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Novel μ_5-Coordination Modes of Aryl and Alkyl Ethynides and Classification of Metal–Ligand Interactions in Silver(I) Complexes

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Abstract: Novel μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2$ and μ_5-$\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ coordination modes of alkyl and aryl ethynide moieties are found in silver(I) complexes **1**–**5**, and the metal–ligand distances can be classified into σ, π and mixed (σ,π) types. With the consistent square-pyramidal capping Ag_5 baskets of the ethynide moiety as supramolecular synthons, a series of two- and three-dimensional coordination networks are obtained.

Keywords: argentophilicity • coordination modes • coordination polymers • metal–ligand interactions • silver complexes

Introduction

Recent interest in the study of d^{10}-metal ethynide complexes is spurred by their structural diversity[1] and potential application as photoluminescent materials.[2] Diverse coordination modes of the ethynide moiety, abetted by metallophilic interactions[3] between coinage metal centers (Cu, Ag, and Au), usually lead to the formation of clusters, multinuclear aggregates, or extended solid-state architectures.[4] However, although a plethora of coinage metal ethynide complexes are known, the significant metal–ethynide interactions and their classification have not been thoroughly investigated.

Our previous studies on double and multiple salts of silver(I) acetylenediide (Ag_2C_2) and silver(I) 1,3-butadiynediide (Ag_2C_4) demonstrated that each terminal carbon atom of an ethynide moiety can at most bind to four silver atoms.[5] This stimulated us to carry out similar studies on silver(I) complexes of aryl and alkyl ethynides. Herein we report the synthesis and structural characterization of the silver(I) complexes **1**–**5**, in which the aryl or alkyl ethynide ligand exhibits the highest ligation number[6] to date.

$2\,AgC{\equiv}CC_6H_5 \cdot 6\,AgC_2F_5CO_2 \cdot 5\,CH_3CN$ (**1**)

$AgC{\equiv}CC_6H_5 \cdot 3\,AgCF_3CO_2 \cdot CH_3CN$ (**2**)

$AgC{\equiv}CC_6H_4C{\equiv}N\text{-}4 \cdot 3\,AgCF_3CO_2 \cdot x\,H_2O$ ($x = 0.3$) (**3**)

$AgC{\equiv}C\mathit{t}Bu \cdot 6\,AgCF_3CO_2 \cdot 2\,CH_3CN \cdot 6\,H_2O$ (**4**)

$AgC{\equiv}C\mathit{t}Bu \cdot 2\,Ag_2(O_2CCF_2CF_2CO_2) \cdot 9\,H_2O$ (**5**)

Results and Discussion

The known coordination modes of the phenylethynide anion in complexes containing Group 11 metal ions are illustrated in Scheme 1. The most common ones are μ_1 (mode **I**)[7] and μ_2-η^1,η^2 (**II**),[8] and the higher modes μ_3-η^1,η^1,η^1 (**IIIa**),[9] μ_3-η^1,η^1,η^2 (**IIIb**),[10] μ_4-$\eta^1,\eta^1,\eta^1,\eta^1$ (**IVa**, M = Ag, M′ = Cu),[11a] and μ_4-$\eta^1,\eta^1,\eta^2,\eta^2$ (**IVb**, M = Cu)[11b] have been reported. As to the *tert*-butylethynide anion, μ_3- and μ_4-coordination modes are found in some organometallic complexes.[12]

To obtain silver–ethynide aggregates with higher ligation numbers and more complex coordination modes of the ethynide moiety, we synthesized the crude polymeric compounds $[AgC{\equiv}CC_6H_5]_n$ (**6**),[13] $[AgC{\equiv}CC_6H_4C{\equiv}N\text{-}4]_n$ (**7**), and $[AgC{\equiv}C\mathit{t}Bu]_n$ (**8**) as starting materials. Complex **7** was synthesized and characterized for the first time. Generally, compound **8** can be prepared from the reaction of a silver salt with *tert*-butylacetylene in the presence of NEt_3.[14] We report here a new synthesis of **8** by the reaction of silver nitrate with an equimolar quantity of lithium *tert*-butylethynide (generated in situ from *tert*-butylacetylene and *n*BuLi) in THF under an inert atmosphere of nitrogen at room temperature. The new

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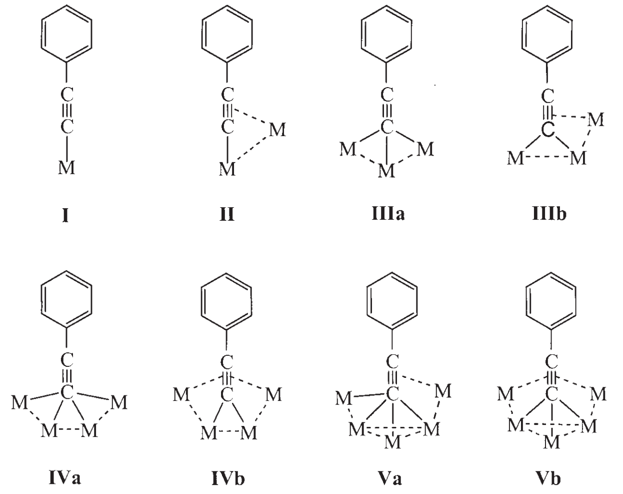

Scheme 1. Coordination modes of the phenylethynide anion in transition metal complexes. (Complexes exhibiting modes **II** to **IVb** can be heterometallic).

complexes **1**–**5** were then obtained from the crystallization of the corresponding crude polymeric silver ethynide in a concentrated aqueous solution of $AgCF_3CO_2$ or $AgC_2F_5CO_2$ plus $AgBF_4$, the latter being used to increase the silver(I) ion concentration.[15] A solvent mixture of water and acetonitrile was used to improve the solubility of **6**–**8** in the syntheses.

