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Structural Diversity of Silver(I) 4,6-Dipyridyl-2-Aminopyrimidine Complexes: Effect of Counteranions and Ligand Isomerism

Ying-Nan Chi,[†] Kun-Lin Huang,[†,‡] Feng-Yun Cui,[†] Yan-Qing Xu,[†] and Chang-Wen Hu*,[†]

The Institute for Chemical Physics and Department of Chemistry, Beijing Institute of Technology, Beijing 100081, China, and College of Chemistry, Chongqing Normal University, Chongqing 400047, China

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Using two ligands, 4,6-bis(2-pyridyl)-2-aminopyrimidine (L1) with two N,N′-chelating sites and 4-(2-pyridyl)-6-(4-pyridyl)-2-aminopyrimidine (L2) (as the isomer of L1) containing one chelating site and one bridging unit, a series of novel Ag(I) complexes varying from zero- to two-dimensions have been prepared and their crystal structures determined via single-crystal X-ray diffraction. The two ligands are employed for the first time in coordination chemistry. The structures of compounds **1**–**3** are directed by the counteranions adopted in the reaction system: The reaction of L1 with $AgNO_3$ yielded a dimer $[Ag_2L1_2](NO_3)_2$ (**1**). The reaction of L1 with $AgCF_3SO_3$ led to a one-dimension "V-shaped" chain $\{[AgL1](CF_3SO_3)\}_n$ (**2**). When AgSCN was used, a one-dimension ladder $\{[Ag_2L1(SCN)_2]\cdot H_2O\}_n$ (**3**) was obtained. While ligand L2 reacted with $AgNO_3$, a two-dimension $\{[Ag_2(L2)_2](NO_3)_2\cdot H_2O\}_n$ (**4**) was prepared with the help of an argentophilic interaction. Compounds **1**–**4** display room-temperature photoluminescence.

Introduction

The rational design and construction of novel discrete and polymeric metal−organic complexes has been the subject of enormous studies in recent years, not only due to their structural and topological novelty[1] but also for their potential applications as functional materials such as catalysis, molecular recognition, separation, and nonlinear optics.[2] The structure of metal−organic complexes is highly influenced by many factors such as the coordination geometry of metal ions, the structure of organic ligands, the solvent system, the counteranion, and the ratio of ligands to metal ions.[3−7] In addition, the secondary forces such as hydrogen-bonding, $\pi-\pi$ stacking, and host−guest interactions must be considered as well. For obtaining novel structural motifs with predictable properties, a large number of organic ligands were designed and utilized. Among them, there is an increasing interest in the N,N′-chelating ligands, especially the N,N′-

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* To whom correspondence should be addressed. E-mail: cwhu@bit.edu.cn. Phone: +86-10-68912667. Fax: ++86-10-68914780.

[†] Beijing Institute of Technology.

[‡] Chongqing Normal University.

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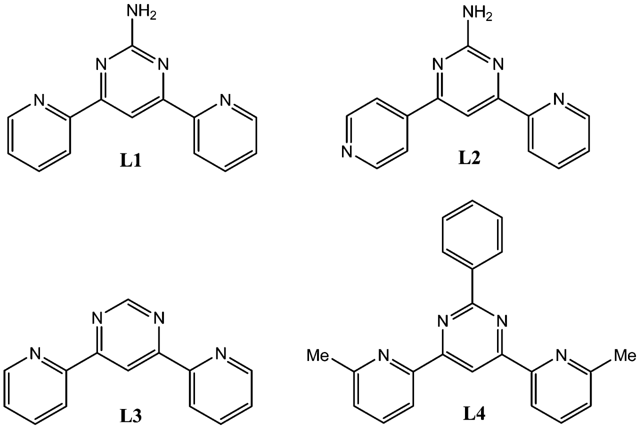
Chart 1. Structural Drawings of Ligands L1−L4



chelating oligopyridine ligands,[8] for instance 2,2′-bipyridine and its derivatives.[9]

During the investigation of coordination chemistry of N,N′-chelating oligopyridine ligands, our attention is attracted by 4,6-bis(2-pyridyl)-2-aminopyrimidine ligand (L1, in Chart 1). The L1 ligand contains two bidentate binding sites with the capability of bridging two metal ions in chelating way, while the amino group can interact with crystallographic water molecules or counteranions through hydrogen bondings. However, the coordination chemistry of this ditopic ligand has not yet been explored, despite the fact that L1 was synthesized by Takagi in 2002.[10] And the ligands structurally similar to the bis(bidentate) ligand L1 are rare; to the best of our knowledge, only 4,6-bis(2-pyridyl)-pyrimidine (L3) and 4,6-bis(6-methylpyridine-2-yl)-2-phenylpyrimidine (L4) were reported (Chart 1). For L3 ligands, several mono- and dinuclear complexes were documented,[11] but only $L3[M(hfac)_2]_2$ (M = Mn, Co, Ni, Cu; hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) were characterized by X-ray diffraction.[11a] While the reactions of L4 with Cu(I), Ag(I), and Zn(II) ions lead to [2 × 2] grid architectures, only the Ag(I) complex has a single-crystal result.[12] Thus, we hope that the L1 ligands could possibly generate new architectures which would enrich the structural database of this kind of ligand.

To investigate the influence of the structural change of ligands on the crystal structure, the 4-pyridine group was used instead of the original 2-pyridine group; thus, a new compound 4-(2-pyridyl)-6-(4-pyridyl)-2-aminopyrimidine (L2) (Chart 1) was prepared in the yield of 60% and characterized by IR and ^{1}H NMR. Compared with the structure of L1, one chelating unit is retained in L2 while another chelating site is changed (Chart 1). Thus, the coordination modes exhibited by L1 and L2 would be different.

The complexes of Ag(I) have been of great interest in recent years owing to their rich bonding modes and coordination geometries.[13] The structure of Ag(I) compounds can be controlled by the structure of organic ligands as well as counteranions. For example, the effect of ligand isomerism on the structural diversity of silver(I) complexes was examined by Lee and his co-workers.[14] When 4-(2-pyridyl)-pyrimidine reacted with $AgBF_4$, $AgCF_3SO_3$, and $AgNO_3$, the effect of conteranions on the structures was documented.[15] So we first chose different silver(I) salts to react with L1 ligands to explore the role of counteranions on resulting structures. Second, we designed and synthesized the new L2 ligand, the isomer of L1, to examine the influence induced by structural change of ligands. As a result, four Ag(I) compounds, namely, $[Ag_2L1_2](NO_3)_2$ (**1**), $\{[AgL1](CF_3SO_3)\}_n$ (**2**), $\{[Ag_2L1(SCN)_2]\cdot H_2O\}_n$ (**3**), and $\{[Ag_2(L2)_2](NO_3)_2\cdot H_2O\}_n$ (**4**) [L1 = 4,6-bis(2-pyridyl)-2-aminopyrimidine; L2 = 4-(2-pyridyl)-6-(4-pyridyl)-2-aminopyrimidine], were synthesized and characterized by X-ray analysis.

