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3D Coordination Networks Based on Supramolecular Chains as Building Units: Synthesis and Crystal Structures of Two Silver(I) Pyridyldiethynides

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Two silver(I) pyridyldiethynides, [$Ag_2(3,5\text{-}C_2PyC_2) \cdot 4CF_3CO_2Ag \cdot 4H_2O$] (**A**) and [$Ag_2(3,5\text{-}C_2PyC_2) \cdot 3AgNO_3 \cdot H_2O$] (**B**), were synthesized by reactions of 3,5-diethynylpyridine with silver trifluoroacetate and silver nitrate in high yield, respectively. X-ray crystallographic studies revealed that in **A** pyridyldiethynide groups connect Ag_{11} cluster units to generate 1D supramolecular chains as bridging ligands, where each ethynide group interacts with four silver atoms. These supramolecular chains bearing pyridyl groups are linked by silver ions to form wavelike layers, which are further connected by trifluoroacetate ligands to afford a 3D coordination network. However, **B** exhibits a different structural feature, where two ethynide groups in one pyridyldiethynide ligand coordinate to three and four silver atoms, respectively. These silver ethynide cluster units are linked through silver-ethynide and argentophilic interactions, leading to a double silver chain by sharing silver atoms in these units. In **B**, the silver double chains are further connected by bridging pyridyldiethynide groups to generate 2D networks, which interact through the Ag−N coordination bonds between silver atoms and pyridyl groups in the adjacent layers to generate a 3D coordination network. In these two compounds, trifluoroacetate and nitrate groups exhibit different bonding modes, indicating that the counterion is an important factor influencing the structures of supramolecular chains and coordination networks.

Introduction

In the past few decades, tremendous progress has been made in supramolecular chemistry. A large number of beautiful and functional supramolecular architectures have been constructed, starting with well-defined building blocks via self-assembly processes, among which most are generated with single metal ions and ligands with predesigned geometries as building units.[1–3] By using di- or polymetal complexes as building block precursors, it is demonstrated that assembled supramolecules may possess some novel properties and the structures are more easily controlled because of metal−metal interactions and variable binding modes in these units.[4,5] In the past decade, Mak and his co-workers have systematically studied the bonding and structures of novel silver(I) clusters of acetylenediide (C_2^{2-}),[6] 1,3-butadiynediide (C_4^{2-}),[7,8] alkylethynide,[8,9] phenyleneethynide,[8–10] and thiopheneethynide.[11] Crystallographic studies revealed that each ethynide moiety of an alkyl- or

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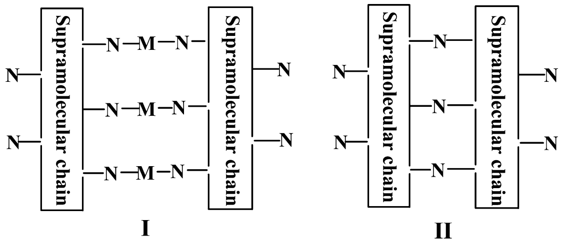
arylethynide group usually interacted with three, four, or five silver atoms, but the ligation numbers and structures of silver ethynide clusters were influenced by many factors.[6] These silver ethynide clusters are potential building blocks to assemble supramolecular complexes through ethynide−silver interaction, $\pi-\pi$ stacking, and argentophilicity or by introduction of bi- or polydental ligands containing nitrogen or oxygen atoms as linkers.[6,12] Recently, Mak reported a class of silver(I) phenylenediethynides, in which some novel silver chains were observed, and their structures were dependent upon the geometries of phenylenediethynides.[8,13] Because the nitrogen atom in the pyridyl group has a strong ability to coordinate to the silver ion, we wonder if when phenylenediethynide ligands are substituted by pyridyldiethynide groups, these silver chain complexes can be utilized as novel building units (super metalloligands) to construct new coordination networks.[14–16] Following this idea, two possible routes to new networks are proposed as follows (Scheme 1): the supramolecular chains bearing pyridyl groups are linked by single silver ions through the N−Ag−N bonds (mode I) and the nitrogen atoms in the pyridyl groups directly coordinate to the silver atoms in the silver chains (mode II). Herein the synthesis and crystal structures of two silver(I) pyridyldiethynides, namely, $[Ag_2(3,5\text{-}C_2PyC_2)\cdot 4CF_3CO_2Ag\cdot 4H_2O]$ (**A**) and $[Ag_2(3,5\text{-}C_2PyC_2)\cdot 3AgNO_3\cdot H_2O]$ (**B**), are reported, and the effect of counterions on the structures of coordination networks is discussed based upon the structures of two compounds.

