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Diverse intermolecular interactions in silver(I)-organic frameworks constructed with flexible supramolecular synthons

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ABSTRACT

Three ligands bearing terminal ethynide moiety attached via pendent arm to a phenyl skeleton have been used in synthesis of three silver (I) complexes, namely, $[(AgL1)(AgCF_3CO_2)_3]_n$ (1), $\{[(AgL2)(AgCF_3CO_2)_6(H_2O)_2] \cdot (H_2O)_6\}_n$ (2) and $[(AgL3) \cdot (AgCF_3CO_2)_5(H_2O)]_n$ (3), in which several unconventional intermolecular interactions (silver-ethynyl, silver-aromatic, argentophilicity and $C-H\cdots\pi$) have been shown to play vital role in the formation and stabilization of supramolecular structures. In 1, butterfly-shaped Ag₄ baskets are interconnected together by trifluoroacetate groups to lead to a layer structure, which is also consolidated by silver-aromatic interactions, adjacent layers are then linked into a three-dimensional supramolecular architecture through weak $C-H\cdots F$ hydrogen bonding. In 2, ladder type chains are associated into three-dimensional supramolecular architecture through weak to groups with the assistance of argentophilic interactions and silver-aromatic interaction give rise to a 2D coordination network, which are further united by $C-H\cdots\pi$ interaction to produce a three-dimensional supramolecular framework.

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1. Introduction

The design and synthesis of new supramolecular synthons with multi-center binding sites for constructing new kinds of nonclassical coordination/organometallic supramolecular architectures are of great current interest [1–7]. In the construction of solid-state frameworks, coordinate covalent bonding [8–12] and noncovalent interactions are two well-established essentials of crystal engineering. Indeed, the latter one lies the foundation of an enormous family of supramolecular synthons [13–15]. Furthermore, weaker interactions such as $C-H\cdots\pi$, for example, may also dominate in molecular association, and packing thus playing an increasingly important role as a persistent structural motif in structure formation [16–19].

Following our investigation of the coordination chemistry of silver ethynediide (Ag_2C_2) [20–22], we have conducted systematic studies on various complexes containing silver(I) 1,3-butadiynediide (Ag_2C_4)

** Corresponding author. The College of Chemistry and Molecular Engineering, Zhengzhou University, Science Road 100#, Zhengzhou 450001, PR China. Tel.: +86 852 2609 6279; fax: +86 852 2603 5057. [23]. Furthermore, utilizing new metal-ligand supramolecular synthons of the type $R-C \equiv C \supset Ag_n(R = aryl or alkyl; n = 4, 5)$ [24,25] and $Ag_n \subset C \equiv C - R - C \equiv C \supset Ag_n (R = 0, m, p - C_6H_4; n = 4, 5)$ [26], we have obtained a series of metal-organic networks stabilized by argentophilic and silver–ethynide (σ , π and mixed σ , π) interactions. Recently, we have explored the employment of several ligands with one or more ethynyl groups attached to phenyl, biphenyl, or naphthyl skeleton via a flexible -CH2-O- link for the construction of MOFs consolidated by both silver(I)-ethynide and silver(I)-aromatic interactions [27-30]. By utilizing new metal-ligand supramolecular synthons of the type p-X–C₆H₅OCH₂C \equiv C \supset Ag_n (X = I, Br; n = 4, 5) [31] and *o*-, *m*-, *p*-Cl-C₆H₅OCH₂C \equiv C \supset Ag_n (*n* = 4, 5) [32], we have obtained a series of metal-organic networks, which provides unequivocal evidence for the existence of the Ag···Br-aryl, Ag···I-aryl and Ag···Cl-aryl interactions. Recently, Zhang group reported three phenylethynes bearing one or two carboxylic groups, as well as one methyl carboxylate for comparison purposes, are utilized as ligands to construct a new class of silver-organic networks and to investigate the relationship between the structure of the network and the number of carboxylate groups attached to the phenylethynide ligands [33]. Notably, the change of substituent group of the phenyl ring affects the overall final structures. As a continuation of our research, herein we report the syntheses and structural characterization of three silver (I) complexes assembled

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with supramolecular synthons $C_6H_4-CH_2-C\equiv C\supset Ag_n$, $C_6H_4-O-CH_2-C\equiv C\supset Ag_n$ and $C_6H_4-CH_2-O-CH_2-C\equiv C\supset Ag_n$ (Scheme 1), which bearing terminal ethynide moiety attached via pendent arm to the phenyl skeleton, respectively: $[(AgL1)(AgCF_3CO_2)_3]_n$ (1), $\{[(AgL2)(AgCF_3CO_2)_6(H_2O)_2] \cdot (H_2O)_6\}_n$ (2) and $[(AgL3) \cdot (AgCF_3CO_2)_5(H_2O)_1_n$ (3).

