Inorg. Chem. **2004**, *43*, 5603–5612

Inorganic Chemistry
Article

New Ag(I)-Containing Coordination Polymers Generated from Multidentate Schiff-Base Ligands

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Received February 17, 2004

The coordination chemistry of the multidentate Schiff-base ligands 2,5-bis(3-methylpyrazinyl)-3,4-diaza-2,4-hexadiene (L5) and 2,5-bis(pyrazinyl)-3,4-diaza-2,4-hexadiene (L6) with inorganic Ag(I) salts has been investigated. Six new Ag(I)-coordination polymers were prepared by solution reactions and fully characterized by infrared spectroscopy, elemental analysis, thermogravimetric analysis, and single-crystal X-ray diffraction. $[Ag(L5)]ClO_4 \cdot 0.5CH_3OH$ (**1**, orthorhombic, *Fdd*2; $a = 20.0896(11)$ Å, $b = 48.224(3)$ Å, $c = 7.8432(4)$ Å, $Z = 16$), $[Ag(L5)]PF_6 \cdot 0.5CH_3OH$ (**2**, orthorhombic, *Fdd*2; $a = 20.7255(11)$ Å, $b = 46.166(2)$ Å, $c = 8.4332(4)$ Å, $Z = 16$), $[Ag(L5)]SbF_6 \cdot 0.5CH_3OH$ (**3**, orthorhombic, *Fdd*2; $a = 21.5481(11)$ Å, $b = 45.196(2)$ Å, $c = 8.7331(4)$ Å, $Z = 16$), and $[Ag(L5)](BF_4) \cdot 0.5CH_3OH$ (**4**, orthorhombic, *Fdd*2; $a = 19.8897(11)$ Å, $b = 48.358(3)$ Å, $c = 7.7491(5)$ Å, $Z = 16$) were obtained by combination of L5 with $AgClO_4 \cdot xH_2O$, $AgPF_6$, $AgSbF_6$, and $AgBF_4$, respectively, in a methylene chloride/methanol mixed solvent system. Compounds **1**–**4** are isostructural and feature noninterpentrating three-dimensional zeolite-like networks. $[Ag_4(L6)_4](PF_6)_4 \cdot CHCl_3$ (**5**, tetragonal, $P\bar{4}c2$; $a = 16.1067(3)$ Å, $b = 16.1067(3)$ Å, $c = 14.4935(5)$ Å, $Z = 2$) was generated from the reaction of L6 with $AgPF_6$ in a chloroform/ethanol mixed solvent system. It forms with a unique one-dimensional nanometer-tube that can be considered a new polymeric motif based on the {AgN5} coordination sphere. The tubes are square with crystallographic dimensions of 10.3 × 10.0 Å. The tubes are further linked together through weak interpolymer C–H···F hydrogen bonding interactions into a novel H-bonded three-dimensional network containing square tubes, in which uncoordinated PF_6^- counterions and chloroform guest molecules are located. Compound **6** ($[Ag(\mu\text{-}C_6H_6N_2O)](SO_3CF_3)$, monoclinic, $P2_1/c$; $a = 12.3435(6)$ Å, $b = 20.3548(10)$ Å, $c = 9.0861(5)$ Å, $Z = 8$**)** was obtained by combination of $AgSO_3CF_3$ and L6 in a methylene chloride/benzene mixed solvent system. In **6**, 2-acetylpyrazine, which was generated from the hydrolysis reaction of L6 in the presence of $CF_3SO_3^-$ and a small quantity of water in solvent, chelates the Ag(I) centers through the carbonyl O-donor, and the vicinal pyrazine N-donor, furthermore, uses the *para*-N atoms to link other Ag(I) centers into one-dimensional zigzag chains. The triflate anions link the chains into a three-dimensional network by somewhat long Ag···O contacts.

Introduction

Owing to their potential as new functional solid materials,[1–4] interest in self-assembled coordination polymers with specific network topologies has grown rapidly, and has focused on structure building and the deliberate design of polymeric coordination compounds.[5–8] In principle, some control over network topology can be gained by judicious selection of reaction-influencing factors, such as the chemical structure of the organic spacers (ligands), the coordination geometry preference of the metal, the inorganic counterions, and the

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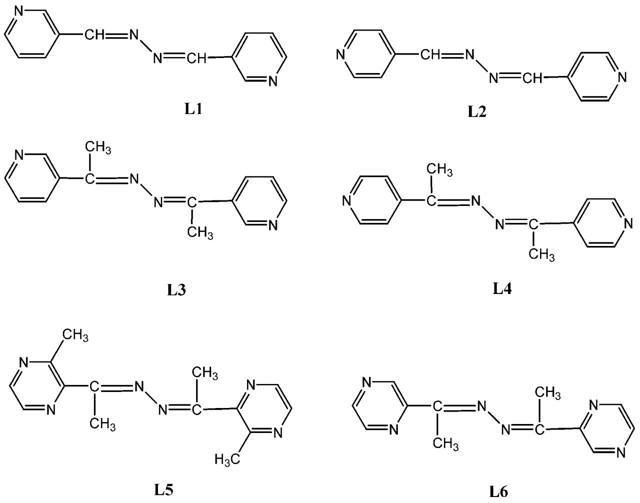
10.1021/ic049787a CCC: $27.50 © 2004 American Chemical Society
Published on Web 08/06/2004

metal-to-ligand ratio.[9−12] So far, among the many diverse efforts to find key factors in the development of extended structures, the dominant synthetic strategy has been to select different organic ligands. During the past few years, many one-, two-, and three-dimensional coordination polymers have been generated from transition metal templates with rigid and flexible pyridyl-containing bidentate or multidentate organic spacers. Two excellent reviews by Zubieta and Schröder summarize some of these.[12]

Scheme 1. Rigid Organic Bipyridine- and Bipyrazine-Type Ligands Used in the Construction of Coordination Polymer Frameworks



Double Schiff-base ligands, due to their specific geometry, including the different relative orientation of N-donors and the zigzag conformation of the spacer moiety ($-\mathrm{CR{=}N{-}N{=}CR}-$) between the two terminal coordination groups, may result in coordination polymers with novel network patterns not achievable by other rigid linking ligands, such as 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethyne, and 1,2-bis(4-pyridyl)ethene. On the other hand, $-\mathrm{CR{=}N}-$ and other organic functional groups such as $-\mathrm{OH}$, $-\mathrm{COOH}$, $-\mathrm{CHO}$, $-\mathrm{CONH_2}$, and $-\mathrm{C{\equiv}N}$ have been shown to be very important for molecular-based photonic, electronic, and ionic devices.[13] We reported a series of Schiff-base ligands with terminal pyridyl groups, namely 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (L1), 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (L2), 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene (L3), and 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (L4) (Scheme 1), and a series of new coordination polymers with novel patterns based on them.[14] Moreover, the $-\mathrm{CR{=}N{-}N{=}CR}-$ functional group in this type of ligand can potentially form hydrogen bonds (acting as the acceptor) with donor groups to generate supramolecular systems with interesting host−guest chemistry.[14c]

All the known Schiff-base ligands L1−L4 (Scheme 1), however, bind metal ions in a bidentate coordinating mode and the N-donors on $-\mathrm{CR{=}N{-}N{=}CR}-$ spacer are never involved in metal coordination environment. Very recently, we designed and synthesized two new Schiff-base ligands, namely 2,5-bis(3-methylpyrazinyl)-3,4-diaza-2,4-hexadiene (L5) and 2,5-bis(pyrazinyl)-3,4-diaza-2,4-hexadiene (L6),[14d] which can be considered as the new members of this double Schiff-base ligand family (Scheme 1). Compared to L1−L4, L5 and L6 have more structural information, including their molecular geometry and coordination preferences. Herein, we report the synthesis, X-ray single crystal structures, and luminescent properties of five novel coordination polymers, namely $[\mathrm{Ag(L5)}]\mathrm{ClO_4}\cdot0.5\mathrm{CH_3OH}$ (**1**), $[\mathrm{Ag(L5)}]\mathrm{PF_6}\cdot0.5\mathrm{CH_3OH}$ (**2**), $[\mathrm{Ag(L5)}]\mathrm{SbF_6}\cdot0.5\mathrm{CH_3OH}$ (**3**) and $[\mathrm{Ag(L5)}](\mathrm{BF_4})\cdot0.5\mathrm{CH_3OH}$ (**4**), and $[\mathrm{Ag_4(L6)_4}](\mathrm{PF_6})_4\cdot\mathrm{CHCl_3}$ (**5**), based on multidentate Schiff-base ligands L5 and L6, respectively, and one polymeric compound $[\mathrm{Ag}(\mu\text{-}\mathrm{C_6H_6N_2O})](\mathrm{SO_3CF_3})$ (**6**) based on 2-acetylpyrazine which was generated from the hydrolysis reaction of L6 in the presence of $\mathrm{CF_3SO_3^-}$ and a small quantity of water in solvent.

