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Self-Assembled Silver Polyhedra with Embedded Acetylide Dianion Stabilized by Perfluorocarboxylate and 4-Hydroxyquinoline Ligands

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Four new silver(I) double salts $(L_2H)_4[Ag_{10}(C_2)(CF_3CO_2)_{12}(L)_2]\cdot 5H_2O$ (**1**), $[Ag_8(C_2)(CF_3CO_2)_6(L)_6]$ (**2**), $[(Ag_2C_2)(AgC_2F_5CO_2)_6(L)_3(H_2O)]\cdot H_2O$ (**3**), and $(L\cdot H_3O)_2[Ag_{11}(C_2)_2(C_2F_5CO_2)_9(H_2O)_2]\cdot H_2O$ (**4**) incorporating the hitherto unexplored ligand 4-hydroxyquinoline (L) have been synthesized by the hydrothermal method. Compound **1** features an unprecedented bicapped square-antiprismatic Ag_{10} silver cage with an embedded C_2^{2-} moiety, whereas the discrete supermolecule **2** bears a rhombohedral Ag_8 core similar to that previously found in $Ag_2C_2\cdot 6AgNO_3$. Compound **3** contains a discrete supramolecular complex whose core is a $(C_2)_2@Ag_{16}$ double cage constructed from the edge-sharing of two monocapped square antiprisms, which is completely surrounded by 12 pentafluoropropionate, 6 4-hydroxyquinoline, and 2 aqua ligands. The layer structure in **4** is constructed from a sinuous anionic silver column composed of fused irregular monocapped trigonal antiprisms each encapsulating a C_2^{2-} dianion, with $L\cdot H_3O^+$ species serving as hydrogen-bond connectors to adjacent columns.

Introduction

Rapid advances in the chemistry of compounds containing silver acetylide, Ag_2C_2, stem from their intriguing structural features.[1] The acetylide dianion C_2^{2-} has a flexible coordination environment, being able to form σ, π, and/or mixed Ag−C interactions. Of particular interest is the fact that silver(I) can display noncovalent $d^{10}-d^{10}$ closed-shell[2] attractive Ag···Ag (i.e., argentophilic[3]) interactions, providing an extra dimension of complexity that leads to the generation of polyhedral silver cages of various geometries each encapsulating an acetylide dianion. Previous studies in our laboratory on Ag_2C_2-containing systems have shown that the formation of this type of $C_2@Ag_n$ polyhedra is quite labile and can be influenced by many factors. For example, to satisfy the charge balance and coordination environment of silver(I), coexisting anions such as nitrate, fluoride, perchlorate, tetrafluoroborate, and triflate, as well as fluoro-substituted carboxylates and dicarboxylates, have been introduced to the Ag_2C_2-containing reaction systems to obtain a wide range of novel double, triple, and quadruple salts.[1,4] Subsequently, the influence of neutral ancillary ligands such as aliphatic nitriles and crown ethers was explored.[5] The introduction of the macrocyclic *N*-donor ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane then led to the isolation of two novel mixed-valent silver(I,II) complexes.[6] Furthermore, the role of quaternary ammonium cations (Et_4N^+, Me_3BzN^+) in the generation of polynuclear aggregates containing Ag(I) and C_2^{2-} ions has also been explored.[7] Recently, the utilization of $C_2@Ag_n$ polyhedra as building blocks for supramolecular assembly of new coordination frameworks through the incorporation of bifunc-

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Table 1. Crystallographic Data for Compounds **1**−**4**

