Inorg. Chem. **2006**, *45*, 5822–5829

Inorganic Chemistry
Article

Synthesis, Crystal Structure, and Characterization of New Tetranuclear Ag(I) Complexes with Triazole Bridges

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Received January 27, 2006

The self-assembly of Ag(I) ions with 3,5-dimethyl-4-amino-1,2,4-triazole (L_1) and 4-salicylideneamino-1,2,4-triazole (L_2) gave two novel complexes, $[Ag_4(\mu_2\text{-}L_1)_6][Ag_4(\mu_2\text{-}L_1)_6(CH_3CN)_2](ClO_4)_8\cdot 2H_2O$ (**1**) and $[Ag_4(\mu_2\text{-}L_2)_6(CH_3CN)_2](AsF_6)_4\cdot 2H_2O$ (**2**), both of which contain tetranuclearic clusters constructed via Ag(I) ions and six N1,N2-bridged triazoles with a Ag_4N_{12} core. When 4-(6-amino-2-pyridyl)-1,2,4-triazole (L_3) was employed, $\{[Ag_4(\mu_2\text{-}L_3)_4(\mu_3\text{-}L_3)_2](CF_3SO_3)_4\cdot H_2O\}_n$ (**3**), $\{[Ag_4(\mu_2\text{-}L_3)_4(\mu_3\text{-}L_3)_2](ClO_4)_4\}_n$ (**4**), and $\{[Ag_4(\mu_2\text{-}L_3)_2(\mu_3\text{-}L_3)_4](PF_6)_4\cdot CH_3CN\cdot 0.75H_2O\}_n$ (**5**) were isolated. **3** and **4** are 1D polymers, while **5** is a 2D polymer. 1D and 2D coordination polymers are constructed via the self-assembly of Ag_4N_{12} cores as secondary building units (SBUs). The connection of these SBUs can be represented as a ladderlike structure for 1D polymers and a 4.8^2 net for 2D polymers. Electrospray ionization mass spectrometry measurements and NMR (^1H and ^{13}C) studies demonstrate that the tetranuclear SBU retains its integrity and the coordination polymers decompose into the tetranuclear Ag_4N_{12} core in solution. **2** exhibits blue emission in the solid state and green emission in solution at ambient temperature. Strong blue fluorescence for complexes **3**–**5** in the solid state can be assigned to the intraligand fluorescent emission.

Introduction

The design, synthesis, and characterization of multinuclear coordination clusters have attracted considerable attention in inorganic chemistry because of their intrinsic aesthetic appeal[1] and their possible use as models for enzyme active sites,[2] precursors for new materials,[3] heterogeneous catalysts,[4] and fluorescent materials.[5] For example, in manganese carboxylate chemistry, the rational synthesis of cluster complex $[Mn_3]$,[6a] $[Mn_8]$,[6b] $[Mn_9]$,[6c] $[Mn_{12}]$,[6d] and $[Mn_{22}]$[6e] single-molecule magnets was reported based on different carboxylate acid ligands. The rationalization for the formation of metal clusters has received much attention in recent years, such as in the reaction of $RuCl_2(PPh_3)_3$ with S^{2-} sources to give tetra-, penta-, and hexanuclear clusters.[7] However, controlling the nuclearities for clusters of a large number of metals is very difficult and requires an ingenious approach to the design of a single ligand. A more practical approach is based on the propensity of metal ions, given the proper coordination environment, to self-assemble into a cluster.

It is well-known that Ag(I) is a favorable and fashionable ion for the construction of coordination clusters because of

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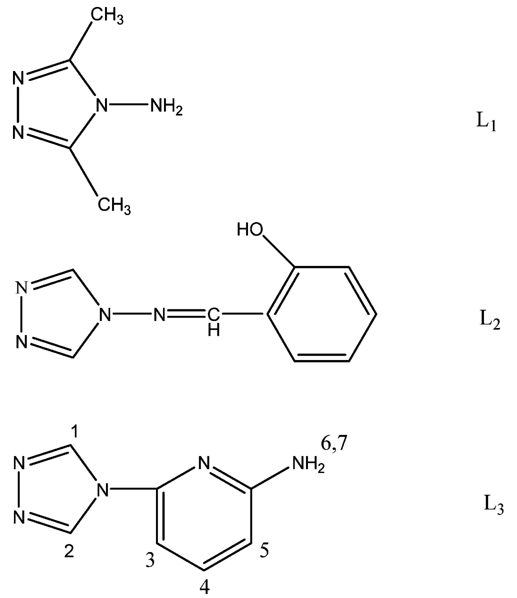
10.1021/ic060155t CCC: $33.50

its coordination diversity and flexibility as well as its positive coordination tendency with various donor atoms, such as O, S, P, I, etc.[8] For example, Fenske et al. reported a series of metal-rich silver(I) chalcogenide clusters.[9a−c] Tetrahedral Ag_4 clusters with dithiolate ligands, such as $[Ag_4(S_2C_2H_4(C_6H_4))_3]^{2-}$ and $[Ag_4(S_2CdC(CN)_2)_4]^{4-}$, and the polyselenide species $[Ag_4(Se_4)_3]^{2-}$, $[Ag_4(Se_4)_4]^{4-}$, and $[Ag_4(Se_4)_{3-x}(Se_5)_x]^{2-}$ have been reported.[9d] Various Ag(I) clusters based on halogen-containing ligands are also documented.[9e,f] 1,2,4-Triazole and, in particular, its derivatives are very interesting as bridging ligands,[10] which have the potential possibility of coordinating with metal ions to fulfill the coordination requirements of clusters. In previous reports, the self-assembly of 1,2,4-triazole derivatives and Ag(I) ions gave dinuclear $Ag_2(admtrz)_2(CF_3CO_2)_2$ (admtrz = 4-amino-3,5-dimethyl-1,2,4-triazole),[11a] 2D and 3D coordination polymers with various channels,[11b] a uninodal $4.^{9}6^{6}$ net based on $[Ag_5(3,5\text{-}Ph_2\text{-}trz)_6]^-$ clusters (3,5-Ph_2-trz = 3,5-diphenyl-1,2,4-triazole),[11c] and a 3D polymeric cation constructed via $\{Ag_3[tz_2(CH_2)]_4\}^{6+}$ units [$tz_2(CH_2)$ = bis(1,2,4-triazol-1-yl)methane].[11d] For multinuclear coordination compounds, no relevant studies and information concerning molecular self-assemblies of tetranuclear Ag(I) clusters based on triazole ligands as secondary building units (SBUs) have been presented, and we are hopeful that this work will fill the gap.