Experimental Section

Materials. All of the silver(I) salts were purchased from commercial sources and used without further purification. Organic solvents with analytical purity were supplied by commercial sources and used as received. Infrared spectra were obtained (as KBr pressed pellets) using a Nicolet 170SXFT/IR spectrometer. ^{1}H NMR spectra (for L1 and L2) were recorded using a Bruker DPX 500 spectrometer. X-ray powder diffraction (XPRD) of samples was collected on a Japan Rigaku D/max γ A X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation ($\lambda = 0.154\,060$ nm). The C, H, and N elemental analyses were performed on Perkin-Elmer 2400 CHN elemental analyzer. Excitation and emission spectra were obtained on a RF-5301PC spectrofluorometer equipped with a 450 W xenon lamp as the excitation source, and the measurements were performed at room temperature.

Synthesis of L1 and L2. L1 and L2 were prepared according to previously reported synthetic procedures.[10] The synthetic procedure of new L2 ligand was similar to that of L1. Data for L2: yield 60%; mp 180−182 °C; ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) δ 8.77 (2H, d, 4-pyridyl), 8.01 (2H, d, 4-pyridyl), 8.42 (1H, s, pyrimidyl), 5.23 (2H, s, amino group), 8.74 (1H, m, $J = 5$ Hz, 2-pyridyl), 8.41 (1H, d, $J = 8.0$ Hz, 2-pyridyl), 7.86 (1H, m, $J = 7.5$ Hz, 8.0, 2-pyridyl), 7.42 (1H, m, $J = 7.5$, 5.0 Hz, 2-pyridyl); IR (KBr, cm^{-1}) ν 3329 (m), 3206 (m), 1649 (s), 1576 (s), 1558 (s), 1531 (s), 1478

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Table 1. Crystallographic Data for Compounds **1**−**4**^{a}

param	**1**	**2**	3	**4**
formula	$C_{28}H_{22}Ag_2N_{12}O_6$	$C_{30}H_{22}Ag_2F_6N_{10}O_6S_2$	$C_{16}H_{13}Ag_2N_7OS_2$	$C_{28}H_{24}Ag_2N_{12}O_7$
fw	*838.32*	*1012.44*	*599.19*	*856.33*
a (Å)	*8.091(9)*	*15.531(2)*	*4.006(5)*	*11.2715(19)*
b (Å)	8.980(10)	13.370(2)	11.815(15)	19.707(3)
c (Å)	10.786(12)	17.639(3)	21.03(3)	14.105(2)
α (deg)	96.802(14)	90	90.00	90
β (deg)	90.398(17)	90	93.53(2)	109.619(2)
γ (deg)	109.199(14)	90	90.00	90
space group	$P\bar{1}$	Pbca	$P2/c$	$C2/c$
D_{calc} (g cm^{-3})	1.897	1.836	2.003	1.927
Z	1	4	2	4
cryst system	triclinic	orthorhombic	monoclinic	monoclinic
V (Å^3)	734.0(14)	3662.8(10)	993(2)	2951.2(9)
M	1.401	1.271	2.204	1.399
F(000)	416	2000	584	1704
cryst size	0.37 × 0.31 × 0.21	0.42 × 0.29 × 0.18	0.70 × 0.12 × 0.03	0.38 × 0.23 × 0.1
reflcns collcd	3446	18 108	4617	7711
unique reflcns	2462	3230	1728	2616
Goof	1.016	1.084	0.974	1.078
R1 [$I > 2\delta(I)$]	0.0633	0.0429	0.0743	0.0324
wR2 [$I > 2\delta(I)$]	0.1893	0.1063	0.1685	0.0697
R1 (all data)	0.0865	0.0639	0.1472	0.0467
wR2 (all data)	0.2343	0.1251	0.2044	0.0762

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

(m), 1371 (m), 1237 (w), 1134 (w), 1065 (w), 999 (w), 828 (m), 783 (s), 746 (w), 640 (m), 620 (w), 408 (m).

Synthesis of $[Ag_2L1_2](NO_3)_2$ (1). A solution of L1 (1 mmol, 24.9 mg) in acetonitrile (5 mL) was carefully layered on the top of a 5 mL aqueous solution of $AgNO_3$ (1 mmol, 17.0 mg). The whole reaction system was kept in darkness at room temperature, and yellow cubic crystals were obtained after 3 days. The crystals were filtered off, washed with distilled water and acetonitrile, and left to dry in darkness at room temperature. Yield: 31.4 mg, 75%. Anal. Calcd for $C_{28}H_{22}Ag_2N_{12}O_6$: C, 40.12; H, 2.64; N, 20.05. Found: C, 40.01; H, 2.81; N, 19.89. IR (KBr, cm^{-1}): ν 3406 (w), 3305 (w), 3205 (w), 1623 (s), 1572 (s), 1564 (s), 1473 (s), 1422 (w), 1385 (vw), 1383 (s), 1364 (s), 1335 (s), 1305 (s), 1235 (m), 1160 (w), 1058 (w), 1013 (m), 858 (w), 826 (w), 797 (w), 775 (s), 749 (w), 689 (w), 657 (m), 633 (w), 513 (w), 413 (w).

Synthesis of $\{[AgL1](CF_3SO_3)\}_n$ (2). Compound **2** was prepared by a procedure similar to that for compound **1**. Yield: 35.9 mg, 71%. Anal. Calcd for $C_{30}H_{22}Ag_2F_6N_{10}O_6S_2$: C, 35.59; H, 2.19; N, 13.83. Found: C, 35.72; H, 2.28; N, 13.65. IR (KBr, cm^{-1}): ν 3382 (m), 3312 (m), 3224 (m), 3112 (w), 1631 (s), 3116 (w), 3072 (w), 1580 (s), 1571 (s), 1556 (s), 1476 (s), 1460 (s), 1420 (m), 1364 (s), 1283 (s), 1242 (s), 1159 (s), 1107 (w), 1059 (w), 1029 (s), 1007 (w), 860 (w), 842 (w), 797 (w), 780 (s), 758 (w), 740 (w), 697 (w), 660 (m), 639 (s), 591 (w), 575 (w), 517 (w), 430 (w).

