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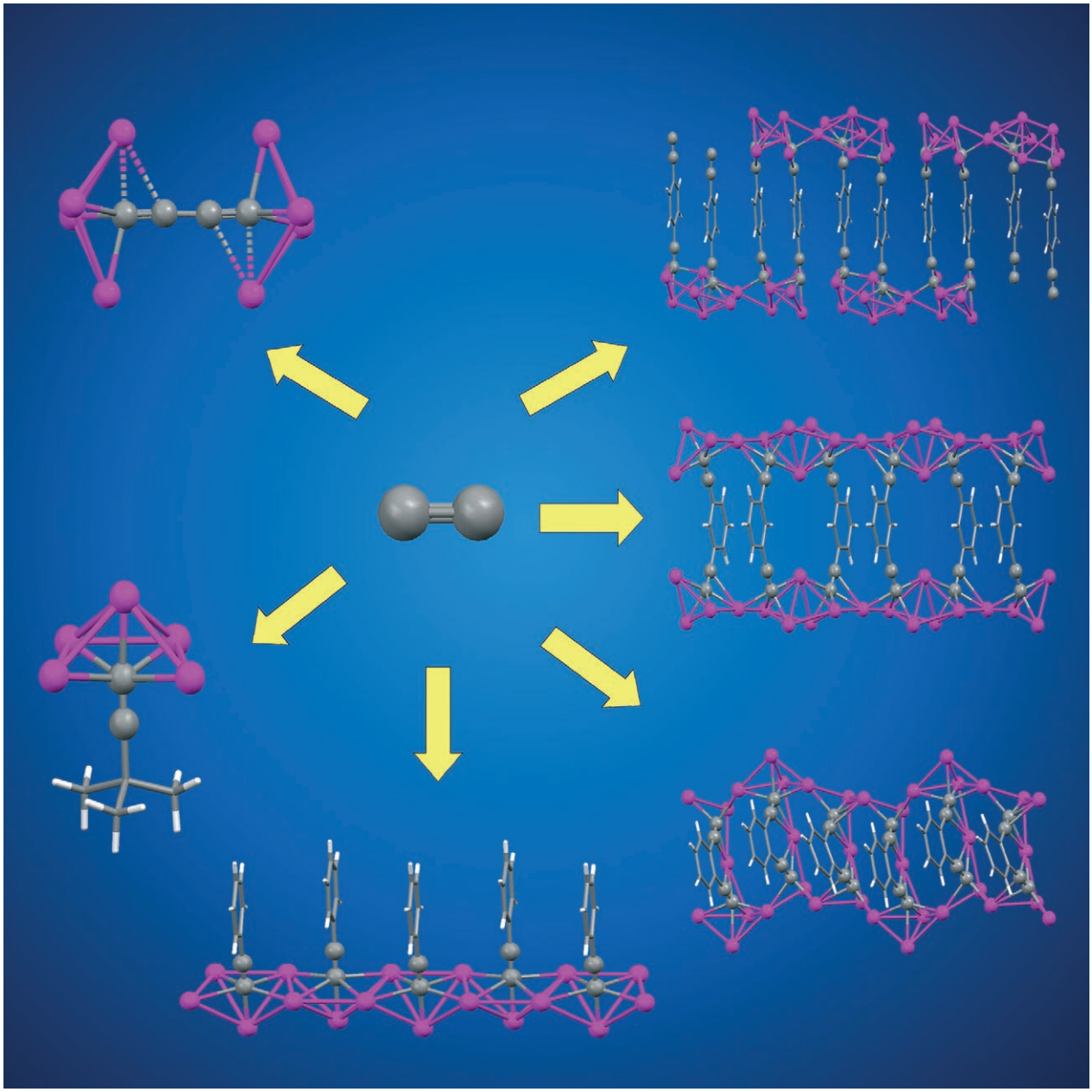
Multinuclear Silver Ethynide Supramolecular Synthons for the Construction of Coordination Networks

Thomas C. W. Mak* and Liang Zhao[a]

Dedicated to Prof. Howard C. Clark on the occasion of his 78th birthday



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Abstract: The invariant appearance of the μ_8 coordination mode for the C_4^{2-} dianion in its silver(I) complexes, with four silver(I) atoms attached to each terminal ethynide moiety, implies that the $Ag_4{\subset}C{\equiv}C{-}C{\equiv}C{\supset}Ag_4$ species may be considered as a new type of supramolecular synthon for the construction of 1D, 2D, and 3D coordination polymers. This Focus Review covers recent results on the synthesis and structural characterization of silver(I) arylethynide and alkylethynide complexes, which established the existence and utility of analogous polynuclear supramolecular synthons $R{-}C{\equiv}C{\supset}Ag_n$ (R = aryl or alkyl; $n = 4$, 5) and $Ag_n{\subset}C_2{-}R{-}C_2{\supset}Ag_n$ (R = *p*-, *m*-, *o*-C_6H_4; $n = 4$, 5). The interplay of silver–ethynide bonding, which can be classified into σ, π, and mixed (σ,π) types, with argentophilicity, π–π stacking, and other weak interactions highlights the complexity and challenge in building coordination networks of silver ethynide complexes.

Keywords: coordination modes · coordination polymers · ethynide · silver · supramolecular synthons

1. Introduction

Recent growing interest in the study of metal ethynide complexes stems from their structural diversity[1] and technological application as precursors of nonlinear optical materials,[2] luminescent materials,[3] and rigid-rod molecular wires.[4] Spectroscopic and crystallographic evidence has amply demonstrated that the ethynide group serves as a good σ-donor and weak π-acceptor ligand to form a large variety of metal alkynyl complexes.[1c,i] Furthermore, the ethynide ligand can also function as a good π donor through pπ–dπ overlap with metal atoms to produce a series of cluster complexes and multinuclear aggregates.[5]

Silver acetylenediide (Ag_2C_2), also called silver acetylide or silver carbide in the older literature, has been known as a highly explosive material for one and a half centuries.[6] Since 1998, our systematic studies on the coordination modes of small inorganic polyatomic anions such as CN^-, SCN^-, $SeCN^-$, N_3^-, and C_2^{2-}[7] by using the d^{10} silver(I) ion as a probe have led to conceptual development of the highest ligation number (HLN), namely, the largest number of coordination bonds that a particular anion can form with neighboring metal centers in a crystalline environment.[7c] Among a series of double and multiple salts of silver acetylenediide,[7d–f] the $^-C{\equiv}C^-$ species is mostly encapsulated in a silver(I) cage of 6–10 vertices, which implicitly suggests an HLN of five for the ethynide moiety $R{-}C{\equiv}C^-$. This stimulated us to carry out further work on silver(I) complexes that contain the $^-C{\equiv}C{-}C{\equiv}C^-$ and $R{-}C{\equiv}C^-$ moieties (R = aryl or alkyl).