2. Experiments

2.1. Reagents

Commercially available 3-phenyl-1-propyne (97%), phenyl propargyl ether (97%), and benzyl propargyl ether (98%) were from Alfa Aesar and used without further purification.

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

2.1.1. Synthesis of $[AgL1]_n$ (4)

Silver nitrate (0.778 g, 4.58 mmol) was dissolved in acetonitrile (50 mL). Then HL (0.532 g, 4.58 mmol) and triethylamine (0.634 mL, 4.58 mmol) were 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 de-ionized water (3 × 10 mL), and then stored in wet form at -10 °C in a refrigerator. Yield: 85%. IR: ν 2039 cm⁻¹ (w, $\nu_{c}\equiv_{C}$).

2.1.2. Synthesis of $[AgL2]_n$ (5) and $[AgL3]_n$ (6)

These polymeric materials were prepared by a similar synthetic procedure using HL2 and HL3, respectively. [AgL2]_n (**5**) Yield: 73%, IR: ν 2025 cm⁻¹ (w, $\nu_C \equiv_C$), [AgL3]_n (**6**) Yield: 80%, IR: ν 2046 cm⁻¹ (w, $\nu_C \equiv_C$).

2.1.3. Synthesis of complexes 1-3

2.1.3.1. $[(AgL1)(AgCF_3CO_2)_3]_n$ (1). AgCF_3CO_2 (0.440 g, 2 mmol) was dissolved in 1 mL water. Then $[AgL1]_n$ (\approx 15 mg) solid was added to the solution. After stirring for about half an hour, the solution was filtered and the filtrate stored at -10 °C in refrigerator. One day later, needle crystals of 1 were deposited in about 55% yield. *Anal.* Calcd for C₁₅H₇Ag₄F₉O₆ (885.69): C 20.34, H 0.80. Found: C 20.38, H 0.87%.

2.1.3.2. {[$(AgL2)(AgCF_3CO_2)_6(H_2O)_2$] · $(H_2O)_6$] $_n$ (**2**). The procedure is also similar to the synthesis of **1** except that [AgL2] $_n$ (\approx 15 mg) was used instead of [AgL1] $_n$. Two day later, needle crystals of **2** were deposited in about 60% yield. *Anal.* Calcd for C₂₁H₂₃Ag₇F₁₈O₂₁ (1708.48): C 14.76, H 1.36. Found: C 14.79, H 1.42%.



Scheme 1. Structural formulas used as ligands in forming new silver(I)-ethynide complexes.

2.1.3.3. $[(AgL3) \cdot (AgCF_3CO_2)_5(H_2O)]_n$ (**3**). The procedure is also similar to the synthesis of **1** except that adding AgBF₄ (0.382 g, 2 mmol) and $[AgL3]_n$ (≈ 25 mg) was used instead of $[AgL1]_n$. After several days, needle crystals of **3** were deposited in about 45% yield. *Anal.* Calcd for C₂₀H₁₁Ag₆F₁₅O₁₂ (1375.51): C 17.46; H 0.81. Found: C 17.52, H 0.74%.

2.2. X-ray crystallographic analysis

Selected crystals were used for data collection on a Bruker SMART APEX–II CCD diffractometer equipped with graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature using the ω -scan technique. An empirical absorption correction was applied using the SADABS program [34]. The structures were solved by the direct method and refined by full matrix least squares on F^2 using the SHELXTL program package [35]. Most of the CF₃ moieties of CF₃CO₂ groups in compounds **1**–**3** 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. [(AgL1)(AgCF₃CO₂)₃]_n (**1**)

In the crystal structure of **1**, there is one independent anionic ligand, in which the ethynide group $(C1\equiv C2)$ is bound to a butterfly-shaped Ag₄ basket in the $\mu_4 - \eta^1$, η^2 , η^2 , η^2 mode. In **1**, the anionic ligand L1 adopts a non-planar conformation, in which the torsion angles C4–C3–C2–C1 is 59.40(2)°. The distances between silver atoms range from 2.869(5) to 2.981(5) Å, implying the presence of significant argentophilic interaction [36–40]. As shown in Fig. 1, three phenyl carbon atoms coordinate to Ag4#1 to form silver–aromatic interactions in an unusual η^3 mode, with the bond lengths of 2.554(5), 2.874(6), and 2.917(5) Å, which all fall within the range of silver–aromatic interaction [40–43]. To our knowledge, there are only a few examples of the η^3 mode [28,29,44–47]. Neighboring two independent Ag₄ baskets are interconnected together by trifluoroacetate groups (O1–O2, O3–O4 and O5–O6)

able 1
X-ray crystal data and structure refinement for compounds 1–3.