Scheme 1. Two possible routes to coordination networks using supramolecular chains as building units.



Experimental Section

Materials. 3,5-Diethynylpyridine was prepared according to the literature method.[17] $AgNO_3$, CF_3CO_2Ag, and NH_4BF_4 were purchased from commercial sources and used without further purification.

Caution! *Silver ethynide complexes are potentially explosive and should be handled in small amounts with extreme care.*

$[Ag_2(3,5\text{-}C_2PyC_2)\cdot 4CF_3CO_2Ag\cdot 4H_2O]$ (A). To a 5 mL vial containing solid 3,5-diethynylpyridine (0.0030 g, 0.024 mmol) were added a few drops of distilled water and excess solid silver nitrate (0.0300 g, 0.177 mmol). This mixture was stirred for 20 min to generate an off-white precipitate. After washing with distilled water two times to remove the excess $AgNO_3$ and nitric acid released from the reaction and exchange of the anion with ammonium tetrafluoroborate (0.10 g, 0.954 mmol), a pale-yellow solid was obtained. This solid was dissolved in a concentrated solution of silver trifluoroacetate (about 1 mL of distilled water, 0.30 g of CF_3CO_2Ag, 1.464 mmol) to give a saturated solution. Diffusion of water to this solution at 65 °C over 1–2 days afforded **A** as pale-yellow blocks in about 70% yield. Anal. Calcd for $C_{34}H_{22}N_2O_{24}F_{24}Ag_{12}$: C, 15.75; H, 0.86; N, 1.08. Found: C, 15.70; H, 0.91; N, 1.02. IR: 2005 (vw, $\upsilon(C{\equiv}C)$), 1688 (vs, $\upsilon(CF_3CO_2^-)$) cm^{-1}.

$[Ag_2(3,5\text{-}C_2PyC_2)\cdot 3AgNO_3\cdot H_2O]$ (B). To a 5 mL vial containing solid 3,5-diethynylpyridine (0.0030 g, 0.024 mmol) were added a few drops of distilled water and excess solid silver nitrate (0.0300 g, 0.177 mmol). This mixture was stirred for 20 min to generate an off-white precipitate. After washing with distilled water two times to remove the excess $AgNO_3$ and nitric acid released from the reaction, a pale-yellow solid was obtained. This solid was dissolved in a concentrated solution of silver nitrate (0.6 mL of distilled water, 0.20 g of $AgNO_3$, 1.177 mmol) to give a saturated solution. Diffusion of water to this solution at 65 °C over 1–2 days afforded **B** as yellow needles in about 80% yield. Anal. Calcd for $C_9H_5N_4O_{10}Ag_5$: C, 12.45; H, 0.58; N, 6.45. Found: C, 12.53; H, 0.55; N, 6.24. IR: 2025 (vw, $\upsilon(C{\equiv}C)$), 1384 (vs, $\upsilon(NO_3^-)$) cm^{-1}.

Physical Measurements. Elemental analysis was performed with a Perkin-Elmer elemental analyzer. The FT-IR spectrum was recorded on a Bruker Equinox55 spectrometer.

