6480 *Inorg. Chem.* **2009**, *48*, 6480–6489
DOI: 10.1021/ic900346p

Inorganic Chemistry
Article

Assembly of Silver(I) Two- and Three-Dimensional Coordination Networks with Complementary Tridentate Heteroaryl Ethynide Ligands†

Liang Zhao and Thomas C. W. Mak*

*Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong
Shatin, New Territories, Hong Kong SAR, P.R. China*

Received February 20, 2009

Three pairs of complementary nitrogen heteroaryl ligands [2,6-($C\equiv C$)$_2$-py and 2-$C\equiv C$-pym; 2,5-($C\equiv C$)$_2$-py and 2-$C\equiv C$-pyz; 3,5-($C\equiv C$)$_2$-py and 5-$C\equiv C$-pym (py = pyridine, pyz = pyrazine, pym = pyrimidine)], wherein a ring nitrogen atom in one is interchanged with a carbon atom bearing an ethynyl substituent in the other, have been used to generate seven silver(I) complexes (**1**−**7**), in which silver infinite chains and two-dimensional coordination networks bridged by heteroaryl ethynide ligands were obtained as pre-programmed. 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. The fusion of $C\equiv C\supset Ag_n$ ($n = 3, 4$) building units yields multinuclear silver aggregates in **1**−**6** whose nuclearities range from seven to twelve. The crystal structure of **7** displays a honeycomb layer composed of Ag_4 baskets alternately linked by pyrimidinyl-5-ethynide ligands. In addition, complex **1** features an infinite chain composed of an alternate arrangement of twist-boat water hexamers and bridging silver atoms.

Introduction

The designed synthesis and property exploration of group 11 metal (M = Cu, Ag, and Au) cluster complexes have attracted much interest because of the uniqueness of metallophilicity between group 11 metal centers.[1] This kind of metallophilic interaction is weaker than covalent or ionic bonds but stronger than van der Waals interactions, and is roughly comparable in strength to typical hydrogen bonds.[2] As a result, these metallophilic interactions have been extensively harnessed as a crystal-engineering tool for enhancing structural dimensionality, leading to the manifestation of desirable properties of new functional materials. In the past decade, our group has conducted a systematic research program on the synthesis and structural characterization of silver(I) double and multiple salts containing polyatomic anionic ligands such as azide,[1g] cyanide,[1h] thiocyanate,[1i] selenocyanate,[1i,1j] acetylenediide ($^-C\equiv C^-$),[1k] aryl- and alkyl-ethynide ($RC\equiv C^-$),[3] and 1,3-butadiynediide ($^-C\equiv C-C\equiv C^-$),[4] which bring cationic silver ions together via the electrostatic effect and stabilize the resulting metal aggregates to achieve high nuclearity numbers. In addition, the ethynide moiety can function as a good σ- and π-donor through $p\pi-d\pi$ overlap with silver atoms to engender a series of cluster complexes, wherein a four- or five-membered silver aggregate consistently embraces it.[5] Although this multinuclear silver-ethynide motif $C\equiv C\supset Ag_n$ ($n = 3-5$) is stable enough to act as a novel metal−ligand supramolecular synthon, its assembly in a pre-programmed arrangement is impaired by the variable coordination environment around the silver(I) atom, in contrast to the common, directional bonding geometries

---

[†] Dedicated to the memory of Prof. Robert Bau (1944−2008).

*To whom correspondence should be addressed. E-mail: tcwmak@cuhk.edu.hk.

(1) (a) Yam, V. W.-W.; Cheng, E. C.-C. *Angew. Chem., Int. Ed.* **2000**, *39*, 4240–4244. (b) Mingos, D. M. P.; Vilar, R.; Rais, D. *J. Organomet. Chem.* **2002**, *641*, 126–133. (c) Schwerdtfeger, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 1892–1895. (d) Sevillano, P.; Fuhr, O.; Kattannek, M.; Nava, P.; Hampe, O.; Lebedkin, S.; Ahlrichs, R.; Fenske, D.; Kappes, M. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3702–3708. (e) Ahlrichs, R.; Eichhoefer, A.; Fenske, D.; May, K.; Sommer, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 8254–8257. (f) Anson, C.; Eichhoefer, A.; Issac, I.; Fenske, D.; Fuhr, O.; Sevillano, P.; Persau, C.; Stalke, D.; Zhang, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 1326–1331. (g) Guo, G.-C.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 3268–3270. (h) Guo, G.-C.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 3183–3185. (i) Guo, G.-C.; Mak, T. C. W. *Chem. Commun.* **1999**, 813–814. (j) Wang, Q.-M.; Guo, G.-C.; Mak, T. C. W. *Polyhedron* **2001**, *20*, 2683–2687. (k) Mak, T. C. W.; Zhao, X.-L.; Wang, Q.-M.; Guo, G.-C. *Coord. Chem. Rev.* **2007**, *251*, 2311–2333.

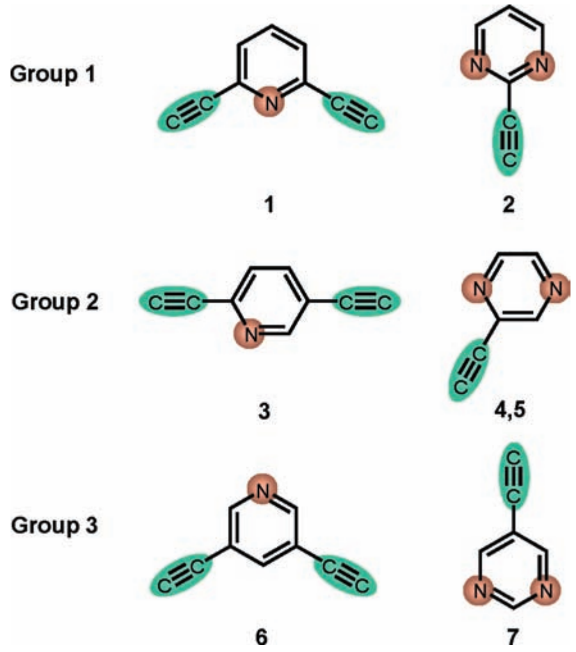
(2) (a) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, *24*, 391–400. (b) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597–636. (c) Schmidbaur, H. *Gold: progress in chemistry, biochemistry, and technology*; Wiley: New York, 1999.

(3) (a) Zhao, L.; Mak, T. C. W. *J. Am. Chem. Soc.* **2005**, *127*, 14966–14967. (b) Zhao, L.; Wong, W.-Y.; Mak, T. C. W. *Chem.—Eur. J.* **2006**, *12*, 4865–4872. (c) Zhao, L.; Zhao, X.-L.; Mak, T. C. W. *Chem.—Eur. J.* **2007**, *13*, 5927–5936. (d) Zhao, L.; Mak, T. C. W. *Organometallics* **2007**, *26*, 4439–4448. (e) Zhao, L.; Chen, X.-D.; Mak, T. C. W. *Organometallics* **2008**, *27*, 2483–2489.

(4) (a) Zhao, L.; Mak, T. C. W. *J. Am. Chem. Soc.* **2004**, *126*, 6852–6853. (b) Zhao, L.; Du, M.; Mak, T. C. W. *Chem. Asian J.* **2007**, *2*, 1240–1257.

(5) Mak, T. C. W.; Zhao, L. *Chem. Asian J.* **2007**, *2*, 456–467.

Scheme 1. Three Pairs of Complementary Tridentate Heteroaryl Ethynyl Ligands[a]



[a] The silver(I) complexes **1**−**7** derived from each ligand are indicated by their numbers in bold type.

of other transition metal centers, typically octahedral, square planar, or tetrahedral,[6] by which metal ions or their polynuclear clusters can be linked through polydentate ligands to generate desired multidimensional architectures.

In our choice of suitable polydentate ligands for linking silver clusters, the $C{\equiv}C{\supset}Ag_n$ supramolecular synthon is grafted onto a six-membered nitrogen heterocycle to obtain three pairs of complementary tridentate ligands, wherein a ring nitrogen atom in one is interchanged with a carbon atom bearing an ethynyl substituent in its counterpart (Scheme 1). Herein we report the synthesis of a series of six new polymeric silver(I) heteroaryl ethynides in crude form, from which seven complexes were generated by the incorporation of trifluoroacetate, namely, $2,6\text{-}(AgC{\equiv}C)_2\text{-py}\cdot 8AgCF_3CO_2\cdot 10H_2O$ (**1**), $2\text{-}(AgC{\equiv}C)\text{-pym}\cdot 4AgCF_3CO_2$ (**2**), $2,5\text{-}(AgC{\equiv}C)_2\text{-py}\cdot 4AgCF_3CO_2$ (**3**), $2\text{-}(AgC{\equiv}C)\text{-pyz}\cdot 4AgCF_3CO_2\cdot H_2O$ (**4**), $2\text{-}(AgC{\equiv}C)\text{-pyz}\cdot 5AgCF_3CO_2\cdot Me_3NCH_2CO_2\cdot 2H_2O$ (**5**), $3,5\text{-}(AgC{\equiv}C)_2\text{-py}\cdot 6AgCF_3CO_2\cdot 3.5H_2O$ (**6**), and $5\text{-}(AgC{\equiv}C)\text{-pym}\cdot 3AgCF_3CO_2\cdot 3H_2O$ (**7**) (py = pyridine, pyz = pyrazine, pym = pyrimidine). Structural characterization of this series of complexes by single crystal X-ray analysis has revealed that the number and relative location of the nitrogen atom(s) and ethynide substituent(s) on the heteroaryl ring act as controlling factors to induce the assembly of their coordination architectures.[7] The present work can be compared to a recent report of the preparation and structural characterization of two silver double salts of the pyridyldiethynide ligand $3,5\text{-}(C_2)_2\text{py}$.[8]

Experimental Section

Reagents. 3,5-Dibromopyridine, 2,5-dibromopyridine, 2,6-dibromopyridine, 5-bromopyrimidine, 2-bromopyrimidine, 2-chloropyrazine, and trimethylsilylacetylene were obtained commercially and used without further purification. Acetonitrile and triethylamine were purified according to standard procedures. All synthetic reactions yielding polymeric starting materials were carried out under a nitrogen atmosphere. All other reagents were of analytical grade and used as received. Infrared spectra were obtained from KBr pellets on a Nicolet Impact 420 FTIR spectrometer in the 400−4000 cm^{-1} region. Elemental analysis (C, H, N) was performed by the Medac Ltd. Brunel Science Center, United Kingdom.