compd	**1**	**2**	**3**	**4**
empirical formula	$(L_2H)_4[Ag_{10}(C_2)(CF_3CO_2)_{12}(L)_2]\cdot 5H_2O$	$[Ag_8(C_2)(CF_3CO_2)_6(L)_6]$	$[(Ag_2C_2)(AgC_2F_5CO_2)_6(L)_3(H_2O)]\cdot H_2O$	$(L\cdot H_3O)_2[Ag_{11}(C_2)_2(C_2F_5CO_2)_9(H_2O)_2]\cdot H_2O$
fw	4004.61	2436.04	2336.62	3084.22
cryst syst	monoclinic	rhombohedral	monoclinic	monoclinic
space group	$C2/c$	$R\bar{3}$	$P2_1/n$	$P2_1$
a (Å)	23.888(1)	15.5003(5)	16.4520(7)	16.050(2)
b (Å)	22.439 (1)	15.5003(5)	21.7398(9)	14.869(2)
c (Å)	27.508(1)	28.833(1)	18.7289(7)	16.887 (2)
α (deg)	90	90	90	90
β (deg)	106.661 (1)	90	105.350 (1)	98.977(2)
γ (deg)	90	120	90	90
V (Å^3)	14125 (1)	5999.2(4)	6459.7(5)	3980.7(7)
Z	4	1	4	2
λ (Å)	0.71073	0.71073	0.71073	0.71073
T (K)	293(2)	293(2)	293(2)	293(2)
D_c (mg/m^3)	1.878	2.023	2.399	2.563
μ (mm^{-1})	1.481	2.026	2.526	2.819
R1^a (obsd)	0.0665	0.0374	0.0707	0.0484
wR2^a (all)	0.2247	0.0959	0.2260	0.1218

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

tional exodentate pyridyl-type ligands has engendered distinctly different crystal structures from discrete to 1D, 2D, and 3D.[8]

Our conceived strategy in the present work is to investigate the assembly of $C_2@Ag_n$ cages with a heterocylic tautomeric compound[9] as an additional component, while taking the influence of coexisting anions into account. The hitherto unexplored ligand 4-hydroxyquinoline (L) was chosen as it could presumably coordinate to silver(I) through its O or N atom, bearing in mind that the steric bulk of the fused benzene ring and potential silver−aromatic interaction[5c,7b,10] might turn out to be significant structure-controlling factors. Here we report the isolation and structural characterization of four new silver(I) double salts, namely $(L_2H)_4[Ag_{10}(C_2)(CF_3CO_2)_{12}(L)_2]\cdot 5H_2O$ (**1**), $[Ag_8(C_2)(CF_3CO_2)_6(L)_6]$ (**2**), $[(Ag_2C_2)(AgC_2F_5CO_2)_6(L)_3(H_2O)]\cdot H_2O$ (**3**), and $(L\cdot H_3O)_2[Ag_{11}(C_2)_2(C_2F_5CO_2)_9(H_2O)_2]\cdot H_2O$ (**4**).

Experimental Section

All chemicals were purchased from ACROS and Aldrich and used without further purification. Ag_2C_2 was prepared as described previously.[1a] *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 in alkaline solution via slow decomposition.*[11] *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 operating at 50 kV and 30 mA using Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Data collection and reduction were performed using the SMART and SAINT software, with frames of 0.3° oscillation in the range $1.5° < \theta < 28°$.[12]An empirical absorption correction was applied using the SADABS program.[13] The structures were solved by direct methods. For **2** and **4**, all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL version 5.1 package.[14] For **1**, some of the water oxygen atoms showed positional disorder with half or quarter site occupancy and were refined with isotropic temperature factors. Some terminal C and F atoms of the pentafluoropropionate groups in **3** exhibited large thermal motion and were subjected to suitable restraints in the refinement. The crystal data and details of refinement for **1**−**4** are summarized in Table 1, and selected bond distances are listed in the legends for figures.

$(L_2H)_4[Ag_{10}(C_2)(CF_3CO_2)_{12}(L)_2]\cdot 5H_2O$ (1). Excess Ag_2C_2 (∼0.5 g, 2 mmol) was added to 1 mL of a concentrated 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, 34 mg (0.23 mmol) of 4-hydroxyquinoline (L) was added to the filtrate. The resulted suspension was placed in a 25 mL Teflon-lined stainless steel reaction vessel and subjected to hydrothermal conditions at 108 °C for 24 h, then cooled to room temperature at 6 °C/h.[8] Colorless rhombus-like crystals were isolated in ∼18% yield. Anal. Calcd for **1**: C, 34.79; H, 2.11; N, 3.50. Found: C, 33.94; H, 1.97; N, 3.63.