X-ray Structure Determinations. Suitable single crystals were selected and mounted onto the end of a thin glass fiber. X-ray intensity data were measured on a Bruker SMART APEX CCD-based diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least squares using the *SHELXTL* crystallographic software package.[18] Anisotropic displacement

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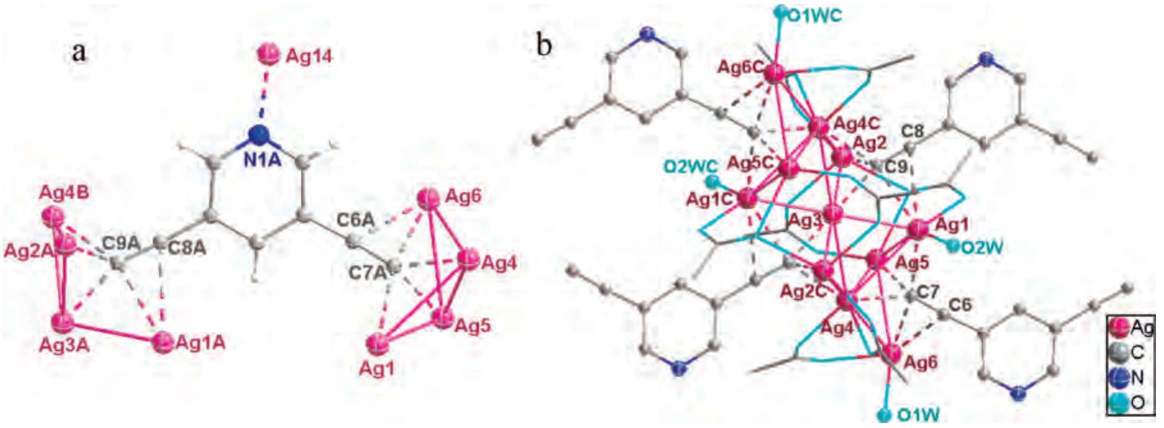

Figure 1. (a) Coordination mode of the 3,5-pyridyldiethynide ligand in **A**. (b) Ag_{11} cluster unit (unit **1**) with four coordinated ethynide groups and four water molecules in **A**. Other atoms and ligands are omitted for clarity. Symmetry code: A, $-x$, $2 - y$, $-z$; B, $1 + x$, y, z; C, $-1 - x$, $2 - y$, $-z$. Selected bond distances (Å): C6−C7 1.216(10); C8−C9 1.201(10); Ag···Ag 2.830(3)−3.368(4).

