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Note

# Assembly of silver(I) one- and two-dimensional coordination frameworks with 2-ethynyl-4,6-dimethylpyrimidine ligand

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ABSTRACT

The reactions of ethynide ligands and silver(I) trifluorocarboxylate under solvent evaporation conditions yielded two silver-organic frameworks, namely, $[(AgL)(AgCF_3CO_2)_4(H_2O)_2]$ (**1**) and $[(AgL)(AgCF_3CO_2)_3]$ (**2**) (HL = 2-ethynyl-4,6-dimethylpyrimidine). In complex **1**, $Ag_{10}$ aggregates are linked by trifluoroacetate groups to produce infinite chains, which are further linked through interchain hydrogen bonds into a three-dimensional supramolecular framework. In **2**, $Ag_8$ aggregates are fused together through trifluoroacetate groups to give rise to 2D metal-organic layer. These structural differences indicate that molar ratio of the molecular components plays important role in defining the overall structures of metal-organic frameworks.

## 1. Introduction

Silver(I)-ethynide complexes have attracted much interest owing to their structural diversity [1–6]. To the best of knowledge, intriguing structures are mainly dependent on diverse coordination modes of the alkynyl moiety together with argentophilic interaction [7,8]. Moreover, the construction of silver(I)-ethynide complexes totally relies on the self-assembly process in solution, which contain variable influencing factors, such as organic ligands, solvents, counterions, the molar ratio of reactants, and such factors play important roles in the construction of the overall architectures of these complexes. Hitherto most of the silver(I)-ethynide complexes with various structures have been reported; nevertheless, it is still a great challenge to predict the exact structure of assembly products in crystal engineering, because the noncovalent supramolecular interactions, such as C—H·F, O—H·O hydrogen bonding play vital role in the formation and stabilization of supramolecular structures [9–13]. Recently, several groups have explored pyridyldiethynides or pyrimidinylethynides, in which the relative positions and bonding preference between the ethynide group and ring nitrogen atom act as controlling factors to produce various structural building units for the formation of multidimensional coordination networks [5d,5e,6]. Because the nitrogen atom has a strong ability to coordinate to the silver ion, we wonder if some derivatives of pyrimidinylethynides can be used to construct interesting coordination networks. Based on the aforementioned considerations and our previous work [5,14], we have designed and synthesized a new ethynide ligand 2-ethynyl-4,6-dimethylpyrimidine to construct new organosilver(I) compounds. Herein we report the syntheses and structural characterization of two new silver(I)-ethynide complexes, namely $[(AgL)(AgCF_3CO_2)_4(H_2O)_2]$ (1) and $[(AgL)(AgCF_3CO_2)_3]$ (**2**), in which $[AgL]_n$ act as a starting material adopting different coordination modes to silver(I) atoms.

## 2. Experiments

### 2.1. Reagents

4,6-dimethyl-2-iodopyrimidine was prepared according to the literature method [15]. 2-ethynyl-4,6-dimethylpyrimidine was synthesized by the literature method via the Sonogashira coupling reaction between the corresponding heteroaryl compounds and trimethylsilylacetylene followed by desilylation with $K_2CO_3$ in methanol [16]. Commercially available trimethylsilylacetylene, acetonitrile and triethylamine were used without further purification. Polymeric starting materials $[AgL]_n$ were prepared according to the literature method [17]. All synthetic reactions yielding organic ligands and polymeric starting materials were carried out under a nitrogen atmosphere.

