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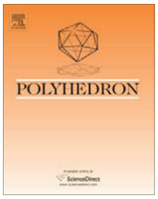

Coordination networks constructed with supramolecular synthon R_X–C≡C⊃Ag_n ($n = 4, 5$; R_X = halophenyl)

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Eight new silver(I) double salts: $AgL^1{\cdot}2AgCF_3COO$ (**1**), $AgL^1{\cdot}3AgNO_3$ (**2**), $2AgL^2{\cdot}5AgCF_3COO{\cdot}2CH_3CN{\cdot}H_2O$ (**3**), $4AgL^3{\cdot}6AgCF_3COO{\cdot}5CH_3CN$ (**4**), $4AgL^4{\cdot}6AgCF_3COO{\cdot}5CH_3CN$ (**5**), $2AgL^5{\cdot}4AgCF_3COO{\cdot}NC(CH_2)_4CN$ (**6**), $2AgL^5{\cdot}4AgCF_3COO{\cdot}2CH_3CN$ (**7**) and $AgL^6{\cdot}2CF_2(CF_2COOAg)_2{\cdot}2CH_3CN$ (**8**) (L^1 = 4-iodophenylethynide; L^2 = 3,4-dichlorophenylethynide; L^3 = 3-chlorophenylethynide; L^4 = 3-bromophenylethynide; L^5 = 2-chlorophenylethynide; L^6 = 2-fluorophenylethynide) have been synthesised and characterized by X-ray crystallography. All compounds contain the silver–halophenylethynide supramolecular synthon R_X–C≡C⊃Ag_n ($n = 4, 5$). In particular, the three-dimensional supramolecular structures in **1** and **2** are stabilized by strong Ag···I interactions, while that in **3** is consolidated by both Ag···Cl and van der Waals type F···Cl interactions. In isomorphous compounds **4** and **5**, the presence of respective F···Cl or F···Br contact contributes to the stability of the network. The silver aggregates in **6**, **7** and **8** are stabilized by Ag···Cl or Ag···F interactions between the *ortho*-halo substituent and the Ag_n basket.

1. Introduction

The silver(I) cation, like other easily-polarizable metal cations, tends to associate with 'soft' non-metals such as sulfur, selenium, tellurium and iodine. Accordingly, intermolecular interactions of the type Ag···X (X = F, Cl, Br, I) have been used in the design and assembly of supramolecular structures [1]. Besides using halogen ions in their bare forms [2], several reports have demonstrated the feasibility of using X-aryl moieties to incorporate silver···halogen interactions into coordination networks. The Ag···I-aryl interaction (with Ag···I distances in the range of 2.719–3.357 Å) commonly occurs [1], while Ag···Br-aryl and Ag···Cl-aryl are less studied [3], and Ag···F-aryl is rarely reported.

In recent years, we have carried out a systematic investigation on the construction of silver–organic coordination networks based on silver–ethynide supramolecular synthons, which comprise silver aggregates stabilized by argentophilicity and silver–ethynide interactions of the σ, π and mixed (σ, π) types [4]. Among the compounds studied thus far, two examples exhibit significant silver···halogen interaction involving the F^- and $PF_2O_2^-$ ions [5]. Therefore, it is of interest to us to investigate the role played by the silver···halogen interactions in coordination network assembly based on the silver–ethynide supramolecular synthon [4b,6]. In this paper, we report the synthesis and structure characterization of eight new silver(I) halophenylethynide complexes: $AgL^1{\cdot}2AgCF_3COO$ (**1**), $AgL^1{\cdot}3AgNO_3$ (**2**), $2AgL^2{\cdot}5AgCF_3COO{\cdot}2CH_3CN{\cdot}H_2O$ (**3**), $4AgL^3{\cdot}6AgCF_3COO{\cdot}5CH_3CN$ (**4**), $4AgL^4{\cdot}6AgCF_3COO{\cdot}5CH_3CN$ (**5**), $2AgL^5{\cdot}4AgCF_3COO{\cdot}NC(CH_2)_4CN$ (**6**), $2AgL^5{\cdot}4AgCF_3COO{\cdot}2CH_3CN$ (**7**) and $AgL^6{\cdot}2CF_2(CF_2COOAg)_2{\cdot}2CH_3CN$ (**8**) (L^1 = 4-iodophenylethynide; L^2 = 3,4-dichlorophenylethynide; L^3 = 3-chlorophenylethynide; L^4 = 3-bromophenylethynide; L^5 = 2-chlorophenylethynide; L^6 = 2-fluorophenylethynide), which are stabilized by both silver(I)–ethynide and silver(I)···halogen interactions. In addition, C—H···X (X = Br, Cl) hydrogen bonds exist in **4** and **5**, respectively, and multiple halogen···halogen van der Waals interactions contribute to network stabilization in **3**, **4**, **5** and **6**.

2. Experimental

2.1. General

All chemicals are used as received from Aldrich® with no further purification. Degassing and desiccation are not performed for solvents of analytical reagent grade.

2.1.1. Synthesis of polymeric silver(I) halophenylethynides

$[AgL^1]_n$. (4-Iodophenylethynyl)trimethylsilane (1.00 g, 3.33 mmol) was dissolved in a mixed solvent of 20 mL acetonitrile, 2 mL triethylamine and 40 mL methanol, to which was subsequently added 10 mL acetonitrile solution containing dissolved silver nitrate (0.623 g, 3.66 mmol). A white precipitate formed immediately. After stirring for 10 h, the crude polymeric product was filtered off and washed with 20 mL acetonitrile, 10 mL diethyl

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ether and 10 mL distilled water trice, and then stored under −10 °C in wet form. Yield: 72% (based on TMS-C$\equiv$CPhI-4). IR: $\nu = 2034\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

$[AgL^2]_n$. 3,4-Dichlorophenylacetylene (1.00 g, 5.85 mmol) was dissolved in a mixture of 2 mL triethylamine and 60 mL acetonitrile, to which a 10 mL acetonitrile solution of silver nitrate (1.00 g, 5.88 mmol) was subsequently added. After stirring for 10 h, the crude polymeric salt was filtered off and washed with 20 mL acetonitrile and 10 mL distilled water trice, and then stored under −10 °C in wet form. Yield: 80%, IR: $\nu = 2026\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$). Similar procedures were conducted in obtaining the following four crude polymeric silver salts.

$[AgL^3]_n$. This material was prepared employing 3-chlorophenylacetylene. Yield: 80%, IR: $\nu = 2010\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

$[AgL^4]_n$. This material was prepared employing 3-bromophenylacetylene. Yield: 80%, IR: $\nu = 2010\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

$[AgL^5]_n$. This material was prepared employing 2-chlorophenylacetylene. Yield: 60%, IR: $\nu = 2025\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

$[AgL^6]_n$. This material was prepared employing 2-fluorophenylacetylene. Yield: 56%, IR: $\nu = 2054\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

2.1.2. Synthesis of silver(I) halophenylethynide complexes

*2.1.2.1. $AgL^1\cdot 2AgCF_3COO$ (**1**).* $AgBF_4$ (0.384 g, 2 mmol) and $AgCF_3COO$ (0.220 g, 1 mmol) were dissolved in 1 mL distilled water, and subsequently $[AgL^1]_n$ (~0.050 g) was added. The mixture was stirred vigorously for 1 h. During that time, 0.1 mL acetonitrile was introduced. The undissolved solid was then filtered off, and the filtrate stored under 25 °C in the dark. Crystallization happened two weeks later. Elemental Analysis (calculated): C: 18.78% (18.56%), H: 0.51% (0.52%). IR: $\nu = 2032\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

*2.1.2.2. $AgL^1\cdot 3AgNO_3$. (**2**).* $AgNO_3$ (0.600 g, 3.5 mmol) was dissolved in a mixture of 1 mL distilled water and 0.2 mL acetonitrile, and subsequently $[AgL^1]_n$ (~0.050 g) was added. The mixture was stirred for 1 h. The undissolved solid was then filtered off, and the filtrate was stored under 25 °C in the dark. Crystallization happened two weeks later. Elemental Analysis (calculated): C: 11.16% (11.38%), H: 0.50% (0.48%). IR: $\nu = 2022\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

