CRYSTAL GROWTH & DESIGN
Article
pubs.acs.org/crystal

Argentophilic Infinite Chain, Column, and Layer Structures Assembled with the Multinuclear Silver(I)−Phenylethynide Supramolecular Synthon

Published as part of the Crystal Growth & Design virtual special issue In Honor of Prof. G. R. Desiraju

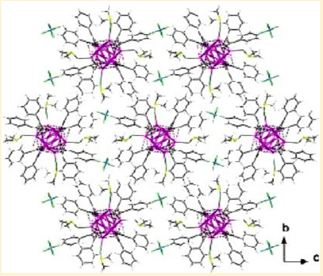
Ping-Shing Cheng,[†] Samipillai Marivel,[†] Shuang-Quan Zang,[‡] Guang-Gang Gao,[§] and Thomas C. W. Mak*[,†]

[†]Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, People's Republic of China

[‡]Department of Chemistry, Zhengzhou University, Zhengzhou, 450001, People's Republic of China

[§]Heilongjiang Engineering Technical Centre of Irradiation Cross-linking Materials, 3 World Road, Jiamusi, 154004, People's Republic of China

Supporting Information



ABSTRACT: Nine silver(I) complexes bearing the phenylethynide ligand and different ancillary anions, namely, double salts $AgC\equiv CPh\cdot AgNO_3$ (**1**), $2AgC\equiv CPh\cdot AgNO_3$ (**2**), $[Ag_5(C\equiv CPh)_4(DMSO)_2]X$ [X = BF_4 (**3A**), ClO_4 (**3B**), PF_6 (**3C**), AsF_6 (**3D**), SbF_6 (**3E**)], $2AgC\equiv CPh\cdot 5AgO_2CCF_3\cdot 4DMSO$ (**4**), and a triple salt $10AgC\equiv CPh\cdot 2AgOTf\cdot AgNO_3\cdot 3DMSO$ (**5**), have been synthesized and shown to possess coordination frameworks that are assembled with the supramolecular synthon $Ph-C\equiv C\supset Ag_n$ (n = 3, 4, 5). Different argentophilic layers are found in nitrate complexes **1** and **2**, which are crystallized from water and mixed water/DMSO, respectively. Difficulty was encountered in growing quality crystals of complexes **3A**−**3E**, **4**, and **5** bearing weakly coordinating anions, but DMSO proved to be a good solvent for crystallization by functioning as a coligand. The isostructural compounds **3A**−**3E** exhibit the same type of pseudohexagonal packing of infinite silver columns, with the ancillary anionic component filling the intervening space and linking adjacent columns via weak hydrogen bonds. Three-dimensional supramolecular frameworks based on similar packing of silver chains and columns, respectively, are found in double salt **4** and triple salt **5**.

INTRODUCTION

The study of metal−ethynide complexes has drawn considerable interest due to their structural diversity[1] and potential application as photoluminescent materials,[2] precursors of nonlinear optical materials,[3] and rigid-rod molecular wires.[4] Diverse coordination modes of the ethynide moiety to the coinage metal center (Cu, Ag, and Au) facilitate the onset of metallophilic interactions,[5] usually leading to the formation of clusters, multinuclear aggregates, or extended solid-state architectures.[6]

Over a dozen years ago, we initiated a systematic investigation on the synthesis and structural characterization of crystalline silver(I) complexes containing various ethynide-containing ligands, including the all-carbon dianions C_2^{2-} and C_4^{2-} and carbon-rich monoanions of the type $R-C_2^-$ (R = alkyl, aryl, heteroaryl).[7] In such complexes, the terminal carbon atom of the ethynide ligand that carries a formal negative charge is invariably surrounded by three to six Ag(I) atoms. The corresponding polynuclear cationic silver(I)-ethynediide, -1,3-butadiene-1,4-diide, and -ethynide aggregates may be designated as $C_2@Ag_n$ (n = 6−8), $Ag_4\subset C\equiv C-C\equiv C\supset Ag_4$, and $R-C\equiv C\supset Ag_n$ (n = 3−6), respectively, with the overall charges omitted for simplicity. In view of their frequent occurrence and robustness, such structural patterns can be regarded, in accordance with Desiraju's seminal definition of *supramolecular synthon* in the context of crystal engineering,[8] as novel multinuclear metal−ligand supramolecular synthons[9] for the designed construction of a wide variety of organosilver(I) compounds composed of discrete molecules, including large-nuclearity clusters,[10] as well as one- to three-dimensional networks.[11]

In contrast to the chemical behavior of Ag_2C_2[12] and Ag_2C_4,[13] silver(I) aryl ethynide is sparingly soluble in a concentrated aqueous solution of a soluble silver(I) salt, so that its double and multiple silver(I) salts cannot be readily obtained in crystalline form. Hitherto most of the reported silver(I) aryl ethynide complexes have been synthesized with the incorporation of phosphine[14] or carboxylate-supporting ligands,[15] except for four aryl or heteroaryl ethynide complexes with silver(I) nitrate[16] and one with silver(I) triflate.[17] Notably, both

Received: May 20, 2012
Revised: July 16, 2012
Published: July 19, 2012

© 2012 American Chemical Society

dx.doi.org/10.1021/cg300691n | *Cryst. Growth Des.* 2012, 12, 4519−4529

Table 1. Crystallographic Data for Compounds 1−5

compound	**1**	**2**	**3A**	**3B**	**3C**	**3D**	**3E**	**4**	**5**
empirical formula	$C_8H_5Ag_2NO_3$	$C_{16}H_{10}Ag_3NO_3$	$C_{36}H_{20}Ag_5BF_4O_2S_2$	$C_{36}H_{20}Ag_5ClO_6S_2$	$C_{36}H_{20}Ag_5F_6O_2PS_2$	$C_{36}H_{20}Ag_5AsF_6O_2S_2$	$C_{36}H_{15}Ag_5F_6O_2SbS_2$	$C_{68}H_{68}Ag_{14}F_{30}O_{28}S_8$	$C_{86}H_{50}Ag_{13}F_6NO_{11}S_4$
formula weight	378.87	587.86	1174.80	1187.44	1232.96	1276.91	1318.70	1834.94	2917.82
crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$Pca2_1$ (No. 29)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a [Å]	21.936(1)	16.918(1)	8.580(1)	8.545(1)	8.505(1)	8.462(1)	8.413(1)	14.146(1)	35.168(7)
b [Å]	16.025(1)	6.513(1)	14.894(1)	26.880(1)	27.457(2)	27.714(4)	16.722(1)	16.183(1)	14.390(3)
c [Å]	7.604(1)	13.605(1)	16.645(1)	17.597(1)	17.857(1)	17.932(2)	16.746(1)	23.228(2)	19.492(4)
α [°]	90	90	67.43(1)	90	90	90	114.11(1)	90.74(2)	90
β [°]	90	92.96(1)	85.22(1)	103.51(1)	103.080(1)	102.69(3)	99.08(1)	95.36(2)	109.19(4)
γ [°]	90	90	82.42(1)	90	90	90	94.42(1)	105.89(2)	90
V [Å^3]	2672.9(2)	1497.1(1)	1945.8(2)	3930.0(3)	4061.9(5)	4102.4(10)	2096.9(2)	5087.9(8)	9316(3)
Z	12	4	2	4	4	4	2	4	4
D_{calc} (g/cm^3)	2.824	2.608	2.005	2.007	2.016	2.067	2.088	2.395	2.080
μ(Mo−Kα) (mm^{-1})	4.369	3.897	2.628	2.663	2.568	3.304	3.079	2.916	2.822
F(000)	2136	1112	1120	2272	2352	2424	1238	3512	5560
reflections collected	42026	32799	48456	112525	136681	24429	43059	154060	117068
independent reflections	5664	3601	7655	9431	7574	5721	8059	18340	11480
observed reflections [$I > 2\sigma(I)$]	4827	3343	6480	6768	6340	3378	6258	16293	8232
parameters	416	209	443	463	472	462	420	1354	599
goodness-of-fit	0.933	1.038	1.426	1.068	1.065	1.031	1.224	1.140	5.973
R_1 [$I > 2\sigma(I)$]	0.0272	0.0225	0.0421	0.0387	0.0423	0.0521	0.0763	0.0504	0.0340
wR_2 (all data)	0.0603	0.0625	0.1200	0.0974	0.1108	0.1132	0.1614	0.1319	0.1078

nitrate and triflate belong to the class of strongly coordinating ligands for the synthesis of metal complexes.