$[Ag_8(C_2)(CF_3CO_2)_6(L)_6]$ (2). This compound was obtained serendipitously from an attempt to trap CN^- inside the silver cage by introducing AgCN into the reaction system. Excess Ag_2C_2 (∼0.5

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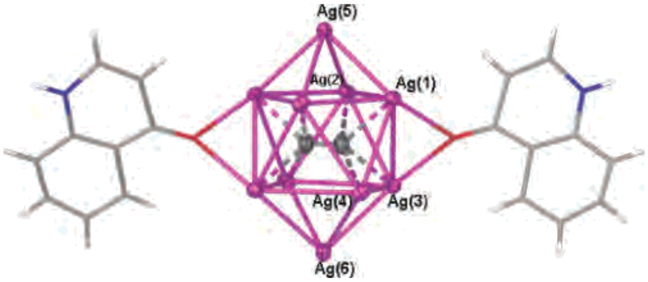

Figure 1. Bicapped square antiprismatic $C_2@Ag_{10}$ core of the supramolecular anion $[Ag_{10}(C_2)(CF_3CO_2)_{12}(L)_2]^{4-}$ in **1**. A 2-fold symmetry axis passes through Ag(5) and Ag(6). Atoms are drawn at 30% thermal ellipsoids. Selected bond distances (Å): C1−C1a 1.05(2), C1−Ag1 2.19(1), C1−Ag3 2.19(1), C1−Ag4 2.43(1), C1−Ag2a 2.46(1), Ag1−Ag2 3.084(1), Ag1−Ag3 3.136(1), Ag1−Ag4 3.151(1), Ag1−Ag5 2.911(1), Ag1−Ag2a 3.031(1), Ag2−Ag4 3.208(1), Ag2−Ag5 2.956(1), Ag2−Ag3a 3.238(1), Ag3−Ag4 2.993(1), Ag3−Ag6 2.933(1), Ag3−Ag4a 3.316(1), Ag4−Ag6 2.964(1). Symmetry codes: (a) x, y, z; (b) $-x + 1$, y, $-z + {}^1/_2$.

g, 2 mmol) and AgCN (∼0.3 g, 2 mmol) were added to 1 mL of a concentrated aqueous solution of $AgCF_3CO_2$ (2 mmol) and $AgBF_4$ (1 mmol) in a plastic beaker with stirring until saturated. The undissolved amount of Ag_2C_2 and AgCN was filtered off, and 36 mg (0.25 mmol) of L was added to the filtrate. The resulted suspension was treated with the hydrothermal method as described. Colorless blocklike crystals were isolated in ∼36% yield. Anal. Calcd for **2**: C, 33.53; H, 1.74; N, 3.45. Found: C, 32.72; H, 1.68; N, 3.37.

$[(Ag_2C_2)(AgC_2F_5CO_2)_6(L)_3(H_2O)]\cdot H_2O$ (3). Excess Ag_2C_2 (∼0.5 g, 2 mmol) was added to 1 mL of a concentrated aqueous solution of $AgC_2F_5CO_2$ (2 mmol) in a plastic beaker with stirring until saturated. The undissolved amount of Ag_2C_2 was filtered off, and then, 30 mg (0.21 mmol) of L was added to the filtrate. The resulting suspension was treated under hydrothermal conditions to yield colorless blocklike crystals in ∼30% yield. Anal. Calcd for **3**: C, 24.16; H, 1.08; N, 1.80. Found: C, 23.02; H, 1.12; N, 1.73.

$(L\cdot H_3O)_2[Ag_{11}(C_2)_2(C_2F_5CO_2)_9(H_2O)_2]\cdot H_2O$ (4). Excess Ag_2C_2 (∼0.5 g, 2 mmol) was added to 1 mL of a concentrated aqueous solution of $AgC_2F_5CO_2$ (2 mmol) and $AgBF_4$ (2 mmol) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, and then, 31 mg (0.21 mmol) of L was added to the filtrate. The resulting suspension was subjected to hydrothermal synthesis to give colorless blocklike crystals in ∼10% yield. Anal. Calcd for **4**: C, 19.08; H, 0.85; N, 0.91. Found: C, 20.06; H, 0.87; N, 0.85.

Results and Discussion

As described before, Ag_2C_2 readily dissolves in a concentrated aqueous solution of a silver salt to form polyhedral species $C_2@Ag_n$ ($n = 6-9$). For instance, double salts of general formula $Ag_2C_2\cdot mR_fCO_2Ag$ can be obtained using silver(I) perfluorocarboxyaltes, and the presence of $AgBF_4$ further contributes to the dissolution of Ag_2C_2 and possible isolation of a triple salt. Comparison of the present work with our previous study of the $Ag_2C_2/AgBF_4/R_fCO_2Ag$ system[5,8] shows that the introduction of 4-hydroxyquinoline as a new component expands the scope of generating new structures.

