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Assembly of Discrete, One-, Two-, and Three-Dimensional Silver(I) Supramolecular Complexes Containing Encapsulated Acetylide Dianion with Nitrogen-Donor Spacers

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

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

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The first successful attempt to construct supramolecular entities via incorporation of bifunctional exodentate ligands into the silver acetylide system is reported. Coordination assembly with nitrogen-donor spacers led to the formation of five distinct supramolecular complexes, namely $[(Ag_2C_2)(AgCF_3CO_2)_4(pyz)_2]_n$ (**1**), $[(Ag_2C_2)_2(AgCF_3CO_2)_{10}(CF_3CO_2)_4(DabcoH)_4(H_2O)_{1.5}]\cdot H_2O$ (**2**), $[(Ag_2C_2)(AgCF_3CO_2)_4(CF_3CO_2)(bpaH)]_n$ (**3**), $[(Ag_2C_2)(AgCF_3CO_2)_8(bpa)_4]_n$ (**4**), and $[(Ag_2C_2)_2(AgCF_3CO_2)_{10}(bppz)_2(H_2O)]_n$ (**5**) (pyz = pyrazine; Dabco = 1,4-diazabicyclo[2.2.2]octane; bpa = 1,2-bis(4-pyridyl)ethane; bppz = 2,3-bis(2-pyridyl)pyrazine). Complex **1** is a three-dimensional framework composed of silver columns cross-linked by pyrazine bridges, whereas **2** contains a discrete supermolecule whose core is a Ag_{14} double cage that is completely surrounded by trifluoroacetate, aqua, and terminal monoprotonated Dabco ligands. Complex **3** has a branched-tree architecture with one terminal of the bpa ligand attached to the silver backbone and the other exposed and protonated. In **4**, neutral decanuclear $[(Ag_2C_2)(AgCF_3CO_2)_8]$ units are interlinked by bpa spacers adopting both gauche and anti conformations to generate a layer structure. Another two-dimensional network was formed with bppz serving as an angular bridging ligand in **5**, in which the building unit is a silver quadruple cage containing 24 silver atoms.

Introduction

The construction of supramolecular arrays through coordination chemistry has developed into a central theme of supramolecular chemistry.[1] Many novel supramolecular complexes have been produced with single metal centers linked by bi- or multifunctional ligands.[2] Cotton and coworkers have used dimetal units to build a variety of supramolecular systems containing metal−metal bonds,[3] while other groups have utilized intact cluster precursors such as $[Re_6Se_8]$ to construct extended (ligand-bridged) arrays.[4] Furthermore, Yaghi and O'Keeffe et al. have employed secondary and tertiary building units in the assembly of metal−organic frameworks.[5]

Our previous work on the chemistry of silver acetylide (Ag_2C_2) has demonstrated that $C_2@Ag_n$ polyhedra and fused double cages $(C_2)_2@Ag_{2n-m}$ (n vertexes, m shared atoms) generally occur in its double, triple, and quadruple salts due to the preference of C_2^{2-} for imprisonment inside a silver polyhedron.[6,7] However, as $C_2@Ag_n$ cages are quite labile and their formation can be influenced by many factors,[8] the number of silver vertexes and cage shape are unpredictable.

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

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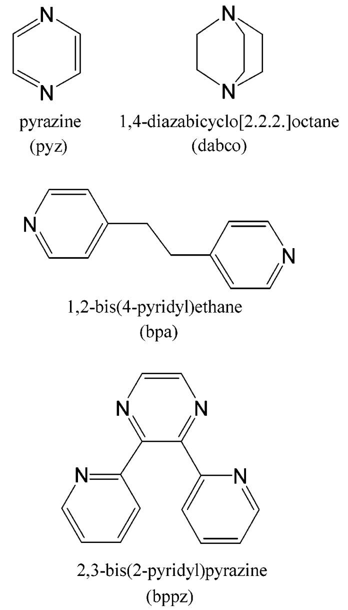
Chart 1



Our conceived strategy in using $C_2@Ag_n$ polyhedra as building blocks for supramolecular assembly of new coordination frameworks is to introduce linear bifunctional linkages between agglomerated components that are generated in situ. Such a synthetic approach has led to the isolation of five supramolecular complexes showing distinctly different crystal structures (discrete, 1D, 2D, and 3D), namely $[(Ag_2C_2)(AgCF_3CO_2)_4(pyz)_2]_n$ (**1**), $[(Ag_2C_2)_2(AgCF_3CO_2)_{10}(CF_3CO_2)_4(DabcoH)_4(H_2O)_{1.5}]\cdot H_2O$ (**2**), $[(Ag_2C_2)(AgCF_3CO_2)_4(CF_3CO_2)(bpaH)]_n$ (**3**), $[(Ag_2C_2)(AgCF_3CO_2)_8(bpa)_4]_n$ (**4**), and $[(Ag_2C_2)_2(AgCF_3CO_2)_{10}(bppz)_2(H_2O)]_n$ (**5**) (pyz = pyrazine; Dabco = 1,4-diazabicyclo[2.2.2]octane; bpa = 1,2-bis(4-pyridyl)ethane; bppz = 2,3-bis(2-pyridyl)pyrazine; Chart 1), which are described in this report.

Experimental Section

Chemicals were used as purchased from commercial vendors without further purification (silver salts from ACROS and nitrogen-donor ligands from Aldrich). Ag_2C_2 was prepared as described previously.[6] *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. For safety, we used moist Ag_2C_2 in all preparations*.

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.[9] The structures were solved by the direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package.[10] In the structure of **2**, the asymmetric unit contains two aqua ligands (one exhibiting half site occupancy) and one lattice water molecule, which are hydrogen-bonded to each other. The crystal data and X-ray structure analysis parameters are summarized in Table 1. Selected bond distances are available as Supporting Information.

