Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 670 (2003) 235–242

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Structural varieties in double salts of silver acetylide containing ancillary anions and terminal ligands

Quan-Ming Wang [a], Guo-Cong Guo [b], Thomas C.W. Mak [a,*]

[a] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, Hong Kong SAR, People's Republic of China*
[b] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China*

Received 18 October 2002; received in revised form 2 January 2003; accepted 2 January 2003

Dedicated to Prof. Qian-Er Zhang on the occasion of his 75th birthday

---

Abstract

New double salts $Ag_2C_2 \cdot 6AgO_2CCHF_2$ (**1**), $[HPyCH_2OH][Ag_9(C_2)(CF_3CO_2)_9(HPyCH_2OH)(H_2O)] \cdot 0.5H_2O$ ($PyCH_2OH = 4$-(hydroxymethyl)pyridine) (**2**), $Ag_2C_2 \cdot 5CF_3SO_3Ag \cdot 2MeCN \cdot 2H_2O$ (**3**) and $Ag_2C_2 \cdot 8CF_3SO_3Ag \cdot 2EtCN \cdot 3H_2O$ (**4**) have been synthesized by dissolving Ag_2C_2 in an aqueous solution of the corresponding silver salt followed by the addition of an ancillary ligand. Complex **1** has a three-dimensional structure in which unprecedented basket-like silver cages are inter-connected by difluoroacetate ligands. In **2**, centrosymmetric $(C_2)_2@Ag_{14}$ double cages with each half taking the shape of a triangulated dodecahedron are linked through additional silver atoms to generate an infinite chain, and unsupported silver(I)–silver(I) interactions exist between neighboring chains. Of the two independent 4-(hydroxymethyl)pyridinium ions in **2**, one acts in the *O*-ligating mode, which is observed for the first time, while the other merely serves to provide charge balance and space-filling. Both **3** and **4** are layer-type structures in which the basic building unit is a distorted monocapped octahedron and monocapped trigonal prism, respectively.

Keywords: Silver; Acetylide; Double salt; Argentophilicity; Difluoroacetate; Trifluoroacetate; Triflate

---

1. Introduction

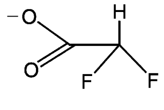
Silver alkynyl ($R-C\equiv C^-$) compounds have been extensively investigated [1], and there exist several examples of silver–ethyne ($HC\equiv CH$) [2] and –ethynyl ($HC\equiv C^-$) binding [3]. However, the silver–ethynediyl ($^-C\equiv C^-$, acetylide dianion, IUPAC name acetylenediide) interaction is seldom studied till recently [4–6] due to the explosive nature of silver acetylide, Ag_2C_2, in the anhydrous state and its insolubility in most solvents, which present serious difficulties in synthesis and characterization. Double salts of silver acetylide have the general formula $Ag_2C_2 \cdot mAgX$, where X is the co-existing anion. Previous studies in our laboratory have shown that different kinds of silver cages each encapsulating an acetylide dianion, $C_2@Ag_n$ ($n = 6$–9), can be obtained by varying the types of ancillary anions ($X = F$, ClO_4 or NO_3) [5,7]. In order to study the influence of co-existing anions on the self-assembly of Ag_2C_2-containing systems, we have conducted research on a series of double salts of silver acetylide with silver perfluorocarboxylates [8], as well as several triple [9] and quadruple [10] salts containing these two components. The fluoro-substituted carboxylates (or sulfonate) employed in the synthesis include trifluoroacetate, pentafluoropropionate, trifluoromethanesulfonate (triflate), as well as dicarboxylates such as tetrafluorosuccinate and hexafluoroglutarate [11]. Recently, the influence of neutral ancillary ligands such as aliphatic nitriles [8] and crown ethers [12] has been explored, and mixed-valent silver(I,II) compounds have been obtained in the presence of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane [13]. Furthermore, the role of quaternary ammonium ions as additional components has also been

---

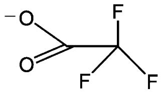
* Corresponding author. Fax: +852-2603-5057.
E-mail address: tcwmak@cuhk.edu.hk (T.C.W. Mak).

0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00013-5

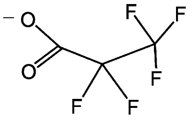
investigated, leading to the generation of some extraordinary structures [14].



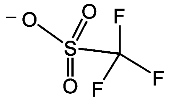
difluoroacetate



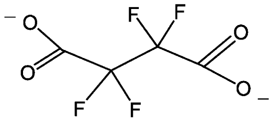
trifluoroacetate



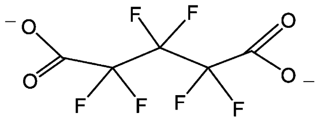
pentafluoropropionate



trifluoromethanesulfonate (triflate)



tetrafluorosuccinate



hexafluoroglutarate

Herein we report four new double salts of silver acetylide with silver difluoroacetae, trifluoroactate and trifluoromethanesulfonate formulated as $Ag_2C_2\cdot 6CHF_2CO_2Ag$ (**1**), $[HPyCH_2OH][Ag_9(C_2)(CF_3CO_2)_9(HPyCH_2OH)(H_2O)]\cdot 0.5H_2O$ (**2**), $Ag_2C_2\cdot 5CF_3SO_3Ag\cdot 2MeCN\cdot 2H_2O$ (**3**) and $Ag_2C_2\cdot 8CF_3SO_3Ag\cdot 2EtCN\cdot 3H_2O$ (**4**).