In 1991, Pyykkö and Runeberg predicted the existence and properties of the C_4^{2-} species, the higher homologue of C_2^{2-}, in carbide form.[8] Recently we obtained silver 1,3-butadiynediide, Ag_2C_4, as a light-gray powder through the reaction of Li_2C_4 (generated in situ from the reaction of hexachloro-1,3-butadiene or 1,4-bis(trimethylsilyl)-buta-1,3-diyne with *n*BuLi) with $AgNO_3$ in a 1:2 molar ratio in THF under an inert atmosphere of nitrogen at room temperature.[9] Ag_2C_4 behaves like its lower homologue Ag_2C_2, being insoluble in most solvents and highly explosive in the dry state when subjected to heating (over 130 °C) or mechanical shock. In two structurally related double salts, $Ag_2C_4{\cdot}6AgNO_3{\cdot}nH_2O$ ($n = 2$, 3), the $^-C{\equiv}C{-}C{\equiv}C^-$ dianion consistently adopts a μ_8 coordination mode with each terminal capped by four silver atoms, thus indicating that the HLN of each ethynide moiety in the C_4^{2-} dianion is four. Therefore, $Ag_4{\subset}C{\equiv}C{-}C{\equiv}C{\supset}Ag_4$ may be perceived as a novel type of supramolecular synthon for the assembly of coordination networks.

In contrast to the rich variety of supramolecular synthons that involve hydrogen bonding and other intermolecular interactions,[10] there are only a few examples of the metalloligand type for the construction of coordination networks.[11] By extending our investigation through the use of various aryl and alkyl ethynide ligands, two new supramolecular synthons, $Ag_n{\subset}C_2{-}R{-}C_2{\supset}Ag_n$ (R = *p*-, *m*-, *o*-C_6H_4; $n = 4$, 5)[12] and $R{-}C{\equiv}C{\supset}Ag_n$ (R = aryl or alkyl; $n = 4$, 5),[13] were established, and the coordination modes of the ethynide moieties therein were fully elucidated and classified. By utilizing these supramolecular synthons, along with argentophi-

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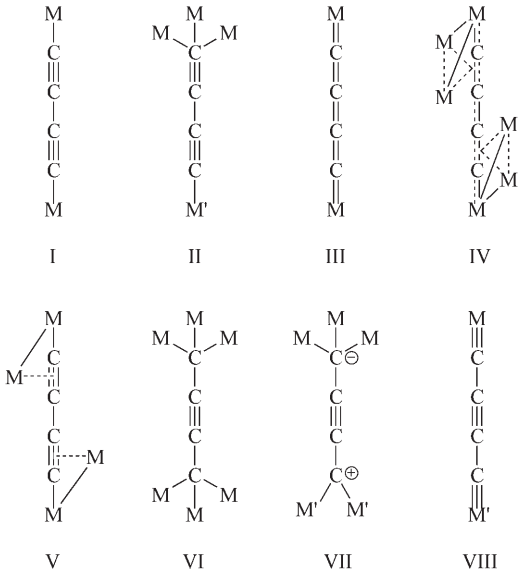
licity, π–π stacking, silver–aromatic interaction, and hydrogen bonding, a series of 1D, 2D, and 3D networks were obtained.

In general, crystalline silver(I) complexes containing the aforementioned supramolecular synthons can be synthesized by dissolving the crude polymeric $[R{-}C{\equiv}C{-}Ag]_n$ compounds in a concentrated aqueous or water/nitrile solution of the corresponding silver salts.

2. Metal Complexes of 1,3-Butadiynediide (C_4^{2-}) and the Supramolecular Synthon $Ag_4{\subset}C{\equiv}C{-}C{\equiv}C{\supset}Ag_4$

The known coordination modes of a naked tetracarbon chain in transition-metal complexes are illustrated in Scheme 1 (modes I–VIII). Linear mode I is a relatively common bonding type that occurs in numerous homometallic (M = Ru,[14] Pt,[15] Fe,[16] Au,[17] Mn,[18] Re,[19] W,[20] Rh[21]) and some heterometallic complexes (M = W, M′ = Rh or Ir;[22a] M = W, M′ = Pt or Ir;[22b] M = Ru, M′ = Hg;[22c] M = Ru, M′ = Au[22d]). Bruce et al. and Yam et al. independently reported mode II in their synthesis of molecular rods[23a] and luminescent materials,[23b,c] respectively. The symmetrical μ_2,μ_2 mode (mode V) also occurs in metal complexes of 1,3-butadiynediide.[24] In mode IV, the tetracarbon chain exhibits extensive electron delocalization, leading to bond-length averaging.[25] Mode III (M = Re)[26] shows a typical cumulenic structure. In modes VI (M = Co),[27] VII (heterometallic, M = Ru, M′ = Fe),[28] and VIII (heterometallic, M = Co, M′ = W),[29] bond shift occurs with interconversion between single and triple bonds, and in the last instance each terminal carbon atom is triply bonded to a metal center.



Scheme 1. Coordination modes of the naked linear tetracarbon (C_4) ligand in metal complexes.

Notably, in all crystalline silver(I) complexes containing 1,3-butadiynediide, the linear $^{-}C{\equiv}C{-}C{\equiv}C^{-}$ ligand invariably exhibits an unprecedented μ_8 coordination mode, each terminal being capped by four silver(I) atoms to form a $[Ag_4C_4Ag_4]$ aggregate. The σ-type and π-type Ag–C interactions play different roles in the formation of the symmetrical or unsymmetrical μ_8 coordination modes (Figure 1). Furthermore, other coexisting anionic and/or neutral ligands also influence the coordination environment of each terminal ethynide, resulting in a butterfly-shaped, barblike, or planar Ag_4 basket. In general, the Ag···Ag distances within the Ag_4 basket are shorter than 3.4 Å (twice the van der Waals radius of the silver atom), suggesting the existence of significant argentophilic interactions.[7,30]

Abstract in Chinese:

近年來，金屬炔基化合物因其結構多樣性以及在非線性光學材料、發光材料和分子線化合物的合成製備中的應用而引起廣泛關注。在進行1,3-丁二炔二負離子銀化合物的結構研究中，我們發現 C_4^{2-} 的 μ_8 配位模式，即每一個末端炔基負離子與四個一價銀原子配位，廣泛且穩定地在此類化合物的結構中出現。因此，我們推斷 $Ag_4{\subset}C{\equiv}C{-}C{\equiv}C{\supset}Ag_4$ 可以作爲超分子合成子應用於一維或多維配位網絡的構建。在本綜述中，我們將介紹一系列芳香環炔基配體和烷基炔基配體的合成及其銀化合物的結構特徵，建立同類型的 $R{-}C{\equiv}C{\supset}Ag_n$ (R = 芳基或烷基; n = 4, 5) 及 $Ag_n{\subset}C_2{-}R{-}C_2{\supset}Ag_n$ (R = *p*-, *m*-, *o*-C_6H_4; n=4, 5) 超分子合成子。我們利用晶體結構數據對炔—銀成鍵方式進行了分類，歸納爲 σ、π 和混合 (σ, π) 三種類型，並結合一些弱相互作用，包括銀–銀親和作用、π–π 堆積、以及氫鍵等構建多種超分子網絡。

Thomas C. W. Mak *received his PhD from The Univ. of British Columbia in 1963. He was a NASA Research Associate (1963–1965) at the Univ. of Pittsburgh and an Assistant Professor (1965–1969) at the Univ. of Western Ontario. In 1969 he joined The Chinese Univ. of Hong Kong, where he is Professor Emeritus and Wei Lun Research Professor. His research interests are in chemical crystallography, with particular focus on supramolecular assembly. He has published over 900 papers. In 2001 he was elected as a member of the Chinese Academy of Sciences.*

