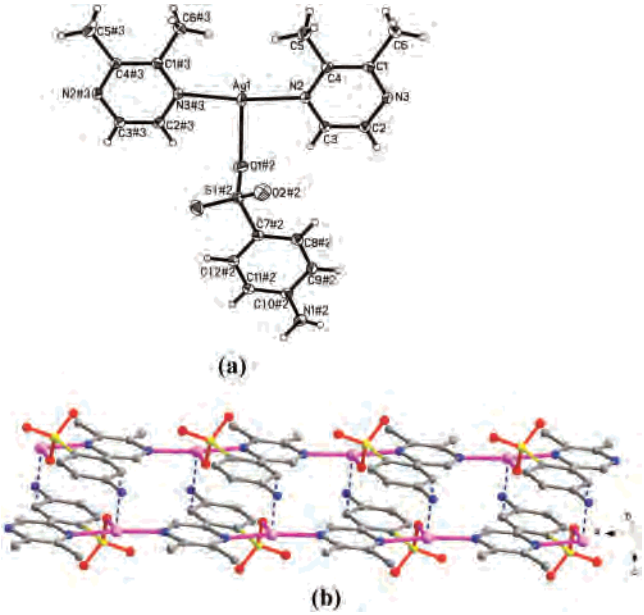


Figure 3. (a) Coordination environment of the Ag(I) in **2**. (b) Double-chain structure through weak Ag···C interactions in **2** (Ag···C: dashed lines).

weakly associated double-chain structure. In addition, two sulfonate oxygen atoms and the amino group of L1 anion are involved in hydrogen-bonding interactions (Supporting Information Table S1). As a result, the 1D polymeric chains of the compound **2** are linked to form a 2D sheet through the hydrogen-bonding interactions (Supporting Information Figure S2). Furthermore, these 2D layers are linked into a 3D network by weak Ag···C interactions between the adjacent chains.

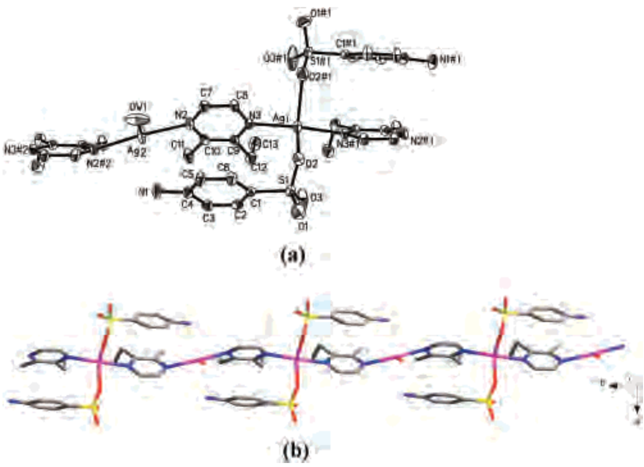


Figure 4. (a) View of **3** showing the coordination environments around the Ag(I) centers. (b) Infinite zigzag chain structure of **3**.

In $[Ag_2(2,3\text{-Pyr})_3][SbF_6]_2$ (**14**),[12] the Ag(I) centers exhibit a planar coordination geometry, intermediate between trigonal and T-shaped, consisting of three nitrogen atoms from three 2,3-Pyr ligands. The SbF_6^- anion only acts as a counteranion in **14**. Compound **14** shows a unique 3D "racemate" structure, whereas compound **2** shows a 1D chain structure. The structural changes may be explained by the coordination effect of anion. Since sulfonate anion has stronger coordination ability than SbF_6^- anion, the sulfonate anions replace part of the coordination sites of 2,3-Pyr ligands, and the dimensionality of the network is decreased.

Structure of $[Ag_2(L1)_2(2Et,3Me\text{-}Pyr)_2(H_2O)]$ (3). As illustrated in Figure 4a, compound **3** contains two kinds of crystallographically unique silver ions. Ag(1) is coordinated by two nitrogen atoms from two 2Et,3Me-Pyr molecules and two oxygen atoms from two L1 ligands, showing a distorted N_2O_2 tetrahedral geometry. The Ag(2) center is three-coordinated by two nitrogen atoms from two 2Et,3Me-Pyr molecules and one water molecule disordered over two sites with occupancies of 0.5 and 0.5, exhibiting a distorted "T"-shaped coordination. The silver cations are bridged by 2Et,3Me-Pyr molecules to form a 1D "zigzag" chain (Figure 4b). Within the chain structure, there are $\pi-\pi$ interactions between the pyrazine rings and the benzene rings with a distance of 3.55 Å. In the compound **2**, the pyrazine rings are coplanar in the same chain, whereas the adjacent pyrazine rings of the "zigzag" chain have a dihedral angle of 52.0° in **3**. The significant change is believed to be caused by the replacement of one methyl group by one ethyl group. Hydrogen-bonding interactions in **3** are similar to those in **2**, and compound **3** also forms a 2D sheet structure of L1 ligands just as that observed in **2** (Supporting Information

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[12] Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Chem. Commun.* **1996**, 1393.

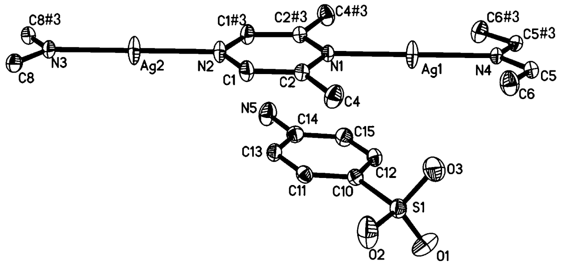

Figure 5. Coordination environments of Ag1 and Ag2 in compound **4**.