Experimental Section

Materials and Methods. $\mathrm{Ag(ClO_4)}\cdot x\mathrm{H_2O}$, $\mathrm{AgPF_6}$, $\mathrm{AgSbF_6}$, 2-acetyl-3-methylpyrazine, and hydrazine (35 wt. % solution in water) were obtained from Acros and used without further purification. L6 was prepared according to the literature method.[14d] Infrared spectroscopy (IR) samples were prepared as KBr pellets, and spectra

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were obtained in the 4000−400 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. ^{1}H NMR data were collected using a JEOL FX 90Q NMR spectrometer. Chemical shifts are reported in δ relative to TMS. Element analyses were performed on a Perkin-Elmer model 240C analyzer. All fluorescence measurements were carried out on a Cary Eclipse spectrofluorimeter (Varian, Australia) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric analysis (TGA) was conducted on a TA Instruments SDT 2960 simultaneous DTA-TGA in a N_2 atmosphere using a heating rate of 10 °C/min. Compounds **1**−**5** were heated from 30 to 550 °C.

Caution! One of the crystallization procedures involves AgClO4, which is a strong oxidizer.

Preparation of 2,5-Bis(3-methylpyrazine)-3,4-diaza-2,4-hexadiene (L5). 2-Acetyl-3-methylpyrazine (1.50 g, 11 mmol) was dissolved in ethanol (30 mL), followed by dropwise addition of the hydrazine solution (35 wt % solution in water, 0.21 g, 5.5 mmol) in ethanol (8 mL). After two drops of formic acid were added, the mixture was stirred at room temperature for 48 h. After removal of the solvent under vacuum, the residue was extracted with methylene chloride and washed with water several times. The organic phase was dried over $MgSO_4$ and filtered, and, upon removal of the solvent, an analytically pure bright yellow crystalline solid was obtained in 96% yield. ^{1}H NMR ($CDCl_3$, ppm): 8.48 (s, 4 H, pyrazinyl), 2.93 (s, 6 H, $-CH_3$), 2.37 (s, 6 H, $-CH_3$). IR (KBr, cm^{-1}): 3100(m), 3000(m), 2940(w), 1628(s), 1460(s), 1430(s), 1410(s), 1355(s), 1300(m), 1180(m), 1160(s), 1094(s), 978(s), 841(s). Anal. Calc. for $C_{14}H_{16}N_6$: C, 66.22; H, 5.41; N, 28.38%. Found: C, 66.24; H, 5.39; N, 28.27%.

Preparation of $[Ag(C_{14}H_{16}N_6)]ClO_4\cdot 0.5CH_3OH$ (1). A methanol solution (5 mL) of $Ag(ClO_4)\cdot xH_2O$ (16.2 mg, 0.078 mmol) was slowly diffused into a methylene chloride solution (5 mL) of L5 (10.5 mg, 0.039 mmol) at room temperature. Colorless crystals formed in about one week. The yield was 78%. IR (cm^{-1}, KBr pellet): 3500(s), 3100(m), 3000(w), 2930(m), 1628(s), 1430(s), 1410(s), 1375(m), 1350(m), 1310(m), 1165(s), 1100(s), 1090(s), 980(s), 850(s). Anal. Calcd for $AgC_{14.5}H_{18}N_6O_{4.5}Cl$: C, 35.39; H, 3.66; N, 17.08%. Found: C, 35.40; H, 3.65; N, 17.07%.

Preparation of $[Ag(C_{14}H_{16}N_6)]PF_6\cdot 0.5CH_3OH$ (2). A methanol solution (5 mL) of $AgPF_6$ (18.8 mg, 0.074 mmol) was slowly diffused into a methylene chloride solution (5 mL) of L5 (10.0 mg, 0.037 mmol) at room temperature. Colorless crystals formed in about one week. The yield was 84%. IR (cm^{-1}, KBr pellet): 3500(s), 3100(m), 3000(m), 2940(w), 1628(s), 1460(m), 1430(s), 1410(s), 1355(s), 1300(m), 1095(s), 978(m), 840(vs). Anal. Calcd for $AgC_{14.5}H_{18}N_6O_{0.5}PF_6$: C, 32.39; H, 3.35; N, 15.64%. Found: C, 32.37; H, 3.37; N, 15.63%.

Preparation of $[Ag(C_{14}H_{16}N_6)]SbF_6\cdot 0.5CH_3OH$ (3). A methanol solution (5 mL) of $AgSbF_6$ (23.0 mg, 0.067 mmol) was slowly diffused into a methylene chloride solution (5 mL) of L5 (9.0 mg, 0.034 mmol) at room temperature. Colorless crystals formed in about one week. The yield was 91%. IR (cm^{-1}, KBr pellet): 3500(s), 3100(w), 3000(w), 2940(w), 1628(s), 1460(m), 1430(s), 1410(s), 1355(s), 1300(w), 1160(m), 1098(s), 978(w), 842(s), 652(vs). Anal. Calcd for $AgC_{14.5}H_{18}N_6O_{0.5}SbF_6$: C, 27.71; H, 2.87; N, 13.38%. Found: C, 27.78; H, 2.82; N, 13.34%.

Preparation of $[Ag(C_{14}H_{16}N_6)]BF_4\cdot 0.5CH_3OH$ (4). A methanol solution (5 mL) of $AgBF_4$ (14.6 mg, 0.075 mmol) was slowly diffused into a methylene chloride solution (5 mL) of L5 (10.0 mg, 0.037 mmol) at room temperature. Colorless crystals formed in about three weeks. The yield was 67%. IR (cm^{-1}, KBr pellet): 3500(s), 3110(w), 3000(w), 2930(w), 1630(s), 1530(m), 1430(s), 1410(s), 1378(m), 1305(w), 1168(m), 1100(vs), 1050(vs), 850(m), 735(s). Anal. Calcd for $AgC_{14.50}H_{18}BF_4N_6O_{0.50}$: C, 36.32; H, 3.76; N, 17.54%. Found: C, 36.34; H, 3.70; N, 17.45%.

Preparation of $[Ag_4(C_{12}H_{12}N_6)_4](PF_6)_4\cdot CHCl_3$ (5). An ethanol solution (5 mL) of $AgPF_6$ (18.0 mg, 0.071 mmol) was slowly diffused into a $CHCl_3$ solution (5 mL) of L6 (8.7 mg, 0.036 mmol). Bright yellow crystals formed in about two weeks. The yield was 67%. IR (cm^{-1}, KBr pellet): 3095(m), 1618(s), 1520(m), 1474(s), 1410(s), 1367(s), 1305(w), 1170(s), 1108(s), 1050(m), 1018(s), 845(vs). Anal. Calcd for $C_{49}H_{49}Ag_4Cl_3F_{24}N_{24}P_4$: C, 28.11; H, 2.34; N, 16.06%. Found: C, 28.21; H, 2.24; N, 16.11%.