Liang Zhao *earned his BS in chemistry from Peking Univ. in 2002 and worked for one year as a Research Assistant in the State Key Laboratory for Structural Chemistry of Unstable and Stable Species at Peking Univ. Subsequently he enrolled at The Chinese Univ. of Hong Kong to pursue his PhD under the guidance of Prof. Thomas C. W. Mak. His research project concentrates on the design, synthesis, and structural characterization of silver(I) complexes containing ethynide and 1,3-butadiynediide ligands.*

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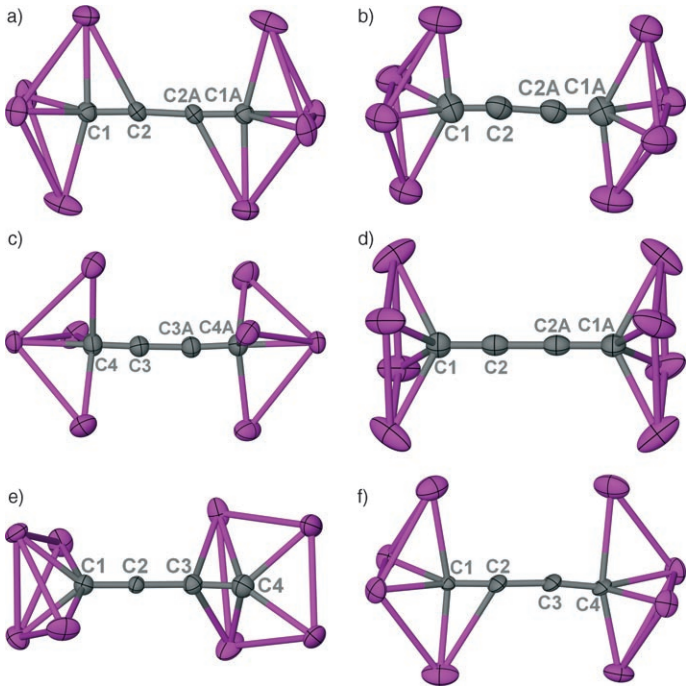

Figure 1. Observed coordination modes of the C_4^{2-} dianion. a) Symmetrical μ_8 coordination mode with two butterfly-shaped baskets in $Ag_2C_4{\cdot}6AgNO_3{\cdot}nH_2O$ ($n=2$, 3). b) Symmetrical μ_8 coordination mode with only Ag–C σ bonds in $Ag_2C_4{\cdot}16AgC_2F_5CO_2{\cdot}6CH_3CN{\cdot}8H_2O$. c) Barb-like μ_8 coordination mode with two linearly coordinated silver–ethynide bonds in $2Ag_2C_4{\cdot}2AgF{\cdot}6AgNO_3{\cdot}H_2O$. d) Symmetrical μ_8 coordination mode with two parallel planar Ag_4 units in $[Ag_{16}(C_4)(C_2F_5CO_2)_{16}(H_2O)_8]{\cdot}2H_3O^+{\cdot}14H_2O$. e) Unsymmetrical μ_8 coordination mode with one terminal butterfly-shaped Ag_4 basket and one terminal planar Ag_4 unit in $Ag_2C_4{\cdot}6AgCF_3CO_2{\cdot}7H_2O$. f) Unsymmetrical μ_8 coordination mode with two butterfly-shaped Ag_4 baskets in $Ag_2C_4{\cdot}4AgNO_3{\cdot}AgPF_2O_2{\cdot}Ag_3PO_4$. In this and subsequent figures, all coexisting anionic and neutral ligands are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

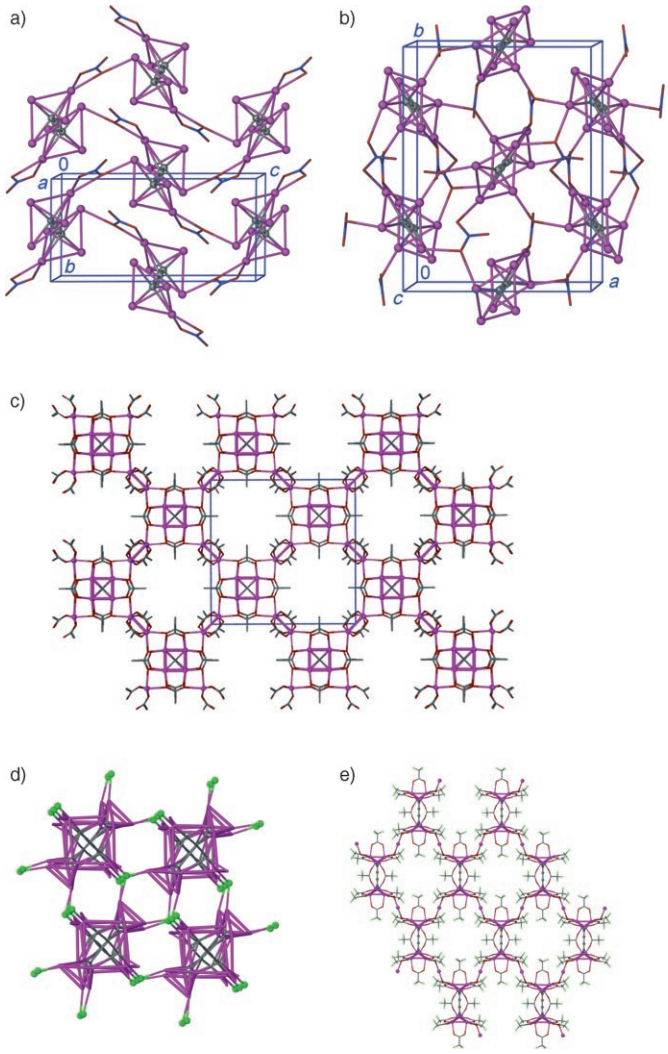

Figure 2. Some examples of 2D and 3D coordination networks in complexes of Ag_2C_4. a) Pseudohexagonal array of $[Ag_4C_4Ag_4]$ aggregates linked by an independent nitrate group into a layer perpendicular to [100] in $Ag_2C_4{\cdot}6AgNO_3{\cdot}2H_2O$. b) Pseudohexagonal array of $[Ag_4C_4Ag_4]$ aggregates connected by eight independent nitrate groups in $Ag_2C_4{\cdot}6AgNO_3{\cdot}3H_2O$. c) (4,4) Network in $[Ag_{16}(C_4)(C_2F_5CO_2)_{16}(H_2O)_8]{\cdot}2H_3O^+{\cdot}14H_2O$ composed of $[Ag_4C_4Ag_4]$ aggregates connected by $[Ag_2(\mu\text{-}O_2CC_2F_5)_2]$ bridging units. d) 3D coordination network in $2Ag_2C_4{\cdot}2AgF{\cdot}6AgNO_3{\cdot}H_2O$ connected by μ_3 fluorine atoms. e) Rosette layer in $Ag_2C_4{\cdot}10AgCF_3CO_2{\cdot}2[(Et_4N)CF_3CO_2]{\cdot}4(CH_3)_3CCN$ composed of $[Ag_4C_4Ag_4]$ aggregates connected by one external silver atom and two trifluoroacetate groups.