Synthesis of $\{[Ag_2L1(SCN)_2]\cdot H_2O\}_n$ (3). AgSCN (1 mmol, 16.6 mg) was dissolved in the saturated aqueous solution of KSCN (5 mL), and then L1 (1 mmol, 24.9 mg) in acetonitrile (5 mL) was carefully layered on the top of mixture solution of AgSCN and KSCN. The whole reaction system was kept in darkness at room temperature, and yellow needle crystals were obtained after 2 days. The crystals were filtered off, washed with distilled water and acetonitrile, and left to dry in darkness at room temperature. Yield: 36.6 mg, 61%. Anal. Calcd for $C_{16}H_{13}Ag_2N_7OS_2$: C, 32.07; H, 2.19; N, 16.36. Found: C, 32.11; H, 2.22; N, 16.42. IR (KBr, cm^{-1}): ν 3460 (w), 3349 (w), 2117 (s), 2103 (s), 1622 (s), 1580 (s), 1473 (s), 1418 (w), 1364 (m), 1308 (w), 1225 (m), 1175 (w), 1156 (w), 1099 (w), 1055 (w), 970 (w), 797 (m), 773 (s), 744 (m), 660 (m), 635 (w), 428 (w), 402 (w).

Synthesis of $\{[Ag_2(L2)_2](NO_3)_2\cdot H_2O\}_n$ (4). Compound **4** was prepared by a procedure similar to that for compound **1**. Yield: 35.5 mg, 83%. Anal. Calcd for $C_{28}H_{24}Ag_2N_{12}O_7$: C, 39.27; H, 2.82; N, 19.63. Found: C, 39.08; H, 2.93; N, 19.55. IR (KBr, cm^{-1}): ν 3290 (w), 3155 (w), 3089 (w), 1633 (m), 1572 (s), 1538 (s), 1505 (w), 1476 (m), 1422 (w), 1385 (s), 1366 (s), 1320 (w), 1300 (w), 1218 (m), 1064 (w), 1006 (w), 828 (m), 822 (w), 798 (m), 780 (m), 764 (w), 744 (w), 728 (w), 693 (w), 673 (w), 657 (m), 639 (w), 484 (w), 460 (w), 442 (w).

X-ray Crystallographic Analysis. Suitable single crystals of complexes **1**−**4** were mounted on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation source ($\lambda = 0.071\,03$ Å) at 298 K. All absorption corrections were performed with the SADABS program. All the structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in the calculated positions. All calculations were performed using the SHELXTL-97 program.[16] The crystallographic details of **1**−**4** are summarized in Table 1. Selected bond lengths and angles of **1**−**4** are listed in Table 2, and selected hydrogen bonding parameters of **1**−**4** are shown in Table 3.

Results and Discussion

Synthesis and IR Spectroscopy. The syntheses of complexes **1**−**4** were summarized in Scheme 1. The formation of the products was not significantly affected by changes of the reaction mole ratio of ligands to metal ions or organic solvents, and the resultant crystals were insoluble in water and common organic solvents. The NO_3^- and $CF_3SO_3^-$ ions yield zero-dimension compound **1** and one-dimension compound **2**, respectively. When counteranions SCN^- were used and coordinated with the metal ions, the one-dimension coordination polymer **3** was isolated. The two-dimension compound **4** was obtained from the reaction of the L2 ligand (the isomer of L1) with $AgNO_3$.

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Table 2. Selected Bond Lengths (Å), Angles (deg), and Important Distance for **1-4**[a]

dist (Å)		angle (deg)	
		Complex **1**	
Ag(1)−N(4)	2.226(9)	N(4)−Ag(1)−N(1)	67.9(3)
Ag(1)−N(5)$^{\#1}$	2.275(10)	N(2)$^{\#1}$−Ag(1)−N(1)	83.8(3)
Ag(1)−N(2)$^{\#1}$	2.413(8)	N(5)$^{\#1}$−Ag(1)−N(2)$^{\#1}$	70.4(3)
Ag(1)−N(1)	2.682(8)	N(4)−Ag(1)−N(5)$^{\#1}$	155.9(3)
Ag(1)···O(1)	2.914(10)	N(5)$^{\#1}$−Ag(1)−N(2)$^{\#1}$	70.5(3)
Ag(1)···O(2)	**3.012(9)**	**O(1)···Ag(1)···O(2)**	**42.2(2)**
		Complex **2**	
Ag(1)−N(5)	2.306(5)	N(5)−Ag(1)−N(1)	114.08(15)
Ag(1)−N(4)	2.325(5)	N(5)−Ag(1)−N(2)	69.10(14)
Ag(1)−N(1)	2.416(4)	N(4)−Ag(1)−N(2)	108.71(15)
Ag(1)−N(2)	2.477(4)	N(4)−Ag(1)−N(1)	69.88(16)
Ag(1)···O(2)$^{\#1}$	**2.933(8)**	**N(5)−Ag(1)−N(4)**	**136.2(2)**
		Complex **3**	
Ag(1)−N(3)	2.315(11)	N(3)−Ag(1)−N(1)	69.8(3)
Ag(1)−N(1)	2.411(9)	N(3)−Ag(1)−S(1)	129.9(3)
Ag(1)−S(1)$^{\#1}$	2.519(5)	N(1)−Ag(1)−S(1)	108.8(3)
Ag(1)−S(1)	2.538(5)	Ag(1)$^{\#2}$−S(1)−Ag(1)	104.76(18)
S(1)−C(9)	1.659(12)	C(9)−S(1)−Ag(1)	102.8(5)
N(4)−C(9)	**1.129(13)**	**N(4)−C(9)−S(1)**	**175(2)**
		Complex **4**	
Ag(1)−N(5)$^{\#1}$	2.167(3)	N(5)$^{\#1}$−Ag(1)−N(1)	172.05(11)
Ag(1)−N(1)	2.238(3)	N(5)$^{\#1}$−Ag(1)−N(4)	115.62(11)
Ag(1)−N(4)	2.381(3)	N(1)−Ag(1)−N(4)	72.31(10)
Ag(1)−Ag(1)$^{\#2}$	3.0839(8)	N(5)#1−Ag(1)−Ag(1)$^{\#2}$	89.83(9)
N(3)−C(1)	1.336(5)	N(1)−Ag(1)−Ag(1)$^{\#2}$	88.03(8)
C(2)−C(12)	1.487(5)	N(4)−Ag(1)−Ag(1)$^{\#2}$	100.53(8)

[a] Symmetry code for **1**: (#1) $-x + 1, -y + 1, -z$; (#2) $x + 1, y, z$. Symmetry code for **2**: (#1) $x, -y + 1/2, z + 1/2$. Symmetry code for **3**: (#1) $x - 1, y, z$; (#2) $x + 1, y, z$. Symmetry code for **4**: (#1) $x - 1/2, y - 1/2, z$; (#2) $-x + 1, y, -z + 1/2$.

