J. Am. Chem. Soc. **2001,** *123,* 7594−7600

Argentophilicity and Solvent-Induced Structural Diversity in Double Salts of Silver Acetylide with Silver Perfluoroalkyl Carboxylates

Quan-Ming Wang and Thomas C. W. Mak*

Contribution from the Department of Chemistry, The Chinese University of Hong Kong,
Shatin, New Territories, Hong Kong SAR, P. R. China

Received December 27, 2000

Abstract: A series of novel double salts of silver(I) were isolated by dissolving Ag_2C_2 in a concentrated aqueous solution of R_FCO_2Ag ($R_F = CF_3$, C_2F_5) and $AgBF_4$. Different ancillary solvento ligands such as H_2O, CH_3CN, and C_2H_5CN were found to affect the crystallization process that led to the assembly of various silver(I) cages with embedded C_2^{2-} ions. $2Ag_2C_2{\cdot}12CF_3CO_2Ag{\cdot}5H_2O$ (**1**) consists of two independent $C_2@Ag_7$ cages, each having the shape of a basket with a square base. $Ag_2C_2{\cdot}6CF_3CO_2Ag{\cdot}3CH_3CN$ (**2**) contains a zigzag chain of edge-sharing triangulated dodecahedra, and $4Ag_2C_2{\cdot}23CF_3CO_2Ag{\cdot}7C_2H_5CN{\cdot}2.5H_2O$ (**3**) features an unusual double-walled silver column constructed from the fusion of four different kinds of irregular polyhedra. $Ag_2C_2{\cdot}10C_2F_5CO_2Ag{\cdot}9.5H_2O$ (**4**), $Ag_2C_2{\cdot}9C_2F_5CO_2Ag{\cdot}3CH_3CN{\cdot}H_2O$ (**5**), and $Ag_2C_2{\cdot}6C_2F_5CO_2Ag{\cdot}2C_2H_5CN$ (**6**) all contain an edge-sharing double cage with each single cage in the shape of a square antiprism, a capped square antiprism, and a triangulated dodecahedron, respectively.

Introduction

The binding of silver(I) to alkenes[1] and aromatics[2] has a long history, and current interest in this type of silver−π interaction, especially in complexes involving arenes[3] and fullerenes,[4] has generated interesting information on their structural aspects and physical properties. Silver compounds containing substituted ethynyl ligands ($R{-}C{\equiv}C^-$) have also been extensively investigated,[5] and there exist a few examples of silver−ethyne ($HC{\equiv}CH$)[6] and −ethynyl ($HC{\equiv}C^-$) binding.[7] However, the silver−ethynediyl ($^-C{\equiv}C^-$, acetylide dianion, IUPAC name acetylenediide) interaction was seldom studied until recently[8−11] due to the explosive nature of Ag_2C_2 and its insolubility in most solvents, which present serious difficulties in synthesis and characterization.

The significance of argentophilicity, namely, the $d^{10}-d^{10}$ closed-shell attraction[12] that promotes the aggregation of silver(I) centers, has been supported by recent spectroscopic and structural evidence.[8−11,13,14] Taking advantage of argentophilic interaction and the versatile coordination capability of C_2^{2-}, we have prepared a series of silver(I) double salts formulated as $Ag_2C_2{\cdot}8AgF$,[9a] $Ag_2C_2{\cdot}2AgClO_4{\cdot}2H_2O$,[9b] and $Ag_2C_2{\cdot}mAgNO_3$ ($m = 1, 5, 5.5, 65$),[9c] as well as two intriguing isomorphous triple salts $Ag_2C_2{\cdot}AgF{\cdot}4CF_3SO_3Ag{\cdot}2L$ ($L = CH_3CN$, C_2H_5CN) exhibiting a honeycomb network.[10] Very recently, we reported a quadruple salt $2Ag_2C_2{\cdot}3AgCN{\cdot}15CF_3CO_2Ag{\cdot}2AgBF_4{\cdot}9H_2O$, which features an elliptic column constructed from a novel $(C_2)_2@Ag_{13}$ double cage and $[Ag_4CN]$ and $[Ag_6(CN)_2]$ fragments.[11] In all these silver(I) double/multiple salts, the C_2^{2-} species is always encapsulated inside an Ag_n ($n = 6, 7, 8, 9$) polyhedral cage and stabilized through mixed $\sigma-\pi$ interactions with its vertexes. Since this coordination mode of C_2^{2-} is much more flexible versus the linear end-to-end bridging mode in the $\{[AgC_2]^-\}_n$ infinite chain of ternary alkali metal silver acetylides $MAgC_2$ (M = Li, Na, K, Rb, Cs)[15] and the planar μ_4-η^1,η^2 mode in the tetranuclear cation $[Cu_4(\mu\text{-dppm})_4(C_2)]^{2+}$,[16] the structures of the silver acetylide-containing systems are quite unpredictable.

In the construction of inorganic coordination polymers, the ligand functionality,[17] the nature of anion,[18] and the solvent [19] are all crucial to the type of solid-state architecture obtained. In regard to silver acetylide-containing systems, our interest has been directed toward an understanding of the assembly process

---

* To whom correspondence should be addressed. Fax: (852) 2603-5057. E-mail: tcwmak@cuhk.edu.hk.

[1] Mak, T. C. W. In *Molecular Structure: Chemical Reactivity and Biological Activity*; Stezowski, J. J., Huang, J. L., Shao, M. C., Eds.; Oxford University Press: New York, 1988; pp 325−344 and references therein.

[2] (a) Hall, E. A.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1968**, 622. (b) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 5407 and references therein.

[3] (a) Munakata, M.; Ning, G. L.; Suenaga, Y.; Kuroda-Sowa, T.; Maekawa, M.; Ohta, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 4555. (b) Munakata, M.; Wu, L. P.; Ning, G. L. *Coord. Chem. Rev.* **2000**, *198*, 171. (c) Lindeman, S. V.; Rathore, R.; Kochi, J. K. *Inorg. Chem.* **2000**, *39*, 5707.

[4] Olmstead, M. M.; Maitra, K.; Balch, A. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 231.

[5] (a) Janssen, M. D.; Köhler, K.; Herres, M.; Dedieu, A.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Am. Chem. Soc.* **1996**, *118*, 4817. (b) Lang, H.; Köhler, K.; Blau, S. *Coord. Chem. Soc.* **1995**, *143*, 113.

[6] Dias, H. V. R.; Wang, Z.-Y.; Jin, W.-C. *Inorg. Chem.* **1997**, *36*, 6205.

