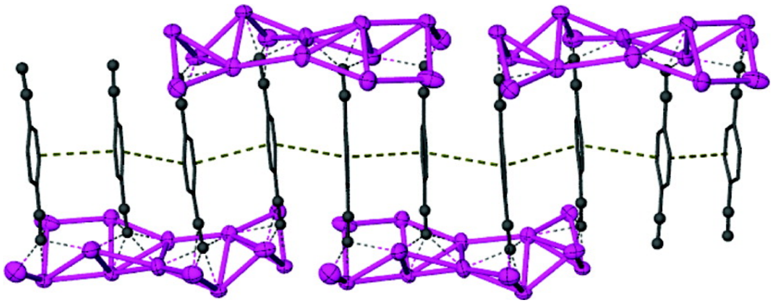
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Assembly of Polymeric Silver(I) Complexes of Isomeric Phenylenediethynides with the Supramolecular Synthons Ag□ CRC □Ag (R = *p*-, *m*-, *o*-CH; *n* = 4, 5)

Liang Zhao, and Thomas C. W. Mak

J. Am. Chem. Soc., **2005**, 127 (43), 14966-14967• DOI: 10.1021/ja054176i • Publication Date (Web): 05 October 2005



ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Published on Web 10/05/2005

Assembly of Polymeric Silver(I) Complexes of Isomeric Phenylenediethynides with the Supramolecular Synthons $Ag_n\subset C_2{-}R{-}C_2\supset Ag_n$ (R = *p*-, *m*-, *o*-C_6H_4; $n = 4, 5$)

Liang Zhao and Thomas C. W. Mak*

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

Received June 24, 2005; E-mail: tcwmak@cuhk.edu.hk

Recently, we reported the synthesis of silver(I) 1,3-butadiynediide, Ag_2C_4, and showed that in two structurally related double salts, $Ag_2C_4{\cdot}6AgNO_3{\cdot}nH_2O$ ($n = 2, 3$), the linear $^{-}C{\equiv}C{-}C{\equiv}C^{-}$ dianion exhibits an unprecedented μ_8-coordination mode, each terminal being capped by four silver(I) atoms.[1] This suggests that the $Ag_4\subset C_2{-}C_2\supset Ag_4$ moiety may be conceived as a synthon for the assembly of coordination networks,[2] by analogy to the plethora of well-known supramolecular synthons that involve hydrogen bonding and weaker intermolecular interactions.[3]

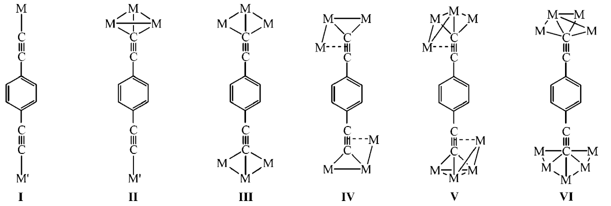
To establish the general utility of a new class of supramolecular synthons of the type $Ag_n\subset C_2{-}R{-}C_2\supset Ag_n$, we considered the simple case in which the bridging R group is a *p*-phenylene ring. With reference to 1,3-butadiynediide as a standard, the *p*-phenylenediethynide dianion has a lengthened linear π-conjugated backbone, and its aromatic ring is potentially capable of partaking in $\pi-\pi$ stacking[4] and silver−aromatic interaction.[5] The isomeric *m*- and *o*-phenylenediethynides were also investigated in order to probe the influence of varying the relative orientation of the pair of terminal ethynide groups.

Herein, we report the synthesis and structural characterization of three silver(I) double salts containing isomeric phenylenediethynide dianions,[6] namely, $2[Ag_2(p\text{-}C{\equiv}CC_6H_4C{\equiv}C)]{\cdot}11AgCF_3CO_2{\cdot}4CH_3CN{\cdot}2CH_3CH_2CN$ (**1**), $Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C){\cdot}6AgCF_3CO_2{\cdot}3CH_3CN{\cdot}2.5H_2O$ (**2**), and $3[Ag_2(o\text{-}C{\equiv}CC_6H_4C{\equiv}C)]{\cdot}14AgCF_3CO_2{\cdot}2CH_3CN{\cdot}9H_2O$ (**3**), in which the corresponding $Ag_n\subset C_2{-}C_6H_4{-}C_2\supset Ag_n$ ($n = 4, 5$) synthons engender a broken silver(I) double chain, a silver(I) double chain, and an unprecedented silver(I) layer, respectively.

