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Elliptic Column Consolidated by Acetylide Dianion, Cyanide, and Trifluoroacetate in a Novel Quadruple Salt of Silver(I)

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In keeping with recent interest in the $d^{10}-d^{10}$ closed-shell attraction,[1] spectroscopic and structural evidence for the less explored Ag(I)−Ag(I) interaction, termed argentophilicity, has been gathering at a rapid pace.[2] By taking advantage of argentophilic interaction that promotes the aggregation of silver(I) centers into various polyhedra, we have obtained a variety of double salts of the general formula mAgY·nAgZ·xL (Y, Z = different anions; L = solvate molecule that may be present)[3−5] and furthermore succeeded in synthesizing some rare examples of silver(I) triple salts of the type lAgX·mAgY·nAgZ·xL.[6] Noting that the previously achieved triple salts involved the separate use of AgCN [6a] and Ag_2C_2,[6b] we attempted to incorporate both components into a crystalline lattice together with two other kinds of silver salts, thereby generating an unprecedented quadruple salt. Following such a strategy, the first silver(I) salt containing four different kinds of anions, namely $2Ag_2C_2 \cdot 3AgCN \cdot 15CF_3CO_2Ag \cdot 2AgBF_4 \cdot 9H_2O$ **1**, has been isolated.[7]

Single-crystal X-ray analysis revealed that **1** consists of an interesting nanoscale columnar structure, which is built up from three kinds of fundamental units: **A**, **B**, and **C**. Unit **A** (Figure 1) is a double cage made of thirteen silver atoms and two encapsulated acetylenediide (C_2^{2-}) species, which can be viewed as two $C_2@Ag_8$ polyhedra sharing a triangular face. These two single cages are related by a 2-fold axis passing through Ag(1) and the midpoint of the line joining Ag(2) and Ag(2a). Each polyhedron is best described as a trigonal prism [Ag(1)Ag(2)-Ag(2a)Ag(4)Ag(3)Ag(5)] with two of its rectangular faces capped by Ag(6) and Ag(7). The mean deviation of the atoms constituting the three rectangular faces of the trigonal prism lies in the range 0.067−0.090 Å. The edges of the [$C_2@Ag_8$] bicapped trigonal prism lie in the range of 2.879(1)−3.316(1) Å (within twice the van der Waals radius of silver atom), except two considerably longer ones at Ag(3)···Ag(4) = 3.869 Å and Ag(4)···Ag(5) = 4.199 Å.

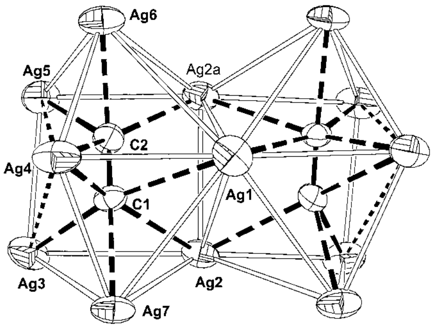

Figure 1. Unit **A** consisting of a double cage fused from two bicapped silver trigonal prisms. Polyhedral edges that are longer than 3.40 Å (twice the van der Waals radius of silver atom) are represented by broken lines. Selected bond ditances [Å]: C(1)−C(2) 1.16(1), C(1)−Ag(1) 2.58(1), C(1)−Ag(2) 2.48(1), C(1)−Ag(3) 2.29(1), C(1)−Ag(4) 2.30(1), C(1)−Ag(7) 2.145(9), C(2)−Ag(1), 2.746, C(2)−Ag(2a) 2.38(1), C(2)−Ag(4) 2.59(1), C(2)−Ag(5) 2.18(1), C(2)−Ag(6) 2.19(1). Symmetry code: (a) $1 - x, y, 3/2 - z$.

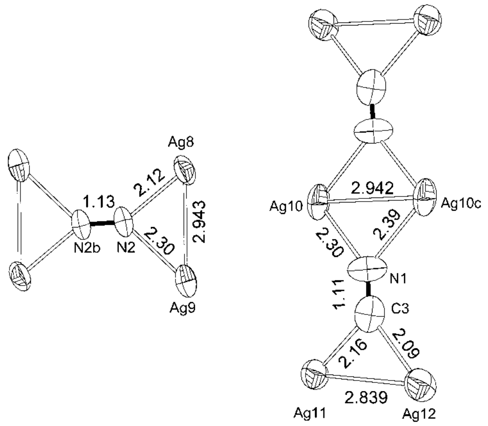

Figure 2. Structural fragments (a) [Ag_4CN] (Unit **B**) and (b) [$Ag_6(CN)_2$] (Unit **C**). Symmetry codes: (b) $1 - x, y, 1/2 - z$; (c) $1 - x, 1 - y, 1 - z$.