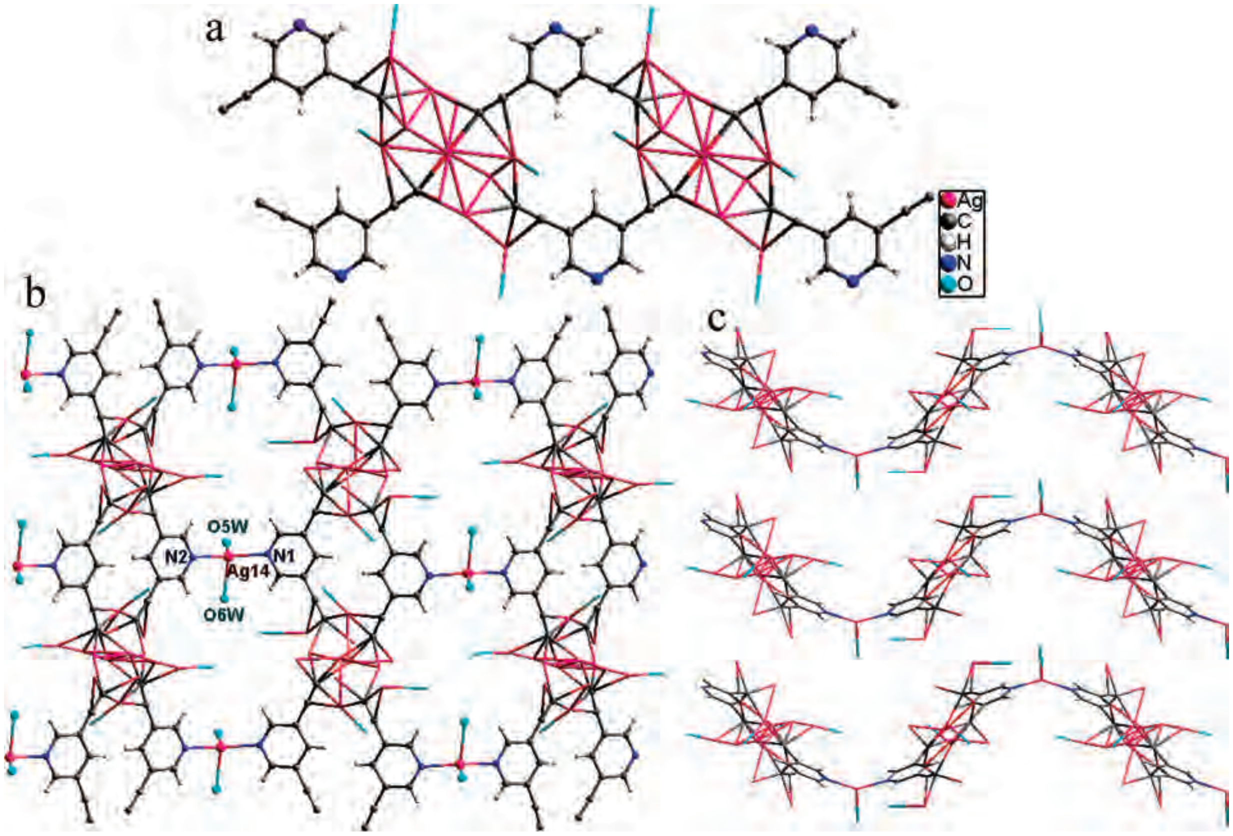

Figure 2. (a) Supramolecular chain in **A** viewed along the b direction. (b) 2D coordination network viewed along the b direction. (c) 2D wavelike layers viewed along the a direction. The bridged trifluoroacetate groups are omitted for clarity. Selected bond distances (Å): Ag14−N1 2.197(6); Ag14−N2 2.208(6); Ag14−O5W 2.56(4); Ag14−O6W 2.624.

parameters were applied to all non-hydrogen atoms except for one atom (C34) in compound **A**. The hydrogen atoms, except for those of water molecules, were included and were generated geometrically.

(a) Crystal data for [$Ag_2(3,5\text{-}C_2PyC_2)\cdot 4CF_3CO_2Ag\cdot 4H_2O$] (A): $C_{34}H_{22}N_2O_{24}F_{24}Ag_{12}$, $M = 2592.98$, triclinic, space group $P\bar{1}$, $a = 10.800(1)$ Å, $b = 11.629(1)$ Å, $c = 25.318(2)$ Å, $\alpha = 89.094(1)°$, $\beta = 87.425(1)°$, $\gamma = 78.440(1)°$, $V = 3112.1(4)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 2.767$ g cm^{-3}, $\mu = 3.829$ mm^{-1}, $F(000) = 2424$. A total of 17 985 reflections (11 987 independent, $R_{int} = 0.0172$) were measured. Final agreement indices were R1 = 0.0582 and wR2 = 0.1613 and GOF = 1.034 for 883 parameters and 9843 reflections [$I > 2\sigma(I)$]. All eight independent trifluoroacetate groups exhibit orientational disorder. Two silver atoms (Ag3 and Ag11) located on a mirror symmetry have two disordered positions with an occupancy ratio of 0.5:0.5. Silver (Ag12) and oxygen (O16) atoms are disordered at two positions in a ratio of 0.5:0.5. One non-hydrogen atom (C34) was refined isotropically. Hydrogen atoms of water molecules were not included in the refinement.