Single-crystal X-ray analysis revealed that compound **1** contains a novel Ag_{10} silver cage of symmetry 2. The cage is best described as a bicapped square antiprism as illustrated in Figure 1. Atoms sets Ag1−Ag2−Ag1a−Ag2a and Ag3−Ag4−Ag3a−Ag4a are each coplanar with a maximum deviation of 0.0201 and 0.0164 Å, respectively. Atoms Ag5 and Ag6 lie on a 2-fold axis, capping the faces Ag1−Ag2−Ag1a−Ag2a and Ag3−Ag4−Ag3a−Ag4a, respectively.

A C_2^{2-} species is accommodated in the cage with its molecular axis aligned parallel to the two square planes. The C1−C1a bond length 1.05(2) Å is significantly shorter than the C−C triple bond lengths in acetylene (1.205 Å),[15] CaC_2 (1.191 Å),[16] the ternary alkali metal silver acetylides $CsAgC_2$ and $KAgC_2$ (1.217(7) and 1.223(6) Å, respectively),[17] and the double and triple salts of silver acetylide in the range 1.175(7)−1.225(7) Å. The observed Ag−C distances vary in the range from 2.19(1) to 2.46(1) Å and are slightly longer than typical Ag−C σ bonds (e.g., 2.087(3) and 2.108(6) Å in $Ag_2C_2\cdot 2AgClO_4\cdot 2H_2O$).[1c]

Twelve trifluoroacetate ligands in the μ-O,O′ mode and two L ligands in the μ-O coordination mode bridge the edges of $C_2@Ag_{10}$ to form an anionic $[Ag_{10}(C_2)(CF_3CO_2)_{12}(L)_2]^{4-}$ unit. Compound **1** represents the first example of metal-coordinated 4-hydroxyquinoline, although some complex crystal structures of related quinolones that form coordinate bonds with metal ions have been reported.[9g]

Some of the lattice water molecules in **1** exhibit positional disorder with half or quarter site occupancy. An anomalous feature of **1** is the overall charge balance. A plausible explanation is that the uncoordinated L ligands are arranged in pairs whose O atoms are bridged by a proton. Furthermore, the $(L_2H)^+$ cations are attached to the Ag_{10} core via hydrogen bonds with their N−H groups serving as hydrogen bond donors and the trifluoroacetate ligands serving as acceptors ($N_5\cdots O_8 = 2.922$ Å, $H\cdots O_8 = 2.070$ Å, $\theta = 170.7°$; $N_2\cdots O_5 = 2.930$ Å, $H\cdots O_5 = 2.079$ Å, $\theta = 170.5°$).

Our pervious work on the chemistry of silver acetylide has demonstrated that $C_2@Ag_n$ cages and fused double cages $(C_2)_2@Ag_{2n-m}$ (n vertices, 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. The maximum value of n for all the previous structures is nine,[1b,5a,7c] and the $C_2@Ag_{10}$ single cage in **1** further extends this to 10.

The rhombohedral Ag_8 core in compound **2** is similar to that found in $Ag_2C_2\cdot 6AgNO_3$.[1a] Likewise the encapsulated acetylide dianion is disordered about a crystallographic 3-fold axis that bisects the C≡C bond and passes through two opposite corners of the Ag_8 rhombohedron.

Apart from the μ-O,O′ trifluoroacetate ligands, there are six L ligands surrounding the polynuclear core, each bridging an edge in the μ-O mode. In contrast to $Ag_2C_2\cdot 6AgNO_3$, in which the discrete cationic silver polyhedra are interlinked by NO_3^- anions to form a three-dimensional network, **2** features a discrete $C_2@Ag_8$ cluster enveloped by bulky L and hydrophobic trifluoroacetate, which prevent further linkage of adjacent silver polyhedra (Figure 2).

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Figure 2. Space-filling drawing of the discrete supermolecule in **2** viewed along its 3-fold symmetry axis. Trifluoroacetate ligands have been omitted for clarity. Color legend: carbon, gray; nitrogen, blue; hydrogen, white; silver, purple; oxygen, red.