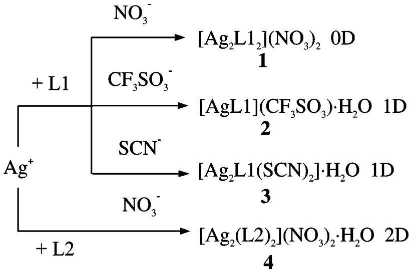
Table 3. Hydrogen Bonds in **1**−**4**[a]

D-H···A	D−H	H···A	D···A	<(DHA)
		Complex **1**		
N(3)−H(3A)···O(2)$^{\#2}$	0.860	2.575	3.140(12)	124.23
N(3)−H(3B)···O(2)$^{\#1}$	**0.860**	**2.251**	**3.070(11)**	**158.46**
		Complex **2**		
N(3)−H(3A)···O(1)$^{\#1}$	0.86	2.18	2.860(11)	135.5
N(3)−H(3B)···O(2)$^{\#4}$	0.86	2.17	2.956(7)	151.8
		Complex **3**		
O(1)−H(9)···N(4)	**0.84(2)**	**2.24(2)**	**3.022(18)**	**154(6)**
		Complex **4**		
N(3)−H(3B)···O(3)$^{\#4}$	0.86	2.06	2.836(5)	150.0
O(4)−H(15)···O(2)$^{\#5}$	0.846	2.074	2.822	147.10

[a] Symmetry codes for **1**: (#1) $-x + 1, -y + 1, -z$; (#2) $x + 1, y, z$. Symmetry codes for **2**: (#1) $x, -y + 1/2, z + 1/2$; (#4) $-x + 1/2, -y, z + 1/2$. Symmetry codes for **4**: (#4) $x, y, z - 1$; (#5) $-x + 3/2, -y + 1/2, -z + 1$.

The chief part of the IR spectrum of **1** is similar to that of the L1 ligand. There are three new strong peaks at 1383, 1335, and 1305 cm^{-1} which are incorporated into a broad band in the region of 1400−1270 cm^{-1}. For compound **2**, the asymmetric and symmetric stretching vibrations of the −NH$_2$ group (at 3382 and 3312 cm^{-1}) are similar to that of free ligand L1, two peaks at 1283 and 1159 cm^{-1} of **2** become stronger and sharper than those of L1, and a new strong peak appears at 1032 cm^{-1}. The IR spectrum of **3** exhibiting ν(CN) stretching bands at 2117 and 2103 cm^{-1} (>2100 cm^{-1}) indicates the coordination of the S atom of SCN$^-$ anion,[17] and this is in agreement with the crystal result of **3**. In the spectrum of **4**, the single peak at 1633 cm^{-1} is weaker than the corresponding peak for L2. Moreover, the peak at 1385 cm^{-1} in **4** is stronger than that in L2 and the several peaks at 1400−1270 cm^{-1} in **4** are incorporated into a broad band; similar phenomena are also observed in the spectrum of **1**.

Scheme 1. Synthesis of Compounds **1**−**4**



X-ray Crystal Structures. Crystal Structure 1. The structure of **1** is constructed from two ligands and two silver ions with an Ag···Ag separation of 6.155 Å. As shown in Figure 1, each L1 chelates two separate silver ions through the four aromatic N atoms. Every Ag atom is coordinated with four aromatic N atoms from two ligands [N(1), N(4); N(2A), N(5A)] with distorted tetrahedral geometry, and the Ag−N$_{\text{pyridine}}$ bond lengths [2.226 and 2.275 Å for Ag(1)−N(4) and Ag(1)−N(5A)] are similar, while Ag−N$_{\text{pyrimidine}}$ bond lengths [2.413 and 2.682 Å for Ag(1)−N(1) and Ag(1)−N(2A)] are much longer than Ag−N$_{\text{pyridine}}$. The acute angles at the chelate sites of L1 [67.69° for N(1)−Ag(1)−N(4) and 70.44° for N(2A)−Ag(1)−N(5A)] account for the obviously distorted surrounding of silver ions. Besides the strong coordination interactions between Ag and N donors, weak interactions are found between Ag(I) and O atoms of nitrate ion: Ag(1)···O(1) = 2.914 Å; Ag(1)···O(2) = 3.012 Å.

In crystal **1**, each pyridine ring is approximately on the same plane, but the pyrimidine ring is a little distorted. The three aromatic rings are far from coplanar; the dihedral angles between the pyrimidine ring and 2-pyridine ring containing N(4) and 2-pyridine ring containing N(5) are 37.9 and 18.5°, respectively, and the dihedral angles between two pyridine

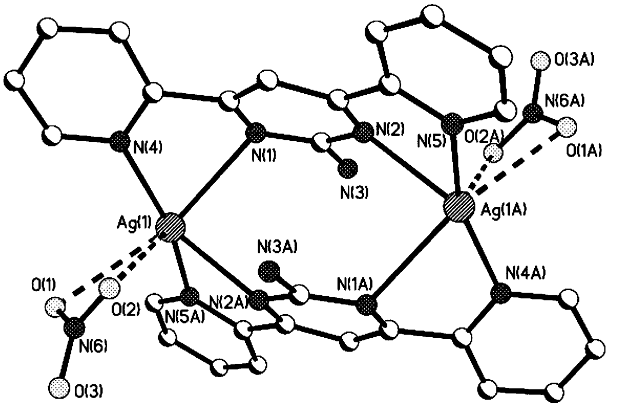


Figure 1. View of the dimer in compound **1**. The dashed lines represent the weak interactions between Ag and O of nitrate ion. All H atoms are omitted for clarity. Symmetry codes: (A) $1 - x, 1 - y, -z$.