	1	2	3
Empirical formula	C15H7Ag4F9O6	C21H23Ag7F18O21	C ₂₀ H ₁₁ Ag ₆ F ₁₅ O ₁₂
Formula weight	885.69	1708.48	1375.51
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	Pī	Pī
a (Å)	10.3230(4)	11.2918(17)	11.1059(7)
b (Å)	10.5140(4)	12.0123(18)	11.8958(7)
<i>c</i> (Å)	19.2746(8)	17.865(3)	13.5635(8)
α (°)	90	106.166(3)	77.289(5)
β(°)	99.6220(10)	98.041(3)	67.902(6)
γ (°)	90	105.055(3)	85.119(5)
V (Å ³)	2062.6(1)	2187.9(6)	1619.6(2)
Ζ	4	2	2
Dcalc (g cm ⁻³)	2.852	2.593	2.821
F(000)	1656	1616	1288
Reflections collected	22836	31152	12094
Independent reflections	3660	7695	5698
R(int)	0.0259	0.0756	0.0322
Data/restraints/parameters	3660/67/379	7695/51/624	5698/148/515
GOF on F ²	1.034	1.079	1.030
$R_1[(I > 2\sigma (I))]$	0.0267	0.0491	0.0503
$wR_2[(I > 2\sigma (I))]$	0.0575	0.1421	0.1442
R ₁ (all data)	0.0356	0.0589	0.0645
wR ₂ (all data)	0.0610	0.1497	0.1586
Max/min (<i>e</i> Å ⁻³)	0.847, -0.730	2.164, -1.552	1.819, -1.021



Fig. 1. Atom labeling and coordination mode of L1 in **1** (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms, and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. Selected bond lengths [Å]: C1=C2 1.196(6), Ag1-C1 2.125(5), Ag2-C1 2.305(5), Ag2-C2 2.734(6), Ag3-C1 2.353(5), Ag3-C2 3.017(6), Ag4-C1 2.363(5), Ag4-C2 2.841(6), Ag1...Ag2 2.946(6), Ag1...Ag3 2.869(6), Ag1...Ag4 2.976(6), Ag2...Ag3 2.869(5), Ag3...Ag4 2.981(6). Symmetry code: #1-*x*, 1-*y*, 1-*z*. Atom color codes: Ag purple, C gray, O orange. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and their symmetry-related molecules in $\mu_3 - \eta^1$, η^2 and $\mu_4 - \eta^2$, η^2 modes, respectively, to furnish an infinite chain (Fig. 2a). The infinite chains are also interconnected by trifluoroacetate groups (05–06 and 05#1–06#1) in $\mu_4 - \eta^2$, η^2 mode, to lead to a layer structure, which is consolidated by silver–aromatic interactions

(Fig. 2b and c). Finally, an association of layers through weak $C5-H5\cdots F1$ (C5-F1 3.45(2) Å, $\angle CHF$ 124.48(1)°) hydrogen bonding generate a 3D supramolecular network (Fig. S1).

3.2. {[(AgL2)(AgCF₃CO₂)₆(H₂O)₂]·(H₂O)₆}_n (**2**)