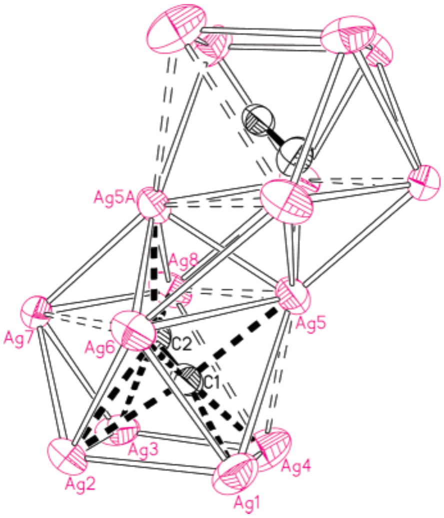

Figure 3. Double cage unit $(C_2)_2@Ag_{16}$ generated from two monocapped square antiprisms in $[(Ag_2C_2)(AgC_2F_5CO_2)_6(L)_3(H_2O)]\cdot H_2O$ (**3**). Atoms are drawn at 30% thermal ellipsoids. The Ag···Ag distances longer than 3.4 Å (twice the van der Waals radius of silver atom) are represented by broken open lines. The C−Ag bonds are only shown in the lower half for clarity. Selected bond distances (Å): C1−C2 1.18(1), C1−Ag1 2.15(1), C1−Ag2 2.462(9), C1−Ag4 2.423(9), C1−Ag5 2.389(9), C1−Ag6 2.394(9), C2−Ag2 2.71(1), C2−Ag3 2.63(1), C2−Ag7 2.23(1), C2−Ag8 2.23(1), C2−Ag5a 2.43(1), Ag1−Ag2 3.042(1), Ag1−Ag4 2.781(2), Ag1−Ag6 3.026(1), Ag2−Ag3 2.925(1), Ag2−Ag6 3.048(1), Ag2−Ag7 2.928(1), Ag3−Ag4 2.977(2), Ag3−Ag7 3.025(1), Ag3−Ag8 2.879(1), Ag5−Ag6 3.211(1), Ag7−Ag8 2.972(1), Ag5−Ag5a 2.967(2), Ag6−Ag5a 3.138(1), Ag7−Ag5a 3.005(1), Ag8−Ag5a 2.966(1). Symmetry codes: (a) *x*, *y*, *z*; (b) $-x + 1$, $-y + 1$, $-z + 1$.

In the crystal structure of **3**, the core is a centrosymmetric double cage composed of 16 silver(I) atoms, with each single cage encapsulating an acetylide dianion, as shown in Figure 3. Each single cage is in the form of a distorted monocapped square antiprism. Atom sets Ag1−Ag2−Ag3−Ag4 and Ag5−Ag6−Ag7−Ag8 are each coplanar within 0.020 and 0.030 Å, respectively, making a dihedral angle of 9.8°. Atom Ag5a caps Ag5−Ag6−Ag7−Ag8, and two single cages share an edge Ag5···Ag5a to form the double cage. A C_2^{2-} species is enclosed in each silver polyhedron and stabilized by eight σ-type and one π-type interactions. The Ag−C bond lengths range from 2.15(1) to 2.71(1) Å. The C1−C2 bond length 1.18(1) Å lies close to the lower limit of 1.175(7)−1.225(7) Å found in the double and triple salts of silver acetylide, suggesting that the degree of metal-to-ligand back-bonding is very low in such a silver-rich environment.[18]

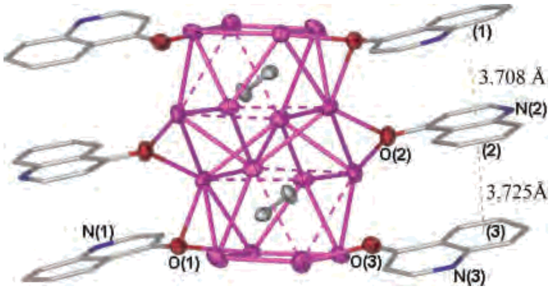

Figure 4. Structure of the centrosymmetric supermolecule in **3**. Pentafluoropropionate and aqua ligands have been omitted for clarity.

The $(C_2)_2@Ag_{16}$ double cage is surrounded by 12 pentafluoropropionate ligands acting in the μ-O,O′ coordination mode, and each silver atom of type Ag1 is further coordinated to one aqua ligand at a distance of 2.34(1) Å. Apart from these, there are six L ligands surrounding the $(C_2)_2@Ag_{16}$ unit. The whole supermolecule is shown in Figure 4. It is notable that the ligand behavior of the three independent L ligands in **3**, of which one is monodentate and the other two function in the μ-O coordination mode in linking the Ag···Ag edges, differs markedly from that in **1**. The hydrophobic tails of the pentafluoropropionate ligands, together with the terminal and bridging L and aqua ligands, prevent further linkage between adjacent silver polyhedra, yielding a unique discrete supermolecule.