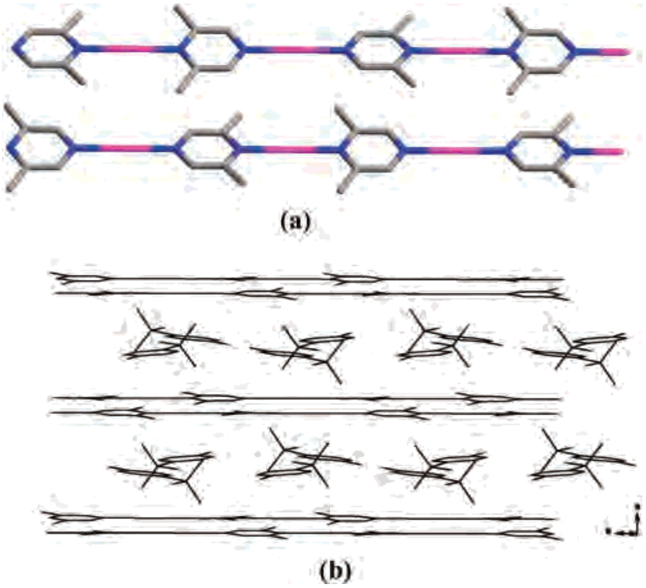

Figure 6. (a) Polymeric chain structure in **4**. (b) Packing diagram of compound **4**.

Figure S3a). Unlike **2**, the adjacent layers in **3** are connected via Ag−O coordinative interactions instead of Ag−C interactions to result in a 3D network (Supporting Information Figure S3b).

Part of the structure of **4** is shown in Figure 5. The L1 anion in **4** does not show any bonding actions with silver cations; it only acts as a counteranion. There are two kinds of unique sliver ions in the structure of **4**. Both Ag(1) and Ag(2) are coordinated by two nitrogen atoms from different 2,6-Pyr ligands. Ag(1)−N distances are somewhat shorter than Ag(2)−N distances. Ag ions are bridged by 2,6-Pyr molecules to form a chain structure (Figure 6a). These chains are arranged in a parallel mode to form a layer structure, and uncoordinated L1 anions intercalate the space between adjacent layers (Figure 6b).

Water clusters have been widely studied both theoretically and experimentally.[13] A variety of water clusters, [$(H_2O)_n$, $n = 2-18$] found in a number of crystal hosts have been characterized and display different configurations. The water clusters [$(H_2O)_2$ and $(H_2O)_3$] in silver(I) sulfonate frameworks have been reported in our previous work.[3a] There exist $(H_2O)_4$ tetramers in the structure of **4**, and the geometrical parameters of the water tetramer and its association with L1 ligands are provided in Table S1 (see the Supporting Information). As shown in Figure 7, the two lattice water molecules in **4** assemble into a centrosymmetric tetramer with OW···OW distances of 2.813(7) Å, whereas these distances in regular ice, liquid water, and water vapor are 2.74, 2.85, and 2.98 Å, respectively.[13c] As is well-known, water molecules frequently show a three-coordinate mode through hydrogen-bond interactions;[14] however, four oxygen atoms of this water tetramer show four- or two-coordinate modes. OW1 behaves as an acceptor as well as a donor, whereas OW2 behaves as a donor only. Four oxygen atoms in the water tetramer form an approximate parallelogram, and four O atoms from two L1 ligands and two OW1 atoms from two water tetramers assemble through hydrogen bonds in an approximate octagon with six oxygen atoms and two sulfur atoms each at corner. The parallelogram and the octagon in turn arrange themselves to form an infinite 1D chain structure.

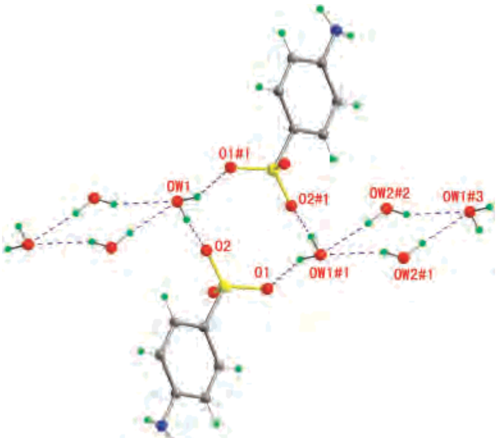

Figure 7. Water tetramers and the infinite 1D hydrogen-bonding chain in **4**. H-bonds: dashed lines.

A related compound [$Ag(CF_3CO_2)$(2,6-Pyr)] (**15**)[15] was a 2D polymeric solid, in which the Ag−(2,6-Pyr) chains are bridged by carboxylate oxygen atoms. As could be expected, the type of anion has a strong influence upon the topology of the coordination networks.

Structure of Ag(L1)(2,5-Pyr) (5). Compound **5** has an infinite 2D structure. As shown in Figure 8, each Ag(I) center adopts a distorted tetrahedral coordination geometry which consists of two $N_{2,5-\text{Pyr}}$ donors, one N_{amino} donor, and one $O_{\text{sulfonate}}$ donor from two different L1 anions. Silver ions are bridged by 2,5-Pyr molecules to form a 1D polymeric chain, and the Ag(I) atoms of adjacent chains are further connected by L1 anions via sulfonate oxygen atoms and amino nitrogen atoms to result in the formation of a 2D network (Figure 9a). The net consists of the metallomacrocyclic rings of Ag_4(2,5-Pyr)$_2$(L1)$_2$ (Figure 9b). This ring is divided into two parts through one hydrogen bond between one uncoordinated

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(13) (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. (d) Carballo, R.; Covelo, B.; Lodeiro, C.; Vazquez-Lopez, E. M. *CrystEngComm* **2005**, *7*, 294. (e) Li, D.; Wang, Y.; Luan, X.; Liu, P.; Zhou, C.; Ma, H.; Shi, Q. *Eur. J. Inorg. Chem.* **2005**, 2678. (f) Mukhopadhyay, U.; Bernal, I. *Cryst. Growth Des.* **2005**, *5*, 1687. (g) Keutsch, F. N.; Cruzan, J. D.; Saykally, R. J. *Chem. Rev.* **2003**, *103*, 2533. (h) Pal, S.; Sankaran, N. B.; Samanta, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1741. (i) Ye, B.-H.; Ding, B.-B.; Weng, Y.-Q.; Chen, X.-M. *Inorg. Chem.* **2004**, *43*, 6866.

