7608 *J. Am. Chem. Soc.* **2000,** *122,* 7608−7609

Novel Honeycomb-Like Layered Structure: The First Isomorphous Triple Salts of Silver Acetylide

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

Received April 13, 2000

In contrast to its isoelectronic analogues N_2, NO^+, CO, and CN^-, C_2^{2-} (common name acetylide dianion, IUPAC name acetylenediide) does not function as a terminal ligand but exhibits the most versatile coordination behavior through σ, π, and various combinations of σ and π bonding to multiple metal centers.[1−3] In compounds containing Ag_2C_2 as a component, argentophilic interactions[4] promotes the aggregation of silver(I) cations into a polyhedral cage that encloses the acetylide dianion, which in turn acts like a "glue" to stabilize the silver cage.

A series of double salts of the general formula $Ag_2C_2 \cdot mAgX$, where X = Cl, I, NO_3, H_2AsO_4, or $^1/_2EO_4$ (E = S, Se, Cr, W) and m is the molar ratio, has been known for half a century.[5] Recently we have prepared several silver double salts formulated as $Ag_2C_2 \cdot 8AgF$,[1a] $Ag_2C_2 \cdot 2AgClO_4 \cdot 2H_2O$[1b] and $Ag_2C_2 \cdot mAgNO_3$ (m = 1, 5, 5.5 and 6)[1c] by dissolving Ag_2C_2 in a concentrated aqueous solution of AgF, $AgClO_4$, and $AgNO_3$, respectively. Their structures exhibit a variety of novel silver cages each encapsulating a C_2^{2-} anion ($C_2@Ag_n$, n = 6, 7, 8, 9). However, there is as yet no information on any silver triple salt of stoichiometric formula $Ag_2C_2 \cdot mAgX \cdot nAgY$ in the literature, as they are less likely to form in comparison with double salts from the thermodynamic point of view. This study reports two unprecedented, nearly isomorphous triple salts of the formula $Ag_2C_2 \cdot AgF \cdot 4AgCF_3SO_3 \cdot RCN$ (R = CH_3 **1**, C_2H_5 **2**).

Compound **1** was obtained by dissolving silver acetylide in an aqueous solution of silver trifluoromethanesulfonate (triflate) and silver tetrafluoroborate in the presence of acetonitrile.[6] The original objective of addition of $AgBF_4$ was to increase the silver(I) concentration to promote the dissolving of Ag_2C_2. However, the experimental result indicates that $AgBF_4$ plays a key role in the formation of the triple salt by functioning as a suitable precursor of AgF. It has been demonstrated that, in some instances, hydrolysis of the BF_4^- ion into F^- and species such as $BF_3(OH)^-$ and $BF_2(OH)_2^-$ can occur in the reactions of transition metal (also including silver) tetrafluoroborates.[7] The gradual release of F^- from BF_4^- favors the crystallization of the triple salt, as using AgF directly in the preparation invariably leads to the formation of the relatively stable complex $Ag_2C_2 \cdot 8AgF$. In addition, **2** was prepared in a similar manner by employing C_2H_5CN instead of CH_3CN.[8]