$[(Ag_2C_2)(AgCF_3CO_2)_4(pyz)_2]_n$ (1). Excess Ag_2C_2 (moist, ~0.5 g) was added to 1 mL of an aqueous solution of $AgCF_3CO_2$ (2 mmol) and $AgBF_4$ (2 mmol) in a plastic beaker with stirring until saturated. The undissolved amount of Ag_2C_2 was filtered off, and then 40 mg of pyz was added to the filtrate. The resulted suspension was transferred to a thick-wall Pyrex glass tube. The tube was subsequently flame-sealed with great care and placed in a furnace. The temperature of the furnace was elevated to 115 °C and kept for 24 h and then cooled to room temperature at 6°/h. Colorless prismatic crystals of **1** were isolated in over 50% yield. Anal. Calcd for $C_{18}H_8Ag_6F_{12}N_4O_8$: C, 16.84; H, 0.63; N, 4.37. Found: C, 16.28; H, 0.52; N, 4.04.

$[(Ag_2C_2)_2(AgCF_3CO_2)_{10}(CF_3CO_2)_4(DabcoH)_4(H_2O)_{1.5}]\cdot H_2O$ (2). Compound **2** was synthesized in the manner described above using 1,4-diazabicyclo[2.2.2]octane (56 mg) instead of pyz. Colorless platelike crystals of **2** were obtained in over 50% yield. Anal. Calcd for $C_{56}H_{57}Ag_{14}F_{42}N_8O_{30.5}$: C, 18.49; H, 1.58; N, 3.08. Found: C, 17.90; H, 1.35; N, 2.78.

$[(Ag_2C_2)(AgCF_3CO_2)_4(CF_3CO_2)(bpaH)]_n$ (3). Compound **3** was synthesized in the same manner using 1,2-bis(4-pyridyl)ethane (92 mg) instead of pyz. Colorless needlelike crystals of **3** were obtained in ca. 45% yield. Anal. Calcd for $C_{24}H_{13}Ag_6F_{15}N_2O_{10}$: C, 20.28; H, 0.92; N, 1.97. Found: C, 20.53; H, 0.90; N, 1.75.

$[(Ag_2C_2)(AgCF_3CO_2)_8(bpa)_4]_n$ (4). Compound **4** in the form of colorless blocklike crystals was obtained by repeating the above procedure for **3** but leaving out $AgBF_4$. Although **4** was obtained in low yield (below 5% and also mixed with some needles of **3** and a large quantity of unidentified brown powder), the synthesis was reproducible.

$[(Ag_2C_2)_2(AgCF_3CO_2)_{10}(bppz)_2(H_2O)]_n$ (5). Compound **5** was synthesized in the same manner as **1** using 2,3-bis(2-pyridyl)pyrazine (46 mg) instead of pyz. Colorless blocklike crystals of **5** were obtained in ca. 40% yield. Anal. Calcd for $C_{52}H_{22}Ag_{14}F_{30}N_8O_{21}$: C, 19.67; H, 0.70; N, 3.53. Found: C, 19.36; H, 0.72; N, 3.46.

Results and Discussion

The addition of pyrazine (pyz) to a mixed aqueous solution of silver trifluoroacetate and silver tetrafluoroborate containing dissolved silver acetylide afforded a pale yellow precipitate, which was then manipulated under hydrothermal condition to give X-ray-quality crystals of **1**. Hydrothermal treatment is normally not advisable for such a potentially explosive system; however, it did provide an effective route to obtain single crystals for structural characterization. The deployment of $AgBF_4$ favors the dissolving of Ag_2C_2 as found in previous studies.[8a] When 1,4-diazabicyclo[2.2.2]octane (Dabco) was used instead of pyz in an attempt to make a three-dimensional analogue, a discrete supermolecule **2** was isolated. A plausible explanation is that Dabco is a stronger Lewis base than pyz and is easier protonated at one end, which makes it function as a unidentate ligand. This prevents the silver cages from further connection with other

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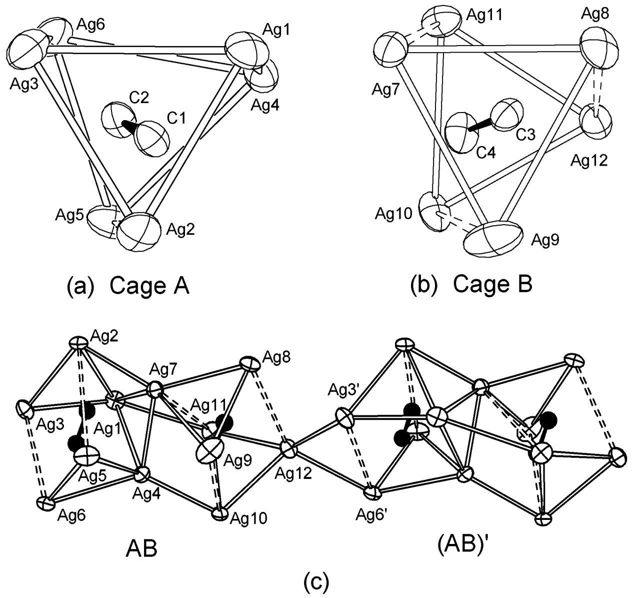
Table 1. Crystallographic Data for Compounds **1**−**5**