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

$[3,5\text{-}(AgC{\equiv}C)_2\text{-py}]_n$, $[2,5\text{-}(AgC{\equiv}C)_2\text{-py}]_n$, $[2,6\text{-}(AgC{\equiv}C)_2\text{-py}]_n$, $[2\text{-}(AgC{\equiv}C)\text{-pyz}]_n$, $[5\text{-}(AgC{\equiv}C)\text{-pym}]_n$, and $[2\text{-}(AgC{\equiv}C)\text{-pym}]_n$. 3,5-Diethynylpyridine, 2,5-diethynylpyridine, 2,6-diethynylpyridine, 2-ethynylpyrazine, 5-ethynylpyrimidine, and 2-ethynylpyrimidine were synthesized by the literature method via the Sonogashira coupling reaction between the corresponding mono- or dihalo substituted heteroaryl compounds and trimethylsilylacetylene followed by desilylation with K_2CO_3 in methanol.[9] In a 100 mL Schlenk flask, silver nitrate (0.690 g, 4.0 mmol) was added to a solution of acetonitrile (50 mL). Then an acetonitrile solution (5 mL) containing a half-molar quantity of 3,5-diethynylpyridine, 2,5-diethynylpyridine, or 2,6-diethynylpyridine, or containing an equimolar amount of 2-ethynylpyrazine, 5-ethynylpyrimidine or 2-ethynylpyrimidine, and triethylamine (2.0 mL) were added with vigorous stirring for 24 h. The yellow precipitate was collected by filtration, washed thoroughly with 3 × 10 mL of acetonitrile and 3 × 20 mL of deionized water, and stored in wet form. IR spectrum: $[3,5\text{-}(AgC{\equiv}C)_2\text{-py}]_n$ 2014 cm^{-1} (w, ν C≡C); $[2,5\text{-}(AgC{\equiv}C)_2\text{-py}]_n$ 2020 cm^{-1} (w, ν C≡C); $[2,6\text{-}(AgC{\equiv}C)_2\text{-py}]_n$ 2019 cm^{-1} (w, ν C≡C); $[2\text{-}(AgC{\equiv}C)\text{-pyz}]_n$ 2013 cm^{-1} (m, ν C≡C); $[5\text{-}(AgC{\equiv}C)\text{-pym}]_n$ 2020 cm^{-1} (w, ν C≡C); $[2\text{-}(AgC{\equiv}C)\text{-pym}]_n$ 2017 cm^{-1} (w, ν C≡C).

$2,6\text{-}(AgC{\equiv}C)_2\text{-py}\cdot 8AgCF_3CO_2\cdot 10H_2O$ (1). $[2,6\text{-}(AgC{\equiv}C)_2\text{-py}]_n$ (∼0.1 g) was added to a concentrated aqueous solution (1 mL) of $AgCF_3CO_2$ (0.220 g, 1 mmol) and $AgBF_4$ (0.382 g, 2 mmol) in a beaker with stirring until saturation. The excess $[2,6\text{-}(AgC{\equiv}C)_2\text{-py}]_n$ was filtered off. The filtrate was then placed in the dark at room temperature. After a few days, transparent yellow prismatic crystals of **1** were deposited in ∼65% yield. mp 216.7−218.0 °C. Elemental analysis for $C_{25}H_{23}F_{24}O_{26}NAg_{10}$, found (calcd): C, 13.06 (13.12); H, 1.01 (1.01); N, 0.44 (0.61). IR spectrum: 2038 cm^{-1} (vw, ν C≡C).

$2\text{-}(AgC{\equiv}C)\text{-pym}\cdot 4AgCF_3CO_2$ (2). $AgCF_3CO_2$ (0.223 g, 1 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of deionized

---

(6) (a) Caulder, D. L.; Raymond, K. N. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1440–1442. (b) Stang, P. J. *Chem.—Eur. J.* **1998**, *4*, 19–27. (c) Gianneschi, N. C.; Tiekink, E. R. T.; Rendina, L. M. *J. Am. Chem. Soc.* **2000**, *122*, 8474–8479. (d) Tabellion, F. M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 7740–7741. (e) Iengo, E.; Zangrando, E.; Minatel, R.; Alessio, E. *J. Am. Chem. Soc.* **2002**, *124*, 1003–1013. (f) Campbell, K.; Kuehl, C. J.; Ferguson, M. J.; Stang, P. J.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 7266–7267. (g) Iengo, E.; Zangrando, E.; Geremia, S.; Graff, R.; Kieffer, B.; Alessio, E. *Chem.—Eur. J.* **2002**, *8*, 4670–4674. (h) Su, C.-Y.; Cai, Y.-P.; Chen, C.-L.; Smith, M. D.; Kaim, W.; Zur Loye, H.-C. *J. Am. Chem. Soc.* **2003**, *125*, 8595–8613. (i) Addicott, C.; Das, N.; Stang, P. J. *Inorg. Chem.* **2004**, *43*, 5335–5338. (j) Natarajan, R.; Savitha, G.; Moorthy, J. N. *Cryst. Growth Des.* **2005**, *5*, 69–72. (k) Steel, P. J. *Acc. Chem. Res.* **2005**, *38*, 243–250. (l) Yang, H.-B.; Ghosh, K.; Northrop, B. H.; Stang, P. J. *Org. Lett.* **2007**, *9*, 1561–1564. (m) Yamaguchi, T.; Tashiro, S.; Tominaga, M.; Kawano, M.; Ozeki, T.; Fujita, M. *Chem. Asian J.* **2007**, *2*, 468–476. (n) Wang, Y.; Cheng, P.; Song, Y.; Liao, D.-Z.; Yan, S.-P. *Chem.—Eur. J.* **2007**, *13*, 8131–8138.

(7) Zhao, L. *Multinuclear Silver-Ethynide Supramolecular Synthons for the Construction of Coordination Networks*. PhD Thesis, The Chinese University of Hong Kong, **2007**.

(8) Zhang, T.; Kong, J.; Hu, Y.; Meng, X.; Yin, H.; Hu, D.; Ji, C. *Inorg. Chem.* **2008**, *47*, 3144–3149.

(9) Schultheiss, N.; Barnes, C. L.; Bosch, E. *Cryst. Growth Des.* **2003**, *3*, 573–580.

Table 1. Crystallographic Data of Compounds **1**−**7**

compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_{25}H_{23}F_{24}O_{26}NAg_{10}$	$C_{14}H_3F_{12}O_8N_2Ag_5$	$C_{17}H_3F_{12}O_8NAg_6$	$C_{14}H_5F_{12}O_9N_2Ag_5$	$C_{21}H_{18}F_{15}O_{14}N_3Ag_6$	$C_{21}H_{10}F_{18}O_{15.5}NAg_8$	$C_{12}H_9F_9O_9N_2Ag_4$
FW	2287.98	1094.53	1224.42	1112.53	1468.57	1729.20	927.64
crystal system	monoclinic	triclinic	triclinic	monoclinic	triclinic	triclinic	orthorhombic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Pbca$
a/Å	18.436(2)	7.960(1)	10.588(2)	8.619(1)	12.193(3)	10.725(1)	15.524(2)
b/Å	16.755(1)	11.693(1)	11.175(2)	21.695(3)	12.464(3)	11.518(1)	16.061(2)
c/Å	20.244(2)	14.170(2)	11.273(2)	13.353(2)	13.515(3)	17.748(2)	17.232(2)
α/deg	90	70.202(2)	89.024(4)	90	97.352(4)	99.149(2)	90
β/deg	114.322(3)	74.579(2)	76.971(4)	108.238(2)	105.052(4)	103.438(2)	90
γ/deg	90	83.495(2)	74.107(4)	90	107.880(4)	104.697(2)	90
V/Å^3	5698.5(8)	1195.8(2)	1248.5(4)	2371.7(5)	1838.8(8)	2006.6(4)	4296.6(8)
Z	4	2	2	4	2	2	8
D_c/g cm^{-3}	2.648	3.040	3.257	3.110	2.645	2.850	2.850
μ/mm^{-1}	3.509	4.161	4.751	4.202	3.273	3.964	3.719
$R_1{}^a$ ($I > 2\sigma$)	0.0371	0.0307	0.0405	0.0306	0.0341	0.0407	0.0319
w$R_2{}^b$ (all data)	0.1073	0.0787	0.1180	0.0746	0.0910	0.1183	0.0863
GOF	1.020	1.027	1.039	1.028	1.038	1.023	1.056

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

water. Then [2-(AgC≡C)-pym]$_n$ (~0.1 g) solid was added to the solution. After stirring for about half an hour, the solution was filtered, and the filtrate was allowed to stand at room temperature in the dark. After several days, pale yellow crystals of **2** were deposited in ~40% yield. Compound **2** decomposes above 170 °C. Elemental analysis for $C_{14}H_3F_{12}O_8N_2Ag_5$, found (calcd): C, 15.50 (15.36); H, 0.18 (0.28); N, 2.27 (2.56). IR spectrum: 2006 cm^{-1} (w, ν C≡C).