*2.1.2.3. $2AgL^2\cdot 5AgCF_3COO\cdot 2CH_3CN\cdot H_2O$ (**3**).* $AgBF_4$ (0.384 g, 2 mmol) and $AgCF_3COO$ (0.220 g, 1 mmol) were dissolved in 1 mL distilled water, and subsequently $[AgL^2]_n$ (~0.050 g) was added. The mixture was stirred vigorously for 1 h. During that time, 0.1 mL acetonitrile was introduced. The undissolved solid was then filtered off, and the filtrate stored under 25 °C in the dark. Small plate-like crystals were obtained two months later. Elemental analysis (calculated): C: 20.30% (20.45%), H: 1.06% (0.92%), IR: $\nu = 2048\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

*2.1.2.4. $4AgL^3\cdot 6AgCF_3COO\cdot 5CH_3CN$ (**4**).* $AgBF_4$ (0.384 g, 2 mmol) and $AgCF_3COO$ (0.220 g, 1 mmol) were dissolved in 1 mL distilled water, and subsequently $[AgL^3]_n$ (~0.050 g) was added. The mixture was stirred vigorously for 1 h. During that time, 0.4 mL acetonitrile was introduced. The undissolved solid was then filtered off, and the filtrate stored under 25 °C in the dark. Plate-like crystals were obtained in one week. Elemental analysis (calculated): C: 25.75% (25.90%), H: 1.40% (1.25%). IR: $\nu = 2065,\ 2000\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

*2.1.2.5. $4AgL^4\cdot 6AgCF_3COO\cdot 5CH_3CN$ (**5**).* $AgBF_4$ (0.384 g, 2 mmol) and $AgCF_3COO$ (0.220 g, 1 mmol) were dissolved in 1 mL distilled water, and subsequently $[AgL^4]_n$ (~0.050 g) was added. The mixture was stirred vigorously for 1 h. During that time, 0.4 mL acetonitrile was introduced. The undissolved solid was then filtered off, and the filtrate stored under 25 °C in the dark. Needle-like crystals were obtained in one week. Elemental analysis (calculated): C: 23.85% (24.18%), H: 1.28% (1.16%). IR: $\nu = 2048,\ 2012\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

*2.1.2.6. $2AgL^5\cdot 4AgCF_3COO\cdot NC(CH_2)_4CN$ (**6**).* $AgBF_4$ (0.384 g, 2 mmol) and $AgCF_3COO$ (0.220 g, 1 mmol) were dissolved in the mixture of 1 mL distilled water, 0.5 mL acetonitrile and 0.1 mL adiponitrile, to which $[AgL^5]_n$ (~0.050 g) was added subsequently. The mixture was stirred for 4 h. The undissolved solid was then filtered off. Colorless block-like crystals were formed one week later. Elemental analysis (calculated): C: 24.21% (24.37%), H: 1.20% (1.09%). IR: $\nu = 2041\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

*2.1.2.7. $2AgL^5\cdot 4AgCF_3COO\cdot 2CH_3CN$ (**7**).* $AgBF_4$ (0.384 g, 2 mmol) and $AgCF_3COO$ (0.220 g, 1 mmol) were dissolved in 1 mL distilled water, and subsequently $[AgL^5]_n$ (~0.050 g) was added. The mixture was stirred vigorously for 1 h. During that time, 0.4 mL acetonitrile was introduced. The undissolved solid was then filtered off, and the filtrate stored under 25 °C in the dark. Plate-like crystals were obtained in one week. Elemental analysis (calculated): C: 23.19% (23.15%), H: 1.10% (0.97%). IR: $\nu = 2058\ \text{cm}^{-1}$ ($\nu_{C\equiv C}$).

*2.1.2.8. $AgL^6\cdot 2Ag_2C_3F_6(COO)_2\cdot 2CH_3CN$ (**8**).* $AgBF_4$ (0.384 g, 2 mmol), hexafluoroglutaric acid (0.120 g, 0.5 mmol) and Ag_2O (0.116 g, 0.5 mmol) were dissolved in a mixture of 1 mL distilled water and 0.2 mL acetonitrile, to which $[AgL^6]_n$ (~0.050 g) was added subsequently. The mixture was stirred for 4 h and filtered afterwards. Colorless needle-like crystals were formed after two weeks. Elemental analysis (calculated): C: 21.81% (21.72%), H: 1.00% (0.83%). IR: $\nu = 2057\ \text{cm}^{-1}$ (w, $\nu_{C\equiv C}$).

2.2. X-ray crystallography

Selected crystals were used for data collection on a BrukerAXS Kappa APEX2 CCD diffractometer at 293 K using frames of oscillation range 0.5° (Phi scan and Omega scan) with $2° < \theta < 28°$ (compound **1**, **2**, **3**, **6**, **7**, **8**) or on a BrukerAXS SMART 1000 CCD diffractometer at 293 K using frames of oscillation range 0.3° (Omega scan) with $2° < \theta < 28°$ (compound **4**, **5**). Empirical absorption corrections based on multi-scan method were applied using the SADABS program [7]. The structures were solved by the direct method and refined by full-matrix least squares based on F^2 using the programs in SHELXTL package [8]. The crystal data and details of refinement are summarized in Table 1.

3. Results and discussion

3.1. $AgL^1\cdot 2AgCF_3COO$ (**1**)

As shown in Fig. 1, compound **1** features a centrosymmetric Ag_6 aggregate derived from two inversion-related Ag_4 baskets sharing one silver edge (Ag3⋯Ag3a). An ethynide group (C1$\equiv$C2) is attached to each Ag_4 basket in the μ_4–$\eta^2, \eta^2, \eta^1, \eta^1$ ligation mode. The distances between silver atoms range from 2.815(1) to 3.238(1) Å, suggesting the existence of significant argentophilic interaction. Such silver baskets and ethynide ligation mode are consistent with those in the previously established $R–C\equiv C\supset Ag_n$ ($n = 4, 5$) supramolecular synthon [4b,6].

The connection of Ag_6 aggregates by bridging trifluoroacetate ligands across crystallographic inversion centers gives rise to a two-dimensional coordination network, as shown in Figs. 1 and 2. The carboxyl group containing oxygen atoms (O3, O4) adopts the μ_4–O,O,O',O' ligation mode generates a centrosymmetric $(AgCF_3COO)_2$ unit (Fig. 2). The distance between two silver atoms (Ag1⋯Ag1a) within this unit is 2.993(1) Å, which lies within the argentophilic distance range; under such linkage, the silver

Table 1
Crystallographic data of compound **1**–**8**.

