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Ligand-Induced Disruption of Polyhedral C$_2$@Ag$_n$ Cage Assembly in Silver Acetylenediide Complexes

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Summary: The use of pyrazine-2-carboxamide as an ancillary ligand in hydrothermal synthesis yielded two new silver acetylenediide complexes exhibiting novel C$_2$@Ag$_n$ motifs: an unprecedented open fishlike Ag$_6$(μ_6-C$_2$) aggregate and the first example of two C_2^{2-} dianions entrapped inside a partially disrupted Ag$_{13}$ cage.

The smallest molecular fragment of carbon, C$_2$, is extremely reactive. Methods of stabilizing the C$_2$ unit involve (1) derivatization at both ends to form the organic acetylenes RC$_2$R,[1] (2) the formation of organometallic ethynyl complexes [M]C$_2$R,[2] (3) acetylenediide bridging between metal centers to form a [M]$_2$(μ-C$_2$) or end-capped [M]$_m$(μ_n-C$_2$) moiety ([M] = metal complex fragment),[3] and (4) encapsulation of acetylenediide in a polyhedral cage, which is symbolized by C$_2$@[M]$_n$ ([M] has been limited to silver(I) thus far).[4]

Silver acetylenediide, Ag$_2$C$_2$, is an explosive powder that is sensitive to heat and mechanical shock. Though insoluble in most solvents, it dissolves readily in a concentrated aqueous solution of one or more soluble silver(I) salts to form a wide variety of double and multiple salts, whose crystal structures are built of polyhedral cages of the type C$_2$@Ag$_n$ ($n = 6-10$). The synthetic strategy takes advantage of three synergistic factors: (i) Coulombic attraction, (ii) the versatile coordination modes of C_2^{2-} involving σ, π, and/or mixed (σ, π) Ag−C interactions, and (iii) argentophilicity, namely the d^{10}−d^{10} closed-shell attractive interaction that promotes the aggregation of silver(I) centers.[5] Examples of trigonal-pyramidal, octahedral, rhombohedral, triangulated-dodecahedral and various capped-polyhedral cages that encapsulate C_2^{2-} have been found,

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(1) Examples: (a) Shimizu, T.; Miyasaka, D.; Kamigata, N. *Org. Lett.* **2000**, *2*, 1923. (b) Marsella, M. J.; Kim, I. T.; Tham, F. *J. Am. Chem. Soc.* **2000**, *122*, 974. (c) Brizius, G.; Pschirer, N. G.; Steffen, W.; Stitzer, K.; Loye, H. C. Z.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2000**, *122*, 12435. (d) Blanchet, J.; Bonin, M.; Chiaroni, A.; Micouin, L.; Riche, C.; Husson, H.-P. *Tetrahedron Lett.* **1999**, *40*, 2935. (e) Hennrich, G.; Lynch, V. M.; Anslyn, E. V. *Chem. Eur. J.* **2002**, *8*, 2274. (f) Sydora, O. L.; Wolczanski, P. T.; Lobkovsky, E. B. *Angew. Chem., Int. Ed.* **2003**, *42*, 2685.

(2) Examples: (a) Siu, P. K. M.; Lai, S.-W.; Lu, W.; Zhu, N.-Y.; Che, C.-M. *Eur. J. Inorg. Chem.* **2003**, *15*, 2749. (b) Rosenthal, U. *Angew. Chem., Int. Ed.* **2003**, *42*, 1794.

(3) Examples: (a) Low, P. J.; Bruce, M. I. *Adv. Organomet. Chem.* **2002**, *48*, 71. (b) Lang, H.; George, D. S. A.; Rheinwald, G. *Coord. Chem. Rev.* **2000**, *206/207*, 101. (c) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178−180*, 431. (d) Bruce, M. I. *Coord. Chem. Rev.* **1997**, *166*, 91. (e) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 179. (f) Akita, M.; Moro-oka, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 420. (g) Kockelmann, W.; Ruschewitz, U. *Angew. Chem., Int. Ed.* **1999**, *38*, 3492.