2,5-(AgC≡C)$_2$-py·4AgCF$_3$CO$_2$ (3) and 3,5-(AgC≡C)$_2$-py·6-AgCF$_3$CO$_2$·3.5H$_2$O (6). A synthetic procedure similar to that yielding compound **1** with [2,5-(AgC≡C)$_2$-py]$_n$ and [3,5-(AgC≡C)$_2$-py]$_n$ instead of [2,6-(AgC≡C)$_2$-py]$_n$ was utilized to get yellow block crystals of **3** in ~30% yield and pale yellow prismatic crystals of **6** were deposited in ~25% yield. Compound **3** turns black and decomposes above 220 °C. Elemental analysis for $C_{17}H_3F_{12}O_8NAg_6$, found (calcd): C, 16.80 (16.68); H, 0.34 (0.25); N, 1.37 (1.14). IR spectrum: 2024 cm^{-1}(w, ν C≡C). Compound **6**: mp 253.0−254.9 °C with decomposition. Elemental analysis for $C_{21}H_{10}F_{18}O_{15.5}NAg_8$, found (calcd): C, 14.29 (14.59); H, 0.55 (0.58); N, 0.69 (0.81). IR spectrum: 2007 cm^{-1} (vw, ν C≡C).

2-(AgC≡C)-pyz·4AgCF$_3$CO$_2$·H$_2$O (4) and 5-(AgC≡C)-pym·3AgCF$_3$CO$_2$·3H$_2$O (7). 2-(AgC≡C)-pyz·4AgCF$_3$CO$_2$·H$_2$O (**4**) and 5-(AgC≡C)-pym·3AgCF$_3$CO$_2$·3H$_2$O (**7**) were obtained by similar synthesis method for compound **2** but utilizing [2-(AgC≡C)-pyz]$_n$ and [5-(AgC≡C)-pym]$_n$ instead [2-(AgC≡C)-pym]$_n$, respectively. Pale yellow crystals of **4** were deposited in ~50% yield. mp 132.1−134.4 °C. Elemental analysis for $C_{14}H_5F_{12}O_9N_2Ag_5$, found (calcd): C, 15.33 (15.11); H, 0.40 (0.45); N, 2.21 (2.52). IR spectrum: 2021 cm^{-1} (w, ν C≡C). Pale yellow crystals of **7** were deposited in ~45% yield. mp 124.8−126.2 °C. Elemental analysis for $C_{12}H_9F_9O_9N_2Ag_4$, found (calcd): C, 15.74 (15.54); H, 0.62 (0.98); N, 2.84 (3.02). IR spectrum: 1996 cm^{-1} (vw, ν C≡C).

2-(AgC≡C)-pyz·5AgCF$_3$CO$_2$·Me$_3$NCH$_2$CO$_2$·2H$_2$O (5). AgCF$_3$CO$_2$ (0.220 g, 1 mmol) and AgBF$_4$ (0.382 g, 2 mmol) were dissolved in deionized water (1 mL). Then [2-(AgC≡C)-pyz]$_n$ (~0.1 g) was added to the solution. After stirring for an hour with the addition of trimethylammonioacetate (betaine, ~0.15 g), the solution was filtered off. After standing for several days, pale yellow block crystals of **5** were collected in about 60% yield. mp 112.4−113.6 °C. Elemental analysis for $C_{21}H_{18}F_{15}O_{14}N_3Ag_6$, found (calcd): C, 17.39 (17.18); H, 1.10 (1.24); N, 2.60 (2.86). IR spectrum: 2046 cm^{-1} (w, ν C≡C).

X-ray Crystallographic Analysis. Data for complexes **1**−**7** were collected at 293 K with Mo Kα radiation on a Bruker SMART 1000 CCD diffractometer with frames of oscillation range 0.3°. During data reduction, an empirical absorption correction was applied by using the SADABS program.[10] All structures were solved by direct methods, and non-hydrogen atoms were located from difference Fourier maps. All non-hydrogen atoms, unless otherwise noted, were subjected to anisotropic refinement by full-matrix least-squares on F^2 by using the SHELXTL program.[11] The crystal data and X-ray structure refinement parameters are summarized in Table 1. The refinement details are described in the Supporting Information. CCDC-711566−711572 (**1**−**7**, respectively) contain the supplementary crystallographic data for this paper, which can be obtained free of charge from The Cambridge Crystallographic Data Centre at http://www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The polymeric silver heteroaryl ethynide crude materials [3,5-(AgC≡C)$_2$-py]$_n$, [2,5-(AgC≡C)$_2$-py]$_n$, [2,6-(AgC≡C)$_2$-py]$_n$, [2-(AgC≡C)-pyz]$_n$, [5-(AgC≡C)-pym]$_n$, and [2-(AgC≡C)-pym]$_n$ were synthesized via the reaction of the corresponding ethynyl-substituted heteroaryl compounds with silver nitrate in the presence of triethylamine. Employment of a concentrated aqueous solution of silver trifluoroacetate and silver tetrafluoroborate, the latter being added to increase the silver(I) ion concentration requisite for the formation of $-C{\equiv}C{\supset}Ag_n$ supramolecular synthon,[12] to dissolve the respective polymeric starting materials yielded complex **1**−**7**.

Description of Crystal Structures. In the crystal structure of 2,6-(AgC≡C)$_2$-py·8AgCF$_3$CO$_2$·10H$_2$O (**1**), the Ag5 and Ag6 atoms each exhibits 2-fold positional disorder. Each ethynide group of the heteroaryl ligand (left formula, group 1 in Scheme 1 shows its neutral form) is encapsulated in a Ag$_4$ butterfly shaped basket with silver-ethynide σ-type interaction in the range of 2.199(6)−2.282(5)Å and π-type at Ag4−C2 = 2.512(5) Å. The nitrogen atom N1 located

---

[10] Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; Univ. of Göttingen: Göttingen, Germany, 1996.

[11] Sheldrick, G. M. *SHELXTL 5.10 for Windows NT: Structure Determination Software Programs*; Bruker Analytic X-Ray Systems, Inc.: Madison, WI, 1997.

[12] Wang, Q.-M.; Mak, T. C. W. *Chem. Commun.* **2000**, 1534–1536.

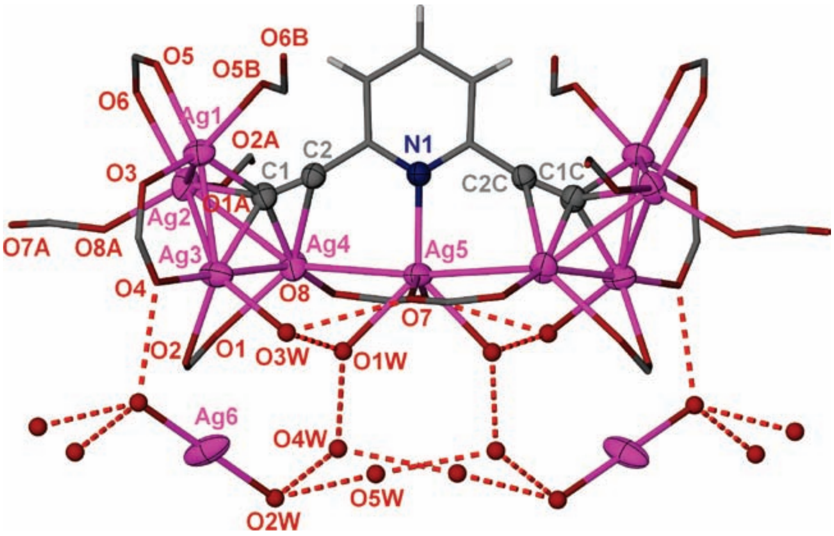


Figure 1. Atom labeling (thermal ellipsoids are drawn at the 50% probability level) and coordination mode of pyridyldiethynide ligand [2,6-(C≡C)$_2$-py]$^{2-}$ in 2,6-(AgC≡C)$_2$-py·8AgCF$_3$CO$_2$·10H$_2$O (**1**). Of the 2-fold disordered Ag5 and Ag6 atoms, only one position of each is shown. Hydrogen bonds are indicated by dashed lines. Trifluoromethyl moieties of CF$_3$CO$_2^-$ ligands are omitted for clarity. Hydrogen bond and selected Ag···Ag distances (Å): O1W−O3W 2.927, O1W−O4W 2.688, O2W−O4W 2.829, O2W−O5W 2.686, O2W−O4 2.711, O4W−O5W 2.798, O3W−O7 2.864; Ag1···Ag2 2.831(1), Ag1···Ag3 2.791(1), Ag2···Ag3 3.015(1), Ag2···Ag4 3.034(1), Ag3···Ag4 2.977(1), Ag4···Ag5 3.147(1). Symmetry code: A 1/2 − *x*, 1/2 − *y*, 1 − *z*; B −*x*, −*y*, 1 − *z*; C −*x*, *y*, 1/2 − *z*.