Another noteworthy characteristic of **3** is the existence of intramolecular π−π stacking interactions. The centroid−centroid distances between phenyl rings belonging to adjacent 4-hydroxyquinoline moieties are 3.708 and 3.725 Å, which fall within the normal range of π−π stacking interactions. The dihedral angles between the corresponding phenyl groups are 5.0° and 5.5°, respectively.

In previous work, we have investigated the influence of terminal ligation presented by aliphatic nitriles, crown ethers and 1,4-diazabicyclo[2.2.2]octane, whose presence usually lower the dimensionality of the resulting crystal structure, such that discrete polynuclear molecules are isolated in some cases.[5,8] An analogous role is played by 4-hydroxyquinoline as a terminal or bridging ligand in **1**, **2**, and **3**, which along with Ag(I), C_2^{2-}, and $R_fCO_2^-$ facilitate the assembly of the supramolecular aggregates.

In contrast to **1**, **2**, and **3**, in which the silver polyhedra are discrete, compound **4** has a quite different structure which comprises the L ligand, H_3O^+ species, and the anionic polymeric system $[Ag_{11}(C_2)_2(C_2F_5CO_2)_9(H_2O)_2]_\infty^{2-}$. The basic building unit in the latter is an Ag_{12} double cage composed of two irregular monocapped trigonal antiprisms sharing a common edge, Ag1−Ag4 (Figure 5). In the left cage, atom sets Ag1Ag2Ag3 and Ag4Ag5Ag6 constitute two triangular faces making a dihedral angle of 6.2°, with Ag7 capping the upper face. As to the right antiprism, the two triangular faces Ag4Ag9Ag10 and Ag1Ag6aAg8 are almost parallel, making a dihedral of 3.3°, with Ag11 capping the Ag4Ag9-

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(18) Halet, J.-F.; Mingos, D. M. P. *Organometallics* **1988**, *7*, 51.

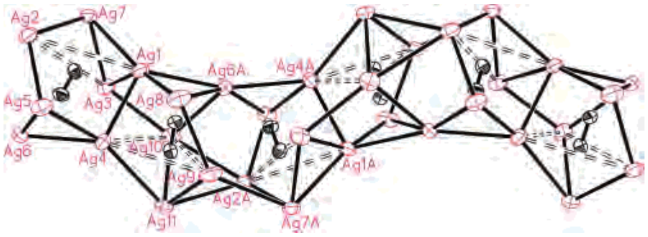


Figure 5. Portion of the sinuous silver column generated from the fusion of monocapped trigonal antiprisms in **4**.

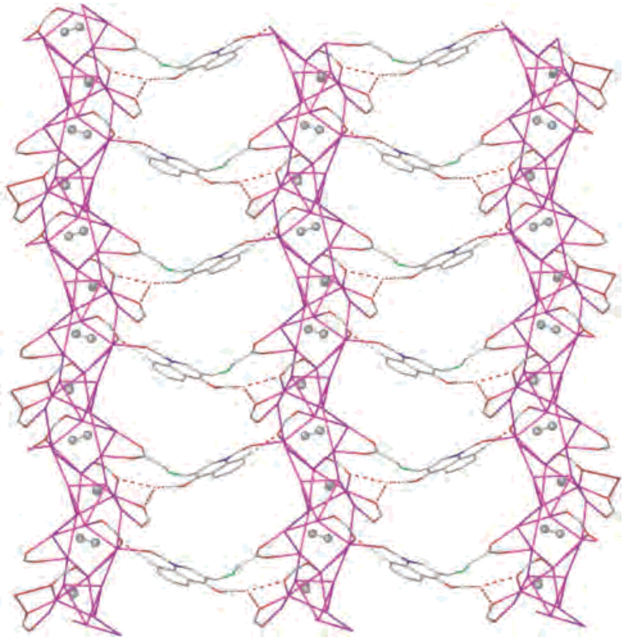


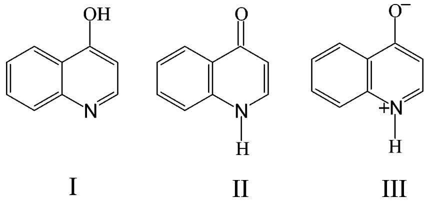
Figure 6. Schematic showing the layer structure in compound **4**. The F, H, and O atoms that do not participate in the formation of hydrogen bonds have been omitted for clarity. Black balls indicate C_2^{2-} species. Color legend: carbon, gray; nitrogen, blue; hydrogen, white; silver, purple; oxygen, red; fluorine, green.