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{12}H_4O_4$ F_6IAg_3	$C_8H_4N_3O_9$ Ag_4I	$C_{30}H_{14}N_2O_{11}$ $Ag_7Cl_4F_{15}$	$C_{54}H_{31}N_5O_{12}$ $F_{18}Ag_{10}Cl_4$	$C_{54}H_{31}N_5O_{12}$ $F_{18}Ag_{10}Br_4$	$C_{30}H_{16}N_2O_8$ $Ag_6Cl_2F_{12}$	$C_{28}H_{14}N_2O_8$ $Ag_6Cl_2F_{12}$	$C_{22}H_{10}N_2O_8$ Ag_5F_{13}
Fw	776.66	844.52	1760.32	2504.34	2682.18	1478.57	1452.53	1216.67
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P* 1	*Cc*	*Cc*	*P* 1	*P* 1	*P* 1	*P* 1	*P* 1
a (Å)	8.3284(5)	8.9094(4)	23.416(1)	14.695(5)	14.846(5)	11.9499(4)	12.008(6)	9.2084(2)
b (Å)	10.0353(6)	25.562(1)	7.2186(4)	15.336(6)	15.362(5)	13.8333(4)	13.150(7)	13.3717(6)
c (Å)	11.0673(7)	7.1395(3)	27.567(2)	17.685(7)	17.715(5)	13.9590(4)	13.706(7)	13.9829(4)
α (°)	84.762(1)	90.00	90.00	73.350(5)	73.298(5)	114.503(1)	67.21(1)	113.748(1)
β (°)	74.189(1)	112.045(1)	102.212(2)	70.084(5)	70.934(5)	94.962(1)	81.68(1)	104.932(1)
γ (°)	71.732(1)	90.00	90.00	83.571(5)	84.054(5)	107.901(1)	80.18(1)	95.177(1)
V (Å^3)	845.11(9)	1507.1(1)	4554.3(4)	3590(2)	3657(2)	1936.1(1)	1959(2)	1485.7(1)
Z	2	4	4	2	2	2	2	2
Dc (mg/m^3)	3.052	3.722	2.567	2.317	2.436	2.536	2.463	2.720
Total reflection	28,642	26,840	49,585	24,230	20,845	70,980	79,851	23,152
Reflection [$I > 2\sigma(I)$]	2882	2675	7438	9689	7085	6457	5645	5423
Parameters	252	215	712	931	873	575	557	441
R_{int}	0.0271	0.0261	0.0397	0.0365	0.0536	0.0231	0.0426	0.0193
R_1 (obsd)	0.0271	0.0181	0.0336	0.0485	0.0689	0.0220	0.0380	0.0216
wR_2 (all)	0.0619	0.0431	0.0770	0.1334	0.1870	0.0481	0.0951	0.0538
S (GooF)	1.053	1.110	1.039	1.022	1.007	1.089	1.016	1.086
ρ_{max} (eÅ^{-3})	1.285	0.926	1.164	1.635	1.511	0.990	1.141	1.212
$-\rho_{min}$ (eÅ^{-3})	1.335	1.216	1.295	1.387	1.092	0.885	1.115	1.202

aggregates are extended into an infinite silver chain along the *a* direction. Furthermore, the Ag_6 aggregates in parallel silver chains are also cross-linked by the other independent trifluoroacetate ligand (containing O1, O2) acting in the μ_3–*O*,*O*,*O*′ mode to form a web-like layer in the *ab* plane, as shown in Figs. 1 and 2. It is notable that bridging between silver chains is assisted by silver···fluoro close contact. The bridged Ag2···F9 distance is 3.088(1) Å, being slightly shorter than the sum of van der Waals radii of F and Ag on the Bondi scale [9]. This kinds of close contact between silver and fluorine rarely occurs, though an example of this interaction was reported in our previous work on the crystal structure of $Ag_2C_4{\cdot}2AgF{\cdot}10AgC_2F_5CO_2{\cdot}CH_3CN{\cdot}12H_2O$ [5].

As shown in Fig. 3, the iodophenyl ethynide ligands are arrayed between the above-mentioned web-like layers, alternatively running parallel or anti-parallel with respect to the *c* axis. Their ethynide terminals are inserted into corresponding silver baskets, while

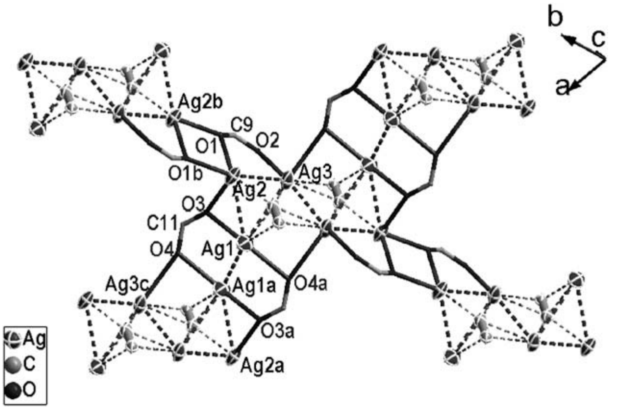


Fig. 2. Two-dimensional coordination network lying in the *ab* plane of complex **1**. CF_3 moieties of trifluoroacetate ions are omitted for clarity. Symmetry code: a 2 − *x*, −*y*, 1 − *z*; b 1 − *x*, 1 − *y*, 1 − *z*; c 1 + *x*, *y*, *z*.

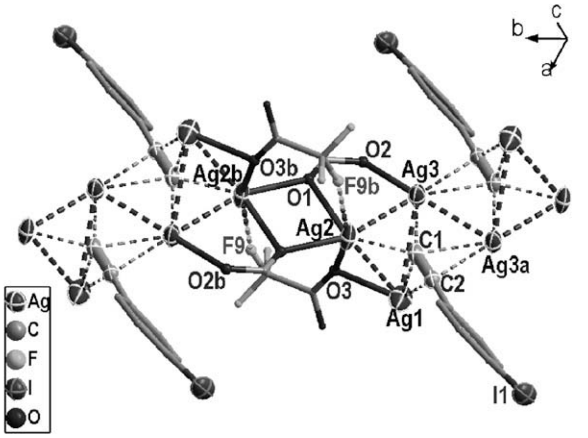


Fig. 1. Two Ag_6 aggregates in complex **1**, which are linked by carboxyl groups and Ag···F close contacts. For clarity, some CF_3 moieties of trifluoroacetate anions and all hydrogen atoms are omitted. Selected bond lengths [Å]: C1≡C2 1.222(6), C1···Ag1 2.341(5), C1···Ag2 2.164(5), C1···Ag3 2.253(4), C1···Ag3a 2.523(5), C2···Ag1 2.842(5), C2···Ag3a 2.673(5), Ag1···Ag2 3.026(1), Ag1···Ag3 3.238(1), Ag2···Ag3 2.781(1), Ag3···Ag3a 2.815(1). Symmetry code: a 1 − *x*, −*y*, 1−*z*; b 1 − *x*, 1 − *y*, 1 − *z*.

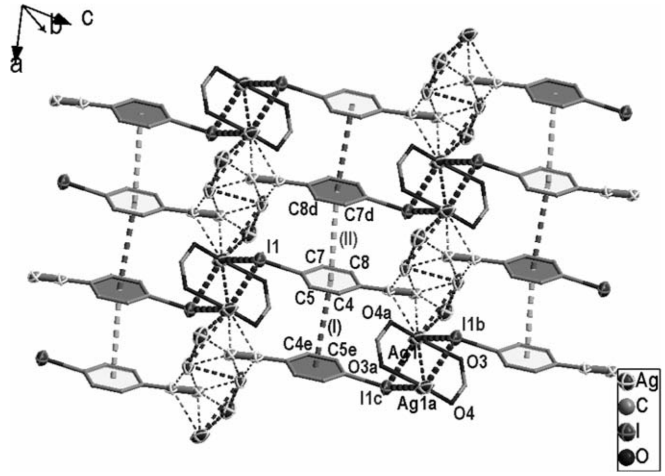


Fig. 3. Packing diagram of complex **1** in the *ac* plane. Trifluoroacetate anions are omitted for clarity, except for one bridging carboxyl moiety. Symmetry code: a 2 − *x*, −*y*, 1 − *z*; b *x*, *y*, 1 + *z*; c 2 − *x*, −*y*, −*z*; d 1 − *x*, −*y*, −*z*; e 2 − *x*, −*y*, −*z*.

each iodophenyl group is coordinated to a pair of silver atoms of the $(AgCF_3COO)_2$ structural unit by adopting the μ_2–*I* mode. The distance between silver and iodine atoms are 2.906(1) Å (Ag1···I1c) and 3.394(1) Å (Ag1···I1b), indicating the presence of strong silver···iodine interactions. The interlaced phenyl rings are stacked via two types of edge-to-edge π···π interaction of intermediate strength [6b]: C4–C5···C5e–C4e 3.670(1) Å and C7–C8···C8d–C7d 3.563(1) Å. The corresponding center-to-center distances of adjacent phenyl rings are 4.149(1) Å (**I**) and 4.199(1) Å (**II**). Thus the iodophenyl ethynide ligands connect the web-like layers altogether to generate a 3D network.