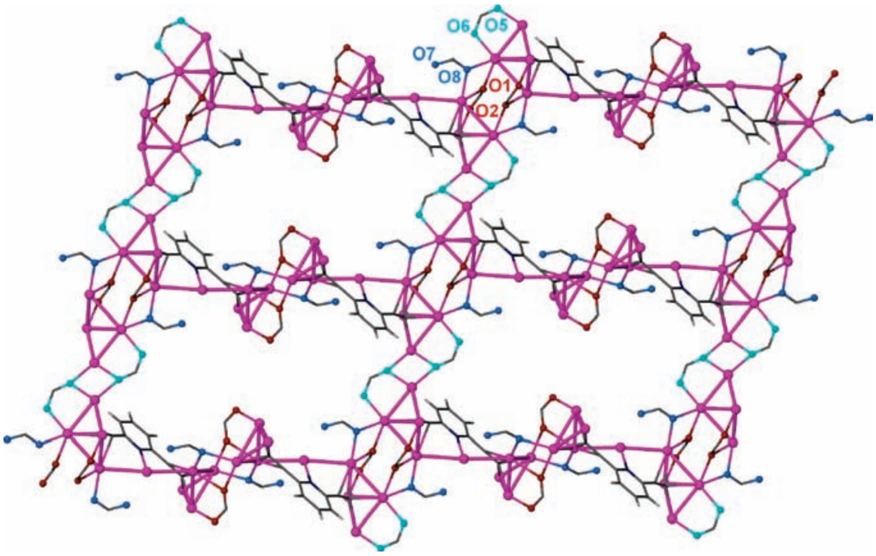


Figure 2. (4,4) Coordination network in **1** orientated parallel to the (−1 1 1) plane, which is constituted through the linkage of dumbbell-like Ag$_9$ aggregates by trifluoroacetate groups O1−O2 (red), O5−O6 (light blue), and O7−O8 (cyan). Other ligands are omitted for clarity.

between two ethynide moieties is expected to coordinate to a bridging silver atom, which presumably connects two Ag$_4$ silver aggregates surrounding two ethynide substituents on the pyridine ring. As shown in Figure 1, such two C_2-related Ag$_4$ baskets are linked by central silver atom Ag5 as pre-designed to generate a Ag$_9$ aggregate. The bridging silver atom Ag5 is coordinated by both nitrogen atom N1 and two C_2-related trifluoroacetate groups (O7−O8). The Ag···Ag distances within this Ag$_9$ aggregate lie in the range of 2.791(1)−3.147(1) Å, being much lower than twice the van der Waals radius of silver (3.4 Å) and hence suggesting the existence of significant argentophilic interactions.[2b,13] The C≡C moiety retains its triple bond feature at a distance of 1.204(7) Å but takes a bent configuration with a C−C≡C bond angle of 170.4(5)°, in contrast with its carbocyclic prototype Ag$_2$(m-C≡CC$_6$H$_4$C≡C)·6AgCF$_3$CO$_2$·3CH$_3$CN·2.5H$_2$O wherein this type of bond angles range from 177(1) to 178(1)°.[3a] Each Ag···Ag edge of this dumbbell-like Ag$_9$ aggregate is spanned by one trifluoroacetate group via the μ_2-*O,O′* mode. Furthermore, three independent trifluoroacetate groups (O1−O2, O5−O6, and O7−O8) and their inversion-related units adopt the μ_3-η^1,η^2 mode to interweave these Ag$_9$ aggregates along two directions to

---

[13] (a) Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098–1110. (b) Omary, M. A.; Webb, T. R.; Assefa, Z.; Shankle, G. E.; Patterson, H. H. *Inorg. Chem.* **1998**, *37*, 1380–1386. (c) Majumdar, P.; Kamar, K. K.; Goswami, S.; Castineiras, A. *Chem. Commun.* **2001**, 1292–1293. (d) Pan, L.; Woodlock, E. B.; Wang, X.; Lam, K.-C.; Rheingold, A. L. *Chem. Commun.* **2001**, 1762–1763. (e) Song, H.-B.; Zhang, Z.-Z.; Hui, Z.; Che, C.-M.; Mak, T. C. W. *Inorg. Chem.* **2002**, *41*, 3146–3154. (f) Yoshida, Y.; Muroi, K.; Otsuka, A.; Saito, G.; Takahashi, M.; Yoko, T. *Inorg. Chem.* **2004**, *43*, 1458–1462. (g) Chen, X.-D.; Du, M.; Mak, T. C. W. *Chem. Commun.* **2005**, 4417–4419.

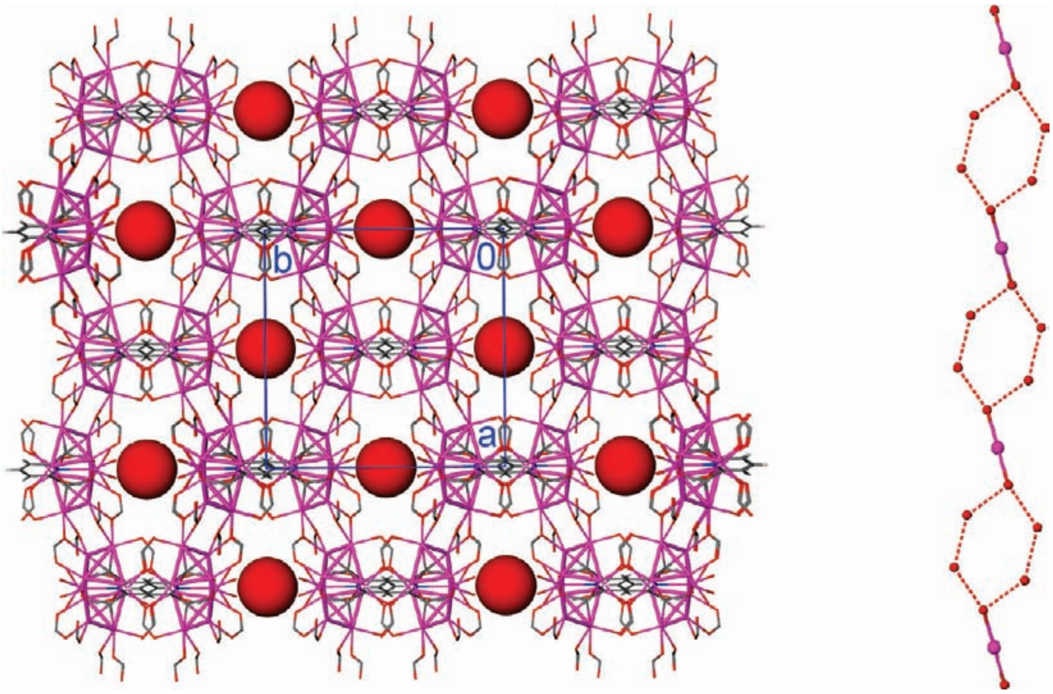


Figure 3. 3-D coordination network in **1** containing a series of parallel channels (cross-section represented by circle at the left) each accommodating a silver-bridged water hexamer chain (details illustrated at the right).

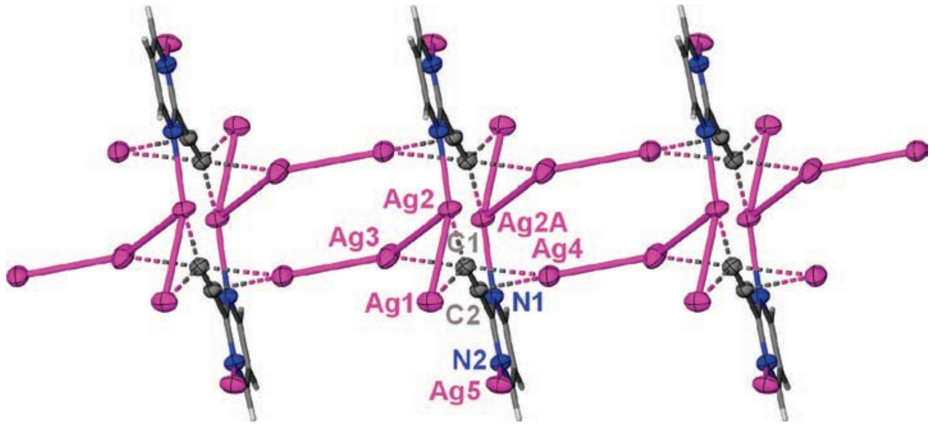


Figure 4. Silver chain in 2-(AgC≡C)-pym·4AgCF$_3$CO$_2$ (**2**) and coordination modes of pyrimidinyl-2-ethynide ligands with atom labeling (30% thermal ellipsoids; only one position of the 2-fold disordered Ag5 atom is shown). Symmetry code: A $1-x$, $-y$, $1-z$. Selected bond lengths and distances (Å): C1−C2 1.212(5), Ag1···Ag2 2.779(1), Ag2···Ag3 3.354(1), Ag3···Ag4 3.087(1).

produce a (4,4) network parallel to the (−1 1 1) plane (Figure 2).

Interestingly, three of the five independent water molecules in **1** (O2W, O4W, and O5W) constitute a twist-boat water hexamer, which is bridged by an external bi-coordinated silver atom Ag6 and further stabilized by the hydrogen bonds between this water hexamer and two aqua ligands (O1W and O3W) upon the assistance of trifluoroacetate groups (O3−O4 and O7−O8) (Figure 1). Although such water hexamer extensively exists in a large number of crystalline compounds,[14] the water hexamer chain linked by metal atoms is rarely reported. These water hexamer chains are accommodated in a series of channels along the [001] direction of a three-dimensional (3-D) coordination network, which is constructed through the linkage of the (4,4) networks by remaining trifluoroacetate groups (Figure 3).