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{18}H_8Ag_6F_{12}N_4O_8$	$C_{56}H_{57}Ag_{14}F_{42}N_8O_{30.5}$	$C_{24}H_{13}Ag_6F_{15}N_2O_{10}$	$C_{66}H_{48}Ag_{10}F_{24}N_8O_{16}$	$C_{52}H_{22}Ag_{14}F_{30}N_8O_{21}$
fw	1283.50	3638.28	1421.58	2743.82	3174.96
cryst system	orthorhombic	orthorhombic	monoclinic	monoclinic	triclinic
space group	Pbca	Pbca	$P2_1/c$	$C2/c$	$P\bar{1}$
a, Å	23.979(1)	22.768(1)	14.4014(5)	17.198(1)	14.6896(9)
b, Å	20.8297(8)	17.8221(8)	28.426(1)	23.451(1)	17.575(1)
c, Å	24.342(1)	47.066(2)	8.5790(3)	20.311(1)	17.946(1)
α, deg	90	90	90	90	66.592(1)
β, deg	90	90	100.276(1)	92.087(2)	75.107(1)
γ, deg	90	90	90	90	68.777(1)
V, Å^3	12158.5(9)	19098(1)	3455.7(2)	8186.0(8)	3928.8(4)
Z	16	8	4	4	2
T, K	293(2)	293(2)	293(2)	293(2)	293(2)
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ, mm^{-1}	3.912	2.959	3.470	2.458	3.545
ρ_{calcd}, g/cm^3	2.805	2.531	2.732	2.226	2.684
R$_1$^{a} (obsd)	0.0544	0.0658	0.0340	0.0486	0.0649
wR$_2$^{a} (all)	0.1502	0.1543	0.0773	0.1447	0.1708

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

units. This is consistent with the fact that pyz is one of the most common exo-bidentate ligands while there are few structures based on a Dabco bridging ligand. Additionally, Dabco is much bulkier compared to pyz, which influences the assembly process of silver cages and results in the formation of a quite different structure. In a similar reaction with the longer and more flexible spacer 1,2-bis(4-pyridyl)ethane (bpa), complex **3** and a minor product **4** were isolated. Compound **3** can be prepared in an improved yield under different reaction conditions. In **3**, the bpa ligand was also found to be protonated at one of its pyridyl groups. However, bpa was successfully incorporated as a neutral connector between silver cages in **4**. When the angular connector 2,3-bis(2-pyridyl)pyrazine (bppz) was introduced into the Ag_2C_2/$AgCF_3CO_2$/$AgBF_4$ system to generate **5**, a two-dimensional network was constructed.



(a) Cage A (b) Cage B

(c)

Figure 1. Structural components in $[(Ag_2C_2)(AgCF_3CO_2)_4(pyz)_2]_n$ (**1**): (a) cage A (distorted trigonal prism); (b) cage B (trigonal antiprism); (c) silver column AB(AB)′⋯ running parallel to the *b* direction. Atoms are drawn as 35% thermal ellipsoids. Polyhedral edges that are longer than 3.40 Å (twice the van der Waals radius of silver atom) are represented by broken open lines. Selected bond distances (Å): C(1)−C(2) 1.21(1), C(1)−Ag(1) 2.216(7), C(1)−Ag(2) 2.186(7), C(1)−Ag(3) 2.374(8), C(1)−Ag(4) 2.692(7), C(1)−Ag(7) 2.378(8), C(2)−Ag(4), 2.363(7), C(2)−Ag(5) 2.203(7), C(2)−Ag(6) 2.129(7), C(2)−Ag(3) 2.660(7), C(3)−C(4) 1.17(1), C(3)−Ag(7) 2.437(8), C(3)−Ag(8) 2.109(7), C(3)−Ag(9) 2.270(7), C(3)−Ag(12) 2.583(8), C(4)−Ag(10) 2.143(7), C(4)−Ag(11) 2.293(9), C(4)−Ag(12) 2.532(8), C(4)−Ag(9) 2.700(9); Ag(1)⋯Ag(2) 2.9445(8), Ag(1)⋯Ag(3) 3.0326(9), Ag(1)⋯Ag(4) 3.2442(9), Ag(2)⋯Ag(3) 3.0355(8), Ag(4)⋯Ag(5) 3.2229(9), Ag(4)⋯Ag(6) 3.2047(9), Ag(5)⋯Ag(6) 2.9400(9), Ag(7)⋯Ag(8) 3.1543(9), Ag(7)⋯Ag(9) 3.2636(9), Ag(8)⋯Ag(9) 3.313(1), Ag(10)⋯Ag(11) 3.1818(9), Ag(10)⋯Ag(12) 3.0880(8), Ag(11)⋯Ag(12) 3.0396(9).

X-ray analysis showed that complex **1** is a three-dimensional framework composed of pyz-linked silver columns. The fundamental unit of the each column is a double cage that is made up of two kinds of silver polyhedra, an irregular trigonal prism (A) and a trigonal antiprism (B) each enclosing an acetylide dianion (Figure 1). For cage A, the triangular faces Ag1Ag2Ag3 (edge lengths 2.9445(8)−3.0355(8) Å) and Ag4Ag5Ag6 (edge lengths 2.9400(9)−3.2229(9) Å) make a dihedral angle of 21.5°. For cage B, triangular face Ag7Ag8Ag9 (edge lengths 3.1543(9)−3.313(1) Å) is nearly parallel to Ag10Ag11Ag12 (edge lengths 3.0396(9)−3.1818(9) Å) with dihedral angle 8.7°, and the twist angle between them is about 30° along the projection direction. Thus, cage B is better described as a trigonal antiprism rather than a twisted trigonal prism. The two types of cages are fused together to form a double cage AB, with atom Ag7 of cage B linked to Ag1, Ag2, and Ag4 of cage A and Ag4 of cage A bound to Ag7, Ag10, and Ag11 of cage B as shown in Figure 1c. An alternative description is that cage Ag1Ag2Ag3Ag4Ag5Ag6Ag7 and Ag4Ag7Ag8Ag9Ag10Ag11Ag12 share an edge Ag4⋯Ag7 to form the double cage. Such a double cage AB is connected to an adjacent cage (AB)′, which is generated from AB by the *b* glide, through linkage of vertex (Ag12) to edge (Ag3′⋯Ag6′). Thus a silver column is generated in an arrangement of AB(AB)′AB(AB)′⋯ parallel to the *b* direction (Figure 1c). There are four independent pyz ligands in each asymmetric unit, which generate eight linkages around each double cage (Figure 2). Such pyz connectors cross-link neighboring silver columns to construct a three-dimensional framework with channels running parallel to the *b* direction as shown in Figure 3. The square cross section