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(17) Kazuo, N. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley & Sons: Weinheim, Germany, 1986.

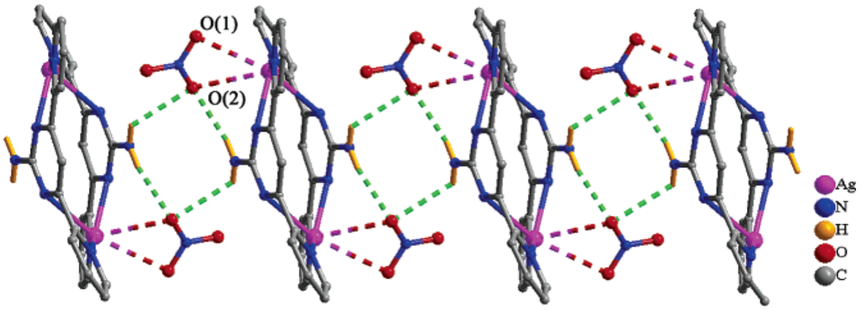

Figure 2. View of a 1-D chain in **1** formed by the hydrogen-bonding interactions between amino groups and nitrate ions. The green dashed lines represent the hydrogen-bonding interactions, and red-pink double-colored dashed lines represent the weak interactions between Ag and O of nitrate ion.

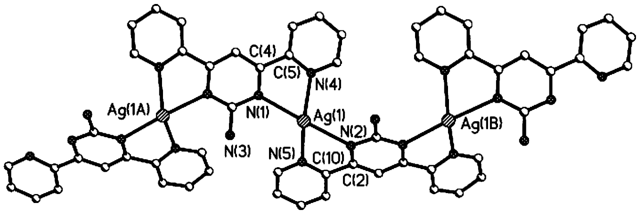

Figure 3. Coordination environments of Ag atoms in **2**. All H atoms are omitted for clarity. Symmetry codes: (A) $1/2 - x$, $-1/2 + y$, z; (B) $1/2 - x$, $1/2 + y$, z.

rings are 33.9°. In the dimer, the two pyrimidine rings are parallel to each other, while the two amino groups on pyrimidine rings point to contrary directions. The O(2) atom of nitrate as a hydrogen-bonding acceptor bridges two amino groups of separate molecules to build 1-D supramolecular chains (Figure 2). In **1**, nitrate ions do not coordinate with Ag ions, but weak interactions between Ag(1)···O(1) and Ag(1)···O(2) may prevent the compound from developing toward a high dimension.

Crystal Structure 2. When $AgCF_3SO_3$ was used instead of $AgNO_3$, compound **2** was obtained. In **2**, the ligands bridge the Ag^+ ions to form 1-D chains with the Ag(1)···Ag(1A) distance of 6.686 Å and the coordination fashion of L1 ligands is as same as that in **1**, namely, as we predicted (see Figure 3). Each Ag^+ ion coordinates with four N atoms from two L1, building a seriously distorted tetrahedral geometry around the metal atom. The $\mathrm{Ag-N_{pyrimidine}}$ bond lengths (average value 2.446 Å) are longer than the $\mathrm{Ag-N_{pyridine}}$ ones (average value 2.316 Å); the acute angles consisting of an Ag^+ ion and chelating N atoms are 69.10 and 69.88°. In this case, the L1 ligands are in a staggered arrangement along the chain, and the dihedral angle between the planes defined by Ag(1)−N(2)−C(2)−C(10)−N(5) and Ag(1)−N(1)−C(4)−C(5)−N(4) is ca. 50.5°. Then the chain looks like a “V-shaped” channel along the *b*-axis, and the metal ions and amino groups point to the tip of the “V” (see Figure 4a). As is shown in Figures 4b and S3 (Supporting Information), F(1), F(2), F(3), and O(1) atoms of $CF_3SO_3^-$ are disordered and O(1′) and O(2) atoms interact with the two adjacent amino groups through hydrogen bonding. So the anions chain is formed with the participation of amino groups under the “V-shaped” channel along the *b*-axis, and L1 is arranged away from the anions probably due to the large volume of $CF_3SO_3^-$ anions. In **2**, just one weak interaction between the O(2) atom of $CF_3SO_3^-$ and Ag [Ag(1)···O(2A) = 2.933 Å; symmetry code for A: x, $1/2 - y$, $1/2 + z$] is observed.

As in **1**, two pyridine rings of L1 are almost coplanar, and the pyrimidine ring is slightly distorted. The dihedral angles between pyrimidine ring and two pyridine rings are 13.9 and 11.4°, respectively; the one between two pyridine rings is 14.0°. All the dihedral angles in compound **2** are obviously smaller than those observed in compound **1**, and this indicates that greater distortion of L1 is required by the dimer motif.

Although the same silver salts and solvent were used, the structural motif in **2** is very different from the reported [2 × 2] grid structure formed by 4,6-bis(6-methylpyridine-2-yl)-2-phenylpyrimidine (L4) mentioned in the Introduction.[12] This result suggests that the structural motif is influenced by the substitution on the 2-position of the pyrimidine ring.

Crystal Structure 3. Since NO_3^- and $CF_3SO_3^-$ counter-anions gave distinct structures (**1** and **2**), it is of interest to examine the effect of other anions that could possibly coordinate with silver ions. When the L1 ligand reacted with $[Ag(SCN)_2]^-$ prepared by AgSCN dissolved in the saturated aqueous solution of KSCN, a new compound **3** was obtained.

