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An unusual silver–ethynide polymeric chain containing centrosymmetric Ag_{14} cluster segments stabilized by mixed carboxylate ligands

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ABSTRACT

From the reaction of $AgC{\equiv}C{}^tBu$ with 9-hydroxy-9-fluorenecarboxylic acid (HL) and $AgCF_3CO_2$, we have isolated a new type of organosilver(I) coordination polymeric chain, namely $\{[Ag_{14}(C{\equiv}C{}^tBu)_8(L)_2(CF_3CO_2)_4]\cdot 2CH_3OH\}_n$, which contains centrosymmetric $[Ag_{14}(C{\equiv}C{}^tBu)_8(CF_3CO_2)_2]^{4+}$ cluster segments bridged by pairs of L and trifluoroacetate ligands.

The chemistry of metal ethynyl complexes is of great interest because of their structural diversity and technological application as precursors of nonlinear optical materials, luminescent probes, and rigid-rod molecular wires [1–4]. Among a wide range of candidate metals, the Group 11 elements (Cu, Ag and Au) are frequently employed in the syntheses of novel ethynyl complexes due to their enhanced metallophilic interaction that overcomes repulsion between cationic metal centers [5–11]. The silver(I) ethynyl derivatives are less explored because of their sensitivity to light and tendency to yield highly insoluble polymers/oligomers. Recently, we and other groups have prepared and structurally characterized a series of silver(I)–ethynide coordination polymeric networks [12–17] and high-nuclearity clusters [18–31] based on the multinuclear metal–ligand supramolecular synthon $R-C{\equiv}C \supset Ag_n$ ($n = 3, 4, 5$; R = alkyl, aryl, heteroaryl).

In 1999 the reaction of $[AgC{\equiv}C{}^tBu]_n$ with $AgBF_4$ in molar ratio 2:1 was reported to yield a polymeric undulated ribbon structure $[Ag_3(C{\equiv}C{}^tBu)_2^+]_n$ [32]. Envisioning that such soluble species might be good precursors for the preparation of new silver(I)–ethynide complexes, we have developed a synthetic strategy by introducing phosphonate and phosphonate-functionalized oxovanadate or oxovanadate as capping ligands for trapping oligomeric silver(I)–ethynide clusters. Recently we isolated a series of mixed-metal giant clusters with the silver(I)–*tert*-butylethynide moiety and various phosphonate-functionalized oxovanadate building blocks as their surface components, as well as different numbers and kinds of anionic species as their encapsulated templates: for example $\{(NO_3)_2@Ag_{16}(C{\equiv}CPh)_4[({}^tBuPO_3)_4V_4O_8]_2(DMF)_6(NO_3)_2\}$ [31] and $\{Cl_2@Ag_{21}(C{\equiv}C{}^tBu)_9[({}^tBuPO_3)_3V_3O_6(OH)]_2[({}^tBuPO_3)VO_2(OH)](MeOH)_2(H_2O)_2\}$ [30]. We also employed neat *tert*-butylphosphonic acid as a precursor and successfully generated new silver(I) ethynide networks and clusters, for example $3AgC{\equiv}CPh\cdot Ag_2^tBuPO_3\cdot Ag^tBuPO_3H\cdot 2AgNO_3$ and $[\{Ag_8(Cl@Ag_{14})\}(C{\equiv}C{}^tBu)_{14}({}^tBuPO_3)_2F_2(H_2O)_2]BF_4\cdot 3.5H_2O$ [16].

In the present work, we report our successful combination of 9-hydroxy-9-fluorenecarboxylic acid (HL) with the supramolecular synthon ${}^tBuC{\equiv}C \supset Ag_n$ ($n = 3, 4$) to generate a novel organosilver coordination polymer, namely $\{[Ag_{14}(C{\equiv}C{}^tBu)_8(L)_2(CF_3CO_2)_4]\cdot 2CH_3OH\}_n$ (**1**) [33], which has been characterized by elemental analysis, infrared spectroscopy and single-crystal X-ray analysis [34]. HL is known to function as a plant growth regulator, which restrains the generation of abscisic acid and regulate plant root calcium transport [35]. Furthermore, in the anionic L ligand, the hydroxy and carboxylate groups provide different potential coordination sites for metal coordination.

The reaction of HL with $AgC{\equiv}C{}^tBu$ and $AgCF_3CO_2$ in CH_3OH yielded colorless prismatic crystals of **1**. An IR vibration band at 2005 cm^{-1} confirmed the presence of the $C{\equiv}C$ functional group. Of the four independent *tert*-butylethynide ligands in the asymmetric unit, the ethynide group composed of C37 and C38 is bound to a silver triangle in the $\mu_3-\eta^1,\eta^1,\eta^1$ coordination mode. The remaining three ethynide groups (C15≡C16, C23≡C24 and C31≡C32) are each capped by a butterfly-shaped Ag_4 basket in the $\mu_4-\eta^1,\eta^1,\eta^1,\eta^2$ or $\mu_4-\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode, as shown in Fig. 1.