2 AgC≡CC$_6$H$_5$·6 AgC$_2$F$_5$CO$_2$·5 CH$_3$CN (1): In the crystal structure of **1**, there are two independent phenylethynide anions. The ethynide group composed of C1 and 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 **Va** in Scheme 1),[16] and the other one comprising C9 and C10 by a butterfly-shaped Ag_4 basket in a μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$ coordination mode, as shown in Figure 1. With an inversion center located at the center of the Ag1···Ag1A bond, two Ag_5 baskets share an edge to engender a Ag_8 aggregate, whereas another Ag_8 aggregate results from fusion of a pair of inversion-related Ag_4 baskets. Two adjacent Ag_8 aggregates are linked by two pentafluoropropiolate groups (O7–O8 and O11–O12) via μ_3-O,O′,O′ and μ_2-O,O′ coordination modes, respectively, to generate an infinite column along the [111] direction. The other four pentafluoropropiolate groups are all bonded to one Ag–Ag edge of the Ag_4 or Ag_5 baskets by the μ_2-O,O′ mode, and the five independent acetonitrile groups (N1–N5) coordinate to different silver atoms (Figure 2).

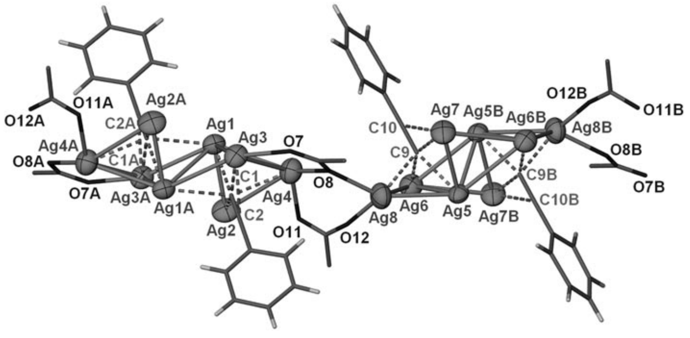

Figure 1. Atom labeling (50% thermal ellipsoids) and coordination modes of the independent phenylethynide ligands in **1**. Adjacent Ag_8 aggregates are connected by two pentafluoropropionate groups (O7–O8 and O11–O12). Other pentafluoropropionate groups, acetonitrile molecules, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1–C2 1.21(2), C9–C10 1.17(2), Ag···Ag 2.843(1)–3.351(2). Symmetry code: A: $-x, -y, -z$; B: $1-x, 1-y, 1-z$.

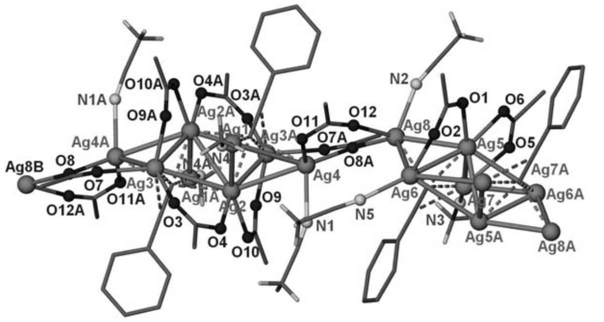

Figure 2. Coordination modes of pentafluoropropionate and acetonitrile ligands in complex **1**. CF_3 moieties of pentafluoropropionate groups and hydrogen atoms of phenyl rings are omitted for clarity.

The infinite columns arranged in a hexagonal array are interconnected by relatively weak C5–H···F14 (H–F14 2.503 Å), C42–H···O2 (H–O2 2.420 Å) and C42–H···O5 (H–O5 2.566 Å)[17] hydrogen bonds to form a three-dimensional network (Figure 3).

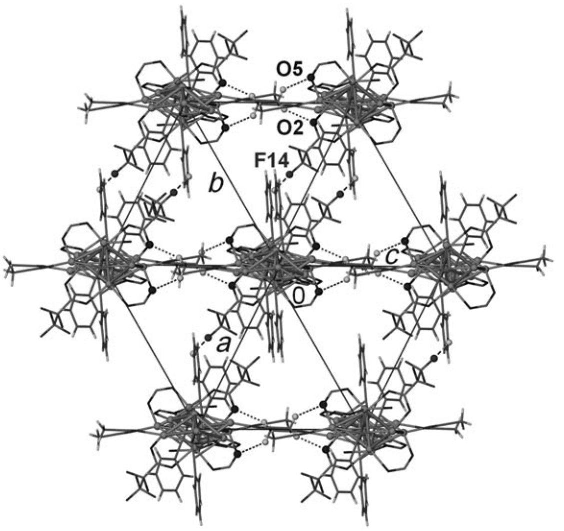

Figure 3. Hexagonal array of coordination chains in complex **1** cross-linked by weak C5-H···F14 (H–F14 2.503 Å), C42–H···O2 (H–O2 2.420 Å) and C42–H···O5 (H–O5 2.566 Å) hydrogen bonds to form a three-dimensional network. Other ligands are omitted for clarity.

$AgC{\equiv}CC_6H_5{\cdot}3\,AgCF_3CO_2{\cdot}CH_3CN$ (2): In an attempt to achieve an ordered arrangement of the aromatic rings of phenylacetylide ligands in a 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 **2**, an infinite array of parallel phenyl rings stabilized by π–π stacking (center-to-center distance 4.189 Å) indeed occurs (Figure 4). Furthermore, a unique μ_5-$\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode of the phenylethynide group (mode **Vb** in Scheme 1) is observed for the first time. The capping square-planar Ag_5 basket is composed of atoms Ag1, Ag2, Ag2A, Ag2B, and Ag2C; the Ag1−C1 bond length of 2.06(2) Å is in good agreement with those observed in $[Ag_4\{\mu\text{-}(C{\equiv}CC_6H_5)_4\}(PCy_3)_2]$,[8a] which exhibit coordination mode **II** (2.048–2.055 Å). Furthermore, only the simple μ_2-O,O′ coordination mode is observed for all trifluoroacetate groups in this structure, in which two carboxylic ligands span the same Ag2A−Ag2B edge of the Ag_5 basket. The external silver atom Ag3, which bears one acetonitrile group, is bonded to the Ag_5 basket through an argentophilic interaction with Ag1, which is further strengthened by the connection of the trifluoroacetate group O1−O2 (Figure 5).

