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Ligand- and Anion-Controlled Formation of Silver Alkynyl Oligomers from Soluble Precursors

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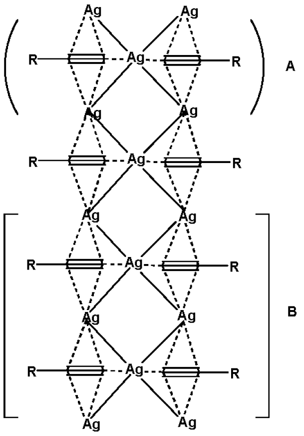
Novel silver(I) alkynyl cluster complexes ($[Ag_5(bpy)_4(C{\equiv}CBu^t)_2]^{3+}$, $[Ag_8(bpy)_6(C{\equiv}CBu^t)_4]^{4+}$, and $[Ag_{12}(bpy)_4(C{\equiv}CBu^t)_6(CF_3CO_2)_6]$) have been synthesized by reacting soluble polymeric precursors with bipyridine ligands, and control of the nuclearity can be achieved by varying the molar ratio of the reactants and using different types of anions.

The chemistry of d^{10} alkynyl complexes is of great interest because of their rich structural diversity and potential applications in NLO, luminescence, and organic optoelectronics.[1] Simple coinage-metal alkynyl compounds $[RC{\equiv}CM]_n$ usually have polymeric structures and are not soluble in common organic solvents, which preclude detailed structural studies. Thus X-ray powder diffraction has been used to acquire insights on the structures of polymeric $[RC{\equiv}CM]_n$ (M = Cu, Ag, Au) solids.[2] Compared to other coinage-metal alkynyl compounds, silver(I) derivatives are less explored because of their sensitivity to light and tendency to yield highly insoluble polymers/oligomers. In most of the known silver alkynyl aggregates, phosphines are employed as capping ligands.[3] It is noted that Mak et al. have prepared and structurally characterized a series of coordination polymeric networks based on silver alkynyl supramolecular synthons by dissolution of $[RC{\equiv}CAg]_n$ in concentrated aqueous solutions of various soluble silver salts.[4]

Interestingly, when bulky alkynes are used, the reaction of $[Bu^tC{\equiv}CAg]_n$ with $AgBF_4$ in a 2:1 ratio led to the formation of a polymeric undulated ribbon structure $[Ag_3(C{\equiv}CBu^t)_2{}^+]_n$,[5] as shown in Scheme 1. Abu-Salah et al. isolated a rhombohedral silver alkynyl complex $[Ag_{14}(C{\equiv}CBu^t)_{12}](BF_4)_2$ by running the reaction at a molar ratio of 6:1 for $[Bu^tC{\equiv}CAg]_n$ and $AgBF_4$,[6] while Mingos et al. reported anion-templated rhombohedral silver alkynyl cages $[Ag_{14}(C{\equiv}CBu^t)_{12}X]^+$ (X = F, Cl, Br).[7] Envisioning that these soluble species might be good precursors for the preparation of new silver alkynyl clusters, we have developed a synthetic strategy by introducing 2,2′-bipyridine (bpy) as an optimal capping ligand for trapping oligomeric silver alkynyl clusters exhibiting nuclearities ranging from 5 to 12. Herein, we reported the synthesis and structures of a series of silver alkynyl complexes having stoichiometric formulas $[Ag_5(bpy)_4(C{\equiv}CBu^t)_2]X_3$ (X = BF_4, **1**; CF_3SO_3, **2**), $[Ag_8(bpy)_6(C{\equiv}CBu^t)_4]X_4$ (X = BF_4, **3**; CF_3SO_3, **4**), and $[Ag_{12}(bpy)_4(C{\equiv}CBu^t)_6(CF_3CO_2)_6]$, **5**.

Scheme 1



Reaction of $Bu^tC{\equiv}CAg$ with $AgBF_4$ in methanol in a 2:1 ratio gave a clear solution, to which bpy was added. A white solid was obtained after solvent removal, which was then

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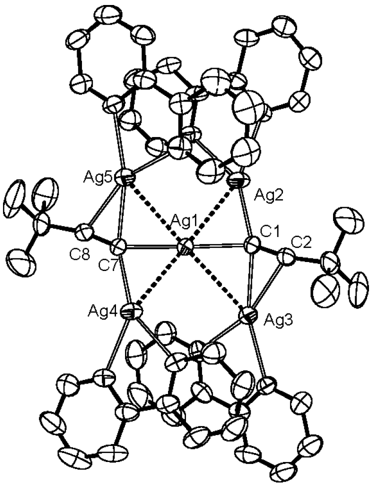

Figure 1. ORTEP drawing of the pentanuclear cation of $[Ag_5(bpy)_4(C{\equiv}CBu^t)_2](BF_4)_3$ (**1**) at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Ag1 · · · Ag2 = 2.764(1), Ag1 · · · Ag3 = 2.991(1), Ag1 · · · Ag4 = 2.764(1), Ag1 · · · Ag5 = 2.996(1), Ag1−C1 = 2.100(8), Ag1−C7 = 2.101(8), Ag2−C1 = 2.156(8), Ag3−C1 = 2.275(8), Ag4−C2 = 2.366(9), Ag4−C7 = 2.135(8), Ag5−C7 = 2.255(8), Ag5−C8 = 2.333(9).