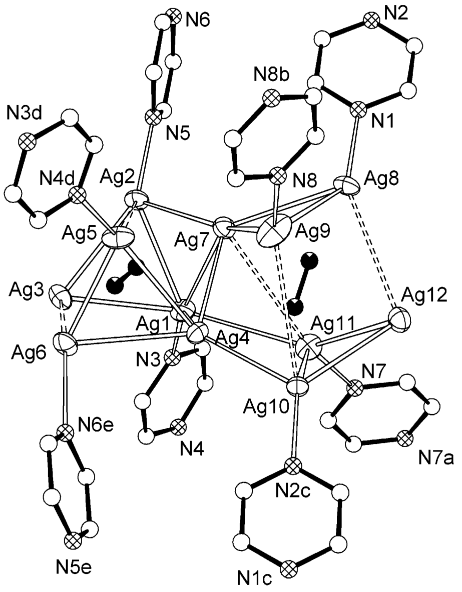


Figure 2. Pyrazine linkages surrounding the double silver cage AB in **1**. Symmetry codes: (a) $-x, 1 - y, -z$; (b) $1 - x, 1 - y, -z$; (c) $^1/_2 - x, 1 - y, -^1/_2 + z$; (d) $^1/_2 + x, ^1/_2 - y, -z$; (e) $x, ^1/_2 - y, -^1/_2 + z$.

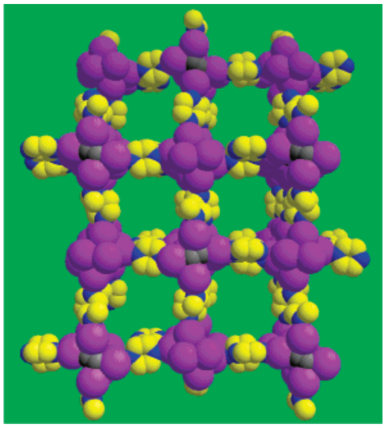


Figure 3. Space-filling drawing of the three-dimensional framework of **1** viewed along the *b* direction. Trifluoroacetate ligands have been omitted for clarity. Color legend: carbon of pyz, yellow; carbon of C_2^{2-}, gray; nitrogen, blue; silver, purple.

of each channel has dimensions of about 12 Å × 12 Å (*a*/2 by *c*/2), and the trifluoromethyl groups fill the channels. The Ag−N bond lengths are in the range of 2.180(6)−2.312(6) Å, which is comparable to 2.193(3)−2.519(8) Å in a series of polymeric frameworks constructed from single Ag(I) centers and pyz linkages.[11] Complex **1** represents the first example of a supramolecular array generated from the incorporation of bifunctional ligands into the silver acetylide system.

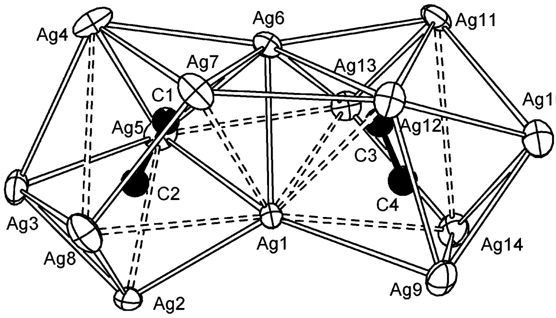


Figure 4. Central core (double cage) consisting of 14 silver(I) atoms in $[(Ag_2C_2)_2(AgCF_3CO_2)_{10}(CF_3CO_2)_4(DabcoH)_4(H_2O)_{1.5}]\cdot H_2O$ (**2**). Atoms are drawn as 35% thermal ellipsoids. Polyhedral edges that are longer than 3.40 Å (twice the van der Waals radius of silver atom) are represented by broken open lines. Selected bond distances (Å): C(1)−C(2) 1.22(1), C(1)−Ag(1) 2.517(7), C(1)−Ag(4) 2.181(7), C(1)−Ag(5) 2.421(8), C(1)−Ag(6) 2.284(7), C(1)−Ag(7) 2.271(8), C(2)−Ag(2), 2.197(8), C(2)−Ag(3) 2.267(7), C(2)−Ag(5) 2.608(8), C(2)−Ag(8) 2.217(7). C(3)−C(4) 1.21(1), C(3)−Ag(1) 2.580(7), C(3)−Ag(6) 2.439(8), C(3)−Ag(11) 2.163(7), C(3)−Ag(12) 2.504(8), C(3)−Ag(13) 2.224(8), C(4)−Ag(1) 2.418(7), C(4)−Ag(9) 2.102(8), C(4)−Ag(10) 2.539(7), C(4)−Ag(12) 2.468(8), C(4)−Ag(14) 2.294(8); Ag(1)···Ag(2) 2.9803(8), Ag(2)···Ag(3) 2.8214(9), Ag(3)···Ag(4) 3.282(1), Ag(5)···Ag(6) 3.2073(9), Ag(6)···Ag(7) 2.9744(9), Ag(7)···Ag(8) 3.0527(9), Ag(1)···Ag(5) 3.2915(9), Ag(1)···Ag(6) 3.0430(8), Ag(2)···Ag(8) 2.942(1), Ag(3)···Ag(5) 3.189(1), Ag(3)···Ag(8) 3.060(1), Ag(4)···Ag(5) 3.183(1), Ag(4)···Ag(6) 3.121(1), Ag(4)···Ag(7) 3.239(1), Ag(1)···Ag(9) 3.3453(9), Ag(9)···Ag(10) 2.980(1), Ag(10)···Ag(11) 3.121(1), Ag(12)···Ag(6) 3.2287(9), Ag(6)···Ag(13) 2.9748(9), Ag(13)···Ag(14) 3.106(1).