In the present study, we have developed a modified crystallization method to obtain new complexes of silver(I) phenylethynide in combination with various ancillary silver(I) salts in order to address two issues: (a) the influence of various weakly coordinating inorganic anions on supramolecular assembly with the multinuclear synthon $\mathrm{Ph{-}C{\equiv}C{\supset}Ag}_n$ (n = 4, 5); and (b) the factors that favor the generation of argentophilic silver(I) columns and layers. Herein we report the synthesis and structural characterization of a series of nine silver(I) phenylethynide complexes, namely, double salts $\mathrm{AgC{\equiv}CPh{\cdot}AgNO_3}$ (**1**), $\mathrm{2AgC{\equiv}CPh{\cdot}AgNO_3}$ (**2**), $\mathrm{[Ag_5(C{\equiv}CPh)_4(DMSO)_2]X}$ [X = BF_4 (**3A**), ClO_4 (**3B**), PF_6 (**3C**), AsF_6 (**3D**), SbF_6 (**3E**)], $\mathrm{2AgC{\equiv}CPh{\cdot}5AgO_2CCF_3{\cdot}4DMSO}$ (**4**), and the triple salt $\mathrm{10AgC{\equiv}CPh{\cdot}2AgOTf{\cdot}AgNO_3{\cdot}3DMSO}$ (**5**), in which the anionic component plays a vital role in dictating the assembly of argentophilic and coordination networks.

■ EXPERIMENTAL SECTION

General Comments. In general, crystalline silver double and multiple salts containing phenylethynide as a component can be obtained from slow evaporation of crude polymeric silver(I) phenylethynide $\mathrm{[AgC{\equiv}CAr]}_n$ in a concentrated aqueous or water/acetonitrile solution of $AgNO_3/AgBF_4/AgCF_3CO_2$. However, silver(I) phenylethynide is sparingly soluble in a concentrated aqueous solution of AgWCA, where WCA represents a weakly coordinating inorganic anion. Therefore we used DMSO to replace water or water/acetonitrile as a reaction medium in combining polymeric silver(I) phenylethynide with various water-soluble silver salts ($AgNO_3$, $AgBF_4$, $AgClO_4$, $AgPF_6$, $AgAsF_6$, $AgSbF_6$, AgO_2CCF_3, and AgOTf) to yield new double and triple salts. After filtration, the filtrate was transferred to a test tube, and water was layered over it for crystallization via slow liquid diffusion.

Reagents. All chemicals and solvents were commercially available and used without further purification. Polymeric $[AgC{\equiv}CPh]_n$ was prepared according to the literature method.[18,19]

Caution! *Silver-ethynide complexes are potentially explosive in the dry state when subjected to heating or mechanical shock and should be used in small quantities with extreme care.*

Syntheses and Characterization. *[AgC≡CPh·AgNO₃] (**1**).* $AgNO_3$ (0.510 g, 3 mmol) was dissolved in deionized water (1 mL), and $[AgC{\equiv}CPh]_n$ (≈ 30 mg) solid was added to the solution. After stirring for about half an hour, the solution was filtered. After a few days, colorless plate-like crystals were collected in ca. 40% yield. Compound **1** melts at 178.1−179.9 °C. Elemental analysis for $C_8H_5O_3NAg_2$, found (calcd): C, 25.69 (25.36); H, 1.71 (1.33); N, 3.38 (3.70). IR spectrum: 2012 cm^{-1} (w, ν C≡C).

*[2AgC≡CPh·AgNO₃] (**2**).* $[AgC{\equiv}CPh]_n$ (≈ 100 mg) was added to 1 mL of a concentrated DMSO of $AgNO_3$ (0.510 g, 3 mmol) in a beaker. After stirring for about half an hour, the solution was filtered and transferred to a test tube. Next, water was layered over the solution, and the test tube was left undisturbed in the ambient environment. After several days, colorless plate-like crystals were obtained in ca. 80% yield. Compound **2** decomposes above 170 °C. Elemental analysis for $C_{16}H_{10}O_3NAg_3$, found (calcd): C, 32.79 (32.69); H, 1.73 (1.71); N, 2.34 (2.38). IR spectrum: 2012 cm^{-1} (w, ν C≡C).

*[Ag₅(PhC≡C)₄(DMSO)₂]X [X = BF₄ (**3A**), ClO₄ (**3B**), PF₆ (**3C**), AsF₆ (**3D**), SbF₆ (**3E**)].* AgX (1 mmol) was dissolved in DMSO (1 mL), and $[AgC{\equiv}CPh]_n$ (≈ 0.1 g) was then added to the solution. After stirring for 1 h, the solution became clear and was transferred to a test tube. Water was layered over the solution. After one week, yellow needle-shaped crystals were obtained in ca. 75% yield. All compounds decompose above 120 °C. **3A**, $C_{36}H_{32}BF_4O_2S_2Ag_5$, elemental analysis found (calcd): C, 36.69 (36.43), H, 2.78 (2.72). IR spectrum: 2006 cm^{-1} (w, ν C≡C); **3B**, $C_{36}H_{32}ClO_6S_2Ag_5$, found (calcd): C, 36.49 (36.05), H, 2.71 (2.69). IR spectrum: 2011 cm^{-1} (w, ν C≡C); **3C**, $C_{36}H_{32}PF_6O_2S_2Ag_5$, found (calcd): C, 34.79 (34.73), H, 2.56 (2.59). IR spectrum: 2018 cm^{-1} (w, ν C≡C); **3D**, $C_{36}H_{32}AsF_6O_2S_2Ag_5$, found (calcd): C, 33.69 (33.54), H, 2.71 (2.50). IR spectrum: 2009 cm^{-1} (w, ν C≡C); **3E**, $C_{36}H_{32}SbF_6O_2S_2Ag_5$, found (calcd): C, 32.54 (32.37), H, 2.30 (2.41). IR spectrum: 2009 cm^{-1} (w, ν C≡C).

*[2AgC≡CPh·5AgCF₃CO₂·4DMSO] (**4**).* $AgCF_3CO_2$ (0.440 g, 2 mmol) was dissolved in 1 mL of DMSO. $[AgC{\equiv}CPh]_n$ (≈ 50 mg) was added to the solution. After stirring for about half an hour, the solution was filtered and transferred to a test tube. And then, water was layered over the solution and the test tube was stored in a refrigerator at 4 °C. After several days, pale yellow needle-shaped crystals of **4** were obtained in ca. 25% yield. Compound **4** melts from 136.0 to 137.7 °C. Elemental analysis for $C_{34}H_{34}O_{14}F_{15}S_4Ag_7$, found (calcd): C, 22.51 (22.26); H, 1.79 (1.87). IR spectrum: 2014 cm^{-1} (vw, ν C≡C).

*[10AgC≡CPh·2AgOTf·AgNO₃·3DMSO] (**5**).* $AgNO_3$ (0.085 g, 0.5 mmol) and AgOTf (0.514 g, 2 mmol) were dissolved in DMSO (1 mL) in a beaker. $[AgC{\equiv}CPh]_n$ (≈ 100 mg) was then added to the solution. After stirring for about half an hour, the solution was filtered and transferred to a test tube. Next, water was layered over the solution, and the test tube was stored in a refrigerator at 4 °C. After several days, pale yellow needle-like crystals of **5** were obtained in ca. 20% yield. Compound **5** decomposes above 120 °C. Elemental analysis for $C_{88}H_{68}F_6O_{12}NS_5Ag_{13}$, found (calcd): C, 34.89 (35.14); H, 2.34 (2.28); N, 0.58 (0.47). IR spectrum: 2008 cm^{-1} (w, ν C≡C).

X-ray Crystallographic Analysis. Selected crystals were used for data collection on a Bruker SMART APEX−II CCD diffractometer at 293 K (for **1**, **2**, **3A**−**3E**, and **5**) and 150 K (for **4**) using frames of oscillation range 0.5°, with $2° < \theta < 28°$. An empirical absorption correction was applied using the SADABS program.[20] The structures were solved by the direct method and refined by full matrix least-squares on F^2 using the SHELXTL program package.[21] The crystal data and parameters for X-ray structure analysis are summarized in Table 1.

RESULTS AND DISCUSSION

Description of Crystal Structures. *AgC≡CPh·AgNO₃ (**1**).* In the crystal structure of **1**, there are three independent phenylethynide anions each attached to a butterfly-shaped Ag_4 basket in different coordination modes. The ethynide moieties C1≡C2 and C17≡C18 act in the μ_4-$\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode, and the other ethynide group C9≡C10 adopts the μ_4-$\eta^1,\eta^2,\eta^2,\eta^2$ mode (Figure 1).

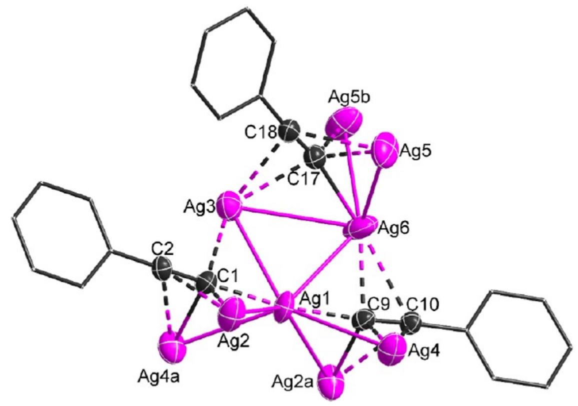


Figure 1. Atom labeling and coordination modes of independent phenylethynide ligands in $AgC{\equiv}CPh{\cdot}AgNO_3$ (**1**) (50% thermal ellipsoids). Hydrogen atoms and nitrate anions are omitted for clarity. Symmetry codes: a $1 - x, -y, 0.5 + z$; b $0.5 - x, y, 0.5 + z$. Selected bond lengths [Å]: C1≡C2 1.24(1), C9≡C10 1.22(1), C17≡C18 1.21(1), Ag···Ag 2.860(1)−3.268(1).