[7] Yamazaki, S.; Deeming, A. J.; Speel, D. M.; Hibbs, D. E.; Hursthouse, M. B.; Malik, K. M. A. *Chem. Commun.* **1997**, 963.

[8] Guo, G.-C.; Mak, T. C. W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3183

[9] (a) Guo, G.-C.; Zhou, G.-D.; Wang, Q.-G.; Mak, T. C. W.*Angew. Chem., Int. Ed.* **1998**, *37*, 630. (b) Guo, G.-C.; Wang, Q.-G.; Zhou, G.-D.; Mak, T. C. W. *Chem. Commun.* **1998**, 339. (c) Guo, G.-C.; Zhou, G.-D.; Mak, T. C. W. *J. Am. Chem. Soc.* **1999**, *121*, 3136.

[10] Wang, Q.-M.; Mak, T. C. W. *J. Am. Chem. Soc.* **2000**, *122*, 7608.

[11] Wang, Q.-M.; Mak, T. C. W. *J. Am. Chem. Soc.* **2001**, 123, 1501.

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

[13] (a) Rawashdeh-Omary, M. A.; Omary, M. A.; Patterson, H. H. *J. Am. Chem. Soc.* **2000**, *122*, 10371. (b) Omary, M. A.; Webb, T. R.; Assefa, Z.; Shankle, G. E.; Patterson, H. H. *Inorg. Chem.* **1998**, *37*, 1380.

[14] Che, C.-M.; Tse, M.-C.; Chan, M. C. W.; Cheung, K. K.; Phillips, D. L.; Leung K.-H. *J. Am. Chem. Soc.* **2000**, *122*, 2464.

[15] Kockelmann, W.; Ruschewitz, U. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3492.

[16] Yam, V. W.-W.; Fung, W. K.-M.; Cheung, K.-K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1100.

10.1021/ja0043441 CCC: $20.00

of both the silver cages and the resulting crystal structures. Thus far, all reported compounds in this category have either layer-type or network structures, with the component $C_2@Ag_n$ cages sharing common vertexes or linked by bridging ligands. To lower the dimensionality of the resulting crystal structures, as bridging groups we choose trifluoroacetate (tfa) and pentafluoropropionate (pfp), which bear bulky hydrophobic tails, in contrast to the small inorganic anions (e.g., fluoride, nitrate, and perchlorate) used previously. However, difficulties were encountered in isolating double salts of the type $Ag_2C_2{\cdot}m$Ag(tfa) or $Ag_2C_2{\cdot}m$Ag(pfp) using conventional methods such as variation of the concentration of reactants, temperature, or solvent and hydrothermal synthesis. Noting that $AgBF_4$ has extremely high solubility in water and BF_4^- is a classical noncoordinating anion, we developed a new strategy by adding sufficient $AgBF_4$ to the reaction solution, thereby increasing the silver ion concentration to promote the dissolution of Ag_2C_2. Application of such a procedure successfully led to the isolation of a series of novel double salts of silver(I) acetylide: $2Ag_2C_2{\cdot}12CF_3CO_2Ag{\cdot}5H_2O$ (**1**), $Ag_2C_2{\cdot}6CF_3CO_2Ag{\cdot}3CH_3CN$ (**2**), $4Ag_2C_2{\cdot}23CF_3CO_2Ag{\cdot}7C_2H_5CN{\cdot}2.5H_2O$ (**3**), $Ag_2C_2{\cdot}10C_2F_5CO_2Ag{\cdot}9.5H_2O$ (**4**), $Ag_2C_2{\cdot}9C_2F_5CO_2Ag{\cdot}3CH_3CN{\cdot}H_2O$ (**5**), and $Ag_2C_2{\cdot}6C_2F_5CO_2Ag{\cdot}2C_2H_5CN$ (**6**). The synthesis and X-ray structural characterization of **1**−**6** are reported in this paper, and the role of the perfluoroalkyl carboxylato and solvento ligands in generating the crystal structures is also discussed.

Experimental Section

Chemicals were used as purchased from Aldrich and ACROS without further purification. Ag_2C_2 was prepared as described previously.[9] **CAUTION**: Thoroughly dried Ag_2C_2 detonates easily upon mechanical shock or heating, and only a small quantity should be used in any chemical reaction.

Synthesis of $2Ag_2C_2{\cdot}12CF_3CO_2Ag{\cdot}5H_2O$ (1). Ag_2C_2 was added to 1 mL of a concentrated aqueous solution of CF_3CO_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, and the filtrate was placed in a desiccator charged with P_2O_5. Colorless prismatic crystals of **1** were obtained in ∼30% yield after several days.

Synthesis of $Ag_2C_2{\cdot}6CF_3CO_2Ag{\cdot}3CH_3CN$ (2). Ag_2C_2 was added to 1 mL of a concentrated aqueous solution of CF_3CO_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, and a few drops of CH_3CN were added to the filtrate. ([Note: excess CH_3CN 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 needlelike crystals of **2** were obtained in over 50% yield after several days.

Synthesis of $4Ag_2C_2{\cdot}23CF_3CO_2Ag{\cdot}7C_2H_5CN{\cdot}2.5H_2O$ (3). The previous procedure was repeated using C_2H_5CN in place of CH_3CN. Colorless blocklike crystals of **3** were obtained in over 50% yield after several days.

Synthesis of $Ag_2C_2{\cdot}10C_2F_5CO_2Ag{\cdot}9.5H_2O$ (4). Ag_2C_2 was added to 1 mL of a concentrated aqueous solution of $C_2F_5CO_2Ag$ 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 rhombic platelike crystals of **4** were obtained in ∼30% yield after several days.

Synthesis of $Ag_2C_2{\cdot}9C_2F_5CO_2Ag{\cdot}3CH_3CN{\cdot}H_2O$ (5). Ag_2C_2 was added to 1 mL of a concentrated aqueous solution of $C_2F_5CO_2Ag$ 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, and a few drops of CH_3CN were added to the filtrate. The resulting solution was placed in a desiccator charged with P_2O_5. Colorless blocklike crystals of **5** were obtained in ∼20% yield after several days.

Synthesis of $Ag_2C_2{\cdot}6C_2F_5CO_2Ag{\cdot}2C_2H_5CN$ (6). The previous procedure was repeated using C_2H_5CN in place of CH_3CN. Colorless platelike crystals of **6** were obtained in ∼30% yield after several days.

All six compounds can be kept stable for a few weeks when stored in the dark, but they decompose readily in common solvents such as water, ethanol, and acetonitrile.