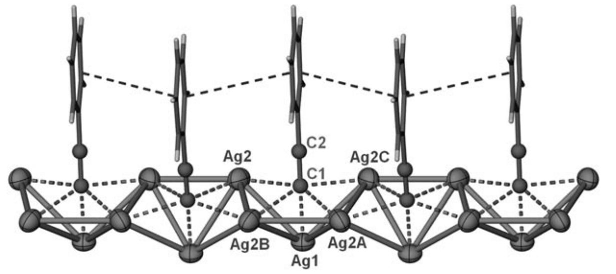

Figure 4. Coordination mode of the $C_6H_5C{\equiv}C^-$ ligand in **2** with atom labeling (50 % thermal ellipsoids). The silver column is connected by edge sharing between adjacent square-pyramidal Ag_5 aggregates, and continuous π···π stacking of phenyl rings occurs on one side of the column. Trifluoroacetate groups and acetonitrile molecules are omitted for clarity. Selected bond lengths [Å]: C1−C2 1.22(2), Ag···Ag 3.017(2)–3.215(2). Symmetry code: A: $\tfrac{1}{2}+x, y, -\tfrac{1}{2}-z$; B: $\tfrac{1}{2}-x, 1+y, \tfrac{1}{2}-z$; C: $-x, y, z$.

Interestingly, the Ag_5 baskets are fused through argentophilic interactions through edge-sharing to form an infinite coordination column along the [100] direction (Figure 4), with continuous π–π stacking of phenyl rings lying on the same side of the column. Linkage of adjacent columns by a weak Ag···Ag interaction (3.603 Å) between two external silver atoms of type Ag3 along the *c* direction, and by weak hydrogen bonds of 2.415 Å (F11−H) between F11···H6A−C6 along the *b* direction, generates a three-dimensional network (Figure 6).

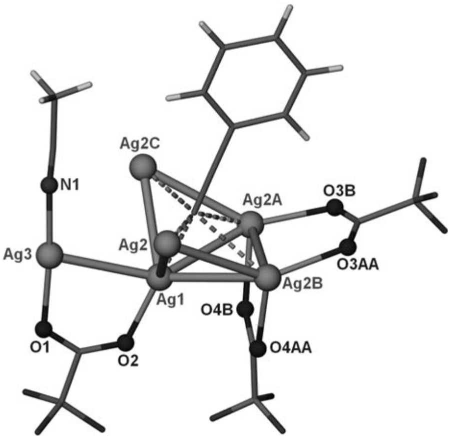

Figure 5. Coordination modes of trifluoroacetate and acetonitrile ligands in complex **2**.

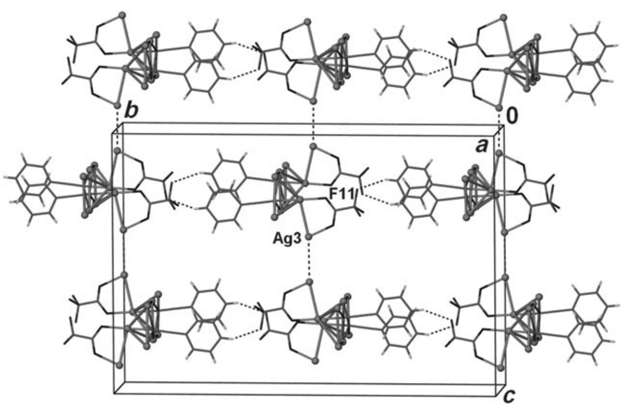

Figure 6. Silver columns (viewed end-on) in complex **2** are linked by weak Ag···Ag interactions (3.603 Å) along the *c* direction, and further consolidated by weak hydrogen bonds between F11···H6A−C6 along the [010] direction (F11−H 2.415 Å), to give a three-dimensional network. Other ligands are omitted for clarity.

$AgC{\equiv}CC_6H_4C{\equiv}N\text{-}4{\cdot}3\,AgCF_3CO_2{\cdot}\boldsymbol{x}H_2O$ ($\boldsymbol{x}$ = 0.3) (3): Considering the role of acetonitrile in facilitating the crystallization of ethynide-containing silver(I) complexes, we decided to investigate the use of an aromatic ligand that incorporates the isoelectronic groups $-C{\equiv}C^-$ and $-C{\equiv}N$, and subsequently obtained the new complex **7** and its double salt **3**, which crystallizes in the higher-symmetry space group *Ibam*. The ethynide moiety C1−C2 in **3** also exhibits the μ_5-$\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode (mode **Vb**), but with a much shorter carbon−carbon triple bond distance of 1.10(2) Å, in contrast with the corresponding values in complexes **1** (1.21(2) Å) and **2** (1.22(2) Å), which can be attributed to the electron-withdrawing effect of the *p*-C≡N substituent. In addition, two Ag_5 baskets share an edge to yield a Ag_8 aggregate with an inversion center located at the center of the Ag1−Ag1A bond (Figure 7). One group O3−O4 binds one edge of the Ag_5 basket Ag2−Ag3 through a simple μ_2-O,O′ coordination mode. The other one O1−O2 acts as a bridging ligand to link all Ag_5 units together through the μ_3-O,O′,O′ mode to form a silver column along the *c* direction (Figure 8).

Bridged by cyano groups of $4\text{-}C{\equiv}NC_6H_4C{\equiv}C{\supset}Ag_5$ moieties, these silver columns are interwoven to produce a three-

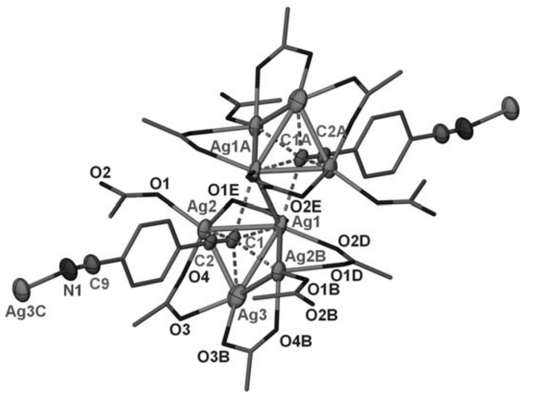

Figure 7. The μ_5-coordination mode of the $4\text{-C}\equiv\text{NC}_6\text{H}_4\text{C}\equiv\text{C}^-$ ligand in **3** with atom labeling (40% thermal ellipsoids). The acetylide-coordinated Ag_5 unit and its inversion-related counterpart are fused by sharing one edge Ag1−Ag1A. The Ag···Ag distances lie in the range 2.89(1)–3.079(2) Å. All fluorine and hydrogen atoms are omitted for clarity. Symmetry code: A: $1-x$, $1-y$, $1-z$; B: x, y, $1-z$; C: $-\frac{1}{2}+x$, $\frac{1}{2}-y$, z; D: $1-x$, y, $\frac{1}{2}+z$; E: $1-x$, y, $\frac{1}{2}-z$.