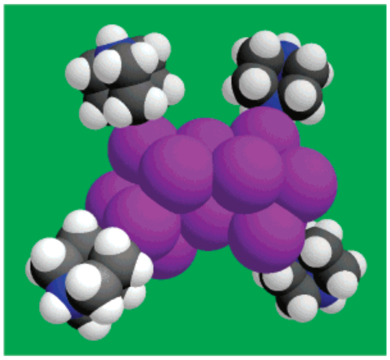


Figure 5. Space-filling drawing of the discrete supermolecule in **2**. Trifluoroacetate and aqua ligands have been omitted for clarity. Color legend: carbon, gray; nitrogen, blue; hydrogen, white; silver, purple.

In the crystal structure of **2,** the core is a double cage comprised of 14 silver atoms with each single cage encapsulating an acetylide dianion. Each single cage is in the form of a distorted triangulated dodecahedron, and two such cages share an edge Ag1···Ag6 to form the double cage shown in Figure 4. This double cage exhibits pseudosymmetry 2 along the line Ag1···Ag6. Apart from trifluoroacetate and aqua ligands, there are four monoprotonated Dabco ligands surrounding the whole unit, each terminally coordinated to a vertex (Ag4, Ag8, Ag11, and Ag14, respectively) of the silver double cage. This discrete supermolecule is shown in Figure 5. In previous work, we have investigated the influence of terminal ligation presented by nitriles and crown ethers,[8a,12] whose presence usually lower the dimension of the resulting structure, and discrete molecules are isolated in some cases. The same role is played by $DabcoH^+$ as a terminal ligand, which together with Ag(I), C_2^{2-}, and $CF_3CO_2^-$ facilitate the assembly of the supramolecular aggregate in **2**. The latter may be compared with rhombohedral silver cages with an encapsulated halide anion at the center and the population of bulky alknyl ligands on the exterior surface.[13]

Complex **3** has a branched-tree architecture, in which the basic building block is a distorted square antiprism (Figure

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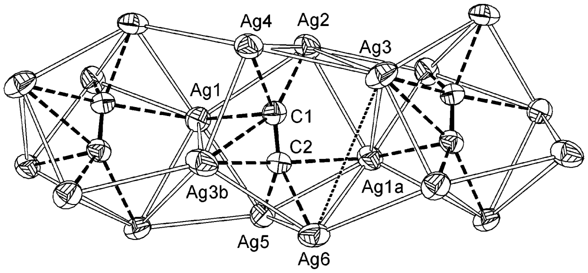


Figure 6. Portion of silver column generated form fusion of square antiprismatic units in $[(Ag_2C_2)(AgCF_3CO_2)_4(CF_3CO_2)(bpaH)]_n$ (**3**). Symmetry codes: (a) $-x, 1/2 - y, 1/2 + z$; (b) $-x, 1/2 - y, -1/2 + z$. Selected bond distances (Å): Ag(1)···Ag(2) 3.3011(5), Ag(2)···Ag(1a) 3.2006(5), Ag(1a)···Ag(5) 3.1254(5), Ag(1)···Ag(5) 2.9321(5), Ag(3)···Ag(4) 3.2250(6), Ag(4)···Ag(3b) 2.9728(5), Ag(3b)···Ag(6) 3.2434(6).

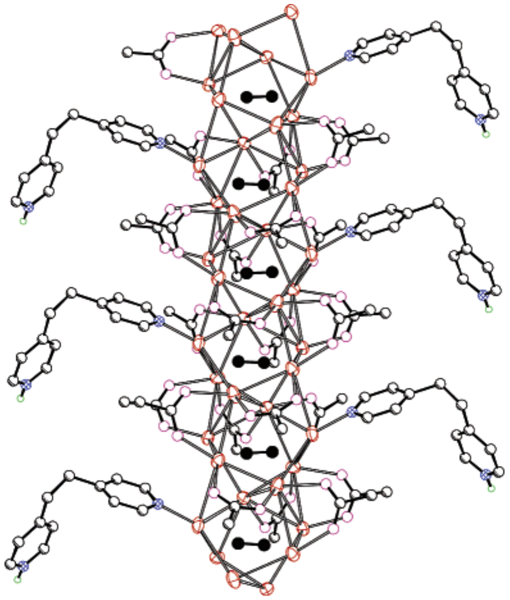
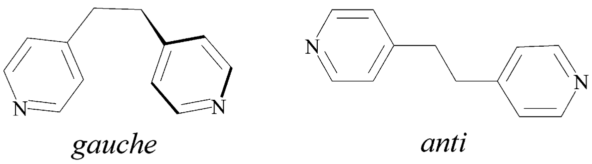


Figure 7. Infinite branched-tree architecture in **3**.

