CHEMISTRY
A EUROPEAN JOURNAL

Betaine-Induced Assembly of Neutral Infinite Columns and Chains of Linked Silver(I) Polyhedra with Embedded Acetylenediide

Xiao-Li Zhao, Quan-Ming Wang, and Thomas C. W. Mak*[a]

This work is dedicated to Professor Khi-Rui Tsai on the occasion of his 92nd birthday

Abstract: Ten polymeric silver(I) double salts containing embedded acetylenediide: $[(Ag_2C_2)_2(AgCF_3CO_2)_9(L^1)_3]$ (**1**), $[(Ag_2C_2)_2(AgCF_3CO_2)_{10}(L^2)_3]\cdot H_2O$ (**2**), $[(Ag_2C_2)(AgCF_3CO_2)_4(L^3)(H_2O)]\cdot 0.75\,H_2O$ (**3**), $[(Ag_2C_2)_{1.5}(AgCF_3CO_2)_7(L^4)_2]$ (**4**), $[(Ag_2C_2)(AgCF_3CO_2)_7(L^5)_2(H_2O)]$ (**5**), $[(Ag_2C_2)(AgC_2F_5CO_2)_7(L^1)_3(H_2O)]$ (**6**), $[(Ag_2C_2)(AgCF_3CO_2)_7(L^1)_3(H_2O)]\cdot 2\,H_2O$ (**7**), $[(Ag_2C_2)(AgC_2F_5CO_2)_6(L^3)_2]$ (**8**), $[(Ag_2C_2)_2(AgC_2F_5CO_2)_{12}(L^4)_2(H_2O)_4]\cdot H_2O$ (**9**), and $[(Ag_2C_2)(AgCF_3CO_2)_6(L^3)_2(H_2O)]\cdot H_2O$ (**10**) have been isolated by varying the types of betaines, the perfluorocarboxylate ligands employed, and the reaction conditions. Single-crystal X-ray analysis has shown that **1**–**4** all have a columnar structure composed of fused silver(I) double cages, with C_2^{2-} species embedded in its stem and an exterior coat comprising anionic and zwitterionic carboxylates. For **5** and **6**, single silver(I) cages are linked into a beaded chain through both types of carboxylate ligands. In **7**, two different coordination modes of L^1 connect the silver(I) polyhedra into a chain. For **8**, the μ_2-O,O′ coordination mode of L^3 connects the silver(I) double cages into a chain. Compound **9** exhibits a two-dimensional architecture generated from the cross-linkage of double cages by $C_2F_5CO_2^-$, L^4, and $[Ag_2(C_2F_5CO_2)_2]$ units. Similar to **9**, **10** is also a two-dimensional structure, which is formed by connecting the chains of linked double cages through $[Ag_2(CF_3CO_2)_2]$ bridging.

Keywords: acetylenediide • betaines • carboxylates • coordination polymers • silver

Introduction

In the course of our investigation on the double/multiple salts of silver acetylenediide (Ag_2C_2), a series of complexes were prepared by using perfluoroalkyl carboxylates as co-existing anions together with various ancillary ligands.[1] With quaternary ammonium cations of different shapes and sizes (e.g. Et_4N^+ and Me_3BzN^+) as structure-inducing agents, anionic discrete and polymeric silver(I) aggregates with embedded C_2^{2-} species were successfully prepared and characterized.[2] To obtain neutral aggregates, a conceivable strategy is to incorporate the carboxylate and ammonio functional groups into the same ligand, that is, to employ a class of zwitterionic compounds whose prototype is the trimethylammonio derivative commonly called betaine ($Me_3N^+CH_2COO^-$, IUPAC name trimetylammonioacetate).[3,4] Owing to their permanent bipolarity and overall charge neutrality, betaine and its derivatives (considered as carboxylate-type ligands) have distinct advantages over most carboxylates in the study of coordination polymers: 1) synthetic access to water-soluble metal carboxylates; 2) generation of new structural varieties, such as complexes with metal centers bearing additional anionic ligands, and those with variable metal to carboxylate molar ratios; 3) easy synthetic modification of ligand property by varying the substituents on the quaternary nitrogen atom or the backbone between the two polar terminals.[5]

It is of interest to incorporate betaine and its derivatives into the Ag_2C_2/AgR_fCO_2 system, as each zwitterionic ligand furnishes a carboxylate group without bringing in an accompanying silver(I) ion. Thus, the resulting silver(I) complex may comprise more carboxylate groups than that when organic cations are employed to provide charge balance in the assembly of anionic aggregates in some double salts of silver acetylenediide.[6] Moreover, the substituents on the quaternary nitrogen atom can be modified to explore the influence of the polarity and steric bulk of various betaines. Furthermore, the effect of different co-existing perfluorocarboxylate anions is also a factor to be investigated. Herein we report

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[a] X.-L. Zhao, Dr. Q.-M. Wang, Prof. T. C. W. Mak
Department of Chemistry, The Chinese University of Hong Kong
Shatin, New Territories, Hong Kong SAR (P. R. China)
Fax: (+852) 260-35-057
E-mail: tcwmak@cuhk.edu.hk

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DOI: 10.1002/chem.200401182

the structural diversity observed in a series of ten new double salts of silver(I) acetylenediide **1–10**:

$[(Ag_2C_2)_2(AgCF_3CO_2)_9(L^1)_3]$ **1**

$[(Ag_2C_2)_2(AgCF_3CO_2)_{10}(L^2)_3] \cdot H_2O$ **2**

$[(Ag_2C_2)(AgCF_3CO_2)_4(L^3)(H_2O)] \cdot 0.75\,H_2O$ **3**

$[(Ag_2C_2)_{1.5}(AgCF_3CO_2)_7(L^4)_2]$ **4**

$[(Ag_2C_2)(AgCF_3CO_2)_7(L^5)_2(H_2O)]$ **5**

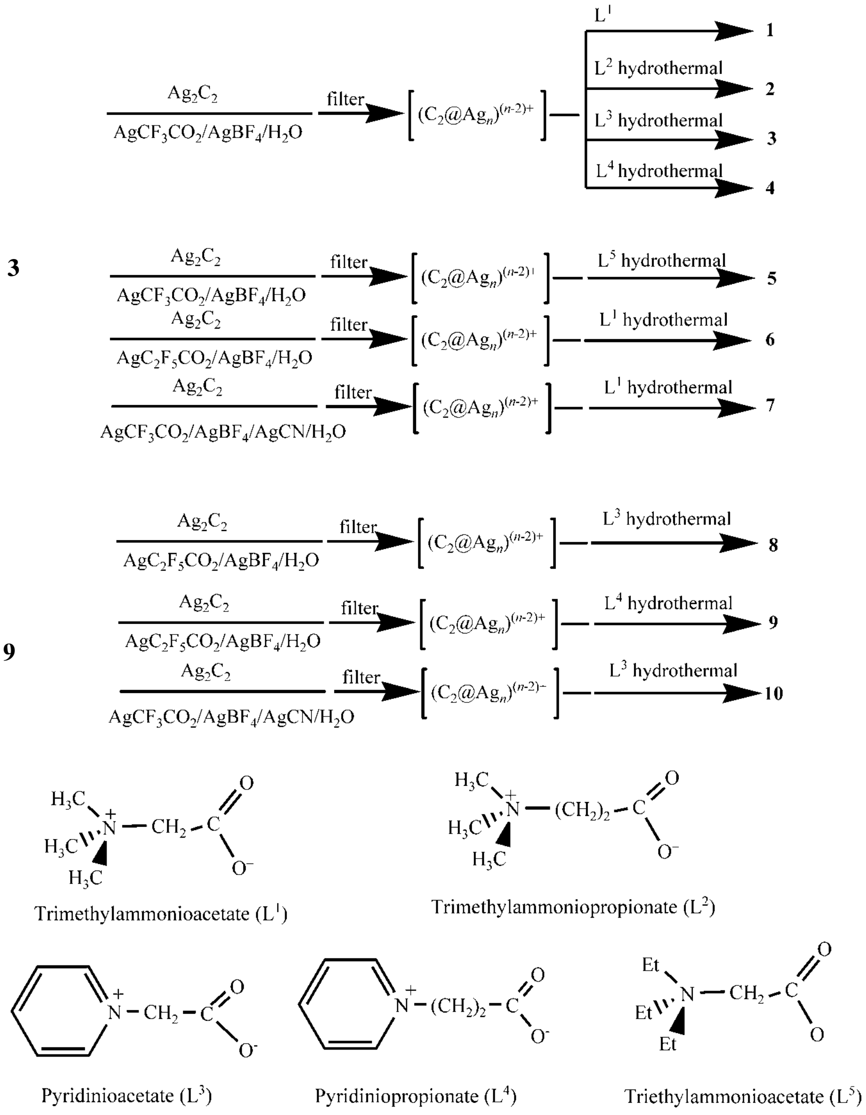
$[(Ag_2C_2)(AgC_2F_5CO_2)_7(L^1)_3(H_2O)]$ **6**