Furthermore, the $[Ag_4C_4Ag_4]$ aggregates can be further linked by coexisting anionic ligands, such as nitrate or perfluorocarboxylic groups, to produce a series of 2D or 3D coordination networks. As illustrated in the structure of $Ag_2C_4{\cdot}6AgNO_3{\cdot}2H_2O$,[9] the $[Ag_4C_4Ag_4]$ aggregates arranged in a pseudohexagonal array are connected by one nitrate group acting in the μ_3-*O*,*O*′,*O*″ and *O*,*O*′ chelating modes to form a thick layer perpendicular to [100] (Figure 2a). Linkage of adjacent layers by the two remaining independent nitrate groups, abetted by O–H···O(nitrate) hydrogen bonding involving the aqua ligand, then generates a 3D network. Similarly, the $[Ag_4C_4Ag_4]$ aggregates in $Ag_2C_4{\cdot}6AgNO_3{\cdot}3H_2O$ constitute a pseudohexagonal array perpendicular to [001], giving rise to a thick layer consolidated by eight nitrate groups (Figure 2b). The layers are further interconnected by the four remaining nitrate groups plus six aqua ligands to yield a 3D network.

In the crystal structure of $[Ag_{16}(C_4)(C_2F_5CO_2)_{16}(H_2O)_8]{\cdot}2H_3O^+{\cdot}14H_2O$, each $[Ag_4C_4Ag_4]$ aggregate connects with eight such units via $[Ag_2(\mu\text{-}O_2CC_2F_5)_2]$ moieties to form a (4,4) network (Figure 2c). Through the linkage of the C_4 carbon chain perpendicular to this planar network, a series of infinite channels are aligned along the [001] direction, which fully accommodate the C_2F_5 moieties of the pentafluoropropionate ligands.

In the crystal structure of triple salt $2Ag_2C_4{\cdot}2AgF{\cdot}6AgNO_3{\cdot}H_2O$, the $[Ag_4C_4Ag_4]$ aggregates are mutually connected through the linkage of nitrate groups and sharing of silver atoms to form a silver column. The fluorine atoms then bridge these silver columns through the μ_3 mode to produce a structurally robust 3D coordination network (Figure 2d).

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With an external silver atom and two carboxylic oxygen atoms as bridging groups, the $[Ag_4C_4Ag_4]$ aggregates within the complex $Ag_2C_4{\cdot}10AgCF_3CO_2{\cdot}2[(Et_4N)CF_3CO_2]{\cdot}4(CH_3)_3CCN$ are linked to form a rosette layer, in which the C_4^{2-} dianion acts as the shared border of two petals (Figure 2e).

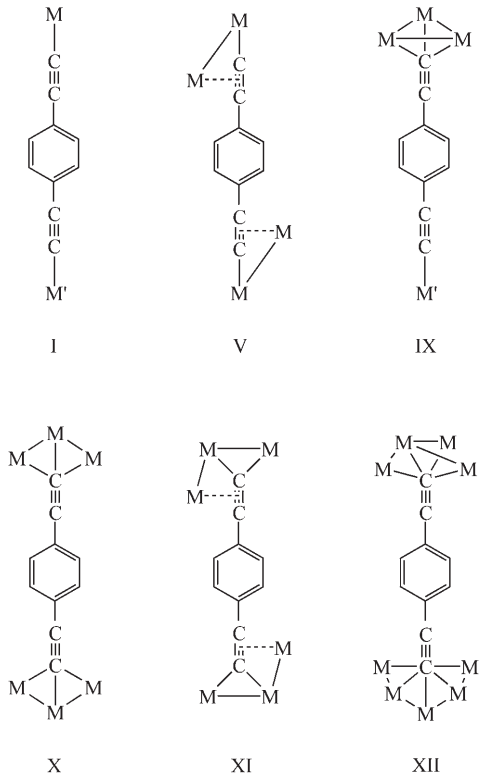
The structural study of silver(I) complexes containing 1,3-butadiynediide mentioned above suggests that the $Ag_4{\subset}C_2{-}R{-}C_2{\supset}Ag_4$ moiety may be conceived as a supramolecular synthon for the assembly of coordination networks, by analogy to the plethora of well-known supramolecular synthons that involve hydrogen bonding and other weaker intermolecular interactions.[10]

3. Metal Complexes of Isomeric Phenylenediethynides and the Supramolecular Synthons $Ag_n{\subset}C_2{-}R{-}C_2{\supset}Ag_n$ (R=*p*-, *m*-, *o*-C_6H_4; $n=4, 5$)

π–π Stacking is an important noncovalent intermolecular interaction that commonly dictates self-assembly when extended structures are formed from building blocks with aromatic moieties.[31] To establish the general utility of a new class of supramolecular synthons of the type $Ag_n{\subset}C_2{-}R{-}C_2{\supset}Ag_n$, the *p*-phenylene ring was introduced as the bridging R group on the grounds that, 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 π–π stacking and silver–aromatic interactions.[32] The isomeric *m*- and *o*-phenylenediethynides were also investigated to probe the influence of varying the relative orientation of the pair of terminal ethynide groups.

The reported coordination modes of the transition-metal complexes of *p*-phenylenediethynide and its derivatives are presented in Scheme 2 (modes I, V, IX–XI). The mode that occurs most frequently is μ_1,μ_1 mode I, in which the terminal metal atoms can be palladium,[33] iridium,[34] platinum,[35] gold,[3a,36] rhodium,[37] or manganese[38] in homometallic complexes, and also iron and rhenium in heterometallic complexes.[39] The symmetrical μ_2,μ_2 mode V was reported recently by Lalinde and co-workers through the reaction of $[\{Pt(PPh_3)_2\}_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}(1,4\text{-}HC{\equiv}C)_2C_6H_4\}]$ with *cis*-$[PtR_2S_2]$ complexes.[40] The higher coordination μ_3 modes IX,[41] X, and XI[42] of the ethynide moiety observed in copper and silver complexes have been reported by Yam et al.[23b,c]

In the crystal structure of $2[Ag_2(p\text{-}C{\equiv}CC_6H_4C{\equiv}C)]{\cdot}11AgCF_3CO_2{\cdot}4CH_3CN{\cdot}2CH_3CH_2CN$,[12] the *p*-phenylenediethynide ligand exhibits the highest ligation number reported to date for the ethynide moiety in an unprecedented μ_5-η^1 mode XII, as opposed to three or fewer in other *p*-phenylenediethynide transition-metal complexes (see above). The Ag_{14} aggregate, which is 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 π–π stacking, is connected to its symmetry equivalents generated



Scheme 2. Coordination modes of the *p*-phenylenediethynide dianion in transition-metal complexes.

from one of the sites located either between phenylene rings IA and I or 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 of two trifluoroacetate groups (Figure 3a).

In contrast to the single known μ_1,μ_1 coordination mode of *m*-phenylenediethynide in its transition-metal complexes,[38,43] this ligand exhibits different terminal ethynide bonding modes, namely, μ_4-$\eta^1,\eta^1,\eta^1,\eta^1$ and μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$, in the crystal structure of $Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C){\cdot}6AgCF_3CO_2{\cdot}3CH_3CN{\cdot}2.5H_2O$.[12] 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, which is further consolidated by π–π interaction between each pair of adjacent *m*-phenylene rings (Figure 3b).