3.2. $AgL^1\cdot 3AgNO_3$ (**2**)

In the non-centrosymmetric structural unit (Fig. 4) of compound **2**, the ethynide group (C1≡C2) inserts into a stand-alone Ag_4 basket in the μ_4–$\eta^2, \eta^2, \eta^1, \eta^1$ ligation mode, being similar to that in complex **1**. The distances between the silver atoms range from 2.909(1) to 3.021(1) Å. Three of the four silver atoms are coordinated by nitrate ions. There is one intramolecular C—H···O hydrogen bond between C8 and O9, in which the C···O distance is 3.177(6) Å and ∠OHC is 165°.

As shown in Fig. 4, adjacent structural units in compound **2** are linked by nitrate ions (upper limit of Ag—O bonding distance taken as 2.61 Å) [10] and silver···iodo interactions in the μ_2–*I* mode: each unit is connected to twelve neighboring ones (see Supplementary Material) to yield a three-dimensional network directly. The Ag···I distances are 3.211(1) Å for Ag1···I1 and 2.814(1) Å for Ag4···I1, respectively. With reference to the van der Waals radii of silver (1.72 Å) and iodine (1.95 Å) on the Bondi scale [9], the two contacts are ranked as strong silver···iodo interactions.

Along the *b* direction, the contents in the *ac* plane are arranged in the infinite sequence: silver baskets, nitrate ions, silver baskets, organic ligands, ... As shown in Fig. 5, the phenyl rings are interlaced by 60° and stacked alternately, forming face-to-face π···π interaction (centroid-to-centroid distance 3.595(1) Å) along the *c* direction. Alternatively, adjacent layers containing the π stacks are linked via silver···iodo interaction and bridged by nitrate anions attached to silver baskets: each iodine atom interacts with two vertices belonging to silver baskets in adjacent layers, and the linkages of nitrate anions occur mainly between silver baskets that are aligned head-to-head. In this manner, a three-dimensional network built by nitrate linkages and silver···iodo interactions is stabilized by inter-layer π···π interaction.

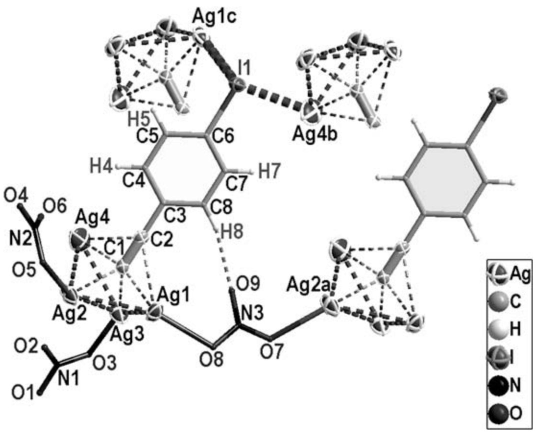


Fig. 4. Coordination geometry in **2** (50% thermo ellipsoids for Ag atoms), and the bridging of adjacent units. Selected bond lengths [Å]: C1≡C2 1.225(7), C1···Ag1 2.308(6), C1···Ag2 2.234(5), C1···Ag3 2.191(6), C1···Ag4 2.304(6), C2···Ag1 2.873(6), C2···Ag4 2.683(6), Ag1···Ag2 3.054(1), Ag1···Ag3 3.012(1), Ag2···Ag3 2.947(1), Ag2···Ag4 3.011(1), Ag3···Ag4 2.909(1), O9···C8 3.177(5). Symmetry code: a 1 + *x*, *y*, 1 + *z*; b 1 + *x*, 1 − *y*, 0.5 + *z*; c *x*, 1 − *y*, 0.5 + *z* .

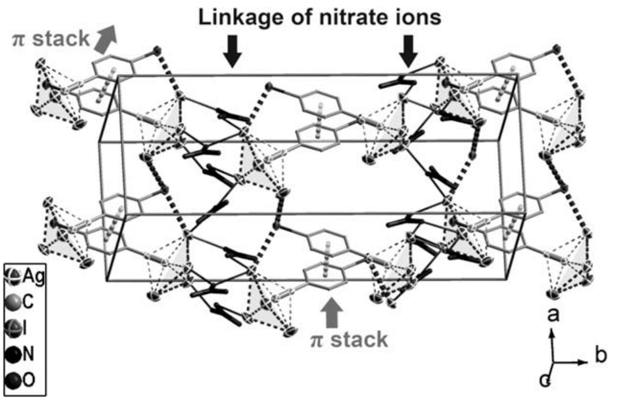


Fig. 5. Unit-cell content of complex **2**. Hydrogen atoms are omitted for clarity. Only those nitrate anions that bridge the silver baskets are included.

3.3. $2AgL^2\cdot 5AgCF_3COO\cdot 2CH_3CN\cdot H_2O$ (**3**)

In the structural unit of compound **3**, two parallelly aligned 3,4-dichlorophenylethynide ligands are inserted into separate Ag_5 baskets by adopting the μ_5–$\eta^2, \eta^2, \eta^2, \eta^1, \eta^1$ and μ_4–$\eta^2, \eta^2, \eta^2, \eta^1$ ligation modes. The silver baskets share one edge to give an Ag_8 aggregate, and such aggregates are anchored and stabilized by trifluoroacetate anions (Fig. 6). The Ag_8 aggregates are further connected together by sharing type Ag5···Ag6 edges of length 3.201(1) Å to form a silver chain. Two types of face-to-face π···π interactions occur between neighboring phenyl rings to form a zigzag stack alongside the extended silver chain. The distances between the ring centroids are 3.999(1) and 3.899(1) Å (average inter-planar distance: 3.63 and 3.71 Å), respectively.

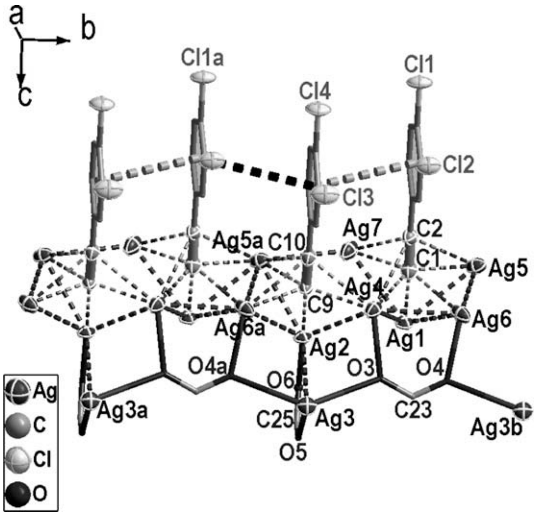


Fig. 6. Metal-ligand bonding in **3**. All hydrogen atoms, acetonitrile molecules, a water molecule, and CF_3 moieties of trifluoroacetate anions are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.191(11), C9≡C10 1.216(10). C1···Ag1 2.089(7), C1···Ag4 2.524(8), C1···Ag5 2.567(7), C1···Ag6 2.662(8), C1···Ag7 2.413(7), C2···Ag4 2.984(8), C2···Ag5 2.989(7), C2···Ag7 2.677(7), C9···Ag2 2.070(7), C9···Ag4 2.387(7), C9···Ag5a 2.476(7), C9···Ag6a 2.362(7), C10···Ag4 2.780(7), C10···Ag5a 2.959(7), C10···Ag6a 2.732(7), Ag1···Ag4 3.136(1), Ag1···Ag5 3.020(1), Ag1···Ag6 3.179(1), Ag1···Ag7 3.009(1), Ag2···Ag3 3.080(1), Ag2···Ag5a 2.951(1), Ag2···Ag6a 3.065(1), Ag4···Ag2 2.954(1), Ag4···Ag6 2.920(1), Ag5···Ag6 3.201(1), Ag7···Ag5a 3.097(1). Symmetry code: a *x*, *y* − 1, *z*; b *x*, *y* + 1, *z*.