2. Results and discussion

Our synthetic strategy is based on the working hypothesis that depolymerization of silver acetylide occurs upon dissolving in a concentrated aqueous solution of a soluble silver salt to afford various polyhedral $C_2@Ag_n$ ($n \geq 6$) cage species. The assembly of such $C_2@Ag_n$ aggregates to form a crystalline complex is dependent on many factors such as co-existing anions, cations and ancillary ligands, as well as the stoichiometric ratios of the reactants.

The choice of co-existing fluorocarboxylate in a double salt $Ag_2C_2\cdot mR_fCO_2Ag$ is based on the fact that an aqueous solution of R_fCO_2Ag provides a sufficiently high concentration of silver(I) ions requisite for dissolving silver acetylide. The adduct formation of Ag_2C_2 with CHF_2CO_2Ag can be carried out readily in aqueous solution in the presence of $AgBF_4$ as a promoter [8], leading to crystallization of $Ag_2C_2\cdot 6CHF_2CO_2Ag$ **1**. Compound **1** is a very stable phase, and is invariably obtained irrespective of the reaction conditions such as concentration, solvent and even hydrothermal synthesis.

Single-crystal X-ray analysis established that **1** contains a $C_2@Ag_7$ cage as shown in Fig. 1. This cage is in the shape of a basket that is found for the first time, with a twofold axis passing through Ag1 and bisecting the C1–C1a triple bond. Such a cage is more open than the convex polyhedra reported previously. The acetylide dianion is accommodated in the silver basket and symmetrically bound to all seven vertices with Ag–C distances ranging between 2.155(7) and 2.497(7) Å. The C1–C1a bond length 1.24(1) Å is in fair agreement with the triple bond lengths found in acetylene (1.205 Å) [15] and CaC_2 (1.191 Å) [16]. The Ag···Ag distances lie in the range 2.8133(9)–3.2041(8) Å, which are shorter than twice the van der Waals radius of silver (3.40 Å) and are comparable to the interatomic contact of 2.89 Å in silver metal [17], being suggestive of the existence of argentophilic interaction [18].

The $C_2@Ag_7$ cages are inter-linked by difluoroacetate ligands to form a 2D network, as shown in Fig. 2. The three independent difluoroacetate ligands can be divided into two types: type (O11) difluoroacetate acting as a bridge within the layer, and the other type (O21 and O31) not only functioning in this manner but also connecting adjacent layers through type Ag5 atoms to generate a 3D structure, as shown in Fig. 3.

The introduction of 4-(hydroxymethyl)pyridine (4-pyridyl carbinol, pyridine-4-methanol, hereafter abbreviated as $PyCH_2OH$) as an ancillary ligand into the $Ag_2C_2 + AgCF_3CO_2$ system led to the isolation of compound **2**, which comprises a discrete *N*-protonated species $[HPyCH_2OH]^+$ and a polymeric anionic system $[Ag_9(C_2)(CF_3CO_2)_9(HPyCH_2OH)(H_2O)]_\infty^-$. The basic building unit in the latter is a centrosymmetric double

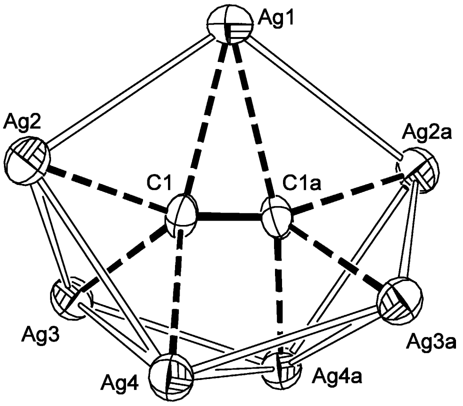


Fig. 1. Basket-like silver cage in $Ag_2C_2\cdot 6CHF_2CO_2Ag$ **1**, in which an acetylide ion is symmetrically encapsulated. Ag(I) atoms are drawn as 50% thermal ellipsoids. Selected bond distances (Å). C1–C1a, 1.24(1); C1–Ag1, 2.497(7); C1–Ag2, 2.115(7); C1–Ag3, 2.211(7); C1–Ag4, 2.330(7). Ag···Ag, 2.8133(9)–3.2041(8) Å. Symmetry code: (a) $3/2-x$, $1-y$, z.

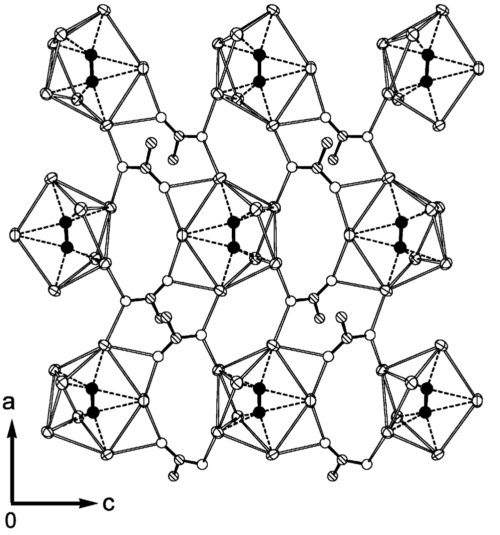


Fig. 2. Two-dimensional network in **1** generated from $C_2@Ag_7$ polyhedra connected by bridging difluoroacetate ligands. The F atoms are omitted for clarity.