$[(Ag_2C_2)(AgCF_3CO_2)_7(L^1)_3(H_2O)] \cdot 2\,H_2O$ **7**

$[(Ag_2C_2)(AgC_2F_5CO_2)_6(L^3)_2]$ **8**

$[(Ag_2C_2)_2(AgC_2F_5CO_2)_{12}(L^4)_2(H_2O)_4] \cdot H_2O$ **9**

$[(Ag_2C_2)(AgCF_3CO_2)_6(L^3)_2(H_2O)] \cdot H_2O$ **10**



Scheme 1.

Results and Discussion

As described in our previous reports, Ag_2C_2 readily dissolves in a concentrated aqueous solution of one or more silver(I) salts to form labile polyhedral species of the type $C_2@Ag_n$ ($n = 6–10$). Introduction of betaine and its derivatives then affects the assembly process of these species during crystallization. The same preparative procedure under hydrothermal conditions was used for all compounds except **1** (Scheme 1). It is of interest that new aspects of structural diversity are observed in not only the specific geometries of the $C_2@Ag_n$ silver cages, but also their organization into one- and two-dimensional structures in the crystalline state.

$[(Ag_2C_2)_2(AgCF_3CO_2)_9(L^1)_3]$ (1): Compound **1** is composed of two kinds of silver cages: a triangulated dodecahedron (cage **A**) and a bicapped trigonal prism (cage **B**), each encapsulating an acetylenediide dianion (Figure 1).

Cage **A** is composed of two atom sets Ag1a-Ag1-Ag2-Ag3 and Ag4-Ag5-Ag6-Ag7, which are each coplanar with mean deviation of 0.04 and 0.09 Å from the corresponding least-squares plane, respectively, making a dihedral angle of 87.2°. This cage encloses a C_2^{2-} species with Ag–C bond lengths in the range of 2.181(9)–2.700(9) Å. Cage **A** and **A′** share edge Ag1···Ag1a to form a centrosymmetric double cage **AA′**.

In cage **B**, two triangular faces Ag3-Ag8-Ag9 and Ag10-Ag11-Ag13b constitute a trigonal prism, and Ag12 and

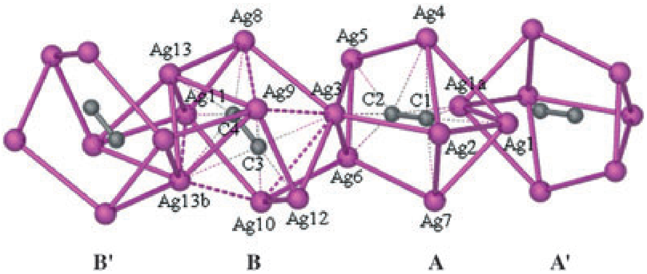


Figure 1. Double cages **AA′** and **B′B** sharing vertices of type Ag3 to generate an infinite chain **B′B AA′ B′B AA′**······ running along the *a* direction in **1**. **A**: triangulated dodecahedron; **B**: bicapped trigonal prism. The Ag···Ag distances longer than 3.4 Å (twice the van der Waals radius of silver) are represented by thick broken lines. The Ag–C bonds are represented by thin broken lines. Selected bond lengths [Å]: C1–C2 1.23(1), C1–Ag1 2.317(8), C1–Ag2 2.181(9), C1–Ag4 2.366(9), C1–Ag1a 2.514(9), C1–Ag7 2.362(9), C2–Ag1a 2.522(8), C2–Ag3 2.283(8), C2–Ag4 2.700(9), C2–Ag5 2.199(8), C2–Ag6 2.201(9), C3–C4, 1.18(1), C3–Ag3 2.403(9), C3–Ag9 2.428(8), C3–Ag10 2.260(8), C3–Ag12 2.143(8), C3–Ag13b 2.573(9), C4–Ag8 2.256(9), C4–Ag9 2.491(9), C4–Ag11 2.284(9), C4–Ag13 2.316(9), C4–Ag13b, 2.627(9). Symmetry code: a: $1-x$, $-y$, $-z$; b: $-x$, $-y$, $-z$.

Ag13 each caps a rectangular face. The mean least-squares plane deviation of the atoms constituting the three rectangular faces of the trigonal prism lies in the range 0.04–0.12 Å. A C_2^{2-} dianion is also accommodated in this cage and lies closer to the uncapped rectangular face Ag3-Ag10-Ag11-Ag8. The Ag–C bond lengths vary between 2.143(8) and 2.627(9) Å. Similar to the case of **AA′**, cage **B** and **B′** share edge Ag13···Ag13b to give the centrosymmetric double cage **B′B**.

A linear array of double cages **AA′** and **B′B** share vertices of type Ag3 with additional Ag6···Ag10 contacts to generate an infinite silver column **B′BAA′B′BAA′**··· running along the *a* direction (Figure 1).

The trifluoroacetate and L^1 ligands function as μ_2- or μ_3-bridges across the Ag···Ag edges of the silver column to form a hydrophobic coat around it, a cross-sectional view is presented in Figure 2 to show the inner silver column and its surrounding sheath. This columnar structure is totally neutral, as opposed to the case of the mixed-valence silver(I,II) complex that contains an anionic column $[Ag^{I}_{6}(C_2)(CF_3CO_2)_5(H_2O)]$ accompanied by $[Ag^{II}(tmc)(BF_4)]^+$ ion (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) for charge balance.[6a] In the crystal structure of **1**, the columns are packed in parallel arrangement along the *a* direction.