When we designed a ligand (right formula, group 1 in Scheme 1) complementary to 2,6-diethynylpyridine, it was anticipated that the nitrogen atoms at both sides of the ethynide moiety would connect with adjacent $-C\equiv C\supset Ag_n$ silver aggregates and extend along the N···N axis to generate an infinite coordination chain or a higher-dimensional network. In the crystal structure of 2-(AgC≡C)-pym·4AgCF$_3$CO$_2$ (**2**), atom Ag5 is

---

[14] (a) Custelcean, R.; Afloroaei, C.; Vlassa, M.; Polverejan, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3094–3096. (b) Moorthy, J. N.; Natarajan, R.; Venugopalan, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 3417–3420. (c) Doedens, R. J.; Yohannes, E.; Khan, M. I. *Chem. Commun.* **2002**, 62–63. (d) Venkataramanan, B.; James, W. L. G.; Vittal, J. J.; Suresh, V. *Cryst. Growth Des.* **2004**, *4*, 553–561. (e) Ma, B.-Q.; Sun, H.-L.; Gao, S. *Chem. Commun.* **2005**, 2336–2338. (f) Prasad, T. K.; Rajasekharan, M. V. *Cryst. Growth Des.* **2006**, *6*, 488–491. (g) Estrader, M.; Ribas, J.; Tangoulis, V.; Solans, X.; Font-Bardķa, M.; Maestro, M.; Diaz, C. *Inorg. Chem.* **2006**, *45*, 8239–8250. (h) Zhai, Q.-G.; Lu, C.-Z.; Chen, S.-M.; Xu, X.-J.; Yang, W.-B. *Inorg. Chem. Commun.* **2006**, *9*, 819–822.

disordered over two positions. The central ethynide moiety of the pyrimidinyl-2-ethynide ligand coordinates to four silver atoms in trigonal pyramidal geometry. As shown in Figure 4, two adjacent silver-ethynide aggregates are linked by nitrogen atom N1 of each 2-pyrimidylethynide ligand to form a ten-membered macrocycle. However, the other nitrogen atom N2 on the pyrimidine ring simply bonds to a peripheral silver atom Ag5 mostly because of the short Ag−N bond distance and crowded coordination environment. Instead, these macrocycles perpendicularly connect with each other by the linkage of two parallel [$Ag_2(CF_3CO_2)_2$] units composed of two silver atom (Ag3 and Ag4) and two independent trifluoroacetate groups (μ_2-{O1−O2} and μ_3-{O5−O6}), constituting a double silver chain along the *a* direction. Adjacent silver chains are further cross-bridged by the external silver atom Ag5 and two trifluoroacetate groups (μ_2-{O3−O4} and μ_3-{O7−O8}), finally resulting in a two-dimensional (2-D) coordination network parallel to the *ab* plane (Figure 5). Trifluoromethyl groups and pyrimidine rings protruding on both sides of the coordination plane hinder further linkage along the *c* direction to construct a 3-D network.

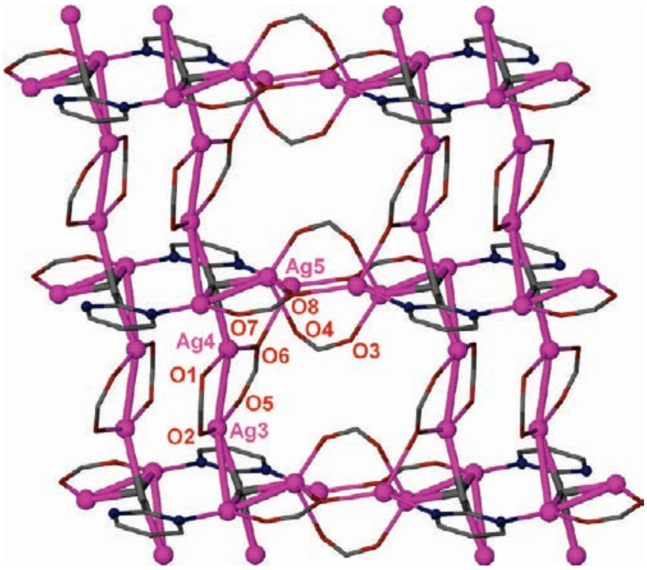


Figure 5. 2-D Coordination network in **2** cross-bridged by external silver atom Ag5 and trifluoroacetate groups O3−O4 and O7−O8.

In the crystal structure of 2,5-(AgC≡C)$_2$-py·4AgCF$_3$CO$_2$ (**3**), atoms Ag1, Ag2, Ag3, Ag4, and Ag5 are each disordered over two positions. Two independent ethynide groups (C1≡C2 and C8≡C9) of the pyridyl-2,5-diethynide ligand (left formula, group 2 in Scheme 1 shows the neutral form), which are located at opposite positions, adopt different modes to bond to a butterfly shaped Ag$_4$

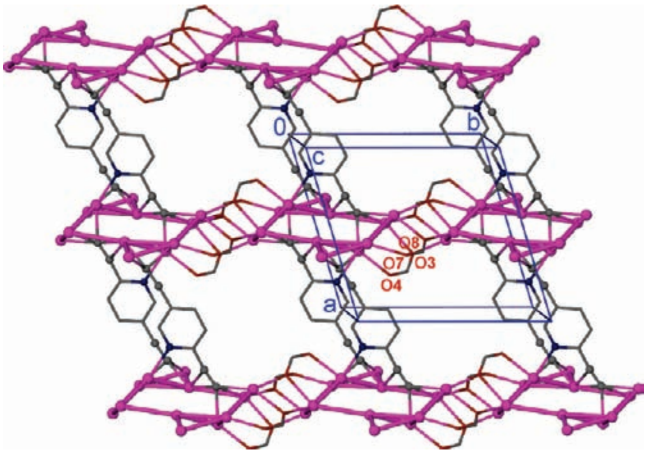


Figure 7. 2-D Coordination network parallel to the *ab* plane in complex **3** formed through the linkage of pyridyldiethynide-pillared silver chains by trifluoroacetate groups O3−O4 and O7−O8. Trifluoromethyl moieties and other ligands are omitted for clarity.

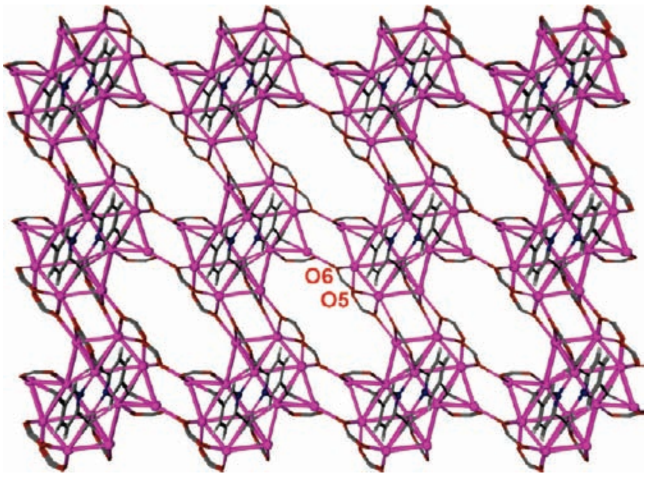


Figure 8. 3-D Coordination network in **3** viewed along the *a* axis.

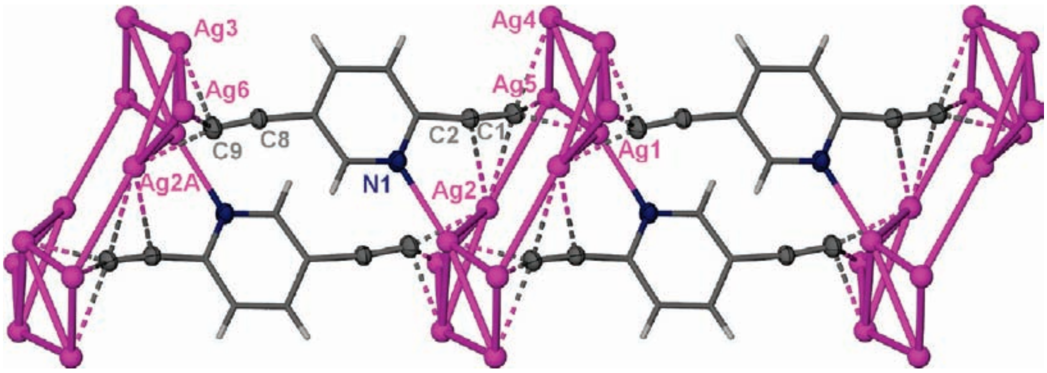


Figure 6. Twelve-membered silver aggregate with atom labeling in 2,5-(AgC≡C)$_2$-py·4AgCF$_3$CO$_2$ (**3**) (of disordered Ag1, Ag2, Ag3, Ag4, and Ag5 atoms, only one position of each is shown). Trifluoroacetate ligands are omitted for clarity. Symmetry code: A −*x*, −*y*, 1 − *z*. Selected bond lengths and distances (Å): C1−C2 1.211(8), C8−C9 1.226(8), Ag···Ag 2.821(2)−3.276(3).