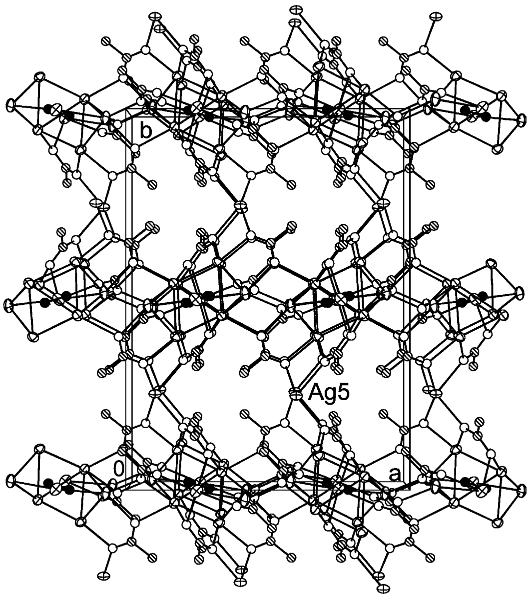


Fig. 3. Crystal structure of **1** with labeling of Ag5 that links adjacent layers.

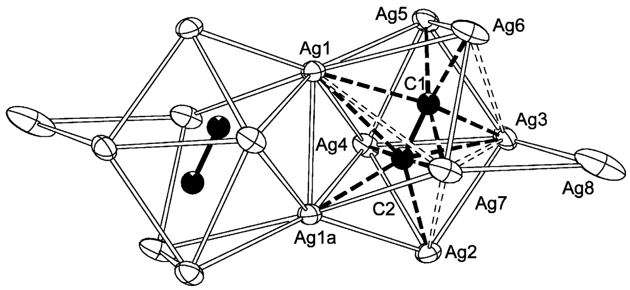


Fig. 4. Centrosymmetric edge-sharing $(C_2)_2@Ag_{14}$ double silver(I) cage in $[HPyCH_2OH][Ag_9(C_2)(CF_3CO_2)_9(HPyCH_2OH)(H_2O)]\cdot 0.5H_2O$ (**2**), each half having the shape of a triangulated dodecahedron. The thermal ellipsoids are drawn at the 35% probability level. Ag···Ag distances greater than 3.4 Å are represented by broken open lines. The sivler(I) to acetylide bonds in the left half are omitted for clarity. Selected bond distances: C1–C2, 1.25(1); C1–Ag1, 2.509(8); C1–Ag3, 2.290(7); C1–Ag5, 2.238(8); C1–Ag6, 2.123(7); C1–Ag7, 2.648(8); C2–Ag1, 2.624(8); C2–Ag1a, 2.279(8); C2–Ag2, 2.175(8); C2–Ag3, 2.614(8), C2–Ag4, 2.373(9); C2–Ag7, 2.446(9). Ag···Ag, 2.8522(9)–3.379(1) Å. Symmetry code: (a) $-x$, $-y$, $-z$.

cage with each half taking the shape of a triangulated dodecahedron, as shown in Fig. 4. The polyhedron is composed of two atom sets Ag1Ag1aAg2Ag3 and Ag4Ag5Ag6Ag7, which are each coplanar within 0.002 and 0.022 Å, respectively, making a dihedral angle of 84.7°; this cage also encloses a C_2^{2-} ion.

Silver atoms of type Ag9 are linked to each half of the $(C_2)_2@Ag_{14}$ double cage through bridging by a pair of trifluoacetate ligands, and each Ag9 atom is additionally coordinated by two aqua ligands and the oxygen atom of a terminal 4-(hydroxymethyl)pyridinium ligand, $[HPyCH_2OH]^+$, at Ag9–O1 = 2.438(7) Å, and the Ag9–O1–C016 bond angle is 131.8(6)°. The protonated pyridyl nitrogen atom N2 forms a donor hydrogen bond with O2W ($1-x$, $-1-y$, z) at a distance of 2.826 Å. Thus, a building unit is formed as illustrated in Fig. 5. Such units are inter-connected by the aqua ligands (on Ag9) to generate a polymeric chain running along the $[10\bar{1}]$ direction. A significant feature is that unsupported silver(I)–silver(I) contacts exist between neighboring chains with an Ag8···Ag8 ($1-x$, $-y$, $-z$) distance of 3.384 Å, which is slightly shorter than twice the van der Waals radius of silver (3.4 Å). This along with other precedents of ligand-unsupported Ag(I) aggregates in the literature [18a,19] provide further corroborative evidence for the importance of argentophilicity. Taking these inter-chain silver(I)–silver(I) contacts into consideration, the crystal structure can be regarded as a layer-type network (Fig. 6). A discrete $[HPyCH_2OH]^+$ cation is accommodated in each rectangular void within the

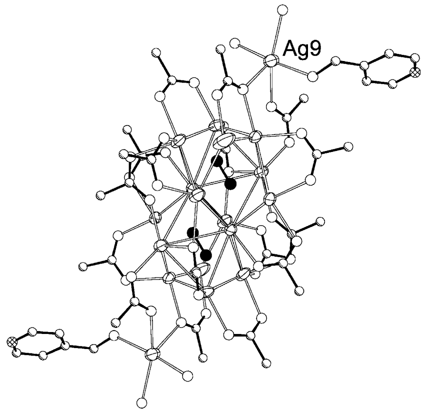


Fig. 5. Building unit in **2** showing the linkage of the double cage to a pair of silver atom of type Ag9 each carrying an *O*-bonded 4-(hydroxymethyl)pyridinium ligand. Black balls indicate C_2^{2-} species. F and H atoms have been omitted for clarity.