The asymmetric unit of **2** contains seven crystallographically independent Ag(I) ions, six trifluoroacetate ions, two coordinated water molecules (O1W and O2W) and six free water molecules (from O3W to O8W). As shown in Fig. 3, the ethynide group composed of C1 and C2 is capped by a square-pyramidal Ag₅ basket in the $\mu_5 - \eta^1$, η^1 , η^2 , η^2 , η^2 coordination mode. The peripheral Ag6 atom is hitched to the Ag₅ basket by a pair of μ_3 -0,0',0' trifluoroacetate groups (O6, O7, O7 and O8, O8, O9) and the aqua ligand O1W. The Ag7 atom is coordinated to four water molecules (05W, 06W, 07W and 08W) give rise to an Ag(H₂O)₄ unit, and such unit is hitched to the Ag₅ basket by O4W, O6W and O8W through hydrogen bonding (08W···O3 2.828(9) Å, 08W···O4 2.998(9) Å, O6W···O4W 2.809(8) Å, O4W···O6 2.932(7) Å). Linkage of two square-pyramidal Ag₅ baskets by a pair of inversion-related trifluoroacetate groups (012-013 and 012#2-013#2) produces a Ag₅-($\mu_3-\eta^1$, η^2 -CF₃CO₂)₂-Ag₅ building unit. Moreover, two phenyl carbon atoms (C7 and C8) coordinate to the silver atom Ag6#1 by the $\mu - \eta^2$ mode with bond lengths of 2.411 (2) and 2.507 (1) Å, respectively, implying the presence of significant Ag(I)aromatic interaction. Adjacent units are further linked through silver–aromatic interaction along the *b* axis to engender an infinite one-dimensional ladder type chain (Fig. 4a). Notably, Ag(H₂O)₄



Fig. 2. (a) Silver (1) chain structure in complex 1 along the *b* axis. (b) (left) Layer structure in **1**. (right) Silver(1)-organic cycle formed via silver(1)-aromatic interactions, which also consolidate the 2D layer structure. All hydrogen atoms and CF₃ moieties of CF₃CO₂ are omitted for clarity. Symmetry codes: #1-x, 1-y, 1-z; #2-x, -1/2 + y, 3/2-z.



Fig. 3. Atom labeling and coordination mode of L2 in **2** (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms, and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. Selected bond lengths [Å]: C1=C2 1.198(7), Ag1-C1 2.206(6), Ag2-C1 2.287(6), Ag3-C1 2.365(6), Ag3-C2 3.024(7), Ag4-C1 2.422(6), Ag4-C2 2.388(8), Ag5-C1 2.381(6), Ag5-C2 2.801(9), Ag1-··Ag2 2.831(8), Ag1-··Ag3 2.862(8), Ag1-··Ag4 2.907(8), Ag1-··Ag5 2.875(8), Ag2-··Ag3 2.970(8), Ag2···Ag5 3.016(8), Ag4-··Ag5 3.031(9). Symmetry code: #1 x, 1 + y, z. Atom color codes: Ap purple, C gray, O orange and Green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

units and free water molecules (O3W and O4W) reside in the interchain void space and further connect the adjacent chains to yield an intricate three-dimensional supramolecular architecture extending a and c directions (Fig. S2). In the rich hydrogen-bonding system, the water molecules, especially O4W, O6W and O7W form rich hydrogen bonds. O4W acts as donors to hydrogen bond to O2 and O6, and as acceptors hydrogen bonded by O6W and O7W, respectively. O6W acts as donors to hydrogen bond to O11 and O4W, and as an acceptor hydrogen bonded by O5W. O7W acts as donors to hydrogen bond to O3W and O4W, and as an acceptor hydrogen bonded by O2W. In **2**, the free water molecules covering the surface of the silver aggregates hinder the formation of coordination polymer. Adjacent silver aggregates associated together just through silver-aromatic interaction and rich hydrogen-bonding system to lead to a three-dimensional supramolecular architecture. This structural feature is different from our previous work using the same ligand [29], in which a series of four complexes are formed through hydrogen bonding and aryl $\pi \cdots \pi$ and oxo lone pair $\cdots \pi$ interaction and silver-aromatic interaction, respectively.

3.3. $[(AgL3) \cdot (AgCF_3CO_2)_5(H_2O)]_n$ (3)

The asymmetric unit of **3** contains six crystallographically independent Ag(I) ions, five trifluoroacetate ions, and one coordinated water molecule. In the crystal structure of **3**, the anionic ligand L3 also adopts a non-planar conformation, in which the torsion angles C4-O1-C3-C2 is 72.96(9)°. As shown in Fig. 5, the $\mu_5 - \eta^1$, η^1 , η^2 , η^2 , η^2 ethynide group (C1=C2) is inserted into a square-pyramidal Ag₅ basket as in complex **2**. The peripheral Ag6 atom is hitched to the Ag₅ basket by a pair of μ_3 -0,0',0' trifluoroacetate groups (04, 05, 05 and 06, 06, 07) and the aqua ligand O1W. Moreover, two phenyl carbon atoms (C7 and C8) coordinate to the silver atom Ag6#1 by the μ - η^2 mode with bond lengths of 2.397(1) and 2.463(1) Å, respectively, implying the presence of significant Ag(I) $-\pi$ interaction. Such two independent Ag₅ baskets are glued together through trifluoroacetate groups (04–05, 08–09, 04#3–05 #3 and 08#4–09#4) in the μ₃-0,0',0' mode to furnish an infinite chain (Fig. 6a). Finally, association of chains through a pair of trifluoroacetate groups (O10-O11 and 010#2–011#2) in the μ_3 -0,0',0' mode, which together with argentophilic interactions (Ag5...Ag5#2) and Ag(I) $-\pi$ interaction,