On the other hand, metal−organic frameworks (MOFs) are of great current interest because of the possibilities for various applications and intriguing topological terms. Of the structural types commonly found in MOFs, the majority are based on three-, four-, and six-connected topologies in which d- and f-block ions act as nodes.[12] Compared with d- or f-block ions, metal-cluster-based nodes generally have larger sizes and more coordination sites but smaller steric hindrance when coordinated by organic ligands. Recently, metal clusters substituted for single metal atoms have been used as nodes or as SBUs for MOFs.[13] For example, this happens in several polymeric Cu(II) complexes in which the trinuclear triangular metal clusters as SBUs constructed 1D and 2D coordination polymers.[14] In our previous studies, a series of MOFs from one to three dimensions were formed via triazole-bridged trinuclear Cd(II) clusters as SBUs.[15]

Chart 1



As part of an ongoing research project dealing with the coordination chemistry of triazole ligands,[15,16] herein we report the self-assembly of Ag(I) ions with 3,5-dimethyl-4-amino-1,2,4-triazole (L_1), 4-salicylideneamino-1,2,4-triazole (L_2), and 4-(6-amino-2-pyridyl)-1,2,4-triazole (L_3), as shown in Chart 1. Five novel complexes, $[Ag_4(\mu_2\text{-}L_1)_6][Ag_4(\mu_2\text{-}L_1)_6(CH_3CN)_2](ClO_4)_8\cdot 2H_2O$ (**1**), $[Ag_4(\mu_2\text{-}L_2)_6(CH_3CN)_2](AsF_6)_4\cdot 2H_2O$ (**2**), $\{[Ag_4(\mu_2\text{-}L_3)_4(\mu_3\text{-}L_3)_2](CF_3SO_3)_4\cdot H_2O\}_n$ (**3**), $\{[Ag_4(\mu_2\text{-}L_3)_4(\mu_3\text{-}L_3)_2](ClO_4)_4\}_n$ (**4**), and $\{[Ag_4(\mu_2\text{-}L_3)_2(\mu_3\text{-}L_3)_4](PF_6)_4\cdot CH_3CN\cdot 0.75H_2O\}_n$ (**5**), were synthesized and characterized via X-ray single-crystal diffraction, elemental analyses, photoluminescence measurements, mass spectrometry (MS), and NMR studies.

Experiment Section

Materials. The triazole ligands L_1−L_3 were synthesized according to literature methods.[15,17] All other reagents and solvents were commercially available and were used without further purification. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The photoluminescence spectrum was measured by a MPF-4 fluorescence spectrophotometer with a Xe arc lamp as the light source. The NMR spectra were recorded on a 300-MHz Inova spectrometer with a 5-mm switchable probehead. Electrospray ionization (ESI) MS spectra were obtained with a Sciex Qstar Pulsar and the ESI source.

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Table 1. Crystal Data and Structure Refinement Information for **1**−**5**

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{26}H_{53}Ag_4Cl_4N_{25}O_{17}$	$C_{29}H_{29}Ag_2As_2F_{12}N_{13}O_4$	$C_{23}H_{22}Ag_2F_6N_{15}O_{6.5}S_2$	$C_{21}H_{21}Ag_2Cl_2N_{15}O_8$	$C_{44}H_{46.5}Ag_4F_{24}N_{31}O_{0.75}P_4$
fw	1561.21	1217.23	1006.42	898.16	2032.98
temp (K)	293(2)	293(2)	293(2)	293(2)	293(2)
cryst syst	triclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a (Å)	12.1358(14)	10.916(5)	10.385(5)	10.5018(12)	19.313(3)
b (Å)	14.3945(17)	14.096(7)	11.587(6)	11.7713(12)	12.0597(19)
c (Å)	16.6517(19)	14.855(7)	16.145(8)	13.8021(14)	29.931(5)
α (deg)	86.7310(10)	73.113(6)	71.728(5)	74.0660(10)	90
β (deg)	89.616(2)	68.652(6)	78.920(6)	82.3620(10)	96.289(3)
γ (deg)	70.2940(10)	75.128(6)	70.204(6)	67.7500(10)	90
V (Å^3)	2733.8(5)	2007.7(17)	1727.8(15)	1517.7(3)	6929.3(18)
Z	2	2	2	2	4
$F(000)$	1552	1188	994	888	3990
ρ (Mg/m^3)	1.897	2.013	1.934	1.963	1.949
abs coeff (mm^{-1})	1.692	2.721	1.352	1.540	1.332
data/restraints/params	9558/98/734	7001/252/699	6004/3/496	5291/64/514	12239/1/980
GOF	1.080	1.025	1.078	1.070	0.876
R1[a] $[I = 2\sigma(I)]$	0.0377	0.0578	0.0405	0.0396	0.0563
wR2[a] (all data)	0.1102	0.2004	0.1193	0.1149	0.1721