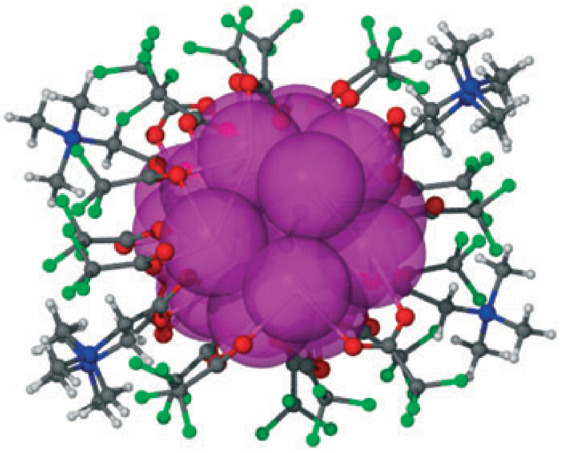


Figure 2. Perspective view along the *a* direction showing a hydrophobic sheath surrounding the silver column with enclosed C_2^{2-} species in **1**.

$[(Ag_2C_2)_2(AgCF_3CO_2)_{10}(L^2)_3]\cdot H_2O$ (2): When L^2 with a more flexible arm that links the two polar terminal groups, as compared to L^1, was used in the reaction under hydrothermal condition, neutral compound **2** crystallized as the principal product. The core is a double cage comprising fifteen silver atoms with each single cage encapsulating an acetylenediide dianion. As shown in Figure 3, the double cage is generated from the edge-sharing of a square-antiprism (cage **A**) and a distorted bicapped trigonal-prism (cage **B**). For cage **A**, atom sets Ag1-Ag2-Ag3-Ag4 and Ag5-Ag6-Ag7-Ag8 are each coplanar within 0.06 Å, making a dihedral angle of 9.8°. A C_2^{2-} species is accommodated in the silver cage and stabilized by eight σ and one π bonding interactions with its vertices in the range 2.131(9)–2.70(1) Å. Atom Ag9 further bridges two silver atoms Ag3 and Ag6 with bond lengths Ag3···Ag9 3.038(1) Å, Ag6···Ag9 3.379(1) Å.

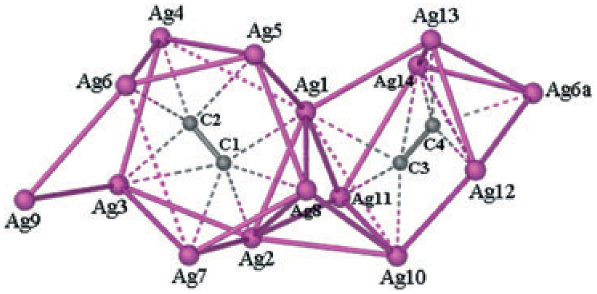


Figure 3. Double cage in **2** arising from the fusion of a square-antiprism with a distorted bicapped trigonal-prism. Polyhedral edges that are longer than 3.40 Å are represented by thick broken lines. Selected bond lengths [Å]: C1–C2 1.15(1), C3–C4 1.17(1), C1–Ag1 2.53(1), C1–Ag2 2.24(1), C1–Ag3 2.70(1), C1–Ag7 2.39(1), C1–Ag8 2.19(1), C2–Ag3 2.34(1), C2–Ag4 2.131(9), C2–Ag5 2.53(1), C2–Ag6 2.413(9), C3–Ag1 2.40(1), C3–Ag10 2.18(1), C3–Ag11 2.18(1), C3–Ag14 2.704(9), C4–Ag6a 2.289(9), C4–Ag12 2.297(9), C4–Ag13 2.18(1), C4–Ag14 2.506(9). Symmetry code: a: $x+{}^1/_2, -y+{}^1/_2, -z+1$.

Cage **B** is best described as a distorted bicapped trigonal prism, in which atoms sets Ag1-Ag10-Ag11 and Ag12-Ag13-Ag14 constitute two triangular faces making a dihedral angle of 14.5°. Atoms Ag2 and Ag6a cap the faces Ag1-Ag10-Ag11 and Ag12-Ag13-Ag14, respectively. The enclosed C_2^{2-} species is coordinated to the silver atoms through six σ and one π interactions in the range 2.179(8)–2.70(1) Å.

Cage **A** and cage **B** share the face Ag1···Ag2···Ag8 to form a double cage. Double cages of the type share vertices of the type Ag6a, together with further connection of Ag4a···Ag12 and Ag5a···Ag14, to form a helical column along the *a* direction. Also, complex **2** represents the first and only example of a helical silver(I) column with encapsulating C_2^{2-} dianion.

Similar to the case of **1**, such a column is surrounded by a hydrophobic sheath composed of trifluoroacetate and L^2 ligands. Monodentate, μ_2-O,O′ together with μ_3-O,O,O′ coordination modes of trifluoroacetate co-exist in compound **2**. An interesting feature is the rare coordination mode of L^2, which function as both μ_4-O,O,O,O′ and μ_2-O,O′ at the outer surface of the helical silver column (Figure 4).

$[(Ag_2C_2)(AgCF_3CO_2)_4(L^3)(H_2O)]\cdot 0.75\,H_2O$ (3): When the synthetic procedure of **2** was repeated with L^3 instead of L^2 at 80 °C, compound **3** was obtained. In the crystal structure of **3**, the core is a centrosymmetric double cage composed of twelve silver(I) atoms, with each single cage encapsulating an acetylenediide dianion. Each single cage is in the form of an irregular monocapped trigonal prism. Atom sets Ag1-Ag2-Ag3 and Ag1a-Ag4-Ag5 constitute two triangular faces making a dihedral angle of 2.4°. Atom Ag6 caps Ag1a-Ag4-Ag5, and two such single cages share an edge Ag1-Ag1a to form the double cage. A C_2^{2-} species is enclosed in each

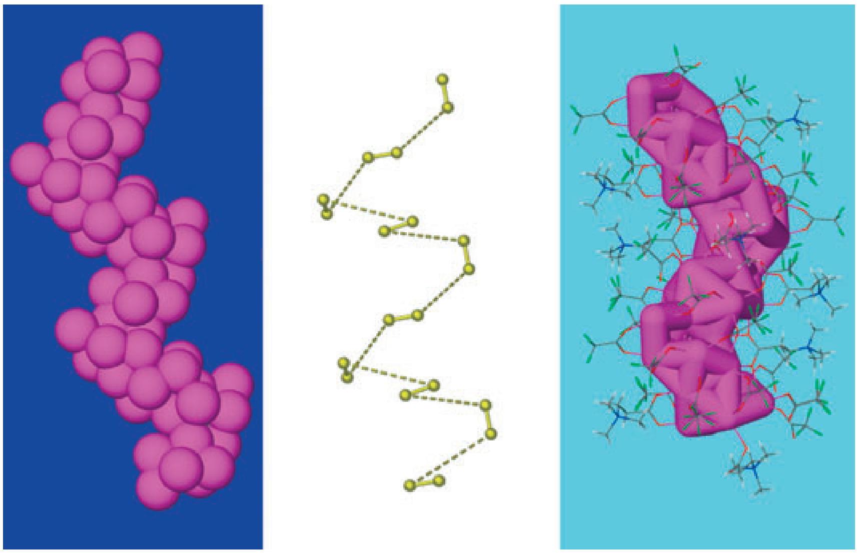


Figure 4. Left: Space-filling drawing of a portion of the helical column of **2**. Center: Trace of acetylenediide dianions hidden inside helical column; note that the broken lines do not indicate interactions. Right: Perspective view of the infinite silver(I) column with C_2^{2-} species embedded in its inner core and an exterior coat comprising anionic and zwitterionic carboxylates.

silver polyhedron and stabilized by multiple σ and π Ag–C interactions in the range 2.077(9)–2.491(8) Å. Of the water molecules in the asymmetric unit, one serves as an aqua ligand bonded to Ag1 at 2.368(8) Å, and the other are located in lattice sites.