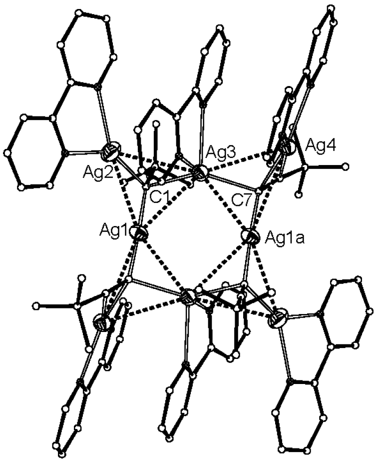

Figure 2. Centrosymmetrically related structure of the octanuclear cation of $[Ag_8(bpy)_6(C{\equiv}CBu^t)_4](BF_4)_4$ (**3**). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Ag1 · · · Ag2 = 2.976(1), Ag1 · · · Ag3 = 2.9945(8), Ag2 · · · Ag3 = 3.202(1), Ag3 · · · Ag1a = 2,8742(9), Ag4 · · · Ag1a = 3.3509(8), Ag1−C1 = 2.092(8), Ag2−C1 = 2.140(9), Ag3−C1 = 2.350(7), Ag3−C7 = 2.256(8), Ag4−C7 = 2.263(7), Ag1a−C7 = 2.097(8). Symmetry code: (a) $-x + 1/2$, $-y + 1/2$, $-z + 1$.

dissolved in hot MeOH/EtOH. Colorless blocklike crystals of **1** were isolated in ~56.3% yield after slow cooling. The purity of the bulk product was confirmed by powder XRD and elemental analysis (see Supporting Information).[8] An IR vibration band at 2055 cm^{-1} confirmed the presence of the C≡C group. Single-crystal X-ray analysis indicated that compound **1** consists of a cationic pentanuclear silver cluster and BF_4^- counteranions.[9] Five silver(I) atoms aggregate together through bridging by two alkynyl ligands. As shown in Figure 1, the five silver(I) atoms can be divided into three chemically distinct types. The central silver atom Ag(1) is coordinated by two terminal alkyl C atoms and also involved in secondary bonding with four surrounding silver atoms. Atoms Ag(2) and Ag(4) are of the second type, each being ligated by one C atom of an alknyl group and a chelating bpy ligand. The third type Ag(3) and Ag(5) is each coordinated by both C atoms of an alkynyl group and a chelating bpy ligand. The argentophilic Ag · · · Ag interactions range from 2.764(1) to 2.996(1) Å, which are significantly shorter than twice the van der Waals radius of the silver atom.

Changing BF_4^- to $CF_3SO_3^-$ led to the isolation of **2**, which has essentially the same structure as **1**.[10]

As shown in Scheme 1, the pentanuclear motif is exactly a portion of the polymeric silver alkynyl structure of $[Ag_3(C{\equiv}CBu^t)_2{}^+]_n$ (part A). Thus bpy ligands function like chemical scissors to chop this motif from the polymeric ribbon. Accordingly, an attempt was made to control the nuclearity by adjusting the ratio of the reactants. With a molar ratio of 4:4:6 for Bu^{t}C≡CAg, $AgBF_4$ and bpy, a new cationic cluster **3** containing eight silver(I) centers was successfully isolated.[11]

IR vibration bands at 1961 and 2004 cm^{-1} confirmed the presence of the C≡C group in **3**. As shown in Figure 2, the centrosymmetric octanuclear cation contains a nearly planar arrangement of eight silver atoms bound together solely by four μ_3-alkynyl ligands, each functioning in the μ_3-bridging mode. The silver atoms are arranged in three rows of 3, 2, and 3, and each of the six bpy ligands chelates a silver atom in row 1 or 3. If the bpy ligands were removed from the structure, the molecular configuration would be very similar to moiety B in Scheme 1.

The structure of the octasilver cation can be viewed as the fusion of four Ag_3 triangles sharing corners Ag1, Ag3, Ag1a, and Ag3a.

Compound **4** was prepared by using AgOTf instead of $AgBF_4$, and its cationic structure is similar to that of **3**.[12]

Changing the noncoordinating anion BF_4^- to the weakly coordinating anion $CF_3SO_3^-$ did not affect the formation of the cationic cluster. However, a surprising structural change was observed when the coordinating anion trifluoroacetate (tfa) was introduced into the system. Compound **5** was isolated in a synthetic procedure similar to that for **1**, except that $AgCF_3CO_2$ was used instead of $AgBF_4$.