An argentophilic silver(I) layer in the crystal structure of **1** is formed from the cross-linkage of an alternating arrangement of parallel double (colored red; composed of Ag1, Ag2, and Ag3) and single (colored purple; Ag5 and Ag6) zigzag chains, with silver(I) atoms of type Ag4 (colored green) strengthening the layer through additional Ag···Ag interaction (Figure 2).

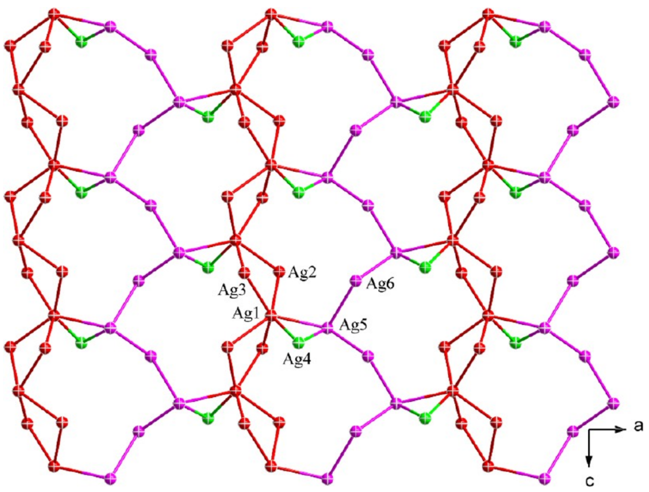


Figure 2. Argentophilic layer in the crystal structure of **1**. Color codes for atoms: normally purple is used for Ag in all figures, but different colors are used as required to facilitate description of structural features: Ag1, Ag2, and Ag3 red; Ag4, green; Ag5 and Ag6, purple.

Unusually short cationic contacts between adjacent d^{10} Ag(I) centers in the range 2.80−3.30 Å (less than 3.40 Å, twice the van der Waals radius of metallic silver) that give rise to layer-type structures are known to exist in many crystalline silver(I) oxo-salts such as $KAgCO_3$, Ag_2CO_3, and $AgBO_2$ for well over a half-century, although such layers were not referred to as argentophilic in the early literature.[22] In contrast, the occurrence of silver(I) layers in organometallic compounds is rare, the few reported examples being $Ag_2C_2 \cdot 2AgClO_4 \cdot 2H_2O$,[23] $3[Ag_2(o\text{-}C{\equiv}CC_6H_4C{\equiv}C)] \cdot 14AgCF_3CO_2 \cdot 2CH_3CN \cdot 9H_2O$,[24] and $Ag_2(2,5\text{-}C{\equiv}CpyC{\equiv}C) \cdot 3AgNO_3$.[25] Compound **1** provides the first example of a corrugated, thick silver(I) layer stabilized by argentophilicity.

The corrugated silver(I)-layer structure is additionally stabilized by nitrate ions exhibiting different coordination modes: (O1−O2−O3) μ_2-*O,O′*, (O4−O5−O6) μ_2-*O,O′* and (O7−O8−O9) μ-O. As shown in Figure 3, the phenyl ethynide groups arranged on both sides of the thick silver(I) layer are involved in pairwise offset face−to−face π−π interaction (inter-centroid distance, 4.169 Å) and weak C−H···O(nitrate) hydrogen bonds (C4···O8, 3.279 Å; C8···O1, 3.278 Å; C16···O9 3.301 Å; C20···O1, 3.233 Å).

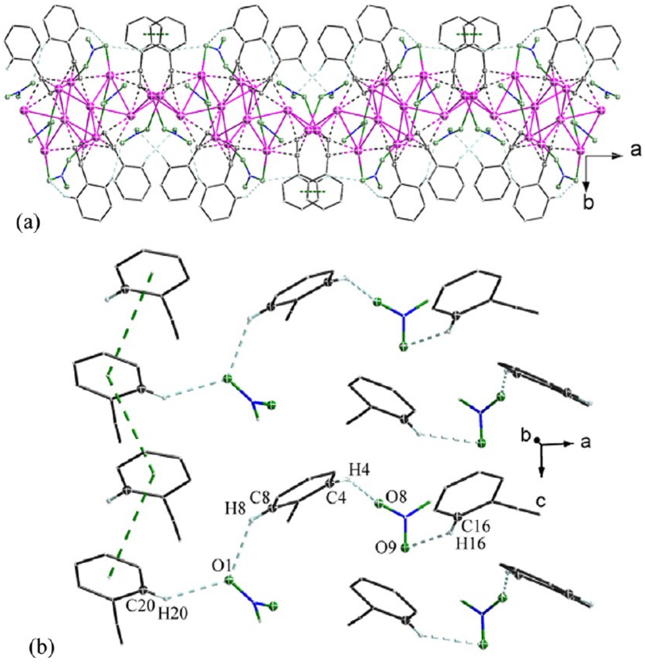


Figure 3. (a) Side view of the corrugated silver(I)-phenylethynide layer in **1** assembled by argentophilic interaction and nitrate ligands. (b) Weak interactions (π−π: green dotted line; C−H···O hydrogen bond: turquoise dotted line) contributing to stabilization of the silver(I)- phenylethynide layer structure. Color codes for atoms: Ag, purple; C, gray; H, turquoise; O, green; N, blue.

2AgC≡CPh·AgNO$_3$ *(2).* Compound **2** was obtained from the crystallization of $[AgC{\equiv}CPh]_n$ in a DMSO solution of $AgNO_3$, instead of an aqueous solution of $AgNO_3$ as in the formation of complex **1**. In the crystal structure of **2**, there are two independent phenylethynide anions (C1≡C2) and (C9≡C10), which are bound to Ag_3 baskets in the μ_3-η^1,η^1,η^2 and μ_3-η^1,η^2,η^2 coordination modes, respectively (Figure 4).

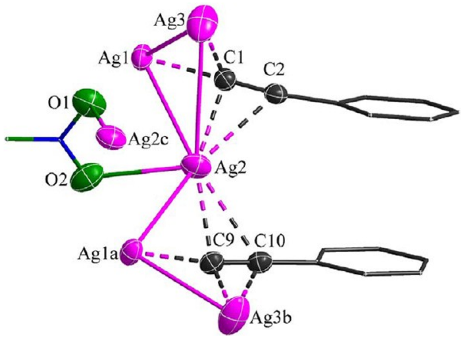


Figure 4. Atom labeling and coordination modes of the phenylethynide and nitrate ligands in $2AgC{\equiv}CPh \cdot AgNO_3$ (**2**) (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Symmetry codes: a $1 - x, -0.5 + y, 0.5 - z$; b $x, 0.5 - y, -0.5 + z$; c $1 - x, -0.5 + y, 0.5 - z$. Selected bond lengths [Å]: C1≡C2 1.22(1), C9≡C10 1.22(1), Ag···Ag 2.895(1)−3.359(1).

As shown in Figure 5a, the silver atoms are united together through argentophilic interaction to form a herringbone silver(I) layer on the *bc* plane, which is constructed by the corner-linkage of chairlike Ag_6 aggregates formed by the double linkage between two inversion-related silver(I) triangles (Ag1, Ag2, Ag3; Ag1d, Ag2d, Ag3d; colored blue to facilitate visualization).

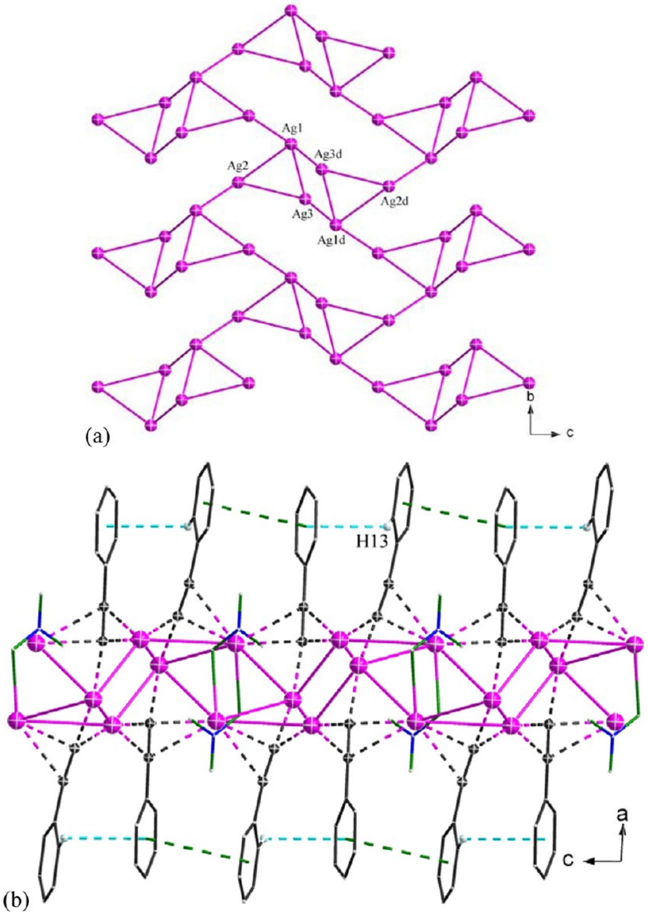


Figure 5. (a) Herringbone silver(I) layer of **2** formed from argentophilic interaction between chairlike Ag_6 aggregates. Symmetry codes: (b) side view of argentophilic layer in **2** assembled by π−π stacking, C−H···O hydrogen bonding and bridging nitrate ligands on both sides. Color scheme for atoms: Ag, purple; C, gray; H, turquoise; O, orange; N, blue. Green and turquoise dotted lines represent π−π and C−H···π interactions, respectively.