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

Preparations. **$[Ag_4(\mu_2\text{-}L_1)_6][Ag_4(\mu_2\text{-}L_1)_6(CH_3CN)_2](ClO_4)_8\cdot 2H_2O$ (1).** A solution of $AgClO_4$ (0.20 mmol) in acetonitrile (10 mL) was slowly added into a H_2O solution (10 mL) of L_1 (0.4 mmol). The mixture was stirred for about 30 min and filtered. Colorless crystals suitable for X-ray analyses were obtained by slow evaporation of the filtrate in the dark, and the yield was 72% [based on Ag(I) salts]. Elem anal. Calcd for **1**: C, 20.00; H, 3.42; N, 22.43. Found: C, 19.67; H, 3.59; N, 22.88. ^{1}H NMR (DMSO-d_6, ppm): 6.03 (s, 2H), 2.49 (s, 6H). ^{13}C NMR (DMSO-d_6, ppm): 154.9 (2C), 10.9 (2C).

$[Ag_4(\mu_2\text{-}L_2)_6(CH_3CN)_2](AsF_6)_4\cdot 2H_2O$ (2). A solution of $AgAsF_6$ (0.20 mmol) in acetonitrile (10 mL) was slowly added into a H_2O solution (10 mL) of L_2 (0.4 mmol). The mixture was stirred for about 30 min and filtered. Colorless crystals suitable for X-ray analyses were obtained by slow evaporation of the filtrate in the dark, and the yield was 65% [based on Ag(I) salts]. Elem anal. Calcd for **2**: C, 28.62; H, 2.40; N, 14.96. Found: C, 28.35; H, 2.27; N, 14.56. ^{1}H NMR (DMSO-d_6, ppm): 8.91 (s, 1H), 8.79 (s, 2H), 7.56−7.51 (d, 1H), 7.35−7.32 (t, 1H), 6.90−6.87 (m, 2H), 3.52 (s, 1H). ^{13}C NMR (DMSO-d_6, ppm): 159.1 (1C), 157.2 (2C), 140.7 (1C), 135.0 (1C), 128.3 (1C), 120.4 (1C), 118.6 (1C), 117.5 (1C).

$\{[Ag_4(\mu_2\text{-}L_3)_4(\mu_3\text{-}L_3)_2](CF_3SO_3)_4\cdot H_2O\}_n$ (3). A solution of $AgCF_3SO_3$ (0.20 mmol) in acetonitrile (10 mL) was slowly added into a H_2O solution (10 mL) of L_3 (0.4 mmol). The mixture was stirred for about 30 min and filtered. Colorless crystals suitable for X-ray analyses were obtained by slow evaporation of the filtrate in the dark, and the yield was 68% [based on Ag(I) salts]. Elem anal. Calcd for **3**: C, 27.45; H, 2.20; N, 20.88. Found: C, 27.89; H, 2.58; N, 20.46. ^{1}H NMR (DMSO-d_6, ppm): 9.25 (s, 2H), 7.61−7.66 (t, 1H), 6.94−6.96 (d, 1H), 6.52−6.54 (d, 3H). ^{13}C NMR (DMSO-d_6, ppm): 160.2 (2C), 145.3 (1C), 141.7 (1C), 113.6 (1C), 108.8 (1C), 101.1 (1C).

$\{[Ag_4(\mu_2\text{-}L_3)_4(\mu_3\text{-}L_3)_2](ClO_4)_4\}_n$ (4). A solution of $AgClO_4$ (0.20 mmol) in acetonitrile (10 mL) was slowly added into a H_2O solution (10 mL) of L_3 (0.4 mmol). The mixture was stirred for about 30 min and filtered. Colorless crystals suitable for X-ray analyses were obtained by slow evaporation of the filtrate in the dark, and the yield was 56% [based on Ag(I) salts]. Elem anal. Calcd for **4**: C, 28.08; H, 2.36; N, 23.39. Found: C, 28.43; H, 2.86; N, 23.75. ^{1}H NMR (DMSO-d_6, ppm): 9.23 (s, 2H), 7.64−7.58 (t, 1H), 6.90−6.93 (d, 1H), 6.49−6.51 (d, 3H). ^{13}C NMR (DMSO-d_6, ppm): 160.2 (2C), 145.3 (1C), 141.5 (1C), 113.6 (1C), 108.9 (1C), 101.1 (1C).

$\{[Ag_4(\mu_2\text{-}L_3)_2(\mu_3\text{-}L_3)_4](PF_6)_4\cdot CH_3CN\cdot 0.75H_2O\}_n$ (5). A solution of $AgPF_6$ (0.20 mmol) in acetonitrile (10 mL) was slowly added into a H_2O solution (10 mL) of L_3 (0.4 mmol). The mixture was stirred for about 30 min and filtered. Colorless crystals suitable for X-ray analyses were obtained by slow evaporation of the filtrate in the dark, and the yield was 45% [based on Ag(I) salts]. Elem anal. Calcd for **5**: C, 25.99; H, 2.31; N, 21.36. Found: C, 26.25; H, 2.71; N, 21.85. ^{1}H NMR (DMSO-d_6, ppm): 9.23 (s, 2H), 7.63−7.58 (t, 1H), 6.90−6.93 (d, 1H), 6.48−6.51 (d, 3H). ^{13}C NMR (DMSO-d_6, ppm): 159.9 (2C), 145.2 (1C), 141.7 (1C), 119.3 (1C), 109.6 (1C), 102.9 (1C).