6). Silver cages of this type share edges and are consolidated by additional Ag···Ag interactions to generate an infinite chainlike silver column along the *c* direction that serves as the backbone of the herringbone array (Figure 7). One terminal of the bpa ligand is protonated and the other is coordinated to a silver atom of type Ag6, and such ligation results in the attachment of cationic branches to the silver backbone. In contrast to the extensively studied rigid ligand 4,4′-bipyridine, the less exploited flexible bpa ligand can adopt gauche and anti conformations as shown below,[14] and this conformational freedom has been shown to engender supramolecular isomerism in coordination polymers.[15] In the present case, the bpaH ligand adopts the gauche conformation and forms a donor hydrogen bond [N2−H···O21$(-x, 1 - y, -1 - z)$, 2.755 Å and 157.1°] with a carboxylate group of a neighboring chain, thus generating an undulated layer (Figure 8).



Interestingly, both gauche and anti conformations of bpa are observed in compound **4**. The building unit in **4** is a neutral decanuclear silver aggregate $[(Ag_2C_2)(AgCF_3CO_2)_8]$ of symmetry 2, which is composed of a distorted square antiprismatic $C_2@Ag_8$ core, together with two additional silver atoms of type Ag5 and eight bridging $CF_3CO_2^-$ groups (Figure 9). Each $[(Ag_2C_2)(AgCF_3CO_2)_8]$ unit is surrounded by eight bpa bridging ligand, of which four adopt the anti conformation (on silver atoms of type Ag1 and Ag4) while the other four take the gauche form (on silver atoms of type Ag3 and Ag5). The $[(Ag_2C_2)(AgCF_3CO_2)_8]$ moieties are connected by anti-type bpa ligands to form a chain along the *a* direction, and such chains are further interlinked by gauche-type bridges to generate a two-dimensional network parallel to the *ab* plane (Figure 10). The distance between the centroids of two pyridyl rings belonging to two independent *anti*-bpa ligands is 3.79 Å, which falls within the limit of $\pi-\pi$ stacking interactions. The dihedral angles between the two pyridyl rings are 62.3° for *anti*-bpa and 85.0° for *gauche*-bpa. When viewed along the *a* direction (cross-section perspective), the gauche-type bpa ligands resemble arches spanning over neighboring chains. The layers pack in the ABAB··· pattern with each Ag_8 unit located above the center of a rhombic polygon of an adjacent layer. Thus, the arches of adjacent layers inlay each other to fill the packing void. The flexibility of bpa is a key factor in the formation of this 2D structure, as the coexistence of both conformations favors the connection between building units to achieve efficient packing.

Another two-dimensional network was also found with bppz as the bridging ligands in **5**. The building unit of **5** is a silver quadruple cage possessing $\bar{1}$ symmetry (Figure 11), which is composed of two kinds of single cages A and B. Cage A is a monocapped trigonal prism Ag3Ag8Ag9Ag10-Ag11Ag12 with Ag2 capping a rectangular face, and cage B is a bicapped trigonal prism Ag3Ag4Ag5Ag6Ag7Ag1a with Ag1 and Ag2 each capping one rectangular face. Cage A and B share silver edge Ag2···Ag3 to form a double cage, and two such double cages related by an inversion center share edge Ag1···Ag1a to generate a basic building unit. These Ag_{24} quadruple cage units are connected by bridging carboxylate groups to form a chain along the [01$\bar{1}$] direction. The bppz ligand functions as a μ_2-bridge with two N donors chelating Ag7 (or Ag8) belonging to the quadruple cage and the other two chelating Ag14 (or Ag13), each of these silver atoms being further linked by a carboxylate to a neighboring quadruple cage to generate a 2D network (Figure 12).

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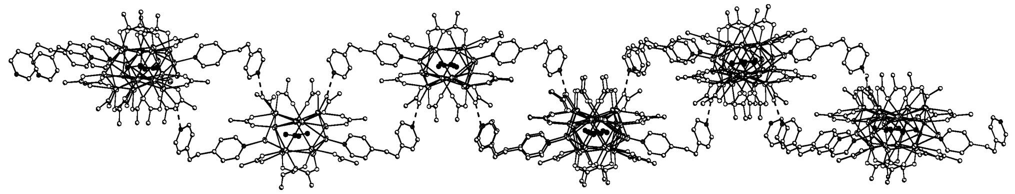

Figure 8. Undulated two-dimensional network of **3** generated from the linkage of herringbone chains by N−H···O hydrogen bonds shown as dotted lines.

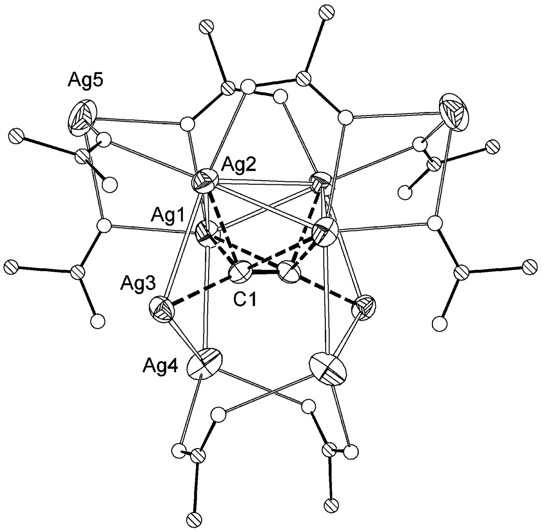

Figure 9. [$(Ag_2C_2)(AgCF_3CO_2)_8$] building unit of symmetry 2 in [$(Ag_2C_2)(AgCF_3CO_2)_8(bpa)_4$]$_n$ (**4**). Selected bond distances (Å): Ag(1)···Ag(2) 3.0545(8), Ag(2)···Ag(3) 2.9608(8), Ag(3)···Ag(4) 3.0636(8), Ag(4)···Ag(1) 2.9882(9), Ag(1)···Ag(2a) 2.9340(8), Ag(2)···Ag(2a) 3.368(1). Symmetry code: (a) −*x*, *y*, 1/2 − *z*.