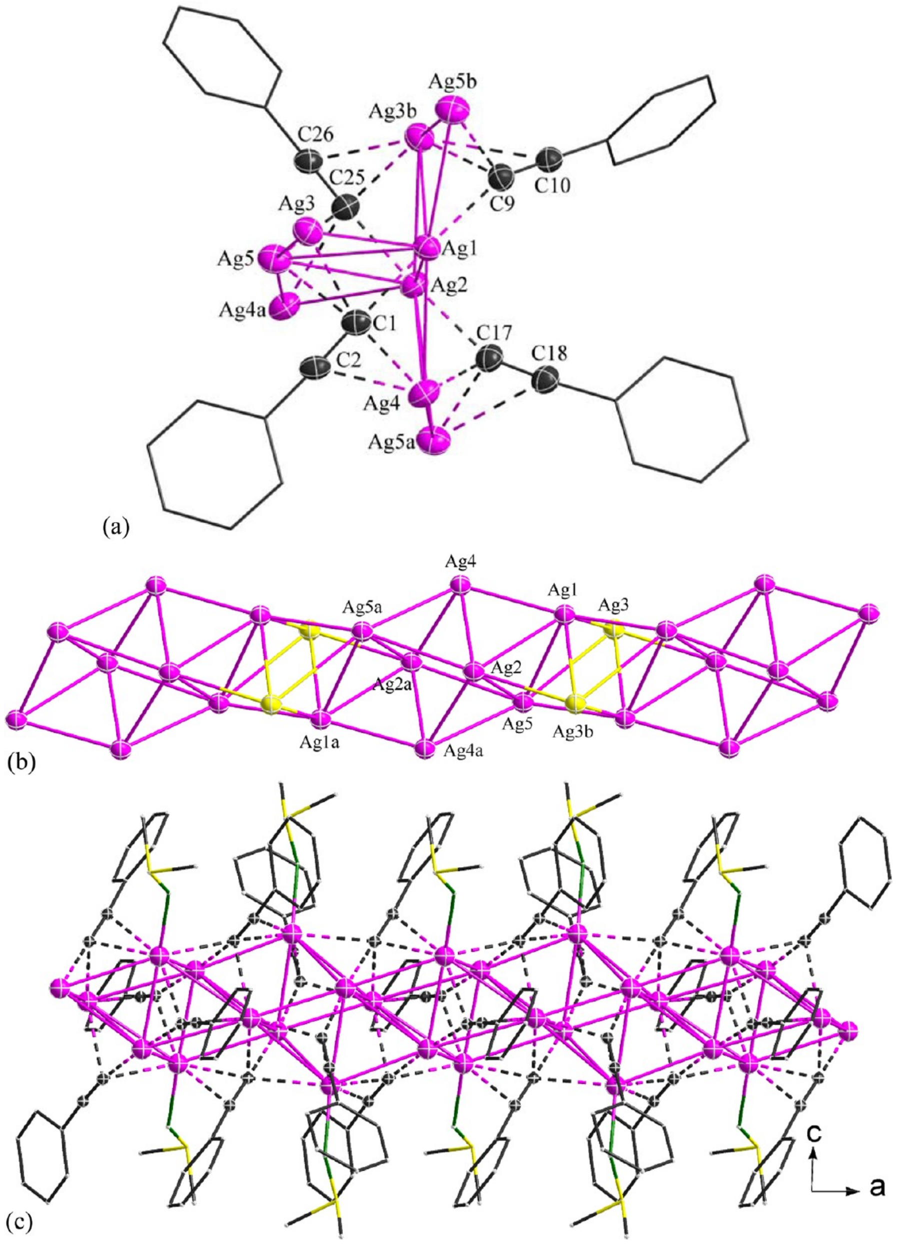


Figure 6. (a) Atom labeling and coordination modes of the phenylethynide ligands in **3A**. The silver(I) and ethynide carbon atoms are drawn as 30% thermal ellipsoids, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.23(1), C9≡C10 1.21(1), C17≡C18 1.20(1), C25≡C26 1.22(1), Ag···Ag 2.904(1)−3.377(1). (b) Characteristic cationic silver(I) column in the isostructural series of complexes **3A** to **3E** formed from the linkage of a linear array of centrosymmetric Ag_8 rhombic prisms (colored purple) by atoms Ag3 and Ag3b (colored yellow). (c) Coordination of silver(I) column by surrounding phenylethynide anions and DMSO ligands. Symmetry codes: a $1 - x$, $1 - y$, $1 - z$; b $2 - x$, $1 - y$, $1 - z$.

As shown in Figure 5b, the nitrate ligand adopts the μ_2-*O,O′* mode to consolidate the silver(I) layer. Adjacent phenyl rings of ethynide ligands arranged on both sides of the silver(I) layer interact through both offset face-to-face $\pi-\pi$ interaction (intercentroid distance 3.603 Å) and edge-to-face C−H···π interaction (H···center, 2.859 Å with a C−H···centroid angle of 115°), the latter being shorter than the normal C−H···π interaction of 3.05 Å [1.05 times the sum of accepted van der Waals radii of hydrogen (1.20 Å) and carbon (1.70 Å)].[26] Such π-related interactions further stabilize the silver(I)-layer structure.

*[Ag5(PhC≡C)4(DMSO)$_2$]X [X= BF$_4$ (**3A**), ClO$_4$ (**3B**), PF$_6$ (**3C**), AsF6 (**3D**), SbF$_6$ (**3E**)].* Complexes **3A**−**3E** bearing common, weakly coordinating inorganic ions constitute an isostructural series of complexes that exhibit essentially the same type of crystal structure. In particular, **3C** and **3D** are isomorphous as both belong to space group $P2_1/c$ with very similar unit-cell dimensions.

The crystal structure of compound **3A**, which contains the BF_4^- anion, is described as a representative example. Here the ethynide moieties C1≡C2 and C25≡C26 are each capped by a butterfly-shaped Ag_4 basket in the μ_4-η^1,η^1,η^1,η^2 coordination mode, whereas ethynides C9≡C10 and C17≡C18 adopt the μ_3-η^1,η^1,η^1 and μ_3-η^1,η^2,η^2 coordination modes, respectively (Figure 6a). The four independent silver(I) atoms (Ag1, Ag2, Ag4, Ag5) and their inversion-related counterparts form a Ag_8

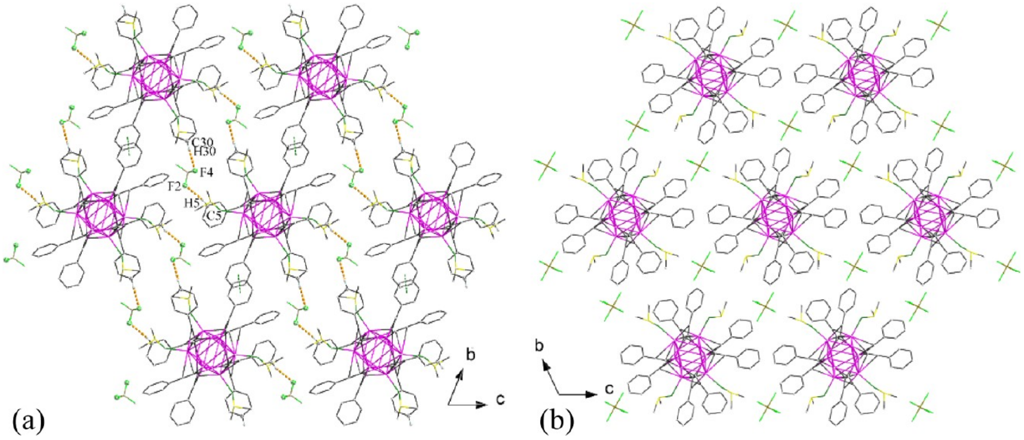


Figure 7. Packing of silver(I) columns (viewed end-on) in complexes (a) **3A** and (b) **3E**, which are linked by weak hydrogen bonds to give a three-dimensional supramolecular network. In the case of **3A**, face-to-face $\pi-\pi$ interaction of phenyl rings occurs between adjacent silver columns in the *b* direction.

rhombic prism, and fusion of a linear array of such polyhedra via bridging atoms Ag3 and Ag3b yields an infinite cationic silver(I) column directed along the *a*-axis (Figure 6b). This silver column is coordinated by the surrounding phenylethynide and DMSO ligands (Figure 6c).