(14) Jeffrey, G. A.; Maluszynska, H. *Acta Crystallogr.* **1990**, *B46*, 546.

(15) Brammer, L.; Burgard, M. D.; Eddleston, M. D.; Rodger, C. S.; Rath, N. P.; Adams, H. *CrystEngComm* **2002**, *4*, 239.

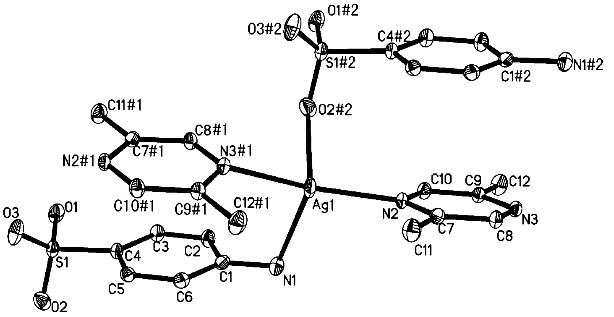


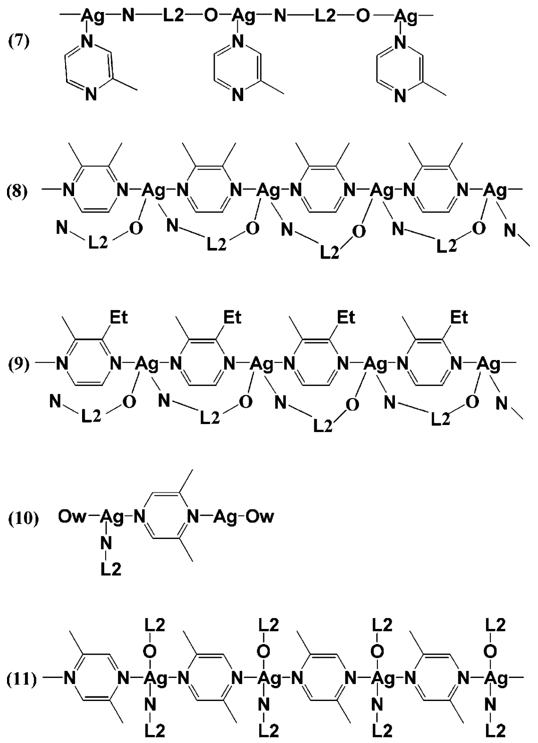
Figure 8. Coordination environment of Ag(I) in **5**.

sulfonate O atom and amino N atom, and each ring has two $\pi-\pi$ interactions between pyrazine rings and benzene rings, with the centroid−centroid distances being 3.66 and 3.69 Å, respectively.

As shown in Supporting Information Figure S4, these 2D nets stack to form the overall structure of **5**. There exist interlamellar N−H$\cdots$O hydrogen bonds between sulfonate oxygen atoms and amino groups. The corresponding hydrogen-bonds data were listed in Table S1. These interlamellar hydrogen bonds stitch these 2D nets into a 3D supramolecular structure. A related compound [Ag(CF$_3$CO$_2$)(2,5-Pyr)] (**16**) shows a 3D polymeric framework rather than a 2D sheet structure.[15]

In order to further survey the structural influence of the substituting groups of pyrazine derivatives and sulfonate anions, compounds **6**−**11** containing 6-amino-1-naphthalenesulfonate anions have been synthesized, and their structures were determined by the X-ray diffraction method. The arrangements of the pyrazine derivatives in compounds **7**−**11** are shown in Scheme 5.

Scheme 5 Arrangements of the Pyrazine Derivatives in Compounds **7**−**11**



Structure of [Ag(H$_2$O)$_2$](L2)·H$_2$O] (6). As shown in Figure 10, compound **6** has a mononuclear structure. The silver center is two-coordinated by two water molecules. Unexpectedly, the L2 anion does not coordinate to the silver ion but acts as a counteranion. In addition, there are lattice water molecules which are hydrogen-bonded to the sulfonate oxygen atoms and amino nitrogen atoms from L2 ions. The geometric parameters of the hydrogen bonds are summarized in Table S1.

Structural Analysis of [Ag(L2)(2-Pyr)] (7). Compound **7** possesses one kind of crystallographically unique silver ion in the structure (Figure 11). Ag(1) is coordinated by one nitrogen atom from the 2-Pyr ligand, one amino nitrogen atom, and one sulfonate oxygen atom from two different L2 anions, showing a distorted trigonal coordination environment. Each L2 anion coordinates to two Ag ions through one oxygen atom and the amino nitrogen atom. Silver(I) centers are bridged by L2 anions to form a polymeric helical chain propagating along the *b*-axis. Surprisingly, the 2-Pyr ligand acts as a monodentate ligand, attaching to the helical chain of L2 anions and Ag ions (Figure 12).

As shown in Figure 13, adjacent helices are linked through hydrogen-bonding interactions to form 2D layers parallel to the *ab* plane. These layers are further extended into 3D networks through the weak $\pi-\pi$ stacking interactions between pyrazine rings of the adjacent layers, with the centroid−centroid distance being 3.72 Å.