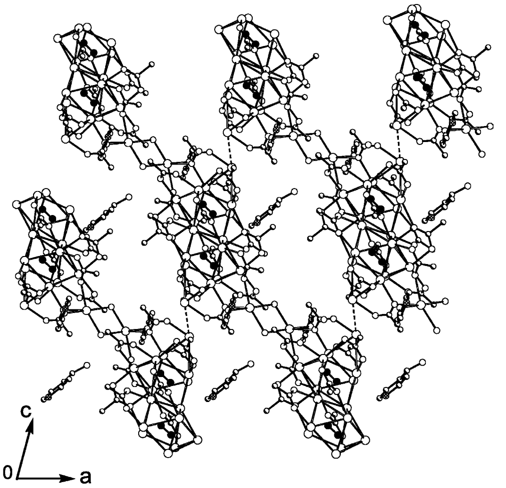


Fig. 6. Layer structure of **2** with chains running parallel to [$10\bar{1}$] connected by unsupported silver(I)-silver(I) contacts (represented by broken lines), viewed along the *b* direction. The discrete 4-(hydroxymethyl)pyridinium ions are accommodated in the cavities. Black balls indicate C_2^{2-} species. F and H atoms have been omitted for clarity.

layer and stabilized by hydrogen bonds: O2···O11 ($-x$, $-y$, $1-z$) 2.764Å, O2···O1W (x, y, $1+z$) 2.768 Å and N2···O82 (x, $1+y$, z) 2.828 Å.

The ligand behavior of 4-(hydroxymethyl)pyridine with its ring nitrogen coordinated to a metal center has been documented with structural details in [$Cu_2(PyCH_2OH)_2(OAc)_4$] [20] and with spectroscopic data in $K_2[Co(NO)(CN)_4(PyCH_2OH)]\cdot H_2O$ [21]. However, to our knowledge ligation via the oxygen atom of the *N*-protonated form of $PyCH_2OH$ in a metal complex is found for the first time.

We have previously shown that silver acetylide can form triple salts of the formula $Ag_2C_2\cdot AgF\cdot 4AgCF_3SO_3\cdot RCN$ ($R = CH_3$, C_2H_5) displaying honeycomb-like layered structures [9]. However, no double salt of silver acetylide with silver triflate has been reported so far. New double salts **3** and **4** are now obtained by dissolving silver acetylide in an aqueous solution of silver trifluoromethanesulfonate (triflate) followed by addition of acetonitrile or propionitrile. The main difference in the present procedure from the preparation of the triple salts is that $AgBF_4$ is not used here so that the release of AgF is avoided [9,22].

Single-crystal X-ray analysis revealed that $Ag_2C_2\cdot 5CF_3SO_3Ag\cdot 2MeCN\cdot 2H_2O$ (**3**) has a layered structure that is constructed from a distorted monocapped octahedron. As illustrated in Fig. 7(a), atom sets Ag2Ag3Ag4 and Ag5Ag6Ag7 constitute two triangular faces making a dihedral angle of 4.9°. These two faces have a twist angle of about 58°, and atom Ag1 caps the upper triangular face. Atom Ag1 and the centroids of the two triangular faces are almost co-linear (angle about 176°), and a view of the silver cage down its idealized C_3 axis is shown in Fig. 7(b). A C_2^{2-} anion is completely encapsulated in this silver cage with π interaction to Ag2 and Ag3 (C2–Ag4 2.853Å is too long to be taken as effective binding) as well as σ bonding to Ag1, Ag5, Ag6 and Ag7. The C(1)–C(2) bond length is 1.17(1) Å, the Ag–C distances fall in the range 2.12(1)–2.607(9) Å, and the Ag···Ag distances range from 2.938(1) to 3.332(1) Å.

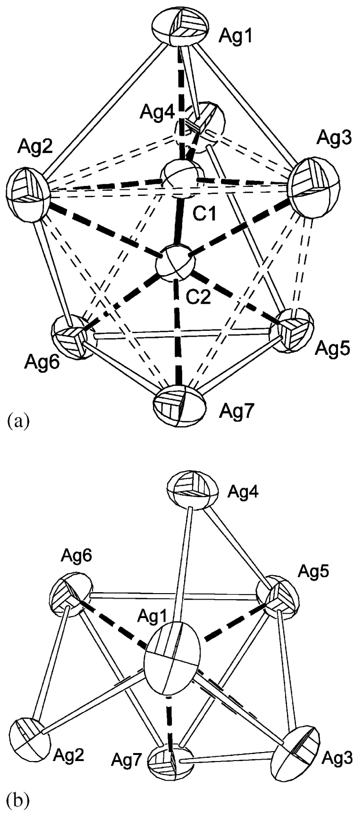


Fig. 7. (a) Monocapped octahedral $C_2@Ag_7$ cage in $Ag_2C_2\cdot 5CF_3SO_3Ag\cdot 2MeCN\cdot 2H_2O$ (**3**). The thermal ellipsoids are drawn at the 35% probability level. Ag···Ag distances greater than 3.4 Å are represented by broken open lines. Selected bond distances: C1–C2, 1.17(1); C1–Ag1, 2.12(1); C1–Ag2, 2.41(1); C1–Ag3, 2.258(9); C1–Ag4, 2.32(1); C2–Ag2, 2.545(8); C2–Ag3, 2.607(9); C2–Ag5, 2.267(8); C2–Ag6, 2.200(9); C2–Ag7, 2.201(9). Ag···Ag, 2.938(1)–3.332(1) Å. (b) The $C_2@Ag_7$ cage viewed down its idealized C_3 axis.