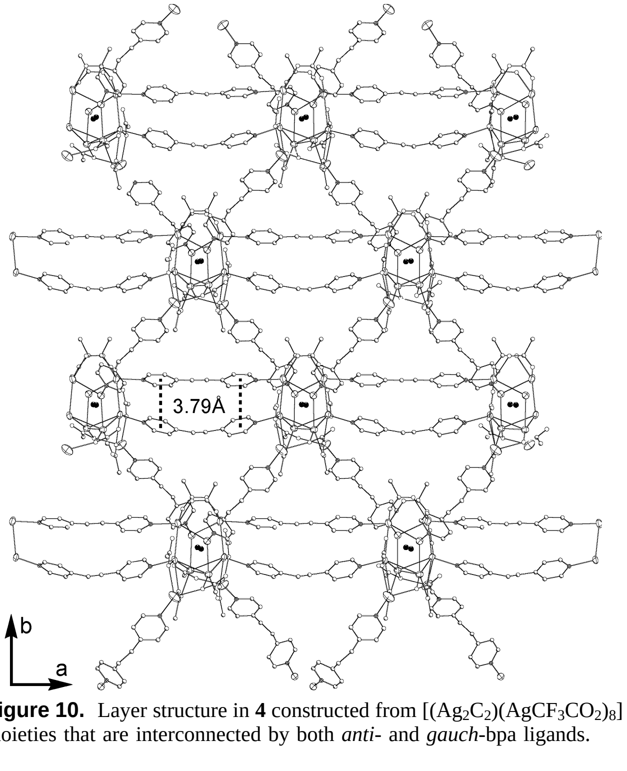

Figure 10. Layer structure in **4** constructed from [$(Ag_2C_2)(AgCF_3CO_2)_8$] moieties that are interconnected by both *anti*- and *gauch*-bpa ligands.

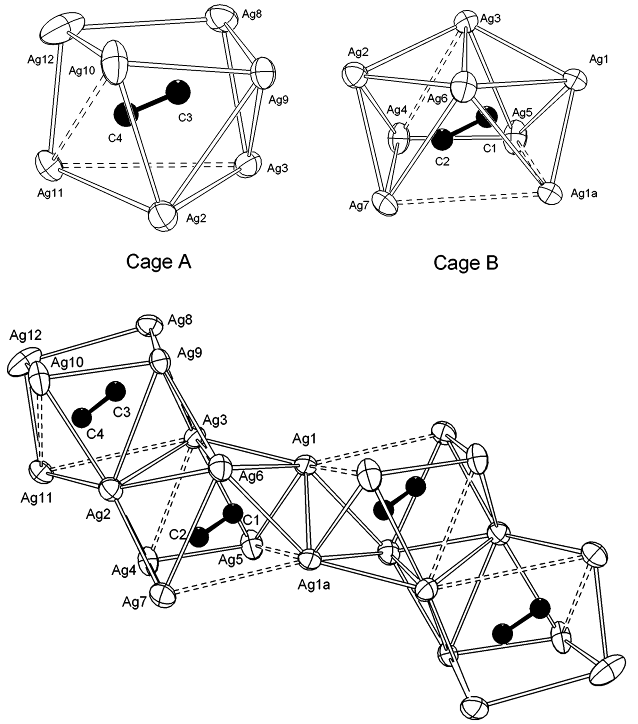

Figure 11. Centrosymmetric Ag_{24} quadruple cage units composed of edge-sharing of two types of cages, A and B, in [$(Ag_2C_2)_2(AgCF_3CO_2)_{10}(bppz)_2\cdot(H_2O)$]$_n$ (**5**). Selected bond distances (Å): Ag(1)···Ag(1a) 2.821(1), Ag(1)···Ag(3) 3.001(1), Ag(1)···Ag(5) 3.027(1), Ag(1)···Ag(6) 3.291(1), Ag(2)···Ag(3) 3.097(1), Ag(2)···Ag(4) 2.999(1), Ag(2)···Ag(6) 3.023(1), Ag(2)···Ag(7) 3.039(1), Ag(3)···Ag(5) 3.364(1), Ag(5)···Ag(4) 2.848(1), Ag(4)···Ag(7) 3.193(1), Ag(1a)···Ag(6) 3.298(1), Ag(6)···Ag(7), Ag(2)···Ag(10) 3.268(1), Ag(2)···Ag(11) 3.304(1), Ag(3)···Ag(8) 3.132(1), Ag(3)···Ag(9) 3.147(1), Ag(8)···Ag(9) 2.844(1), Ag(9)···Ag(10) 2.987(1), Ag(10)···Ag(12) 2.988(2), Ag(11)···Ag(12) 2.897(1).

The trifluoroacetate ligands exhibit different kinds of coordination modes in complex **1** and **2**. One monodentate and 7 μ-O,O′ trifluoroacetate ligands are present in the asymmetric unit of **1**, while 1 μ_3-O,O,O′ and 13 μ-O,O′ trifluoroacetate ligands surround the core of the supermolecule in **2**. Similarly, both μ_2- and μ_3-modes of trifluoroacetate ligands are found in complexes **3**−**5**. The various coordination modes of trifluoroacetate ligands found in complexes **1**−**5** are illustrated in Chart 2, and the relevant range and average of observed Ag−O distances are listed in Table 2.