Preparation of $[Ag(C_6H_6N_2O)](SO_3CF_3)$ (6). An ethanol solution (5 mL) of $AgSO_3CF_3$ (19.9 mg, 0.077 mmol) was slowly diffused into a CH_2Cl_2 solution (5 mL) of L6 (9.2 mg, 0.038 mmol). Yellow crystals formed in about one week. The yield was 63%. IR (cm^{-1}, KBr pellet): 3100(w), 3000(w), 2940(w), 1689(s), 1628(s), 1435(s), 1410(s), 1355(s), 1260(vs), 1165(vs), 1095(s), 1045(s), 850(m), 760(m). Anal. Calcd for $AgC_7H_6F_3N_2O_4S$: C, 22.16; H, 1.58; N, 7.39%. Found: C, 22.17; H, 1.61; N, 7.34%.

Single-Crystal Structure Determination. Suitable single crystals of **1**−**6** were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 150 K on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å).[15] The raw frame data for **1**−**6** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[15] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[15] None of the crystals showed evidence of crystal decay during data collection. Compounds **1**−**4** crystallized in an unusual space group, *Fdd*2, as determined by the systematic absences in the intensity data, intensity statistics, and the successful solution and refinement of the structures. In all three structures, the asymmetric unit contains one Ag(I) center, one L5 ligand, and one counterion (ClO_4^- for **1**, PF_6^- for **2**, SbF_6^- for **3**, and BF_4^- for **4**), all located on general positions. One-half of a disordered MeOH molecule of crystallization is also present, disordered about a 2-fold axis. Hydrogen atoms were not located or calculated for the disordered species. Except for the MeOH, all non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The final absolute structure (Flack) parameter is 0.01(2) (**1**), −0.01(2) (**2**), −0.04(3) (**3**) and −0.03(2) (**4**), respectively, indicating the correct absolute structure and the absence of inversion twinning. Compound **5** crystallized in the tetragonal system. The space groups $P\bar{4}c2$, $P4_2cm$, and $P4_2/mcm$ were indicated by the pattern of systematic absences in the intensity data. The noncentrosymmetric space group $P\bar{4}c2$ was eventually confirmed by successful solution and refinement of the data. No reasonable solution could be obtained in the other space group candidates, and upon completion of the refinement in $P\bar{4}c2$ a check for missed symmetry was performed,[15] which verified the space group. The asymmetric unit consists of one Ag(I) center and one independent L5 ligand, a disordered $CHCl_3$ molecule of crystallization, and the symmetry-independent atoms of three PF_6^- anions, as follows: P(1) is located on a site of point symmetry D_2; three independent F atoms are associated with P(1)

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Table 1. Crystallographic Data for **1**−**3**

compound	**1**	**2**	**3**
formula	$C_{14.50}H_{18}AgClN_6O_{4.50}$	$C_{14.50}H_{18}AgF_6N_6O_{0.50}P$	$C_{14.50}H_{18}AgF_6N_6O_{0.50}Sb$
fw	491.67	537.19	627.97
cryst syst	orthorhombic	orthorhombic	orthorhombic
a (Å)	20.0896(11)	20.7255(11)	21.5481(11)
b (Å)	48.224(3)	46.166(2)	45.196(2)
c (Å)	7.8432(4)	8.4332(4)	8.7331(4)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
V (Å^3)	7598.5(7)	8068.9(7)	8505.2(7)
space group	$Fdd2$	$Fdd2$	$Fdd2$
Z value	16	16	16
ρ calc. (g/cm^3)	1.719	1.769	1.962
μ (Mo Kα) (mm^{-1})	1.238	1.148	2.258
temp (K)	150	150	150
no. of observations ($I > 3\sigma$)	3811	4122	3984
residuals: $R1$; $wR2$[a]	0.0273; 0.0580	0.0307; 0.0740	0.0427; 0.0916

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Crystallographic Data for **4**−**6**

compound	**4**	**5**	**6**
formula	$C_{14.50}H_{18}AgBF_4N_6O_{0.50}$	$C_{49}H_{49}Ag_4Cl_3F_{24}N_{24}P_4$	$C_7H_6AgF_3N_2O_4S$
fw	479.03	2091.83	379.07
cryst syst	orthorhombic	tetragonal	monoclinic
a (Å)	19.8897(11)	16.1067(3)	12.3435(6)
b (Å)	48.358(3)	16.1067(3)	20.3548(10)
c (Å)	7.7491(5)	14.4935(5)	9.0861(5)
α (deg)	90	90	90
β (deg)	90	90	98.5230(10)
γ (deg)	90	90	90
V (Å^3)	7453.3(8)	3759.99(16)	2257.7(2)
space group	$Fdd2$	$P\bar{4}c2$	$P2(1)c$
Z value	16	2	8
ρ calc. (g/cm^3)	1.708	1.848	2.230
μ (Mo Kα) (mm^{-1})	1.134	1.331	2.020
temp (K)	150	150	150
no. of observations ($I > 3\sigma$)	3581	2694	4654
residuals: $R1$; $wR2$[a]	0.0238; 0.0567	0.0628; 0.1543	0.0305; 0.0663

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

and all reside on 2-fold axes. P(2) is located on a site of C_2 symmetry and is surrounded by four independent F atoms, two of which are on 2-fold axes. P(3) is disordered over two orientations around a position of C_2 symmetry with six associated independent F atoms, one of which is on a 2-fold axis. Refinement of the P(3) anion with half-occupancies appropriate for 2-fold disorder resulted in inflated displacement parameters as well as a violation of electroneutrality. Refinement of the P(3) anion occupancy gave a value near $^1/_4$ with reasonable displacement parameters, and subsequently the occupancy was fixed at $^1/_4$ for the final cycles. The P(3) anion site is therefore a 50/50 mix of the disordered P(3) anion and either void space or unidentifiable disordered solvent molecule atoms. The presence of nonnegligible residual electron density around the P(3) site indicates the latter. The chloroform molecule is also disordered about a site of D_2 symmetry. Finally, atoms of the uncoordinated terminus of the L5 ligand (near N(6)) show elongated displacement ellipsoids, suggesting minor unresolved disorder of this end of the ligand. Eventually all non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in idealized positions and included as riding atoms. After the final refinement cycle, the absolute structure (Flack) parameter was 0.06(8), indicating the lack of inversion twinning. A total of 63 restraints (SHELX SADI and DFIX) were used to model the anion and solvent disorder. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least squares technique.[15] Compound **6** crystallizes in the space group $P2_1/c$ based on systematic absences in the intensity data. The asymmetric unit consists of two Ag(I) centers, two 2-acetylpyrazine ligands and two triflate anions. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in idealized positions and included as riding atoms. Crystal data, data collection parameters, and refinement statistics for **1**−**6** are listed in Tables 1 and 2. Relevant interatomic bond distances and bond angles for **1**−**6** are given in Tables 3−8.

Table 3. Interatomic Distances (Å) and Bond Angles (deg) with esds () for **1**[a]

Ag−N(6)#1	2.250(2)	Ag−N(2)	2.319(2)
Ag−N(1)#2	2.343(2)	Ag−N(3)	2.581(2)
N(6)#1−Ag−N(2)	147.92(9)	N(6)#1−Ag−N(1)#2	113.70(8)
N(2)−Ag−N(1)#2	97.89(8)	N(6)#1−Ag−N(3)	97.09(8)
N(2)−Ag−N(3)	68.37(8)	N(1)#2−Ag−N(3)	122.94(8)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + ^1/_2, -y, z - ^1/_2$; #2 $x + ^1/_4, -y + ^1/_4, z + ^1/_4$; #3 $x - ^1/_4, -y + ^1/_4, z - ^1/_4$; #4 $-x + ^1/_2, -y, z + ^1/_2$.