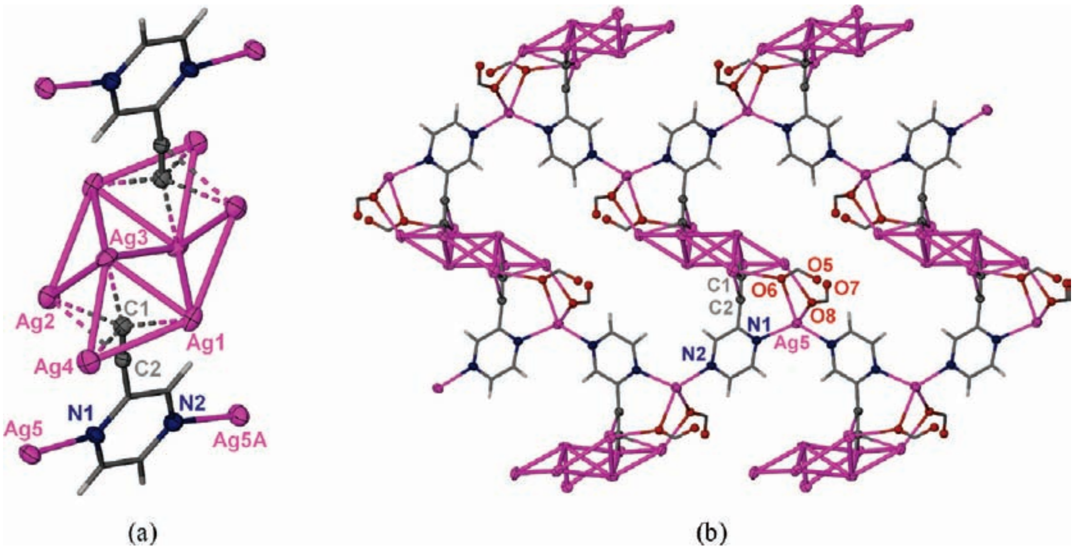


Figure 9. (a) Coordination modes of pyrazinyl-2-ethynide ligand with atom labeling (50% thermal ellipsoids; only one position of disordered Ag4 is shown) in 2-(AgC≡C)-pyz·$4AgCF_3CO_2\cdot H_2O$ (**4**). Symmetry code: A $1/2 + x$, $1/2 - y$, $1/2 + z$. Selected bond lengths and distances (Å): C1−C2 1.225(5), Ag1···Ag2 3.217(1), Ag1···Ag3 2.821(1), Ag1···Ag4 3.018(3), Ag1···Ag3′ 3.275(1), Ag2···Ag3 2.913(1), Ag3···Ag4 2.921(3), Ag3···Ag3′ 3.004(1). (b) 2-D coordination network in **4** containing a series of 32-membered macrocycles.

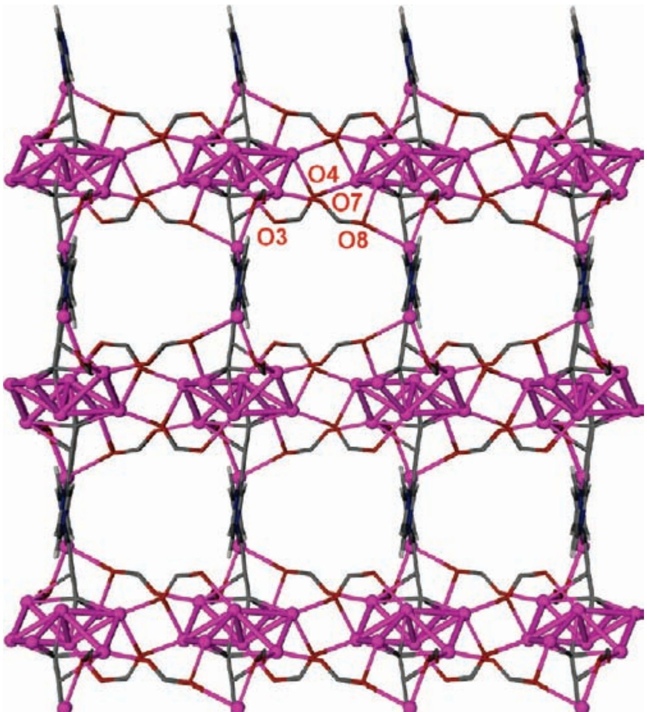


Figure 10. 3-D coordination network in **4** with a series of channels along the [1 0 1] direction.

basket and a trigonal Ag_3 aggregate, respectively (Figure 6). Two pairs of inversion-related Ag_3 and Ag_4 baskets condense mutually by sharing central silver atoms of type Ag2 to constitute a twelve-membered silver aggregate with four pyridyldiethynide ligands evenly located on both sides. The heterocyclic rings of two pyridyldiethynide ligands on the same side are parallel to each other and stabilized by mild $\pi\cdots\pi$ interaction (shortest carbon to carbon distance = 3.24 Å). Further prolongation through the linkage of a series of pyridyldiethynide-pillared Ag_{12} aggregates results in the formation of a silver chain, in which the nitrogen atom N1 points inward and bonds to an adjacent Ag_{12} aggregate to consolidate the whole silver chain. Furthermore, these infinite silver chains are bridged by trifluoroacetate groups (O3−O4 and O7−O8) and their inversion-related units in a μ_3-η^1,η^2 mode to generate a (4,4) network parallel to the *ab* plane (Figure 7). Linkage of these 2-D coordination networks by a series of μ_3-η^1,η^2 trifluoroacetate groups of type O5−O6 along the *c* direction gives rise to a 3-D coordination network (Figure 8).

We subsequently investigated the coordination mode and supramolecular architecture construction of 2-ethynylpyrazine (right formula, group 2 in Scheme 1), the complementary ligand of 2,5-diethynylpyridine in **3**. In the crystal structure of 2-(AgC≡C)-pyz·$4AgCF_3CO_2\cdot H_2O$ (**4**), atom Ag4 is disordered over two positions. The ethynide moiety of the pyrazinyl-2-ethynide ligand is also enveloped by a butterfly shaped Ag_4 basket (Figure 9a). Nevertheless, two nitrogen atoms of the pyrazinyl ring each directly bonds to an external silver atom of type Ag5, thus forming a zigzag silver-pyrazinyl string with a series of pendant silver-ethynide aggregates. On the other hand, pairs of Ag_4 baskets of adjacent zigzag chains fuse together through Ag···Ag interactions to generate an octanuclear aggregate. Consequently, these Ag_8 aggregates are fastened by ethynide moieties and linked by the silver-pyrazinyl string to produce a 2-D coordination network parallel to the (1 0 −1) plane, in which a series of remarkable 32-membered macrocycles are acquired by use of three different connection geometries between the ethynide moiety and nitrogen atoms on the pyrazinyl ring: 60° between N1 and C1≡C2, 120° between N2 and C1≡C2, and 180° between N1 and N2 (Figure 9b). Two trifluoroacetate groups O5−O6 and O7−O8 acting as adhesive ligands are used to consolidate this 2-D network. Adjacent 2-D networks are further linked by μ_3 trifluoroacetate groups O3−O4 and O7−O8 to produce a 3-D coordination network with channels directed along the [1 0 1] direction (Figure 10).

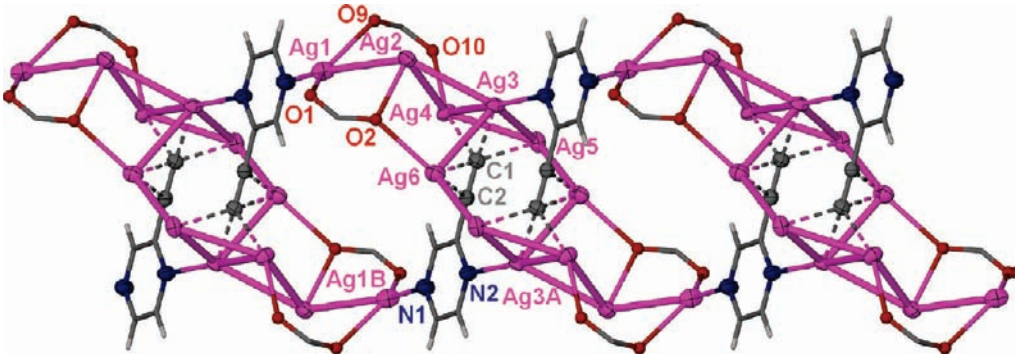


Figure 11. Twelve-membered silver aggregate with atom labeling (50% probability level) and a double-strand silver chain in 2-$(AgC{\equiv}C)$-pyz$\cdot$5-$AgCF_3CO_2\cdot Me_3NCH_2CO_2\cdot 2H_2O$ (**5**). Symmetry code: A $1-x, -y, 1-z$; B $1-x, 1-y, 1-z$. Selected bond lengths and distances (Å): C1−C2 1.214(5), Ag1$\cdots$Ag2 3.152(1), Ag2$\cdots$Ag3 3.156(1), Ag2$\cdots$Ag4 3.054(1), Ag3$\cdots$Ag4 2.924(1), Ag3$\cdots$Ag5 2.884(1), Ag3$\cdots$Ag6 2.985(1), Ag4$\cdots$Ag5 3.045(1), Ag5$\cdots$Ag6 3.060(1).