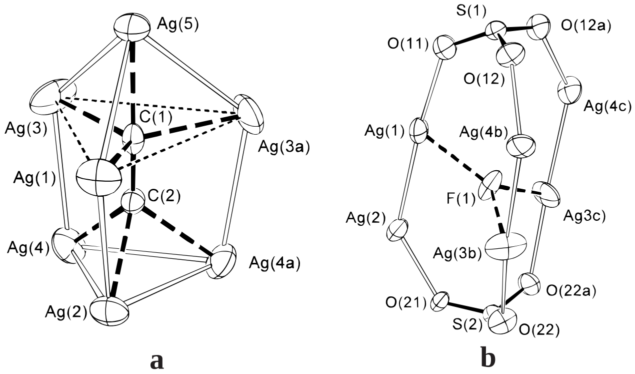

Figure 1. (a) Cage A: monocapped trigonal prism $C_2@Ag_7$ at a site of symmetry m (atoms are drawn as 50% thermal ellipsoids). Symmetry code: (a) x, $^1/_2 - y$, z. Selected bond distances (Å): C(1)−C(2) 1.21(1), Ag(1)−C(1) 2.319(9), Ag(3)−C(1) 2.242(5), Ag(5)−C(1) 2.14(1), Ag(2)−C(2) 2.21(1), Ag(4)−C(2) 2.208(7), Ag(1)···Ag(2) 2.886(1), Ag(1)···Ag(5) 3.003(1), Ag(2)···Ag(4) 2.910(1), Ag(3)···Ag(4) 2.878(1), Ag(3)···Ag(5) 2.978(1), Ag(4)···Ag(4a) 2.970(1). (b) Cage B: trigonal lantern of site symmetry m generated from bridging of the Ag···Ag edges of three adjacent type A cages by a μ_3-fluoride and two μ_3-triflates (50% thermal ellipsoids). The CF_3 groups are omitted for clarity. Symmetry codes: (a) x, $^1/_2 - y$, z; (b) $^1/_2 - x$, $-y$, $^1/_2 + z$; (c) $^1/_2 - x$, $^1/_2 + y$, $^1/_2 + z$. Selected bond distances (Å): Ag(1)−F(1) 2.289(6), Ag(1)−O(11) 2.388(8), Ag(2)−O(21) 2.212(6), Ag(3b)−F(1) 2.222(3), Ag(3b)−O(22) 2.442(5), Ag(4b)−O(12) 2.255(5).

The crystal structure of **1** is constructed from two kinds of silver cages: Ag_7 of type A (Figure 1a) and $Ag_6(\mu_3\text{-}F)(\mu_3\text{-}CF_3SO_3)_2$ of type B (Figure 1b). As illustrated in Figure 1a, the C_2^{2-} anion is completely encapsulated in a trigonal prism capped on the top triangular face, and the resulting type A cage is different from the $[C_2@Ag_7]$ moiety in $Ag_2C_2 \cdot 5AgNO_3$, where the seventh silver atom is 2-fold disordered and capping occurs on one rectangular face. The atoms Ag(1), Ag(2), Ag(5), C(1), and C(2) all lie in a mirror plane. Ag−C distances fall in the range 2.14−2.32(1) Å. The C(1)−C(2) bond length of 1.21(1) Å is in agreement with the C−C triple bond lengths found in acetylene (1.205 Å),[9] CaC_2 (1.191 Å),[10] and the ternary alkali metal silver acetylides $CsAgC_2$ and $KAgC_2$ [1.217(7) and 1.223(6) Å, respectively].[2] The Ag···Ag distances in cage A range from 2.878(1) to 3.003(1) Å, which are comparable to the interatomic contact of 2.89 Å in silver metal.[11]

There are two kinds of well-ordered triflate anions: S(1) (short designation for the triflate group containing the S(1) atom) and S(2) function as bridging ligands while S(3) and S(4) serve as

---

[1] (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.

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

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

[4] (a) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597. (b) Omary, M. A.; Webb, T. R.; Assefa, Z.; Shankle, G. E.; Patterson, H. H. *Inorg. Chem.* **1998**, *37*, 1380.

[5] Vestin, R.; Ralf, E. *Acta Chem. Scand.* **1949**, *3*, 101.

[6] Ag_2C_2 was prepared as described previously.[1] **CAUTION**: thoroughly dried Ag_2C_2 detonates easily upon mechanical shock, and only a small quantity should be used in any chemical reaction. Compound **1** was prepared by adding Ag_2C_2 to 1 mL of a concentrated aqueous solution of $AgCF_3SO_3$ 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 MeCN were added to the filtrate. (Note: excess MeCN 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 platelike crystals of **1** were obtained in ∼30% yield after several days. The product is light-sensitive and decomposes readily in common solvents such as water, ethanol, and acetonitrile. Crystal data for **1**: $C_8H_3Ag_7F_{13}NO_{12}S_4$, orthorhombic, space group *Pnma* (no. 62), $a = 27.847(4)$ Å, $b = 7.389(1)$ Å, $c = 12.864(2)$ Å, $V = 2646.8(7)$ Å^3, $Z = 4$, $D_c = 3.602$ g cm^{-3}, $T = 293$ K. Full-matrix least-squares refinement on F^2 (241 variables) converged to R1 = 0.0461, wR2 = 0.1071 for 2206 independent reflections with $I > 2\sigma(I)$.