(4) Examples: (a) Guo, G.-C.; Zhou, G.-D.; Mak, T. C. W. *J. Am. Chem. Soc.* **1999**, *121*, 3136. (b) Guo, G.-C.; Zhou, G.-D.; Wang, Q.-G.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 630. (c) Zhao, X.-L.; Wang, Q.-M.; Mak, T. C. W. *Inorg. Chem.* **2003**, *42*, 7872. (d) Zhao, X.-L.; Mak, T. C. W. *Dalton* **2004**, 3212. (e) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 399−410, 443.

(5) (a) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597. (b) Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098. (c) Guo, G.-C.; Mak, T. C. W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3183. (d) Omary, M. A.; Webb, T. R.; Assefa, Z.; Shankle, G. E.; Patterson, H. H. *Inorg. Chem.* **1998**, *37*, 1380. (e) 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.

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while extended structures involving edge- or face-sharing $C_2@Ag_n$ ($n = 7-9$) aggregates are also known.[4] Noting that the previously observed structural motifs are all convex polyhedra with only one C_2^{2-} entrapped in each cage, two questions naturally arise. Can the $C_2@Ag_n$ cage be opened to form a $[M]_m(\mu_n\text{-}C_2)$ species? In addition, is it possible to construct a large single cage for holding two or more C_2^{2-} dianions? With these two issues in mind, we attempted to interfere with the assembly process through the incorporation of a multidentate ligand with strong chelating and bridging affinity into the reaction system, anticipating that the competition between it and C_2^{2-} for coordination to silver might lead to fragmented $C_2@Ag_n$ cages. We selected pyrazine-2-carboxamide as a structure-directing component, in view of its very short spacer length and chelating capacity.[6] Furthermore, the introduction of the amide functionality could conceivably disrupt the assembly of $C_2@Ag_n$ via the formation of hydrogen bonds. Proceeding on this premise, we answered both queries in the affirmative through the hydrothermal synthesis of new silver(I) complexes **1** and **2** that exhibit novel $C_2@Ag_n$ motifs.[7]

$$Ag_{12}(C_2)_2(CF_3CO_2)_8(2\text{-pyzCONH}_2)_3$$

1

$$Ag_{20}(C_2)_4(C_2F_5CO_2)_8(2\text{-pyzCOO})_4(2\text{-pyzCONH}_2)(H_2O)_2$$

2

The double salt **1** was prepared by dissolving Ag_2C_2 in an aqueous solution of CF_3CO_2Ag and $AgBF_4$ followed by the addition of pyrazine-2-carboxamide. The afforded precipitate was then subjected to hydrothermal conditions.[8] The basic structural unit of **1** comprises the fusion of a distorted-triangular-dodecahedral Ag_8 cage containing an embedded C_2^{2-} dianion (cage **A**) and an open fishlike $Ag_6(\mu_6\text{-}C_2)$ motif (Figure 1a). The encapsulated C_2^{2-} species (C1−C2 = 1.21(1) Å) exhibits multiple σ and π interactions with the cage silver(I) atoms in the range 2.14(1)−2.58(1) Å.