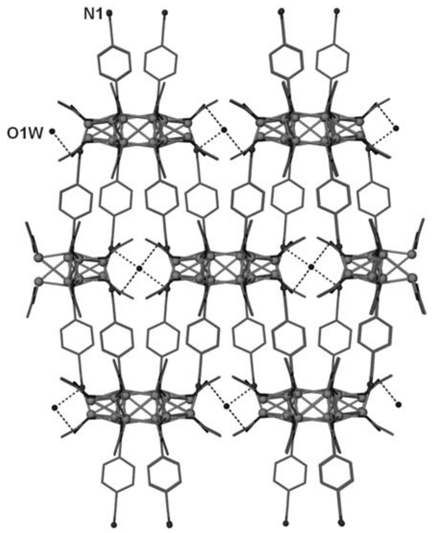

Figure 9. Three-dimensional network in complex **3** cross-linked by two isoelectronic moieties: cyano group $\text{-C}\equiv\text{N}$ and acetylide $\text{C}\equiv\text{C}^-$. Water molecules partially filling a one-dimensional channel are stabilized by four O1W−H···O3 (O1W−O3 2.796 Å, dashed bonds) and two O1W−H···N1 (O1W−N1 2.675 Å, dashed bonds) hydrogen bonds. Other ligands are omitted for clarity.

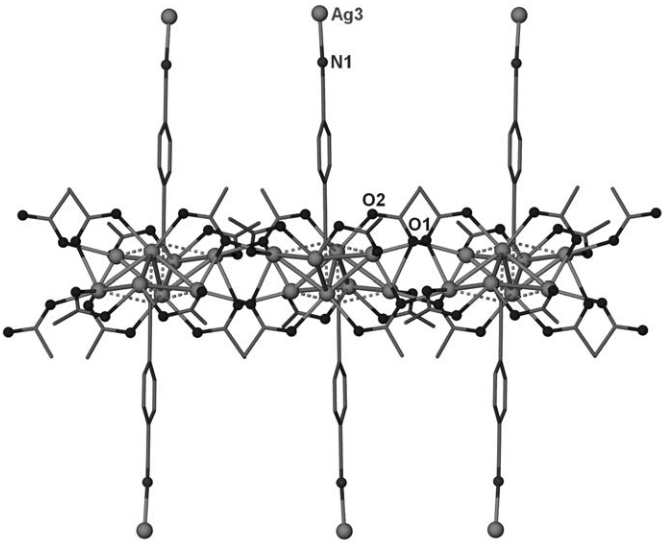

Figure 8. One-dimensional silver column in complex **3** bridging by trifluoroacetate group O1−O2 through μ_3-O,O′,O′ coordination mode. Hydrogen atoms and CF_3 groups of trifluoroacetate ligands are omitted for clarity.

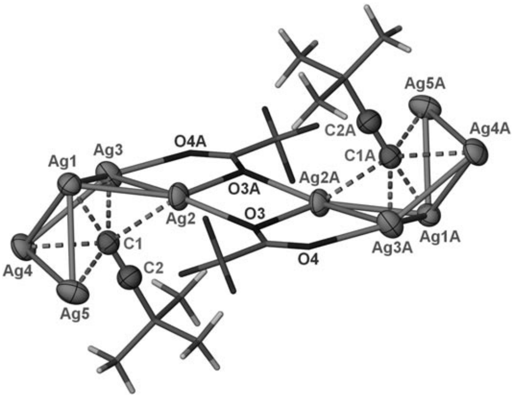

Figure 10. Coordination mode of the $t\text{BuC}\equiv\text{C}^-$ ligand in **4** with atom labeling (50% thermal ellipsoids). The Ag···Ag distances lie in the range 2.873(1)–3.130(1) Å. Other trifluoroacetate groups, acetonitrile molecules and hydrogen atoms are all omitted for clarity. Symmetry code: A: $1-x$, $1-y$, $-z$.

dimensional network, in which an infinite channel partially filled with water molecules is found (Figure 9). Although all phenyl rings are parallel to each other, no π–π interaction arises in view of the remarkably large inter-ring separation (8.592 Å).

$\mathbf{AgC\equiv C\mathit{t}Bu\cdot 6\,AgCF_3CO_2\cdot 2\,CH_3CN\cdot 6\,H_2O}$ (4): In the crystal structure of **4**, the alkyl ethynide moiety C1−C2 taking the μ_5-η^1,η^1,η^1,η^2,η^2 coordination mode (mode **Vb** in Scheme 1, Ph replaced by *t*Bu) lies perpendicular to the plane comprising silver(I) atoms Ag2, Ag3, Ag4, and Ag5, pointing almost linearly at Ag1 (Figure 10). The C1−C2 triple bond length is 1.18(1) Å, in good agreement with the values observed in other silver *tert*-butylethynide complexes (1.171–1.221 Å,[18a] 1.207–1.224 Å[18b]). Utilizing two μ_3-O,O′,O′ coordination groups (O5−O6, O7−O8) and a water molecule O1W as linkage components, the external silver atom Ag6 bearing one acetonitrile group N1 is connected together with the square-pyramidal Ag_5 (Ag1–Ag5) basket. Linkage of two square-pyramidal Ag_5 baskets by a pair of inversion-related trifluoroacetate groups (O3−O4 and O3A−O4A) produces a Ag_5-(μ_3-η^1,η^2-CF_3CO_2)$_2$-Ag_5 building unit, and such units are connected by O1W through hydrogen bonding (O1W−H···O4, O1W−O4 2.758 Å) to generate a winding infinite chain along the *a* direction. The remaining trifluoroacetate groups (O1−O2, O9−O10, O11−O12) each coordinates with one edge of the Ag_5 basket to stabilize this $[Ag_5(tBu{-}C\equiv C)]^{4+}$ cationic moiety. Acetonitrile group N2, together with two aqua molecules (O3W and O6W), bond to silver atom Ag7 and constitute an independent peripheral unit, which is trapped in the crystal structure of **4** by a large number of hydrogen bonds (Figure 11). By utilizing the external silver atom Ag7 and the remaining water molecules (O2W–O6W) as bridging groups, adjacent infinite chains are cross-linked in the [001] direction through hydrogen bonds involving four trifluoroacetate groups (O1–O2, O3–O4, O9–O10, O11–O12) to generate a two-dimensional network parallel to the (010) plane (Figure 12).