Each double cage is connected to an adjacent cage through linkage of the type Ag3–Ag6b, Ag2–Ag5b, Ag6–Ag3b, and Ag5–Ag2b to generate an infinite column along the *a* direction (Figure 5).

Both the trifluoroacetate and L^3 ligands function as μ_2-bridges across the Ag···Ag edges of the silver column to form a hydrophobic coat around it (Figure 5).

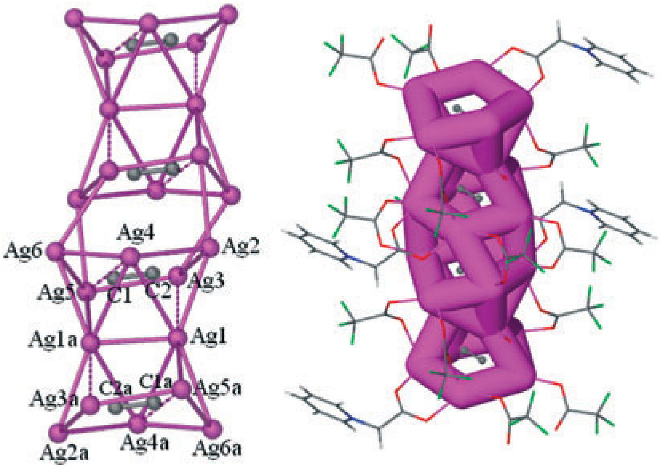


Figure 5. Left: Portion of silver column generated from fusion of the centrosymmetric double cages in **3**. Symmetry code: a: $-x, -y+1, -z$; b: $-x+1, -y+1, -z$. Selected bond lengths [Å]: C1–C2 1.23(1), C1–Ag1a 2.321(7), C1–Ag4 2.491(8), C1–Ag5 2.211(8), C1–Ag6 2.095(8), C2–Ag1 2.335(7), C2–Ag2 2.077(9), C2–Ag3 2.300(8), C2–Ag4 2.469(8). Right: Perspective view of the infinite silver(I) column with C_2^{2-} species embedded in its inner core and an exterior coat comprising anionic and zwitterionic carboxylates.

$[(Ag_2C_2)_{1.5}(AgCF_3CO_2)_7(L^4)_2]$ (4): Compound **4** contains a Ag_{15} double cage, which is generated from vertex-sharing of two types of polyhedra each encapsulating an acetylenediide dianion, namely a distorted triangulated dodecahedron (cage **A**) and a slightly distorted cube (cage **B**; Figure 6).

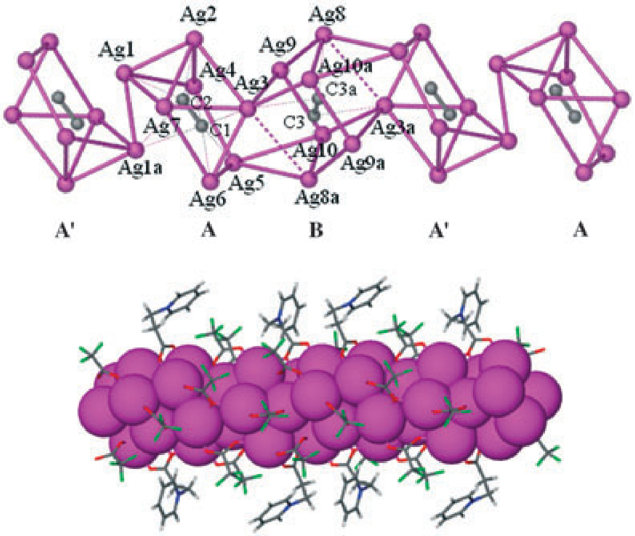


Figure 6. Top: Portion of an infinite column generated from cage **A** (distorted triangulated dodecahedron), **A′** and **B** (slightly distorted cube) in the **A′ABA′AB**··· sequence along the *a* direction in **4**. Polyhedral edges that are longer than 3.40 Å are represented by thick broken lines; the Ag–C bonds are represented by thin broken lines. Selected bond lengths [Å]: C1–C2 1.174(9), C3–C3a 1.21(1), C1–Ag1a 2.587(6), C1–Ag3 2.499(7), C1–Ag4 2.560(7), C(1)–Ag(5) 2.157(7), C1–Ag6 2.384(7), C2–Ag1 2.313(7), C2–Ag2 2.216(6), C2–Ag4 2.434(6), C2–Ag7 2.238(7), C2–Ag1a 2.617(6), C3–Ag9 2.362(6), C3–Ag10 2.198(6), C3–Ag3a 2.548(6), C3–Ag8a 2.279(6). Bottom: Space-filling drawing of the infinite silver(I) column with C_2^{2-} species embedded in its inner core and an exterior coat comprising anionic and zwitterionic carboxylates.

For cage **A**, atoms sets Ag1-Ag2-Ag3-Ag1a and Ag4-Ag5-Ag6-Ag7 are each coplanar within 0.20 and 0.09 Å, respectively, making a dihedral angle of 98.2°. This cage encloses a C_2^{2-} species with Ag–C bond lengths in the range of 2.157(7)–2.617(6) Å. Cage **A** and **A**′ share edge Ag1···Ag1b to form a centrosymmetric double cage **AA**′.

For cage **B**, the edge lengths of the cube lie in the range 2.8235(7)–3.505 Å. A C_2^{2-} ion is also accommodated in this cage and is σ-bonded to its adjacent silver atoms in the range 2.198(6)–2.548(6) Å.

Cage **A** and **B** are further fused together through sharing of the vertex Ag3, with further connection of Ag5–Ag10 (3.3293(8) Å) Ag5–Ag8a (3.3537(8) Å) to generate a double cage. A linear array of double cage **AA**′ and **B** result in an infinite column **AA′BAA′B···** along the *a* direction. The silver column in **4** is also surrounded by a hydrophobic sheath composed of μ_2-O,O and μ_3-O,O,O′ coordination modes of trifluoroacetate and L^4 ligands (Figure 6).

$[(Ag_2C_2)(AgCF_3CO_2)_7(L^5)_2(H_2O)]$ (5): Compound **5** was obtained by hydrothermal synthesis using the same starting materials $Ag_2C_2/AgBF_4/AgCF_3CO_2$ for compounds **1**–**4** with the addition of ligand L^5. The basic building block is a distorted monocapped cube. Atom sets Ag1-Ag2-Ag3-Ag2a and Ag4-Ag5-Ag6-Ag5a are each coplanar with a maximum deviation of 0.08 and 0.06 Å, respectively, making a dihedral angle of 3.7°. Atom Ag7 caps the upper face. A C_2^{2-} species is enclosed in the silver polyhedron and is stabilized by six σ-type and one π-type interactions. The Ag–C bond lengths range from 2.21(2) to 2.58(2) Å. The C1–C2 bond length (1.10(3) Å) lies close to the lower limit of 1.175(7)–1.225(7) Å found in the double and triple salts of silver acetylenediide, suggesting that the degree of metal-to-ligand back-bonding is very low in such a silver-rich environment.

In contrast to compounds **1**–**4**, in which a silver column is generated from fusion of double cages of various geometries, in **5** one of the seven independent trifluoroacetate groups and both L^5 ligands act as μ_3-bridges across adjacent single cage blocks to form a beadlike infinite chain along the *c* direction (Figure 7).