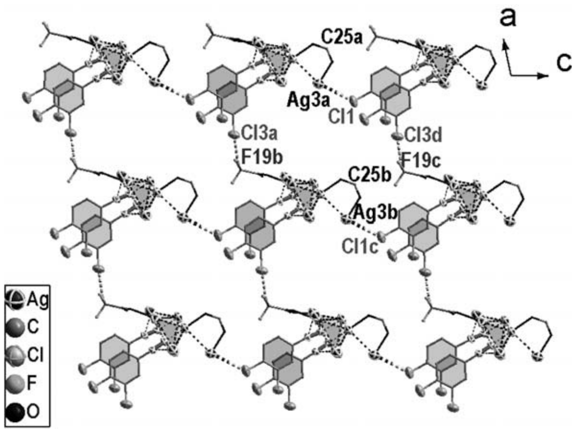


Fig. 7. Packing diagram of **3** viewed along *b* direction. The trifluoroacetate anions containing F19 are displayed, as well as the carboxyl groups of the anions containing C25. Other anions, hydrogen atoms and acetonitrile molecules are omitted for clarity. Symmetry code: a *x*, −*y*, *z* − 0.5; b *x* − 0.5, 0.5−*y*, *z* − 0.5; c *x* − 0.5, 0.5 + *y*, *z*; d *x*, 1 + *y*, *z*.

As shown in Fig. 6, independent atom Ag3 alone lies outside the silver basket and is anchored by type μ_4–*O*,*O*,*O*′,*O*′ (O3–O4) and μ_3–*O*,*O*′ (O5–O6) trifluoroacetate groups with further stabilization by argentophilic interaction (Ag3···Ag2 3.080(1) Å). Weak inter-chain silver···chloro interaction between Ag3 and Cl1 (Ag3···Cl1 3.287(2) Å) occurs in the *c* direction to generate a supramolecular layer, and inter-layer F···Cl contact in the *a* direction is of the van der Waals type [9,11] (F19···Cl3 3.23(1) Å). (Fig. 7).

3.4. 4AgL^3·6AgC$_2$F$_5$COO·5CH$_3$CN (**4**) and 4AgL^4·6AgC$_2$F$_5$COO·5CH$_3$CN (**5**)

Compound **4** and **5** are nearly isomorphous with the same kind of centrosymmetric structural unit. In compound **4** (Fig. 8), four parallel-related ethynides are inserted into respective Ag$_5$ baskets by adopting μ_5–$\eta^2,\eta^2,\eta^2,\eta^1,\eta^1$ (C9$\equiv$C10 and C17$\equiv$C18), μ_5–$\eta^2,\eta^2,\eta^1,\eta^1,\eta^1$ (C25$\equiv$C26) μ_5–$\eta^2,\eta^1,\eta^1,\eta^1,\eta^1$ (C1$\equiv$C2) ligation modes. The only difference in compound **5** is that C17$\equiv$C18 adopts the μ_5–$\eta^2,\eta^2,\eta^1,\eta^1,\eta^1$ mode. By sharing edges, the Ag$_5$ baskets are further united to form a columnar fragment. Four phenyl rings in each fragment are aligned on the same side of the silver column and stacked via weak face-to-face π···π interactions. Each fragment and its inversion-related neighbors share three Ag···Ag edges to generate an infinite column (Fig. 8).

In both **4** and **5**, C—H···X (X = Br, Cl) hydrogen bonds and weak halogen···halogen interactions are observed between the silver

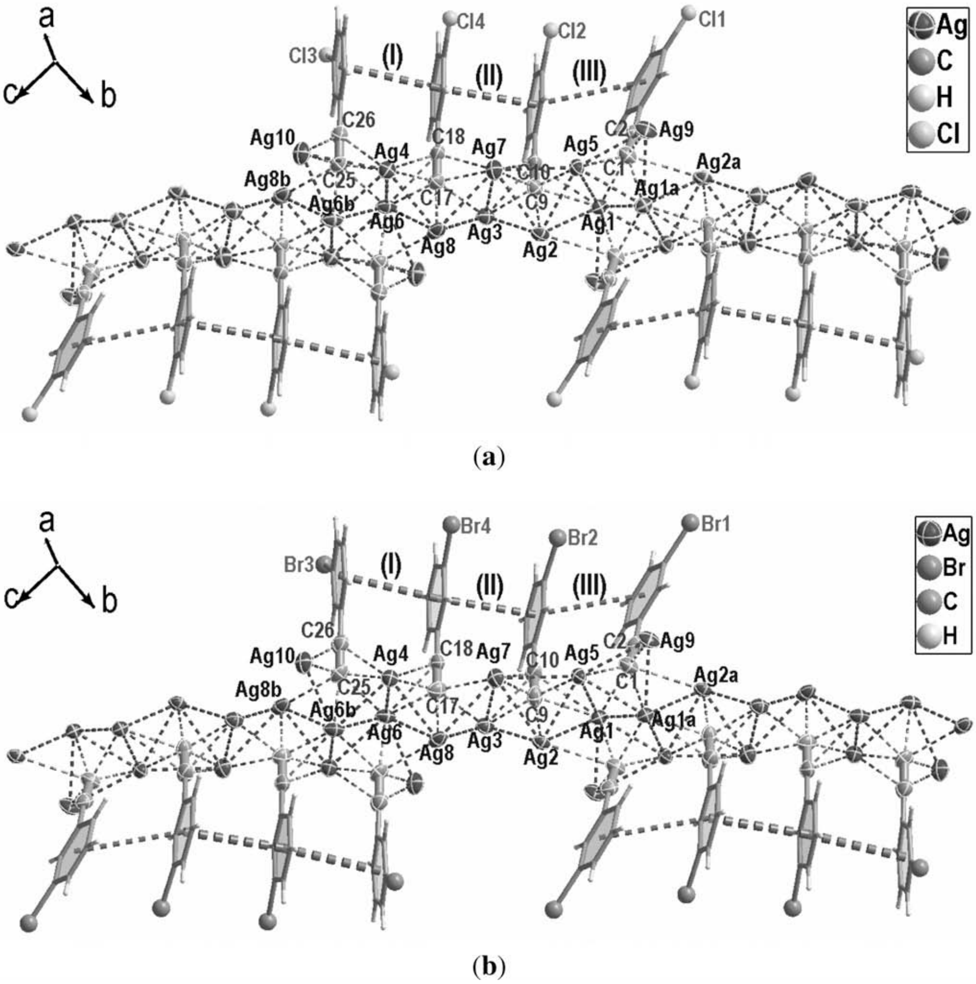
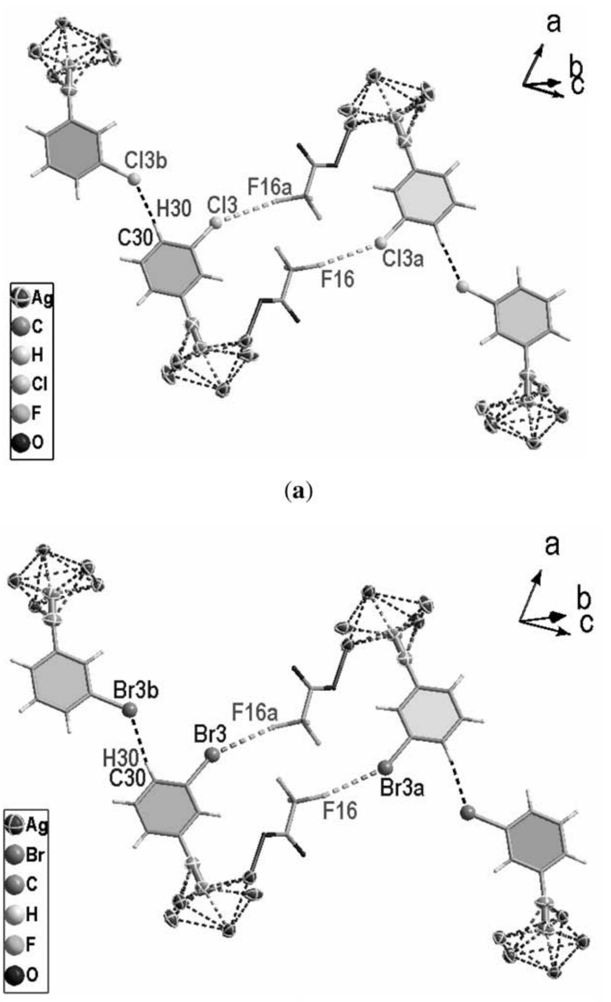