Ag10 face. A C_2^{2-} species is enclosed in each silver polyhedron and stabilizes it via multiple σ and π Ag−C interactions. Two aqua ligands O1w and O2w are coordinated to Ag11 and Ag7 at distances of 2.318(7) and 2.482(6) Å, respectively. Similar to the case of **3**, only the μ-O,O′ coordination mode of pentafluoropropionate ligands is found in **4**.

The double cage is fused to adjacent double cages through sharing of vertices of the type Ag6a, with further connections Ag9−Ag7a and Ag11−Ag2a to generate an infinite, sinuous anionic column along the *c* direction.

Similar to the case of compound **1**, where overall charge balance is provided by pairs of uncoordinated L ligands whose O atoms are bridged by a proton, the O atoms of L and water molecule are bridged by a proton to give the cationic aggregate $L{\cdot}H_3O^+$ in **4**. This is substantiated by the observed interatomic distances of O19⋯O5w = 2.622 Å and O20⋯O4w = 2.564 Å. Notably, the $L{\cdot}H_3O^+$ species not only serves as a structure-inducing agent to provide overall charge balance in the formation of the anionic silver column but also plays a key role in the construction of the layer structure. As shown in Figure 6, the infinite silver columns are further connected by hydrogen bonding with the $L{\cdot}H_3O^+$ ions serving as donors and the F and O atoms of pentafluoropropionate as acceptors [O_{20}−H⋯O_{4w} (*x*, *y*, *z*), D−A = 2.564Å, H⋯A = 1.745 Å, D−H⋯A = 177.2°; N_2−H⋯O_{2w} (*x*, *y*, *z*), D−A = 2.895 Å, H⋯A = 2.095 Å, D−H⋯A = 154.5°; C_{45}−H⋯O_{13} (*x*, *y*, *z*), D−A = 3.433 Å, H⋯A = 2.503 Å, D−H⋯A = 179.7°; C_{42}−H⋯F_{11} (*x*, *y*, *z*-1), D−A = 3.188 Å, H⋯A = 2.354 Å, D−H⋯A = 149.2°].

Scheme 1



Although the neutral L molecule may exist in enol- (**I**), keto- (**II**), and zwitterionic (**III**) tautomeric forms (see Scheme 1), the dominate structure of the L ligand in all four compounds **1**−**4** is **II**. This may be due to the preference of Ag(I) for O- over N-coordination, as well as the use of polar solvent H_2O as the medium of reaction.[19]

The Ag⋯Ag distances of the silver cages in **1**−**4** lie in the ranges 2.911(1)−3.316(1), 2.8690(3)−3.1180(3), 2.781(2)−3.321(1), and 2.887(1)−3.375 (1) Å (within twice the van der Waals radius of silver atom), respectively, being indicative of the existence of significant argentophilic interaction in this class of compounds.[1]

Conclusion

The incorporation of the seldom investigated heterocylic ligand 4-hydroxyquinoline as a new component into the $Ag_2C_2/AgBF_4/R_fCO_2Ag$ system under hydrothermal conditions has yielded four new complexes **1**−**4**, three of which feature discrete high-nuclearity neutral or anionic aggregates. In particular, compound **1** represents the first example of a bicapped square-antiprismatic silver cage, the largest polyhedron found to date, that encapsulates a C_2^{2-} dianion. It is also noteworthy that minor variations in synthetic conditions, such as the addition of $AgBF_4$, resulted in the formation of a new phase **4**. As demonstrated in this study, broadening the chemistry of the silver acetylide system by variation of coexisting anions and ancillary ligands continues to pose challenging problems in the assembly of discrete and extended supramolecular systems. Further study of the incorporation of other classes of organic ligands in the synthesis of double/multiple silver salts is in progress.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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