In the crystal structure of $3[Ag_2(o\text{-}C{\equiv}CC_6H_4C{\equiv}C)]{\cdot}14AgCF_3CO_2{\cdot}2CH_3CN{\cdot}9H_2O$,[12] the ethynide moieties bond to silver atoms through 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-η^1,η^1,η^1, η^1,η^2 (Figure 3c), in contrast to the simple μ_1,μ_1 mode in known *o*-phenylenediethynide transition-metal complexes.[44] 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 π–π stacking. Bridged by an external silver atom through Ag···Ag interaction and three oxygen atoms of two independent trifluoroacetate

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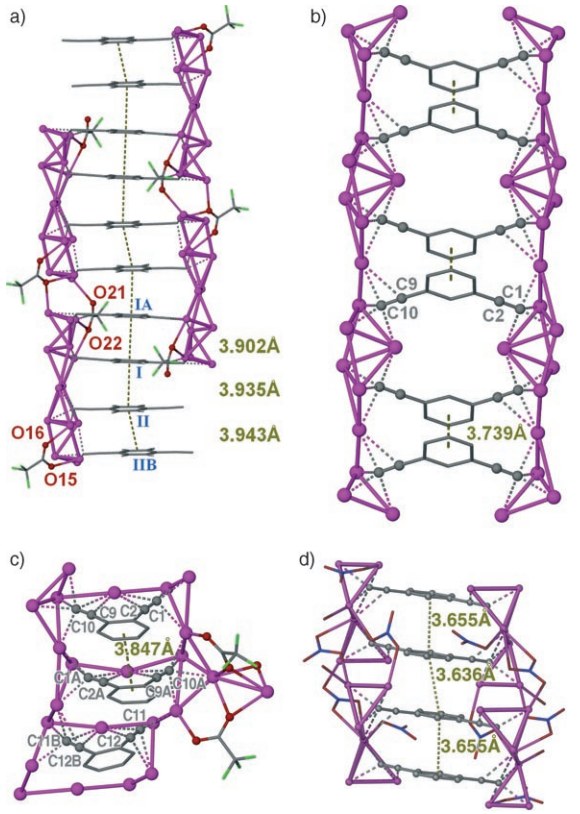

Figure 3. a) Broken silver(I) double chain in $2[Ag_2(p\text{-}C{\equiv}CC_6H_4C{\equiv}C)]\cdot 11AgCF_3CO_2\cdot 4CH_3CN\cdot 2CH_3CH_2CN$ composed of discrete Ag_{14} segments connected by trifluoroacetate groups and stabilized by continuous π–π stacking between parallel *p*-phenylene rings. b) Silver double chain in $Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)\cdot 6AgCF_3CO_2\cdot 3CH_3CN\cdot 2.5H_2O$ assembled by argentophilic and π–π interactions between adjacent pairs of *m*-phenylene rings. c) Broad silver chain in $3[Ag_2(o\text{-}C{\equiv}CC_6H_4C{\equiv}C)]\cdot 14AgCF_3CO_2\cdot 2CH_3CN\cdot 9H_2O$ through the fusion of two narrow silver chains and stabilized by discontinuous π–π stacking between two *o*-phenylene rings. d) Broken silver(I) double chain in $Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)]\cdot 5AgNO_3\cdot 3H_2O$ connected by nitrate groups and stabilized by continuous π–π stacking between parallel *m*-phenylene rings. Color scheme for atoms: Ag = purple, C = gray, O = red, N = blue, F = green.

groups and one water molecule, the silver columns are linked to form a wavelike layer held together by Ag···Ag interaction with *o*-phenylene groups protruding on both sides.

In the crystal structures of the above three complexes, the decreasing separation of the pair of ethynide groups is accompanied by strengthened argentophilic interaction at the expense of weakened π–π stacking to yield sequentially a broken double chain, a double chain, and a silver layer. When the pair of ethynide vectors make an angle of 60°, sharing of a common silver atom for the Ag_n caps occurs in the *o*-phenylenediethynide complex. The structural correlation between various silver ethynide supramolecular synthons affords a rationale for the dominant manifestion of $C_2@Ag_n$ ($n \leq 10$) polyhedra in Ag_2C_2 complexes. If the linear $^-C{\equiv}C{-}C{\equiv}C^-$ chain was 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 (Figure 4).

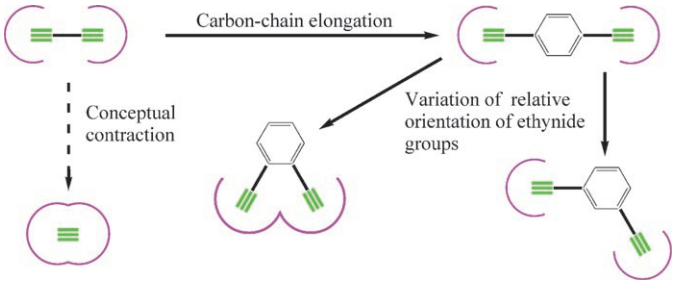

Figure 4. Structural relationship between the supramolecular synthons $Ag_4{\subset}C{\equiv}C{-}C{\equiv}C{\supset}Ag_4$, $Ag_n{\subset}C_2{-}R{-}C_2{\supset}Ag_n$ (R = *p*-, *m*-, *o*-C_6H_4; $n = 4, 5$), and $C_2@Ag_n$ ($n = 6$–10). The circular arc represents an Ag_n ($n = 4, 5$) basket.

In the double salt $Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)]\cdot 5AgNO_3\cdot 3H_2O$, two Ag_7 aggregates are arranged in a face-to-face fashion and bridged by two *m*-phenylenediethynide ligands, which are further stabilized by continuous π–π stacking. Linkage of such $[Ag_{14}(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)_2]$ units by interunit π–π interaction and nitrate groups produces a broken silver(I) double chain (Figure 3d). With reference to $Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)\cdot 6AgCF_3CO_2\cdot 3CH_3CN\cdot 2.5H_2O$, replacement of the trifluoroacetate counteranion by nitrate breaks up the silver double chain, and the π–π interaction between *m*-phenylene rings is converted from pairwise to continuous.

4. Assembly of Arylethynide Supramolecular Synthon $R{-}C_2{\supset}Ag_n$ (R = C_6H_5, 4-MeC_6H_4, 3-MeC_6H_4, 2-MeC_6H_4, 4-*t*BuC_6H_4; $n = 4, 5$)

Although aromatic π–π interaction is popularly employed to build up multidimensional structures through three dominant modes involving face-to-face, offset face-to-face, and edge-to-face contacts between a pair of aromatic rings, the prediction of how the aromatic rings are packed in a given crystal lattice remains a formidable challenge.[45] We therefore undertook to investigate the π–π stacking in the crystal structures of silver(I) complexes of phenylethynide and its derivatives with different substituents (methyl, *tert*-butyl) in various positions (*o*-, *m*-, *p*-) on the aromatic ring.

The most-common coordination modes of the phenylethynide ligand (including those with substituents on the aromatic ring) in transition-metal complexes are μ_1 and μ_2-η^1,η^2 (Scheme 3, modes I and V), which have been extensively reviewed.[1] The higher coordination modes, such as μ_3 (modes Xa,[46] Xb,[47] and Xc[48]) and μ_4 (modes XIa,[49] XIb,[50] and XIc[51]), have also been reported.