The $C_2@Ag_7$ silver cages are linked alternately by a pair of μ_2-triflate ions and a couple of aqua ligands to generate an infinite chain along the *c* direction. Two kinds of μ_3-triflate ions, bidentate (μ_3-O,O,O′) and tridentate (μ_3-O,O′,O″), function as connectors between chains to form a layered network (Fig. 8). A perspective view of the layer viewed along the *a* direction is shown in Fig. 9. Each $C_2@Ag_7$ cage is terminally coordinated by two acetonitrile ligands. All hydrophobic groups are located in the space between adjacent layers.

The compound $Ag_2C_2\cdot 8CF_3SO_3Ag\cdot 2EtCN\cdot 3H_2O$ **4** has also a layered structure, whose basic building unit is a distorted monocapped trigonal prism (Fig. 10). The two triangular faces Ag2Ag3Ag4 and Ag5Ag6Ag7 are

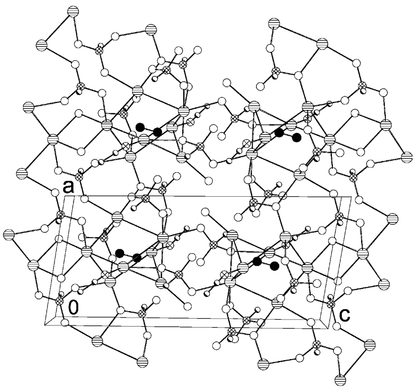


Fig. 8. Layer-type crystal structure of **3**. Black balls indicate C_2^{2-} species. F atoms of triflate ions have been omitted for clarity.

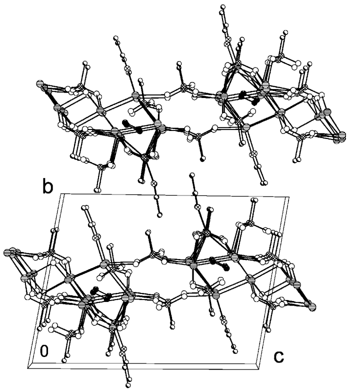


Fig. 9. Crystal structure of **3** viewed along the *a* direction.

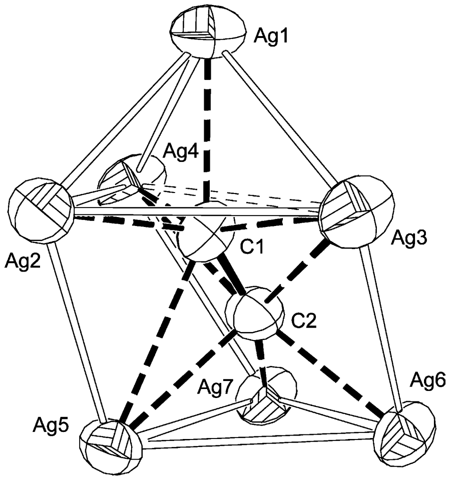


Fig. 10. Slanted monocapped trigonal prismatic $C_2@Ag_7$ cage in $Ag_2C_2 \cdot 8CF_3SO_3Ag \cdot 2EtCN \cdot 3H_2O$ (**4**). The thermal ellipsoids are drawn at the 35% probability level. Ag···Ag distances (greater than 3.4 Å) are represented by broken open lines. Selected bond distances: C1–C2, 1.18(1); C1–Ag1, 2.25(1); C1–Ag2, 2.153(9); C1–Ag3, 2.365(8); C1–Ag4, 2.350(7); C1–Ag5, 2.64(1); C2–Ag3, 2.69(1); C2–Ag4, 2.63(1); C2–Ag5, 2.297(9); C2–Ag6, 2.20(1); C2–Ag7, 2.204(9). Ag···Ag, 2.853(1)–3.298(2) Å.

almost parallel, making a dihedral angle of 3.1°, with Ag1 capping the upper face. The polyhedron exhibits a pronounced lean to one side, and the enclosed C_2^{2-} species is π bound to Ag3, Ag4 and Ag5 while σ binding to the remaining silver atoms. The Ag–C distances fall in the range 2.153(9)–2.69(1) Å, and the C(1)–C(2) bond length is 1.18(1) Å. Short Ag···Ag distances in this cage occur in the range from 2.853(1) to 3.298(2) Å.

These $C_2@Ag_7$ cages are connected by aqua and μ_2-triflate ligands to generate an infinite chain along the *c* direction. Silver atoms of type Ag8, Ag9 and Ag10 are bridged by aqua and triflate ligands to form a short ribbon, which links the chains into a two-dimensional network (Fig. 11).

An interesting structural feature is that the pair of independent acetonitrile ligands in **3** are coordinated to silver atoms on opposite sides of the layer in **3** (Fig. 9), whereas the independent propionitrile ligands in **4** are bound to two neighboring silver atoms and hence situated on the same side of the layer (Fig. 12).

In contrast to the case of triple salts $Ag_2C_2 \cdot AgF \cdot 4AgCF_3SO_3 \cdot RCN$ ($R = CH_3$, C_2H_5) where the ligation of acetonitrile or propionitrile leads to an isomorphous layer-type structure [9], the ancillary nitrile ligands afford different layer-type structures in **3** and **4**. With stronger additional binding of fluoride ions between silver cages in the *iso*-structural triple salts, the layer is more robust and thus the terminal coordination sites can be occupied by either acetonitrile or propionitrile without affecting the assembly process and overall crystal packing.