X-ray Crystallographic Analysis. Suitable crystals sealed inside Lindemann glass capillaries were used for data collection on a Bruker SMART 1000 CCD diffractometer at 293 K using frames of oscillation range 0.3°, with $2° < \theta < 28°$. An empirical absorption correction was applied using the SADABS program.[20] The structures were solved by the direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package.[21] The crystal data and X-ray structure analysis parameters are summarized in Table 1. Selected bond distances are available as Supporting Information.

Two acetonitrile solvent molecules and the F atoms of one tfa in **2** are disordered and were refined isotropically. One Ag atom in **4** is disordered over two positions, being represented by Ag12 with a site occupancy factor (sof) = 0.7 and Ag13 with sof = 0.3. Some terminal C and F atoms of pfp groups in **4**−**6** exhibited large thermal motion and were subjected to suitable restraints in refinement.

Results and Discussion

Although Ag_2C_2 is insoluble in common solvents, it can be dissolved in a concentrated aqueous solution of a soluble silver salt such as AgF, $AgNO_3$, or $AgClO_4$. The mechanism of the dissolution process is not clear at present, but it is conceivable that argentophilicity provides the driving force to transform Ag_2C_2 to some soluble $[C_2@Ag_n]^{(n-2)+}$ species. The addition of $AgBF_4$ is based on the premise that it can provide a sufficiently high concentration of silver(I) ions, which is requisite for dissolving Ag_2C_2. In such a situation, $AgBF_4$ can be regarded as a kind of "silver(I) ion source", which both promotes the dissolution of Ag_2C_2 and favors the crystallization of double salts of Ag_2C_2 and R_FCO_2Ag ($R_F = CF_3$, C_2F_5). In contrast, AgF, $AgClO_4$, and $AgNO_3$ are not suitable substitutes for $AgBF_4$ as an additive, as their use would lead to the deposition of stable products such as $Ag_2C_2{\cdot}8AgF$,[9a] $Ag_2C_2{\cdot}2AgClO_4{\cdot}2H_2O$,[9b] and $Ag_2C_2{\cdot}6AgNO_3$.[9c] Moreover, in some circumstances, $AgBF_4$ can act as the precursor of AgF whose gradual release in situ plays a key role in the formation of some silver acetylide triple salts.[10]

The crystal structure of **1** contains two almost identical $C_2@Ag_7$ cages in the independent unit, which are illustrated in Figure 1. Each silver cage is best described as a basket with a square base. The four basal silver atoms Ag4Ag5Ag6Ag7 deviate from coplanarity by 0.087 Å, the Ag···Ag sides being in the range 2.909(2)−3.182(2) Å with angles 81.84(5)−97.44(5)°. Such a cage has quasi-C_2 symmetry, with both each carbon atom of C_2^{2-} bound to four silver atoms. The Ag−C distances fall in the range of 2.15(1)−2.46(2) Å. The $C_2@Ag_7$ cages are connected to each other through tfa bridges to generate a 2D layer (Figure 2), and such layers are further linked by silver atoms of type Ag15 and Ag16 through further tfa bridges to form a 3D network.

---

[17] (a) MacGillivary, L. R.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325. (b) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W.-S.; Schröder, M. *Chem. Commun*. **1997**, 1005. (c) Blake, A. J.; Champness, N. R.; Khlobystov, A. N.; Lemenovskii, D. A.; Li. W.-S.; Schröder, M. *Chem. Commun.* **1997**, 1339.

[18] Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2327.

[19] (a) Hennigar, T. L.; Macquarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 972. (b) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Li, W.-S.; Schröder, *Inorg. Chem.* **1999**, *38*, 2259.

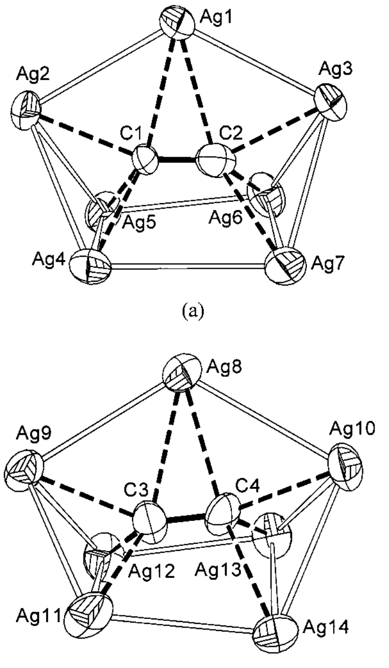
[20] Sheldrick, G. M. SADABS: *Program for Empirical Absorption Correction of Area Detector Data;* University of Gottingen: Germany, 1996.

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

Table 1. Crystallographic Data for Compounds **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
empirical formula	$C_{28}H_{10}Ag_{16}F_{36}O_{29}$	$C_{20}H_9Ag_8F_{18}N_3O_{12}$	$C_{75}H_{40}Ag_{31}F_{69}N_7O_{48.5}$	$C_{32}H_{19}Ag_{12}F_{50}O_{29.5}$	$C_{35}H_{11}Ag_{11}F_{45}N_3O_{19}$	$C_{26}H_{10}Ag_8F_{30}N_2O_{12}$
formula wt	3220.28	1688.26	6470.11	3119.91	2819.04	1975.32
cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	12.795(3)	35.465(3)	17.205(2)	15.600(1)	16.083(1)	11.685(3)
b, Å	13.032(3)	7.8927(6)	32.735(4)	16.949(1)	19.971(2)	16.439(4)
c, Å	20.864(5)	31.241(2)	27.257(4)	17.143(1)	21.994(2)	25.220(6)
α, deg	81.911(5)	90	90	111.716(2)	90	90
β, deg	84.450(5)	121.858(1)	106.021(3)	94.238(2)	94.935(2)	93.486(5)
γ, deg	70.545(4)	90	90	104.719(2)	90	90
V, A^3	3242(1)	7427.5(9)	14755(3)	4001.1(5)	7038.0(9)	4835(2)
Z	2	8	4	2	4	4
T, K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	4.890	4.275	4.167	3.051	3.169	3.339
ρ_{calcd}, g/cm^3	3.298	3.020	2.913	2.590	2.660	2.713
total refl	22368	24087	47304	27111	48704	32153
unique refl	15552	8557	32571	18971	16969	11707
data [$I > \sigma(I)$]	7255	4460	13755	6715	7665	5001
parameters	983	646	2082	1121	999	704
$R_1{}^a$	0.0750	0.0622	0.0595	0.0456	0.0478	0.0504
$wR_2{}^b$	0.1866	0.1791	0.1306	0.1062	0.1241	0.1160

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



(a)

(b)

Figure 1. Two almost identical $C_2@Ag_7$ cages in the independent unit of **1**, which are in the shape of an incomplete capped square antiprism with two diagonal silver atoms of the upper capped face removed. The thermal ellipsoids are drawn at the 50% probability level. Selected bond distances: C1−C2, 1.19(2); C3−C4, 1.19(2); Ag···Ag, 2.739(2)-3.185(2) Å.

