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Silver(I) Ethynide Coordination Networks and Clusters Assembled with *tert*-Butylphosphonic Acid

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Ⓢ *Supporting Information*

ABSTRACT: Variation of the reaction conditions with $AgC\equiv CR$ (R = Ph, $C_6H_4OCH_3$-4, ^tBu), $^tBuPO_3H_2$, and AgX (X = NO_3, BF_4) as starting materials afforded four new silver(I) ethynide complexes incorporating the *tert*-butylphosphonate ligand, namely, $3AgC\equiv CPh\cdot Ag_2{}^tBuPO_3\cdot Ag^tBuPO_3H\cdot 2AgNO_3$ (**1**), $2AgC\equiv CC_6H_4OCH_3\text{-}4\cdot Ag_2{}^tBuPO_3\cdot 2AgNO_3$ (**2**), $[\{Ag_5(NO_3@Ag_{18})Ag_5\}(^tBuC\equiv C)_{16}(^tBuPO_3)_4(H_2O)_3][\{Ag_5(NO_3@Ag_{18})Ag_5\}(^tBuC\equiv C)_{16}(^tBuPO_3)_4(H_2O)_4]\cdot 3SiF_6\cdot 4.5H_2O\cdot 3.5MeOH$ (**3**), and $[\{Ag_8(Cl@Ag_{14})\}(^tBuC\equiv C)_{14}(^tBuPO_3)_2F_2(H_2O)_2]BF_4\cdot 3.5H_2O$ (**4**). Single-crystal X-ray analysis revealed that complexes **1** and **2** display different layer-type coordination networks, while **3** and **4** contain high-nuclearity silver(I) composite clusters enclosing nitrate and chloride template ions, respectively, that are supported by $^tBuPO_3{}^{2-}$ ligands.

Recent growing interest in the study of metal ethynyl complexes stems from their structural diversity and technological application as precursors of nonlinear optical materials, luminescent probes, and rigid-rod molecular wires.[1−4] Of the related but different metal ethynide complexes, the $RC\equiv C\supset Ag_n$ (n = 3−5; R = alkyl, aryl, heteroaryl) metal−ligand supramolecular synthon[5] has been intensively investigated as novel polynuclear building units to assemble organosilver(I) networks[6] and high-nuclearity clusters.[7]

In general, the reactions of phosphonic/arsonic acids with metal salts afford products that vary structurally from discrete molecules to multidimensional coordination polymers,[8] which have potential applications[9] in ion exchange, catalysis, and chemical sensing. Recently, we employed $(Me_4N)_3(H_3V_{10}O_{28})$ as a precursor to react with $AgC\equiv CPh$, $AgNO_3$, and $^tBuPO_3H_2$ in dimethylformamide (DMF) to assemble two novel high-nuclearity silver(I) clusters, i.e., $\{(NO_3)_2@Ag_{16}(PhC\equiv C)_4[(^tBuPO_3)_4V_4O_8]_2(DMF)_6(NO_3)_2\}$ and $\{[(O_2)V_2O_6]_3@Ag_{43}(PhC\equiv C)_{19}[(^tBuPO_3)_4V_4O_8]_3(DMF)_6\}$, in which each phosphonate ligand binds two vanadium(V) atoms to form a $[(^tBuPO_3)_4(V_4O_8)]^{4-}$ structural building unit with its three oxygen atoms linked to silver(I) atoms.[7g]

In the present work, we explored the utility of *tert*-butylphosphonic acid for the synthesis of high-nuclearity silver(I) clusters and successfully generated four new silver(I) ethynide complexes, namely, $3AgC\equiv CPh\cdot Ag_2{}^tBuPO_3\cdot Ag^tBuPO_3H\cdot 2AgNO_3$ (**1**), $2AgC\equiv CC_6H_4OCH_3\text{-}4\cdot Ag_2{}^tBuPO_3\cdot 2AgNO_3$ (**2**), $[\{Ag_5(NO_3@Ag_{18})Ag_5\}(^tBuC\equiv C)_{16}(^tBuPO_3)_4(H_2O)_3][\{Ag_5(NO_3@Ag_{18})Ag_5\}(^tBuC\equiv C)_{16}(^tBuPO_3)_4(H_2O)_4]\cdot 3SiF_6\cdot 4.5H_2O\cdot 3.5MeOH$ (**3**), and $[\{Ag_8(Cl@Ag_{14})\}(^tBuC\equiv C)_{14}(^tBuPO_3)_2F_2(H_2O)_2]BF_4\cdot 3.5H_2O$ (**4**), which have their structures fully characterized by single-crystal X-ray analysis.