Structure of [Ag(L2)(2,3-Pyr)]·1.5H$_2$O (8) and [Ag(L2)(2Et,3Me-Pyr)]·2H$_2$O (9). As shown in Figure 14a, the Ag-

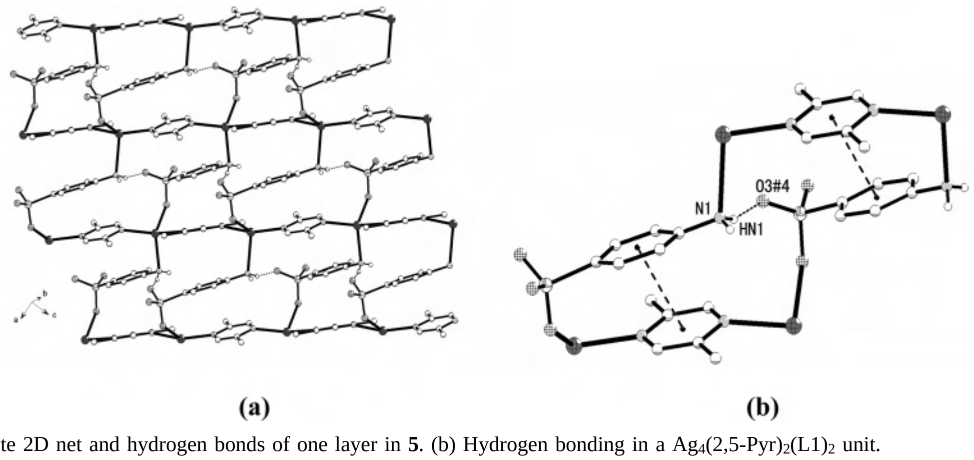


Figure 9. (a) Infinite 2D net and hydrogen bonds of one layer in **5**. (b) Hydrogen bonding in a Ag$_4$(2,5-Pyr)$_2$(L1)$_2$ unit.

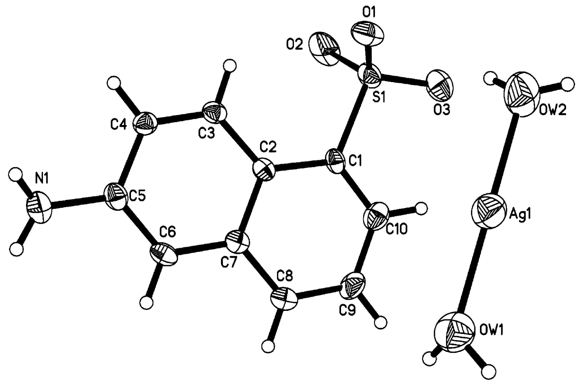


Figure 10. Coordination environment of Ag(I) in **6**.

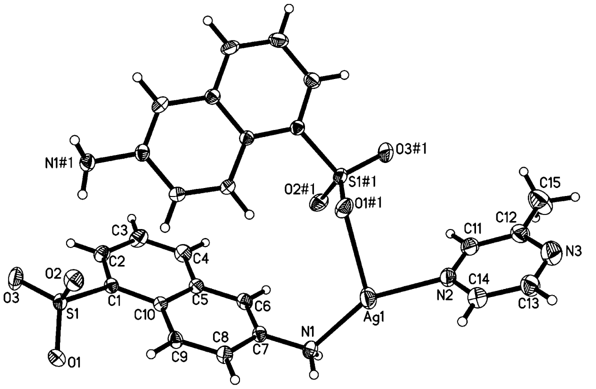


Figure 11. Coordination environment of Ag(I) in **7**.

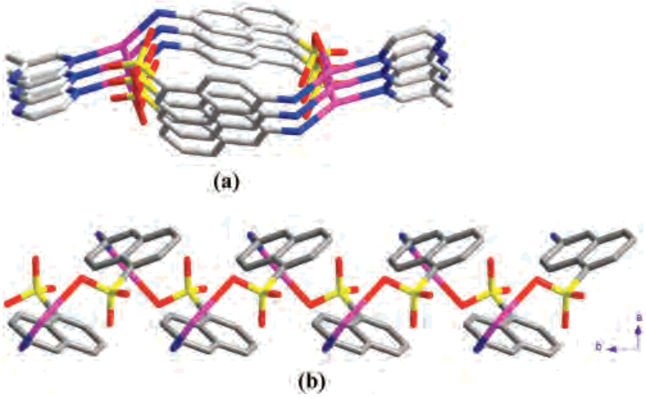


Figure 12. View of a helical chain of **7** [in (b), 2-Pyr ligands are omitted for charity].

(I) center in **8** shows a distorted tetrahedral coordination sphere consisting of two N_{Pyr} donors, one N_{amino} donor, and one $O_{sulfonate}$. The Ag−N_{amino} lengths are considerably longer than those of the Ag−N_{Pyr} bonds, but all Ag−N bond distances are within the normal range observed in N-containing Ag(I) complexes.[10] The Ag−O distance is similar to the reported values.[3a,16] As shown in Figure 14b, Ag ions are bridged by 2,3-Pyr ligands to form a 1D polymeric chain structure, and two adjacent Ag ions are further linked by one L2 anion through one O atom and the N atom. In addition, there are $\pi-\pi$ interactions between pyrazine rings and naphthalene rings of the same chain with the mean distance of 3.59 Å. The structure of **9** is similar to that of **8**, and the diagrams of the structure of **9** are shown in Figure S5 (see the Supporting Information).