A C_2^{2-} species is accommodated in each Ag_8 cage with its molecular axis aligned approximately toward the capping silver atoms Ag(7) and Ag(6) [C(1)−C(2)−Ag(6) = 140(1)°, C(2)−C(1)−Ag(7) = 176(1)°]. The C(1)−C(2) bond length 1.16(1) Å is significantly shorter than the C−C triple bond lengths in acetylene (1.205 Å),[8] CaC_2 (1.191 Å),[9] and the ternary alkali metal silver acetylides $CsAgC_2$ and $KAgC_2$, (1.217(7) and 1.223(6) Å, respectively).[10] As the C−C bond distances found in the double and triple salts of silver acetylide fall in the range 1.175(7)−1.225(7) Å, the bond length observed in **1** lies close to the lower limit, suggesting that the degree of metal-to-ligand back-bonding[11] is very low in such a silver-rich environment. The observed Ag−C distances range from 2.145(9) to 2.59(1) Å; however, Ag(1)··· C(2) at 2.746 Å is too long to be taken as a coordination bond.

The silver polyhedra encapsulating C_2^{2-} that have been found thus far are all single cages that are either connected by bridging ligands or directly linked through vertex-sharing into 2D or 3D

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(7) Ag_2C_2 was prepared as described previously.[5] **CAUTION**: thoroughly dried Ag_2C_2 detonates easily upon mechanical shock and heating, and only a small quantity should be used in any chemical reaction. Excess Ag_2C_2 and AgCN were added to 1 mL of a concentrated aqueous solution of $AgCF_3CO_2$ and $AgBF_4$ (molar ratio ~1:3) in a plastic beaker with stirring until saturated. The undissolved amount of Ag_2C_2 and AgCN were filtered off, and the filtrate was placed in a desiccator charged with P_2O_5. Colorless prismatic crystals of **1** (mp 120−125 °C dec) were obtained in ~50% yield after several days. The compound is very hygroscopic and decomposes readily in common solvents such as water, ethanol, and acetonitrile. Crystal data for **1**: $C_{37}H_{18}Ag_{24}B_2F_{53}N_3O_{39}$, $M = 4746.04$, monoclinic, space group $C2/c$ (No. 15), $a = 26.372(3)$ Å, $b = 25.257(3)$ Å, $c = 15.978(2)$ Å, $\beta = 103.804(2)°$, $V = 10335(2)$ Å^3, $Z = 4$, $D_c = 3.050$ Mg m^{-3}, $T = 293$ K. Full-matrix least-squares refinement on F^2 (12 465 unique data, 712 variables) converged to $R1 = 0.0657$, $wR2 = 0.1996$ for 6230 observed reflections [$I > 2\sigma(I)$].

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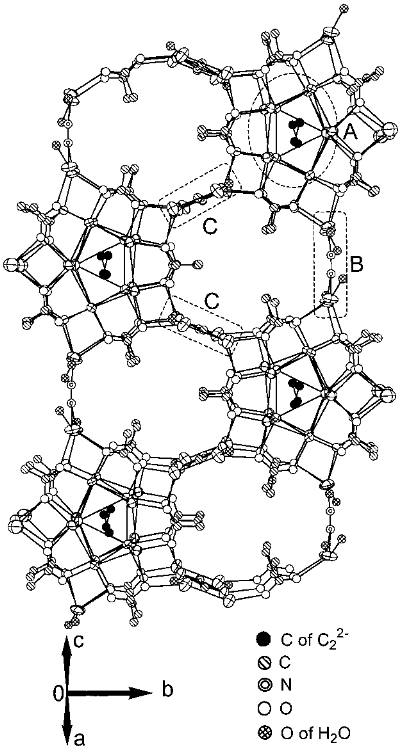

Figure 3. An elliptic column viewed approximately in the [101] direction. Ag(I) atoms are drawn as 35% thermal ellipsoids, and the remaining atoms are differentiated by size and shading. All F atoms have been omitted for clarity. Type **A**, **B**, and **C** units are each outlined by a dotted oval or frame.

networks. Unit **A** represents the first example of a face-sharing double cage with one C_2^{2-} anion located inside each half.