Under the consolidatory influence of argentophilicity, namely the d^{10}–d^{10} closed-shell attraction [23] that promotes the aggregation of silver(I) centers, Ag_2C_2 dissolves readily in a concentrated aqueous solution of a silver salt to generate polyhedral $[Ag_n(C_2)]^{(n-2)+}$ moieties. The present study shows that the assembly of such species is affected by co-existing anions ($CF_2HCO_2^-$,

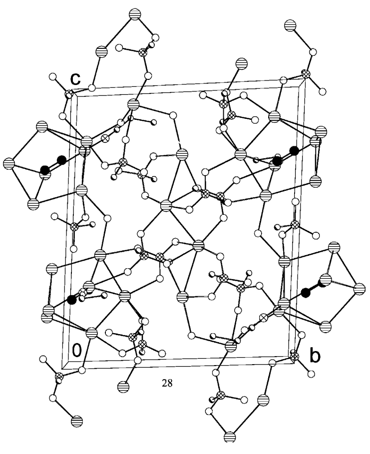


Fig. 11. Layer-type structure of **4**. Black balls indicate C_2^{2-} species. F atoms of triflate ions have been omitted for clarity.

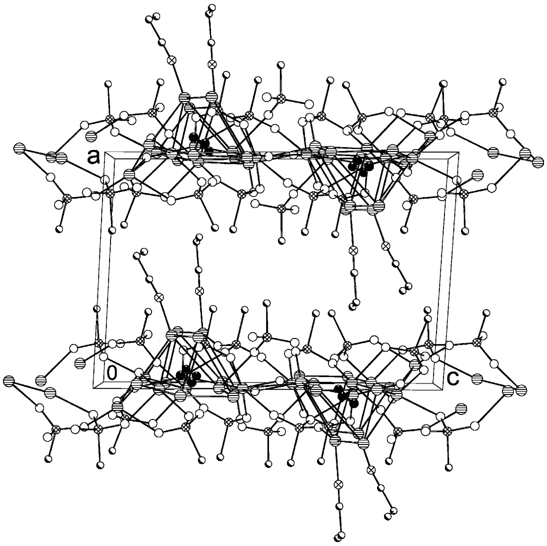


Fig. 12. Crystal structure of **4** viewed along the *b* direction.

$CF_3CO_2^-$, $CF_3SO_3^-$) and ancillary ligands (aqua, aliphatic nitrile and 4-(hydroxymethyl)pyridine) to generate crystal structures exhibiting various cage geometries and network connectivities.

The labile nature of the silver acetylide system poses a considerable challenge to designed assembly, and presently it is not yet possible to employ a specific $[C_2@Ag_n]^{(n-2)+}$ species as a polyhedral building block for supramolecular construction, in contrast to structurally robust entities such as the $[Re_6Se_8]$ unit [24]. However, the incorporation of 4-(hydroxmethyl)pyridine as a new organic component in compound **2** broadens the scope of the silver acetylide system through ligand variation. As further studies on analogous organic-inorganic acetylide-encapsulating systems continue to be further developed, it may be possible to gain better insight into the rational design of discrete and extended supramolecular silver complexes.

3. Experimental

3.1. Materials

All chemicals were purchased from ACROS and Aldrich and used without further purification. Ag_2C_2 was prepared as described previously [5]. Caution: thoroughly dried Ag_2C_2 detonates easily upon mechanical shock, and only a small quantity should be used in any chemical reaction. Excess amount can be disposed in alkaline solution via slow decomposition [25].

3.2. Synthesis of $Ag_2C_2 \cdot 6CHF_2CO_2Ag$ (*1*)

Freshly prepared Ag_2C_2 was added to 1 ml of a concentrated aqueous solution of CHF_2CO_2Ag and $AgBF_4$ (molar ratio ~1:1) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, the filtrate was placed in a desiccator charged with P_2O_5. Colorless block-like crystals of **1** were obtained in ca. 70% yield after several days.

3.3. Synthesis of $[HPyCH_2OH][Ag_9(C_2)(CF_3CO_2)_9(HPyCH_2OH)(H_2O)] \cdot 0.5H_2O$ (*2*)

Ag_2C_2 was added to 1 ml of an aqueous solution of CF_3CO_2Ag (0.442 g, 2 mmol) and $AgBF_4$ (0.389 g, 2 mmol) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, and 50 mg $PyCH_2OH$ was added to the filtrate. The resulting suspension was transferred to a thick-walled glass tube. The tube was subsequently flame-sealed and kept in a furnace at 115 °C for 6 h, and then cooled down to room temperature (r.t.) at $6° h^{-1}$. Colorless prismatic crystals of **2** were isolated in good yield (> 50%). Anal. Found: C, 17.02; H, 0.77; N, 1.15. Calc. for $C_{32}H_{19}N_2O_{21.5}F_{27}Ag_9$: C, 17.01; H, 0.85; N, 1.24%.

3.4. Synthesis of $Ag_2C_2 \cdot 5CF_3SO_3Ag \cdot 2MeCN \cdot 2H_2O$ (*3*)

Compound **3** was prepared by adding Ag_2C_2 to 1 ml of a concentrated aqueous solution of 1.5 g CF_3SO_3Ag in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, and a few drops of MeCN were added to the filtrate. (Note: excess MeCN would lead to deposition of Ag_2C_2 as a white precipitate.) The resulting solution was placed in a desiccator charged with P_2O_5. Colorless block-like crystals of **3** were obtained in ca. 20% yield after several days.