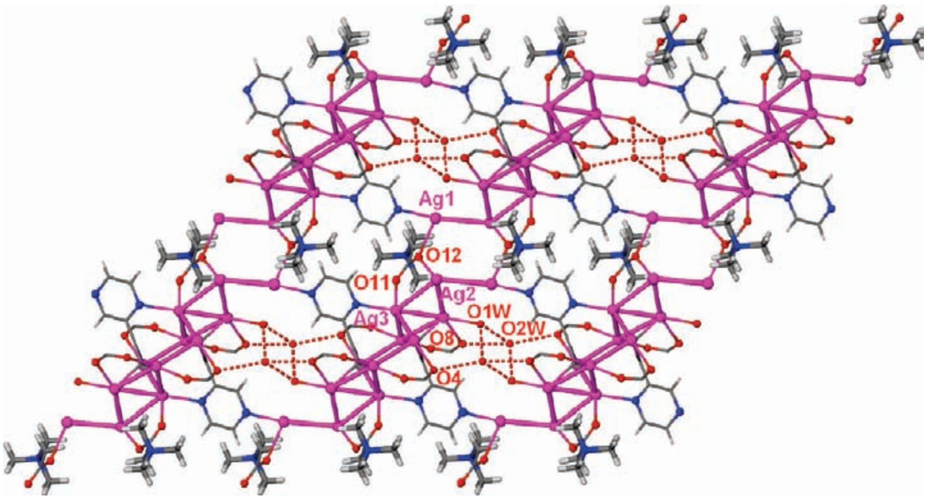


Figure 12. 2-D Coordination network in complex **5** constituted through the linkage of double-strand silver chains by betaine ligands (O11−O12). Hydrogen bonds (Å): O1W−O2W 2.855, O1W−O2WA 2.839, O2W−O4 2.984, O2W−O8 2.863.

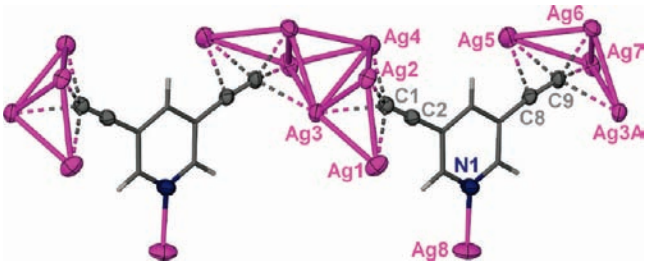


Figure 13. Coordination mode of 3,5-diethynidepyridine ligand with atom labeling (50% thermal ellipsoid) in 3,5-$(AgC{\equiv}C)_2$-py$\cdot 6AgCF_3CO_2\cdot 3.5$-$H_2O$ (**6**). Symmetry code: $1+x, y, z$. Selected bond lengths and distances (Å): C1−C2 1.206(7), C8−C9 1.206(7), Ag1$\cdots$Ag2 3.003(1), Ag1$\cdots$Ag3 2.984(1), Ag2$\cdots$Ag3 2.831(1), Ag2$\cdots$Ag4 2.998(1), Ag3$\cdots$Ag4 2.992(1), Ag3$\cdots$Ag6 2.971(1), Ag3$\cdots$Ag7 2.911(1), Ag4$\cdots$Ag6 2.995(1), Ag4$\cdots$Ag7 3.136(1), Ag5$\cdots$Ag6 3.252(1), Ag5$\cdots$Ag7 3.076(1), Ag6$\cdots$Ag7 2.838(1).

With the addition of a bulky neutral ligand $Me_3NCH_2CO_2$ to the silver trifluoroacetate aqueous solution of $[2\text{-}(AgC{\equiv}C)\text{-pyz}]_n$, pale-yellow crystals of 2-$(AgC{\equiv}C)$-pyz$\cdot 5AgCF_3CO_2\cdot Me_3NCH_2CO_2\cdot 2H_2O$ (**5**) were deposited after one week evaporation in ambient environment. The ethynide moiety C1≡C2 is surrounded by a Ag_4 aggregate as in **4**, which connects with another inversion-related four-membered silver aggregate via Ag$\cdots$Ag interaction. On the other hand, a disilver unit of Ag1−Ag2 attaches on this eight-membered silver segment by Ag$\cdots$Ag interaction together with the connection of two trifluoroacetate groups μ_3-{O1−O2} and μ_2-{O9−O10}, thus constituting a Ag_{12} aggregate. As shown in Figure 11, nitrogen atoms of type N1 and N2 of the four pyrazinyl rings located on both sides of the Ag_{12} aggregate serve as a pair of linking nodes at each side to connect these silver aggregates, therefore yielding a double-strand silver chain along the *b* direction. The bonding fashion of pyrazinyl-ethynide ligand in **5** can be figured as the pyrazinyl-ethynide ligand in **4** undergoing a 180° rotation with respect to the $C{-}C{\equiv}C$ axis. This variation may be due to the steric hindrance of the bulky neutral ligand $Me_3NCH_2CO_2$. Furthermore, the additional betaine ligand of O11−O12 herein acts as a μ_3-η^1,η^2 linking unit to hold these silver chains, consequently leading to the generation of a 2-D coordination network parallel to the *ab* plane (Figure 12). The trimethylammonio moiety of the betaine ligand lies perpendicular to this plane, protruding on both sides to prevent the further linkage of these 2-D networks. In addition, a rhomboid-like water tetramer composed of aqua ligands (O1W) and water molecules (O2W) are stabilized between two pyrazinyl rings via their hydrogen bonds with trifluoroacetate groups of type O3−O4 and O7−O8.

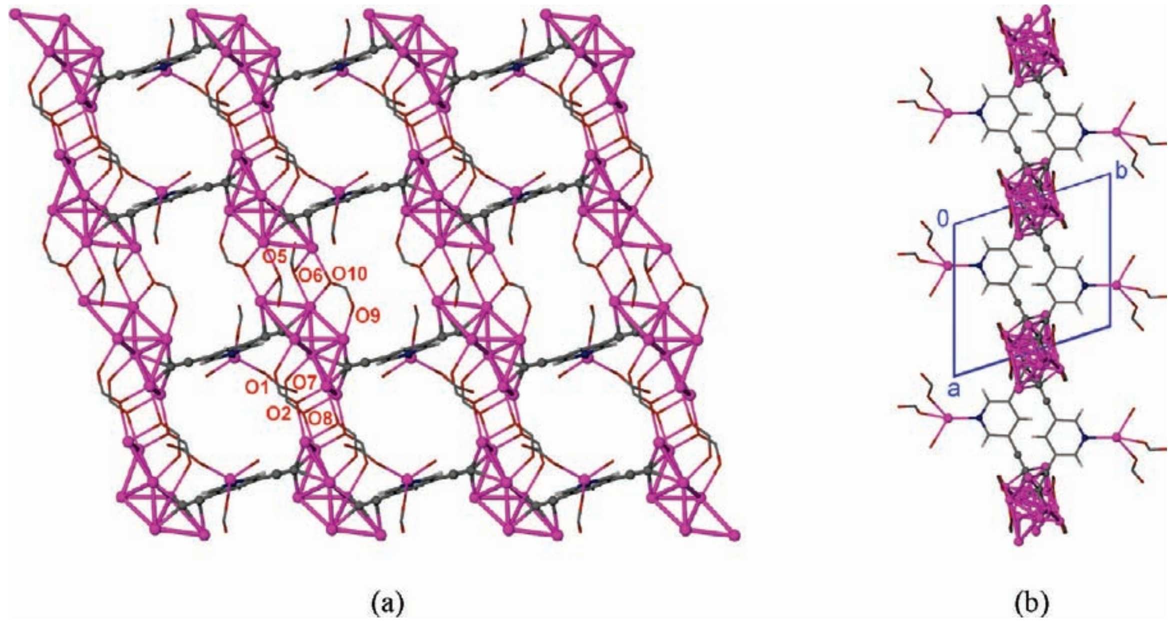


Figure 14. (a) 2-D Coordination network in **6** linked by a series of trifluoroacetate groups and pyridyl-3,5-diethynide ligands. (b) Side view of the 2-D network along the *c* direction.

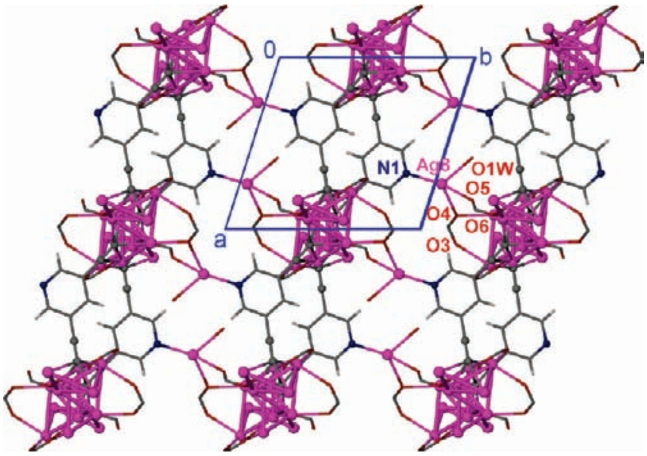


Figure 15. 3-D Coordination network in **6** constructed through the linkage of 2-D networks by pyridyl-3,5-diethynide ligands and trifluoroacetate groups (O3−O4 and O5−O6).