Notably, in the crystal structure of $2AgC{\equiv}CC_6H_5\cdot 6AgC_2F_5CO_2\cdot 5CH_3CN$,[13] one ethynide moiety, C1≡C2, is capped by a square-pyramidal Ag_5 basket in an unprecedented μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2$ coordination mode (mode XIIa), and the other one, C9≡C10, by a butterfly-shaped Ag_4 basket in a μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$ coordination (Figure 5). Two inversion-related Ag_5 baskets share an edge to produce an Ag_8 aggregate, whereas another Ag_8 aggregate results from fusion of a pair

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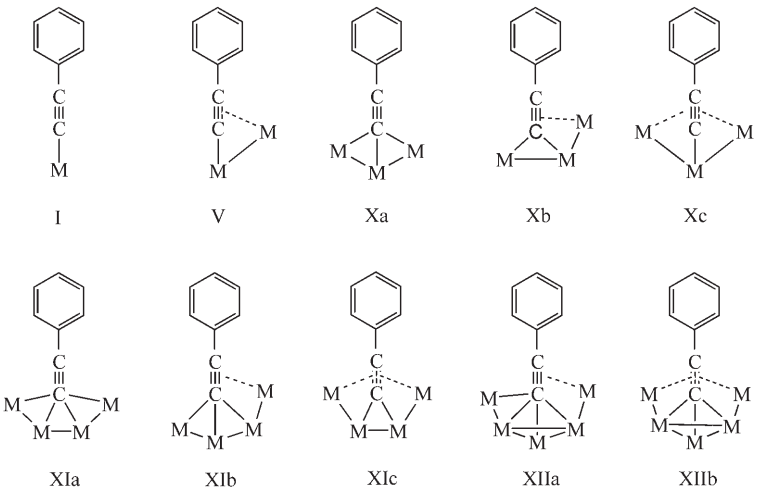

Scheme 3. Coordination modes of the phenylethynide ligand ($C_6H_5C{\equiv}C^-$) in transition-metal complexes.

of inversion-related Ag_4 baskets. Two adjacent Ag_8 aggregates are linked by two pentafluoropropionate groups through μ_3-*O*,*O*′,*O*′ and μ_2-*O*,*O*′ coordination modes to generate an infinite column along the [111] direction. No π–π interaction was observed in this complex.

In an attempt to achieve an ordered arrangement of the aromatic rings of the phenylethynide ligands in supramolecular assembly, the quaternary ammonium salt $(BzMe_3N)BF_4$ (Bz = benzyl) was introduced as an additive in crystallization, with the anticipation that its benzyl group would serve as a π–π induction template. In the resulting complex $AgC{\equiv}CC_6H_5{\cdot}3AgCF_3CO_2{\cdot}CH_3CN$,[13] an infinite array of parallel phenyl rings stabilized by π–π stacking (center-to-center distance 4.189 Å) indeed occurs (Figure 5). Furthermore, a unique μ_5-$\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode (mode XIIb) of the phenylethynide group was observed for the first time, leading to the formation of a capping square-pyramidal Ag_5 basket. Interestingly, the Ag_5 baskets are fused by argentophilic interactions through square edge-sharing to form an infinite coordination column along the [100] direction, with continuous π–π stacking of phenyl rings lying on the same side of the column. This type of π–π stacking matches the stacking mode in the polymeric starting material $[AgC{\equiv}CC_6H_5]_n$, whose polymeric chainlike structure was determined by powder XRD recently.[1k]

Upon replacement of the phenyl group by substituted phenyl groups, the π–π stacking between two phenyl rings was broken gradually by varying the size of the substituent and its position (Figure 6). In the crystal structure of $2AgC{\equiv}CC_6H_4Me\text{-}4{\cdot}6AgCF_3CO_2{\cdot}1.5CH_3CN$, the methyl group has negligible influence on the formation of the silver column stabilized by π–π stacking, which is almost identical with that in $AgC{\equiv}CC_6H_5{\cdot}3AgCF_3CO_2{\cdot}CH_3CN$. In contrast, when the bulky *tert*-butyl group was introduced in the 4-position to form the complex $AgC{\equiv}CC_6H_4t\text{Bu-}4{\cdot}3AgCF_3CO_2{\cdot}CH_3CN$,

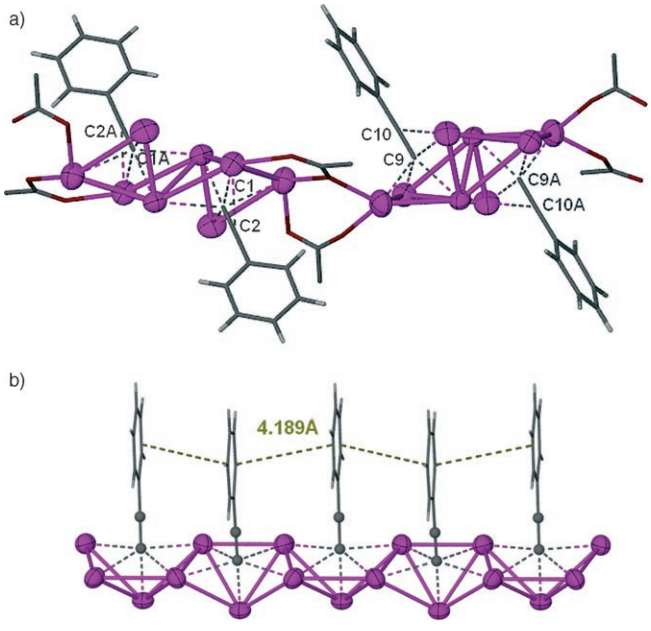

Figure 5. a) Coordination modes of two independent phenylethynide ligands in $2AgC{\equiv}CC_6H_5{\cdot}6AgC_2F_5CO_2{\cdot}5CH_3CN$. b) Coordination mode of the $C_6H_5C{\equiv}C^-$ ligand in $AgC{\equiv}CC_6H_5{\cdot}3AgCF_3CO_2{\cdot}CH_3CN$. The silver column is connected by edge sharing between adjacent square-pyramidal Ag_5 aggregates, and continuous π–π stacking of phenyl rings occurs on only one side of the column. Thermal ellipsoids are drawn at the 50% probability level.

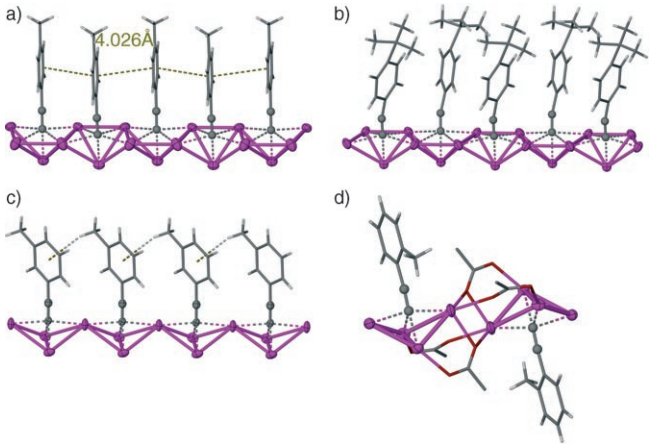

Figure 6. a) Silver column in $2AgC{\equiv}CC_6H_4Me\text{-}4{\cdot}6AgCF_3CO_2{\cdot}1.5CH_3CN$ connected by the fusion of square-pyramidal Ag_5 baskets and stabilized by continuous π–π stacking of phenyl rings. b) Similar silver column in $AgC{\equiv}CC_6H_4t\text{Bu-}4{\cdot}3AgCF_3CO_2{\cdot}CH_3CN$ with disordered *tert*-butylphenyl groups. c) Vertex-sharing silver chain in $AgC{\equiv}CC_6H_4Me\text{-}3{\cdot}2AgCF_3SO_3$ stabilized by C–H···π interactions. d) Coordination chain in $AgC{\equiv}C\text{-}C_6H_4Me\text{-}2{\cdot}4AgCF_3CO_2{\cdot}H_2O$ through the connection of butterfly-shaped Ag_4 baskets by four trifluoroacetate groups. Thermal ellipsoids are drawn at the 50% probability level.