The crystal structure of **3A** consists of a hexagonal packing of parallel coordinated silver columns, with the BF_4^- ion playing a space-filling role as well as linking neighboring columns via weak C−H···F hydrogen bonds (C5···F2, 3.316 Å; C30···F4, 3.407 Å). In view of the small size of the BF_4^- ligand, face-to-face $\pi-\pi$ interaction (4.087 Å) of phenyl rings of adjacent silver columns also occurs (Figure 7a).

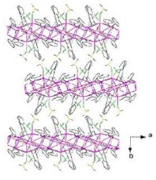
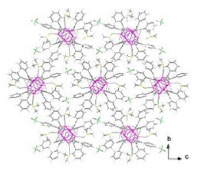
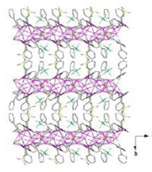
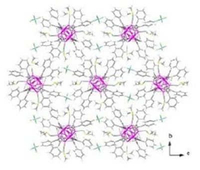
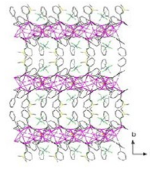
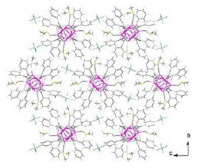
The infinite cationic silver(I) column found in **3A** also exists in the crystal structures of **3B** to **3E**. Despite the large difference in steric bulk of the BF_4^- and SbF_6^- anions, they play the same role in linking the infinite silver(I) columns in **3A** and **3E**, respectively, by weak hydrogen bonds to form a pseudohexagonal network (Figure 7).

In a like manner, when $AgClO_4$, $AgPF_6$, and $AgAsF_6$ are used in turn to generate **3B**, **3C**, and **3D**, respectively, a similar hexagonal array of infinite silver(I) columns are interconnected by weak hydrogen bonds to form a three-dimensional supramolecular network. The crystal structures of **3B** and the isomorphous pair **3C** and **3D** are displayed in Table 2.

Notably, the mode of crystal packing and closest separation between the cationic silver(I) columns can be fine-tuned by varying the size of the ancillary inorganic anion. With a steady increase in the size of WCAs, the separation between adjacent silver(I) columns increases (Table 3).

2AgC≡CPh·5AgO₂CCF₃·4DMSO (**4**). In the crystal structure of **4**, there are four independent phenylethynide anions which are consolidated into a Ag_{15} aggregate via different coordination modes. The ethynide moieties C1≡C2 and C17≡C18 are each capped by a butterfly-shaped Ag_4 basket in the μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$ mode, and the other two ethynide groups C9≡C10 and C25≡C26 are each bound to a square-pyramidal Ag_5 basket in the μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2$ mode, as shown in Figure 8a. This Ag_{15} aggregate is stabilized by continuous $\pi-\pi$ stacking of phenyl rings (intercentroid distances (I)···(II) 4.120 Å, (II)···(III) 3.874 Å, (III)···(IV) 4.087 Å) lying on one side. All trifluoroacetate groups each spans a Ag···Ag edge by the μ_2-*O*,*O*′ mode (Figure 9a).

Table 2. Comparison of Three-Dimensional Supramolecular Structures of 3B, 3C, and 3D

Compound	3D network viewed along *c*-axis	3D network viewed along *a*-axis
3B		
3C		
3D		

Adjacent Ag_{14} aggregates are further fused together through a shared silver atom (Ag14) and a bridging μ_2-DMSO molecule to generate an infinite silver(I) chain along the *b* axis (Figure 9a). The remaining DMSO molecules are each coordinated to the silver chain (three in μ_1 and four in μ_2 mode) at intervals between segments of four phenyl rings. Because of the steric effect of the bridging DMSO molecule, complex **4** exhibits segmented $\pi-\pi$ interactions rather than infinite continuous $\pi-\pi$ stacking among parallel phenyl rings in AgC≡CPh·3AgO₂CCF₃·CH₃CN.[18]

As shown in Figure 9b, the infinite silver(I) chains are interconnected by two kinds of weak hydrogen bonds, that is, C6−H6A···F9 (C14−F9 3.11 Å) and C61−H61B···F22 (C61−F22 3.38 Å), to form a three-dimensional supramolecular structure.

10AgC≡CPh·2AgOTf·AgNO₃·3DMSO (**5**). In the crystal structure of complex **5**, independent atoms Ag1, Ag2, Ag5, Ag6, and Ag7 together with their inversion-related counterparts

Table 3. Variation of Separation between Nearest Silver(I) Columns in Isostructural Complexes 3A−3E with the Presence of Different Ancillary Inorganic WCAs

$[Ag_5(PhC{\equiv}C)_4(DMSO)_2]X$	3A	3B	3C	3D	3E
X	BF_4	ClO_4	PF_6	AsF_6	SbF_6
shortest center to the center distance between adjacent silver(I) columns (Å)	14.89	16.06	16.37	16.51	16.72

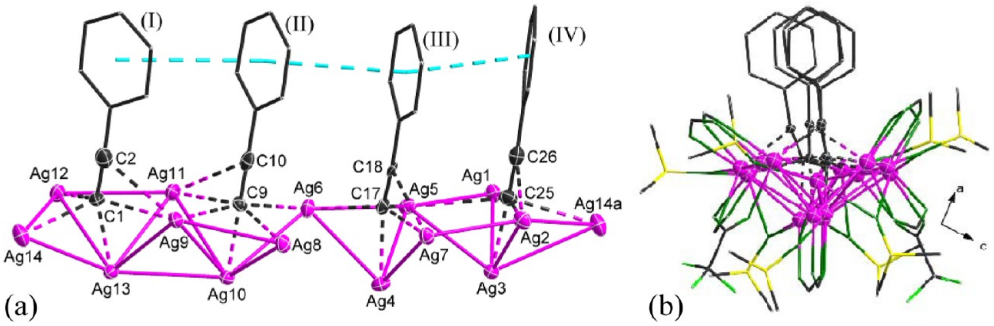


Figure 8. (a) Atom labeling and coordination modes of four independent phenylethynide units in $2AgC{\equiv}CPh{\cdot}5AgO_2CCF_3{\cdot}4DMSO$ (**4**) (50% thermal ellipsoids). The DMSO and $CF_3CO_2^-$ ligands and all hydrogen atoms are omitted for clarity. Symmetry code: a − *x*, −1 + *y*, *z*. Selected bond lengths [Å]: C1≡C2 1.20(1), C9≡C10 1.22(1), C17≡C18 1.23(1), C25≡C26 1.24(1), Ag···Ag 2.896(1)−3.170(1). (b) Side view of silver(I) chain in **4** surrounded by trifluoroacetate ligands and DMSO molecules.

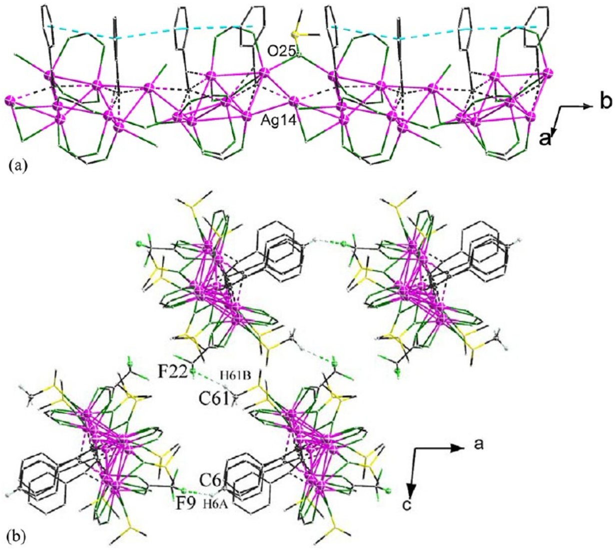


Figure 9. (a) Silver(I) chain in complex **4** connected by sharing the Ag14 atom and bridging DMSO ligand. All hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. (b) Adjacent silver(I) chains (viewed end-on) in complex **4** are linked by weak hydrogen bonds C6−H6A···F9 (C14−F9 3.11 Å) and C61−H61B···F22 (C61−F22 3.38 Å) to give a three-dimensional network.

constitute an argentophilic Ag_{10} incomplete double cubane. An infinite silver(I) column is constructed by fusion of such incomplete double cubanes with a bent Ag_3 unit (Ag3, Ag4, Ag3b) with C_2 symmetry (Figure 10a).

Complex **5** features a neutral silver(I) coordination column stabilized by phenylethynide, triflate, and nitrate anions oriented along the *c*-axis (Figure 10b). All the phenylethynide anions are each capped by three silver atoms. The ethynide moieties C1≡C2, C9≡C10, and C25≡C26 act in the μ_3-η^1,η^1,η^2 coordination mode, and ethynides C17≡C18 and C33≡C34 adopt μ_3-η^1,η^1,η^1 and μ_3-η^1,η^2,η^2 coordination modes, respectively. The triflate and nitrate anions adopt *μ*-O and μ_2-O,O′ coordination modes, respectively, to act as effective counteranions to balance the charge.