Compound **5** is a neutral centrosymmetric silver cluster consisting of twelve silver atoms consolidated by six alkynyl

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(8) ESI-MS studies were carried out for **1**–**5**, but no satisfactory results were obtained.

(9) Crystal data for **1**: $C_{52}H_{52}N_8OB_3F_{12}Ag_5$, a = 27.925(5) Å, b = 16.721(3) Å, c = 24.254(4) Å, V = 11325(3) Å^3, space group *Pccn*, Z = 8, T = 295 K, 60 124 reflections measured, 11 132 unique (R_{int} = 0.0462), final R_1 = 0.0787, R_2 = 0.1925 for 7878 observed reflections [$I > 2\sigma(I)$].

(10) Crystal data for **2**: $C_{56}H_{54}N_8O_{10}S_3F_{12}Ag_5$, a = 17.904(1) Å, b = 16.7075(8) Å, c = 21.784(2) Å, β = 100.523(7)°, V = 6406.6(7) Å^3, space group *C2/c*, Z = 4, T = 295 K, 21 554 reflections measured, 8625 unique (R_{int} = 0.056), final R_1 = 0.0427, R_2 = 0.0940 for 4003 observed reflections [$I > 2\sigma(I)$].

(11) Crystal data for **3**: $C_{84}H_{84}N_{12}B_4F_{16}Ag_8$, a = 29.4664(9) Å, b = 22.1125(6) Å, c = 15.0713(3) Å, β = 113.858(2)°, V = 8981.0(4) Å^3, space group *C2/c*, Z = 4, T = 223 K, 30 559 reflections measured, 10 785 unique (R_{int} = 0.0392), final R_1 = 0.0552, R_2 = 0.1533 for 4643 observed reflections [$I > 2\sigma(I)$].

(12) Crystal data for **4**: $C_{88}H_{88}N_{12}O_{14}S_4F_{12}Ag_8$, a = 12.6079(6) Å, b = 14.485(1) Å, c = 14.5796(6) Å, α = 93.675(5)°, β = 110.905(4)°, γ = 92.933(5)°, V = 2474.4(2) Å^3, space group $P\bar{1}$, Z = 1, T = 295 K, 20 943 reflections measured, 11 274 unique (R_{int} = 0.0392), final R_1 = 0.0640, R_2 = 0.1868 for 5797 observed reflections [$I > 2\sigma(I)$].

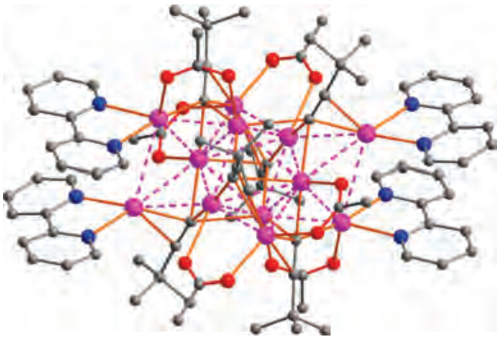

Figure 3. Molecular structure of $[\mathrm{Ag_{12}(bpy)_4(C{\equiv}CBu^t)_6(CF_3CO_2)_6}]$ (**5**). Atom color legend: silver (purple), oxygen (red), nitrogen (blue), and carbon (gray). Hydrogen and fluorine atoms have been omitted for clarity. Ag • • • Ag contacts are shown as broken lines.

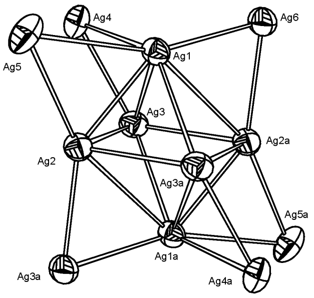

Figure 4. Configuration of the twelve silver(I) centers in **5**, showing six silver atoms attached to the octahedral core. Bond distances (Å): Ag1 • • • Ag2 = 2.8474(6), Ag1−Ag3 = 3.1308(7), Ag1−Ag2a = 3.3337(7), Ag1−Ag3a = 3.0487(7), Ag1−Ag4 = 2.8679(7), Ag1−Ag5 = 3.1781(8), Ag1−Ag6 = 2.8400(7), Ag2−Ag3 = 2.9578(7), Ag2−Ag3a = 3.0035(7), Ag2−Ag5 = 3.0183(8), Ag3−Ag4 = 2.9112(8). Symmetry code: (a) $-x + 1, -y, -z + 1$.