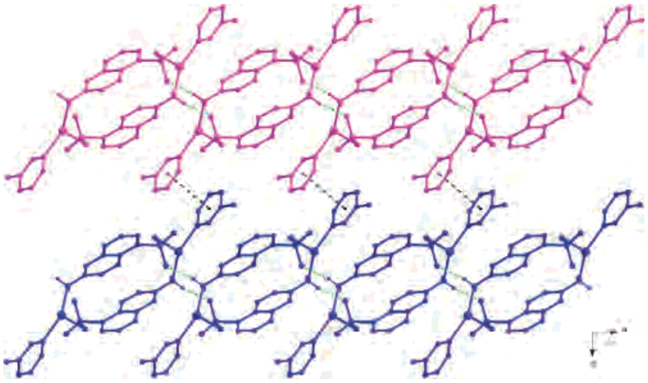


Figure 13. View of the hydrogen bonds between adjacent chains and the $\pi-\pi$ stacking of the layers. Hydrogen atoms are omitted for clarity.

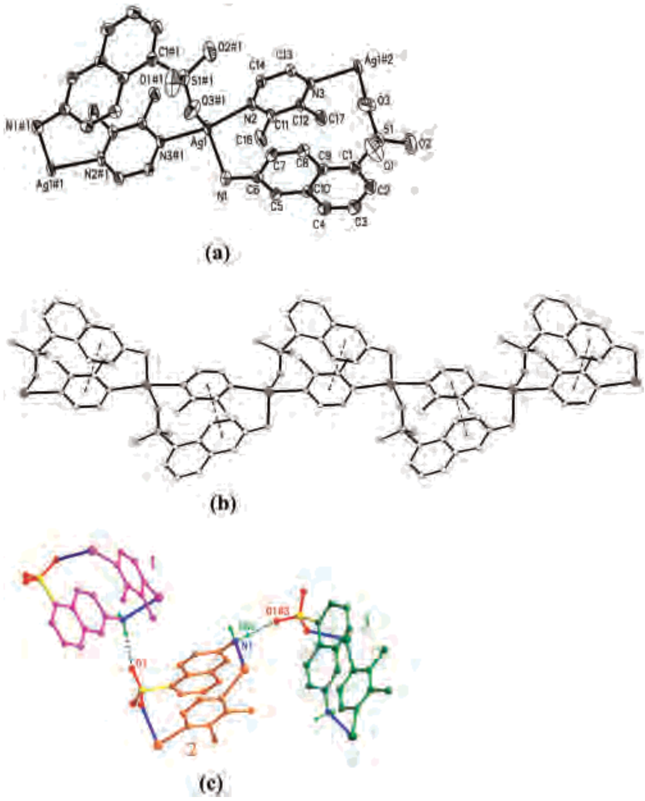


Figure 14. (a) Coordination environment of Ag(I) in **8**. (b) The hinged 1D chain structure of **8**. (c) 1D chains along different direction are interconnected by N−H···O hydrogen bonds in **8** (1, 2, and 3 show three units of three adjacent chains). H atoms are omitted for clarity. H-bonds: dashed lines.

Compounds **8** and **9** show similar packing modes, and these packing modes of the 1D coordination polymers are rather rare.[17] Indeed, the polymeric chains are packed in the trigonal crystallographic system (in space group *R*3*c*) with each near-neighbor chain arranged in the disposition with an inclined angle of 60° to one another (For **8**, see Figures 15, parts a and b). The 1D chains interlace with each other to form a 3D supramolecular structure through hydrogen

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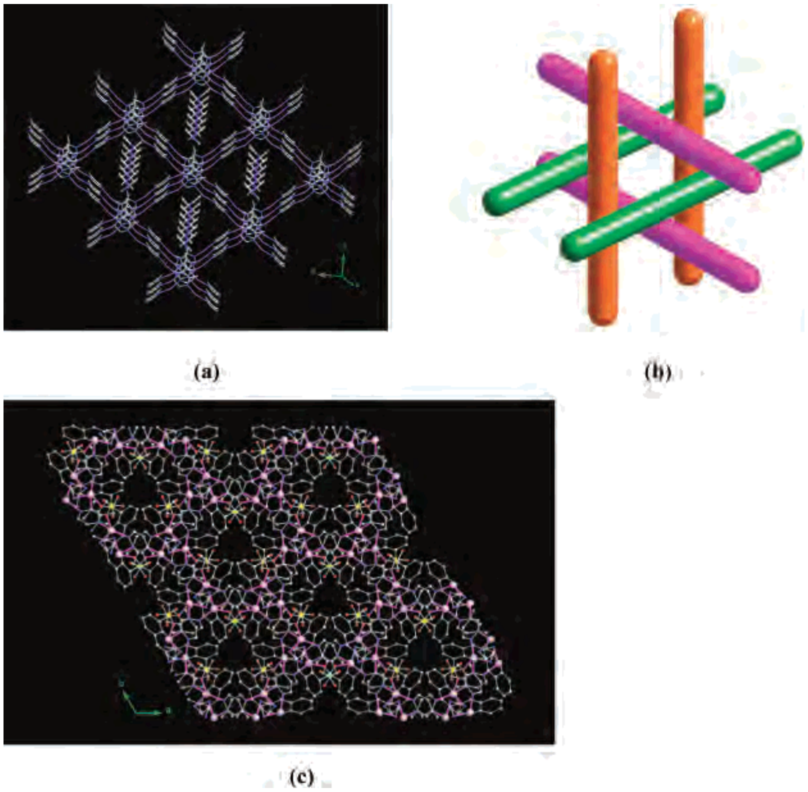

Figure 15. (a) Packed structure of the 1D chains in **8** (L2 anions and water molecules have been omitted for clarity). (b) Schematic representation of the packing mode of the 1D chains in **8**. (c) Packing diagram of **8**. The lattice water molecules are omitted for clarity.

bonds (For **8**, see Figure 15c). As shown in Figure 14c, each amino group of one chain is hydrogen-bonded to one sulfonate O atom from the adjacent chain. Thus the 3D supramolecular structures are fixed by these hydrogen bonds. The packing diagrams for **9** are shown in Figure S6 (see the Supporting Information).