Crystal Structure Determination. Diffraction intensities for five complexes were collected on a computer-controlled Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation with a radiation wavelength of 0.710 71 Å by using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares techniques using the *SHELXS-97* and *SHELXL-97* programs.[18] Anisotropic thermal parameters were assigned to all non-H atoms. The organic H atoms were generated geometrically; the H atoms of the H_2O molecules were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom-scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data and selected bond lengths and angles for **1**−**5** are listed in Tables 1 and S1 (in the Supporting Information), respectively.

Results and Discussion

Preparations. To start, a 2D polymer, **5**, was isolated unexpectedly. As far as we know, N-containing ligands were rarely used to synthesize Ag(I) clusters and tetranuclear Ag(I) clusters based on triazole ligands have never been reported. This led to our exploration of extensive research on the

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reaction of L_3 with other Ag salts. $AgCF_3SO_3$ and $AgClO_4$ were employed to yield **3** and **4**. Crystal analyses indicate that although their topologies and the geometries of the networks have changed, tetranuclear Ag_4N_{12} cores as SBUs are identical with that of **5**. L_2 was adopted to react with $AgAsF_6$ to yield **2** because L_2 has large N4-bridged aromatic substituents in the triazole rings similar to those of L_3 and the coordinating competence of $AgAsF_6$ approximates to $AgPF_6$. Structural analyses illustrate that **2** is a discrete tetranuclear compound because of the hydroxyl group's failure to coordinate with Ag(I) centers and to extend the Ag_4N_{12} core to high dimension like in **3**−**5**.

In **4**, parts of the amino groups bridged Ag atoms and a 1D ladderlike polymer occurs readily. Whether other triazolatosilver complexes based on tetranuclear Ag_4N_{12} cores can be prepared if none of the amino groups in the ligands coordinates with metal centers is questionable. L_1 was applied to react with $AgClO_4$ because of the comparatively larger spacial hindrance of the amino group in L_1 as compared to L_3, which was most unlikely to join metal ions. Crystallography determination explains that **1** gave two kinds of discrete tetranuclear Ag_4 cores: one contains two coordinated CH_3CN molecules and the other does not contain any.

It is noted that the self-assembly of L_1 with $AgClO_4$ and $AgCF_3CO_2$ yielded the tetranuclear complex **1** and a dinuclear complex $Ag_2(admtrz)_2(CF_3CO_2)_2$,[11a] respectively. Significant structural changes may be due to different metal-to-ligand molar ratios and solvents as well as the anions used in the system. On the other hand, the existence of a Ag−Ag interaction is only found in complex **1** because L_2 and L_3 have larger substituents at the 4 positions of the triazole rings in comparison with L_1, which makes the Ag···Ag separation longer. So, complexes **2**−**5** have no Ag−Ag interactions in the tetranuclear units. The formation of tetranuclear units is also different because of the the stereo effect between two dinuclear units.

From the viewpoint of structures, tetranuclear complexes can be considered as two dinuclear units, which are further connected via two N1,N2-bridged triazoles. If the supramolecular interactions, coordination, and stereo effect of the anions make the dinuclear units stable, it is hard to obtain tetranuclear units. The formation of tetranuclear units is also different because of the stereo effect between two dinuclear units. In conclusion, several factors such as the ligand topicity (i.e., the number and position of the coordinating groups),[19a] solvents,[19b] counterions,[19c] and ligand-to-metal ratio[19d] play an important role in the self-assembly process.

Structural Studies. The self-assembly of Ag(I) ions and L_1 gave two kinds of tetranuclear Ag(I) clusters in **1**. The slight difference between them is that two CH_3CN molecules coordinate with one kind of tetranuclear cluster and the other does not. A structural representation of one kind of cluster with an atomic labeling scheme is shown in Figure 1. Each L_1 ligand acts as an N1,N2-bridged motif, and six L_1 ligands link Ag(I) centers through alternating single and double bridges to form Ag_4N_{12} cores. The Ag−N bond distances are in the range of 2.184−2.309 Å. It is noted that the aromatic rings between double-bridged L_1 ligands are parallel and the distances between the planes of two rings are in the range of 3.588−3.639 Å, indicating significant $\pi-\pi$ stacking interactions. Four Ag(I) atoms in a Ag_4N_{12} core are coplanar. The metal−metal distances in the core are 3.322 and 3.271 Å, respectively, indicating weak Ag−Ag interactions.