The reaction of $AgC\equiv CPh$, $AgNO_3$, and $^tBuPO_3H_2$ in DMF afforded colorless crystals of $3AgC\equiv CPh\cdot Ag_2{}^tBuPO_3\cdot Ag^tBuPO_3H\cdot 2AgNO_3$ (**1**). Of the three independent phenylethynide anions in the crystal structure, the ethynide group composed of C17 and C18 is capped by a butterfly-shaped Ag_4 basket in the μ_4-$\eta^1,\eta^1,\eta^1,\eta^1$ coordination mode, and such Ag_4 baskets are bridged by a series of $BuPO_3{}^{2-}$ and $BuPO_3H^-$ anions to afford an infinite coordination chain in the direction of the *a* axis. The remaining two ethynide groups ($C1\equiv C2$ and $C9\equiv C10$) are each bound to a silver triangle in the μ_3-η^1,η^1,η^1 coordination mode, as shown in Figure 1a. Four Ag_3 triangles coalesce by sharing four vertexes to produce a centrosymmetric $4PhC\equiv C\supset Ag_8$ aggregate (Figure 1a), and such aggregates and the coordination chains composed of Ag_4 baskets are cross-bridged by a series of $BuPO_3{}^{2-}$, $BuPO_3H^-$, and $NO_3{}^-$ anions to engender a coordination layer (Figure S1 in the Supporting Information, SI). The $^tBuPO_3{}^{2-}$ unit adopts the μ_6-bridging mode to coordinate to six silver atoms (Figure S2a in the SI). However, in the $^tBuPO_3H^-$ unit, two oxygen atoms coordinate to five silver atoms, and its remaining protonated oxygen atom binds a silver atom (Figure S2b in the SI). The $Ag-O_P$ (O_P = oxygen atom of the *tert*-butylphosphonate ligand) bond lengths range from 2.239(7) to 2.699(7) Å. The nitrate ions adopt μ_1- and μ_4-ligation modes to coordinate to silver atoms, with $Ag-O_N$ (O_N = oxygen atom of the nitrate ligand) distances varying from 2.474(6) to 2.779(6) Å. A packing drawing showing the van der Waals interaction between coordination layers is shown in Figure S3 in the SI.

The synthetic procedure used to obtain $2AgC\equiv CC_6H_4OCH_3\text{-}4\cdot Ag_2{}^tBuPO_3\cdot 2AgNO_3$ (**2**) is similar to that of **1**, except that $AgC\equiv CPh$ was replaced by $AgC\equiv CC_6H_4OCH_3$-4. In the crystal structure of **2**, each independent ethynide moiety ($C1\equiv C2$ or $C10\equiv 11$) is bound to a Ag_4 basket (Figure 1b), and such baskets are mutually connected by vertex-sharing to generate an infinite argentophilic linear chain. These silver ethynide chains are interconnected through the bridging $^tBuPO_3{}^{2-}$ and $NO_3{}^-$ ligands, affording a two-dimensional coordination network (Figure S4 in the SI). The $^tBuPO_3{}^{2-}$ unit adopts the μ_7-bridging mode to coordinate to