This silver(I) column is stabilized by formation of a *π*−*π* interaction cycle which consists of an offset face-to-face *π*−*π* interaction (center-to-center distance 3.913 Å), a C−H···*π*-(ethynide) interaction (H4···midpoint of C9 and C10 = 3.016 Å with a C4−H4···midpoint of C9 and C10 angle 158°, and two edge−to−face C−H···*π* interactions (H31 to center of (II) distance = 2.836 Å with a C−H···centroid angle 143°; H40 to center of (IV) distance = 2.944 Å with a C−H···centroid angle 140°) (Figure 11).

In the crystal structure of **5**, the infinite silver(I) columns arranged in a hexagonal array are interconnected by C30−H30···F2 (C30−F2 3.520 Å) hydrogen bonds to form a three-dimensional supramolecular structure (Figure 12).

■ DISCUSSION

Crystallization Procedure. Polymeric silver(I) phenylethynide readily dissolves in a concentrated aqueous solution of $AgNO_3$, but it has very low solubility in a saturated solution of a soluble silver(I) salt AgX in water, where X represents an inorganic anion in the weakly coordinating series composed of BF_4^-, ClO_4^-, PF_6^-, AsF_6^-, and SbF_6^- (henceforth abbreviated as WCAs). In our attempted preparation of new crystalline silver(I) complexes containing phenylethynide and a monoanion in this series, we explored mixed-solvent systems by employing a water-miscible cosolvent such as methanol, ethanol, acetone, THF, DMF, and DMSO. Subsequently, we found that the solubility of silver(I) phenylethynide can be greatly increased using DMSO as a cosolvent. We therefore modified the crystallization method by layering water over a concentrated DMSO solution of a variety of silver(I) salts, thereby resulting in a high phenylethynide/X molar ratio in the product complexes (see Table 4).

Influence of Solvent and Ancillary Anion. Double salts **1** and **2**, which bear different molar ratios, are obtained from crystallization in water and water/DMSO, respectively. DMSO proved to be a good solvent for crystallization of complexes **3**−**5** by functioning as a ligand. From the available structural data presented in Table 4, it appears that the coordination ability of phenylethynide is weakened when the complex has a high

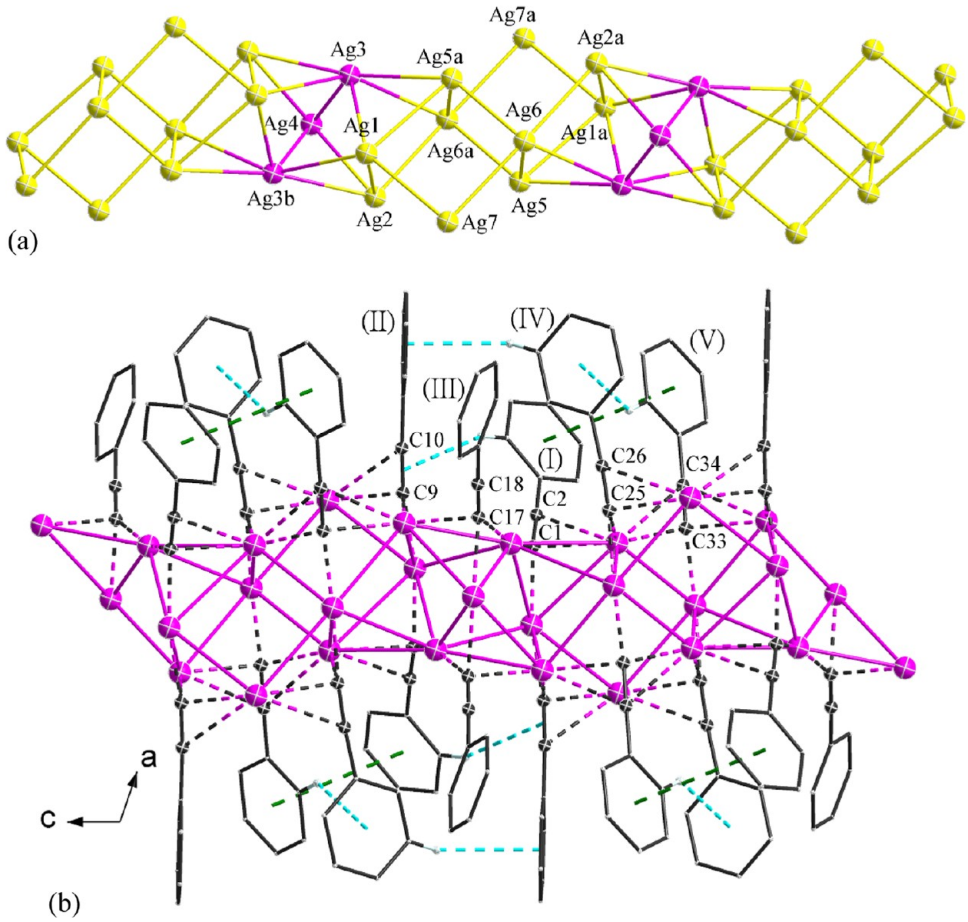


Figure 10. (a) Argentophilic column in **5** formed by fusion of centrosymmetric Ag$_{10}$ incomplete double cubanes (yellow) and C$_2$ bent Ag$_3$ unit (purple). (b) The silver(I) polyhedron column in complex **5** surrounded by phenylethynide ions, whose phenyl rings are engaged in $\pi-\pi$, C−H···π(phenyl) and C−H···π(ethynide) weak interactions. Hydrogen atoms, nitrates, triflates, and DMSO molecules are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.202(8), C9≡C10 1.210(5), C17≡C18 1.198(1), C25≡C26 1.22(1), C32≡C33 1.22(1), Ag···Ag 2.905(1)−3.311(1). Symmetry codes: a: 1 − *x*, 1 − *y*, 1 − *z*; b: 1 − *x*, *y*, 1.5 − *z*.

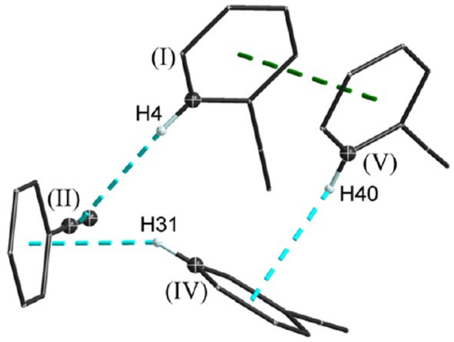


Figure 11. $\pi-\pi$ Interaction cycle in compound **5**. Green dotted line indicates $\pi-\pi$ stacking; turquoise dotted line represents C−H···π interaction.

molar ratio of silver(I) phenylethynide to ancillary silver(I) salt. Moreover, the nature of the ancillary anion also affects the coordination mode of the phenylethynide anion. In DMSO, when AgO$_2$CCF$_3$ was used, the ligation number[27] of phenylethynide is 4 and 5. It decreases to 3 and 4 when a weakly coordinating inorganic anion (WCA) is used. In the presence of the nitrate anion, only three silver atoms are bonded to the ethynide moiety.

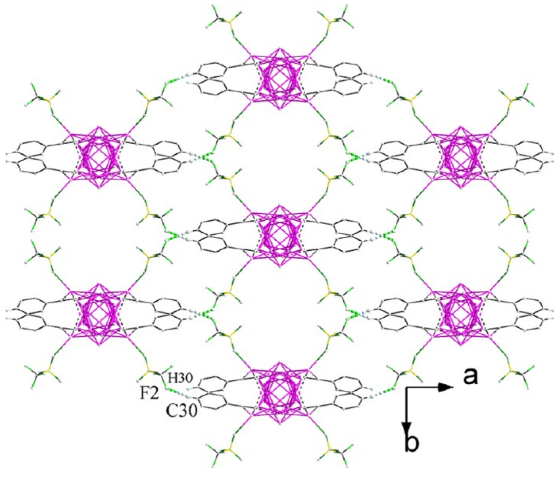


Figure 12. Hexagonal array of coordination columns in complex **5** cross-linked by C30−F2 weak hydrogen bonds to form a three-dimensional supramolecular structure. Other ligands are omitted for clarity.

Crystal growth from DMSO and H$_2$O gives compounds **1** and **2** of different stoichiometry, indicating that the solvent molecule affects the coordination ability of the anionic component. When DMSO is used in place of water, fewer

Table 4. Effect of Solvent and Ancillary Anion X on the Ligation Number of Phenylethynide and AgC_2Ph/AgX Molar Ratio

complex	**4**	**2**	**5**	**3A** to **3E**	$AgC{\equiv}CPh \cdot 3AgO_2CCF_3 \cdot CH_3CN$[18]	**1**
silver(I) salt	AgO_2CCF_3	$AgNO_3$	$AgNO_3$ + AgOTf	WCA[a]	AgO_2CCF_3	$AgNO_3$
solvent	DMSO				$H_2O + CH_3CN$	H_2O
ligation number[b] of phenylethynide	4 and 5	3	3	3 and 4	5	4
ratio of silver(I) phenylethynide to component silver salt	1:2.5	2:1	10:3	4:1	1:3	1:1

[a] WCA = weakly coordinating inorganic anion. [b] Ligation number defined as number of metal ions consolidated by the ligand.

silver(I) ions are bound to the ethynide moiety, thereby lowering the molar ratio of silver(I) phenylethynide to the ancillary silver(I) salt, as well as the ligation number of phenylethynide.