[7] (a) Crabtree, R. H.; Hlatky, G. G.; Holt, E. M. *J. Am. Chem. Soc.* **1983**, *105*, 7302. (b) Hitchcock, P. B.; Lappert, M. F.; Tayler, R. G. *J. Chem. Soc. Chem. Commun.* **1984**, 1082. (c) Hoedt, R. W. M. Ten; Reekijk, J. *Inorg. Chim. Acta* **1981**, *51*, 23.

[8] Compound **2** was prepared in a manner similar to that for **1** using C_2H_5CN instead of CH_3CN. Colorless platelike crystals of **2** were obtained in ∼30% yield. Crystal data for **2**: $C_9H_5Ag_7F_{13}NO_{12}S_4$, orthorhombic, space group *Pnma*, $a = 28.662(8)$ Å, $b = 7.389(2)$ Å, $c = 12.885(3)$ Å, $V = 2729(1)$ Å^3, $Z = 4$, $D_c = 3.528$ g cm^{-3}, $T = 293$ K. Full-matrix least-squares refinement on F^2 (248 variables) converged to R1 = 0.0576, wR2 = 0.1278 for 1699 independent reflections with $I > 2\sigma(I)$.

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

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

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

10.1021/ja001286a CCC: $19.00 © 2000 American Chemical Society
Published on Web 07/22/2000

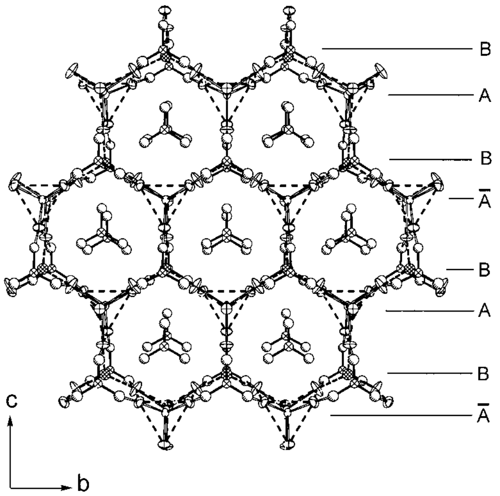

Figure 2. Honeycomb-like layer $\{[(C_2@Ag_7)(\mu_3\text{-}F)(\mu_3\text{-}CF_3SO_3)_2](CF_3SO_3)_2\}_\infty$ in the isomorphous complexes **1** and **2**. Silver atoms are drawn as 50% thermal ellipsoids and the remaining atoms are differentiated by size and shading. The Ag···Ag interactions are outlined by dotted lines. All CF_3 groups are omitted for clarity. Capital letter A stands for a top-capped $C_2@Ag_7$ cage, Ā indicates a bottom-capped $C_2@Ag_7$ cage, and B presents a trigonal lantern $[Ag_6(\mu_3\text{-}F)(\mu_3\text{-}CF_3SO_3)_2]$. A schematic illustration is shown in Figure 1S of the Supporting Information.

guest species that occupy the hexagonal cavities within the honeycomb-like host layer. Fluoride F(1) and triflates S(1) and S(2) all adopt the μ_3-bridging mode to form an interesting lantern-like cage B, with F(1) lying in the middle level and triflate S(1) and S(2) above and below the side edges of three neighboring type A trigonal prisms (Figure 1b). The type A and B cages thus share Ag···Ag edges to form a honeycomb-like layered structure normal to the *a* axis (Figure 2). The type A cages are arranged with their capping Ag atoms pointing alternately up and down in adjacent rows running parallel to the *b* axis. The oxygen atoms of triflates S(3) and S(4) are orientated in a head-to-head manner in the hexagonal void, and each O atom interacts with two neighboring silver atoms at Ag···O distances in the range 2.60−2.88 Å. The hexagonal cross-section of each void is nearly regular, as the three distances between pairs of parallel edges are 7.431, 7.431 and $b = 7.389$ Å (Figure 3). It is noted that honeycomb structures have been found in a silver-1,3,5-tricyanobenzene coordination networks,[12a] a layered niobium oxochloride cluster compound,[12b] and an Fe(III)−Ni(II) cyanide-bridged complex.[12c] An interesting related example is $C_{60}\cdot 5AgNO_3$ in which the fullerene is encapsulated in a zeolite-like 3D network constructed from the inorganic components.[13]