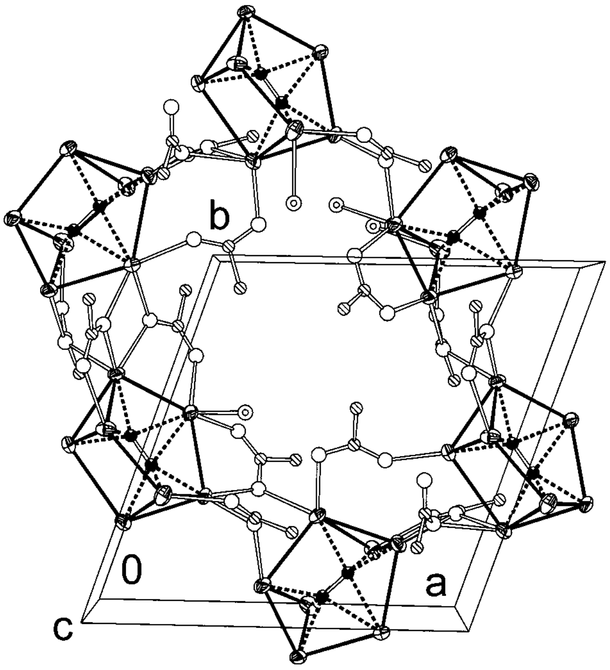


Figure 2. A portion of the layer structure in the three-dimensional network of **1**. Silver(I) cages are highlighted by solid lines.

The fundamental unit in **2** is a distorted triangulated dodecahedron as shown in Figure 3. Atom sets Ag1Ag2Ag3Ag4 and Ag5Ag6Ag5′Ag6′ are each coplanar within 0.087 and 0.010 Å, respectively, making a dihedral angle of 88.3°. This dodecahedron can be regarded as the fusion of two sets of tetrahedra, elongated Ag2Ag3Ag5′Ag6 and flattened Ag1Ag4Ag5Ag6′. The $C_2{}^{2-}$ anion has π interactions with the silver(I) atoms in the latter set with Ag−C bond lengths in the range 2.35(1)−2.67(1) Å. On the other hand, each carbon atom provides a filled sp orbital that overlaps with the empty 5s orbitals of two silver atoms to form a three-center, two-electron (3c−2e) bond. The Ag−C bond lengths in the 3c−2e systems C1Ag5′Ag6 and C2Ag2Ag3 range from 2.20(1) to 2.31(1) Å, which are longer than typical Ag−C σ bonds (e.g., 2.087(3) and 2.108(6) Å in $Ag_2C_2 \cdot 2AgClO_4 \cdot 2H_2O$).[9b] The dodecahedra share edges of the type Ag5−Ag6 to generate a chainlike structure (Figure 4). An alternative description is that the silver atoms of type Ag5 and Ag6 construct a nearly planar zigzag chain with type Ag1, Ag2, Ag3, and Ag4 silver atoms hitched to it through the binding of $C_2{}^{2-}$ ainons. The remaining silver atoms of type Ag7 and Ag8 are attached around the chain via tfa bridges and are both four-coordinated, but the latter has its fourth coordination site saturated by an unsupported Ag8···Ag8′ interaction of 2.917(4) Å. These composite chains are interlinked to each other through such interaction to construct a two-dimensional network oriented parallel to the *bc* plane.

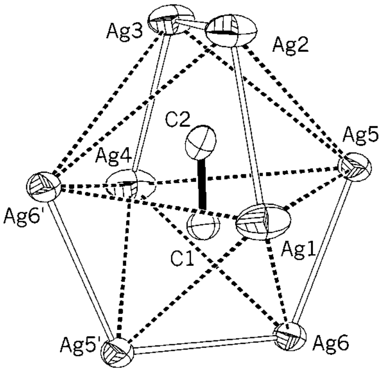


Figure 3. Distorted triangulated Ag_8 dodecahedron in **2**. The thermal ellipsoids are drawn at the 30% probability level. The short and long (longer than 3.3 Å) Ag$\cdots$Ag interactions are shown as open and broken lines, respectively. The bonds between C_2^{2-} and silver atoms are omitted for clarity. Selected bond distances: C1−C2, 1.24(1); Ag$\cdots$Ag, 2.738(2)−3.350 Å.

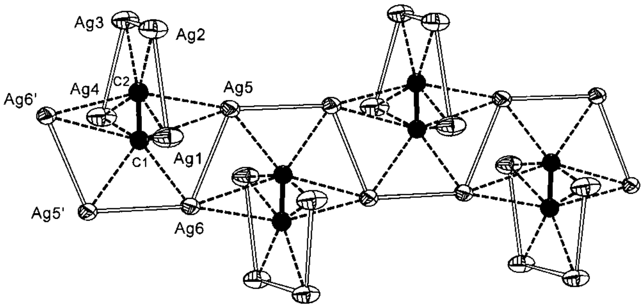


Figure 4. Chainlike structure in **2** resulting from edge-sharing of Ag_8 dodecahedra.

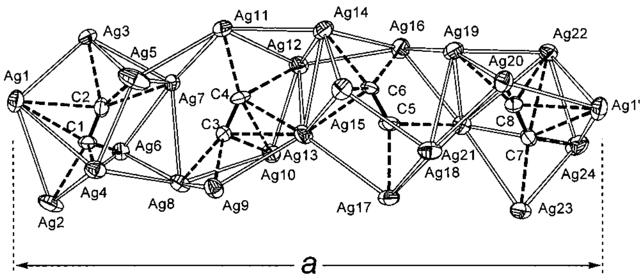


Figure 5. Broadside view of silver(I) column with imbeded C_2^{2-} species in different orientations in **3**. The thermal ellipsoids are drawn at the 30% probability level.