When the ancillary silver salt AgO_2CCF_3 was employed, the steric effect of the trifluoromethyl group is reflected in the generation of an infinite silver(I) coordination chain. In contrast, $AgNO_3$ induces assembly of silver(I)-phenylethynide to form an argentophilic layer. Upon addition of a silver(I) salt of WCA to silver(I)-phenylethynide, the silver layer is rolled up to yield a silver column composed of fused Ag_n polyhedra. The nitrate ions in **1**, DMSO molecules, and the corresponding counterions in **3A**–**3E** and **5** were found to exhibit positional/orientational disorder, which was properly addressed in structure refinement.

π–π Interaction. In our previous studies of silver(I) aryl ethynide complexes, π–π interaction has been demonstrated to play an important role in crystal formation by inducing the assembly of $Ar{-}C{\equiv}C{\supset}Ag_n$ building units to form a silver(I) layer, column, chain, or bridged aggregate.[17] As expected, the aromatic ring of phenylethynide invariably partakes in continuous or discontinuous π–π interaction to give an infinite columnar structure in **4** and layer-type structures in **1** and **2**. However, when WCA is added, π–π interaction is interrupted, and the phenyl rings only surround the silver(I) column to form a hydrophobic shield. The WCA tends to force the silver(I) phenylethynide together to form thick argentophilic columns in **3** and **5**.

Argentophilicity and Silver(I)-Ethynide Supramolecular Synthons. It is well-established that metallophilic attractions[5] are roughly comparable in strength with typical hydrogen bonds. A well-known example is aurophilicity, the propensity for aggregation of Au(I) centers in dinuclear or polynuclear complexes,[28] for which ab initio calculations showed that such cohesive d^{10}-d^{10} interaction, together with significant relativistic effects, can be attributed mainly to dispersion forces.[5] For analogous Ag(I) and Cu(I) complexes, presumably dispersion plays a dominant role while relativistic effects are absent or negligible. Theoretical treatments of dimeric models of linear two-coordinate group 11 complexes at the MP2 level have suggested that metallophilicity decreases in the order Au(I) > Ag(I) > Cu(I),[29] which agrees with chemical intuition. However, later theoretical studies at higher level (CCSD and CCSD(T)) showed that argentophilicity may even exceed aurophilicity in strength.[30]

There is as yet no definitive theoretical study on multinuclear metal–ligand aggregates such as the silver(I)-ethynide supramolecular synthons, which we and other groups have employed to assemble a wide variety of inorganic and organometallic oligomers, high-nuclearity clusters, infinite chains, layers, and three-dimensional frameworks.[7,10] In our working model, the terminal ethynyl carbon atom bearing the negative charge draws neighboring Ag(I) atoms together to facilitate the onset of argentophilicity, such that the binding interaction that consolidates the multinuclear metal–ligand aggregate is considered to be mainly ionic with minor contribution from covalent σ and π components. Accordingly we have adopted the term "silver(I)-ethynide" in preference to "silver(I)-ethynyl" and consistently used it in all our publications. To date, formation of the multinuclear metal–ligand supramolecular synthons is restricted to silver(I), as no analog has yet been found for the other two coinage metals and the transition elements. The fact that analogous multinuclear metal–ligand supramolecular synthons are not formed by copper(I) and gold(I) presumably arises from the insolubility of their salts in common solvents.

■ CONCLUSION

On the basis of the multinuclear metal–ligand supramolecular synthon $Ph{-}C{\equiv}C{\supset}Ag_n$ (n = 3, 4, 5), the present work reports the synthesis and structure of a series of silver(I) complexes containing phenylethynide and inorganic ligands that include the nitrate ion and a series of weakly coordinating anions (WCAs). Crystallization of complexes containing WCAs is made possible only using DMSO as a solvent, which plays the role of an ancillary ligand. A systematic investigation of the effect of variation of the anionic component on supramolecular assembly showed that, to a certain extent, the dimension and pattern of argentophilic aggregation can be controlled by using different ancillary anions, yielding silver(I) layers in **1** and **2** with the nitrate ion, and isostructural complexes **3A**–**3E** that exhibit a three-dimensional supramolecular host network composed of a hexagonal array of infinite silver(I) columns that accommodate the WCA guests. With the incorporation of organic ligand trifluoroacetate and triflate in **4** and **5**, respectively, an infinite silver(I) chain and a thick neutral silver(I) column are obtained.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray structure analysis results of **1**–**5** in CIF format. CCDC reference numbers 865513–865521. This information is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tcwmak@cuhk.edu.hk; fax: (852) 26035057.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support by the Hong Kong Research Grants Council (GRF CUHK 402408 and 402710) and the Wei Lun Foundation for postdoctoral fellowships to Guang-Gang Gao, Shuang-Quan Zang, and Samipillai Marivel, and the award of a Postgraduate Studentship to P.-C. Cheng by The Chinese University of Hong Kong.

■ DEDICATION

Dedicated to Prof. Gautam R. Desiraju on the occasion of his 60th birthday.

■ REFERENCES

(1) (a) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89−124. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197−257. (c) Lotz, S.; Van Rooyen, P. H.; Meyer, R. *Adv. Organomet. Chem.* **1995**, *37*, 219−320. (d) Abu-Salah, O. M. *J. Organomet. Chem.* **1998**, *565*, 211−216. (e) Lang, H.; George, D. S. A.; Rheinwald, G. *Coord. Chem. Rev.* **2000**, *206*−*207*, 101−107. (f) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2586−2617. (g) Bruce, M. I. *Coord. Chem. Rev.* **2004**, *248*, 1603−1625. (h) Wong, W.-Y. *Coord. Chem. Rev.* **2007**, *251*, 2400−2427. (i) Chen, M.-L.; Xu, X.-F.; Cao, Z.-X.; Wang, Q.-M. *Inorg. Chem.* **2008**, *47*, 1877−1879. (j) Berenguer, J. R.; Lalinde, E.; Moreno, M. T. *Coord. Chem. Rev.* **2010**, *254*, 832−875.

(2) (a) Younus, M.; Kohler, A.; Cron, S.; Chawdhury, N.; Al-Madani, M. R. A.; Khan, M. S.; Long, N. J.; Friend, R. H.; Raithby, P. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 3036−3039. (b) Yam, V. W.-W. *Acc. Chem. Res.* **2002**, *35*, 555−563. (c) Wei, Q.-H.; Zhang, L.−Y.; Yin, G.-Q.; Shi, L.-X.; Chen, Z.-N. *J. Am. Chem. Soc.* **2004**, *126*, 9940−9941. (d) Xu, H.-B.; Shi, L.-X.; Ma, E.; Zhang, L.-Y.; Wei, Q.-H.; Chen, Z.-N. *Chem. Commun.* **2006**, *1601*, 1603−1603. (e) Swavey, S.; Swavey, R. *Coord. Chem. Rev.* **2009**, *253*, 2627−2638.

(3) (a) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637−670. (b) Whittal, I. R.; McDonagh, A. M.; Humphrey, M. G. *Adv. Organomet. Chem.* **1998**, *42*, 291−362. (c) Cifuentes, M. P.; Humphrey, M. G. *J. Organomet. Chem.* **2004**, *689*, 3968−3981.

(4) (a) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178*−*180*, 431−509. (b) Yam, V. W.-W.; Wong, K. M.-C. *Top. Curr. Chem.* **2005**, *257*, 785−791. (c) Rigaut, S.; Olivier, C.; Costuas, K.; Choua, S.; Fadhel, O.; Massue, J.; Turek, P.; Saillard, J. Y.; Dixneuf, P. H.; Touchard, D. *J. Am. Chem. Soc.* **2006**, *128*, 5859−5876. (d) Aguirre-Etcheverry, P.; O'Hare, D. *Chem. Rev.* **2010**, *110*, 4839−4864.

(5) (a) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563−594. (b) Pyykkö, P.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 604−605. (c) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597−636. (d) Fernandez, E. J.; López de Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Perez, J.; Laguna, A.; Mohamed, A. A.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 2022−2023. (e) O'Grady, E.; Kaltsoyannis, N. *Phys. Chem. Chem. Phys.* **2004**, *6*, 680−687. (f) Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412−4456. (g) Pyykkö, P. *Inorg. Chim. Acta* **2005**, *358*, 4113−4130. (h) Pyykkö, P. *Chem. Soc. Rev.* **2008**, *37*, 1967−1997. (i) Grimme, S.; Djukic, J.-P. *Inorg. Chem.* **2010**, *49*, 2911−2919. (j) Muñiz, J.; Wang, C.; Pyykkö, P. *Chem.—Eur. J.* **2011**, *17*, 368−377.