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

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**Table 1**
X-ray crystal data and structure refinement for compounds **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{16}H_{11}Ag_5F_{12}N_2O_{10}$ | $C_{14}H_7Ag_4F_9N_2O_6$ |
| Formula weight | 1158.62 | 901.70 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ |
| $a$ (Å) | 8.0217(4) | 9.0235(8) |
| $b$ (Å) | 25.7170(14) | 10.5943(10) |
| $c$ (Å) | 14.8817(7) | 12.3334(13) |
| $\alpha$ (°) | 90 | 84.052(8) |
| $\beta$ (°) | 117.172(4) | 89.602(8) |
| $\gamma$ (°) | 90 | 68.411(9) |
| $V$ (Å$^3$) | 2731.2(2) | 1089.81(2) |
| $Z$ | 4 | 2 |
| Dcalc (g cm$^{-3}$) | 2.818 | 2.748 |
| $F$(000) | 2176 | 844 |
| Reflections collected | 18178 | 6840 |
| Independent reflections | 4795 | 3838 |
| $R$(int) | 0.1248 | 0.0505 |
| Data/restraints/parameters | 4795/30/440 | 3838/13/322 |
| GOF on $F^2$ | 1.021 | 1.065 |
| $R_1[(I > 2\sigma(I)]$ | 0.0730 | 0.0624 |
| $wR_2[(I > 2\sigma(I)]$ | 0.1952 | 0.1192 |
| $R_1$ (all data) | 0.1084 | 0.1001 |
| $wR_2$ (all data) | 0.2450 | 0.1342 |

### *2.1.1. Synthesis of $[AgL]_n$*

Silver nitrate (0.778 g, 4.58 mmol) was dissolved in acetonitrile (50 mL). Then HL (0.605 g, 4.58 mmol) was added with vigorous stirring and the mixture was stirred overnight under a nitrogen atmosphere in darkness. The white precipitate formed was collected by filtration, washed thoroughly with acetonitrile (2 × 10 mL) and methyl alcohol (3 × 10 mL), and then stored in wet form at −10 °C in a refrigerator. Yield: 65%.

### *2.1.2. Synthesis of complexes **1** and **2***

*2.1.2.1. $[(AgL)(AgCF_3CO_2)_4(H_2O)_2]$ (**1**).* $AgCF_3CO_2$ (0.440 g, 2 mmol) was dissolved in 1 mL water. Then $[AgL]_n$ (0.015 g, 0.06 mmol) solid was added to the solution. After stirring for about half an hour, the solution was filtered. After several days, needle crystals of **1** were deposited in about 39% yield. Anal. Calcd for $C_{16}H_{11}Ag_5F_{12}N_2O_{10}$ (1158.62): C 16.59, H 0.96 N 2.42%. Found: C 16.67, H 0.87, N 2.51%.

*2.1.2.2. $[(AgL)(AgCF_3CO_2)_3]$ (**2**).* The procedure is similar to the synthesis of **1** except that $AgCF_3CO_2$ (0.220 g, 1 mmol) were used instead of $AgCF_3CO_2$ (0.440 g, 2 mmol). After several days, needle