Results and Discussion

Synthesis of L5. The multidentate Schiff-base ligand L5 was prepared in quantitative yield by the Schiff-base condensation reaction of 2-acetyl-3-methylpyrazine with hydrazine (35 wt. % solution in water) in ethanol at room temperature. Elemental analysis and ^{1}H NMR and IR spectra

Table 4. Interatomic Distances (Å) and Bond Angles (deg) with esds () for **2**[a]

Ag−N(6)#1	2.240(3)	Ag−N(2)	2.323(3)
Ag−N(1)#2	2.352(3)	Ag−N(3)	2.577(3)
N(6)#1−Ag−N(2)	145.96(10)	N(6)#1−Ag−N(1)#2	110.94(11)
N(2)−Ag−N(1)#2	100.84(11)	N(6)#1−Ag−N(3)	101.49(9)
N(2)−Ag−N(3)	68.67(9)	N(1)#2−Ag−N(3)	123.89(10)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + {}^1/_2, -y, z - {}^1/_2$; #2 $x + {}^1/_4, -y + {}^1/_4, z + {}^1/_4$; #3 $x - {}^1/_4, -y + {}^1/_4, z - {}^1/_4$; #4 $-x + {}^1/_2, -y, z + {}^1/_2$.

Table 5. Interatomic Distances (Å) and Bond Angles (deg) with esds () for **3**[a]

Ag−N(6)#1	2.248(5)	Ag−N(2)	2.293(5)
Ag−N(1)#2	2.349(5)	Ag−N(3)	2.539(5)
N(6)#1−Ag−N(2)	143.95(17)	N(6)#1−Ag−N(1)#2	106.59(17)
N(2)−Ag−N(1)#2	106.45(18)	N(6)#1−Ag−N(3	101.61(16)
N(2)−Ag−N(3)	68.91(17)	N(1)#2−Ag−N(3)	126.72(18)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + {}^1/_2, -y, z - {}^1/_2$; #2 $x + {}^1/_4, -y + {}^1/_4, z + {}^1/_4$; #3 $x - {}^1/_4, -y + {}^1/_4, z - {}^1/_4$; #4 $-x + {}^1/_2, -y, z + {}^1/_2$; #5 $-x + 1, -y, z$.

Table 6. Interatomic Distances (Å) and Bond Angles (deg) with esds () for **4**[a]

Ag(1)−N(6)#1	2.243(2)	Ag(1)−N(1)	2.312(2)
Ag(1)−N(2)#2	2.334(2)	Ag(1)−N(3)	2.561(2)
N(6)#1−Ag(1)−N(1)	148.93(8)	N(6)#1−Ag(1)−N(2)#2	112.79(8)
N(1)−Ag(1)−N(2)#2	97.48(8)	N(6)#1−Ag(1)−N(3)	98.12(8)
N(1)−Ag(1)−N(3)	68.90(8)	N(2)#2−Ag(1)−N(3)	123.57(8)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + {}^1/_2, z - {}^1/_2$; #2 $x + {}^1/_4, -y + {}^1/_4, z + {}^1/_4$; #3 $x - {}^1/_4$, $-y + {}^1/_4$, $z - {}^1/_4$; #4 $-x + 1, -y + {}^1/_2, z + {}^1/_2$; #5 $-x + {}^1/_2, -y + {}^1/_2, z$.

Table 7. Interatomic Distances (Å) and Bond Angles (deg) with esds () for **5**[a]

Ag−N(5)#1	2.271(8)	Ag−N(1)	2.334(9)
Ag−N(3)	2.443(9)	Ag−N(4)#1	2.492(7)
Ag−N(2)#2	2.519(9)		
N(5)#1−Ag−N(1)	147.2(3)	N(5)#1−Ag−N(3)	120.3(3)
N(1)−Ag−N(3)	67.2(3)	N(5)#1−Ag−N(4)#1	68.9(2)
N(1)−Ag−N(4)#1	143.8(3)	N(3)−Ag−N(4)#1	93.3(2)
N(5)#1−Ag−N(2)#2	103.3(3)	N(1)−Ag−N(2)#2	82.8(3)
N(3)−Ag−N(2)#2	134.9(3)	N(4)#1−Ag−N(2)#2	92.0(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-y + 1, -x + 1, -z + {}^1/_2$; #2 $y, -x + 1, -z + 1$; #3 $-y + 1, x, -z + 1$; #4 $-x + 1, -y + 1, z$; #5 $y, x, -z + {}^1/_2$; #6 $-y + 1, -x + 1, -z + {}^3/_2$; #7 $-x, -y + 1, z$; #8 $-x + 2, -y + 2, z$; #9 $-y + 2, -x + 2, -z + {}^3/_2$; #10 $y, x, -z + {}^3/_2$.

are consistent with the formulation of L5. Compared to L1−L4, the solubility of L5 in common organic solvents was clearly enhanced after introducing the four methyl groups, which made crystallization with inorganic metal salts in solutions easy. In addition, the possibility increased for this bipyrazine-type spacer to bind metal ions simultaneously by N-donors on both pyrazinyl group and −MeC═N−N═CMe− spacer, which potentially allows access to frameworks with novel polymeric motifs.

Structural Analysis of 1−4. Compounds **1**−**4** were isolated as colorless air-stable crystals by combination of L5 with $Ag(ClO_4)\cdot xH_2O$, $AgPF_6$, $AgSbF_6$, and $AgBF_4$ in CH_2Cl_2/CH_3OH mixed solvent system, respectively. It is worthwhile to point out that, in these specific reactions, the products do not depend on the ligand-to-metal ratio. Single-crystal X-ray analysis revealed that compounds **1**−**3** are isostructural, and crystallize in an acentric orthorhombic space group *Fdd*2. For example in compound **1** (Figure 1), each Ag(I) center lies in a 3 + 1 capped trigonal planar coordination sphere which is defined by three pyrazinyl N-donors (N(1), N(2), and N(6)) from each of three L5 ligands, one Schiff-base N-donor (N(3)) from one of three L5 ligands. The one of $N_{pyrazinyl}$ atom adopts a chelating coordination mode by incorporation with adjacent $N_{Schiff-base}$ atom to generate a five-membered silver-containing ring. In compounds **1**−**4**, the ligand is bound to Ag(I) centers through four of the six N-donors, including one of the central nitrogens. Thus L5 ligand herein serves as not only a multidentate ligand but also a chelating one. In compounds **1**−**4**, the Ag−$N_{pyrazinyl}$ bond lengths range between 2.240 and 2.352 Å, while the Ag−$N_{Schiff-base}$ bond distances lie in the range of 2.539 to 2.581 Å. All these bond lengths are very close to the corresponding bond lengths found in reported Ag−Schiff-base molecular complexes.[16,17] In compounds **1**−**4**, one $N_{pyrazinyl}$ and one $N_{Schiff-base}$ atoms in L5 remain uncoordinated probably due to the steric arrangement of the ligand. As shown in Figure 2, the ligand in **1**−**4** is severely twisted. Two pyrazinyl groups do not lie in the same plane, and the dihedral angle between them is ca. 20°. The torsion angle of C(6)−N(3)−N(4)−C(9) is 113.5(4)°. For compounds **1**−**4**, there is an interesting change in the unit cell parameters upon increasing the counterion size from BF_4^- to ClO_4^- to PF_6^- to SbF_6^-. The cell volume increases as expected, but does so in an anisotropic way. The shorter *a* and *c* axes expand while the long *b* axis contracts.