Double salts **1**−**3** were obtained from the crystallization of the corresponding polymeric crude compounds $[Ag_2(p\text{-}C{\equiv}CC_6H_4C{\equiv}C)]_n$ (**4**), $[Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)]_n$ (**5**), and $[Ag_2(o\text{-}C{\equiv}CC_6H_4C{\equiv}C)]_n$ (**6**) in a concentrated aqueous solution of $AgCF_3CO_2$. Although complex **4** was synthesized nearly a quarter-century ago,[7] tedious experimental operations and the use of liquid ammonia were required. In the present study, we carried out the reaction of dilithium *p*-phenylenediethynide (generated in situ from 1,4-bis(trimethylsilylethynyl)benzene and *n*-BuLi) with $AgNO_3$ in a 1:2 molar ratio in THF under an inert atmosphere of nitrogen at room temperature to produce complex **4** (contaminated with a small amount of metallic silver). Repeating this synthetic procedure employing 1,3- and 1,2-bis(trimethylsilylethynyl)benzene yielded new complexes **5** and **6**. To improve the solubility of compounds **4**−**6**, a mixed solvent of water and acetonitrile or propionitrile was used.

In the crystal structure of **1**, the *p*-phenylenediethynide ligand exhibits the highest ligation number[8] reported to date for the ethynide moiety, in comparison with three or less in other *p*-phenylenediethynide transition metal complexes (Scheme 1, modes **I**−**IV**).[9,10] As shown in Figure 1a, two independent *p*-phenylenediethynide ligands coordinate to a Ag_{14} aggregate with different μ_4,μ_5-coordination modes, which are depicted as **V** and **VI** in Scheme 1. An unprecedented μ_5-η^1 mode for the ethynide moiety C19−C20 within a square-pyramidal Ag_5 basket is observed for the first time. The Ag_{14} aggregate, being constructed essentially from two independent $Ag_n\subset C_2{-}(p\text{-}C_6H_4){-}C_2\supset Ag_n$ ($n = 4, 5$) synthons through argentophilic interaction and continuous $\pi-\pi$ stacking, is connected to its symmetry equivalents generated from one of the sites located between phenylene rings (IA) and (I), and between (II) and (IIB), to form a broken silver(I) double chain along the *a*-axis, in which adjacent Ag_{14} segments are also bridged by oxygen atoms O15 and O21 of two trifluoroacetate groups (Figure 1b).

Scheme 1. Coordination Modes of the *p*-Phenylenediethynide Dianion in Transition Metal Complexes



In contrast to the only known μ_1,μ_1-coordination mode of *m*-phenylenediethynide in its transition metal complexes,[12] this ligand exhibits different terminal ethynide bonding modes, namely, μ_4-η^1,η^1,η^1,η^1 and μ_4-η^1,η^1,η^1,η^2, in the crystal structure of **2** (Figure S1 in Supporting Information). Through inversion centers located between successive pairs of *m*-phenylene rings, the $Ag_n\subset C_2{-}(m\text{-}C_6H_4){-}C_2\supset Ag_n$ ($n = 4$) synthon is extended along the [100] direction by Ag···Ag interactions to form a silver double chain (Figure 2a), which are further consolidated by $\pi-\pi$ interaction between *m*-phenylene rings protruding alternatively on either side (Figure 2b). Linkage of these silver double chains by (aceto-

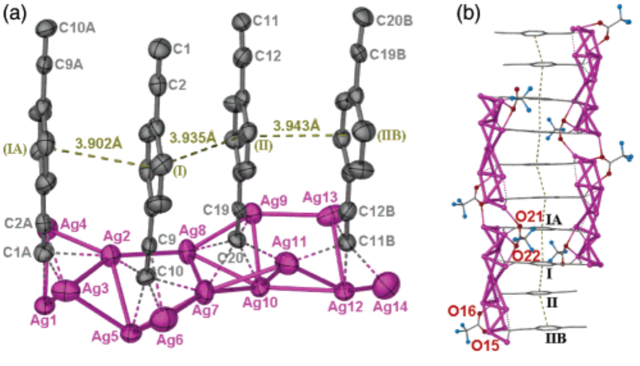


Figure 1. (a) Atom labeling (50% thermal ellipsoids) and coordination modes of the *p*-phenylenediethynide ligands in **1**. Other ligands are omitted for clarity. Symmetry code: A $-x$, $1-y$, $1-z$; B $1-x$, $1-y$, $1-z$. (b) Broken silver(I) double chain in **1** composed of discrete Ag_{14} segments connected by trifluoroacetate groups and stabilized by continuous $\pi-\pi$ stacking between parallel *p*-phenylene rings. Color scheme for atoms: Ag purple, C gray, O red, F cyan.