Compound **3** has a fascinating one-dimensional structure, which is a double-walled silver column with C_2^{2-} species imbedded in it at different orientations. A part of the independent unit, as shown in Figure 5, contains four consecutive $C_2@Ag_n$ cages fused together in a row. The C−C bond lengths of C_2^{2-} anions are all ~1.20 Å. The specific coordination environments of the C_2^{2-} species are separately shown in Figure 6. Cages a and c are essentially in the shape of a monocapped distorted trigonal prism, while cages b and d are not so regular. Cage b can be described as a basket with Ag8Ag9Ag13Ag10 forming the flat bottom and Ag7Ag11Ag12 acting like the handle. Cage d is a severely distorted pentagonal bipyramid, with Ag1′Ag20Ag19Ag21Ag24 in the equatorial plane and one axial atom (Ag23) displaced to one side. This sequence of four fused polyhedra is repeated by the *a* translation to form the inner core of a double-walled silver column with embedded C_2^{2-}. Figure 7 shows an end-on view of the silver column, whose inner core is linked by bridging trifluoroacetato ligands to seven independent silver atoms, each being coordinated by one terminal C_2H_5CN ligand, which form the outer wall. All 31 silver centers in the independent unit that constitute the one-dimensional motif are surrounded by hydrophobic C_2H_5CN and CF_3 groups, which prevent further aggregation of such motifs to generate a higher-dimensional network. The resulting double-walled silver column generated from the fusion of different kinds of $C_2@Ag_n$ polyhedra is unprecedented.

Single-crystal X-ray analysis of **4** revealed a novel centrosymmetric $(C_2)_2@Ag_{14}$ double cage composed of 14 silver atoms, which can be considered as two $C_2@Ag_8$ square antiprisms sharing an Ag1−Ag1′ edge (Figure 8). Atom sets Ag1Ag2Ag3Ag4 and Ag1′Ag5Ag6Ag7 are each coplanar within 0.169 and 0.137 Å, respectively, and the dihedral angle between them is 7.7°. The Ag−C distances fall in the range 2.167(9)−2.560(9) Å. Twelve pfp ligands are coordinated around such a double cage to form a fundamental building unit. These units are connected by $[Ag_2(pfp)_2]$ bridges to generate an infinite chain along the *c* direction, and such chains are further cross-linked through two other $[Ag_2(pfp)_2]$ bridges at different orientations to form a 2D network in the *bc* plane (Figure 9). Identical layers are stacked along the *a* direction with $[Ag_2(pfp)_2]$ fragments pillared between adjacent layers to form a 3D networks, so that peanut-shaped channels are also generated parallel to the *a* direction. The bulky tails of pfp ligands are located in these channels.

When the terminally coordinated ligand acetonitrile was included in the crystallization process that yielded **4**, complex **5** was isolated. Compound **5** features the first example of a discrete molecule composed of a double cage with embedded C_2^{2-} species. This double cage is formed by two inversion-related $C_2@Ag_9$ polyhedra sharing an Ag1−Ag1′ edge; each polyhedron is best described as a square antiprism with one silver atom capping the top face (Figure 10). The silver atoms of the upper and bottom squares, Ag1′Ag2Ag3Ag4 and Ag5Ag6Ag7Ag8, are each almost coplanar within 0.190 and 0.017 Å, respectively, and they are nearly parallel to each other with dihedral angle 7.0°. The encapsulated C_2^{2-} species has its molecular axis oriented parallel to the triangular face Ag3Ag7Ag8, with Ag−C distances in the range 2.167(8)−2.596(8) Å. A similar single cage has been observed in $Ag_2C_2 \cdot 8AgF$,[9a] but the C−C bond runs parallel to the bottom face. Thus, the C_2^{2-} anion is bonded to all nine vertexes of the $C_2@Ag_9$ cage in **5**, but to only eight vertexes of the $C_2@Ag_9$ cage in $Ag_2C_2 \cdot 8AgF$. The structure of the supermolecule in **5** is shown in Figure 11. The $(C_2)_2@Ag_{16}$ double cage is surrounded by 18 pfp ligands, and silver atoms of the type Ag9, Ag10, and Ag11 are attached to its core via pfp bridges. Both Ag9 and Ag10 are coordinated by three O atoms of pfp ligands and an acetonitrile ligand. Ag11 is coordinated by two O atoms of pfp ligands, one aqua ligand, and an acetonitrile ligand. The hydrophobic tails of pfp ligands and the terminally coordinated acetonitrile and aqua ligands prevent further linkage between groups, and a unique discrete supermolecule forms as a result.

Complex **6** was obtained with the presence of propionitrile in crystallization, and its structure also features a centrosymmetric silver double cage with half of it illustrated in Figure 12. One C_2^{2-} anion is encapsulated in each single cage, which can be considered as a distorted dodecahedron formed by the interpenetration of two tetrahedra: elongated Ag1Ag2Ag4Ag7 and flattened Ag1′Ag5Ag3Ag6. The Ag−C distances are in the range 2.171(9)−2.633(9) Å. Two dodecahedra share an edge to generate the $(C_2)_2@Ag_{14}$ double cage fundamental unit. Two silver atoms of the type Ag8 are attached to the double cage via pfp ligands. Ag8 is coordinated by two O atoms of pfp