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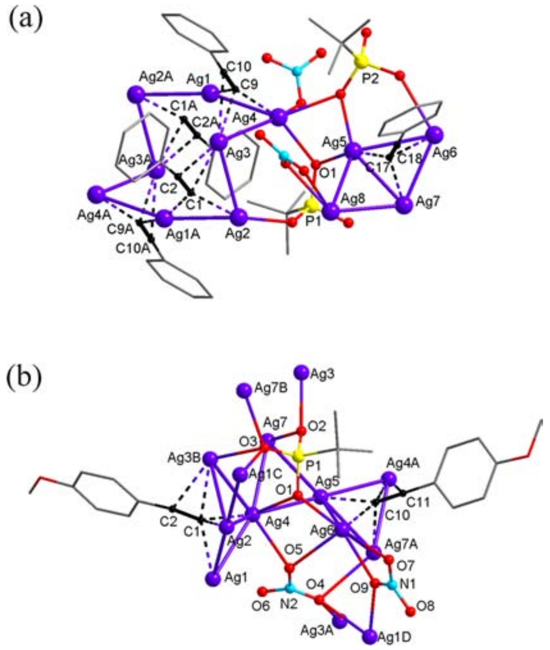

Figure 1. (a) Coordination environment of silver(I) atoms surrounded by three independent phenylethynides, two *tert*-butylphosphonates, and two nitrate ligands in 3AgC≡CPh·$Ag_2{}^tBuPO_3$·Ag^tBuPO_3H·$2AgNO_3$ (**1**), yielding Ag_4 and centrosymmetric Ag_8 aggregates. Symmetry code: A, −*x*, −*y*, 2 − *z*. (b) Coordination environment of silver(I) atoms surrounded by two independent 4-methoxyphenylethynide ligands, one *tert*-butylphosphonate, and two nitrate groups in 2AgC≡$CC_6H_4OCH_3$-4·$Ag_2{}^tBuPO_3$·$2AgNO_3$ (**2**). Note that Ag2 and Ag5 are each located at an inversion center. Symmetry code: A, −*x*, −*y*, −*z*; B, −1 − *x*, −*y*, −*z*; C, −1 − *x*, 1 − *y*, −*z*; D, −*x*, 1 − *y*, −*z*. The C≡C triple bond is represented by a bold rod. The Ag···C bonds are indicated by broken lines. All hydrogen atoms have been omitted for clarity. Color code: Ag, violet; C, gray; O, red; N, sky blue; P, yellow.

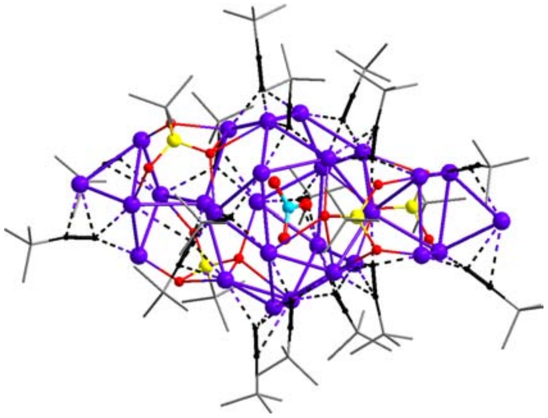

Figure 2. (a) Core skeleton of one of the two nearly identical Ag_{28} clusters in complex **3**. The encapsulated NO_3^- anion is represented by a larger ball-and-stick model. Hydrogen atoms and water molecules are omitted for clarity. The carbon atoms of the ethynide group are represented as small black balls, and their bonds to silver atoms are indicated by broken lines. Color code: Ag, violet; C, gray; O, red; N, sky blue; P, yellow.

seven silver atoms (Figure S2c in the SI), with Ag−O_P bond distances from 2.214(5) to 2.509(5) Å. The two independent nitrate ions adopt μ_2- and μ_5-ligation modes to coordinate to silver atoms, with Ag−O_N distances varying from 2.293(6) to 2.782(6) Å. These two-dimensional coordination networks are interconnected through intermolecular C−H···O interactions to afford a three-dimensional supramolecular architecture (Figure S5 in the SI).