(b) Crystal data for [$Ag_2(3,5\text{-}C_2PyC_2)\cdot 3AgNO_3\cdot H_2O$] (B): $C_9H_5N_4O_{10}Ag_5$, $M = 868.52$, monoclinic, space group $P2_1/n$, $a = 6.923(2)$ Å, $b = 16.732(5)$ Å, $c = 25.13.842(5)$ Å, $\alpha = 90°$, $\beta = 90.074(5)°$, $\gamma = 90°$, $V = 1603.4(9)$ Å^3, $Z = 4$, $T = 293$ K, $D_c = 3.598$ g cm^{-3}, $\mu = 6.065$ mm^{-1}, $F(000) = 1608$. A total of 16 093 reflections (3585 independent, $R_{int} = 0.0531$) were measured. Final agreement indices were R1 = 0.0343 and wR2 = 0.0769 and GOF

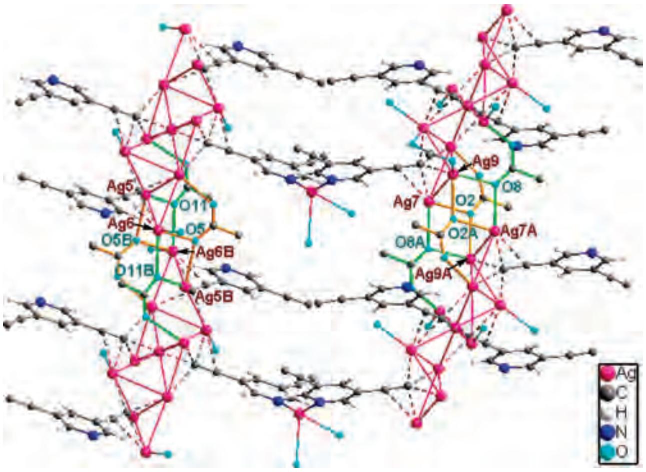

Figure 3. (a) Two independent Ag_{11} units in the adjacent layers are linked by trifluoroacetate groups in **A**, which are indicated by green and yellow colors, respectively. All fluorine atoms and partial bridged trifluoroacetate groups in Ag_{11} units are omitted for clarity. Symmetry code: A, $1 - x$, $1 - y$, $1 - z$; B, x, $-1 + y$, z. Selected bond distances (Å): Ag5−O11 2.260(6); Ag6−O5 2.329(6); O11−Ag6B 2.432(6); O5−Ag5B 2.505(6); Ag7−O2 2.320(7); Ag9−O8 2.281(6); O2−Ag9A 2.416(7); O8−Ag7A 2.451(7).

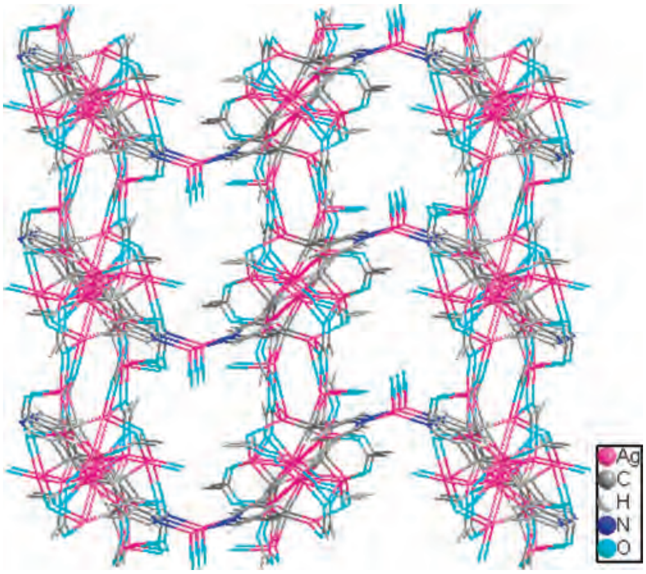

Figure 4. 3D coordination network in **A** viewed along the *a* direction. All fluorine atoms in trifluoroacetate groups are omitted for clarity.

= 1.062 for 255 parameters and 3585 reflections [$I > 2\sigma(I)$]. Hydrogen atoms of water molecules were not included in the refinement.