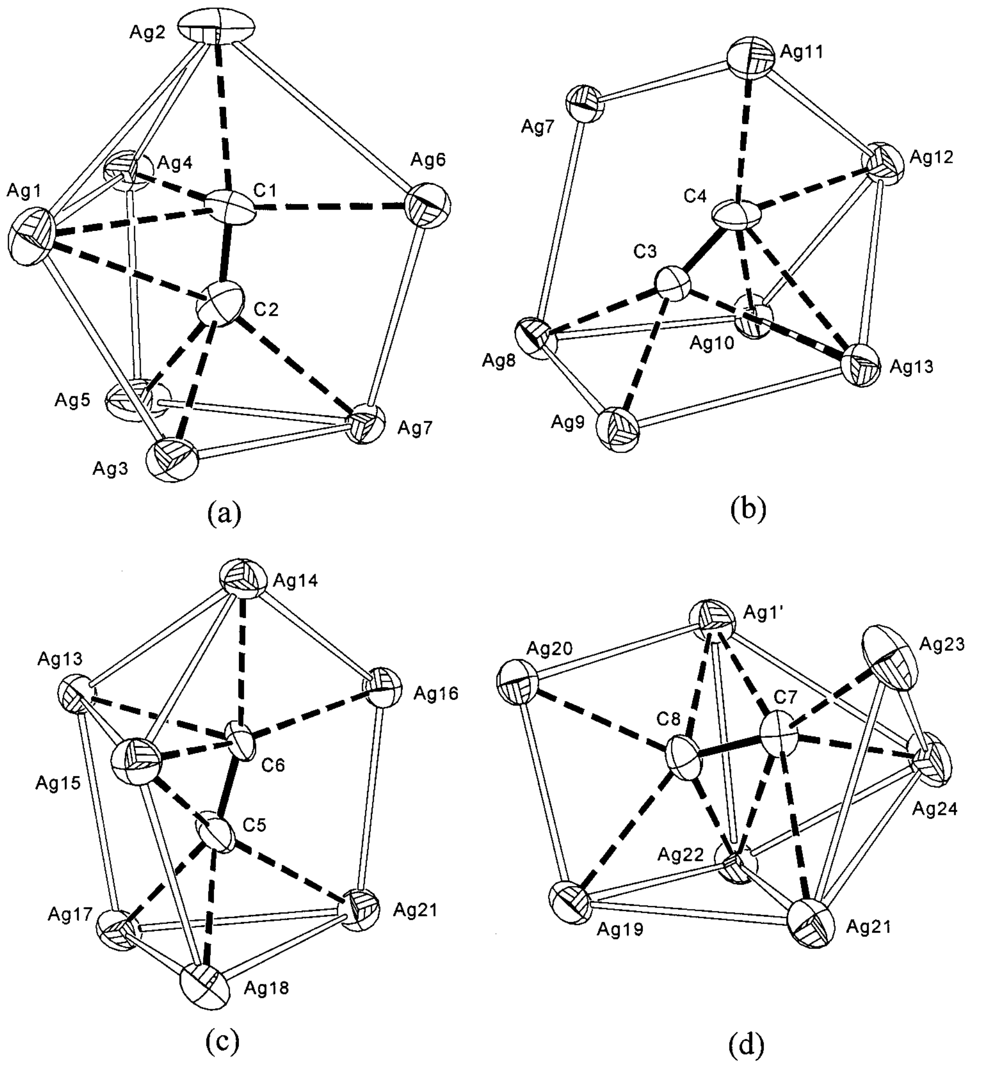


Figure 6. Coordination environments of the four independent C_2^{2-} species in **3**: (a) monocapped trigonal prism; (b) basket; (c) monocapped trigonal prism; (d) distorted pentagonal bipyramid. Selected bond distances: C1−C2, 1.14(1); C3−C4, 1.18(1); C5−C6, 1.20(1); C7−C8, 1.21(1); Ag···Ag, 2.756(1)−3.368(1) Å.

ligands and a terminal propionitrile ligand. There are four pfp bridges between every pair of neighboring units, and thus, a one-dimensional structure is formed (Figure 13). As the chain is surrounded by terminal propionitrile ligands and C_2F_5 groups, further linkage to construct a 2D or 3D network is precluded.

In all known double salts and multiple salts of silver acetylide, the C−C bond length lies in the range of 1.14−1.24 Å, which is compatible with that of 1.205 Å in acetylene[22] and 1.19 Å in CaC_2.[23] This indicates that the entrapped C_2^{2-} ion possesses essentially triple bond character. In contrast, the case is different in ternary lanthanide/transition metal dicarbides, where the dicarbon units exhibit C−C distances in the range 1.32−1.60 Å, which are consistent with their formulation as C_2^{4-} and even C_2.[6−24] In the present instance, the bonding of the C_2^{2-} anion to silver atoms essentially involves a combination of σ and π types, which is very different from the case in silver−aromatic complexes where only metal−ligand π bonding occurs.[25]

The Ag···Ag distances under 3.40 Å (twice the van der Waals radius of silver atom) in **1**−**6** are in the following ranges: 2.739(2)−3.185(2) Å for **1**, 2.738(1)−3.350(1) Å for **2**, 2.756(1)−3.368(1) Å for **3**, 2.811(1)−3.265(1) Å for **4**, 2.845(1)−3.332(1) Å for **5**, and 2.798(1)−3.311(1) for **6**. Many of them are shorter than 2.89 Å (twice the atom radius in metallic silver),[26] and in addition, an unsupported Ag−Ag contact of 2.917(4) Å is found in **2.** These data indicate that there exists a significant attraction between the silver(I) atoms. Molecular orbital analysis has been carried out on several dicarbido transition-metal carbonyl cluster compounds [27] and tetrametallic or high-nuclearity organometallic systems containing an exposed dicarbon fragment,[28] and density functional theory (DFT) calculations have been performed on some dinuclear complexes containing bridging dicarbon units.[29] However, the electronic structure and bonding in the above $C_2@Ag_n$ cages and the nature of the argentophilic interaction still await a detailed theoretical study.

The fact that Ag_2C_2 can be dissolved in a concentrated aqueous solution silver(I) is comparable to the textbook case

---

[22] Herzberg, G.; Spinks, J. W. T. *Z. Phys.* **1934**, *91*, 386.

[23] Atoji, M. *J. Chem. Phys.* **1961**, *35*, 1950.

[24] (a) Cotton, F. A.; Wilkinson, G. C.; Murillo, A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley-Interscience: New York, 1999; p 221. (b) King, R. B. *J. Organomet. Chem.* **1997**, *536*−*537*, 7.

[25] Munakata, M.; Wu, L.-P.; Ning, G.-L.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Maeno, N. *J. Am. Chem. Soc.* **1999**, *121*, 4968.

[26] Emsley, J. *The Elements*; Clarendon: Oxford, U.K., 1989; p 174.

[27] Halet, J. F.; Mingos, M. P. *Organometallics* **1988**, *7*, 51.

[28] (a) Frapper, G.; Halet, J. F. *Organometallics* **1995**, *14*, 5044. (b) Frapper, G.; Halet, J. F.; Bruce, M. I. *Organometallics* **1997**, *16*, 2590.

[29] (a) Belanzoni, P.; Re, N.; Rosi, M.; Sgamellotti, A.; Floriani, C. *Organometallics* **1996**, *15*, 4264. (b) Belanzoni, P.; Re, N.; Sgamellotti, A.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1997**, 4773.