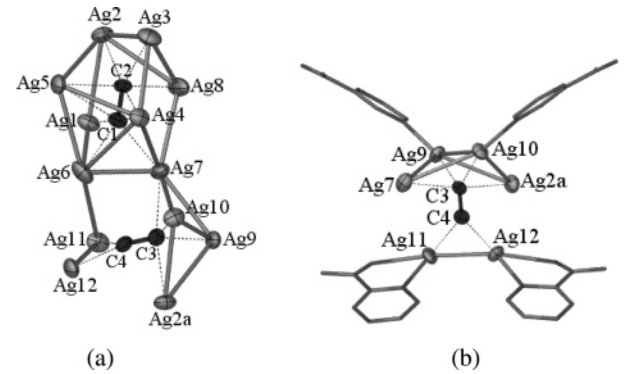

Figure 1. (a) Basic building unit in $Ag_{12}(C_2)_2(CF_3CO_2)_8(2\text{-pyzCONH}_2)_3$ (**1**). Atoms are drawn as 50% thermal ellipsoids. Selected bond lengths (Å): C(1)−C(2) = 1.21(1), C(3)−C(4) = 1.19(1), Ag(1)−C(1) = 2.38(1), Ag(4)−C(1) = 2.37(1), Ag(5)−C(1) = 2.57(1), Ag(6)−C(1) = 2.19(1), Ag(7)−C(1) = 2.33(1), Ag(2)−C(2) = 2.369(9), Ag(3)−C(2) = 2.14(1), Ag(4)−C(2) = 2.58(1), Ag(5)−C(2) = 2.42(1), Ag(8)−C(2) = 2.30(1), Ag(2a)−C(3) = 2.46(1), Ag(7)−C(3) = 2.48(1), Ag(9)−C(3) = 2.148(9), Ag(10)−C(3) = 2.166(9), Ag(11)−C(4) = 2.150(9), Ag(12)−C(4) = 2.137(9). (b) Open fishlike $Ag_6(\mu_6\text{-}C_2)$ motif coordinated by four pyrazine-2-carboxamide ligands. Symmetry code: (a) $-x + 1$, $-y$, $z - {}^1/_2$.

In the $Ag_6(\mu_6\text{-}C_2)$ motif, the atom C3 is embraced by four silver atoms in a butterfly arrangement and C4 bonds to two silver atoms; this kind of assembly can be best described as fishlike. These two sp-hybridized carbon atoms (C3−C4 = 1.19(1) Å) are σ-bonded to the silver atoms in the range 2.137(9)−2.48(1) Å. The distance C4−Ag6 = 2.870 Å is too long for significant Ag−C interaction. Normally the C_2^{2-} species prefers to be enclosed in a cage comprising six or more silver atoms, and therefore the fishlike motif, being a remnant of a broken $C_2@Ag_n$ cage, is both unexpected and novel. Its existence can be rationalized by the fact that it is stabilized by four surrounding pyrazine-2-carboxamide ligands (Ag11−N1 = 2.309(7) Å, Ag11−O17 = 2.468(7) Å, Ag12−N4 = 2.219(7) Å, Ag12−O18 = 2.574(7) Å, Ag9−N2 = 2.245(7) Å, Ag10−N5 = 2.250(7) Å), so that steric overcrowding obstructs the aggregation of silver(I) into a closed cage (Figure 1b).

Cage **A** and the $Ag_6(\mu_6\text{-}C_2)$ motif are fused together to form a $Ag_{13}(C_2)_2$ aggregate via sharing of atom type Ag7 plus a connection of the type Ag6−Ag11. An infinite column running along the *c* direction is constructed by vertex sharing at Ag2. Such a column is further stabilized by the carboxylate groups of trifluoroacetate ligands functioning in both monodentate and bidentate μ-O,O′ coordination modes (see Figure 3 in the Supporting Information for details). A three-dimensional framework is generated via cross-linkage by pyrazine nitrogens between the silver columns, forming channels along the *c* direction, which are filled by the trifluoroacetate groups (see Figure 4 in the Supporting Information).

In the synthesis of the triple salt **2**,[9] a major portion of pyrazine-2-carboxamide underwent hydrolysis to pyrazine-2-carboxylate, resulting in the first example of their coexistence as mixed ligands in a metal complex.