The C−C bond lengths of the acetylide anion in **1**−**5** are in the range 1.16(1)−1.23(1) Å, which indicates that the entrapped C_2^{2-} species retains its triple bond character, in accordance with the previous finding in a variety of $C_2@Ag_n$ cages.[16] In addition, the Ag···Ag distances of the silver cages in **1**−**5** lie in the ranges of 2.8549(8)−3.2636(9), 2.8214(9)−3.3453(9), 2.8886(5)−3.3573(6), 2.9840(8)−3.368(1), and 2.821(1)−3.364(1) Å (within twice the van der Waals radius of the silver atom), respectively. This is indicative of the existence of significant argentophilic interaction.[17]

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Table 2. Range/Average of Ag−O Bond Lengths (Å) for Various Coordination Modes Found in Complexes **1**−**5**

	A	B	C	D
1	2.245(5)		2.301(6)−2.584(7)/2.414(6)	
2			2.221(6)−2.554(6)/2.383(6)	2.422(6)−2.507(7)/2.478(7)
3			2.156(3)−2.499(4)/2.315(4)	
4		2.343(7)−2.542(6)/2.415(6)	2.356(6)−2.575(6)/2.466(6)	2.304(5)−2.578(5)/2.422(5)
5		2.32(1)−2.54(1)/2.43(1)	2.206(7)−2.377(7)/2.298(7)	2.159(7)−2.594(9)/2.389(7)

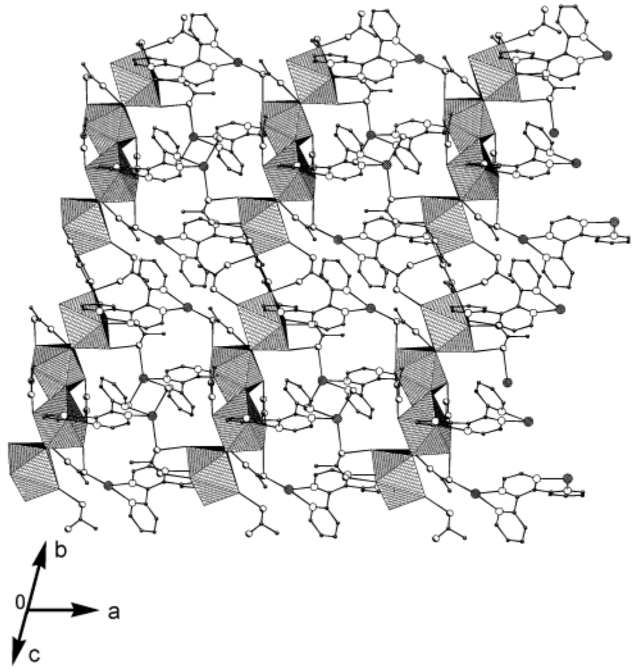
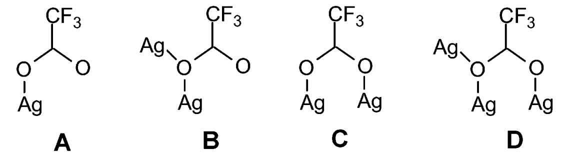


Figure 12. Two-dimensional network of **5** generated from quadruple cage units bridged by bppz ligands.

Compounds **1**, **2**, **3**, and **5** were prepared in the same manner using the same silver(I) starting materials but with different ligands employed. When Ag_2C_2 dissolves in a concentrated aqueous solution of silver trifluoroacetate and silver tetrafluoroborate, some polyhedral species of the type $[C_2@Ag_n]^{(n-2)+}$ ($n \geq 6$) are assumed to form from the depolymerization of Ag_2C_2. Various pyridyl-related ligands affect the assembly process of these species during crystallization under hydrothermal condition. As a result, quite different crystal structures such as discrete (**2**), 1D (**3**), 2D (**5**), and 3D (**1**) are generated.

Efforts have been made to effect ligand-controlled self-assembly of polynuclear lanthanide−oxo/hydroxo complexes by methods ranging from synthetic serendipity to rational supramolecualr design.[18] It is noteworthy that in **1**−**3**, which are assembled with the linear spacer ligands pyrazine, 1,4-diazabicyclo[2.2.2]octane, and 1,2-bis(4-pyridyl)ethane, respectively, the acetylide-encapsulating silver cages $[C_2@Ag_n]^{(n-2)+}$ exhibit different geometries that are fused to different extents, whereas the use of the angular spacer 2,3-bis(2-pyridyl)pyrazine results in a Ag_{24} quadruple cage in **5**. Such an observation indicates that the silver acetylide system is a very labile one and the assembly process is subject to many factors, thus making it intractable to use a specific $[C_2@Ag_n]^{(n-2)+}$ species as an intact building unit like $[Re_6Se_8]$. Therefore, our approach to use the $[C_2@Ag_n]^{(n-2)+}$ species in supramolecular construction is not technically a designed assembly but is more like "serendipitous assembly" as termed by Winpenny in the exploration of polynuclear cage compounds.[19] However, compound **4** obtained by chance sheds a new light on the feasibility of using an acetylide-encapsulating silver polyhedral entity for supramolecular construction. As studies on the $Ag_2C_2/AgCF_3CO_2/AgBF_4$ and related systems continue to be further developed, it will be possible to gradually steer our synthetic approach to supramolecular complexes containing Ag_2C_2 from anticipation toward rational design.

Chart 2



Concluding Remark

The assembly of supramolecular complexes exhibiting a range of discrete to 1D, 2D, and 3D structures via the incorporation of pyridyl-type ligands into the silver acetylide system has been achieved. In **1**, **4**, and **5**, pyz, bpa, and bppz ligands function as linear or angular neutral connectors in the construction of supramolecular architectures containing $C_2@Ag_n$ building blocks generated in situ. As demonstrated in this study, broadening the chemistry of the silver acetylide system by ligand variation continues to pose challenging problems in the designed synthesis of discrete and extended supramolecular systems.

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Supporting Information Available: Five X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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