Starting with the same reaction system $Ag_2C_2/AgCF_3CO_2/AgBF_4$, but under different reaction conditions (evaporation, hydrothermal method at different temperature) and the influence of the versatile ancillary ligands L^1–L^5, an infinite silver column or beaded chain with embedded C_2^{2-} anion in its inner core and an exterior coat comprising anionic and zwitterionic carboxylates is generated in compounds **1**–**5**.

$[(Ag_2C_2)(AgC_2F_5CO_2)_7(L^1)_3(H_2O)]$ (6): In the crystal structure of **6**, the core is a distorted monocapped square prism, as shown in Figure 8. Atom sets Ag1-Ag2-Ag3-Ag4 and Ag5-Ag6-Ag7-Ag8 are each coplanar within 0.07 and 0.04 Å, respectively, making a dihedral angle of 4.9°. Atom Ag9 caps the upper face. A C_2^{2-} species is enclosed inside and stabilized by seven σ-type and one π-type interactions in the range 2.2053(8)–2.5752(8) Å.

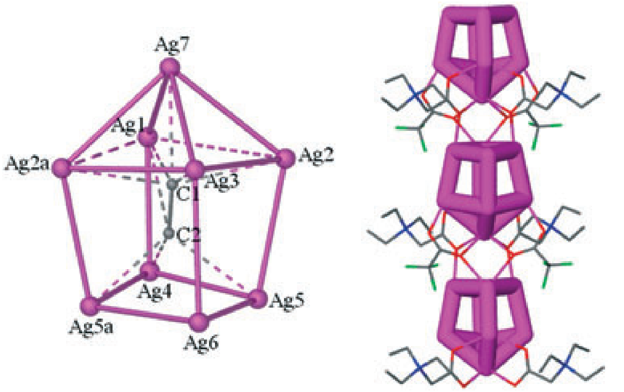


Figure 7. Left: The basic building block of **5** in the shape of distorted monocapped cube. Ag···Ag distances longer than 3.4 Å are represented by thick broken lines. Selected bond lengths [Å]: C1–C2 1.10(3), C1–Ag1 2.45(2), C1–Ag2 2.356(4), C1–Ag3 2.30(2), C1–Ag7 2.40(2), C2–Ag1 2.58(2), C2–Ag4 2.21(2), C2–Ag5 2.25(1). Right: Perspective view of silver(I) chain constructed from $C_2@Ag_9$ polyhedra connected by L^5 and trifluoroacetate bridges. Hydrogen atoms have been omitted for clarity.

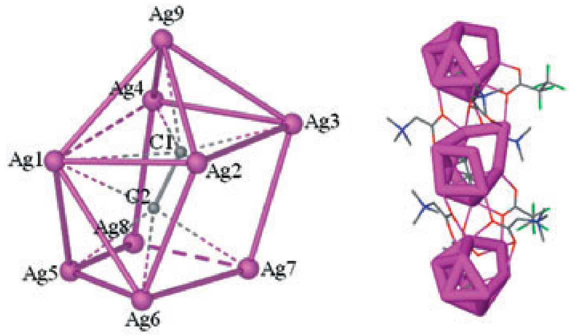


Figure 8. Left: Distorted monocapped square prism in **6**. Ag···Ag distances longer than 3.4 Å are represented by thick broken lines. Right: Portion of silver(I) chain generated from the linkage of discrete silver cage through μ_3-O,O,O′ trifluoroacetate and L^1 ligands acting in μ_4-O,O,O′,O′ and μ_3-O,O,O′ coordination modes. Selected bond lengths [Å]: C1–C2 1.199(1), C1–Ag1 2.5752(8), C1–Ag2 2.3509(6), C1–Ag3 2.2053(8), C1–Ag4 2.3641(7), C1–Ag9 2.2236(8), C2–Ag1 2.3899(8), C2–Ag5 2.2214(9), C2–Ag6 2.2739(9), C2–Ag7 2.2383(8).

The trifluoroacetate ligands exhibit different kinds of coordination modes in **6**, that is, μ-O,O′, μ-O, μ_3-O,O,O′ and μ-O,O. Another interesting feature of **6** is the role played by the L^1 ligands: they act in both μ_4-O,O,O′,O′ and μ_3-O,O,O′ modes, which together with the μ_3-O,O,O′ trifluoroacetate ligands link the $C_2@Ag_9$ motif into a beaded chain (Figure 8).

The replacement of trifluoroacetate ligands in **1** with pentafluoropropionate ligands to give **6** and the modification of the reaction conditions successfully lead to the rupture the fused silver column and result in the beaded chain of connected single cages. A plausible explanation is that the employment of the bulkier pentafluoropropionate ligand prohibited the fusion of the silver cages.

$[(Ag_2C_2)(AgCF_3CO_2)_7(L^1)_3(H_2O)]\cdot 2H_2O$ (7): An attempt to trap the CN^- ion inside the silver cage by introducing AgCN into the reaction system failed, and instead compound **7** was obtained with a structure quite different from that of **1**, showing that the influence of a subtle change for such a reaction system. X-ray single crystal analysis revealed that **7** is a beaded chain composed of L^1-linked discrete $C_2@Ag_9$ cages. The basic building block is a distorted monocapped square antiprism (Figure 9). Atoms sets Ag1-Ag2-Ag3-Ag4 and Ag5-Ag6-Ag7-Ag8 are each coplanar within 0.03 and 0.18 Å, respectively, making a dihedral angle of 4.8°. Atom Ag9 caps the Ag5-Ag6-Ag7-Ag8 face. A C_2^{2-} ion is enclosed in such a polyhedron and stabilized by six σ-type and two π-type interactions. The Ag–C bond lengths range from 2.10(2) to 2.64(2) Å. The C1–C2 bond length of 1.29(3) Å lies close to the upper limit of 1.175(7)–1.225(7) Å found in the double and triple salts of silver acetylenediide.

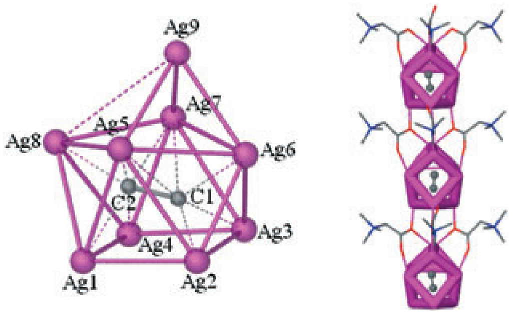


Figure 9. Left: Distorted monocapped square antiprismatic single cage in **7**. The Ag8–Ag9 edge that is longer than 3.40 Å is indicated by a thick broken line. Selected bond lengths [Å]: C1–C2 1.29(3), C1–Ag2 2.23(2), C1–Ag3 2.13(2), C1–Ag5 2.64(2), C1–Ag6 2.22(2), C1–Ag7 2.57(2), C2–Ag1 2.31(2), C2–Ag4 2.31(2), C2–Ag5 2.40(2), C2–Ag7 2.39(2), C2–Ag8 2.10(2). Right: Beadlike chain composed of $C_2@Ag_9$ cages linked by L^1 ligands.

The trifluoroacetate ligands, which exhibit only one kind of coordination mode, namely μ_2-O,O′, surround the core in **7**, while μ_2-O,O, μ_3-O,O,O′ L^1 ligands connect the discrete polyhedra into a beadlike chain (Figure 9).