In the solid state, compounds **1**−**4** present a noninterpenetrating zeolite-like three-dimensional network based on four coordinated silver centers (Figure 3). Parallelogram-like channels running down the crystallographic *c* axis with different dimensions (for example **1**, crystallographic dimensions ca. 3 × 9 and 13 × 7 Å^2) were found. Disordered MeOH guest molecules and uncoordinated counterions (ClO_4^-, PF_6^-, SbF_6^-, and BF_4^-, for **1**−**4**, respectively) are located in the larger channels. Compared to *N*,*N*′-bipyridine-type of Schiff-base ligands L1−L4, the coordination behavior of L5 was dramatically changed due to the steric presence of four methyl and two pyrazinyl groups, which could make it more favorable for incorporating metal ions as both multidentate and chelating ligand into polymeric compounds. Compounds **1**−**4** are air stable and have a similar thermal decomposition behavior, which is reasonable since they possess the same polymeric motif. TGA shows that the MeOH guest molecules were lost during 141−240 °C for **1**, 150−220 °C for **2**, 171−255 °C for **3**, and 240−252 °C for **4**. The frameworks of **1**−**4** were collapsed after removal of guest molecules.

Structural Analysis of 5. To confirm the role of substitutents on pyrazinyl groups in the self-assembly process, L6

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Table 8. Interatomic Distances (Å) and Bond Angles (deg) with esds () for **6**[a]

Ag(1)−N(4)#1	2.242(2)	Ag(1)−N(1)	2.258(2)
Ag(1)−O(1)	2.579(2)	Ag(1)−O(11)	2.582(2)
Ag(1)−O(12)#2	2.701(3)	Ag(2)−N(2)	2.254(2)
Ag(2)−N(3)	2.292(2)	Ag(2)−O(21)	2.510(2)
Ag(2)−O(23)#3	2.565(2)	Ag(2)−O(2)	2.658(3)
N(4)#1−Ag(1)−N(1)	159.44(9)	N(4)#1−Ag(1)−O(1)	91.02(7)
N(1)−Ag(1)−O(1)	68.53(7)	N(4)#1−Ag(1)−O(11)	86.71(8)
N(1)−Ag(1)−O(11)	93.51(8)	O(1)−Ag(1)−O(11)	96.89(8)
N(4)#1−Ag(1)−O(12)#2	89.22(9)	N(1)−Ag(1)−O(12)#2	108.25(9)
O(1)−Ag(1)−O(12)#2	143.18(8)	O(11)−Ag(1)−O(12)#2	119.87(8)
N(2)−Ag(2)−N(3)	151.06(9)	N(2)−Ag(2)−O(21)	119.64(8)
N(3)−Ag(2)−O(21)	82.78(8)	N(2)−Ag(2)−O(23)#3	106.15(8)
N(3)−Ag(2)−O(23)#3	88.79(8)	O(21)−Ag(2)−O(23)#3	94.12(8)
N(2)−Ag(2)−O(2)	86.09(8)	N(2)−Ag(2)−O(2)	86.09(8)
N(3)−Ag(2)−O(2)	66.07(8)	O(21)−Ag(2)−O(2)	119.06(10)
O(23)#3−Ag(2)−O(2)	133.26(10)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $x - 1, y, z - 1$; #2 $-x, -y, -z$; #3 $x, -y + {}^1/_2, z - {}^1/_2$; #4 $x + 1, y, z + 1$; #5 $x, -y + {}^1/_2, z + {}^1/_2$.

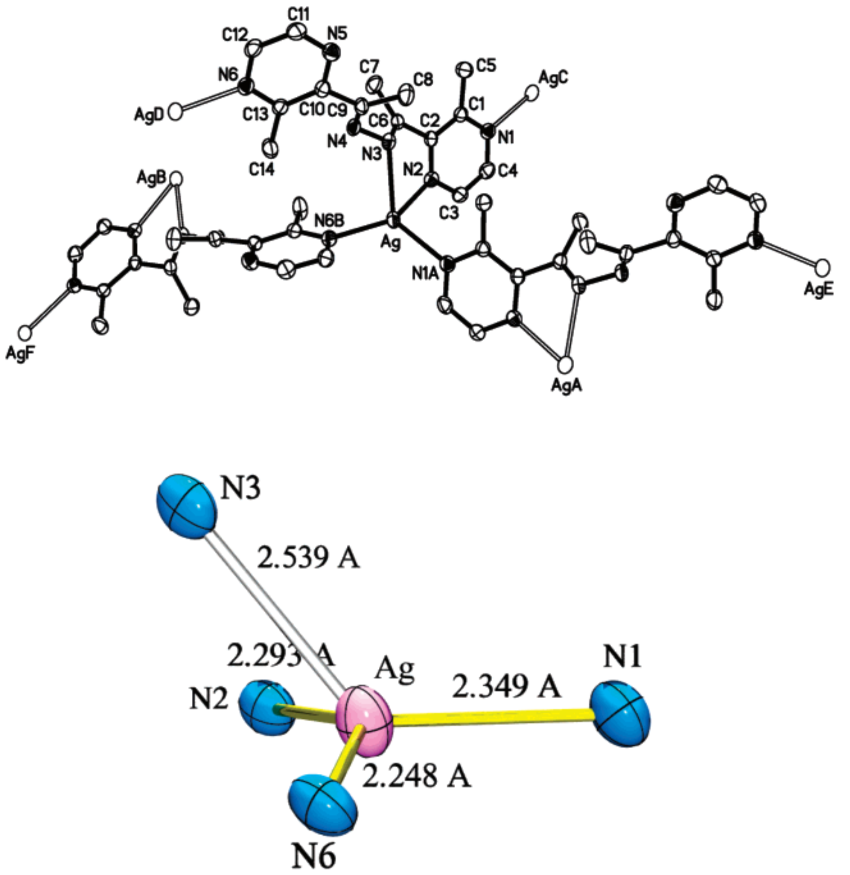

Figure 1. Ag(I) coordination environment in compounds **1**−**4**. Displacement ellipsoids drawn at the 50% probability level.

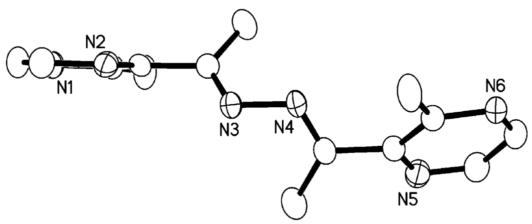

Figure 2. Ligand conformation in **1**−**4**, drawn with 50% probability ellipsoids.

was used instead of L5 to perform the reaction. Compound **5** was obtained as bright yellow crystals by combination of L6 with $AgPF_6$ in a $CHCl_3$/MeOH mixed solvent system at 67% yield. Single-crystal X-ray analysis revealed that the asymmetric unit consists of one Ag(I) center and one independent L6 ligand. As shown in Figure 4, each Ag(I) center lies in a {AgN5} coordination environment which consists of three N-donors (N(1), N(2), and N(5): Ag−N(1) = 2.334(9) Å, Ag−N(2) = 2.519(9) Å, and Ag−N(5) = 2.271(8) Å) from three coordinated pyrazinyl groups and two N-donors (N(3) and N(4): Ag−N(3) = 2.443(9) Å and Ag−N(4) = 2.492(7) Å) from $-C(CH_3){=}N{-}N{=}(CH_3)C-$ spacers. It is worthy to point out that L6 in **5** uses five of six N-donors to bind Ag(I) centers and one terminal $N_{pyrazine}$ is free, which is distinctly different from the coordination