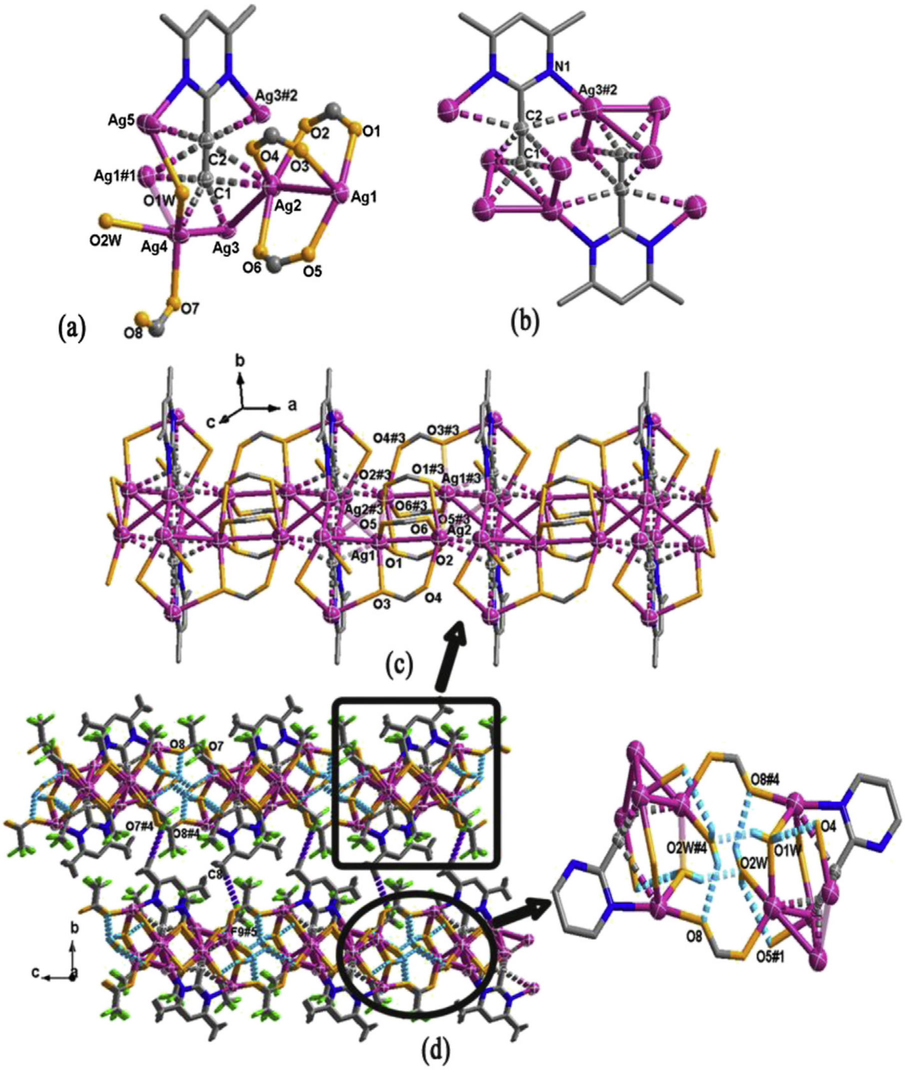

**Fig. 1.** (a) Atom labeling and coordination mode of L in **1** (50% thermal ellipsoids are drawn for silver atoms). (b) View of $Ag_{10}$ aggregate. (c) $Ag_{10}$ aggregates are fused together through trifluoroacetate groups and argentophilic interactions to produce a silver column in **1** along the *a* axis. All hydrogen atoms and $CF_3$ moieties of $CF_3CO_2^-$ are omitted for clarity. (d) (left) View of three-dimensional supramolecular architecture of **1**. (right) View of the hydrogen bonding between the chains. Selected bond lengths [Å]: C1≡C2 1.235(16), Ag1#1–C1 2.471(10), Ag1#1–C2 2.825(12), Ag2–C1 2.545(10), Ag2–C2 2.835(12), Ag3–C1 2.121(11), Ag3#2–C2 2.929(10), Ag4–C1 2.257(11), Ag5–C2 3.067(11), Ag1·Ag2 3.048(14), Ag1·Ag3#1 3.220(14), Ag1·Ag4#1 3.269(15), Ag2·Ag3 3.111(14), Ag3·Ag4 2.822(13). Symmetry codes: #1 $x+1, y, z$; #2 $-x+2, -y+2, -z+1$; #3 $-x+1, -y+2, -z+1$; #4 $-x+3, -y+2, -z+2$; #5 $-x+2, y-1/2, -z+3/2$. Atom color codes: Ag purple, C gray, O orange, N blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

crystals of **2** were deposited in about 45% yield. Anal. Calcd for $C_{14}H_7Ag_4F_9N_2O_6$ (901.70): C 18.65, H 0.78, N 3.11%. Found: C 18.73, H 0.69, N 3.21%.

### 2.2. X-ray crystallographic analysis

Selected crystals were used for data collection on OXFORD Diffraction Gemini Single Crystal diffractometer equipped with graphite monochromatized Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å) at room temperature using the $\omega$-scan technique. An empirical absorption correction was applied using the SADABS program [18]. The structures were solved by the direct method and refined by full matrix least squares on $F^2$ using the SHELXTL program package [19]. The $CF_3$ moieties of $CF_3CO_2^-$ groups in compound **1** were disordered, and the SADI command was used to fix them in the refinements. The crystal data and details of refinement are summarized in Table 1.