Structure of [Ag_2(L2)(2,6-Pyr)(H_2O)$_2$](L2)·H_2O (10). In surprise, compound **10** shows a discrete dinuclear structure (Figure 16). There are two crystallographically unique silver ions and two distinct L2 ligands in **10**. The Ag(1) center is two-coordinated by one N atom from the 2,6-Pyr ligand and one water molecule. The Ag(2) center is three-coordinated by one water molecule, one N atom from the 2,6-Pyr ligand, and one N atom from L2 anion. The other L2 sulfonate anion does not coordinate to the Ag ion, but acts as a counteranion. In the structure of **10**, there exist strong O−H···O and N−H···O hydrogen-bonding interactions, and compound **10** shows a 3D supramolecular structure through extensive intermolecular hydrogen bonds. The geometrical parameters of the hydrogen bonds are provided in Table S1.

Structure of [Ag(L2)(2,5-Pyr)]·H_2O (11). Compound **11** shows an infinite 2D sheet. As shown in Figure 17, the silver ion in **11** is four-coordinated by two N atoms from two 2,5-Pyr ligands and one oxygen atom and one nitrogen atom from two different L2ligands. Silver ions are bridged by 2,5-Pyr molecules to form a 1D polymeric chain, and the Ag(I) ions of adjacent chains are further connected by L1 anions via sulfonate oxygen atoms and amino nitrogen atoms to result in the formation of a 2D network (Figure 18a). There exist intralamellar hydrogen-bonding interactions and $\pi-\pi$ interaction between the pyrazine ring and the naphthalene ring with the mean distance of 3.58 Å (Figure 18b). The

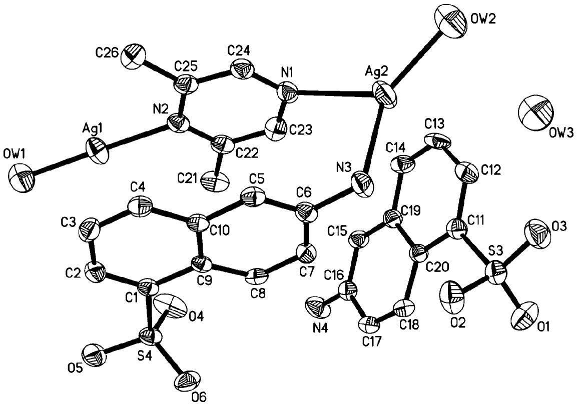

Figure 16. Coordination environments of the silver(I) cations in **10**.

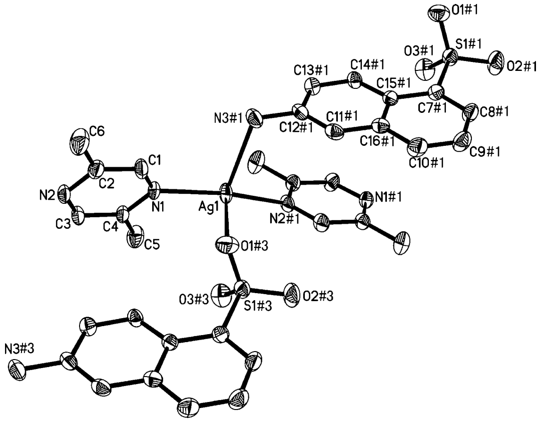

Figure 17. Coordination environment of Ag(I) in **11**.

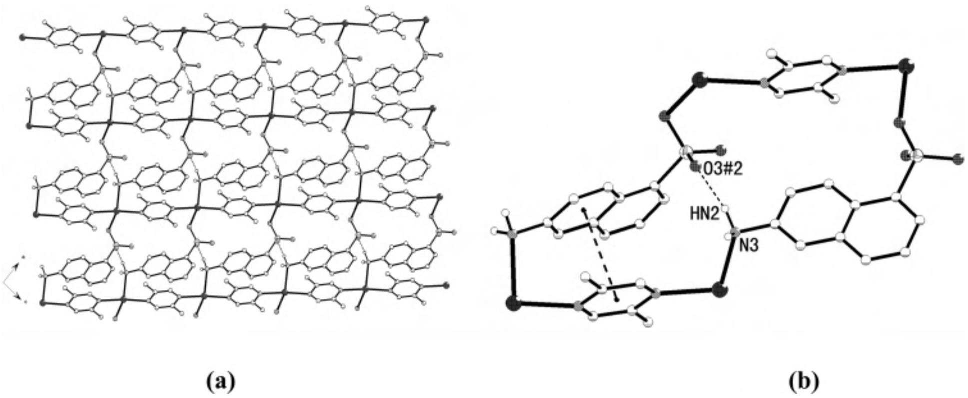

Figure 18. (a) Infinite 2D net and hydrogen bonds of one layer in **11**. (b) Hydrogen bonding in a $Ag_4(2,5\text{-Pyr})_2(L2)_2$ unit. Lattice water molecules are omitted for clarity. H-bonding: dashed lines.