Our next attempt to employ AgC≡C^{t}Bu as a synthetic precursor, with $AgBF_4$ added to the reaction mixture, yielded $[\{Ag_5(NO_3@Ag_{18})Ag_5\}(^tBuC{\equiv}C)_{16}(^tBuPO_3)_4(H_2O)_3]$-$[\{Ag_5(NO_3@Ag_{18})Ag_5\}(^tBuC{\equiv}C)_{16}(^tBuPO_3)_4(H_2O)_4]\cdot 3SiF_6\cdot 4.5H_2O\cdot 3.5MeOH$ (**3**). The unit cell of **3** contains two slightly different Ag_{28} silver clusters, each encapsulating a template nitrate ion: one cluster has three, and the other has four, water molecules coordinated to silver atoms. The enclosed NO_3^- ion coordinates to separate silver atoms by the μ_3-η^1,η^1,η^1 ligation mode, with Ag−O bond distances ranging from 2.696(5) to 2.838(5) Å, which are longer than those found in $\{(NO_3)_2@Ag_{16}(PhC{\equiv}C)_4[(^tBuPO_3)_4V_4O_8]_2(DMF)_6(NO_3)_2\}$ (2.299−2.431 Å).[7g] The Ag_{28} cluster skeleton comprises two Ag_5 aggregates fused into a globular $NO_3@Ag_{18}$ cage on opposite sides (Figures 2 and S6 in the SI). Four *tert*-butylphosphonate ligands, each adopting the μ_6-bridging mode to bind five silver atoms (Figure S2a in the SI), stabilize the cluster shell via Ag−O_P bond lengths ranging from 2.087(6) to 2.829(6) Å. Of the 16 peripheral ^{t}BuC≡C ligands, 12 adopt the μ_3-bridging and 4 the μ_4-bridging mode to coordinate to silver atoms. The crystal packing is consolidated by nine solvated water molecules and seven methanol molecules, each exhibiting half site occupancy. The overall charge balance against the large cationic silver(I) cluster is provided by six hexafluorosilicate counteranions, each having half site occupancy in the crystal structure. Notably, in the preparation of **3**, generation of the hexafluorosilicate ion presumably arises from the reaction of BF_4^- with the SiO_2 component of the glassware.[10]

The reaction of AgC≡C^{t}Bu with $AgBF_4$, $^tBuPO_3H_2$ and a small amount of $(Me_4N)Cl$, with the latter acting as a chloride source, in methanol yielded $[\{Ag_8(Cl@Ag_{14})\}(^tBuC{\equiv}C)_{14}(^tBuPO_3)_2(H_2O)_2F_2]BF_4\cdot 3.5H_2O$ (**4**). Single-crystal X-ray analysis revealed that complex **4** contains a cationic Ag_{22} cluster, which lies on a crystallographic C_2 axis (Figure 3 and S7 in the SI). The cluster skeleton can be described as consisting of a rhombic-dodecahedral Ag_{14} cage that encapsulates a chloride ion, with one vertex covered by a square face of an empty Ag_8 Archimedean antiprism. The resulting Ag_{22} assembly is held together by two *tert*-butylphosphonate ligands, each adopting the μ_5-bridging mode to bind five silver atoms (Figure S2d in the SI) via Ag−O_P bond lengths ranging from 2.116(2) to 2.320(2) Å. The argentophilic Ag···Ag bond distances lie in the range 2.878(2)−3.376(2) Å. The chloride atom does not lie in the center of the Ag_{14} cage, being closer to the shared vertex at a Ag···Cl distance of 2.784(6) Å. The remaining Ag···Cl distances lie in the range of 2.999(6)−3.537(6) Å, which are comparable to those found in $[Ag_{19}(^tBuC{\equiv}C)_{11}(CF_3CO_2)_7Cl]$ (2.940−3.847 Å) and $[Ag_{14}(^tBuC{\equiv}C)_{12}Cl]BF_4$ (3.116−3.297 Å).[11] Each ^{t}BuC≡C ligand adopts the μ_3-bridging mode to link a silver(I) triangle, and a total of 14 ligands are peripherally coordinated to silver atoms to consolidate the cluster. Additionally, two water molecules and two fluoride ions from the disassembly of BF_4^- function as terminal ligands, each coordinating to one silver atom. The crystal packing is further stabilized by four solvated water molecules, three exhibiting half site occupancy and one having quarter site occupancy. The overall charge balance against the silver anionic cluster is provided by one BF_4^- counteranion in the crystal structure.