## 3. Results and discussion

### 3.1. $[(AgL)(AgCF_3CO_2)_4(H_2O)_2]$ (**1**)

The asymmetric unit of **1** contains five crystallographically independent Ag(I) ions, four trifluoroacetate ions, and two coordinated water molecules. As shown in Fig. 1a, the ethynide group (C1≡C2) is enveloped by an unprecedented $\mu_6$-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode. Utilizing three $\mu_2$-O,O′, $\mu_3$-O,O′,O′ and $\mu_4$-O,O,O′,O′ (O5, O6, O3, O3, O4 and O1, O1, O2, O2) trifluoroacetate groups as linkage components, together with the argentophilic interactions (Ag1–Ag2 3.048(14)Å), the external silver atom Ag1 is hitched to the $Ag_6$ basket, within which the argentophilic Ag–Ag distances vary from 2.822(13) to 3.269(15) Å, being shorter than twice the van der Waals radius of silver ions (3.44 Å) [20] and suggesting the presence of significant argentophilic interactions. Adjacent $Ag_6$ baskets are coalesced by sharing Ag3 and Ag3#2 to yield an $Ag_{10}$ aggregate (Fig. 1b). Such $Ag_{10}$ aggregates are linked by three pairs of trifluoroacetate groups (O5–O6, O3–O4 and O1–O2) via $\mu_2$-O,O′, $\mu_3$-O,O′,O′ and $\mu_4$-O,O,O′,O′ coordination modes, respectively, with the assistance of the argentophilic interactions (Ag1–Ag2, Ag1#3–Ag2#3 3.048(14)Å), to generate an infinite column along the *a* axis. The infinite columns are interconnected by the remaining trifluoroacetate group (O7–O8) via $\mu_2$-O,O′ coordination mode to form a two-dimensional coordination polymer parallel to the *ac* plane. There are also relatively weak hydrogen bonds O1W–H·O4 (H–O4 2.813(16)Å), O1W–H·O2W#4 (H–O2W#4 2.809(13) Å), O2W–H·O5#1 (H–O5#1 3.040(3) Å), and O1W–H·O8#4 (H–O8#4 2.823(13) Å), which are further consolidated the layer. Neighboring layers are linked by weak C8–H·F9#5 (H–F9#5 2.588(12) Å) hydrogen bond to form a three-dimensional supramolecular framework, as illustrated in Fig. 1c.

### 3.2. $[(AgL)(AgCF_3CO_2)_3]$ (**2**)

As shown in Fig. 2a, the asymmetric unit of **2** contains four crystallographically independent Ag(I) ions and three trifluoroacetate ions. Different from **1**, the ethynide group (C1≡C2) is enveloped by a square-pyramidal $Ag_5$ basket $\mu_5$-$\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode. The peripheral Ag4 atom is hitched to the $Ag_5$ basket by trifluoroacetate groups in $\mu_3$-O,O′,O′ and $\mu_4$-O,O,O′,O′ (O3–O4 and O5–O6) modes, respectively. The argentophilic Ag–Ag distances vary from 2.870(11) to 2.905(12) Å. Such distances are clearly indicative of the presence of $d^{10}$–$d^{10}$ interactions. Similar to complex **1**, adjacent $Ag_5$ baskets are coalesced by sharing Ag1 and Ag1#1 to yield an $Ag_8$ aggregate (Fig. 2b). Such $Ag_8$ aggregates are linked by two pairs of trifluoroacetate groups (O1–O2, O1#4–O2#4, and O5–O6, O5#3–O6#3) via $\mu_3$-O,O′,O′ coordination modes, to yield an infinite column along the *b* axis. Linkage of adjacent columns by two pair of inversion-related trifluoroacetate groups (O3–O4, O3#2–O4#2, O5–O6, and O5#2–O6#2) produces a two-dimensional layer parallel to the *ab* plane (Fig. 2c). Owing to the pyrimidinyl ring appended on both sides of this silver(I) layer, there is no obvious intermolecular interaction between layers.