10.1021/ja054176i CCC: $30.25

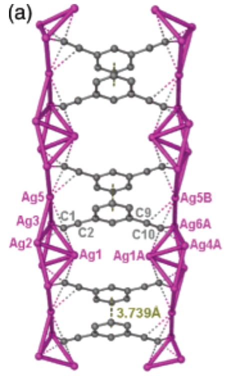


Figure 2. (a) Silver double chain in **2** assembled by argentophilic interaction and $\pi-\pi$ interaction between adjacent pairs of *m*-phenylene rings. Symmetry code: A $1-x, -y, 1-z$; B $-x, -y, 1-z$. (b) Side view of silver double chain, whose axis makes an angle of 71.8° with the line joining the centers of adjacent *m*-phenylene rings.

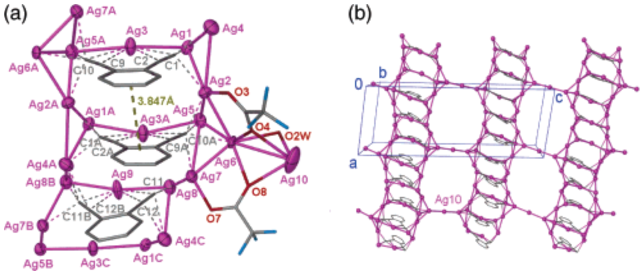


Figure 3. (a) Atom labeling (50% thermal ellipsoids) and coordination modes of two independent *o*-phenylenediethynide ligands in **3**. Symmetry code: A $1-x, y, 1/2-z$; B $-x, y, 1/2-z$; C $x-1, y, z$. (b) Argentophilic layer composed of silver columns cross-bridged by Ag10.

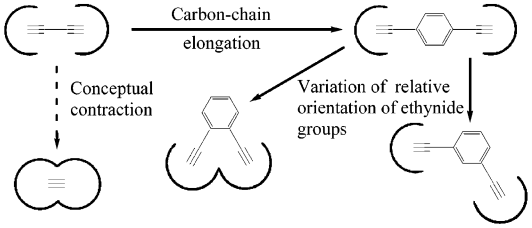
nitrile)C−H···F(trifluoroacetate) hydrogen bonds generates a two-dimensional network (Figure S2).

In the crystal structure of **3**, the ethynide moieties bond to silver atoms via three different coordination modes, μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$, μ_4-$\eta^1,\eta^1,\eta^2,\eta^2$, and μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2$ (Figure 3a), in contrast to the simple μ_1,μ_1 mode existing in known *o*-phenylenediethynide transition metal complexes.[13] The two independent $Ag_n\subset C_2-(o\text{-}C_6H_4)-C_2\supset Ag_n$ ($n = 4, 5$) synthons mutually associate to generate an undulating silver column consolidated by argentophilic interaction and $\pi-\pi$ stacking.

Bridged by silver atom Ag10 through Ag···Ag interaction and three oxygen atoms (O2W, O4, O8), the silver columns are linked to form a wavelike layer with *o*-phenylene groups protruding on both sides (Figure 3b). Although silver(I) layers linked by ancillary organic connectors are very abundant,[14,15] to our knowledge there is only one precedent of a silver(I) layer held together by Ag···Ag interaction.[16] Utilizing the remaining Ag11 atom and three trifluoroacetate groups as linkage components, adjacent undulating silver layers are stacked along [010] to generate a three-dimensional network (Figures S3 and S4). The formation of the silver layer and the network structure is consistent with the unusually high melting point of 220 °C for complex **3**.

The decreasing separation of the pair of ethynide groups in **1**−**3** is accompanied by strengthened argentophilic interaction at the expense of weakened $\pi-\pi$ stacking, yielding a broken double chain, a double chain, and a layer, respectively. When the pair of ethynide vectors make an angle of 60°, sharing of a common silver atom for the Ag_n caps occurs in **3**. The structural correlation between various silver−ethynide supramolecular synthons affords a rationale for the preponderant existence of $C_2@Ag_n$ ($n \leq 10$) polyhedra in Ag_2C_2 complexes.[15] If the linear $^-C{\equiv}C{-}C{\equiv}C^-$ chain were

Scheme 2. Schematic Diagram Showing the Structural Relationship between the Supramolecular Synthons $Ag_4\subset C_2{-}C_2\supset Ag_4$, $Ag_n\subset C_2{-}R{-}C_2\supset Ag_n$ (R = *p*-, *m*-, *o*-C_6H_4; $n = 4, 5$) and $C_2@Ag_n$ ($n = 6{-}10$). The Circular Arc Represents a Ag_n ($n = 4, 5$) Basket



contracted to a C_2^{2-} dumbbell, further overlap between atoms of the terminal Ag_n caps would yield a closed cage with 6−10 vertices (Scheme 2).

Acknowledgment. Financial support by the Hong Kong Research Grants Council (Ref. No. CUHK 401704) is gratefully acknowledged. This work is dedicated to the memory of J. Monteath Robertson (1900−1989).