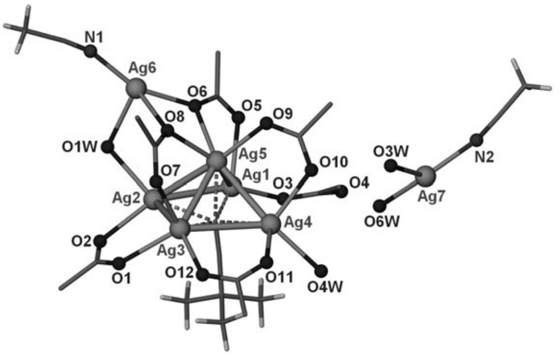

Figure 11. Coordination modes of trifluoroacetate, aqua and acetonitrile ligands in **4**. All fluorine atoms of trifluoroacetate groups are omitted for clarity.

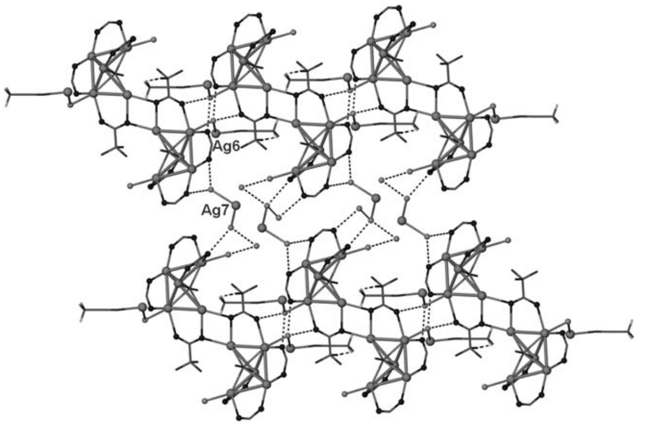

Figure 12. Layer structure in complex **4** linked by O1W–H···O4 (O1W–O4 2.758 Å) and C20–H···F21 (H–F21 2.505 Å) hydrogen bonds between two Ag_5-(μ_3-η^1,η^2-CF_3CO_2)$_2$-Ag_5 building units and further connected by external silver atom Ag7 and the remaining aqua ligands (O2W–O6W, indicated as small gray balls). The *tert*-butyl groups and other ligands are omitted for clarity.

$AgC\equiv CtBu\cdot 2Ag_2(O_2CCF_2CF_2CO_2)\cdot 9H_2O$ (5): To interconnect the planar arrays composed of silver(I) cations and $tBuC\equiv C^-$ anions in complex **4** into a three-dimensional network, tetrafluorobutanedioate was employed as a bridging ligand in **5**. A similar μ_5-η^1,η^1,η^1,η^2,η^2 coordination mode also occurs in this compound (Figure 13). Two tetrafluorobutanedioate groups (O5–O6, O7–O8) act as linkers to form an undulating silver chain by bridging a series of Ag_5 baskets (Figure 14), which are extended along the [010] direction, and further bridged by another tetrafluorobutanedioate group (O1–O4) to generate a three-dimensional network, which contains a series of channels of approximately square cross-section that accommodate the *tert*-butyl groups (Figure 15).

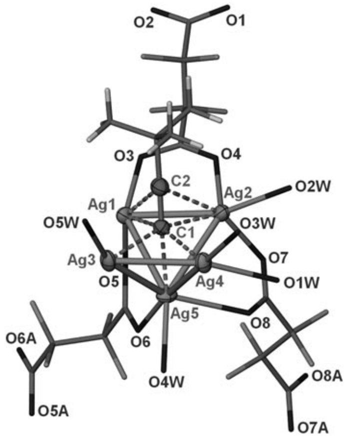

Figure 13. Coordination mode of the $tBuC\equiv C^-$ ligand in **5** with atom labeling (50% thermal ellipsoids). Selected bond lengths [Å]: C1–C2 1.205(5), Ag···Ag 2.831(2)–3.032(3). Symmetry code: A: $-x$, $1-y$, $-z$.

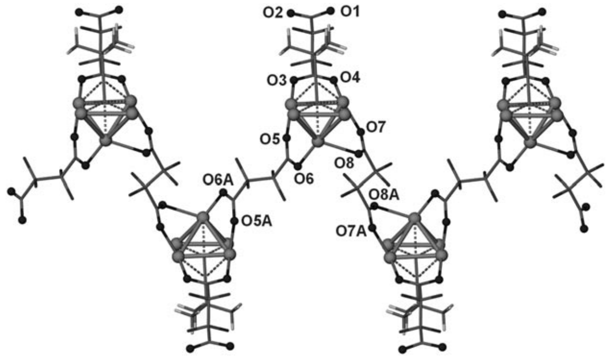

Figure 14. Undulating silver chain in complex **5** linked by two tetrafluorobutanedioate groups O5–O6 and O7–O8.

Notably, the silver–ethynide interactions within the square-pyramidal Ag_5 baskets in **1**–**5** can be classified into three types: σ, π and mixed (σ,π). As listed in Table 1, the σ-bond between the terminal carbon atom C1 of the ethynide moiety and its almost linearly bonded silver atom Ag1 (C2-C1-Ag1 163.3(3)-176(2)°) is much shorter than other Ag–C bonds. With reference to the distances between carbon atom C2 and the remaining silver atoms and the C2-

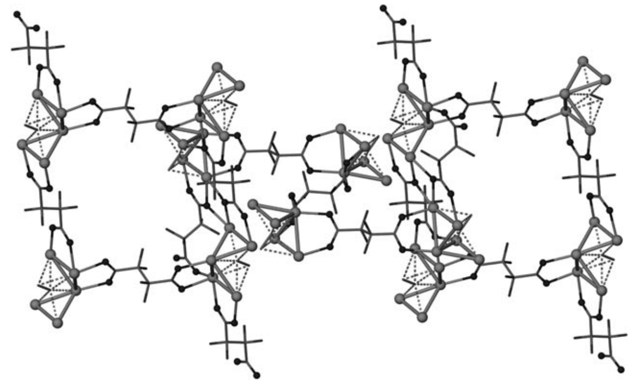

Figure 15. A series of channels in complex **5** linked by bridging tetrafluorobutanedioate ligands. The water molecules, *tert*-butyl groups and other ligands are omitted for clarity.