3.5. Synthesis of $Ag_2C_2 \cdot 8CF_3SO_3Ag \cdot 2EtCN \cdot 3H_2O$ (*4*)

Compound **4** was synthesized by repeating the procedure for **3** but with propionitrile used instead of acetonitrile.

Complexes **1** and **2** are stable in the dark, and compounds **3** and **4** are highly hygroscopic. All four complexes decompose readily in common solvents such as water, ethanol and acetonitrile. The homogeneity of each crystalline compound was indicated by its uniform habit, which was confirmed by measuring the unit-cell data of several hand-picked crystals.

3.6. X-ray crystallography

A selected single crystal of **1**, **2** or **3** was sealed in a glass capillary and mounted on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 30 mA using Mo–K_α radiation ($\lambda = 0.71073$ Å). Data collection and reduction were performed using the SMART and

Table 1
Crystallographic data for complexes **1**–**4**

Compound	**1**	**2**	**3**	**4**
Formula	$C_{14}H_6Ag_8F_{12}O_{12}$	$C_{32}H_{19}Ag_9F_{27}N_2O_{21.5}$	$C_{11}H_{10}Ag_7F_{15}N_2O_{17}S_5$	$C_{16}H_{16}Ag_{10}F_{24}N_2O_{27}S_8$
F_w	1457.15	2259.32	1642.60	2459.49
Color and habit	Colorless block	Colorless prism	Colorless block	Colorless block
Crystal size (mm^3)	0.20 × 0.20 × 0.13	0.48 × 0.28 × 0.26	0.33 × 0.20 × 0.19	0.48 × 0.38 × 0.32
Space group	*Pnna* (no. 52)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Unit cell dimensions				
a (Å)	15.585(1)	14.385(2)	8.179(2)	11.786(2)
b (Å)	20.924(2)	14.596(2)	13.399(3)	14.396(3)
c (Å)	7.8617(7)	15.175(2)	17.475(4)	16.916(3)
α (°)	90	63.014(2)	78.548(4)	84.90(3)
β (°)	90	74.229(2)	78.869(4)	85.61(3)
γ (°)	90	85.978(3)	78.562(4)	75.42(3)
V (Å^3)	2563.6(4)	2727.3(6)	1816.1(6)	2762(1)
Z	4	2	2	2
F(000)	2680	2126	1540	2312
D_{calc} (g cm^{-3})	3.775	2.751	3.004	2.957
μ (mm^{-1})	6.125	3.326	4.127	3.924
θ Range (°)	2.79–28.01	1.47–28.07	1.81–28.05	1.83–25.48
Reflections measured	16277	18347	12345	8955
Unique data (R_{int})	3099(0.0674)	12877(0.0449)	8601(0.0296)	8955
Data with $I > 2\sigma(I)$	1847	8582	4453	8549
Absorption correction	SADABS	SADABS	SADABS	ABSCOR
T_{min}/T_{max}	0.783–1.000	0.468–1.000	0.690–1.000	0.704–1.000
Parameters	228	824	542	784
R_1 (obs.) [a]	0.0359	0.0677	0.0555	0.0624
R_w (all) [b]	0.0784	0.1923	0.1598	0.1826
S (GOF)	0.901	0.976	0.922	1.080
Largest shift/error	0.001	0.001	0.002	0.001
Largest difference peak and hole (e Å^{-3})	1.115, −1.141	2.533, −2.201	1.338, −1.153	1.626, −1.525

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

SAINT software [26], with frames of 0.3° oscillation in the θ range $1.5 < \theta < 28°$. An empirical absorption correction was applied using the SADABS program [27]. For **4**, a single crystal sealed in a capillary was used for data collection on a Rigaku RAXIS IIC imaging plate diffractometer using graphite-monochromated Mo–K_α radiation from a rotating-anode generator powered at 50 kV and 90 mA. ABSCOR correction was applied [28]. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package [29]. In **3**, the oxygen atoms of one triflate ion are disordered over two sets of positions; in **4**, one aqua ligand also exhibits disorder over two positions. The crystal data and details of refinement are summarized in Table 1, and selected bond distances and angles are listed in the legends for figures.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 194800–194803. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work is supported by the Research Grants Council of the Hong Kong Special Administrative Region (project no. CUHK 4268/00P) and a Postdoctoral Fellowship awarded to Q.-M. Wang by The Chinese University of Hong Kong.

References

[1] (a) D.M.P. Mingos, R. Vilar, D. Rais, J. Organomet. Chem. 641 (2002) 126;
(b) V.W.-W. Yam, K.K.-W. Lo, K.M.-C. Wong, J. Organomet. Chem. 578 (2002) 3;
(c) M.D. Janssen, K. Köhler, M. Herres, A. Dedieu, W.J.J. Smeets, A.L. Spek, D.M. Grove, H. Lang, G. van Koten, J. Am. Chem. Soc. 118 (1996) 4817;
(d) H. Lang, K. Köhler, S. Blau, Coord. Chem. Soc. 143 (1995) 113.

[2] H.V.R. Dias, Z.-Y. Wang, W.-C. Jin, Inorg. Chem. 26 (1997) 6205.

[3] S. Yamazaki, A.J. Deeming, D.M. Speel, D.E. Hibbs, M.B. Hursthouse, K.M.A. Malik, Chem. Commun. (1997) 177.