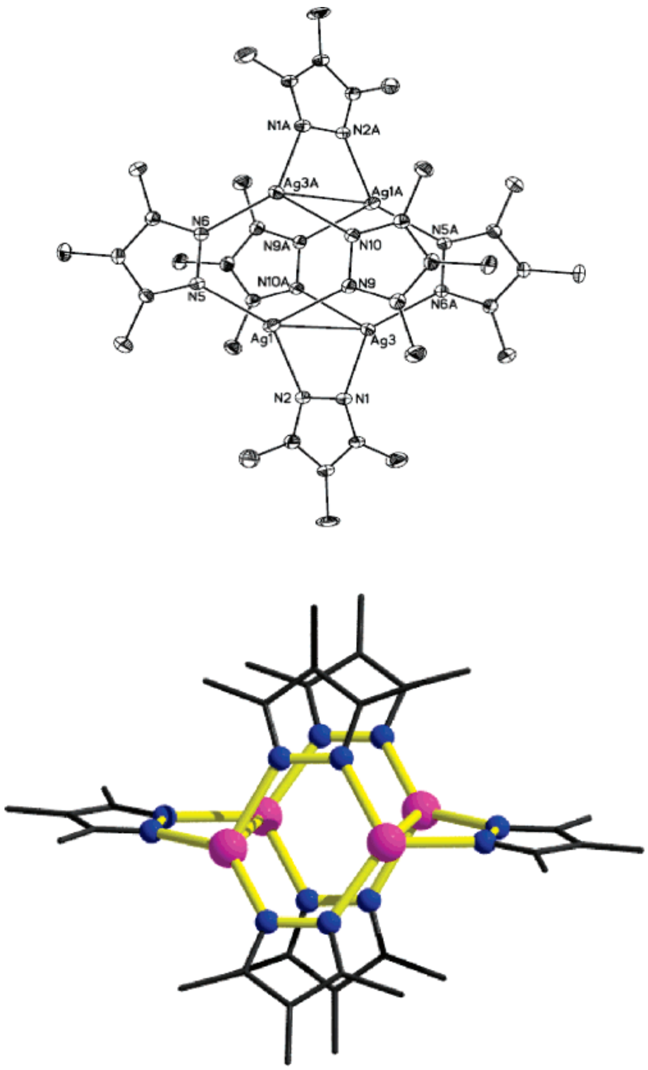

Figure 1. ORTEP drawing of one kind of tetranuclear Ag cluster with an atomic labeling system (up) and the Ag_4N_{12} core (down) in **1**. H atoms are omitted for clarity. Color code: purple, Ag; blue, N; yellow line, bond around the core.

When L_2 was employed, another tetranuclear Ag(I) cluster of complex **2** with a similar Ag_4N_{12} core was isolated. As shown in Figure 2, the core contains two three-coordinated and two four-coordinated metal centers. Six L_2 ligands link Ag(I) through an N1,N2-bridged motif, and the Ag−N distances are in the range of 2.214−2.323 Å. The aromatic rings between double-bridged L_2 ligands are parallel and the distances between the planes of two rings are in the range of 3.416−3.484 Å. The Ag···Ag separations in the SBU are from 3.776 to 5.923 Å, which are over the summed van der Waals radii of two Ag(I) atoms (3.44 Å).[20] The slight

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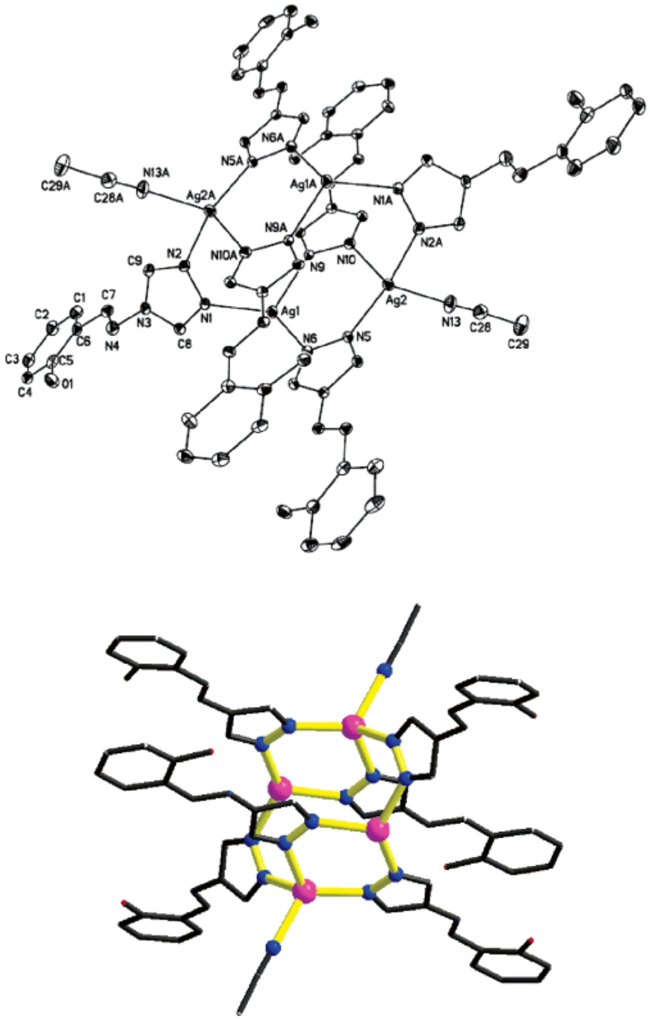

Figure 2. ORTEP drawing with an atomic labeling system (up) and the Ag_4N_{12} core of **2** (down). H atoms are omitted for clarity. Color code: purple, Ag; blue, N; red, O; yellow line, bond around the core.

structural difference of Ag_4N_{12} cores between **1** and **2** are due to different substituents of the triazole ligands. **1** and **2** imply that N1,N2-bridged triazoles are good choices to construct a tetranuclear Ag(I) cluster.

The self-assembly of L_3 with Ag(I) ions resulted in the formation of 1D and 2D MOFs **3**−**5** based on tetranuclear SBUs (Figure 3). The SBU is constructed via six N1,N2-bridged L_3 ligands and four Ag(I) ions, which have a Ag_4N_{12} core similar to those in complexes **1** and **2**. The Ag$\cdots$Ag separations in the tetranuclear unit are over the summed van der Waals radii of two Ag(I) atoms. The amino groups in L_3 can coordinate with Ag(I) ions. Therefore, two L_3 ligands adopt a μ_3-bridged motif in **3** and **4**, while four L_3 ligands adopt a μ_3-bridged motif in **5**. **3** and **4** are 1D coordination polymers, both of which have similar coordination networks. As shown in Figure 4, each tetranuclear SBU is further connected by double bridges through Ag−N bonds to form a 1D ladderlike chain. In **5**, each tetranuclear SBU is linked by four μ_3-bridged L_3 to four neighbor SBUs and a unique 2D coordination layer with a 4.8^2 net is formed (Figure 5). In complexes **3**−**5**, the Ag−N distances between the N atoms of the amino groups and Ag(I) ions are significantly longer than those between the N atoms in the triazole rings and Ag(I) ions, indicating relatively weak coordination bonds.