Results and Discussion

A direct reaction of 3,5-diethynylpyridine with silver nitrate in water led to a white precipitate, which was proposed to be a polymeric complex $[3,5\text{-}C_5H_3N(C{\equiv}C)_2Ag_2 \cdot 0.5AgNO_3]_x$. After washing and exchange of the anion with excess ammonium tetrafluoroborate, this solid was dissolved in a concentrated solution of silver trifluoroacetate to generate a clear solution. Slow diffusion of water to this saturated solution led to crystallization of compound **A** as pale-yellow blocks in high yield at 338 K.[13,19] Almost in a similar way, compound **B** crystallized as yellow needles from an aqueous solution of silver nitrate. The vibrations of ethynide groups appear at 2005 and 2025 cm^{-1} in IR spectra of **A** and **B**, respectively, close to the values observed in other silver phenyleneethynides.[9,13]

In the structure of **A**, each ethynide group coordinates to four silver atoms with μ_4-$\eta^2,\eta^1,\eta^1,\eta^1$ bonding mode and the nitrogen atom in the pyridyl group binds to one silver atom (Figure 1a). Four ethynide groups belonging to four pyridyldiethynide ligands and eleven silver atoms constitute a cluster unit with a center of symmetry, where seven silver atoms are arranged to give a significantly distorted body-centered octahedron and another two ethynide (C6–C7)−Ag_4 units are attached to this octahedron by sharing the Ag···Ag edges. Two ethynide groups (C8–C9) coordinate to the central silver atom (Ag3) in a head-to-head fashion. All of the silver atoms on the surface of the Ag_{11} cluster unit are bridged by trifluoroacetate groups. In **A**, there are two independent cluster units, but both of them exhibit almost similar structural features (Figures 1b and Figure S1 in the Supporting Information). The triple bond lengths (C6–C7, C8–C9, C15–C16, and C17–C18) are in the range of 1.201(10)–1.229(10) Å, in good agreement with that observed in other silver phenyleneethynide complexes.[9,10] The Ag···Ag (2.83–3.37 Å) and Ag···C (2.08–2.70 Å) distances are also normal for phenyleneethynide−silver clusters, comparable with the values found in the literature.[9,20] However, in this crystal, silver atoms (Ag3, Ag11, and Ag12) are found to be disordered, which leads to the difficulty of getting exact values for some Ag···Ag and Ag···C bond distances.

The interesting structural feature of **A** is that these Ag_{11} cluster units are linked by pyridyldiethynide groups to generate an infinite chain, where all of the pyridyl groups point outward (Figure 2a). Obviously this supramolecular chain bearing pyridyl groups could be considered as a super metalloligand. Linkage of these supramolecular chains by silver ions through N(pyridyl)−Ag−N(pyridyl) bonds affords 2D wavelike networks as described in Scheme 1 (mode I; parts b and c of Figure 2). The space-filling drawing suggests that in **A**, mode I in Scheme 1 is preferred because of the steric hindrance from the bridging trifluoroacetate groups in Ag_{11} cluster units. As a linker, the silver ion not only is coordinated by two pyridyl groups in two adjacent chains, but also interacts with two water molecules, adopting a significantly distorted tetrahedral geometry (∠N−Ag−N = 146.9°). The Ag−N bond lengths are 2.197(6) Å (Ag14−N1) and 2.208(6) Å (Ag14−N2), respectively, in agreement with the values observed in silver pyridine complexes.[21] The

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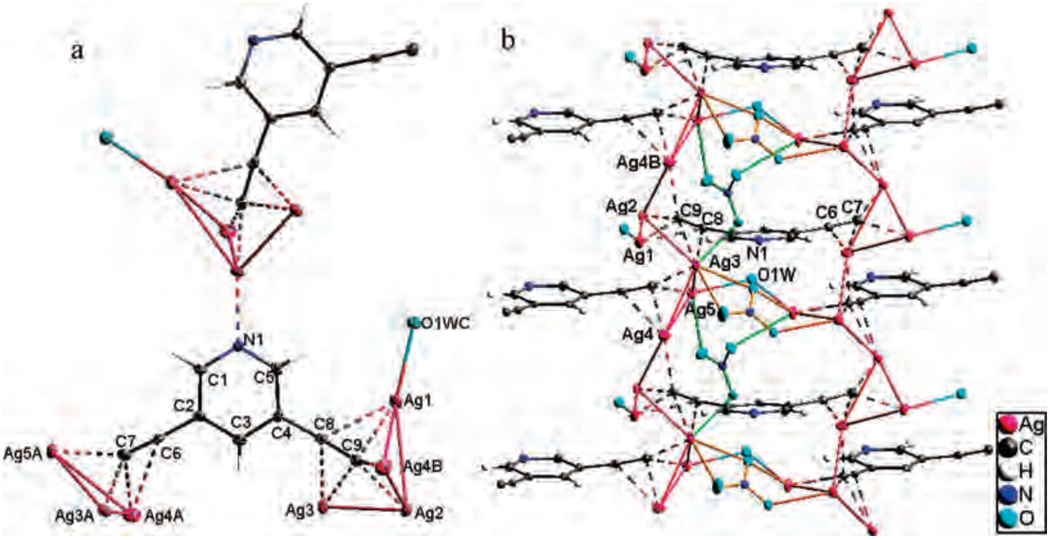