Motif **B** is a cyanide-bridged tetra-silver fragment located at a site of symmetry 2 (Figure 2a). The disordered cyanide group of this [Ag_4CN] fragment is represented by N(2) = $^1/_2$C + $^1/_2$N. Motif **C** (Figure 2b) is a centrosymmetric hexa-silver moiety [$Ag_6(CN)_2$] with three pairs of silver atoms side-on bridged by two ordered cyanides, each being coordinated to four silver atoms. The cyanide ligands in motifs **B** and **C** both adopt the μ_4-$\kappa C,\kappa C$:$\kappa N,\kappa N$ coordination mode that occurs in several precedents: $3AgCN\cdot 2AgF\cdot 3H_2O$[4] and $AgCN\cdot AgF\cdot 4AgCF_3CO_2\cdot 2L$ (L = H_2O or CH_3CN).[6a] The Ag$\cdots$Ag distances are Ag(8)$\cdots$Ag(9) 2.943(2), Ag(10)$\cdots$Ag(10c) 2.942(2), and Ag(11)$\cdots$Ag(12) 2.839(2) Å, which are comparable to the interatomic contact of 2.89 Å in metallic silver.[12]

Structural units **A**, **B**, and **C** are inter-linked through 7.5 independent bridging trifluoroacetato groups to generate the fascinating columnar structure shown in Figure 3. Viewed approximately along the [101] direction, one **B** and two **C** fragments are bridged by nine trifluoroacetato ligands to form a pear-like cavity with their hydrophobic $-CF_3$ tails accommodated in it. Furthermore, motif **A** is connected to neighboring silver atoms via fifteen trifluoroacetato bridges to construct an intriguing pentacle. A noteworthy feature is that the trifluoroacetato ligands adopt two kinds of bridging patterns: μ_3-*O,O*:*O′* and μ_4-*O,O*:*O′,O′* coordination modes with Ag−O distances in the range of 2.263(9)−2.587(8) Å. Only one example containing the μ_4-*O,O*:*O′,O′* coordination mode of $CF_3CO_2^-$ has been reported,[6a] and the coexistence of μ_3 and μ_4 binding modes of trifluoroacetato groups in the same structure is unprecedented.

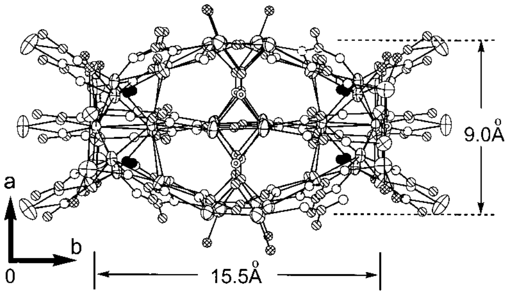

Figure 4. Oval cross section of an elliptic column viewed along the *c* direction. Dimensions of the major and minor diameters are shown. All F atoms have been omitted for clarity.

Alternately arranged pentacles and pear-like cavities are fused in a zigzag fashion along the *c* direction to configure an elliptic column, whose oval cross section is shown in Figure 4. The major and minor diameters of the elliptic girdle of the column are 15.5 and 9.0 Å, respectively. Such cationic columns are aligned parallel to each other along the *c* direction in the crystal structure of **1**. They are further interconnected to form a 3D network through bridging aqua ligands, which together with the noncoordinating BF_4^- anions occupy the space between them (see Supporting Information Figure 1S).

In summary, successful synthesis of the unprecedented quadruple salt **1** is achieved through a judicious combination of argentophilicity and the known coordination modes of selected anionic ligands in a silver(I)-rich environment: (i) the invariable preference of C_2^{2-} for encapsulation within a silver cluster, (ii) the tendency of CN^- to achieve its highest ligation number through the μ_4-$\kappa C,\kappa C$:$\kappa N,\kappa N$ mode, (iii) the bridging capacity of $CF_3CO_2^-$ whose hydrophobic tail also plays a significant role, and (iv) the weakly coordinating behavior of BF_4^-. Further exploration of viable synthetic routes to novel silver multiple salts and the controlling factors relevant to the self-assembly process are in progress.

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

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