The structure of **3** exhibits a novel 1-D ladder (extended along the *a*-axis) formed by L1 linking two 1-D $[AgSCN]_n$ chains with the intrachain Ag···Ag distance of 4.006 Å and the interchain Ag···Ag distance of 6.687 Å. In crystal **3**, the Ag(I) ion is four-coordinated by two N atoms from the chelate site of L1 and two S atoms from two thiocyanate ions, and N_2S_2 coordination builds a distorted tetrahedral geometry around the silver atom (Figure 5). In this case, L1 still acts as a bridge ligand and fixes two Ag^+ ions by its chelating N atoms, but the Ag^+ ion is not the node connecting two ligands as in compounds **1** and **2**. Moreover, the S atoms of thiocyanate ions acting as μ_2-bridges join the Ag^+ ions to form a 1-D chain (Figure 6) while the N atoms do not participate in coordination. As we known, the Ag^+ ion prefers to coordinate with S atoms. So the reported examples self-assembled from AgSCN and an organic N-ligand are rare.[18] In our work, the formation of **3** indicates that, to a certain degree, L1 ligands have strong coordinating ability. In **3**, the Ag(1)−N(1) bond length (2.411 Å) is shorter than the $\mathrm{Ag-N_{pyridine}}$ bond length in **1** or **2**, and Ag(1)−N(3) (2.315 Å) is similar to the average value of $\mathrm{Ag-N_{pyrimidine}}$ (2.316 Å) in **2**. The bond lengths of Ag−S in **3** are not entirely identical [Ag(1)−S(1) = 2.538 Å, Ag(1)−S(1B) = 2.519 Å], and the acute angle of Ag(1)−N(1)−N(3) is responsible

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(18) Liu, X.; Gou, G.-C.; Fu, M.-L.; Liu, X.-H.; Wang, M.-S.; Huang, J.-S. *Inorg. Chem.* **2006**, *45*, 3679−3685.

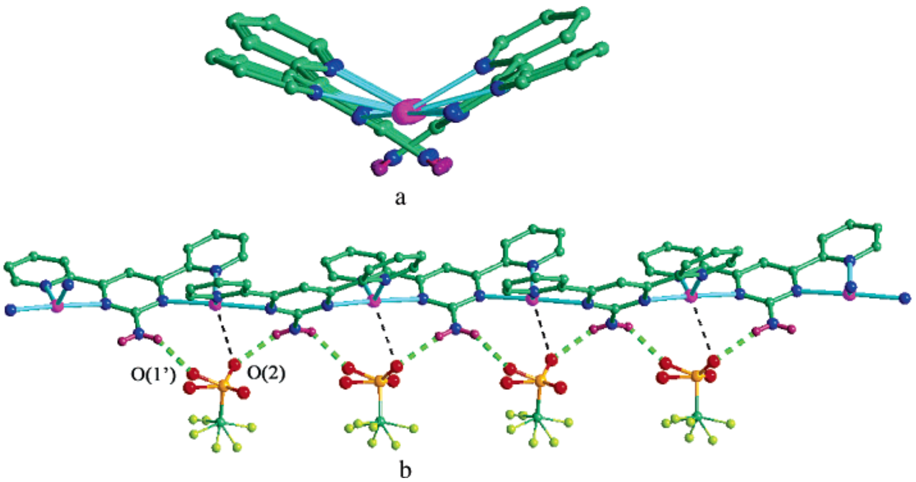

Figure 4. (a) Side view of the chain projected along the *b*-axis. (b) View of the 1-D chain of compound **2**. The hydrogen-bonding interactions between amino groups and O atoms of $CF_3SO_3^-$ are represented by green dashed lines, and the weak interactions between Ag and the O atom of the counteranion are represented by dark dashed lines. Color code: Ag, pink; N, blue; C, green; O, red; F, kelly green; S, yellow; H, dark pink.

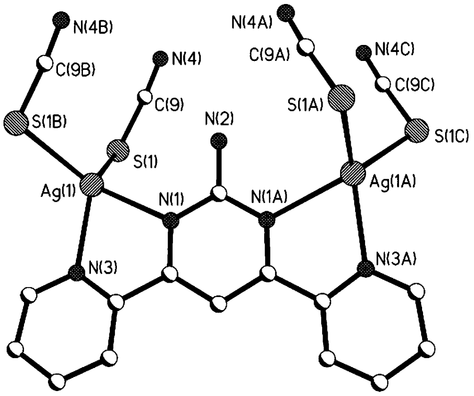

Figure 5. Coordination environment of Ag atoms in compound **3**. All H atoms are omitted for clarity. Symmetry codes: (A) $1 - x, y, 1/2 - z$; (B) $-1 + x, y, z$; (C) $2 - x, y, 1/2 - z$.

for the distorted tetrahedral geometry of Ag^+ ions. Each aromatic ring of L1 is planar; the dihedral angles between the pyrimidine ring and two pyridine rings are the same with the value of 13.1°, and the dihedral angle between two pyridine rings is 24.3°. In the 1-D ladder, every ring of the ligands is parallel to the adjacent corresponding ring and this arrangement not only enhances the stability of compound **3** by $\pi-\pi$ stacking (plane-to-plane distance: 3.497 Å) but also minimizes the steric hindrance.

It is noticeable that the 1-D ladder of compound **3** looks like a crab (projected along the *a*-axis direction) with the ligand L1 as the body of the crab and the SCN^- ions as the clamps (Figure 6b). Crystallographic water molecules are connected with the N atoms of SCN^- via hydrogen bonding ($N\cdots O_w = 3.022$ Å). Unlike compounds **1** and **2**, amino groups in **3** do not participate in the formation of hydrogen bonding; the reason for such phenomena is perhaps that the extended SCN^- ions cover the amino groups, so as to prevent the water molecules from approaching the amino groups to form hydrogen bondings.

In compounds **1**−**3**, L1 adopts identical coordination modes, a bis-chelating ligand binding with two silver atoms, while the different arrangements of the L1 ligands in the three complexes result in three distinct structural motifs.

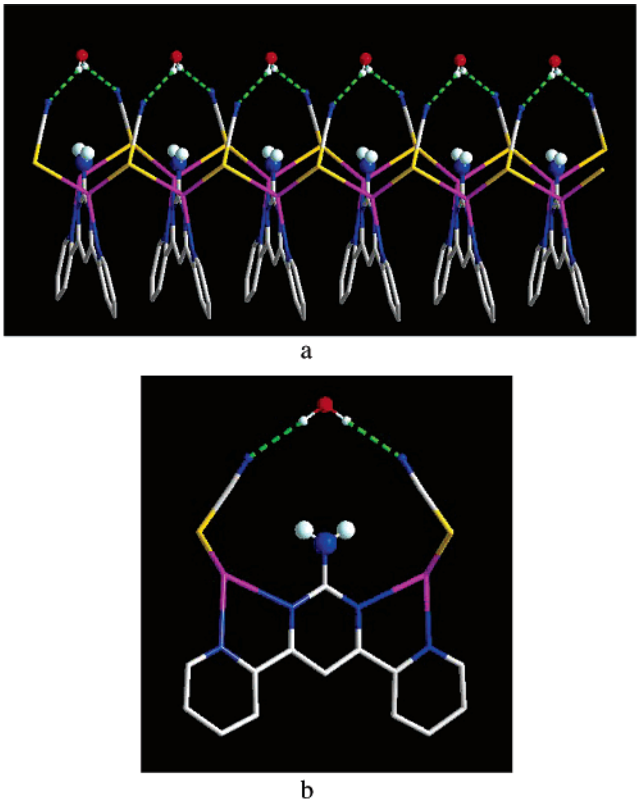

Figure 6. (a) View of a 1-D ladder in **3** along the *a*-axis with water molecules and amino groups in a ball and stick model. Green dashed lines represent the hydrogen-bonding interactions between H_2O and SCN^-. (b) Side view of the 1-D ladder when projected along the *a*-axis. Color code: Ag, pink; N, blue; C, gray; O, red; S, yellow; H, white.