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the π–π stacking system was totally interrupted despite the formation of a similar silver column. On the other hand, substitution of the methyl group at different positions on the phenyl ring also influences the strength of π–π interaction. In the crystal structure of $AgC{\equiv}CC_6H_4Me\text{-}3\cdot 2AgCF_3SO_3$, not only was the strength of π–π stacking sharply decreased, the constitution of the silver chain was also transformed from edge-sharing to vertex-sharing. Eventually, use of the 2-methylphenylethynide ligand broke the π–π stacking in $AgC{\equiv}CC_6H_4Me\text{-}2\cdot 4AgCF_3CO_2\cdot H_2O$ to yield a coordinated chain connected by trifluoroacetate groups.

The stepwise placement of the methyl substituent closer to the ethynide moiety in the series of silver *n*-methylphenylethynide ($n=4$, 3, 2) complexes lowered the ligation number of the ethynide moiety from five to four. Accordingly, the linkage mode of adjacent Ag_n baskets changed from edge-sharing, through vertex-sharing, to bridging by a pair of trifluoroacetate groups, leading to a silver(I) column, a silver chain, and a linear coordination polymer, respectively. The interactions between substituted phenyl rings within these three complexes were concomitantly weakened from π–π stacking in the 4-methyl complex, through C–H···π interaction in the 3-methyl complex, to no interaction in the 2-methyl complex. In summary, π–π stacking in silver(I) phenylethynide complexes can be fine-tuned by altering the substituents and their positions on the phenyl ring, resulting in modification of the linkage mode between $Ar{-}C{\equiv}C{\supset}Ag_n$ ($n=4$, 5) supramolecular synthons.

5. Metal Complexes of *tert*-butylethynide and Assembly of Supramolecular Synthon $t\text{BuC}_2{\supset}\text{Ag}_n$ ($n=4$, 5)

Although the *tert*-butylethynide ($t\text{BuC}{\equiv}\text{C}^-$) ligand occurs in numerous transition-metal complexes, in which it exhibits bonding modes ranging from simple μ_1 to relatively complicated μ_4 types,[52–56] the Group 11 metal *tert*-butylethynide complexes are seldom characterized due to the poor solubility of their polymeric forms $[t\text{BuC}{\equiv}\text{CM}]_n$ (M = Cu, Ag, Au). In 2001, Mingos and co-workers utilized quaternary ammonium chloride or bromide as a template to direct the formation of the cationic cage $[Ag_{14}(C{\equiv}Ct\text{Bu})_{12}X]^+$.[52g,i] Herein we used a concentrated aqueous solution of silver(I) trifluoroacetate to dissolve crude polymeric $[t\text{BuC}{\equiv}\text{CAg}]_n$ and generate the supramolecular synthon $t\text{Bu}{-}C{\equiv}C{\supset}Ag_n$ ($n=4$, 5). In the ensuing study, we focused on the influence of nitrile ligands on the coordination skeletons of ethynide moieties and the configuration of coordination networks.

As shown in Figure 7a, two butterfly-shaped Ag_4 baskets each capping an ethynide moiety in $AgC{\equiv}Ct\text{Bu}\cdot 3AgCF_3CO_2\cdot H_2O$ are connected by two trifluoroacetate groups to form a building unit, and such units are further linked by other trifluoroacetate groups to generate a 2D coordination network.

In the crystal structure of $AgC{\equiv}Ct\text{Bu}\cdot 6AgCF_3CO_2\cdot 2CH_3CN\cdot 6H_2O$ (Figure 7b),[13] the ethynide moiety C1≡C2,

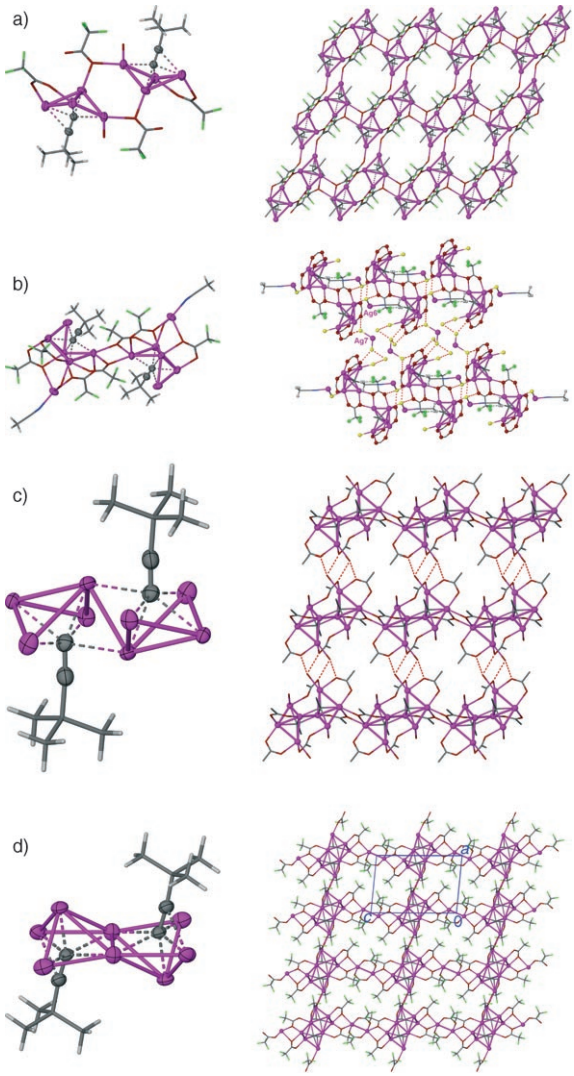

Figure 7. a) Left: Coordination skeleton of the $t\text{BuC}{\equiv}\text{C}^-$ anion in $AgC{\equiv}Ct\text{Bu}\cdot 3AgCF_3CO_2\cdot H_2O$. Right: 2D coordination network connected by trifluoroacetate groups in the μ_3-*O*,*O*′,*O*′ mode. b) Left: Coordination mode of $t\text{BuC}{\equiv}\text{C}^-$ in $AgC{\equiv}Ct\text{Bu}\cdot 6AgCF_3CO_2\cdot 2CH_3CN\cdot 6H_2O$. Two $t\text{Bu}{-}C{\equiv}C{\supset}Ag_5$ units are connected by two trifluoroacetate groups in the μ_3-*O*,*O*′,*O*′ mode to form the building block $Ag_5(\mu_3\text{-}\eta^1,\eta^2\text{-}CF_3CO_2)_2Ag_5$. Right: Layer structure linked by two weak hydrogen bonds and silver atom Ag6 between two building units; further connection is provided by external silver atom Ag7 and the remaining aqua ligands (yellow balls). c) Left: Ag_8 aggregate in $AgC{\equiv}Ct\text{Bu}\cdot 3AgCF_3CO_2\cdot CH_3CH_2CN\cdot 2H_2O$ through slanted-edge sharing of two Ag_5 caps. Right: (4,4) Network connected by coordination bonds along the *a* direction and hydrogen bonding along the *b* direction. d) Left: Ag_8 aggregate in $AgC{\equiv}Ct\text{Bu}\cdot 4AgCF_3CO_2\cdot(CH_3)_3CCN\cdot 2H_2O$ through square-edge sharing of two Ag_5 caps. Right: (4,4) Network linked by one trifluoroacetate group along [001] and one $[Ag_2(\mu_2\text{-}CF_3CO_2)_2]$ bridging unit along the *a* direction. Thermal ellipsoids are drawn at the 50% probability level.