$[(Ag_2C_2)(AgC_2F_5CO_2)_6(L^3)_2]$ (8): When the procedure for **6** was repeated with L^3 instead of L^1, colorless blocklike crystals of **8** were obtained. Single-crystal X-ray analysis revealed that the basic building unit in **8** is a centrosymmetric double cage composed of sixteen silver(I) atoms, in which each single cage encapsulates an acetylenediide dianion. Each single cage is an irregular monocapped trigonal prism with one additional atom. Atoms sets Ag1-Ag2-Ag3 and Ag4-Ag5-Ag6 constitute two triangular faces making a dihedral angle of 7.5°, and atom Ag7 caps the face Ag4-Ag5-Ag6. Two such single cages are linked together to form a double cage through Ag7–Ag7a, Ag7a–Ag5, and Ag7–Ag5a bonds. A C_2^{2-} ion is enclosed in each silver polyhedron and is stabilized by mixed (σ, π) Ag–C interactions in the range 2.19(1)–2.64(1) Å.

The $(C_2)_2@Ag_{16}$ double cage in **8** is surrounded by twelve pentafluoropropionate ligands acting in the μ-O,O′ coordination mode. As regards L^3, although it exhibits only one coordination mode, namely μ_2-O,O′, it can be divided into two types: one kind bridges an Ag–Ag edge, the other kind links a pair of double cages to form an infinite chain, as shown in Figure 10.

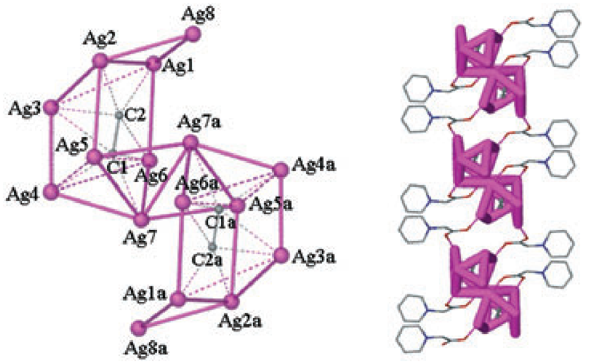


Figure 10. Left: Central core (double cage) consisting of 16 silver(I) atoms in **8**. Polyhedral edges that are longer than 3.40 Å are represented by thick broken lines. Selected bond lengths [Å]: C1–C2 1.21(2), C1–Ag3 2.64(1), C1–Ag4 2.25(1), C1–Ag5 2.30(2), C1–Ag6 2.32(1), C1–Ag7 2.30(1), C2–Ag(1) 2.23(1), C2–Ag2 2.19(1), C2–Ag3 2.31(1), C2–Ag6 2.48(1). Right: Silver(I) chain generated from the linkage of $(C_2)_2@Ag_{16}$ double cages by μ-O,O′ L^3 ligands.

$[(Ag_2C_2)_2(AgC_2F_5CO_2)_{12}(L^4)_2(H_2O)_4]\cdot H_2O$ (9): In contrast to compounds **1**–**8**, in which only an infinite column or chain is formed, compound **9** has a quite different two-dimensional architecture composed of Ag–Ag-bond-linked silver columns. The basic building unit in **9** is a double cage of fourteen silver atoms, in which each cage is a monocapped trigonal prism (Figure 11). For the left cage, atom sets Ag1-Ag2-Ag3 and Ag4-Ag5-Ag6 constitute two triangular faces

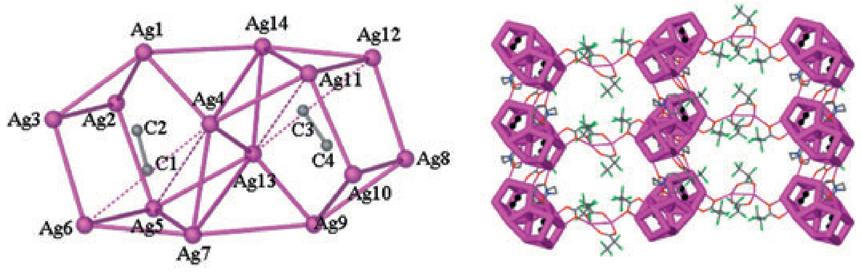


Figure 11. Left: $(C_2)_2@Ag_{14}$ double cage in **9**, with each single cage taking the shape of a monocapped trigonal prism. Polyhedral edges longer than 3.40 Å are represented by broken lines. Right: Two-dimensional architecture generated from the linkage of silver(I) chains by $[Ag_2(C_2F_5CO_2)_2]$ units. Selected bond lengths [Å]: C1–C2 1.09(2), C3–C4 1.16(2), C2–Ag1 2.13(2), C2–Ag2 2.32(1), C2–Ag3 2.30(2), C2–Ag4 2.51(2), C1–Ag4 2.62(2), C1–Ag5 2.24(2), C1–Ag6 2.27(2), C1–Ag7 2.24(2), C4–Ag8 2.21(2), C4–Ag9 2.16(2), C4–Ag10 2.26(2), C3–Ag11 2.33(1), C3–Ag12 2.36(2), C4–Ag12 2.69(2), C3–Ag13 2.42(2), C4–Ag13 2.69(2), C3–Ag14 2.12(2).

making a dihedral angle of 6°, and Ag7 caps the lower face. As regards the right trigonal prism on the right side, the two triangular faces Ag8-Ag9-Ag10 and Ag11-Ag12-Ag13 are almost parallel, making a dihedral angle of 3.3°, and Ag14 caps the Ag11-Ag12-Ag13 face. Two such single cages fused together to form a double cage through linkage of Ag1–Ag14, Ag4–Ag14, Ag4–Ag11, Ag7–Ag9, Ag7–Ag13, and Ag5–Ag13.

Three kinds of coordination mode of the pentafluoropropionate exist in **9**, that is, μ-O, μ_2-O,O′, μ_3-O,O,O′. The μ_3-O,O,O′ type of pentafluoropropionate, together with the μ_4-O,O,O′,O′ mode of L^4, link the discrete double cages into a beaded chain. Cross-linkage of such chains through $[Ag_2(C_2F_5CO_2)_2]$ bridging groups gives rise to a two-dimensional architecture for **9**, as shown in Figure 11.

It is noteworthy that the employment of the bulkier pentafluoropropionate ligand yielded a two-dimensional architecture for **9**, which is at variance with our pervious observation, for example, where the introduction of the bulkier pentafluoropropionate ligand led to discrete supermolecules with ancillary ligation of either [15]crown-5 or [18]crown-6. The compound $Ag_2C_2 \cdot 9\,AgC_2F_5CO_2 \cdot 3\,MeCN \cdot H_2O$ is also a discrete high-nuclearity cluster with bulky acetonitrile as a terminal ligand.

$[(Ag_2C_2)(AgCF_3CO_2)_6(L^3)_2(H_2O)] \cdot H_2O$ (10): Compound **10** was obtained in a similar way to that for **7** except that L^3 was used instead of L^1. Single-crystal analysis revealed that **10** has a two-dimensional architecture. The basic building block in **10** is a centrosymmetric double cage with two embedded C_2^{2-} ions in each triangulated dodecahedron cage (Figure 12). Atom sets Ag1-Ag2-Ag3-Ag4 and Ag5-Ag6-Ag7-Ag7a are each coplanar within 0.02 and 0.23 Å, respectively, making a dihedral angle of 101°. A C_2^{2-} species is enclosed in each silver polyhedron and is stabilized by multiple σ- and π-interactions with silver(I) in the range of 2.121(9)-2.701(9) Å.