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(7) Crystal data for **1**: crystal dimensions 0.77 × 0.23 × 0.16 mm, orthorhombic, space group $Pna2_1$ (No. 33), a = 16.256(1) Å, b = 18.026(1) Å, c = 19.609(1) Å, V = 5746.2(6) Å^3, Z = 4, λ = 0.710 73 Å, ρ_{calcd} = 3.024 g cm^{-3}, μ(Mo Kα) = 4.146 mm^{-1}, R1 = 0.0471, wR2 = 0.1248 for 10 558 observed reflections ($I > 2\sigma(I)$). Crystal data for **2**: crystal dimensions 0.42 × 0.22 × 0.22 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 15.452(1) Å, b = 51.319(4) Å, c = 11.3424(8) Å, β = 96.009(2)°, V = 8945(1) Å^3, Z = 4, λ = 0.710 73 Å, ρ_{calcd} = 3.123 g cm^{-3}, μ(Mo Kα) = 4.428 mm^{-1}, R1 = 0.0667, wR2 = 0.1801 for 10 616 observed reflection ($I > 2\sigma(I)$). Data collection was performed at 293 K with Mo Kα radiation on a Bruker SMART 1000 CCD diffractometer using frames of oscillation range 0.3°, with $1 < \theta < 28°$. Data collection and reduction were performed using the SMART and SAINT software. An empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program.

(8) Ag_2C_2 was prepared as described previously. *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 **1**: Ag_2C_2 was added to 1 mL of a concentrated aqueous solution of CF_3CO_2Ag (0.44 g, 2 mmol) and $AgBF_4$ (0.39 g, 2 mmol) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, and pyrazine-2-carboxamide (61 mg, 0.5 mmol) was added to the filtrate, affording a yellow precipitate which was subjected to hydrothermal conditions at 110 °C for 24 h. Colorless blocklike crystals of **1** were obtained in ~30% yield. Anal. Calcd for $C_{35}H_{15}Ag_{12}F_{24}N_9O_{19}$ **1** (M_r = 2616.00): C, 16.07; H, 0.58; N, 4.82. Found: C, 16.27; H, 0.53; N 4.49. Complex **1** melts at 185.1 °C.

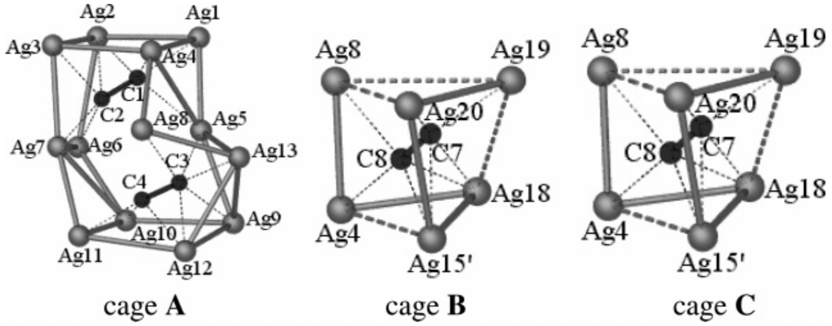

Figure 2. Three different kinds of silver polyhedra in the crystal structure of $Ag_{20}(C_2)_4(C_2F_5CO_2)_8(2\text{-pyzCOO})_4(2\text{-pyzCONH}_2)(H_2O)_2$ (**2**). Ag⋯Ag distances longer than 3.4 Å (twice the van der Waals radius of silver) are represented by thick broken lines. Symmetry code: (′) $x, y, z - 1$.

The basic building block in **2** is an aggregate composed of three polyhedral units: the unprecedented partially opened cage $(C_2)_2@Ag_{13}$ (cage **A**) and two similar distorted $C_2@Ag_6$ trigonal prisms (cages **B** and **C**), as shown in Figure 2.

A pair of C_2^{2-} dianions is completely encapsulated in cage **A**. For simplicity, this Ag_{13} single cage can be visualized as composed of two distorted cubes sharing a common face, with cleavage of four of the edges and capping of the lateral Ag5−Ag9−Ag12−Ag8 face by Ag13 lying 1.9 Å above it. The two embedded C_2^{2-} dianions retain their triple-bond character with similar C−C bond lengths of 1.18(2) Å and exhibit multiple σ and π interactions with the cage silver(I) atoms with Ag−C bond distances in the range 2.14(2)−2.55(2) Å. The Ag⋯Ag distances lie in the range 2.821(2)−3.237(2) Å. The interatomic distances of Ag6⋯Ag5 (4.181 Å), Ag5⋯Ag8 (3.820 Å), Ag7⋯Ag8 (3.692 Å), and Ag8⋯Ag12 (3.738 Å) are too long for significant argentophilic interaction (over twice the van der Waals radius of silver). Cage **A** thus provides the first example of two C_2^{2-} dianions trapped inside a single cage.