We next considered a more even distribution of nitrogen atoms and ethynide substituents on the heterocyclic ring and investigated the bonding modes and coordination network construction using the ligand pair 3,5-diethynylpyridine and 5-ethynylpyrimidine (left and right formula, respectively, group 3 in Scheme 1). In the silver double salt 3,5-$(AgC\equiv C)_2$-py$\cdot 6AgCF_3CO_2\cdot 3.5H_2O$ (**6**), two ethynide moieties ($C1\equiv C2$ and $C8\equiv C9$) each coordinates to a tetranuclear aggregate via the μ_4-η^1 and μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$ modes, respectively. Two tetranuclear aggregates of adjacent 3,5-diethynidepyridine ligands coalesce together by sharing silver atom Ag3 to produce a Ag_7 segment. As shown in Figure 13, the linkage of the Ag_7 segments by continuous silver-ethynide interaction yields an infinite silver chain with a peripheral silver atom Ag8 attaching on it via the coordination of nitrogen atom N1. Notably, the present Ag_7-$(C\equiv C)_2$ aggregate differs from the Ag_{11}-$(C\equiv C)_4$ aggregate in the reported silver double salt 3,5-$(AgC\equiv C)_2$-py$\cdot 4AgCF_3CO_2\cdot 4H_2O$.[8] This can be explained by the fact that fusion of the $C\equiv C\supset Ag_4$ fragments in the latter complex occurs to a greater extent on account of the lower silver ion concentration employed in its synthesis and method of crystallization.

Adjacent pyridylethynide-bridged silver chains are further connected by a series of trifluoroacetate groups (O1−O2, O5−O6, O7−O8, and O9−O10) and their inversion-related ones via the μ_3-O,O',O', μ_2-O,O, μ_3-O,O',O', and μ_3-O,O',O' mode, respectively, to form a 2-D network parallel to the *ac* plane (Figure 14). Each pyridyl group rooted on this 2-D network protrudes outward to coordinate to the external silver atom Ag8, which connects with an adjacent 2-D network via two bridging trifluoroacetate groups (O3−O4 and O5−O6) to form a 3-D coordination network (Figure 15). This structural feature is comparable with that of 3,5-$(AgC\equiv C)_2$-py$\cdot 4AgCF_3CO_2\cdot 4H_2O$,[8] in which the resulting layers are also bridged by N(pyridyl)−Ag−N(pyridyl) units to afford a 3-D coordination network.

In 5-$(AgC\equiv C)$-pym$\cdot 3AgCF_3CO_2\cdot 3H_2O$ (**7**), the butterfly shaped Ag_4 cap of ethynide group $C1\equiv C2$ on the pyrimidine ring is connected by nitrogen atoms of two other pyrimidine rings, thus leading to the formation of a honeycomb structure, wherein each hexagon is composed of three Ag_4 aggregates and three pyrimidinyl-5-ethynide ligands (Figure 16). Extension of this honeycomb metallacycle eventually results in a (6,3) coordination layer. These coordination layers are then bridged by trifluoroacetate groups (O3−O4 and O5−O6) via the μ_3-O,O',O' mode to generate a 3-D coordination network similar to that in complex **4** (Supporting Information, Figure S1). A series of infinite channels directed along the *c* direction accommodate the CF_3 moieties of the trifluoroacetates.

Silver Aggregate. Structure characterization of silver complexes **1**−**7** showed that the nuclearity numbers of silver aggregates therein vary within a broad range from 4 to 12 in the presence of different heteroaryl ethynide ligands.

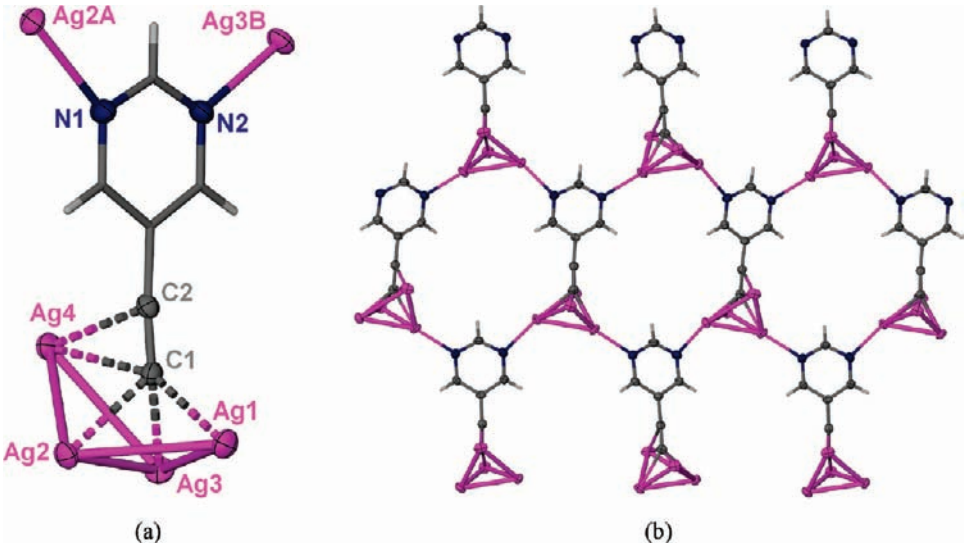


Figure 16. (a) Coordination modes of pyrimidinyl-5-ethynide ligands with atom labeling (30% possibility) in 5-(AgC≡C)-pym·3AgCF$_3$CO$_2$·3H$_2$O (**7**). Symmetry code: A $x - 1/2$, $1\frac{1}{2} - y$, $1 - z$; B $-1/2 + x$, y, $1\frac{1}{2} - z$. Selected bond lengths and distances (Å): C1−C2 1.221(6), Ag1···Ag3 2.873(1), Ag1···Ag2 2.920(1), Ag2···Ag3 2.899(1), Ag2···Ag4 3.211(1), Ag3···Ag4 3.019(1). (b) Honeycomb layer in **7**.

Two generalizations can be formulated from a scrutinized analysis of their crystal structures. (1) For the pyridyldiethynide ligands in **3** and **6**, each ethynide moiety is embraced by a Ag$_n$ (n = 3, 4) aggregate, which coalesces with the other one (in **6**) or more (in **3**) aggregate(s) to constitute a larger aggregate of higher nuclearity. In conformity with the structures of analogous phenylenediethynide silver complexes,[3a] the fusion of two or more $-\mathrm{C{\equiv}C{\supset}Ag}_n$ (n = 4, 5) synthons into a larger assembly decreases the number of silver atoms required for putting a Ag$_n$ cap on each ethynide terminal, which is a pivotal prerequisite for dissolving the corresponding polymeric starting material [R−(C≡CAg)$_{1-2}$]$_n$ in an aqueous solution. In other words, this kind of aggregation lessens the rigorous requirement of a high concentration of silver ions. (2) The positioning of nitrogen atom(s) relative to ethynide(s) also has a crucial impact on the formation of multinuclear silver aggregates. A nitrogen atom located next to the ring carbon atom carrying an ethynide moiety readily coordinates to a silver atom, which may connect with the $-\mathrm{C{\equiv}C{\supset}Ag}_n$ (n = 4, 5) aggregate through argentophilic interaction to yield a higher-nuclearity aggregate. This bonding arrangement gives rise to a dumbbell-like Ag$_9$ aggregate in **1** and a twelve-membered silver aggregate in **3** and **5**.

Silver Chain and 2-D Coordination Network. Six tridentate heteroaryl ethynide ligands are herein employed to construct silver(I) coordination networks by virtue of the relative positions of three bonding sites on the corresponding heterocyclic ring. The concentration of all three bonding sites on one side of the pyridyl-2,6-diethynide ligand in **1** prevents further linkage of the resulting Ag$_9$ aggregate by the pyridyl nitrogen atom; instead, such aggregates are interconnected by trifluoroacetate groups to generate a 3-D coordination network. Similar bonding fashion is also adopted by the pyrimidinyl-2-ethynide ligand in complex **2**; short Ag−N bonding distance and crowded coordination environment of $-\mathrm{C{\equiv}C{\supset}Ag}_4$ species block their mutual connection, resulting only in a ten-membered macrocycle. Moving one bonding site away from the other two leads to the formation of an infinite silver chain in **3** and **5** bridged by heteroaryl ethynide ligands, and a 2-D coordination network in **4**. Finally, an even distribution of three ligation sites on the six-membered nitrogen heterocycle maximizes their linkage efficiency to condense the silver aggregates, consequently forming a trifluoroacetate-bridged 2-D coordination network in **6** and a well-programmed honeycomb-like 2-D network in **7**.

Conclusion

In summary, the present work has investigated the coordination modes of three pairs of complementary tridentate heteroaryl ethynide ligands to silver(I) and demonstrated that the relative locations and bonding preference between the ethynide substitutent(s) and ring nitrogen atom(s) can act as controlling factors to direct the formation of multidimensional coordination networks. Two combinations of three bonding sites on the six-membered heterocycle—one nitrogen atom and two ethynide groups or two nitrogen atoms and one ethynide moiety, lead to specific types of structure building units, such as a discrete multinuclear silver-ethynide aggregate in **1** and **2**, a heteroaryl ethynide-bridged infinite silver chain in **3**, **5** and **6**, and a heteroaryl ethynide-connected 2-D coordination network in **4** and **7**. Consequently, this type of ligand design strategy offers a viable means to control the nuclearity and geometry of silver-ethynide aggregates that dictate the assembly of multidimensional coordination networks.

Acknowledgment. This work is supported by the Hong Kong Research Grants Council (GRF ref. No. CUHK 402405 and 402408) and the Wei Lun Foundation.

Supporting Information Available: Structure refinement details and Figure S1 of **7**. X-ray crystallographic data for **1**−**7** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.