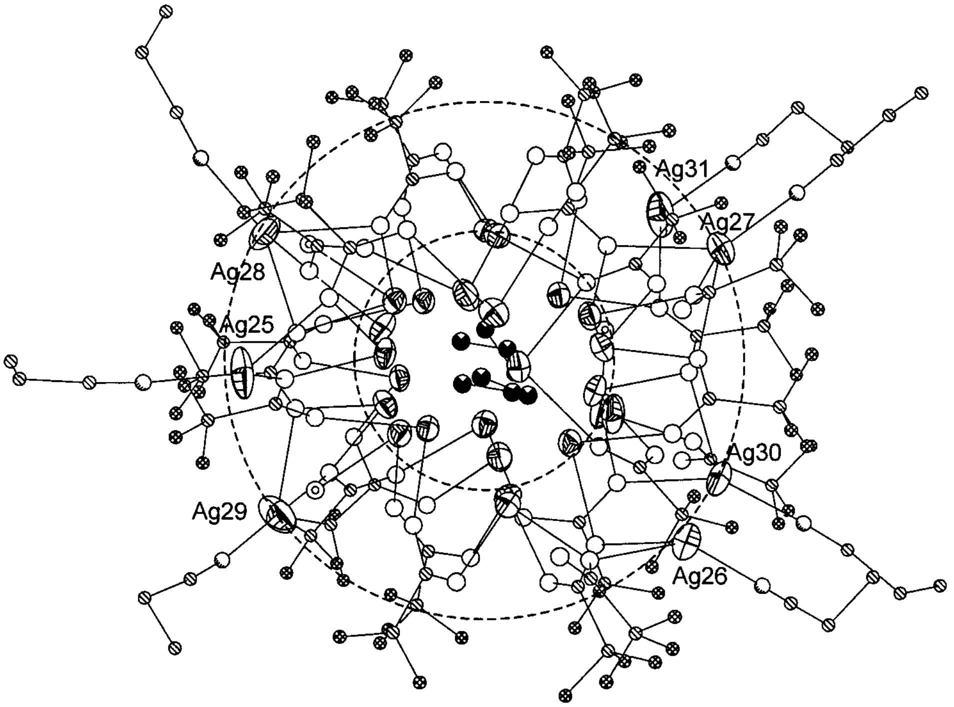


Figure 7. Structure of **3** viewed along the *a* direction, showing a cross section of the double-walled silver column. The row of fused polyhedra, each encapsulating a C_2^{2-} ion, constitutes the inner core, which is linked by bridging tfa ligands to seven independent atoms Ag25−Ag31 in an outer wall. The diameters of the inner and outer walls are about 5 and 9 Å, respectively. The Ag atoms are shown as thermal ellipsoids and the other atoms as spheres of different shading. The Ag···Ag interactions are omitted for clarity.

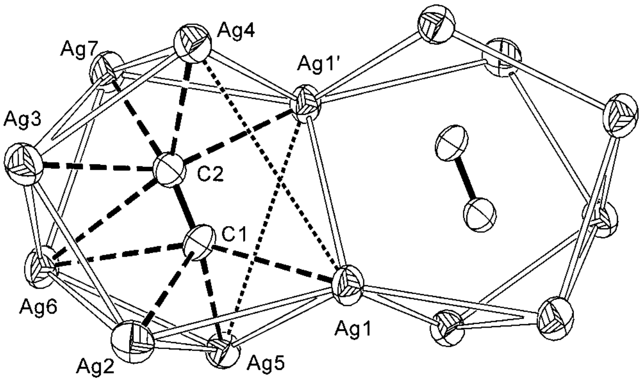


Figure 8. Centrosymmetric edge-sharing $(C_2)_2@Ag_{14}$ double silver(I) cage in **4**, each half having the shape of a square antiprism. The thermal ellipsoids are drawn at the 35% probability level. Ag···Ag distances (longer than 3.4 Å) are represented by broken lines. The sivler(I) to acetylide bonds in the right half are omitted for clarity. Selected bond distances: C1−C2, 1.16(1); Ag···Ag, 2.811(1)−3.265(1) Å.

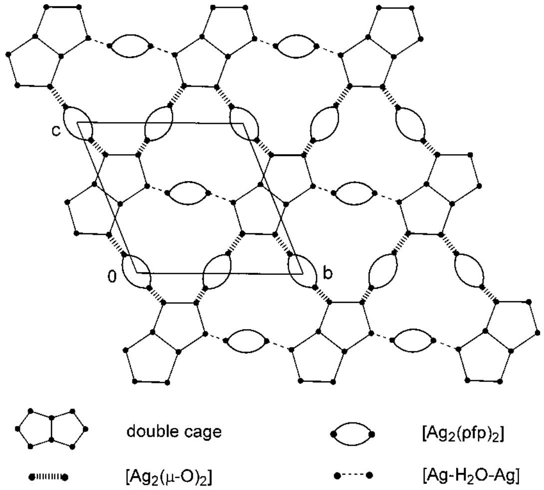


Figure 9. Schematic illustration of one *bc* layer in the 3D network of **4**, showing the linkage of double cages by $[Ag_2(pfp)_2]$, $[Ag_2(\mu\text{-}O)_2]$, and aqua bridges.

that CuI is readily soluble in concentrated KI solution to form $[CuI_4]^{3-}$. As an analogy, it is probable that silver(I) ions in high concentration can break down the polymeric structure of insoluble Ag_2C_2 (whose crystal structure is still unknown) with compensation by the formation of stabilized $[C_2@Ag_n]^{(n-2)+}$ species. Suitable counterions such as fluorinated caboxylates can trap specific cationic species in the crystallization process, with or without the presence of the coordinating solvents such as CH_3CN or C_2H_5CN.

When no nitrile solvent (CH_3CN or C_2H_5CN) was used in crystallization, a hydrated compound was isolated. As aqua ligands and lattice water molecules can be easily enclosed in voids in the structure, 3D networks are generated via bridging carboxylates. When CH_3CN or C_2H_5CN participates in the crystallization process, its coordination to a peripheral silver atom constitutes a steric hindrance to prevent the formation of a 3D network. Thus, lower-dimensional (1D, 2D) and even discrete structures are formed as a result. Different structures are obtained because C_2H_5CN is bulkier than CH_3CN. There is an ideal sequence in the Ag_2C_2/Ag(fta) system, with 3D, 2D, and 1D structures corresponding to the increasing steric influence of H_2O, CH_3CN, and C_2H_5CN. Compound **3** is the only known example of a silver acetylide-containing complex generated from the fusion of different kinds of $C_2@Ag_n$ cages, and the resulting double-walled silver column is unique. In the Ag_2C_2/Ag(pfp) system, **5** turned out to be an exception, and thus far, it is the only example of a discrete molecular compound that contains a double cage among reported silver acetylide-containing systems. In addition, the hexadedanuclear double cage $(C_2)_2@Ag_{16}$ in **5** is the largest among those found so far, in comparison to the tridecanuclear $(C_2)_2@Ag_{13}$ in $2Ag_2C_2\cdot$

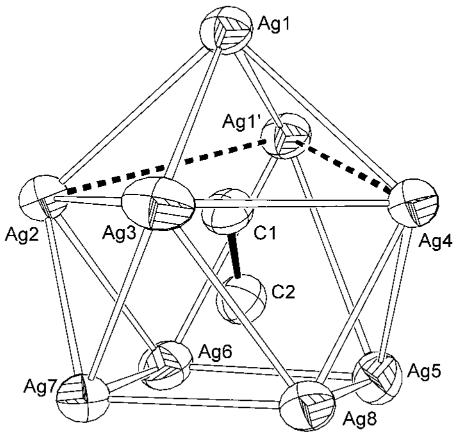


Figure 10. Half of the centrosymmetric double cage of **5** in the shape of a monocapped antiprism. The thermal ellipsoids are drawn at the 35% probability level. Ag···Ag distances (longer than 3.4 Å) are represented by broken lines. Selected bond distances: C1−C2, 1.19(1); Ag···Ag, 2.845(1)−3.332 Å.