MS Spectra and ^{1}H NMR Studies. Importantly, ESI MS measurements demonstrate that the Ag_4N_{12} core retains its integrity and the coordination polymers decompose into the tetranuclear SBUs in solution. In the MS spectrum of **2** (Figure S2 in the Supporting Information), the observed peaks in the positive MS spectrum are *m*/*z* 1747.12 and 1936.91, corresponding to $[Ag_4(L_2)_4(L_2{-}H)_2(AsF_6)]^+$ and $[Ag_4(L_2)_5(L_2{-}H)(AsF_6)_2]^+$, respectively. The spectrum also shows the peaks associated with $[Ag_4(L_2)(L_2{-}H)_5(CH_3CN)_2]^-$ and $[Ag_4(L_2)_2(L_2{-}H)_4(CH_3CN)_2(AsF_6)]^-$ at *m*/*z* 1637.49 and 1827.05, respectively. The peaks of the Ag_4N_{12} core have the appropriate isotopic distribution. The tetranuclear SBUs in coordination polymers are intact in solution; that is, they do not form simply upon crystallization. This is demonstrated by ESI MS of a DMSO solution of **5**. The spectrum, acquired in the cation mode, shows clearly the signal for $[Ag_4(L_3)_6(PF_6)_3]^+$, with an isotopic distribution matching perfectly with the calculated one (Figure S3 in the Supporting Information).

The free ligand L_3 shows the aromatic protons 9.09 (1, 2), 7.61−7.56 (4), 6.88−6.86 (5), and 6.47−6.45 ppm (3, 6, 7) in a DMSO-d_6 solution. The resonance (single) for protons 1,2-H of **4** and **5**, which are adjacent to the metal binding sites, is shifted downfield by $\Delta\delta$ 0.14−9.23 ppm because of the inductive effect of the metal.[21] It is noted that the resonance of the amino group in complexes is not shifted, which implies that the amino groups are uncoordinated with Ag(I) ions in solution. X-ray diffraction reveals that **4** and **5** are coordination polymers constructed via tetranuclear SBU linked through relatively weak $Ag{-}N_{amino}$ bonds and L_3 ligands exist as μ_2- and μ_3-bridged motifs. In solution, ^{1}H NMR studies illustrate that the coordination polymers decompose into tetranuclear SBU because of the breaking of the relatively weak $Ag{-}N_{amino}$ bonds, which is consistent with the MS results.

Solution and Solid-State Emission Spectroscopy. Inorganic−organic hybrid coordination polymers have been investigated for fluorescent properties and for potential applications as luminescent materials, such as light-emitting diodes.[22] Owing to their ability to affect the emission wavelength and strength of organic materials, the syntheses of inorganic−organic coordination polymers by the judicious choice of conjugated organic spacers and transition-metal centers can be an efficient method for obtaining new types of photoluminescent materials, especially for d^{10} or $d^{10}{-}d^{10}$ systems.[16a,23] In the present work, the luminescent properties

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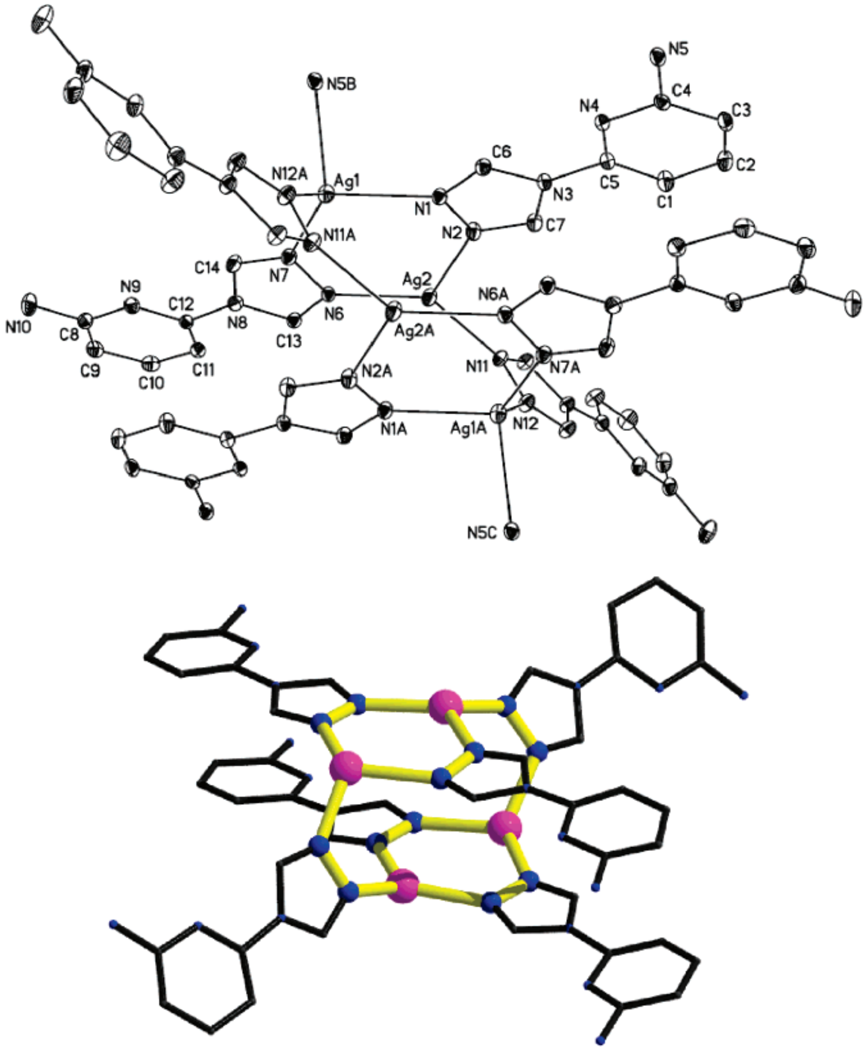