Fig. 8. Extension of silver chain in **4** (**a**) and **5** (**b**). Acetonitrile molecules and trifluoroacetate anions and a minor disordered part of Cl5/Br5 with C55 to C60 (of both) are omitted for clarity. Selected bond lengths [Å], **4**: C1$\equiv$C2 1.203(8), C9$\equiv$C10 1.211(9), C17$\equiv$C18 1.193(9), C25$\equiv$C26 1.200(9), C···Ag: 2.101(7) (C17···Ag8) to 3.022(8) (C18···Ag7), Ag···Ag: 2.882(1) (Ag6···Ag6b) to 3.277(1) (Ag4···Ag10)). **5**: C1$\equiv$C2 1.224(16), C9$\equiv$C10 1.203(16), C17$\equiv$C18 1.205(16), C25$\equiv$C26 1.200(15), C···Ag: 2.131(11) (C17···Ag8) to 3.012(13) (C25···Ag8b), Ag···Ag: 2.883(2) (Ag6···Ag6b) to 3.262(2) (Ag3···Ag7). Symmetry code **4**: a 1 − *x*, 2−*y*, −*z*; b 1 − *x*, 1 − *y*, 1 − *z*. **5**: a 1 − *x*, 2 − *y*, 1 − *z*; b 1 − *x*, 1 − *y*, 2 − *z*. Ring centroid-to-centroid distance in the sequence (**I**), (**II**), (**III**): **4**, 3.844(1), 3.810(1), 4.276(1) Å; **5**: 3.860(1), 3.860(1), 4.219(1), respectively.



(a)

(b)

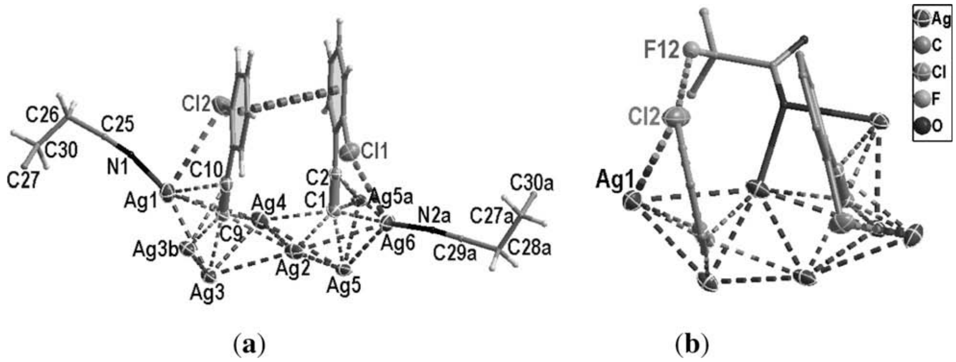
Fig. 9. Weak halogen···halogen interactions and C—H···X (X = Cl, Br) type hydrogen bonds in the crystal structure of **4** (**a**) and **5** (**b**). Symmetry code **4**: a 2 − *x*, 1 − *y*, 1 − *z*; b 2 − *x*, 1 − *y*, −*z*; **5**: a 2 − *x*, 1 − *y*, 2 − *z*; b 2 − *x*, 1 − *y*, 1 − *z*.

columns, leading to a three-dimensional supramolecular architecture [11–13] (Fig. 9). Hydrogen bonds occur between the halogen-substituted phenyl rings: *d*(Cl2b···C30) = 3.380(8) Å, ∠CHCl = 126° for **4**, *d*(Br2b···C30) = 3.456(9) Å, CHBr = 132° for **5**, while halogen···halogen interactions are observed between the Cl or Br atom at the *meta* position of the phenylethynide moiety and a fluorine atom of the CF_3COO^- anion: *d*(Cl3···F16) = 3.195(9) Å for **4** and *d*(Br3···F16) = 3.19(1) Å for **5**. Although the inter-halogen contacts are close to the sums of their van der Waals radii, their presence and attractive nature contribute to the stability of the network. It is noted that in compound **3**, van der Waals type Cl···F interaction also occurs between the *meta* chlorine atom and the fluorine atom of a CF_3COO^- anion.

3.5. $2AgL^5 \cdot 4AgCF_3COO \cdot NC(CH_2)_4CN$ (**6**) and $2AgL^5 \cdot 4AgCF_3COO \cdot 2CH_3CN$ (**7**)

In the structural units of these two complexes, parallelly-related ethynide ligands are inserted into Ag_5 baskets by adopting the μ_5–$\eta^2, \eta^2, \eta^1, \eta^1, \eta^1$(C1≡C2), μ_5–$\eta^2, \eta^1, \eta^1, \eta^1, \eta^1$(C9≡C10) (in **6**) and the μ_5–$\eta^2, \eta^2, \eta^2, \eta^2, \eta^1$(C1≡C2), μ_5–$\eta^2, \eta^2, \eta^1, \eta^1, \eta^1$(C9≡C10) (in **7**) ligation modes, with $\pi\cdots\pi$ interactions occurring between the phenyl rings. The centroid-to-centroid distances are 3.928(1) Å (**6**, average inter-planar distance 3.58 Å) and 3.941(2) Å (**7**, average inter-planar distance 3.54 Å) (Figs. 10 and 11). Both silver···chloro interaction and chloro···fluoro interaction are observed in complex **6** (Ag6···Cl1 3.191(4) Å, Ag7···Cl1 3.006(5) Å, Ag1···Cl2 3.404(1) Å, Cl2···F12 3.165(4) Å; Ag7 and Ag6 together represent a disordered silver atom with site occupancy ratio Ag6:Ag7 = 13:12.). The distance between Cl1 and Ag6/Ag7 is significantly smaller than the sum of their van der Waals radii by 0.3–0.5 Å [9], indicated a strong silver···halogen interaction. On the other hand, both silver···chloro and chloro···fluoro short contacts occur at Cl2, which has never been observed in our previous works. In **7**, only silver···chloro interaction is observed: Cl2···Ag6 3.280(3) Å, indicating a moderately-strong silver···halogen interaction.

In complex **6**, two adjacent inversion-related structural units are held by argentophilic interactions (Ag3···Ag3b and Ag5···Ag5a) to form a silver column in the *a* direction (Fig. 12a), and such columns are further expanded to a two-dimensional supramolecular structure via the linkage of adiponitrile molecules, as shown in Fig. 13a. In **7**, a silver column parallel to *a* axis is similarly formed (sharing edges Ag1···Ag1b and Ag3···Ag3a) (Fig. 12b), which is expanded into a three-dimensional supramolecular structure via the formation of two hydrogen bonds: C5–H5···F18 (C5···F18: 3.274(9) Å, ∠CHF = 170°) and C28–H20···O7 (C28···O7: 3.236(12) Å, ∠CHO = 162°) [13], as shown in Fig. 13b.



(a) (b)

Fig. 10. (**a**) Coordination geometry of complex **6** (thermal ellipsoid 50%). All trifluoroacetate ions, hydrogen labels and disordered groups are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.217(5), C9≡C10 1.224(4), C1···Ag2 2.270(3), C1···Ag4 2.740(3), C1···Ag5 2.193(4), C1···Ag6 2.249(6), C1···Ag5a 2.626(3), C2···Ag6 2.602(6), C2···Ag5a 2.916(3), C9···Ag1 2.236(5), C9···Ag2 2.748(5), C9···Ag3 2.211(3), C9···Ag4 2.285(4), C9···Ag3b 2.532(4), C10···Ag1 2.687(4), C10···Ag3b 2.772(4), Cl1···Ag6 3.191(4), Cl2···Ag1 3.404(1), Ag1···Ag3 3.093(1), Ag1···Ag4 3.299(1), Ag2···Ag3 3.190(1), Ag2···Ag4 2.919(1), Ag2···Ag5 2.810(1), Ag3···Ag3b 2.832(1), Ag3···Ag4 2.780(1), Ag4···Ag5 3.234(1), Ag5···Ag6 3.078(3), Ag5···Ag5a 2.808(1). Symmetry code: a 1 + *x*, *y*, 1 + *z*; b − *x*, 1 − *y*, 1 − *z*. (**b**) Ag···Cl···F interaction. Cl2···F12: 3.165(4) Å.