Supporting Information Available: Experimental details and X-ray crystallographic data for **1**, **2**, and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Zhao, L.; Mak, T. C. W. *J. Am. Chem. Soc.* **2004**, *126*, 6852.
(2) Zhang, H.-X.; Kang, B.-S.; Xu, A.-W.; Liu, H.-Q.; Chen, Z.-N. *Comments Inorg. Chem.* **2002**, *23*, 231.
(3) (a) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311. (b) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375. (c) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565.
(4) (a) Roesky, H. W.; Andruh, M. *Coord. Chem. Rev.* **2003**, *236*, 91. (b) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885. (c) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, U.K., 2000.
(5) (a) Kim, S.; Kim, J. S.; Kim, S. K.; Suh, I.-H.; Kang, S. O.; Ko, J. *Inorg. Chem.* **2005**, *44*, 1846. (b) Chen, C.-L.; Su, C.-Y.; Cai, Y.-P.; Zhang, H.-X.; Xu, A.-W.; Kang, B.-S.; Zur Loye, H.-C. *Inorg. Chem.* **2003**, *42*, 3738. (c) Wang, Q.-M.; Mak, T. C. W. *Chem. Commun.* **2002**, 2682 and references therein.
(6) Synthesis and X-ray analysis of **1**, **2**, and **3** are in the Supporting Information.
(7) Royer, E. C.; Barral, M. C.; Moreno, V.; Santos, A. *J. Inorg. Nucl. Chem.* **1981**, *43*, 705.
(8) Guo, G.-C.; Mak, T. C. W. *Chem. Commun.* **1999**, 813.
(9) Mode I: (a) Chin, C. S.; Kim, M.; Lee, H.; Noh, S.; Ok, K. M. *Organometallics* **2002**, *21*, 4785. [M = Ir]: (b) Chao, H.-Y.; Lu, W.; Li, Y.; Chan, M. C.-W.; Che, C.-M.; Cheung, K.-K.; Zhu, N. *J. Am. Chem. Soc.* **2002**, *124*, 14696. [M = Au]: (c) Behrens, U.; Hoffmann, K.; Kopf, J.; Moritz, J. *J. Organomet. Chem.* **1976**, *117*, 91. [M = Pt]: (d) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *Chem. Commun.* **1991**, 188. [M = Rh]: (e) Wong, K. M.-C.; Lam, S. C.-F.; Ko, C.-C.; Zhu, N.; Yam, V. W.-W.; Roue, S.; Lapinte, C.; Fathallah, S.; Costuas, K. Kahlal, S.; Halet, J.-F. *Inorg. Chem.* **2003**, *42*, 7086. [Heterometallic, M = Re, M′ = Fe].
(10) Modes II, III, and IV: (a) Yam, V. W.-W.; Fung, W. K.-M.; Wong, K. M.-C.; Lau, V. C.-Y.; Cheung, K.-K. *Chem. Commun.* **1998**, 777. [Mode II, M = Cu, M′ = Re]: (b) Yam, V. W.-W.; Fung, W. K.-M.; Cheung, K.-K. *Chem. Commun.* **1997**, 963. [Mode III and IV, M = Cu or Ag].
(11) (a) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597. (b) Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098. See also other references cited in 15a.
(12) (a) Weyland, T.; Costuas, K.; Toupet, L.; Halet, J.-F.; Lapinte, C. *Organometallics* **2000**, *19*, 4228. [M = Fe]: (b) Vicente, J.; Chicote, M.-T.; Abrisqueta, M. D.; Alvarez-Falcón, M. M.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2003**, *22*, 4327 [M = Au].
(13) (a) Onitsuka, K.; Yamamoto, S.; Takahashi, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 174. (b) Tykwinski, R. R.; Stang, P. J. *Organometallics* **1994**, *13*, 3203. (c) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411.
(14) (a) Liu, C.-W.; Liaw, B.-J.; Liou, L.-S.; Wang, J.-C. *Chem. Commun.* **2005**, 1983. (b) Liu, S.-Q.; Konaka, H.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ning, G.-L.; Munakata, M. *Inorg. Chim. Acta* **2005**, *358*, 919. (c) Leznoff, D. B.; Xue, B.-Y.; Batchelor, R. J.; Einstein, F. W. B.; Patrick, B. O. *Inorg. Chem.* **2001**, *40*, 6026.
(15) (a) Zhao, X.-L.; Wang, Q.-M.; Mak, T. C. W. *Chem.*−*Eur. J.* **2005**, *11*, 2094. (b) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 179 and references therein.
(16) Guo, G.-C.; Wang, Q.-G.; Zhou, G.-D.; Mak, T. C. W. *Chem. Commun.* **1998**, 339.

JA054176I