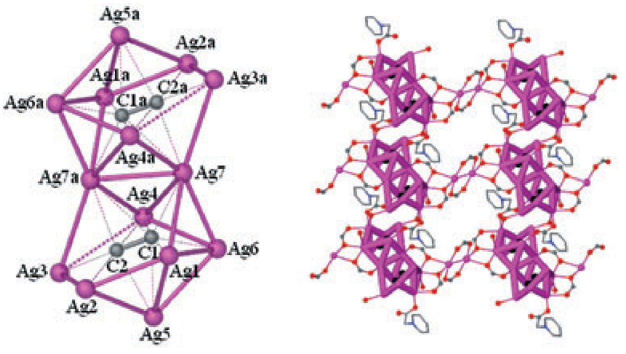


Figure 12. Left: Centrosymmetric double cage in **10**, with each half taking the shape of a triangulated dodecahedron. Selected bond lengths [Å]: C1–C2 1.22(1), C1–Ag1 2.256(9), C1–Ag4 2.351(9), C1–Ag5 2.576(9), C1–Ag6 2.190(9), C1–Ag7 2.362(9), C1–Ag7a 2.701(9), C2–Ag2 2.436(9), C2–Ag3 2.121(9), C2–Ag4 2.443(9), C2–Ag5 2.455(9), C2–Ag7a 2.447(9). Right: Two-dimensional structure formed from the linkage of columns by $[Ag_2(CF_3CO_2)_2]$ units. Some of the L^3 and trifluoroacetate ligands, the CF_3 groups of bridging trifluoroacetate ligands, and hydrogen atoms have been omitted for clarity.

Similar to the case of **8**, L^3 acts only in the μ_2-O,O′ mode to connect the double cages into an infinite chain. An interesting feature of **10** is that the aqua ligands serve as bridging ligands within a chain, as shown in Figure 12. The two-dimensional structure of **10** is consolidated by cross-linkage of the chains through $[Ag_2(CF_3CO_2)_2]$ bridging.

A common structural feature in compounds **5**, **6**, and **9** is that both the betaine derivatives and the perfluoroalkyl carboxylates are involved in the connection of the silver(I) cages into an infinite chain. For compounds **7**, **8**, and **10**, only the betaine derivatives take part in the linkage of discrete silver(I) cages into infinite chains. Another point worthy of note is that irregular or highly distorted silver(I) cages generally occur in all the compounds, which may be due to the competition of the zwitterionic carboxylate groups with the C_2^{2-} dianion for coordination sites around the silver(I) atoms. When the bulky pentafluoropropionate anion is used in place of trifluoroacetate, no fused silver(I) column is generated, although in the case of compound **9** this leads to a layer-type architecture.

Conclusion

In summary, we have shown that it is practicable to incorporate betaines of both trialkylammonio and pyridinio classes, each playing the role of a zwitterionic carboxylate, as new components in the formation of double salts of silver(I) acetylenediide and silver(I) perfluorocarboxylate, leading to the generation of neutral infinite columns of fused silver(I) polyhedra or chains of linked polyhedra, with C_2^{2-} species embedded in the inner core and hydrophobic groups as a surface coat. The work here may shed some light on the self-assembly of fluorinated ligands and carboxylate networks.[7] Since silver(I) coordination compounds of a wide variety of betaines,[8] double betaines,[9] and their tertiary phosphonio analogues[10] have been reported, the present investigation opens the way to further studies on supramolecular assembly with silver acetylenediide.

Experimental Section

Ag_2C_2 was prepared as described previously.[1] Ligand L^1 was commercially available from Aldrich. Ligands L^2, L^3, L^4, L^5 were synthesized according to the literature methods.[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 amounts can be disposed of by slow decomposition in an alkaline solution.*[11] *To ensure safety, we used moist* Ag_2C_2 *in all preparations. Although the double salts of* Ag_2C_2 *are less prone to explosion, they should be handled with extreme care.*

Preparation of $[(Ag_2C_2)_2(AgCF_3CO_2)_9(L^1)_3]$ (1): Freshly prepared Ag_2C_2 was added to an aqueous solution (1 mL) of $AgCF_3CO_2$ (0.442 g, 2 mmol) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, and L^1 (33 mg) was added to the filtrate. The resulting solution was allowed to stand without disturbance, and pale yellow needles of **1** were obtained in almost quantitative yield (based on Me_3bet). Compound **1** is stable in the dark but readily decomposes in common solvents such as water and ethanol. Elemental analysis calcd (%) for $C_{37}H_{33}Ag_{13}F_{27}N_3O_{24}$: C 15.77, H 1.18, N 1.49; found: C 15.90, H 1.14, N 1.40.

Preparation of $[(Ag_2C_2)_2(AgCF_3CO_2)_{10}(L^2)_3]\cdot H_2O$ (2): Excess moistened Ag_2C_2 (ca. 0.5 g, 2 mmol) was added to 1 mL of a concentrated aqueous solution of $AgCF_3CO_2$ (0.446 g, 2 mmol) and $AgBF_4$ (0.409 g, 2.1 mmol) in a plastic beaker with stirring. The undissolved amount of Ag_2C_2 was filtered off, and then L^2 (42 mg) was added to the filtrate. The resulting suspension was placed in a 25-mL Teflon-lined stainless steel reaction vessel and subjected to hydrothermal conditions at 110°C for 36 h, and then cooled to room temperature at 6°C h^{-1}. Colorless blocklike crystals of **2** were isolated in about 60% yield. Elemental analysis calcd (%) for $C_{42}H_{41}Ag_{14}F_{30}N_3O_{27}$: C 16.27, H 1.33, N 1.36; found: C 16.32, H 1.31, N 1.40.

Preparation of $[(Ag_2C_2)(AgCF_3CO_2)_4(L^3)(H_2O)]\cdot 0.75H_2O$ (3): When the procedure for **2** was repeated with L^3 instead of L^2 at 80°C, a mixture of needlelike and blocklike crystals were obtained, which can be separated manually. The needlelike crystals were poor quality and not suitable for X-ray analysis, on the other hand the blocklike crystals of **3** were characterized by X-ray structure analysis. Yield: ca. 20%. Elemental analysis calcd (%) for $C_{17}H_{10.5}NO_{11.75}F_{12}Ag_6$: C 15.86, H 0.82, N 1.09; found: C 15.78, H 0.79, N 1.04.

Preparation of $[(Ag_2C_2)_{1.5}(AgCF_3CO_2)_7(L^4)_2]$ (4): The synthetic procedure for **2** was repeated by using L^4 instead of L^2. Colorless blocklike crystals of **4** were obtained in about 63% yield. Elemental analysis calcd (%) for $C_{33}H_{18}Ag_{10}F_{21}N_2O_{18}$: C 18.02, H 0.83, N 1.27; found: C 17.98, H 0.79, N 1.31.

Preparation of $[(Ag_2C_2)(AgCF_3CO_2)_7(L^5)_2(H_2O)]$ (5): Compound **5** was synthesized in a similar manner to **2** except that L^5 was used instead of L^2. Colorless blocklike crystals were obtained in about 45% yield. Elemental analysis calcd (%) for $C_{32}H_{36}Ag_9F_{21}N_2O_{19}$: C 18.17, H 1.72, N 1.33; found: C 18.32, H 1.69, N 1.35.