Fig. 4. (a) One-dimensional ladder type chain structure in complex **2** along the *b* axis. (b) Layer structure in **2**. (c) The hydrogen bonding between the layers. All hydrogen atoms and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. Symmetry codes: #1 x, 1 + y, z; #2-x, 1-y, -z; #3 1 + x, y, z.

give rise to a 2D coordination network (Fig. 6b). Short distances between the parallel methylene and phenyl ring indicate the existence of C–H··· π interaction (C4–H4A···centroid 2.917(2) Å, with a C4–H4A···centroid angle 146.43(4)°), which are comparable with the results in the literature [48]. Such networks are further bridged by C–H··· π interaction to produce a three-dimensional supramolecular framework (Fig. S3).

3.4. Supramolecular synthons

In contrast to previous reported [23–26], $C_6H_4-CH_2-C\equiv C\supset Ag_n$, $C_6H_4-O-CH_2-C\equiv C\supset Ag_n$ and $C_6H_4-CH_2-O-CH_2-C\equiv C\supset Ag_n$ synthons have much longer flexible arms, which offer a good opportunity to introduce silver(I)–aromatic interactions in the construction of coordination networks of variable dimensions. The invariable appearance of the μ_4 - and μ_5 -ligation modes of the ethynide moiety are also obtained in complexes **1**–**3**. Complexes **1** and **3** display 2D coordination network, which are associated by the C–H···F and C–H···F and C–H···F



Fig. 5. Atom labeling and coordination mode of L3 in 3 (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms, and CF₃ moieties of CF₃CO₂ are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.201(1), Ag1-C1 2.125(5) 2.235(7), Ag2-C1 2.377(7), Ag2-C2 2.978(9), Ag3-C1 2.257(7), Ag4-C1 2.434(8), Ag4-C2 2.551(9), Ag5-C1 2.536(7), Ag5-C2 2.644(8), Ag1...Ag2 2.908(9), Ag1...Ag3 2.773(9), Ag1…Ag4 2.861(9), Ag1…Ag5 3.424(1), Ag2…Ag3 2.915(1), Ag2…Ag4 2.984(9). Symmetry codes: #1 1-x, -y, -z; #2-x, -1-y, -z; #3 1-x, -1-y, -z; #4-x, -y, -z. Atom color codes: Ag purple, C gray, O orange. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cular frameworks, respectively. Complex 2 exhibits an infinite onedimensional ladder type chain, and further linked into threedimensional supramolecular framework through rich hydrogenbonding interaction. A comparison of **1–3** demonstrates that the



Fig. 6. (a) Chain structure of 3. (b) 2D metal-organic network of 3.

structure and dimensionality of the coordination network can be modulated by varying the anionic ligands, even the length of the flexible arms.

4. Conclusion

In summary, we have synthesized and characterized three silver-organic complexes. In the present instance, the silver (I)aromatic interaction has been successfully introduced into silver-ethynide supramolecular chemistry, showing that it is an effective driving force for building novel solid state architectures. Meanwhile, the invariable appearance of the μ_4 - and μ_5 -ligation modes of the ethynide moiety affirms the general utility of the silver–ethynide supramolecular synthon $C_6H_5CH_2C\equiv C \supset Ag_n$, $C_6H_5OCH_2C \equiv C \supset Ag_n$ and $C_6H_5CH_2OCH_2C \equiv C \supset Ag_n$ (n = 4, 5) in coordination network assembly. The interplay of silver-ethynide bonding, argentophilicity, and weak intermolecular interactions such as hydrogen bonding, silver–aromatic, $C-H\cdots\pi$ interactions in these complexes has been shown to play vital role in the formation and stabilization of supramolecular structures. Further studies in this respect are underway in our laboratory.

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Appendix A. Supplementary material

CCDC 832266(1), 858070(2) and 832267(3) 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.

Appendix B. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2012.02.029.

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