Thus, we have reason to believe that the counteranions might create a tuning effect on the formation of crystal structures. Furthermore, we realized that it was difficult to build a highly dimensioned structure from this bis-chelating ligand with Ag(I), so we intentionally broke one chelating site in L1 and a new ligand L2 with one chelating site and one bridging site was synthesized.

Crystal Structure 4. Although great effort was made, we only obtained a crystal structure from L2 and $AgNO_3$. The reaction of L2 with $AgNO_3$ results in the formation of a two-

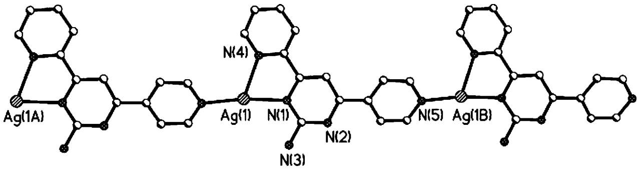

Figure 7. Coordination environments of Ag atoms in **4**. All H atoms are omitted for clarity. Symmetry codes: (A) $-1/2 - x, -1/2 + y, z$; (B) $1/2 + x, 1/2 + y, z$.

dimensional network, and the ligand adopts the coordination mode as we predicted. As shown in Figure 7, each L2 ligand binds two Ag^+ ions via the bridging N atom of 4-pyridyl and the chelating N atoms of pyrimidine ring and 2-pyridine ring. The Ag−N bond lengths range from 2.167 to 2.381 Å, and the N−Ag−N angle ranges from 72.31 to 172.05°. The Ag^+ ion exhibits a distorted trigonal planar geometry. L2 ligands are linked by Ag^+ ions to form a one-dimension chain in head-to-tail fashion where all Ag^+ ions arrange in a line with the Ag···Ag distance of 11.35 Å. Every aromatic ring of L2 is almost planar. The dihedral angles between the central pyrimidine and two terminal pyridine rings are 12.4 and 30.8°, respectively, and the dihedral angle between the two pyridine rings is 35.5°.

In **4**, the three coordinated-N atoms and the Ag center are almost on the same plane, and this kind of orientation allows two Ag^+ ions from adjacent polymers to come close and form a closed-shell metal−metal interaction[19] which is becoming an important element in the construction of fascinating structures recently.[7c,d,18,20] In the structure of **4**, the Ag−Ag interaction with the distance of 3.084 Å appears to be supported by interpolymeric $\pi-\pi$ stacking (plane-to-plane distance: 3.29−3.34 Å). As a result, the Ag−Ag interaction joins the would-be isolated 1-D chains into a 2-D sheet in a crossed way. As shown in Figure 8a, the obtained sheet exhibits a staggered array of interlaced $Ag_8(L2)_4$ rhombic rings which have the dimensions about ca. 19.7 × 11.2 Å (atom-to-atom separation). The result is similar to the structure reported by Klausmeyer,[7c] but the linking fashions of the 1-D chains are different in the two structures. To understand the complicated structure of **4**, the network was simplified in Figure 8b, with the Ag atoms as T-shaped nodes and ligands as well as Ag−Ag interactions as linkers. The crystal packing figure of **4** indicates that the neighboring layers are stacked in ABAB fashion (see Figure S6), and then the size of channel generated by stacking of $Ag_8(L2)_4$ rhombic rings along *c*-axis is rather limited. The crystal water molecules are situated inside the rhombic ring, while the nitrate ions are located between the two adjacent layers (see Figure S7). One crystallographic water molecule connects two adjacent nitrate ions through O_w···O hydrogen bonding to form a linker, which connects two amino groups from every other layer via N−H···O hydrogen bonding. As shown in Figure 9, the hydrogen-bonding interactions assemble the 2-D layers into a 3-D supramolecular architecture.

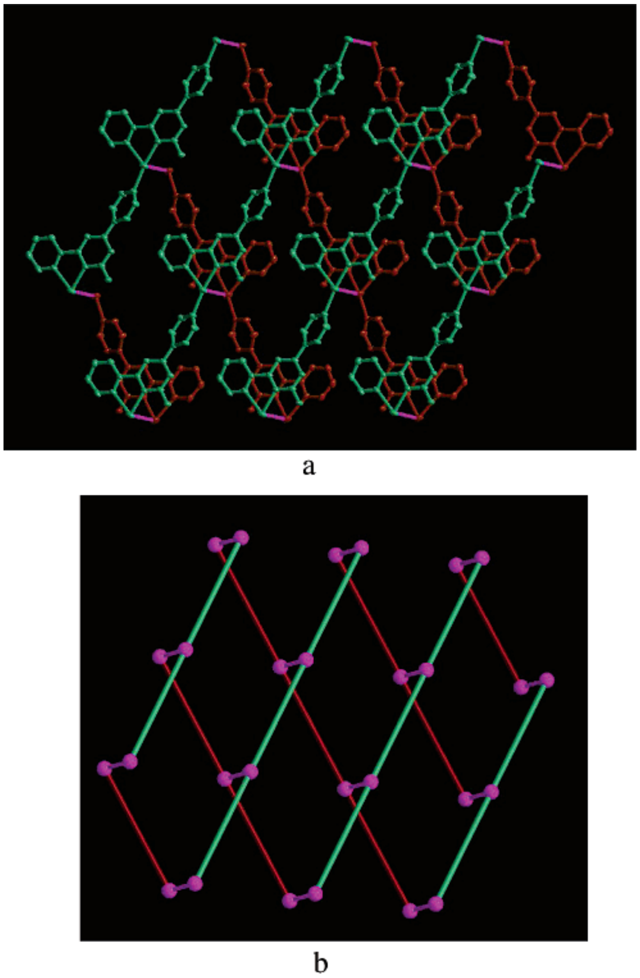

Figure 8. (a) 1-D chains (represented as green polymers) link with 1-D chains (represented as red polymers) through the Ag−Ag argentophilic interactions (represented as pink lines) to form a 2-D layer in **4**. (b) Schematic presentation of the 2-D net described above. The pink balls represent Ag atoms.