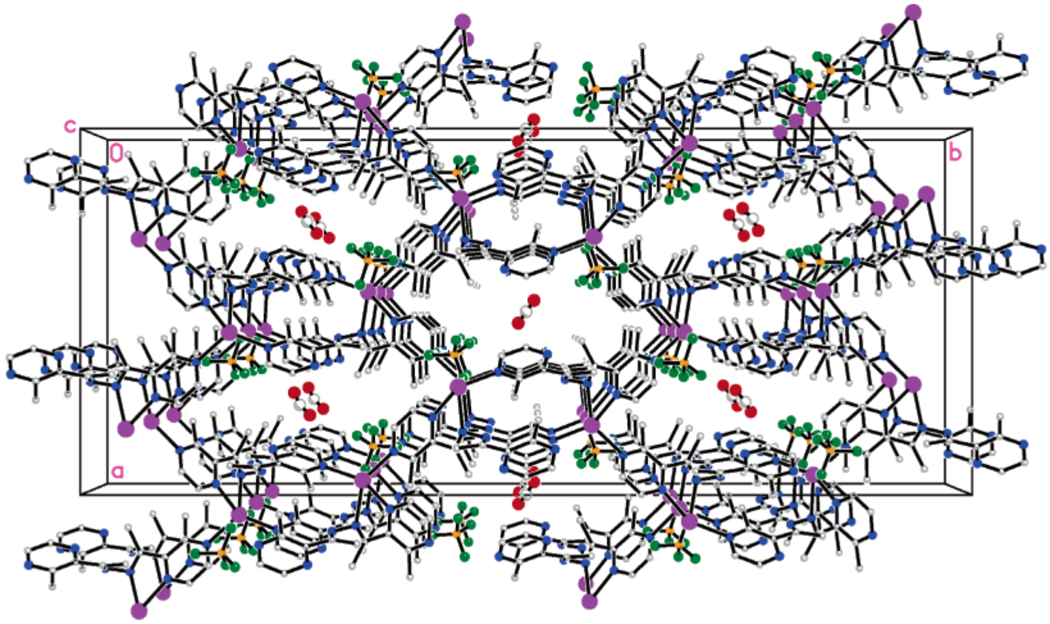

Figure 3. Zeolite-like three-dimensional network in **1**−**4**.

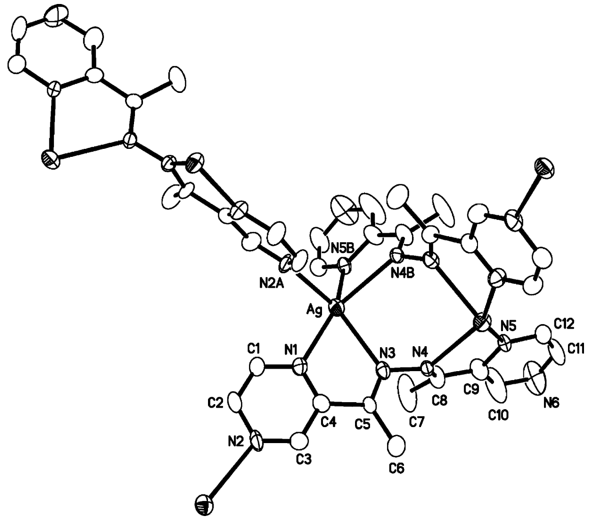

Figure 4. Ag(I) coordination environment in compound **5** (only one Ag(I) complete coordination environment was shown with the label). Displacement ellipsoids drawn at the 30% probability level.

behavior of L5 in **1**−**4**. The four N-donors on $-C(CH_3)=N-N=(CH_3)C-$ spacers incorporate with four pyrazinyl N-donors to chelate two Ag(I) centers into a distorted tetrahedral building block (Figure 4). The intra-building block Ag(I)⋯Ag(I) contact is 4.612(3) Å, which is longer than the sum of the van der Waals radii of two silver atoms, 3.44 Å.[18]

In the solid state, these tetrahedral building blocks are linked together via coordinated pyrazinyl N-donors into a novel infinite one-dimensional metal−organic nanometer-tube along the crystallographic *c* axis. As shown in Figure 5, the tube is square (view down crystallographic *c* axis) with crystallographic dimensions of 10.3 × 10.0 Å,[19] in which the $P(1)F_6^-$ counterions are located and hydrogen bonded to the framework through weak C−H⋯F bonds. The hydrogen bonding system involves the F(2) and C(2) atoms and the H(2) atoms on the pyrazinyl groups of the framework. The F(2)⋯H(2) and F(2)⋯C(2) distances are 2.447(5) and 3.377(5) Å, respectively. The corresponding F(2)⋯H(2)−C(2) angle is 167.20(4)°. It is interesting that these metal−organic one-dimensional tubes are further linked together through six sets of weak C−H⋯F bonds consisting of two F atoms of $P(2)F_6^-$ ions located near Ag(I) centers and three H atoms of pyrazinyl groups (two sets of C(12)−H(12)⋯F(6) with F(6)⋯H(12) = 2.417(5) and F(6)⋯C(12) = 3.291(5) Å; two sets of C(10)−H(10)⋯F(6) with F(6)⋯H(10) = 2.487(5) and F(6)⋯C(12) = 3.253(5) Å; and two sets of C(3)−H(3)⋯F(4) with F(4)⋯H(3) = 2.414(5)

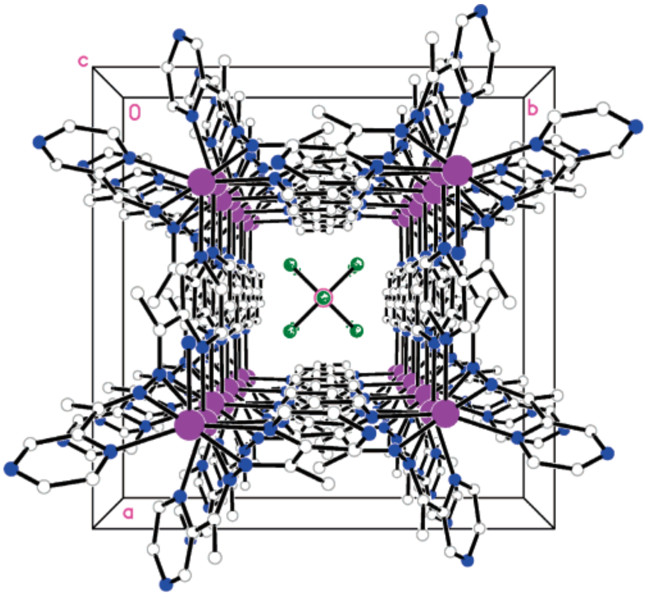

Figure 5. Perpendicular view looking directly down the channel in **5**.

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[18] Bertelli, M.; Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Mater. Chem.* **1997**, *7*, 1271.

[19] The pore dimensions described here are crystallographic scalar quantities, and do not account for the van der Waals radii of the atoms defining the pore.

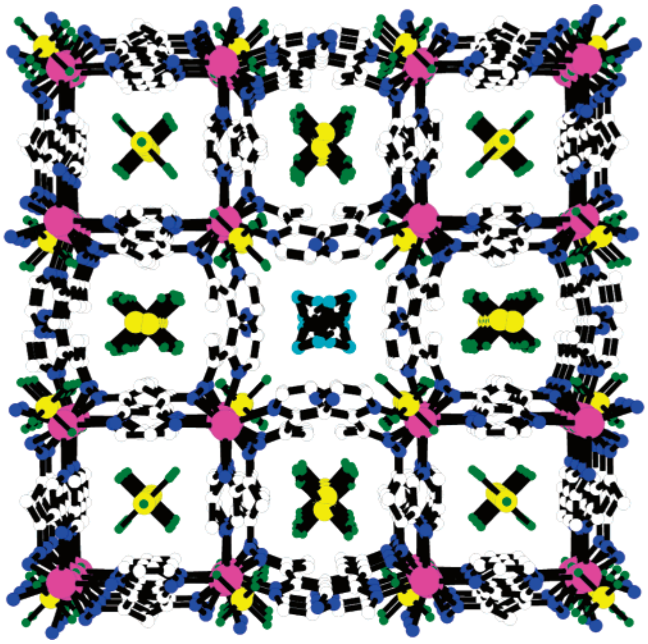

Figure 6. Perspective view of H-bonded three-dimensional framework containing square channels in **5**.