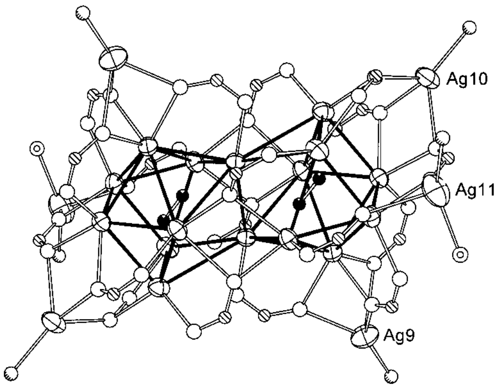


Figure 11. Perspective drawing of the structure of the supermolecule in **5**. The $(C_2)_2@Ag_{16}$ double cage is highlighted by solid lines (only short Ag···Ag distances are shown). The C_2F_5 tails of pfp and the carbon atoms of acetonitrile are omitted for clarity.

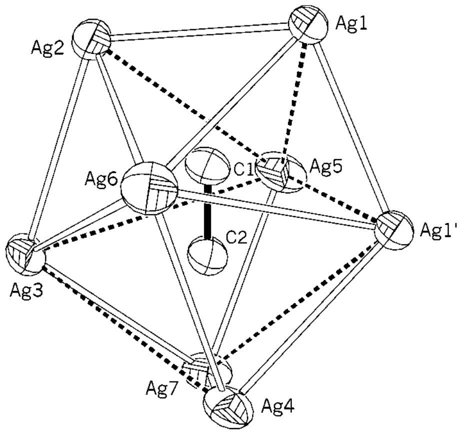


Figure 12. Half of the double cages in **6** in the shape of a triangulated dodecahedron. The thermal ellipsoids are drawn at the 30% probability level. Ag···Ag distances (longer than 3.4 Å) are represented by broken lines. Selected bond distances: C1−C2, 1.19(1); Ag···Ag, 2.798(2)−3.311(1) Å.

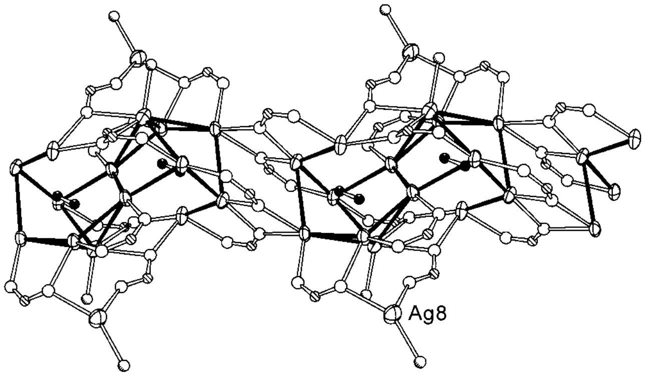


Figure 13. Chain structure derived from the bridging of $(C_2)_2@Ag_{14}$ double cages by carboxylato groups. Each double cage is highlighted by solid lines (only short Ag···Ag distances shown). The C_2F_5 tails of pfp and the carbon atoms of propionitrile are omitted for clarity.

$3AgCN\cdot15CF_3CO_2Ag\cdot2AgBF_4\cdot9H_2O$[11] and the tetradecanuclear $(C_2)_2@Ag_{14}$ in **4** and **6**.

It is noteworthy that the replacement of CH_3CN by C_2H_5CN does not affect the structural integrity of the 2D honeycomb structure in $Ag_2C_2\cdot AgF\cdot4CF_3SO_3Ag\cdot2L$ (L = CH_3CN, C_2H_5CN),[10] which is different from the present case. Another feature is that the silver polyhedra in all three pfp complexes are of the double cage type, implying that their formation is induced by the increased bulk of the C_2F_5 group relative to the CF_3 group. It is easily understood that solvent molecules serving as terminal ligands can influence the crystal structure thus formed; however, precisely how they would affect the assembly of an acetylide-captivating silver cage is beyond our present knowledge. The cages found in **1**−**6** differ from one another, and most are not identical to previously reported ones. Self-assembly in the silver acetylide-containing system is a very complex process, and much study remains to be done.

Concluding Remarks

This work provides some insight into the structural diversity of a series of new double salts containing silver acetylide and silver perfluoroalkyl carboxylates. A variety of $C_2@Ag_n$ single and $(C_2)_2@Ag_n$ double cages make their appearance for the first time, and the specific geometry of the silver cages and their interconnection into larger aggregates are influenced by the bulky hydrophobic tails of the perfluorocarboxylate anions and the terminally coordinated solvento ligands.[30] The series of six silver acetylide complexes display diverse structures from discrete molecule through infinite chain to three-dimensional network, furnishing substantiative evidence for the effectiveness of the $d^{10}-d^{10}$ closed-shell argentophilic interaction. The double-walled columnlike structure constructed from the fusion of different kinds of silver cages in compounds **3** and the largest $(C_2)_2@Ag_{16}$ double cage in discrete supermolecule **5** are both unprecedented among silver complexes.

Acknowledgment. T.C.W.M. dedicates this presentation to the memory of the late Dr. Hson-Mou Chang (1923−2000), mentor and colleague. This work was supported by the Hong Kong Research Grants Council of the Hong Kong Special Administrative Region (Project CUHK 4268/00P).

Supporting Information Available: One table (PDF) and six X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0043441

---

(30) Macrocyclic ligands also can be used as structure-directing agents in the silver acetylide system: (a) Wang, Q.-M.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 1130. (b) Wang, Q.-M.; Mak, T. C. W. *Chem. Commun.* **2001**, 807.