Preparation of $[(Ag_2C_2)(AgC_2F_5CO_2)_7(L^1)_3(H_2O)]$ (6): Excess Ag_2C_2 (ca. 0.5 g) was added to 1 mL of a concentrated aqueous solution of $AgC_2F_5CO_2$ (0.44 g, 2 mmol) and $AgBF_4$ (0.40 g, 2 mmol) in a plastic beaker with stirring until saturated. The undissolved amount of Ag_2C_2 was filtered off, and then L^1 (50 mg) was added to the filtrate. The resulted suspension was treated under hydrothermal conditions at 110°C for 48 h, and then cooled to room temperature at 6°C h^{-1}. Colorless blocklike crystals were isolated in about 42% yield. Elemental analysis calcd

Table 1. Crystal data for compounds **1–10**.

	1	**2**	**3**	**4**	**5**
formula	$C_{37}H_{33}Ag_{13}F_{27}N_3O_{24}$	$C_{42}H_{41}Ag_{14}F_{30}N_3O_{27}$	$C_{17}H_{10.5}Ag_6F_{12}NO_{11.75}$	$C_{33}H_{18}Ag_{10}F_{21}N_2O_{18}$	$C_{32}H_{34}Ag_9F_{21}N_2O_{19}$
crystal system	monoclinic	orthorhombic	triclinic	monoclinic	orthorhombic
space group	$P2_1/c$ (no. 14)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$Cmc2_1$ (no. 36)
a [Å]	18.7164(5)	15.500(1)	8.3681(5)	13.4828(8)	26.814(1)
b [Å]	14.2127(4)	19.005(1)	12.0944(7)	25.250(1)	13.0947(7)
c [Å]	25.5025(8)	25.529(2)	15.9243(9)	15.2296(8)	15.8528(8)
α [°]	90	90	107.866(1)	90	90
β [°]	100.007(1)	90	98.819(1)	103.702(1)	90
γ [°]	90	90	96.667(1)	90	90
V [Å^3]	6680.7(3)	7520.1(9)	1492.8 (2)	5037.2(5)	5566.3(5)
Z	4	4	2	4	4
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	3.865	3.704	3.990	3.946	3.231
ρ_{calcd} [g cm^{-3}]	2.803	2.736	2.866	2.912	2.530
total refl.	44 940	51 288	8268	33 757	19 236
unique refl.	16 107	18 116	5193	12 122	5694
data [$I > 2\sigma(I)$]	7200	11 300	4496	8830	4736
parameters	960	1124	440	757	403
R_1 (obs.)	0.0499	0.0445	0.0617	0.0425	0.0687
wR_2 (all data)	0.1367	0.1114	0.1673	0.1202	0.1710

	6	**7**	**8**	**9**	**10**
formula	$C_{38}H_{33}Ag_9F_{35}N_3O_{21}$	$C_{31}H_{33}Ag_9F_{21}N_3O_{23}$	$C_{34}H_{14}Ag_8F_{30}N_2O_{16}$	$C_{56}H_{18}Ag_{16}F_{60}N_2O_{33}$	$C_{28}H_{14}Ag_8F_{18}N_2O_{18}$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	Cc (no. 9)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	16.0427(8)	14.7622(8)	10.7789(9)	9.9166(7)	9.7561(5)
b [Å]	28.045 (1)	26.258(1)	17.709(1)	36.400(3)	16.3890(9)
c [Å]	16.3879(8)	15.7780(8)	28.183(2)	28.644(2)	28.707 (2)
α [°]	90	90	90	90	90
β [°]	112.091(1)	102.683(1)	97.293(2)	95.766(2)	91.327(1)
γ [°]	90	90	90	90	90
V [Å^3]	6831.9(6)	5966.8(5)	5336.0(8)	10 287(1)	4588.9(4)
Z	4	4	4	4	4
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	2.684	3.024	3.042	3.150	3.483
ρ_{calcd} [g cm^{-3}]	2.434	2.433	2.663	2.655	2.709
total refl.	29 829	15 949	22 990	55 944	25 329
unique refl.	12 038	9514	9363	18 096	8083
data [$I > 2\sigma(I)$]	7721	6527	5547	8336	6692
parameters	955	759	805	1514	695
R_1 (obs.)	0.0541	0.0870	0.0815	0.0712	0.0554
wR_2 (all data)	0.1541	0.2027	0.2265	0.2255	0.1238

(%) for $C_{38}H_{35}Ag_9F_{35}N_3O_{21}$: C 18.27, H 1.41, N 1.68; found: C 18.35, H 1.36, N 1.72.

Preparation of $[(Ag_2C_2)(AgCF_3CO_2)_7(L^1)_3(H_2O)]\cdot 2H_2O$ (7): This compound was obtained serendipitously in an attempt to trap CN^- inside the silver cage by introducing AgCN into the reaction system. Excess Ag_2C_2 (ca. 0.5 g) and AgCN (ca. 0.53 g, 4 mmol) were added to 1 mL of a concentrated aqueous solution of $AgCF_3CO_2$ (0.447 g, 2 mmol) and $AgBF_4$ (0.213 g, 1 mmol) in a plastic beaker with stirring until saturated. The undissolved amount of Ag_2C_2 and AgCN was filtered off, and L^1 (52 mg) was added to the filtrate. The resulting suspension was treated by the hydrothermal method as described above. Colorless blocklike crystals were isolated in about 30% yield. Elemental analysis calcd (%) for $C_{31}H_{39}Ag_9F_{21}N_3O_{23}$: C 17.05, H 1.80, N 1.92; found: C 16.99, H 1.79, N 1.87.

Preparation of $[(Ag_2C_2)(AgC_2F_5CO_2)_6(L^3)_2]$ (8): When the procedure for **6** was repeated with L^3 instead of L^1, colorless blocklike crystals of **8** were obtained in about 65% yield. Elemental analysis calcd (%) for $C_{34}H_{14}N_2O_{16}F_{30}Ag_8$: C 19.09, H 0.66, N 1.31; found: C 19.22, H 0.65, N 1.27.

Preparation of $[(Ag_2C_2)_2(AgC_2F_5CO_2)_{12}(L^4)_2(H_2O)_4]\cdot H_2O$ (9): Compound **9** was synthesized in a similar manner to compound **6** using L^4. Colorless blocklike crystals of **9** were obtained in about 35% yield. Elemental analysis calcd (%) for $C_{56}H_{28}N_2O_{33}F_{60}Ag_{16}$: C 16.36, H 0.69, N 0.68; found: C 16.44, H 0.63, N 0.67.

Preparation of $[(Ag_2C_2)(AgCF_3CO_2)_6(L^3)_2(H_2O)]\cdot H_2O$ (10): When the procedure for **7** was repeated with L^3 instead of L^1, colorless blocklike crystals of **10** were obtained in about 40% yield. Elemental analysis calcd (%) for $C_{28}H_{18}N_2O_{18}F_{18}Ag_8$: C 17.93, H 0.97, N 1.49; found: C 17.41, H 0.86, N 1.37.

X-ray crystallography: Data collection was performed at 293 K on a Bruker SMART 1000 CCD diffractometer using frames of oscillation range 0.3°, with $1.5° < \theta < 28°$. An empirical absorption correction was applied by using the SADABS program[12] to all the compounds except compound **3**. The structures were solved by direct methods, and non-hydrogen atoms were located from difference-Fourier maps. All the non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using the SHELXTL program.[13] Some of the water oxygen atoms in **3** have 1/4 occupancies. The crystal data and details of refinement are given in Table 1.

CCDC-256251—CCDC-256260 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

Financial support from the Hong Kong Research Grants Council (CERG Ref. No. CUHK 401704) is gratefully acknowledged.

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Received: November 20, 2004