Figure 5. (a) Coordination mode of the 3,5-pyridyldiethynide ligand in **B**. (b) Silver double chain and two coordination modes of nitrate groups (marked with gold and green colors) in **B**. Partial nitrate groups are omitted for clarity. Symmetry code: A, 0.5 + *x*, 0.5 − *y*, 0.5 + *z*; B, 1 + *x*, *y*, *z*; C, −0.5 + *x*, 0.5 − *y*, −0.5 + *z*. Selected bond distances (Å): C6−C7 1.214(11); C8−C9 1.231(11); Ag1−O1WC 2.483(5); Ag5−O1W 2.412(5); Ag···Ag 2.801(1)−3.333(1); Ag···O(nitrate) 2.400−2.808.

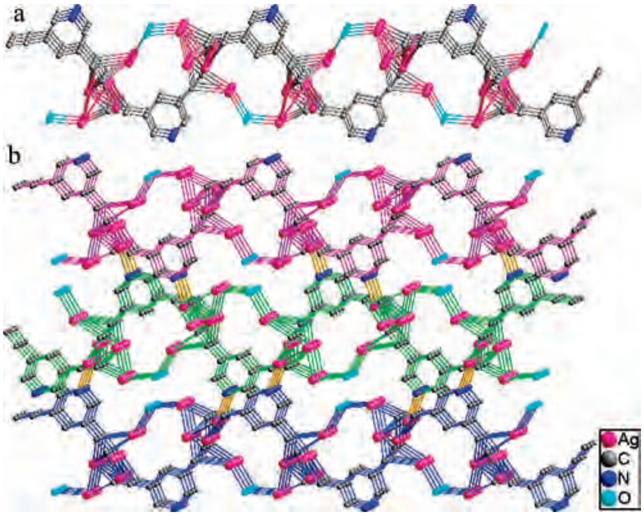

Figure 6. (a) 2D coordination network in **B** constructed from the linkage of silver double chains by pyridyldiethynide groups. (b) 3D coordination network in **B** composed of 2D coordination networks linked through the interaction between silver atoms and pyridyl groups, which are marked with gold color. All nitrate groups are omitted for clarity.

Ag−O5W bond distance is 2.56(4) Å, close to the values found in other silver complexes,[22] but the Ag−O6W bond distance (2.624 Å) is longer, indicating the presence of weak interaction.

The Ag$_{11}$ cluster units in the wavelike layers are further connected by trifluoroacetate groups to afford a broken silver chain along the *b* direction. In Figure 3, it is clearly shown how two independent Ag$_{11}$ cluster units in the adjacent layers are linked by four trifluoroacetate ligands, respectively, where one of the oxygen atoms in each trifluoroacetate group binds to two silver atoms in different Ag$_{11}$ cluster units. The Ag−O bond distances lie in the range of 2.260(6)−2.505(6) Å. A similar phenomenon was also observed in silver(I) *p*-phenylenediethynide.[13] In this way, the wavelike layers are consequentially linked to generate a rigid 3D coordination network (Figure 4), where large 1D channels are found that are filled by the bridged trifluoroacetate groups and lattice–water molecules in the solid state.