Figure 3. Tetranuclear Ag_4 coordination unit of **3** (up) and the tetranuclear SBU in **3**−**5** (down). H atoms are omitted for clarity. Color code: purple, Ag; blue, N; yellow line, bond around the Ag_4 SBU.

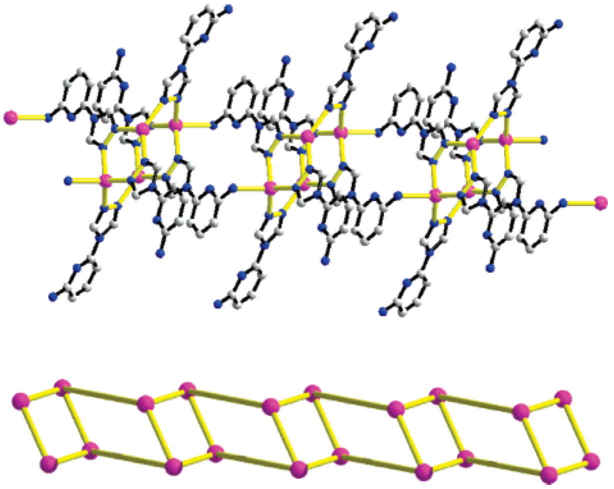

Figure 4. 1D coordination polymeric cations of **3** and **4** (up) and schematic drawing of the 1D chain (down). H atoms are omitted for clarity. Color code: purple, Ag; blue, N; gray, C; yellow line, bond around the tetranuclear Ag_4 core; black line, other bond.

of L_2 and L_3 and the complexes **2**−**5** based on them in the solid state and in a H_2O solution have been investigated.

At ambient temperature, **2** in H_2O is luminescent and shows a broad emission maximum at 514 nm when the excitation is at 328 nm. However, the free ligand L_2 is not emissive in H_2O at ambient temperature. The emission may be derived from metal-to-ligand charge transfer (MLCT). In the solid state, both L_2 and **2** exhibit strong blue emissions with $\lambda_{max} = 435$ nm with excitation at 396 and 379 nm, respectively. Compared with the fluorescent emission of **2** in solution, the emissions are blue-shifted and narrow in the solid state (Figure 6). ESI MS measurement indicates that **2** does not dissociate in acetonitrile. Thus, the large difference of luminescent spectra in the solid state and in solution is unlikely because of decomposition of **2** in solution and may be attributable to different emission processes.

Strong blue light fluorescence for complexes **3**−**5** in the solid state is visible in daylight by irradiation of UV light. The emission spectra are shown in Figure 7, and all of the complexes are excited at 380 ± 2 nm. The main emission bands of the complexes are located at the same position, exhibiting strong blue fluorescence ($\lambda_{max} = 436$ nm) with a slightly different band shape. All complexes also exhibit some low-energy emission bands. The different band shapes in the luminescent emissions might be due to the different structural topologies. The emissions of **3**−**5** are neither MLCT nor ligand-to-metal charge transfer in nature and

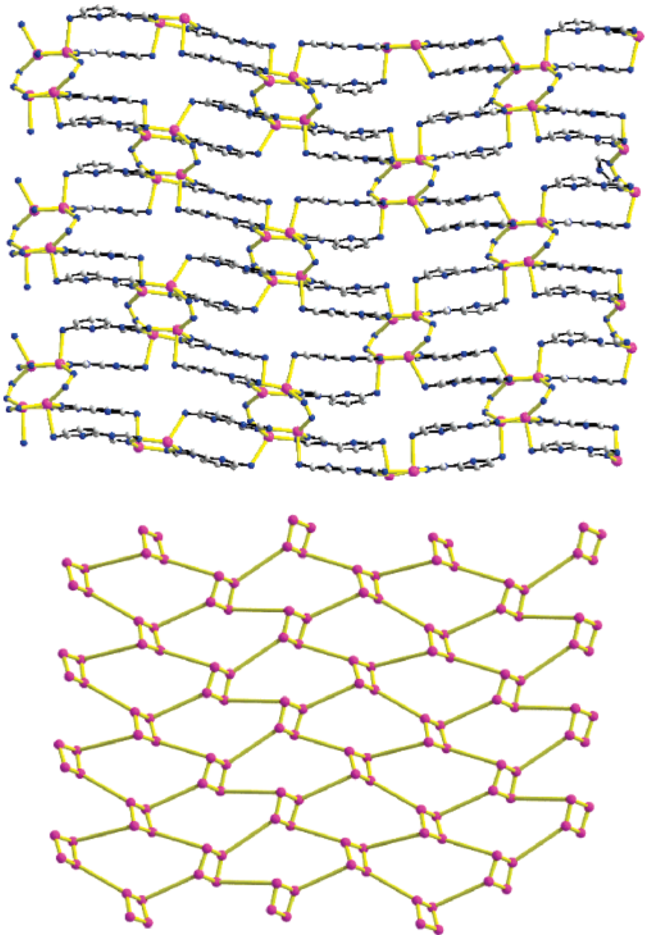

Figure 5. 2D coordination polymer of **5** (up) and schematic drawing of a 2D layer with a 4.8^2 net (down). H atoms are omitted for clarity. Color code: purple, Ag; blue, N; gray, C; yellow line, bond around the Ag_4; black line, other bond. Uncoordinated atoms of μ_2-L_3 are omitted.