which adopts the $\mu_5\text{-}\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode, coordinates to a square-pyramidal Ag_5 basket. Linkage of two Ag_5 baskets by a pair of inversion-related trifluoroacetate groups produces an $Ag_5(\mu_3\text{-}\eta^1,\eta^2\text{-}CF_3CO_2)_2Ag_5$ building unit, and such units are connected by one aqua ligand and silver atom Ag6 through hydrogen bonding to generate a winding infin-

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ite chain along the *a* direction. By utilizing the external silver atom Ag7 and the remaining water molecules as bridging groups, adjacent infinite chains are cross-linked along the [001] direction through hydrogen bonds to generate a 2D hydrogen-bonding network parallel to the (010) plane.

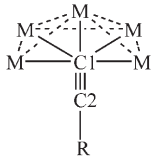
A similar 2D network was observed in the crystal structure of $AgC{\equiv}C\textit{t}Bu{\cdot}3AgCF_3CO_2{\cdot}CH_3CH_2CN{\cdot}2H_2O$, in which the more bulky propionitrile ligand promotes the linkage of two square-pyramidal Ag_5 aggregates through sharing of one slanted edge (Figure 7c). These Ag_8 aggregates are further connected by trifluoroacetate groups to produce a coordination chain, which is bridged by a large number of hydrogen bonds to yield a 2D network. When the bulkier nitrile ligand $\textit{t}BuC{\equiv}N$ was employed, two Ag_5 aggregates in $AgC{\equiv}C\text{-}\textit{t}Bu{\cdot}4AgCF_3CO_2{\cdot}(CH_3)_3CCN{\cdot}2H_2O$ become even closer together by sharing one basal edge (Figure 7d). The resulting Ag_8 aggregates with two *tert*-butylethynide ligands are linked by one trifluoroacetate group along the [001] direction and one $[Ag_2(\mu_2\text{-}CF_3CO_2)_2]$ bridging unit to form a (4,4) coordination network.

The different coordination skeletons and 2D networks of the four complexes above may be rationalized by the fact that 1) the more bulky and hydrophobic nitrile ligands CH_3CH_2CN and $(CH_3)_3CCN$ hinder the approach of the trifluoroacetate groups and aqua ligands to coordination sites, leading to two separate Ag_5 aggregates coalescing into one Ag_8 aggregate by sharing one pyramidal or square edge, and 2) the peripheral silver atoms and trifluoroacetate groups, blocked off by the bulky nitrile groups, can connect mutually to act as bridging units to generate a 2D coordination network, in contrast to the use of hydrogen bonds in the acetonitrile complex.

6. Summary and Outlook

We have carried out an investigation of the HLNs of the 1,3-butadiynediide, phenylenediethynide, phenylethynide, and *tert*-butylethynide ligands through the synthesis and structural characterization of their silver(I) complexes, which led to the establishment of a series of new supramolecular synthons symbolized by $Ag_4{\subset}C{\equiv}C{-}C{\equiv}C{\supset}Ag_4$, $Ag_n{\subset}C_2{-}R{-}C_2{\supset}Ag_n$ ($R = p\text{-}, m\text{-}, o\text{-}C_6H_4$; $n = 4, 5$), and $R{-}C{\equiv}C{\supset}Ag_n$ (R = aryl or alkyl; $n = 4, 5$). The silver–ethynide bonding interactions within these supramolecular synthons can be classified as σ, π, and mixed (σ,π) types according to the measured Ag–C bond lengths and C≡C–Ag bond angles. The values found in some square-pyradimal Ag_5 baskets reported in this review are summarized in Table 1. The interplay of ethynide–silver bonding, argentophilicity, and π–π interaction highlights the complexity and challenge in programming the supramolecular assembly of metal–organic networks.

Table 1. Classification of different types of silver–ethynide interactions within the square-pyramidal Ag_5 baskets in some silver aryl- and alkylethynide complexes.



Complex	Bond type	Bond lengths [Å] and angles [°]			
		C1–M	C2–M	M–M	C2≡C1–M
$2AgC{\equiv}CC_6H_5{\cdot}6AgC_2F_5CO_2{\cdot}5CH_3CN$[13]	σ	2.21(2)	3.396	2.843(1)–3.351(2)	167(1)
	π	2.40(1)	2.69(1)		90.3(9)
	(σ,π)	2.48(1)–2.71(1)	2.858–3.109		97.7–112
$AgC{\equiv}CC_6H_5{\cdot}3AgCF_3CO_2{\cdot}CH_3CN$[13]	σ	2.06(2)	3.269	3.017(2)–3.215(2)	176(2)
	π	2.426(7)	2.772		93.1(7)
	(σ,π)	2.61(1)	3.094		102(1)
$2AgC{\equiv}CC_6H_4Me\text{-}4{\cdot}6AgCF_3CO_2{\cdot}1.5CH_3CN$	σ	2.09(2)–2.14(2)	3.277–3.290	2.975(5)–3.279(7)	177(2)–180(2)
	π	2.415(9)–2.43(1)	2.757–2.758		92.7–94.5
	(σ,π)	2.60(2)–2.66(2)	3.059–3.076		99.9–100.9
$AgC{\equiv}CC_6H_4\textit{t}Bu\text{-}4{\cdot}3AgCF_3CO_2{\cdot}CH_3CN$	σ	2.09(2)	3.283	2.890(9)–3.120(7)	163(3)
	π	2.53(3)	2.644		81.7
	(σ,π)	2.31(3)–2.58(3)	2.845–3.283		97.3–115.4
$AgC{\equiv}C\textit{t}Bu{\cdot}6AgCF_3CO_2{\cdot}2CH_3CN{\cdot}6H_2O$	σ	2.187(7)	3.358	2.873(1)–3.130 (1)	171.9(6)
	π	2.346(7)–2.375(7)	2.740–2.792		94.9(6)–99.4(5)
	(σ,π)	2.312(7)–2.375(7)	2.902–2.913		105.0(6)–108.0(6)
$AgC{\equiv}C\textit{t}Bu{\cdot}3AgCF_3CO_2{\cdot}CH_3CH_2CN{\cdot}2H_2O$	σ	2.283(7)	3.427	2.808(1)–3.105(1)	159.5(6)
	π	2.576(7)	2.876		91.9(5)
	(σ,π)	2.289(7)–2.341(7)	2.724–3.124		95.2–121.1
$AgC{\equiv}C\textit{t}Bu{\cdot}4AgCF_3CO_2{\cdot}(CH_3)_3CCN{\cdot}2H_2O$	σ	2.142(4)	3.301	2.859(1)–3.151(1)	157.3(4)
	π	2.362(5)–2.370(4)	2.539–2.765		83.5(3)–95.7(3)
	(σ,π)	2.441(4)–2.465(4)	3.073–3.190		108.2(3)–117.3(3)

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