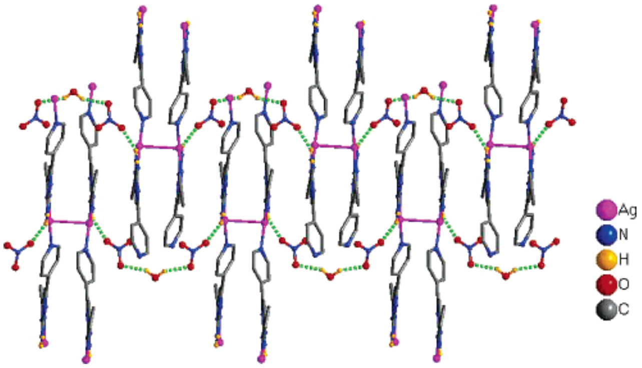

Figure 9. 2-D layers in **4** connected by hydrogen bonding (represented by green dashed lines) to form a 3-D structure. Only parts of the layers are shown for clarity.

Obvious changes were observed from the structures of **1**

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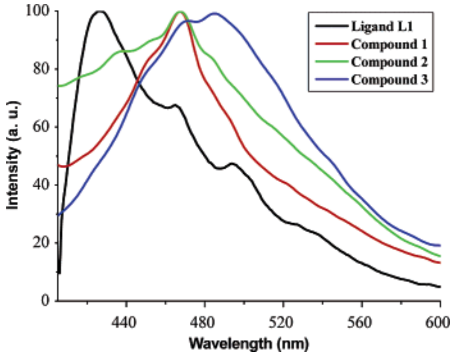

Figure 10. Emission spectra of ligand L1 and compounds **1**−**3** in the solid state at room temperature.

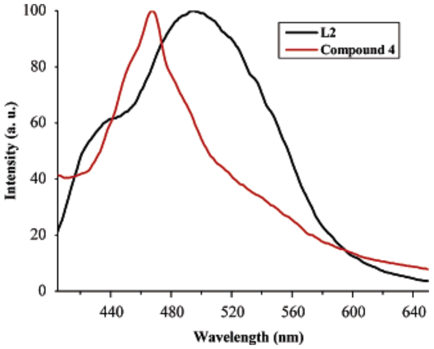

Figure 11. Emission spectra of ligand L2 and compound **4** in the solid state at room temperature.

and **4**, and the dimension of the compounds increase from 0-D (**1**) to 2-D (**4**) assisted by the ligand-supported argentophilic attraction. On the basis of the above results, it is concluded that the position change of one coordinated atom on the ligand leads to the change of the coordination mode and consequently affects the final structure.

Luminescent Properties. Metal complexes are promising luminescent materials. Although the emission spectra of 4,6-bis(2-pyridyl)-2-aminopyrimidine (L1) in solution has been reported,[10] the emission spectra of L1, 4-(2-pyridyl)-6-(4-pyridyl)-2-aminopyrimidine (L2), and their metal complexes in solid state have not yet been investigated. Herein, the luminescent properties of free ligands L1 and L2 as well as compounds **1**−**4** were studied.

The luminescent spectra of L1 and compounds **1**−**3** are shown in Figure 10 (and Figure S1). At ambient temperature, the emission spectrum of L1 shows a main peak at 426 nm with two shoulder peaks at 466 and 495 nm upon excitation at 396 nm, and this emission is probably attributed to the aromatic $\pi^* \rightarrow \pi$ transition of L1. The maximum emission peak of compound **1** is located at 468 nm upon excitation at 367 nm. Compound **2** emits the emission maximum at 467 nm when excited at 358 nm, and compound **3** displays a broad peak with the maximum emission at 485 nm upon excitation at 358 nm. All the emissions of three compounds are in the region of the free ligand L1. The resemblance between compounds **1**−**3** and L1 implies that their luminescent behaviors are L1-based emission. However, compared to that of L1, the maximum emission bands of **1**−**3** are red-shifted. This result is probably due to the coordination of L1 with silver ion. As we known, the intraligand emissions for the same ligand can be effected by its conformations.[21] In the above cases, the conformations of L1 ligands alter to meet with the coordination requirements, and those may result in the changes of the intraligand emissions of L1.[21b] Moreover, similar red shifts were observed in the Ag(I) complexes of multidentated oxadiazole-bridged biphenylamine.[22]

In emission spectrum of L2, one main peak at 495 nm and one shoulder peak at 439 nm upon excitation at 388 nm are observed (Figure 11 and Figure S1). As for ligand L1, the luminescence of L2 may be due to $\pi^* \rightarrow \pi$ electronic transition. Compound **4** exhibits an emission maximum at 468 nm upon excitation at 367 nm with a blue shift of 27 nm in contrast to ligand L2. The resemblance between the emission spectrum of compound **4** and that of free ligand L2 indicates that the luminescence of compound **4** is L2-based emission.

Conclusion

In this work, we have successfully assembled four different metal−organic structures from N,N′-chelating L1 ligands, new L2 ligands, and different silver salts. To the best of our knowledge, the two ligands are for the first time employed in coordination chemistry. Moreover, the structure of compounds **1**−**3** obtained by reacting with L1 is controlled by various counteranions. The effect of ligand isomerism on the structure is also investigated by the introduction of L2. Moreover, the luminescent properties of free ligands L1 and L2 and compounds **1**−**4** have been examined. Studies of 2-aminopyrimidine with aryl substituent groups at the 4 and 6 positions are in progress.

Acknowledgment. The ligands were synthesized with the help of Professor Qun Liu at Northeast Normal University. This work was supported by the Natural Science Foundation of China (NSFC, Grant Nos. 20331010, 90406002, 20671011) and Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP, Grant No. 20030007014).

Supporting Information Available: Crystallographic data in CIF format, excitation spectra, figures of structures, and XPRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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