and six tfa ligands. [13] As shown in Figures 3 and 4, the core of this dodecanuclear silver cluster is an octahedron comprising Ag1, Ag2, Ag3, Ag1a, Ag2a, and Ag3a, and there are six additional silver atoms surrounding it. The six outer-shell silver atoms are connected to the octahedral core through three linking modes: (i) solely by one $\mathrm{Bu^tC{\equiv}C}$ ligand, (ii) by one $\mathrm{Bu^tC{\equiv}C}$ and one tfa ligand, and (iii) by one $\mathrm{Bu^tC{\equiv}C}$ and two tfa ligands. Atoms Ag1, Ag6, Ag2a, Ag5a, Ag1a, Ag6a, Ag2, and Ag5 are coplanar with a mean deviation of 0.06 Å. The argentophilic Ag • • • Ag contacts are in the range of 2.840–3.334 Å.

It is noteworthy that a dodecanuclear silver cluster $[\mathrm{Ag_{12}(CF_3CO_2)_{14}}]^{6-}$ has been reported that has a mixed-valence $\mathrm{Ag_{12}}^{8+}$ core comprising two $\mathrm{Ag_6}^{4+}$ octahedra fused together.[14]

All the alkynyl ligands in compounds **1**–**5** retain their triple-bond character, with C−C bond lengths in the range of 1.18−1.22 Å. Different types of coordination modes of alkynyl ligands were observed, $\mu_3-\eta^1,\eta^1,\eta^2$ in **1** and **2**, $\mu_3-\eta^1,\eta^1,\eta^1$ in **3** and **4**, and $\mu_4-\eta^1,\eta^1,\eta^1,\eta^2$ in **5**. The versatile coordination behavior (both σ- and π-bonding to metal centers) of alkynyl ligands made the formation of diverse structures possible.

A pentanuclear copper(I) analogue of **1**/**2** was prepared through the reaction of $\mathrm{Cu(MeCN)_4}^+$ with $\mathrm{Bu^tC{\equiv}CLi}$ and 2,2′-bpy.[15] However, the structural configurations of **3**–**5** are unprecedented among complexes of the metal alkynyl family.

The absorption and emission spectra of complexes **1**–**5** in methanol (Figures 1S and 2S) are almost the same as that of 2,2′-bpy. This suggested that the photophysical behavior in solution is dominated by bipyridine ligands. However, complexes **1**–**5** displayed weak luminescence in the solid state at room temperature, when these compounds were irradiated at wavelengths greater than 290 nm. As shown in Figures 3S−7S, the emission spectra are relatively complex, and multiple emission maxima were observed ($\lambda_{\mathrm{em}}^{\mathrm{max}}$ at 375, 407, 460, and 534 nm for **1**; $\lambda_{\mathrm{em}}^{\mathrm{max}}$ at 405, 460, and 533 nm for **2**; $\lambda_{\mathrm{em}}^{\mathrm{max}}$ at 368, 404, 456, and 530 nm for **3**; $\lambda_{\mathrm{em}}^{\mathrm{max}}$ at 405, 460, and 534 nm for **4**; $\lambda_{\mathrm{em}}^{\mathrm{max}}$ at 428, 460, and 530 nm for **5**). DFT/B3LYP[16] calculations were carried out to study the electronic structures of **1**, **3**, and **5**. For both **1** and **3**, the HOMO mainly consists of characters from d-orbitals of Ag atoms, p-orbitals of N atoms, and π-bonding orbitals of alkynyl ligands, while the LUMO is essentially the π*-orbital of bipyridine rings. For **5**, the HOMO contains characters from d-orbitals of Ag atoms, p-orbitals of O atoms, and π-bonding orbitals of alkynyl ligands, while its LUMO is a π*-system delocalized over the bipyridine rings. This is quite different from the case in $[\{\mathrm{Pt_2Ag_4(Bu^tC_2)_8}\}\{\mathrm{Ag(bipy)}\}_4](\mathrm{ClO_4})_4$, where Ag(bpy) units are not involved in the excited states. [17]

In summary, the present study presents a facile method for the synthesis of polynuclear silver alkynyl clusters, demonstrating that structural diversity can be controlled by varying the molar ratio of the reactants or utilizing different types of coexisting anions.

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Supporting Information Available: X-ray crystallographic data in CIF format for **1**–**5**, synthetic procedures, characterization data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data for **5**: $\mathrm{C_{88}H_{86}N_8O_{12}F_{18}Ag_{12}}$, a = 13.9275(5) Å, b = 15.0064(6) Å, c = 15.1885(6) Å, α = 61.852(4)°, β = 63.854(4)°, γ = 80.682(5)°, V = 2508.3(2) Å^3, space group $P\bar{1}$, Z = 1, T = 295 K, 18 909 reflections measured, 7781 unique (R_{int} = 0.0274), final R_1 = 0.0370, R_2 = 0.0934 for 5789 observed reflections [$I > 2\sigma(I)$].

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