[4] (a) J. Osterlof, Acta Crystallogr. 7 (1954) 637;
(b) X.-L. Jin, G.D. Zhou, N.-Z. Wu, Y.-Q. Tang, H.-C. Huang, Acta Chim. Sin. 48 (1990) 232. A description of the structure is given in: T.C.W. Mak, G.-D. Zhou, Crystallogrphy in Modern Chemistry: a Resource Book of Crystal Structure, Wiley–Interscience, New York, 1992, p. 288.

[5] G.-C. Guo, G.-D. Zhou, Q.-G. Wang, T.C.W. Mak, Angew. Chem. Int. Ed. Engl. 37 (1998) 630.

[6] W. Kockelmann, U. Ruschewitz, Angew. Chem. Int. Ed. Engl. 38 (1999) 3492.

[7] (a) G.-C. Guo, Q.-G. Wang, G.-D. Zhou, T.C.W. Mak, Chem. Commun. (1998) 339.;
(b) G.-C. Guo, G.-D. Zhou, T.C.W. Mak, J. Am. Chem. Soc. 121 (1999) 3136.

[8] Q.-M. Wang, T.C.W. Mak, J. Am. Chem. Soc. 123 (2001) 7594.

[9] Q.-M. Wang, T.C.W. Mak, J. Am. Chem. Soc. 122 (2000) 7608.

[10] Q.-M. Wang, T.C.W. Mak, J. Am. Chem. Soc. 123 (2001) 1501.

[11] Q.-M. Wang, T.C.W. Mak, Angew. Chem. Int. Ed. Engl. 40 (2001) 1130.

[12] Q.-M. Wang, G.-C. Guo, T.C.W. Mak, J. Cluster Sci. 13 (2002) 63.

[13] (a) Q.-M. Wang, T.C.W. Mak, Chem. Commun. (2001) 807;
(b) Q.-M. Wang, H.K. Lee, T.C.W. Mak, New J. Chem. 26 (2002) 513.

[14] (a) Q.-M. Wang, T.C.W. Mak, Angew. Chem. Int. Ed. Engl., 41 (2002) 4135;
(b) Q.-M. Wang, T.C.W. Mak, Chem. Commun., (2002) 2682.

[15] G. Herzberg, J.W.T. Spinks, Z. Phys. 91 (1934) 386.

[16] M. Atoji, J. Chem. Phys. 35 (1961) 1950.

[17] J. Emsley, The Elements, Clarendon, Oxford, 1989, p. 174.

[18] (a) M.A. Omary, T.R. Webb, Z. Assefa, G.E. Shankle, H.H. Patterson, Inorg. Chem. 37 (1998) 1380 and references therein;
(b) G.-C. Guo, T.C.W. Mak, Angew. Chem. Int. Ed. Engl. 37 (1998) 3183;
(c) C.-M. Che, M.-C. Tse, M.C.-W. Chan, K.-K. Cheung, D.L. Phillips, K.-H. Leung, J. Am. Chem. Soc. 122 (2000) 2464;
(d) M.A. Rawashdeh-Omary, M.A. Omary, H.H. Patterson, J. Am. Chem. Soc. 122 (2000) 10371.

[19] (a) O. Kristiansson, Inorg. Chem. 40 (2001) 5058;
(b) K. Singh, J.R. Long, P. Stavropoulos, J. Am. Chem. Soc. 119 (1997) 2942;
(c) O. Yaghi, H.-L. Li, J. Am. Chem. Soc. 118 (1996) 295;
(d) M.-L. Tong, X.-M. Chen, B.-H. Ye, L.-N. Ji, Angew. Chem. Int. Ed. Engl. 38 (1999) 2237.

[20] N.N. Hoang, F. Valach, M. Melnik, Acta Crystallogr. Sect. C 49 (1993) 467.

[21] R.C. Maurya, D.D. Mishra, S. Mukherjee, J. Dubey, Polyhedron 14 (1995) 1351.

[22] Q.-M. Wang, T.C.W. Mak, Chem. Commun. (2000) 1435.

[23] (a) P. Pyykkö, Chem. Rev. 97 (1997) 597;
(b) M. Jansen, Angew. Chem. Int. Ed. Engl. 26 (1987) 1098.

[24] (a) M.V. Bennett, L.G. Beauvais, M.P. Shores, J.R. Long, J. Am. Chem. Soc. 123 (2001) 8022;
(b) Z.P. Zheng, T.G. Gray, R.H. Holm, Inorg. Chem. 38 (1999) 4888;
(c) B.K. Roland, H.D. Selby, M.D. Carducci, Z.P. Zheng, J. Am. Chem. Soc. 124 (2002) 3222.

[25] D.K. Breitinger, W.A. Herrmann (Eds.), Synthetic Methods of Organometallic and Inorganic Chemistry, vol. 5, Thieme, Stuttgart, 1999, pp. 38–39.

[26] Bruker, SMART 5.0 and SAINT 4.0 for Windows NT, Area Detector Control and Integration Software. Bruker Analytical X-Ray Systems Inc., Madison, WI, 1998.

[27] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen, Göttingen, Germany, 1996.

[28] T. Higashi, ABSCOR, An Empirical Absorption Correction Based on Fourier Coefficient Fitting, Rigaku Corporation, Tokyo, 1995.

[29] G.M. Sheldrick, SHELXTL 5.10 for Windows NT, Structure Determination Software Programs, Bruker Analytical X-Ray Systems Inc., Madison, WI, 1997.