and F(4)$\cdots$C(3) = 3.353(5) Å). Consequently, the packing of the tubes is also in a square motif, as shown in Figure 6, and generates further square channels (crystallographic dimensions of 11.4 × 10.0 Å) between original tubes which contain disordered $P(3)F_6^-$ counterions and $CHCl_3$ guest molecules alternatively along crystallographic *a* axis. When viewed down crystallographic [110] direction, rhombic channels with different dimensions have been found. Large (crystallographic dimensions of 9.8 × 9.8 Å)[19] and small channels (crystallographic dimensions of 4.6 × 4.6 Å)[19] arrange alternately, in which PF_6^- and $CHCl_3$ guest molecules are located (Figure 7). The existence and structural importance of weak C−H$\cdots$X hydrogen bonding interactions are now well established [20] and are observed in many compounds, such as the N$\cdots$H−C interaction in 1,3,5-tricyanobenzene-hexamethylbenzene,[21] the O$\cdots$H−C interaction in $(C_{14}H_{12}N_2)[Cu(opba)]\cdot 3H_2O$ and $Na_2(C_{12}H_{12}N_2)[Cu(opba)]_2\cdot 4H_2O$ (opba = *o*-phenylenebis(oxamate)),[22] and the F$\cdots$H−C interaction in 11-(trifluoromethyl)-15,16-dihydrocyclopenta[α]phenanthren-17-one.[23] These hydrogen bonds, although weak, contribute significantly to the alignment of those one-dimensional tubes into a three-dimensional H-bonded framework in the crystalline state. TGA shows that the $CHCl_3$ guest molecules are lost in the temperature range 90−121 °C and the framework collapsed after removal of guest molecules. It is well-known that many porous systems, upon removal of the included guest molecules, often undergo phase transitions to other more dense structures.[24]

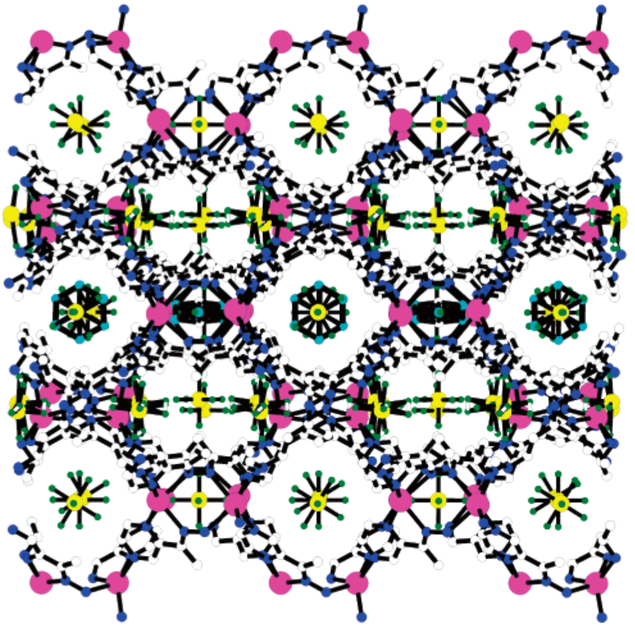

Figure 7. [110] view of H-bonded three-dimensional framework containing rhombic channels with different dimensions.

In contrast to the well-developed molecular square chemistry,[25] efforts on polymeric organic−inorganic coordination square one-dimensional tubes are still unusual, although some inorganic 1-D tubes based on inorganic counterions such as CN^- and $N(CN)_2^-$ have been reported.[26]

Structural analysis of 6. Compound **6** was obtained by reaction of L6 and $AgSO_3CF_3$ in ethanol/CH_2Cl_2 mixed solvent system as yellow crystals at 63% yield. In addition, compound **6** can also be obtained directly by combination of 2-acetylpyrazine with $AgSO_3CF_3$ in the same solvent system, but in somewhat higher yield (76%). The structure is confirmed by single-crystal X-ray analysis, IR spectrum, and elemental analysis. However, under dry condition, single crystals qualified for single-crystal X-ray analysis were not obtained by combination of L6 with AgOTf, although we tried many times including using different solvent systems and metal-to-ligand ratios. It is worthy to point out that, in this reaction, Schiff-base ligand L6 was attacked by water in the presence of $SO_3CF_3^-$ (weak base) and converted to 2-acetylpyrazine which is the starting material for synthesis of L6. It is well-known that imine group is easy hydrolysis especially in the presence of acid or base.[27] As shown in Figure 8, there are two Ag(I) atoms in **6**. The first Ag(I) center lies in a distorted tetrahedral coordination environment which consists of two N-donors (Ag(1)−N(4)#1 = 2.242-

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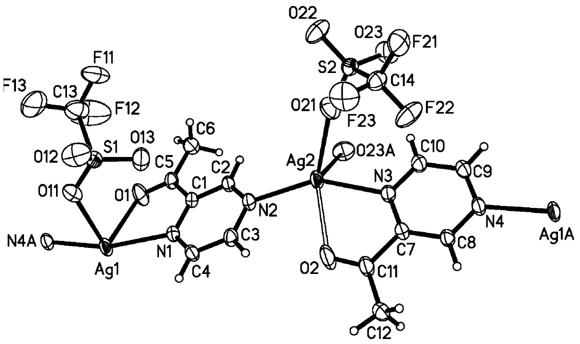

Figure 8. Ag(I) coordination environment in compound **6**. Displacement ellipsoids drawn at the 30% probability level.

(2) and Ag(1)−N(1) = 2.258(2) Å) from two 2-acetylpyrazine ligands, one O-donor (Ag(1)−O(1) = 2.579(2) Å) and from one 2-acetylpyrazine and one triflate O-donor (Ag(1)−O(11) = 2.582(2) Å). The second Ag(I) center adopts a $\{AgN_2O_3\}$ coordination sphere which consists of two N-donors (Ag(2)−N(2) = 2.254(2) and Ag(2)−N(3) = 2.292(2) Å) from two 2-acetylpyridine ligands and one O-donor (Ag(2)−O(2) = 2.658(3) Å) and from one 2-acetylpyrazine ligand and two O-donors (Ag(2)−O(21) = 2.510(2) and Ag(2)−O(23)#3 = 2.565(2) Å) from two triflate counterions. In the solid state, 2-acetylpyrazine ligand chelates the Ag(I) centers through the carbonyl O-donor, and the vicinal pyrazine N-donor, furthermore, uses the *para*-N atoms to link other Ag(I) centers into one-dimensional zigzag chains along the crystallographic [101] direction (Figure 9a). The triflate anions link these chains into a three-dimensional network by somewhat long Ag···O contacts (Figure 9b). There are no guest molecules found in the framework.

Luminescent Properties. Mixed inorganic−organic hybrid coordination polymers have been investigated for fluorescence properties and for potential applications as light-emitting diodes (LEDs).[28] Owing to the ability of affecting the emission wavelength of organic materials, syntheses of inorganic−organic coordination polymers by the judicious choice of organic spacers and transition metal centers can be an efficient method for obtaining new types of electroluminescent materials.[28] The luminescent properties of L5−L6 and compounds **1**−**5** were investigated in the solid state. The fluorescence spectra of L5 and compounds **1**−**4** are shown in Figure 10. L5 exhibits one emission maximum at 420 nm upon photoexcitation at 293 nm. The emission spectra of **1**−**4** exhibit three maxima at 420, 440, and 482 nm (excitation wavelength: 336 nm) for **1**, 420, 440, and 483 nm (excitation wavelength: 333 nm) for **2**, 422, 455, and 482 nm (excitation wavelength: 336 nm)for **3**, and 423, 442, and 484 nm (excitation wavelength: 280 nm) for **4**. Compared to the emission spectrum of L5, compounds **1**−**4** present two more emission bands and are red-shifted. However, no obvious enhancement of the fluorescence intensities is realized. For L6, no significant emission was found in the range of 400−800 nm. For compound **5**, as