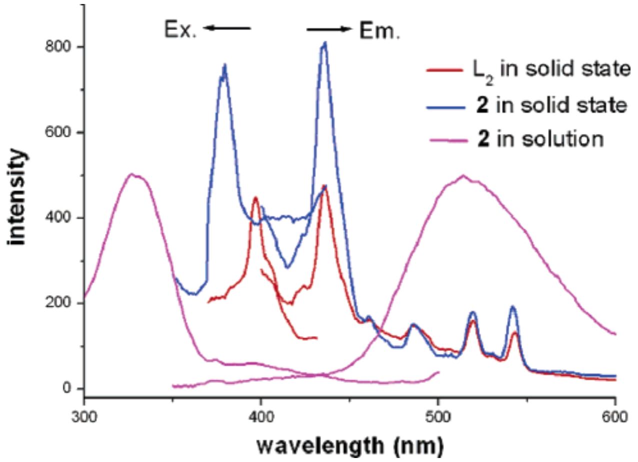

Figure 6. Excitation and emission spectra of L_2 and **2** in the solid state and in a H_2O solution at room temperature (1×10^{-4} mol/L for **2**).

probably are assigned to the intraligand fluorescent emission because very similar emissions are also observed for the free L_3 ligand. The enhancement of intraligand fluorescence in **3**−**5** is probably due to the coordination of L_3 to Ag(I) increasing the conformational rigidity of the ligand, thereby reducing the nonradiative decay of the intraligand (π−π*) excited state.[10] As shown in Figure 8, **3**−**5** exhibit broad blue fluorescence in H_2O. The fluorescent emissions are probably assigned to the intraligand fluorescent emission because similar behaviors are also observed for the free L_3 ligand in a H_2O solution. The coordination of the complexes leads to slight red shifts for the emissions. Compared with the fluorescent emissions of **3**−**5** in solution, the excitations and emissions are red-shifted and narrow, which are attributable to intermolecular interactions in the solid state, most likely π−π stacking interactions.

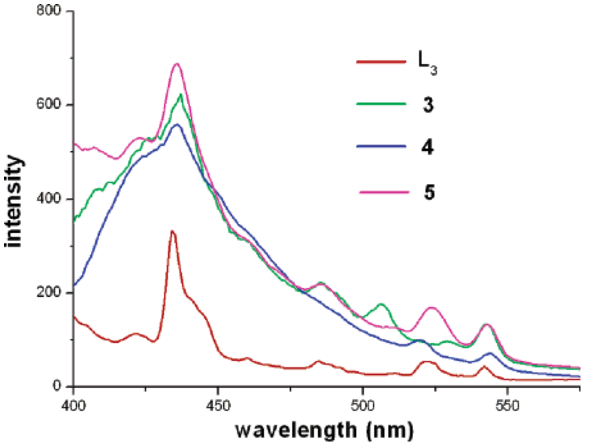

Figure 7. Emission spectra in the solid state at room temperature. All compounds are excited at 380 ± 2 nm.

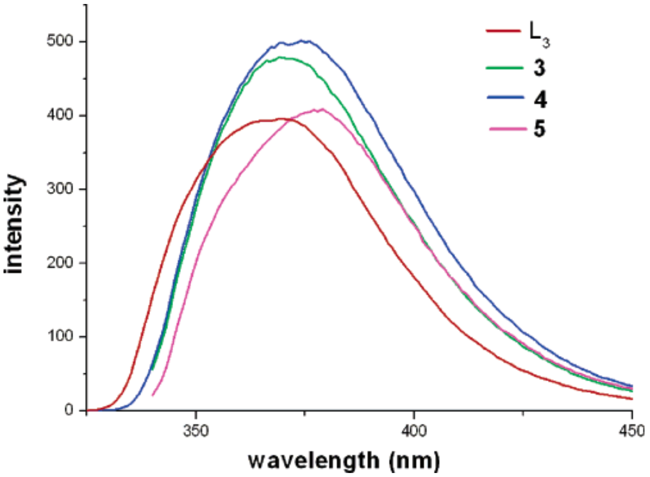

Figure 8. Emission spectra in an aqueous solution at room temperature (1×10^{-4} mol/L for L_3 and **3**−**5**). All compounds are excited at 334 ± 2 nm.

Conclusion

A series of novel complexes based on tetranuclear triazolatosilver(I) units were synthesized and characterized structurally. **1** and **2** contain discrete tetranuclear Ag(I) clusters based on different triazole ligands. When L_3 was employed, coordination polymers **3**−**5** were isolated. **3** and **4** are 1D coordination polymers, while **5** is a 2D coordination polymer, all of which are formed from the self-assembly of tetranuclear SBUs to construct 1D ladderlike structures and a 4.8^2 2D net. The existence of a tetranuclear Ag(I) cluster in solution is supported by the results of MS and ^{1}H NMR studies. **2**−**5** exhibit strong fluorescent emission bands in the solid state and in an aqueous solution at ambient temperature, which renders them with the potential use as fluorescent materials.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grants 20425103 and 90501002), the NSF of Tianjin (Grant 06YFJZJC009000), and the State Key Project of Fundamental Research of MOST (Grant 2005CCA01200), People's Republic of China.

Supporting Information Available: Crystallographic data in CIF format, Table S1, and additional Figures S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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