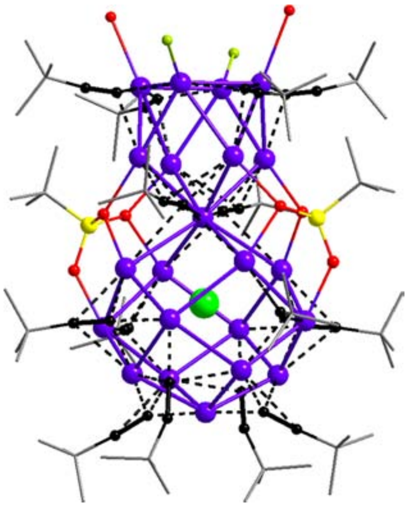

Figure 3. Cl@Ag_{22} cluster skeleton in complex **4**, which lies on a crystallographic C_2 axis. The Cl^- template is represented by a larger green ball. Hydrogen atoms are omitted for clarity. The carbon atoms of the ethynide group are represented as small black balls, and their bonds to silver atoms are indicated by broken lines. Color code: Ag, violet; C, gray; O, red; Cl, green; P, yellow.

Notably, the Cl@Ag_{14} cage is similar to four previously reported silver(I) ethynide clusters, $[Cl@Ag_{14}({}^tBuC{\equiv}C)_{12}]BF_4$,[11b] $[Cl@Ag_{14}({}^iPrC{\equiv}C)_{12}]NO_3$,[7h] $[Cl@Ag_{14}({}^tBuC{\equiv}C)_{12}]OH$,[11a] and $[Cl@Ag_{14}(chxC{\equiv}C)_{12}]Cl$ (chx = cyclohexyl),[7h] and the latter two clusters can be used as precursors to construct two high-nuclearity silver ethynide cluster compounds, $[Cl_6Ag_8@Ag_{30}({}^tBuC{\equiv}C)_{20}(ClO_4)_{12}]\cdot Et_2O$ and $[Cl_6Ag_8@Ag_{30}(chxC{\equiv}C)_{20}(ClO_4)_{10}](ClO_4)_2\cdot 1.5Et_2O$,[7h] which bear the same novel Cl_6Ag_8 central core.

The syntheses and structural characterizations of **1**−**4** showed that the phosphonate species is directly involved in the formation of silver(I) ethynide complexes, and their structures are affected by variation of the silver(I) ethynide precursor, anionic templates, and solvent employed. In the synthesis of **4**, the BF_4^- anion undergoes disassembly in solution, yielding F^- anions as terminal ligands, while the reaction of BF_4^- and SiO_2 derived from glassware afforded SiF_6^{2-} as the counteranion in **3**.

In conclusion, on the basis of the ${}^tBuC{\equiv}C{\supset}Ag_n$ (n = 3−5) metal−ligand supramolecular synthon and the *tert*-butylphosphonate ligand, we have synthesized and structurally characterized four silver(I) ethynide complexes. Compounds **1** and **2** exhibit coordination layer-type architectures, and the latter features an argentophilic infinite chain. Compounds **3** and **4** provide precedents of high-nuclearity silver(I) ethynide $\{Ag_5(NO_3@Ag_{18})Ag_5\}$ and $\{Ag_8(Cl@Ag_{14})\}$ composite clusters bearing nitrate and chloride template ions, respectively. In our previous report on the synthesis of high-nuclearity silver(I) ethynide clusters, ${}^tBuPO_3^{2-}$ constitutes a structural component for building up the cluster shell,[7g] but here in complexes **3** and **4**, it functions as a tripodal strut to support vertex-sharing or fusion of two small silver(I) clusters to form an enlarged composite cluster.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, additional figures, and X-ray crystallographic data in CIF format for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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