(6) (a) McArdle, C. P.; Vittal, J. J.; Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3819−3822. (b) Yam, V. W. W.; Fung, W. K. M.; Cheung, K. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1100−1102.

(7) For reviews, see (a) Mak, T. C. W.; Zhao, X.-L.; Wang, Q.-M.; Guo, G.-C. *Coord. Chem. Rev.* **2007**, *251*, 2311−2333. (b) Mak, T. C. W.; Zhao, L. *Chem. Asian J.* **2007**, *2*, 456−467. (c) Mak, T. C. W.; Zhao, L.; Zhao, X.-L. Supramolecular Assembly of Silver(I)Complexes with Argentophilic and Silver...Carbon Interactions. In *The Importance of Pi-Interactions in Crystal Engineering − Frontiers in Crystal Engineering III*; Tiekink, E. R. T., Zukerman-Schpector, J., Eds.; Wiley: Chichester, 2012; Chapter 13, pp 323−366.

(8) (a) Desiraju, G. R. *Angew. Chem., Int. Ed.* **1995**, *34*, 2311−2327. (b) Reddy, D. S.; Ovchinnikov, Y. E.; Shishkin, O. V.; Struchkov, Y. T.; Desiraju, G. R. *J. Am. Chem. Soc.* **1996**, *118*, 4085−4089. (c) Thalladi, V. R.; Goud, B. S.; Hoy, V. J.; Allen, F. H.; Howard, J. A. K.; Desiraju, G. R. *Chem. Commun.* **1996**, 401−402. (d) Nangia, A.; Desiraju, G. R. *Top. Curr. Chem.* **1998**, *198*, 57−95. (e) Desiraju, G. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 8342−8356.

(9) These persistent structural patterns serve as versatile structure building units in crystal engineering, but logically they should be regarded as multinuclear metal−ligand supramolecular synthons to conform to the classical definition of Desiraju, since each cationic aggregate is held together by weak interatomic/molecular attractive interactions rather than conventional coordination bonding.

(10) (a) Bian, S.-D.; Wu, H.-B.; Wang, Q.-M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5363−5365. (b) Bian, S.-D.; Jia, J.-H.; Wang, Q.-M. *J. Am. Chem. Soc.* **2009**, *131*, 3422−3423. (c) Qiao, J.; Shi, K.; Wang, Q.-M. *Angew. Chem., Int. Ed.* **2010**, *49*, 1765−1767. (d) Gao, G.-G.; Cheng, P.-S.; Mak, T. C. W. *J. Am. Chem. Soc.* **2009**, *131*, 18257−18259. (e) Gruber, F.; Jansen, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 4924−4926. (f) Putaj, P.; Lefebvre, F. *Coord. Chem. Rev.* **2011**, *255*, 1642−1685. (g) Xie, Y.-P.; Mak, T. C. W. *J. Am. Chem. Soc.* **2011**, *133*, 3760−3763. (h) Hau, S. C. K.; Cheng, P.-S.; Mak, T. C. W. *J. Am. Chem. Soc.* **2012**, *134*, 2922−2925. (i) Xie, Y.-P.; Mak, T. C. W. *Chem. Commun.* **2012**, 1123−1125.

(11) (a) Zhao, L.; Wong, W.-Y.; Mak, T. C. W. *Chem.—Eur. J.* **2006**, *12*, 4865−4872. (b) Zhao, L.; Wan, C.-Q.; Han, J.; Chen, X.-D.; Mak, T. C. W. *Chem.—Eur. J.* **2008**, *14*, 10437−10444. (c) Zang, S.-Q.; Mak, T. C. W. *Inorg. Chem.* **2008**, *47*, 7094−7105. (d) Zang, S.-Q.; Han, J.; Mak, T. C. W. *Organometallics* **2009**, *28*, 2677−2683.

(12) (a) Guo, G.-C.; Zhou, G.-D.; Wang, Q.-G.; Mak, T. C. W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 630−632. (b) Guo, G.-C.; Zhou, G.-D.; Mak, T. C. W. *J. Am. Chem. Soc.* **1999**, *121*, 3136−3141.

(13) (a) Zhao, L.; Mak, T. C. W. *J. Am. Chem. Soc.* **2004**, *126*, 6852−6853. (b) Zhao, L.; Du, M.; Mak, T. C. W. *Chem. Asian J.* **2007**, *2*, 1240−1257.

(14) (a) Koshevoy, I. O.; Koskinen, L.; Haukka, M.; Tunik, S. P.; Serdobintsev, P. Y.; Melnikov, A. S.; Pakkanen, T. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3942−3945. (b) Koshevoy, I. O.; Karttunen, A. J.; Lin, Y. C.; Lin, C. C.; Chou, P. T.; Tunik, S. P.; Haukka, M.; Pakkanen, T. A. *Dalton Trans.* **2010**, *39*, 2395−2403. (c) Koshevoy, I. O.; Ostrova, P. V.; Karttunen, A. J.; Melnikov, A. S.; Khodorkovskiy, M. A.; Haukka, M.; Janis, J.; Tunik, S. P.; Pakkanen, T. A. *Dalton Trans.* **2010**, *39*, 9022−9031. (d) Koshevoy, I. O.; Karttunen, A. J.; Shakirova, J. R.; Melnikov, A. S.; Haukka, M.; Tunik, S. P.; Pakkanen, T. A. *Angew. Chem., Int. Ed.* **2010**, *49*, 8864−8866. (e) Koshevoy, I.; Lin, O.C.-L.; Karttunen, A. J.; Janis, J.; Haukka, M.; Tunik, S. P.; Chou, P.-T.; Pakkanen, T. A. *Inorg. Chem.* **2011**, *50*, 2395−2403. (f) Chen, Z.-N.; Zhao, N.; Fan, Y.; Ni, J. *Coord. Chem. Rev.* **2009**, *253*, 1−20.

(15) Mak, T. C. W.; Zhao, L. *Chem. Asian J.* **2007**, *2*, 456−467.

(16) Zhao, L.; Mak, T. C. W. *Inorg. Chem.* **2009**, *48*, 6480−6489.

(17) Zhao, L.; Zhao, X.-L.; Mak, T. C. W. *Chem.—Eur. J.* **2007**, *13*, 5927−5936.

(18) Zhao, L.; Wong, W.-Y.; Mak, T. C. W. *Chem.—Eur. J.* **2006**, *12*, 4865−4872.

(19) Teo, B. K.; Xu, Y.-H.; Zhong, B.-Y.; He, Y.-K.; Chen, H.-Y.; Qian, W.; Deng, Y.-J.; Zou, Y. H. *Inorg. Chem.* **2001**, *40*, 6794−6801.

(20) Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.

(21) (a) Sheldrick, G. M. *SHELX-97: Program Package for Crystal Structure Solution and Refinement*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.

(22) (a) Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098−1110. (b) Omary, M. A.; Webb, T. R.; Assefa, Z.; Shankle, G. E.; Patterson, H. H. *Inorg. Chem.* **1998**, *37*, 1380−1386.

(23) Guo, G.-C.; Wang, Q.-G.; Zhou, G.-D.; Mak, T. C. W. *Chem. Commun.* **1998**, 339−340.

(24) Zhao, L.; Mak, T. C. W. *J. Am. Chem. Soc.* **2005**, *127*, 14966−14967.

(25) Zhang, T.; Song, H.; Dai, X.; Meng, X. *Dalton Trans.* **2009**, 7688−7694.

(26) Similar criteria have been used previously in other studies of the C−H···*π* interaction. For example, see (a) Umezawa, Y.; Tsuboyama, S.; Takahashi, H.; Uzawa, J.; Nishio, M. *Tetrahedron* **1999**, *55*, 10047−10056. (b) Nishio, M. *CrystEngComm* **2004**, *6*, 130−158. (c) Tsuzuki,

S.; Fujii, A. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2584−2594. (d) Gagnon, E.; Maris, T.; Arseneault, P.-M.; Maly, K. E.; Wuest, J. D. *Cryst. Growth Des.* **2010**, *10*, 648−657.

(27) Guo, G.-C.; Mak, T. C. W. *Chem. Commun.* **1999**, 813−814.

(28) (a) Scherbaum, F.; Grohmann, A.; Huber, B.; Krüger, C.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1544−1546. (b) Schmidbaur, H. *Gold: Progress in Chemistry, Biochemistry, and Technology*; Wiley: Chichester, NY, 1999. (c) Schmidbaur, H.; Schier, A. *Chem. Soc. Rev.* **2008**, *37*, 1931−1951. (d) Gimeno, M. C.; Laguna, A. *Chem. Soc. Rev.* **2008**, *37*, 1952−1966. (e) Doerrer, L. H. *Dalton Trans.* **2010**, *39*, 3543−3553.

(29) (a) Hermann, H. L.; Boche, G.; Schwerdtfeger, P. *Chem.—Eur. J.* **2001**, *7*, 5333−5342. (b) Magnko, L.; Schweizer, M.; Rauhut, G.; Schütz, M.; Stoll, H.; Werner, H.-J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1006−1013.

(30) O'Grady, E.; Kaltsoyannis, N. *Phys. Chem. Chem. Phys.* **2004**, *6*, 680−687.