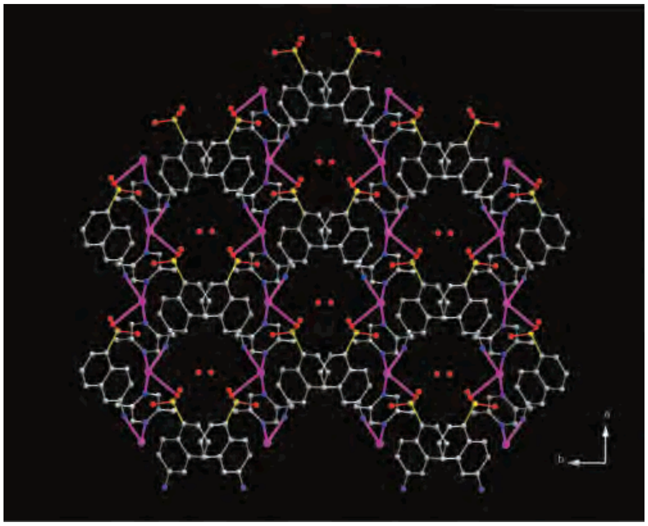

Figure 19. Packing diagram of **11**. Water molecules are omitted for clarity.

sulfonate O atom and amino N atom from two adjacent layers are linked by the lattice water molecule through strong hydrogen bonds (Supporting Information Figure S7). The packing diagram of **11** is shown in Figure 19.

Effect of the Pyrazine Derivatives on the Structures of the Complexes. Compounds **1**−**5** have the same Ag/L1/Pyr ratio of 1:1:1. Since pyrazine derivatives have stronger coordination ability to Ag ions than L1 anion, the structures of these complexes are mainly determined by the nature of the pyrazine derivatives. Due to the geometric property of the 2-Pyr ligand, the silver ions in **1** may have three possible pyrazine-related environments for the polymeric chain of silver ions and 2-Pyr molecules (Scheme 3, I-a, I-b, and I-c). Actually, all silver ions adopt the I-c environment, and this kind of silver ion prefers to be coordinated by one water molecule and one amino N atom rather than O atom of L1 anion [Scheme 4 (1)]. For the polymeric chain of silver ions and symmetric 2,3-Pyr molecules, the silver ions in **2** only have one kind of pyrazine-related environment (Scheme 3 II) and tend to be coordinated by one sulfonate O atom [Scheme 4 (2)]. For compound **3**, the silver ions may have three kinds of pyrazine-related environments (Scheme 3, III-a, III-b, and III-c). In fact, silver ions have two different pyrazine-related environments as shown in Scheme 3, III-b and III-c. The former is further coordinated by one water molecule, whereas the latter is further coordinated by two sulfonate O atoms [Scheme 4 (3)]. For compound **4**, the silver ions may have three kinds of pyrazine-related environments (Scheme 3, IV-a, IV-b, and IV-c). In fact, silver ions have two different pyrazine-related environments as shown in Scheme 3, IV-a and IV-b [Scheme 4 (4)]. Silver ions are not further coordinated by any other atoms, and all L1 anions are uncoordinated. For compound **5**, the silver ions only have one kind of pyrazine-related environment (Scheme 3 V) and can be further coordinated by one sulfonate O atom and one amino N atom from different L1 anions [Scheme 4 (5)]. L1 anions in **5** act as bidentate bridging ligands and lead to the formation of a 2D polymeric structure.

Compounds **7**−**9** and **11** have the same Ag/L2/Pyr ratio of 1:1:1. Like compounds **1**−**5**, compounds **8**, **9**, and **11** contain 1D polymeric chains of Ag ions and pyrazine derivatives due to the coordination character of pyrazine derivatives. For compound **8**, the silver ions only have one kind of pyrazine-related environment (Scheme 3 II) and can be further coordinated by one sulfonate O atom and one amino N atom from different L2 anions [Scheme 5 (8)]. For compound **9**, the silver ions may have three kinds of pyrazine-related environments (Scheme 3, III-a, III-b, and III-c). Unlike compound **3**, silver ions in **9** adopt only one kind of pyrazine-related environment (Scheme 3 III-a). Each silver ion is further coordinated by one sulfonate O atom and one amino N atom from different L2 anions [Scheme 5 (9)]. Like compound **5**, the silver ions in **11** only have one kind of pyrazine-related environment (Scheme 3 V), and each silver ion is further coordinated by one sulfonate O atom and one amino N atom from different L2 anions [Scheme 5 (11)]. L2 anions in **11** also act as bidentate bridging ligands and lead to the formation of a 2D polymeric structure. Although all L2 anions in **8**, **9**, and **11** act as bidentate bridging ligands through N and O atoms, due to the change of the pyrazine derivatives, each L2 anion in **8** and **9** coordinates to two silver ions of the same polymeric chain of silver ions and pyrazine derivatives; however, the L2 anion in **11** coordinates to two silver ions from different polymeric chain of silver ions and 2,5-Pyr ligands, and a 2D polymeric structure of **11** is formed. In compound **7**, there exist polymeric chains of silver ions and L2 anions instead of the expected polymeric chains of silver ions and 2-Pyr ligands.

The 2-Pyr ligand in **7** acts as a monodentate ligand. Although the L2 anions of **7**−**9** and **11** show the same bidentate bridging coordination mode, it can also be seen that the coordination tendency of L2 anions can be adjusted by the pyrazine derivatives, and the substitutions of pyrazine rings can diversify the polymeric frameworks of the complexes. Compound **10** has a different Ag/L2/Pyr ratio of 2:2:1 and shows a dinuclear discrete structure in which two silvers are bridged by one 2,6-Pyr ligand. One L2 anion coordinates to one silver ion via the N atom, and the other L2 anion does not coordinate to silver ions.

Effects of the Sulfonate Anions on the Structures of the Complexes. From the structures of these compounds, it can be seen that sulfonate ions also play an important role in the formation of the structures. The effects of anions on the complexes are discussed below:

(1) L2 anion shows stronger coordination ability to silver ion than L1 anion. L2 anions in **7**−**9** act as bidentate ligands, whereas L1 anions in compounds **1**−**3** act as monodentate ligands. L1 anions in **4** do not coordinate to silver ions; however, half of the L2 anions in **10** coordinate to silver ions.