Cages **B** and **C** each take the shape of a distorted trigonal prism with one encapsulated C_2^{2-} dianion. The trapped C_2^{2-} species retains its triple-bond character (C5−C6 = 1.22(2) Å for cage **B** and C7−C8 = 1.20(2) Å for cage **C**) while having multiple interactions with its adjacent silver atoms (Ag−C = 2.13(2)−2.59(1) Å for cage **B** and 2.12(1)−2.71(2) Å for cage **C**).

The three kinds of silver polyhedra are connected to one another in the **ABCABC**... pattern, sharing edges of the types Ag6−Ag10 and Ag4−Ag8 and vertex of the type Ag15 to generate a column along the *c* direction (see Figure 5 in the Supporting Information for details), which is further stabilized by pentafluoropropionate ligands in both monodentate and bidentate μ-O,O′ coordination modes. The μ-O,O′ and μ_3-O,O,O′ modes of the pyrazine-2-carboxylate ligands further contribute to the consolidation of the column.

The pyrazine-2-carboxamide and four independent pyrazine-2-carboxylate ligands in the asymmetric unit generate eight linkages around each **ABC** aggregate via the pyrazine nitrogens. Such linkers connect the column to form a three-dimensional framework with channels running parallel to the *c* direction. The square cross-section of each channel has dimensions of about 13.6 × 13.6 Å, and the hydrophobic terminals of pentafluoropropionate groups fill the channels (see Figure 6 in the Supporting Information for details).

The basic building units in **1** and **2** differ strikingly from those in structures described in our previous reports, even that using pyrazine as a short exo-bidentate bridging ligand.[4] As the amino group of pyrazine-2-carboxamide does not participate in coordination, hydrogen bonding involving it also affects the self-assembly of $C_2@Ag_n$ motifs in both complexes. Compound **1** is stabilized by various N−H⋯O and N−H⋯F hydrogen bonds between the amino and trifluoroacetate groups. In **2**, hydrogen bonds are formed between the amino group and the aqua ligand.

Labile polyhedral $[Ag_n(C_2)]^{(n-2)+}$ aggregates are generated by dissolving Ag_2C_2 in a concentrated aqueous solution of one or more soluble silver salts. The self-assembly of such polynuclear species is a complex process, and the present study demonstrates, for the first time, that a suitably chosen ancillary ligand such as pyrazine-2-carboxamide, with its proximal ligation sites, short bridging span, and hydrogen-bonding capacity, can override Coulombic and argentophilic interactions to yield disrupted motifs. The rather open $Ag_6(\mu_6\text{-}C_2)$ motif found in compound **1** may be visualized as an intermediate moiety that is prevented by the surrounding pyrazine-2-carboxamide ligands from developing into a polyhedral $C_2@Ag_n$ aggregate during crystal growth.

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Supporting Information Available: X-ray crystallographic data as CIF files for the structure determination of **1** and **2**, and additional figures giving structural details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Complex **2** was synthesized in a manner similar to that for **1** except that $C_2F_5CO_2Ag$ was used as a substitute for CF_3CO_2Ag. Colorless blocklike crystals of **2** were deposited in ~25% yield. Anal. Calcd for $C_{57}H_{21}Ag_{20}F_{40}N_{11}O_{27}$ **2** (M_r = 4209.15): C, 16.27; H, 0.50; N, 3.66. Found: C, 16.29; H, 0.54; N 3.90. Complex **2** melts at 241.2 °C.