The identical honeycomb-like layers stack in the CDCD··· fashion with a layer-to-layer separation of $a/2 = 13.92$ Å. Successive layers C and D are related by an *a* glide plane with symmetry operation $({}^{1}/_{2} + x, y, {}^{1}/_{2} - z)$, such that the monocapped trigonal prisms A or Ā (A stands for a top-capped $C_2@Ag_7$ cage, and Ā indicates a bottom-capped $C_2@Ag_7$ cage) of layer C are stacked on top of those of layer D, while each lantern B of layer C lies directly above the triflate pair S(3) and S(4) that occupy a hexagonal cavity of layer D (Figure 3). Furthermore, this kind of staggered stacking results in close interlayer contacts between the F atoms of triflate ions S(1) and S(2): F(11)···F(11)′ $(-x, -y, 1 - z)$, 2.555; F(12)···F(22)′ $({}^{1}/_{2} + x, y, {}^{3}/_{2} - z)$, 2.662; F(21)···F(21)′ $(1 - x, -y, 1 - z)$, 2.712 Å. Notably, these intermolecular separations are significantly shorter than attractive nonbonded F···F interactions found in 6-perfluorohexylsulfonyl-2-naphthol[14] and a novel S_6-symmetric $(CF_3SO_3^-)_6$ cluster.[15]

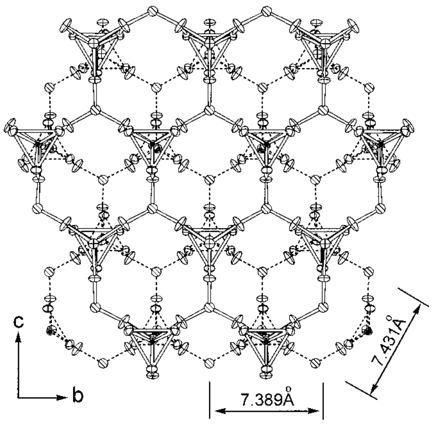

Figure 3. Staggered stacking of honeycomb layer C (open lines) over layer D (dotted lines) viewed along the *a* direction. All $CF_3SO_3^-$ anions are omitted for clarity.

The neutral ligand CH_3CN is terminally coordinated to the capping silver atom Ag(5) of the type A cage, and it can be readily substituted by C_2H_5CN to form the isomorphous complex **2** with its layer structure intact. It is noteworthy that the interlayer separation in **2** is $a/2 = 14.33$ Å, ~0.4 Å larger than that of **1**, which results in weakening of the F···F interactions with corresponding longer distances: F(11)···F(11)′ 2.742, F(12)···F(22)′ 2.964, F(21)···F(21)′ 2.908 Å.

Dissolving Ag_2C_2 in a concentrated aqueous solution of a soluble silver salt may lead to the formation of various $[Ag_n(C_2)]^{(n-2)+}$ species. The self-assembly of such polynuclear species to generate a network is a complex process, and specific $C_2@Ag_n$ cages may be trapped by crystallization in the presence of suitable ancillary anions and neutral ligands. Such a strategy is in a way an extension of Lehn's virtual combinatorial library (VCL) concept.[16] Further investigation of the controlling factors relevant to the self-assembly process in silver multiple salts is in progress in our laboratory.

Acknowledgment. This paper is dedicated to the memory of Professor George Alan Jeffrey (1915−2000). We thank the Hong Kong Research Grants Council Earmarked Grant (CUHK 4022/98P) for financial support.

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

JA001286A

---

(12) (a) Gardner, G. B.; Venkataraman, D.; Moore, J. S.; Lee, S. *Nature* **1995**, *374*, 792. (b) Anokhina, E. V.; Day, C. S.; Essig, M. W.; Lachgar, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1047. (c) Colacio, E.; Domínguez-Vera, J. M.; Ghazi, M.; Kivekäs, R.; Lloret, F.; Moreno, J. M.; Stoeckli-Evans, H. *Chem. Commun.* **1999**, 987.

(13) Olmstead, M. M.; Maitra, K.; Balch, A. L. *Angew. Chem., Int. Ed.* **2000**, *38*, 231.

(14) Kowalik, J.; Vanderveer, D.; Clower, C.; Tolbert, L. M. *Chem. Commun.* **1999**, 2007.

(15) Su, C.-Y.; Kang, B.-S.; Wang, Q.-G.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **2000**, 1831.

(16) Baxter, P. N. W.; Lehn, J.-M.; Rissanen, K. *Chem. Commun.* **1997**, 1323.