(2) The distances between S and N atoms are 5.95 Å (L1 anion) and 6.81 Å (L2 anion), respectively. The distances between the two adjacent Ag ions bridged by pyrazine derivatives in **1**−**5**, **8**, **9**, and **11** range from 7.08 to 7.27 Å. Due to the geometric difference between L1 and L2, L2 anions can bridge the adjacent silver ions of the same polymeric chain to generate the 1D hinged chain structures of **8** and **9** as well as the silvers of different polymeric chains to give rise a 2D polymeric structure of **11**; however, L1 anions only can bridge the silvers of different polymeric chains to produce the 2D polymeric network of **5**.

(3) Although pyrazine derivatives generally have stronger coordination ability to Ag ions than sulfonate anions, the sulfonate anions can influence the coordination between silver ion and the pyrazine derivatives. Compounds **1** and **7** have the same 2-Pyr ligands. The 2-Pyr ligands in **1** act as bidentate bridging ligands to form the 1D polymeric chain; however, the 2-Pyr ligands in **7** act as monodentate ligands. Part of the coordination sites of 2-Pyr ligands in **1** has been replaced by L2 anions in **7**.

(4) The pyrazine derivatives in the Ag−Pyr chains may be arranged in several different modes: head-to-head, head-to-tail, and tail-to-tail. As discussed above, the arrangement of pyrazine derivatives in the Ag−Pyr chains can be modified by sulfonate ions.

(5) The molar ratio of Ag/(pyrazine derivative) of products can be adjusted by changing anions. Under the same synthetic condition, **4** with Ag/L1/(2,6-Pyr) ratio of 1:1:1 was isolated, whereas **10** with Ag/L2/(2,6-Pyr) ratio of 2:2:1 was isolated.

Photoluminescent Properties. Luminescent compounds are of great current interest because of their various applications in chemical sensors, photochemistry, and electroluminescent (EL) display.[18] The luminescent properties of silver carboxylate compounds and silver compounds containing $CF_3SO_3^-$ ions have been investigated.[19,20] However, investigations of silver aromatic sulfonates are seldom.[3a,b] The solid-state photoluminescence properties of compounds **1**−**11** were studied at room temperature. No photoluminescence was observed for compounds **4**, **10**, and free 2-Pyr ligand. The photoluminescence spectra of HL1, HL2, **1**−**3**, **5**−**9**, **11**, **13**, 2,3-Pyr, 2Et,3Me-Pyr, and 2,5-Pyr are depicted in Figure S8 (see the Supporting Information), and the wavelengths of the emission maxima and excitation are listed in Table 3.

Table 3. Wavelengths of the Emission Maxima and Excitation (nm)

compd	**1**	**2**	**3**	**5**	**13**	**HL1**
λ_{em}	440	524	467, 540	467, 538	396, 467	363, 467
λ_{ex}	260	290	290	240	240	290

compd	2-Pyr	2,3-Pyr	2Et,3Me-Py r	2,5-Pyr
λ_{em}		413, 438, 524	457	409, 435, 460
λ_{ex}		387	387	365

compd	**7**	**8**	**9**	**11**	**6**	**HL2**
λ_{em}	435, 542	438	467	430	420	399
λ_{ex}	290	290	290	260	290	320

The emission peaks of HL1, HL2, 2,3-Pyr, 2Et,3Me-Pyr, and 2,5-Pyr may be assigned to $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions of the ligands. The emission peaks of compounds **1**−**3**, **5**−**9**, **11**, and **13** are attributed to charge-transfer transitions and the intraligand transitions ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$).[19a,21,22] Although free 2-Pyr shows no emission at ambient temperature, the coordinated 2-Pyr ligands in **1** and **7** may give $\pi \rightarrow \pi^*$ emission because the coordination of 2-Pyr to Ag(I) may increase the conformational rigidity of 2-Pyr and reduce the nonradiative decay of the excited state. For compounds **1**, **2**, **6**, **8**, **9**, and **11**, the emission peaks of charge-transfer transition and the intraligand transition are mixed together, showing only one emission peak. Compounds **3**, **5**, **7**, and **13** exhibit a main peak with a shoulder, respectively. The main peaks would be assigned to intraligand transitions, whereas the shoulder peaks may be attributed to the emission of charge-transfer transitions.

Due to the introduction of the pyrazine derivative ligands, both the outlines and emission maxima of **1**−**3**, **5**, **7**−**9**, and **11** are different from those of **6** and **13**. These changes may be caused by the following reasons: (1) The introduction of pyrazine derivatives can change the coordination modes of

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the sulfonate anions, and this may change the energy levels of HOMO and LUMO of the sulfonate anions. (2) The coordinated pyrazine derivatives can also contribute to the emission of the complexes. (3) The complexes may display the emission resulted from the charge-transfer transition between silver ion and pyrazine derivatives.

Conclusion

A series of silver sulfonate complexes with pyrazine derivatives with different substitutions have been synthesized. The influence of pyrazine derivatives and sulfonate anions on the structures of the complexes has been investigated. It is found that the different substitutions of the pyrazine rings can adjust the polymeric topology of the framework as well as the coordination modes of sulfonate ligands. On the other hand, since the structural differences of sulfonate anions may change the coordination powers of anions, sometimes this can also influence the coordination behavior of pyrazine derivatives (compounds **1** and **7**). In all, the pyrazine derivative ligands show a stronger influence on the structures of the complexes than the sulfonate anions. However, a sulfonate anion with strong coordination power may also influence the structures of the complexes to some extent.

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Supporting Information Available: X-ray crystallographic files (CIF), hydrogen-bond geometries, diagrams of the structures of compounds **1**−**3**, **5**, **9**, and **11**, and the luminescent spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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