Table 1. Classification of different types of silver-ethynide interactions within the square-pyramidal Ag_5 baskets of complexes **1–5**.

Complex	Bond type	Bond lengths [Å] and angles [°]		
		C1–M	C2–M	C2-C1-M
1	σ	C1–Ag1 2.21(2)		Ag1 167(1)
	π	C1–Ag3 2.40(1)	C2–Ag3 2.69(1)	Ag3 90.3(9)
	(σ,π)	C1–Ag4 2.48(1)	C2–Ag4 2.899	Ag4 98(1)
		C1–Ag1A 2.71(1)	C2–Ag1A 3.109	Ag1A 97.7(9)
		C1–Ag2 2.17(1)	C2–Ag2 2.858	Ag2 112(1)
2	σ	C1–Ag1 2.06(2)		Ag1 176(2)
	π×2	C1–Ag2 2.426(7)	C2–Ag2 2.772	Ag2 93.1(7)
		C1–Ag2C 2.426(7)	C2–Ag2C 2.772	Ag2C 93.1(7)
	(σ,π)×2	C1–Ag2A 2.61(1)	C2–Ag2A 3.094	Ag2A 102(1)
		C1–Ag2B 2.61(1)	C2–Ag2B 3.094	Ag2B 102(1)
3	σ	C1–Ag1 2.25(1)		Ag1 172(1)
	π	C1–Ag2 2.32(1)	C2–Ag2 2.783	Ag2 102.7(5)
		C1–Ag2A 2.32(1)	C2–Ag2A 2.783	Ag2A 102.7(5)
	(σ,π)	C1–Ag1A 2.70(1)	C2–Ag1A 3.087	Ag1A 100(1)
		C1–Ag3 2.45(1)	C2–Ag3 2.950	Ag3 106(1)
4	σ	C1–Ag1 2.187(7)		Ag1 171.9(6)
	π	C1–Ag2 2.346(7)	C2–Ag2 2.792	Ag2 99.4(5)
		C1–Ag5 2.375(7)	C2–Ag5 2.740	Ag5 94.9(6)
	(σ,π)	C1–Ag3 2.312(7)	C2–Ag3 2.902	Ag3 108.0(6)
		C1–Ag4 2.375(7)	C2–Ag4 2.913	Ag4 105.0(6)
5	σ	C1–Ag1 2.186(4)		Ag1 163.3(3)
	π	C1–Ag2 2.473(4)	C2–Ag2 2.682(5)	Ag2 86.4(3)
		C1–Ag3 2.375(4)	C2–Ag3 2.587(4)	Ag3 86.0(3)
	(σ,π)	C1–Ag4 2.331(4)	C2–Ag4 3.013	Ag4 113.0(3)
		C1–Ag5 2.267(3)	C2–Ag5 2.905	Ag5 109.8(3)

C1-Ag bond angles, the π and (σ,π) types of silver–ethynide interactions can be differentiated. The π-type Ag–C2 distances vary from 2.587(4) Å to 2.792(6) Å with C2-C1-Ag angles in the range 86.0(9)–102.7(5)°, in contrast to the longer distances of 2.858–3.094 Å with 97.7(9)–108.0(6)°, corresponding to mixed (σ,π)-type interactions.

Conclusion

Two unprecedented μ_5-coordination modes for the alkyl and aryl ethynide moieties (**Va** and **Vb** in Scheme 1) are observed in silver(I) complexes **1–5**, in contrast to the highest ligation number[6] of four hitherto reported for such ligands. The silver–ethynide interactions within the square-pyramidal Ag_5 baskets of **1–5** are systematically classified as σ, π and mixed (σ,π) types according to the measured Ag–C bond lengths and C≡C-Ag bond angles. This finding provides a rationale for the general occurrence of silver(I) polyhedra of 6–10 vertices with encapsulated $^{-}C{\equiv}C^{-}$ species in a wide variety of double and multiple salts of silver acetylenediide.[5]

Supramolecular synthons, defined as recognition motifs of basic building blocks consolidated by intermolecular interactions, usually involve hydrogen bonding and weaker forces such as π–π stacking and halogen–halogen interactions.[19] In the present study, we have established the utility of a new class of supramolecular synthons, symbolized by $R{-}C{\equiv}C{\supset}Ag_n$ (R = aryl or alkyl; $n = 4, 5$), for the generation of coordination polymeric structures. The interplay of ethynide–silver bonding, argentophilicity, and π–π interaction highlights the complexity and challenge in programming supramolecular assembly of metal-organic networks.

Experimental Section

Reagents: Phenylacetylene (Merck, purity > 97 %), 4-bromobenzonitrile (IL, > 98 %), 3,3-dimethylbut-1-yne (Alfa Aesar, > 98 %), trimethylsilylacetylene (Alfa Aesar, 98 %) and *n*BuLi in hexane (Merck, 1.6 M) were available commercially and used without further purification. 4-Ethynylbenzonitrile was synthesized according to the literature method by the reaction of 4-bromobenzonitrile with trimethylsilylacetylene.[20] Tetrahydrofuran (THF) was purified through refluxing over sodium and benzophenone. All reactions were carried out under a nitrogen atmosphere unless otherwise noted.

CAUTION! *Silver acetylide complexes are potentially explosive and should be handled with care and in small amounts.*

$[AgC{\equiv}CC_6H_5]_n$ (6): Compound **6** was prepared according to the literature method.[13] Silver nitrate (0.742 g, 4.4 mmol) was dissolved in acetonitrile (50 mL). Then phenylacetylene (1.45 mL, 13.2 mmol) and triethylamine (1.83 mL, 13.2 mmol) were added with vigorous stirring for 48 h. The pale yellow precipitate formed was collected by filtration and washed thoroughly with acetonitrile (3×30 mL) and methanol (3×30 mL) successively, and dried under vacuum. Yield: 0.653 g (71 %). IR: $\tilde{\nu} = 2050\ cm^{-1}$ (m, ν(C≡C)).