To explore the effect of the counterion on the structure of the silver pyridyldiethynide coordination network for comparison purposes, **B** was synthesized and structurally characterized. In contrast to **A**, **B** exhibits a completely different coordination network. In **B**, two ethynide groups in one pyridyldiethynide ligand coordinate to Ag$_4$ and Ag$_3$ aggregates with μ_4-η^2,η^2,η^1,η^1 and μ_3-η^2,η^1,η^1 bonding modes, respectively, and the nitrogen atom in the pyridyl group binds to one silver atom in the ethynide−Ag$_4$ unit (Figure 5a). As observed in silver(I) *m*-phenylenediethynide, those Ag$_4$ and Ag$_3$ cluster units are indeed connected one-by-one by sharing silver atoms in these units through ethynide−silver bonding, argentophilic, and silver−nitrate interactions to form a silver double chain.[13] All of the pyridyl groups are parallel and point in the same direction, different from that found in silver *m*-phenylenediethynide, where the phenyl groups are arranged alternately to point in different directions (Figure 5b).[13] On the other side of this silver double chain, water molecules link silver chains by coordinating to silver atoms in Ag$_3$ and Ag$_4$ units in two silver chains as bridging ligands, with Ag−O bond lengths of 2.412(5) and 2.483(5) Å, respectively. The distances of C6–C7 and C8–C9 triple bonds are 1.214(11) and 1.231(11) Å, respectively. The Ag···Ag distances [2.801(1)–3.333(1) Å] are close to the values found in **A**.

As expected, the nitrate groups in **B** exhibit bonding modes different from those of trifluoroacetate ligands. In **B**, two kinds of bonding modes for nitrate groups are observed, which are also depicted in Figure 5b. One is that one nitrate binds to three silver atoms in three silver ethynide cluster units through Ag−O interactions; another mode is that one

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[22] Dong, Y.-B.; Zhang, Q.; Ma, J.-P.; Huang, R.-Q.; Shen, D. Z.; Chen, D. Z. *Inorg. Chem.* **2005**, *44*, 6591–6608.

[23] Kalra, M. K.; Zhang, H.; Son, D. Y. *Inorg. Chem. Commun.* **2004**, *7*, 1019–1022.

nitrate coordinates to three silver atoms in two cluster units, where one oxygen atom interacts with two silver atoms in a bridging mode. The Ag−O bond lengths are in the range of 2.400–2.808 Å, which indicate the presence of Ag−O interactions.[23]

It is interesting that the silver double chains are further linked by pyridyldiethynide groups to form a 2D coordination network (Figure 6a), where all of the pyridyl groups point outward on both sides of this layer, somewhat similar to that found in **A** except for a 1D chain in **A** instead of a 2D network. As shown in Figure 6b, these layers bearing pyridyl groups interact through Ag−N coordination bonds and nitrate−silver interactions (the nitrate groups are not shown) to generate a 3D coordination network. It is worth pointing out that all of the pyridyl groups only coordinate to silver atoms in Ag_4 units in adjacent layers, as depicted in Figure 5a and mode II (Scheme 1). The Ag−N(pyridyl group) bond distance of 2.189(6) Å is indicative of a bonding interaction.[21]

Conclusions

Two silver(I) pyridyldiethynides have been synthesized and structurally characterized for comparison purposes. The obtained results demonstrate that silver ethynide compounds can be used as potential network builders to construct new coordination networks by incorporating extra coordination atoms into these conjugated organic ligands, which expands the scope of rational design for coordination networks or functional materials by choosing suitable building units. This study also shows that the structures of coordination networks of silver(I) pyridyldiethynides are able to be varied by changing the counterions, indicating that the bonding modes and steric hindrances of the counterions could be important factors influencing the structures of supramolecular chains and coordination networks. Further investigation is in progress to obtain new organometallic coordination networks based upon this approach.

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Supporting Information Available: X-ray crystallographic data for **A** and **B** in CIF format, structure unit of compound **2**, and IR spectra of **A** and **B**. This material is available free of charge via the Internet at http://pubs.acs.org.

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