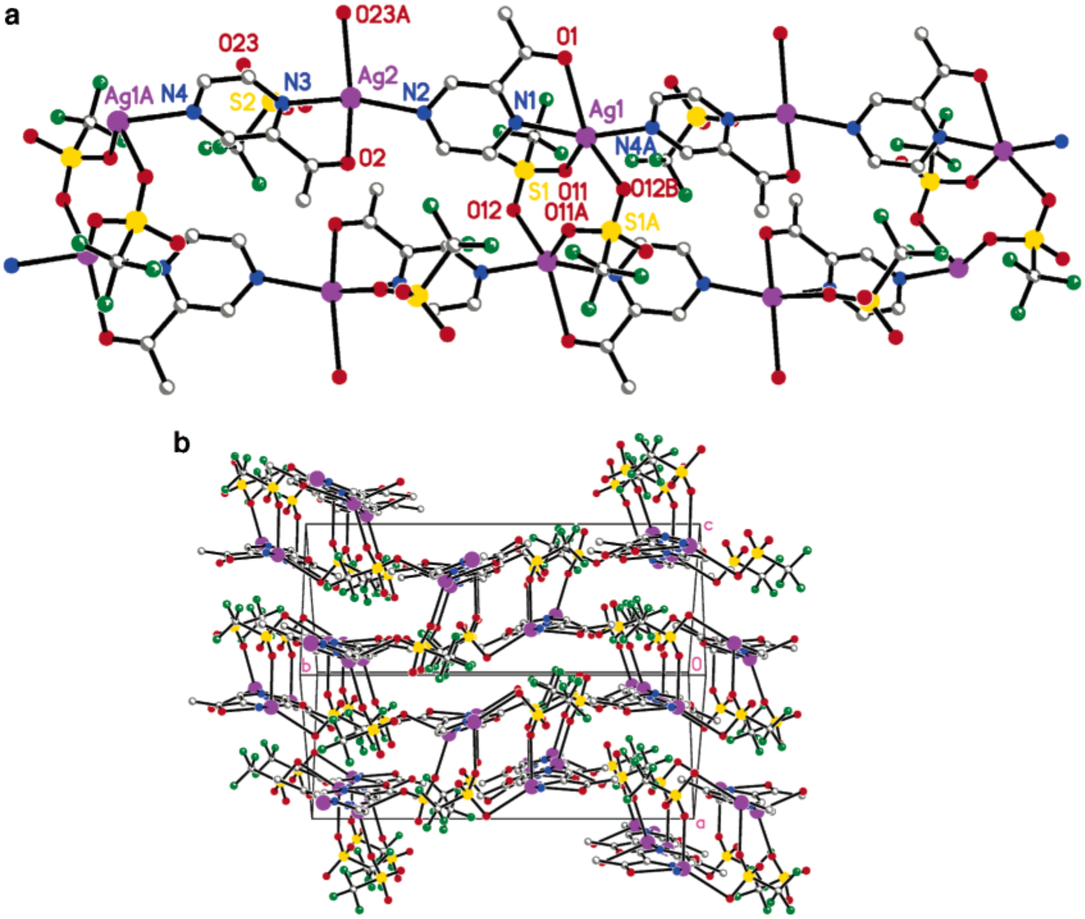

Figure 9. (a) Infinite one-dimensional chains along [101] in **6**. (b) Three-dimensional network in **6**.

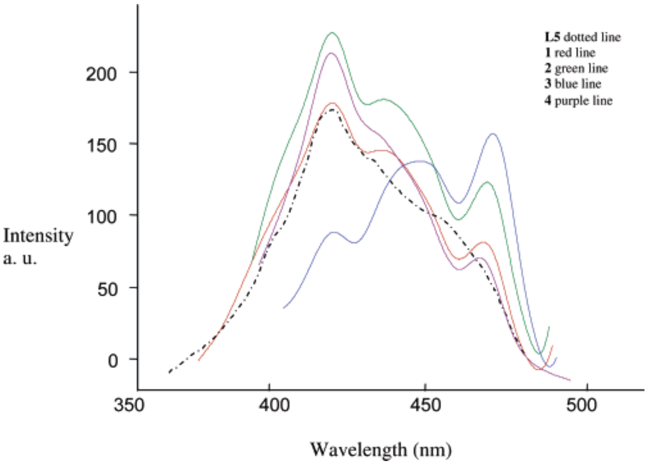

Figure 10. Photoinduced emission spectra of L5 and **1**−**4** in the solid state at room temperature.

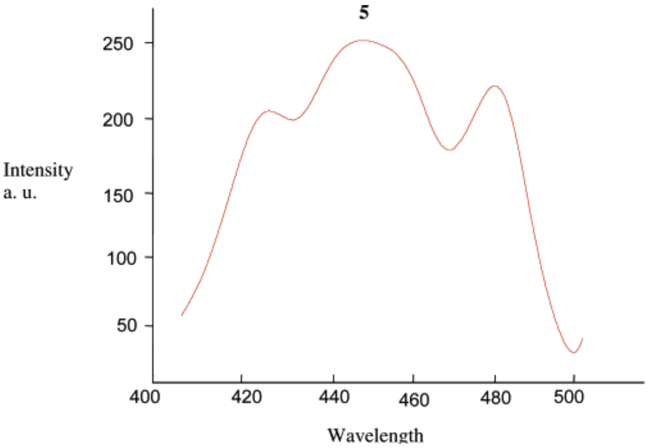

Figure 11. Photoinduced emission spectrum of **5** in the solid state at room temperature.

shown in Figure 11, there are three emission maxima at 423, 448, and 482 nm (excitation wavelength: 336 nm), respectively. The fluorescence properties of the free L5 and L6 were significantly affected by their incorporation into the Ag-containing polymeric compounds **1**−**5**, as evidenced by the large shift for compounds **1**−**4** and fluorescence intensity enhancement in the emissions for **5**. In general, Ag(I) complexes might emit weak photoluminescence at low temperature, and, consequently, compounds **1**−**5** reported herein represent the unusual examples of room-temperature luminescent Ag-containing polymeric compounds.[29] Further work on synthesis of new bipyrazine-type ligands and their coordination chemistry are in progress.

Conclusions

This study demonstrates that the bipyrazine-type double Schiff-base ligands 2,5-bis(3-methylpyrazinyl)-3,4-diaza-2,4-hexadiene (L5) and 2,5-bis(pyrazinyl)-3,4-diaza-2,4-hexadiene (L6) are capable of coordinating Ag(I) metal center through both terminal pyrazinyl nitrogen donors and Schiff-base nitrogen donors, and of generating novel coordination polymers. Varying the R group (from H to $-CH_3$) on the terminal pyrazinyl groups is a decisive factor in determining the coordination environments of the metal centers and, moreover, the topologies of the polymeric products. Bipyrazine-type ligands L5−L6 reported herein resulted in unusual building blocks due to their multidentate and chealting coordination behavior, leading to the construction of polymeric motifs which have not been achieved using bipyridine-type Schiff-base ligands L1−L4. In the solid state, compounds **1**−**5** are luminescent. The emission colors of the free ligands were significantly affected by their incorporation into the Ag-containing polymeric compounds **1**−**5**, as evidenced by the large shift and fluorescence intensity enhancement in the emission. We are currently extending this result by preparing new Schiff-base ligands of this type with different R functional groups and with different orientations of the nitrogen donors on the pyrazinyl rings. We anticipate this approach will be useful for the construction of a variety of new transition metal complexes and luminescent coordination polymers with novel structures that have the potential of leading to new fluorescent materials.

Acknowledgment. We are grateful for financial support from the National Natural Science Foundation of China (20371030 and 20174023), we also thank the Open Fountain of State Key Lab of Crystal Materials for financial support. H.-C.zL. gratefully acknowledges support from the NSF through grant DMR: 0134156.

Supporting Information Available: Crystallographic file for the subject compounds (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC049787A

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