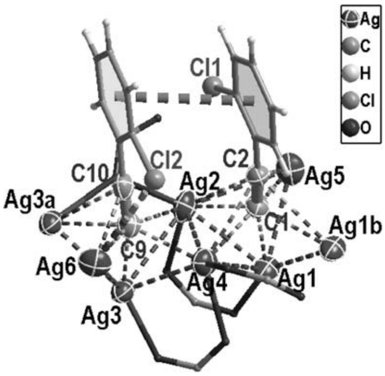


Fig. 11. Coordination geometry of complex **7** (thermal ellipsoid 50%). All CF_3 moieties of trifluoroacetate ions, acetonitrile molecules and hydrogen labels are omitted for clarity. Selected bond lengths [Å]: $C1{\equiv}C2$ 1.219(6), $C9{\equiv}C10$ 1.226(9), C1···Ag1 2.167(5), C1···Ag2 2.320(5), C1···Ag4 2.580(7), C1···Ag5 2.318(6), C1···Ag1b 2.608(5), C2···Ag2 2.982(5), C2···Ag4 2.937(7), C2···Ag5 2.850(7), C2···Ag1b 2.959(5), C9···Ag2 2.778(7), C9···Ag3 2.180(6), C9···Ag4 2.397(6), C9···Ag6 2.297(8), C9···Ag3a 2.599(6), C10···Ag6 2.618(8), C10···Ag3a 2.983(5), Cl2···Ag6 3.280(3), Ag1···Ag2 2.908(1), Ag1···Ag4 3.123(2), Ag1···Ag5 2.988(2), Ag1···Ag1b 2.862(1), Ag2···Ag3 3.160(1), Ag2···Ag4 3.011(2), Ag2···Ag5 3.236(2), Ag3···Ag4 2.804(1), Ag3···Ag6 3.134(2), Ag3···Ag3a 2.818(1). Symmetry code: a $1-x, 1-y, 1-z$; b $2-x, 1-y, 1-z$.

3.6. $AgL^6{\cdot}2CF_2(CF_2COOAg)_2{\cdot}2CH_3CN$ (**8**)

In compound **8**, the 2-fluorophenylethynide ligand is connected to a butterfly-shaped Ag_5 basket by adopting the μ_4–$\eta^2, \eta^2, \eta^1, \eta^1$ ligation mode (Fig. 14). The lone Ag5 atom is coordinated linearly by two acetonitrile ligands and a carboxylate oxygen atom: Ag···O (2.622(2) Å). One of the two independent hexafluoroglutarate dianions adopts a bent conformation to anchor on the Ag_5 basket, while the other one is fully extended. The distance between F13 and Ag2 is 3.106(3) Å, being approximately equal to the sum of their van der Waals radii [9].

By sharing one edge (Ag1···Ag1a), two inversion-related Ag_5 baskets form an Ag_8 aggregate. A halogen···π interaction (Fig. 15) is observed between F3 and the centroid of the phenyl ring belonging to an inversion-related unit (F3···centroid 3.292(2) Å; closest F···C contact F3a···C7 3.351(4) Å) [14] The centrosymmetric Ag_8 aggregates are further linked by bent hexafluoroglutarate dianions to form a silver–organic chain along the *a* axis, in which each carboxyl group adopts the μ_3–*O,O,O′*, mode. Notably, short F···Ag contacts are also observed between fluorine and silver atoms of adjacent Ag_8 aggregates: Ag3···F1c 3.044(2) Å, Ag4···F5c 2.915(2) Å (Fig. 15), being significantly shorter than the sum of their van der Waals radii, 3.19 Å [9]. On the other hand, along the *b* direction, the Ag_8 aggregates are linked by unbent hexafluoroglutaric dianions to yield a two-dimensional metal–organic network.

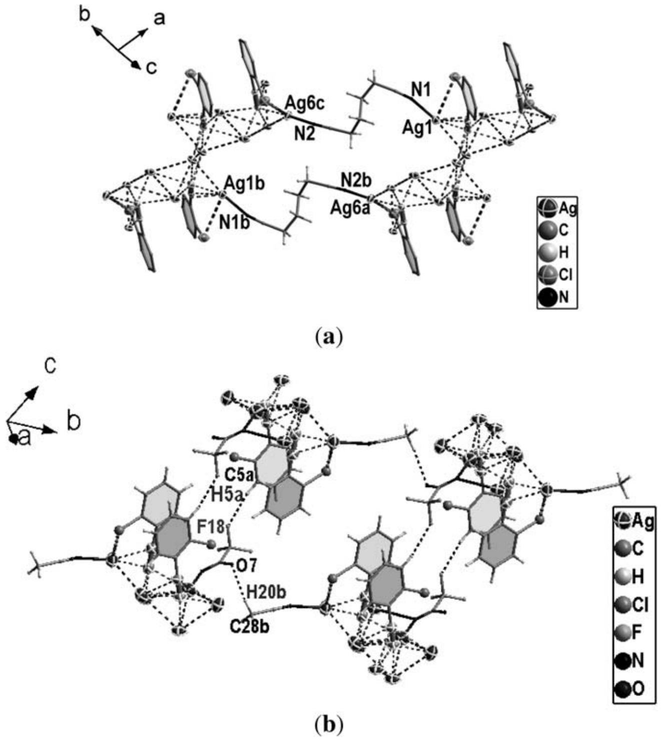


Fig. 13. (**a**) The two-dimensional coordination network of **6**. Symmetry code: a $-x, 1-y, 1-z$; b $1-x, 1-y, -z$; c $x-1, y, z-1$. (**b**) The 3D structure of **7** constructed by hydrogen bonds. Symmetry code: a $1-x, 1-y, 2-z$; b $x, 1+y, z$.

In this two-dimensional framework, the hexafluoroglutaric dianions form a loop structure, and the void space in the middle of it is filled by two linear $Ag(CH_3CN)_2$ moieties (N—Ag—N = 169°) oriented parallel to the *c* axis. The silver atom Ag5 of such a moiety is connected to the surrounding dianions via two weak Ag···O coordination interactions (Ag5···O5 2.622(2) Å, Ag5···O8 2.884(2) Å) and a C—H···F type hydrogen bond (C10···F8 3.296(5) Å, ∠CHF = 155°) A close contact of 3.002(2) Å is also observed between the ligand-unsupported Ag5 atom and F11a in the perfluoro arm of the surrounding dianion. Although this moiety does not serve as a bonding-linkage unit, it fills the ligand-inaccessible void space to stabilize the overall framework structure (Fig. 16).

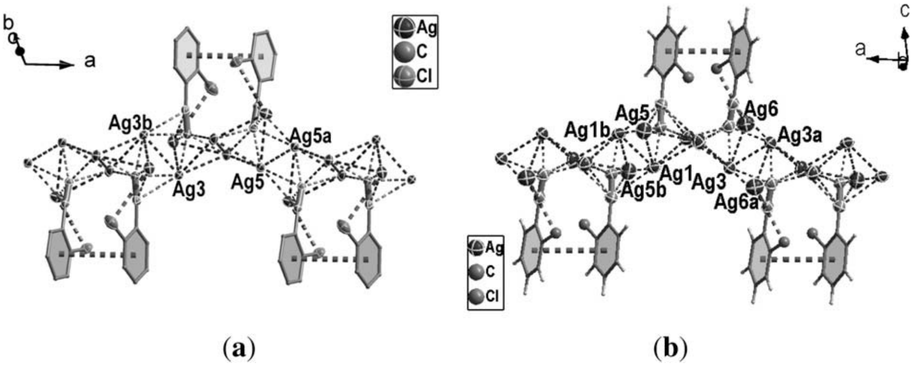


Fig. 12. (**a**) Formation of silver column in complex **6**. Symmetry code: a $1-x, 1-y, 1-z$; b $-x, 1-y, 1-z$. (**b**) Formation of silver column in **7**. Symmetry code: a $1-x, 1-y, 1-z$; b $2-x, 1-y, 1-z$. Hydrogen atoms, trifluoroacetate ions and acetonitrile/adiponitrile molecules are omitted for clarity.