$[AgC{\equiv}CC_6H_4C{\equiv}N\text{-}4]_n$ (7): Compound **7** was synthesized as a yellow powder by the reaction of 4-ethynylbenzonitrile with $AgNO_3$ using a method similar to that employed for complex **6**. IR: $\tilde{\nu} = 2040\ cm^{-1}$ (m, ν(C≡C)), $2221\ cm^{-1}$ (m, ν(C≡N)).

$[\mathrm{AgC{\equiv}C}t\mathrm{Bu}]_n$ (8): In a 100-mL Schlenk flask, THF (20 mL) was cooled to −78 °C in a cold bath. Then *n*BuLi (1.6 M in *n*-hexane, 4.4 mmol) was added by using a syringe, and the mixture was stirred for 15 min at −78 °C. A solution of 3,3-dimethylbut-1-yne (0.329 g, 4.0 mmol) dissolved in THF (5 mL) was added dropwise. The cold bath was then replaced by an ice–water bath and the mixture was stirred for 2 h. Under a stream of nitrogen, $\mathrm{AgNO_3}$ crystals (0.680 g, 4.0 mmol) were added to the flask and dissolved gradually while the mixture was stirred overnight. A white precipitate of crude **8** was isolated by filtration, washed several times with THF, and finally with de-ionized water. Yield: 0.524 g (69.3 %). IR: $\tilde{\nu}$ = 2056 cm^{-1} (m, ν(C≡C)).

$\mathrm{2\,AgC{\equiv}CC_6H_5{\cdot}6\,AgC_2F_5CO_2{\cdot}5\,CH_3CN}$ (1): $\mathrm{AgCF_3CF_2CO_2}$ (0.270 g, 1 mmol) and $\mathrm{AgBF_4}$ (0.382 g, 2 mmol) were dissolved in a mixture of de-ionized water (1 mL) and acetonitrile (0.2 mL). Then $[\mathrm{AgC{\equiv}CC_6H_5}]_n$ (~0.1 g) solid was added to the solution. After stirring for one hour, the solution was filtered and the filtrate was stored in a refrigerator at −10 °C. After several days, pale yellow prismatic crystals of **1** were deposited in about 20 % yield. Compound **1** decomposes above 135 °C. Elemental analysis (%)calcd for $\mathrm{C_{44}H_{25}F_{30}O_{12}N_5Ag_8}$: C 23.64, H 1.12, N 3.11; found: C 23.50, H 1.30, N 2.87; IR: $\tilde{\nu}$ = 2104 cm^{-1} (vw, ν(C≡C)).

$\mathrm{AgC{\equiv}CC_6H_5{\cdot}3\,AgCF_3CO_2{\cdot}CH_3CN}$ (2): $[\mathrm{AgC{\equiv}CC_6H_5}]_n$ (~0.1 g) was added to a concentrated aqueous solution of $\mathrm{AgCF_3CO_2}$ (0.220 g, 1 mL, 1 mmol) and $\mathrm{AgBF_4}$ (0.382 g, 2 mmol) in a beaker with stirring until saturation. The excess $[\mathrm{AgC{\equiv}CC_6H_5}]_n$ was filtered off. Then a solution of $[\mathrm{BzMe_3N}]\mathrm{BF_4}$ in acetonitrile (0.1 mL, 1 M) was added to the filtrate, which was then placed in a refrigerator at −10 °C. After a few days, transparent pale yellow prismatic crystals of **2** were deposited in about 15 % yield. Compound **2** melts with decomposition between 103.2 °C and 105.7 °C. Elemental analysis (%) calcd for $\mathrm{C_{16}H_8F_9O_6NAg_4}$: C 21.06, H 0.88, N 1.53; found: C 21.19, H 0.75, N 1.29; IR: $\tilde{\nu}$ = 2005 cm^{-1} (vw, ν(C≡C)).

$\mathrm{AgC{\equiv}CC_6H_4C{\equiv}N\text{-}4{\cdot}3\,AgCF_3CO_2{\cdot}}x\mathrm{H_2O}$ (x = 0.3) (3): A mixture of water (1 mL) and acetonitrile (0.2 mL) was used to dissolve $\mathrm{AgCF_3CO_2}$ (1 mmol) and $\mathrm{AgBF_4}$ (2 mmol). Then $[\mathrm{AgC{\equiv}CC_6H_4C{\equiv}N\text{-}4}]_n$ (~0.1 g) was added to this mixture with stirring for an hour. The filtered solution was put into a refrigerator at −10 °C and yellow prismatic crystals of **3** were obtained in about 5 % yield after a few days. Compound **3** decomposes above 125 °C. Elemental analysis (%) calcd for $\mathrm{C_{15}H_{4.6}F_9O_{6.3}NAg_4}$: C 19.97, H 0.51, N 1.55; found: C 20.09, H 0.47, N 1.32; IR: $\tilde{\nu}$ = 2090 cm^{-1} (vw, ν(C≡C)), 2264 cm^{-1} (vw, ν(C≡N)).

$\mathrm{AgC{\equiv}C}t\mathrm{Bu{\cdot}6\,AgCF_3CO_2{\cdot}2\,CH_3CN{\cdot}6\,H_2O}$ (4): $\mathrm{AgCF_3CO_2}$ (0.220 g, 1 mmol) and $\mathrm{AgBF_4}$ (0.382 g, 2 mmol) were dissolved in de-ionized water (1 mL). Then $[\mathrm{AgC{\equiv}C}t\mathrm{Bu}]_n$ (~0.1 g) was added to the solution. After stirring for about five minutes, the solution was filtered. To the filtrate was added acetonitrile (0.1 mL), and then the solution was placed in a refrigerator (−10 °C). After one day, colorless crystals of **4** were collected in about 60 % yield. Compound **4** has a melting point ranging from 49.8 °C to 51.4 °C. Elemental analysis (%) calcd for $\mathrm{C_{22}H_{27}F_{18}O_{18}N_2Ag_7}$: C 15.50, H 1.60, N 1.64; found: C 15.10, H 1.37, N 1.29; IR: $\tilde{\nu}$ = 2121 cm^{-1} (m, ν(C≡C)).