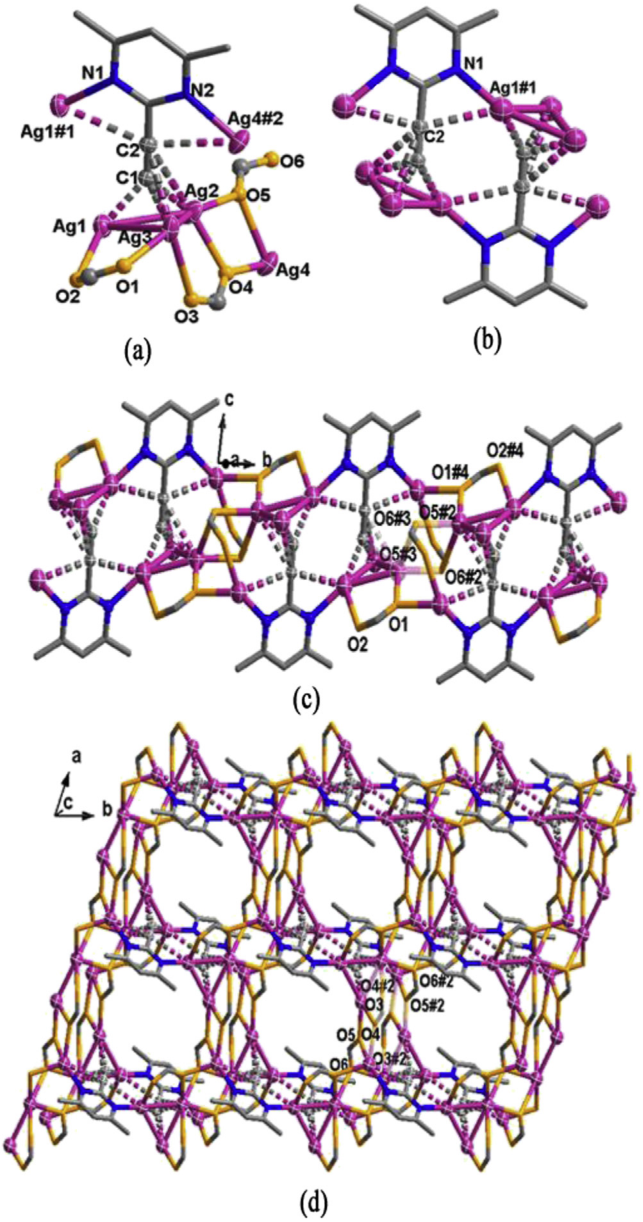

**Fig. 2.** (a) Atom labeling and coordination mode of L in **2** (50% thermal ellipsoids are drawn for silver atoms). (b) View of $Ag_8$ aggregate. (c) $Ag_8$ aggregates are fused together through trifluoroacetate groups to give rise to a silver column in **2** along the *b* axis. (d) (left) View of metal-organic layer of **2**. All hydrogen atoms and $CF_3$ moieties of $CF_3CO_2^-$ are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.198(9), Ag1–C1 2.116(11), Ag2–C1 2.142(10), Ag2–C2 3.094(10), Ag3–C1 2.353(11), Ag3–C2 2.948(11), Ag1#1–C2 3.082(9), Ag4#2–C2 2.993(11), Ag1·Ag2 2.9047(12), Ag1·Ag3 2.8911(12), Ag2·Ag3 2.8698(11). Symmetry codes: #1 $-x+2, -y+1, -z+1$; #2 $-x+1, -y+2, -z+1$; #3 $x+1, y, z$; #4 $-x+2, -y+2, -z+1$. Atom color codes: Ag purple, C gray, O orange, N blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 4. Conclusion

In conclusion, on the basis of the pyrimidinylethynide supramolecular synthon and silver(I) trifluorocarboxylate, we have synthesized and structurally characterized two silver(I) ethynide complexes. It should note that the subtle change of structure influencing factor, such as molar ratio of the molecular components, could affect the overall final structures. In addition, the silver-ethynide, argentophilic, hydrogen-bonding play vital roles in assembly of the coordination polymers with increasing in dimensionality as well as the stability of the framework structure.

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## Appendix A. Supplementary material

CCDC 926172 and 926173 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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