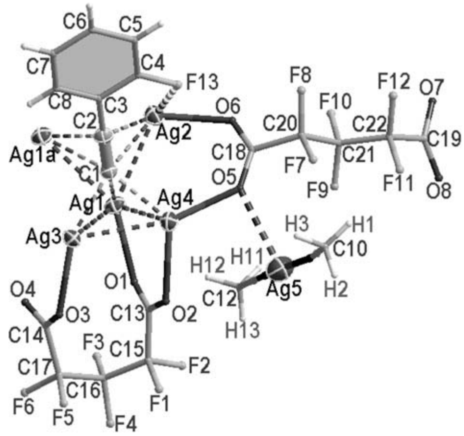


Fig. 14. Coordination geometry and atom labeling of **8**. Labels of hydrogen atoms are omitted. Selected bond lengths [Å]: C1≡C2 1.223(3), C1···Ag1 2.297(3), C1···Ag2 2.513(3), C1···Ag3 2.257(2), C1···Ag4 2.301(3), C1···Ag1a 2.554(3), C2···Ag2 2.609(3), C2···Ag1a 2.671(3), Ag1···Ag2 2.915(1), Ag1···Ag3 2.901(1), Ag1···Ag4 2.829(1), Ag1···Ag1a 3.012(1), Ag3···Ag4 2.876(1), Ag2···F13 3.106(3), O5···Ag5 2.622(2). Symmetry code: a −*x*, 1 − *y*, 1 − *z*.

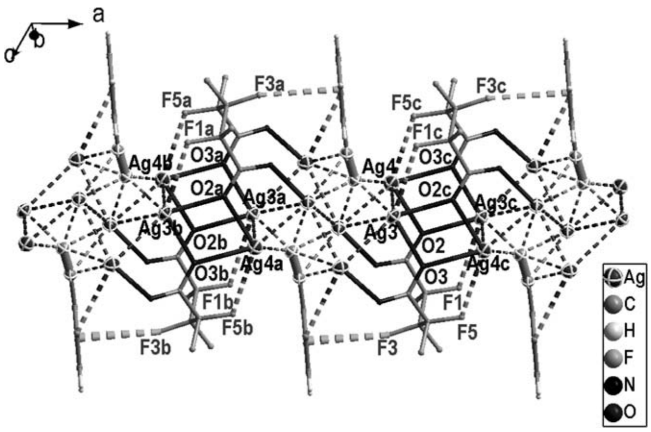


Fig. 15. The bridging linkage of Ag_8 clusters in **8** along the *a* direction. Acetonitrile molecules, Ag5 and the unbent hexafluoroglutarate anion are omitted for clarity. Symmetry code: *a* −*x*, 1 − *y*, 1 − *z*; b *x* − 1, *y*, *z*; c 1 − *x*, 1 − *y*, 1 − *z* .

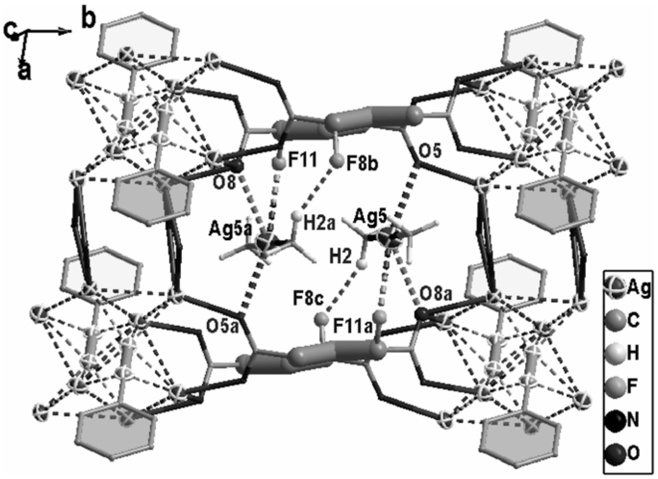


Fig. 16. Packing diagram of complex **8**. Symmetry code: a 1 − *x*, −*y*, 1 − *z*; b − *x*, −*y*, 1 − *z*; c 1 + *x*, *y*, *z*.

4. Conclusion

We have synthesised eight silver(I) halophenyl ethynide complexes bearing the supramolecular synthon $\mathrm{R}_X{-}\mathrm{C}{\equiv}\mathrm{C}{\supset}\mathrm{Ag}_n$ ($n = 4$, 5; R_X = halophenyl). Strong silver···iodo interactions in two of the structures play an important role in constructing high-dimensional coordination networks, while in the other six complexes, silver···chloro interactions and chloro···fluoro, bromo···fluoro interactions are observed. The silver···iodo contacts in crystals are significantly shorter than those of silver···chloro and silver···fluoro, indicating that the silver···iodo interaction has greater strength, since the van der Waals radius of iodine is larger than those of the other two (I: 198 pm, Cl: 175 pm, F: 147 pm).

It is notable that, in compound **1** and **2**, the ligation mode of ethynide ligands toward Ag_n baskets is μ_4– rather than μ_5–, though the latter mode is commonly observed in our previous studies [4b,6]. Moreover, the respective ratios of ancillary ligands to the ethynide ligand are also smaller than expected. This is probably due to the significant strength of the silver···iodine interaction, the μ_2–*I* ligation mode, and the rigidity of the iodophenyl ligand which together account for little accessible void space for the accommodation of ancillary ligands. A better understanding of the role of silver···halogen interactions on stabilization of coordination networks needs to be further investigated.

Within the limited number of complexes reported here, all halogen atoms at the *para* position of the phenyl ring are observed to form silver···halogen interactions, while van der Waals type halogen (Cl, Br)···fluoro interactions are observed on all substituents at the *meta* position. This is an interesting phenomenon unnoticed in the past. On the other hand, *ortho* chloro atoms in **6** and **7** form moderate to strong silver···chloro interactions due to their relatively close location to the silver baskets; for the same reason, they are not involved in the generation of higher-dimensional structures.

The silver···fluoro close contacts observed in **8** are different from the silver···chloro(*ortho*) interactions in **6** and **7**: the strong electron-withdrawing fluoro substituent on the phenyl ring facilitates the formation of charge-induced F···π interaction. On the other hand, though the silver···fluoro interaction that involves contacts significantly shorter than the sum of respective van der Waals radii is not well-recognized due to too few reports in the literature, the occurrence of unusually large number of such contacts in one structure indicated its potentially significant role in the stabilization of coordination networks.

The present report demonstrates the feasibility of using halogen-substituted phenylethynide synthons $\mathrm{R}_X{-}\mathrm{C}{\equiv}\mathrm{C}{\supset}\mathrm{Ag}_n$ ($n = 4$, 5) in the construction of silver(I) coordination and supramolecular networks. Variation on the type and the position of halogen substituents on the phenyl ring leads to network structures of different dimensionality due to the presence of subtle weak interactions in supramolecular organization. Further systematic investigation employing multi-substituted halophenylethynide ligands is required in order to shed additional light on the role of weak supramolecular interactions involving halogen atoms in the stabilization of coordination networks.

Acknowledgment

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Appendix A. Supplementary data

CCDC 723285, 723286, 723287, 723288, 723289, 723290, 723291 and 723292 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.05.004.

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