$\mathrm{AgC{\equiv}C}t\mathrm{Bu{\cdot}2\,Ag_2(O_2CCF_2CF_2CO_2){\cdot}9\,H_2O}$ (5): $\mathrm{Ag_2(O_2CCF_2CF_2CO_2)}$ (0.203 g, 0.5 mmol) and $\mathrm{AgBF_4}$ (0.382 g, 2 mmol) were dissolved in de-ionized water (1 mL). Then $[\mathrm{AgC{\equiv}C}t\mathrm{Bu}]_n$ (~0.1 g) was added with stirring for half an hour and the solution was filtered off. To the filtrate was added acetonitrile (0.1 mL), and then the filtered solution was placed in a refrigerator at −10 °C. After one day, colorless crystals of **5** were collected in about 40 % yield. Compound **5** decomposes above 130 °C. Elemental analysis (%) calcd for $\mathrm{C_{14}H_{27}F_8O_{17}Ag_5}$: C 14.51, H 2.35; found: C 14.33, H 2.20; IR: $\tilde{\nu}$ = 2094 cm^{-1} (m, ν(C≡C)).

X-ray crystallography: Data collection was performed at 293 K on a Bruker SMART 1000 CCD diffractometer using frames of oscillation range 0.3°, with $1.5° < \theta < 28°$. An empirical absorption correction was applied by using the SADABS program[21] to all the compounds. The structures were solved by direct methods, and non-hydrogen atoms were located from difference-Fourier maps. All the non-hydrogen atoms, unless otherwise noted, were refined anisotropically by full-matrix least-squares on F^2 using the SHELXTL program.[22]

Crystal data: **1**, $\mathrm{2\,AgC{\equiv}CC_6H_5{\cdot}6\,AgC_2F_5CO_2{\cdot}5\,CH_3CN}$, $\mathrm{C_{44}H_{25}F_{30}O_{12}N_5Ag_8}$, $M_r = 2248.65$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.195(1)$, $b = 15.233(1)$, $c = 17.313(1)$ Å, $\alpha = 95.004(2)$, $\beta = 97.081(2)$, $\gamma = 113.718(1)°$, $V = 3362.6(4)$ Å^3, $Z = 2$, 11 814 unique reflections ($R_{\mathrm{int}} = 0.0534$), $R1 = 0.0673$, $wR2 = 0.1867$, goodness-of-fit = 0.896 for 5230 observed reflections with $I > 2\sigma(I)$. Five atoms (C22, C25, C31, F25, and F64) were refined isotropically.

2, $\mathrm{AgC{\equiv}CC_6H_5{\cdot}3\,AgCF_3CO_2{\cdot}CH_3CN}$, $\mathrm{C_{16}H_8F_9O_6NAg_4}$, $M_r = 912.70$, orthorhombic, space group *Cmca* (no. 64), $a = 7.374(2)$, $b = 30.430(6)$, $c = 20.717(4)$ Å, $V = 4649(2)$ Å^3, $Z = 8$, 2234 unique reflections ($R_{\mathrm{int}} = 0.0925$), $R1 = 0.0639$, $wR2 = 0.2035$, goodness-of-fit = 1.014 for 1294 observed reflections with $I > 2\sigma(I)$.

3, $\mathrm{AgC{\equiv}CC_6H_4C{\equiv}N\text{-}4{\cdot}3\,AgCF_3CO_2{\cdot}}x\,\mathrm{H_2O}$ ($x = 0.3$), $\mathrm{C_{15}H_{4.6}F_9O_{6.3}NAg_4}$, $M_r = 902.06$, orthorhombic, space group *Ibam* (no. 72), $a = 21.513(3)$, $b = 13.378(2)$, $c = 15.617(2)$ Å, $V = 4494(1)$ Å^3, $Z = 8$, 2066 unique reflections ($R_{\mathrm{int}} = 0.0336$), $R1 = 0.0492$, $wR2 = 0.1732$, goodness-of-fit = 1.070 for 1463 observed reflections with $I > 2\sigma(I)$. The site occupancy of water molecule O1W was derived from the elemental analysis results and structural analysis. The water hydrogen atoms were not included in the structure model.

4, $\mathrm{AgC{\equiv}C}t\mathrm{Bu{\cdot}6\,AgCF_3CO_2{\cdot}2\,CH_3CN{\cdot}6\,H_2O}$, $\mathrm{C_{22}H_{27}F_{18}O_{18}N_2Ag_7}$, $M_r = 1704.50$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.440(1)$, $b = 12.814(2)$, $c = 18.218(2)$ Å, $\alpha = 100.994(2)$, $\beta = 106.988(2)$, $\gamma = 105.691(2)°$, $V = 2351.0(5)$ Å^3, $Z = 2$, 8103 unique reflections ($R_{\mathrm{int}} = 0.0202$), $R1 = 0.0457$, $wR2 = 0.1364$, goodness-of-fit = 1.027 for 6191 observed reflections with $I > 2\sigma(I)$. Hydrogen atoms of water molecules were not included in the refinement.

5, $\mathrm{AgC{\equiv}C}t\mathrm{Bu{\cdot}2\,Ag_2(O_2CCF_2CF_2CO_2){\cdot}9\,H_2O}$, $\mathrm{C_{14}H_{27}F_8O_{17}Ag_5}$, $M_r = 1158.56$, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.815(2)$, $b = 12.816(2)$, $c = 20.109(3)$ Å, $\beta = 96.715(3)°$, $V = 3024.1(9)$ Å^3, $Z = 4$, 7511 unique reflections ($R_{\mathrm{int}} = 0.0299$), $R1 = 0.0296$, $wR2 = 0.0831$, goodness-of-fit = 1.016 for 5916 observed reflections with $I > 2\sigma(I)$. Hydrogen atoms of water molecules were not included in the refinement.

CCDC-279157 (**1**), CCDC-279158 (**2**), CCDC-288078 (**3**), CCDC-279156 (**4**), and CCDC-288077 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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