Two Ag_3 triangles and six Ag_4 baskets coalesce by sharing vertices to form a centrosymmetric $Ag_{14}({}^tBuC{\equiv}C)_8$ cluster, which is further stabilized by a pair of CF_3CO_2 ligands with Ag–O bond distances of

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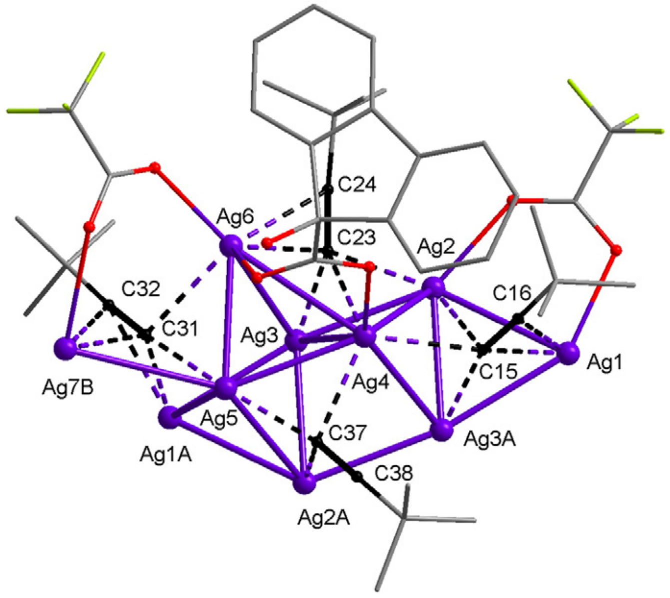

Fig. 1. Coordination environment of silver(I) atoms surrounded by four independent *tert*-butylethynide, one 9-hydroxy-9-fluorenecarboxylate, and two trifluoroacetate ligands in $\{[Ag_{14}(C{\equiv}C^tBu)_8(L)_2(CF_3CO_2)_4]\cdot 2CH_3OH\}_n$ (**1**). The C≡C triple bond is represented by a bold rod. The Ag – C bonds are indicated by broken lines. All hydrogen atoms and methanol molecules have been omitted for clarity. Color codes: Ag, violet; C, gray; O, red; and F, lime. Ag1A – C31 = 2.325(8), Ag1 – C15 = 2.334(9), Ag1 – C16 = 2.647(9), Ag1A – C32 = 2.679(7), Ag2A – C37 = 2.349(9), Ag2 – C23 = 2.521(9), Ag3 – C23 = 2.134(7), Ag3A – C15 = 2.151(8), Ag4 – C37 = 2.429(7), Ag4 – C15 =2.438(9), Ag4 – C23 = 2.519(6), Ag5 – C37 = 2.150(8), Ag5 – C31 = 2.195(7), Ag6 – C23 = 2.376(8), Ag6 – C31 = 2.494(7), Ag6 – C24 = 2.545(8), Ag7B – C31 = 2.256(8), Ag7B – C32 = 2.665(7). Symmetry codes: A 1 − *x*, −*y*, −*z*; and B 2−*x*, −*y*, −*z*.

2.317(5) and 2.369(6) Å (Fig. 2). The resulting $Ag_{14}(^tBuC{\equiv}C)_8(CF_3CO_2)_2$ cluster segments are bridged by a series of L and additional CF_3CO_2 ligands to engender an infinite coordination chain in the direction of the *a* axis (Fig. 3). The L ligand has its carboxylate terminal bridging two adjacent silver atoms, and the 9-hydroxy group functions as a monodentate ligand to coordinate one silver atom, with Ag – O distances varying from 2.343(6) to 2.589(5) Å. However, the bridging CF_3CO_2 ligand coordinates to four silver atoms with Ag – O bond lengths ranging from 2.335(6) to 2.715(6) Å.

The argentophilic Ag···Ag bond distances lie in the range 2.899(2)–3.325(2) Å. Additionally, the crystal structure contains two methanol solvate molecules in the unit cell. Fig. 4 shows the crystal structure with only van der Waals interaction between the coordination polymeric chains.

Notably, the bar-like Ag_{14} cluster in **1** differs markedly from previously reported rhombic-dodecahedral silver(I)–ethynide cages, *e.g.* $[Cl@Ag_{14}(C{\equiv}C^tBu)_{12}]OH$ [19] and $[Cl@Ag_{14}(C{\equiv}Ccyclohexyl)_{12}]Cl$ [28] with encapsulated chloride ions, which have been employed as precursors to synthesize the corresponding iso-structural "cluster-within-cluster" compounds $[Cl_6Ag_8@Ag_{30}(^tBuC{\equiv}C)_{20}(ClO_4)_{12}]\cdot Et_2O$ and $[Cl_6Ag_8@Ag_{30}(chxC{\equiv}C)_{20}(ClO_4)_{10}](ClO_4)_2\cdot 1.5Et_2O$ that bear the same pseudo-O_h cationic Cl_6Ag_8 inner core [28].

The anionic L ligand, with its bulky hydrophobic, outward-extending fluorenyl group, connects adjacent high-nuclearity silver(I)–ethynide cluster segments to generate the coordination polymer chain in **1**. In contrast, silver trifluoroacetate plays a crucial dual role in the present synthesis: (i) as a bridging ligand that stabilizes each Ag_{14} cluster segment, and (ii) cooperates with the L ligand to link up adjacent Ag_{14} cluster segments. Notably, thus far our attempts to prepare related silver(I)–ethynide complexes using other soluble silver salts such as nitrate, tetrafluoroborate and triflate were unsuccessful, which always yielded an intractable pale solid residue.

Combining the metal–ligand supramolecular synthon $^tBuC{\equiv}C \supset Ag_n$ ($n = 3, 4$) (generated *in situ* from a solution of $^tBuC{\equiv}CAg$ and $AgCF_3CO_2$ in methanol) and 9-hydroxy-9-fluorenecarboxylic acid, we have isolated and structurally characterized a new kind of silver(I)–ethynide coordination polymeric complex, in which the 9-hydroxy-9-fluorenecarboxylate and trifluoroacetate ligands bridge two novel condensed Ag_{14} clusters to form a coordination chain architecture. The present study offers broad prospects to future synthetic exploration of silver–ethynide complexes bearing different varieties of carboxylates as structural components.

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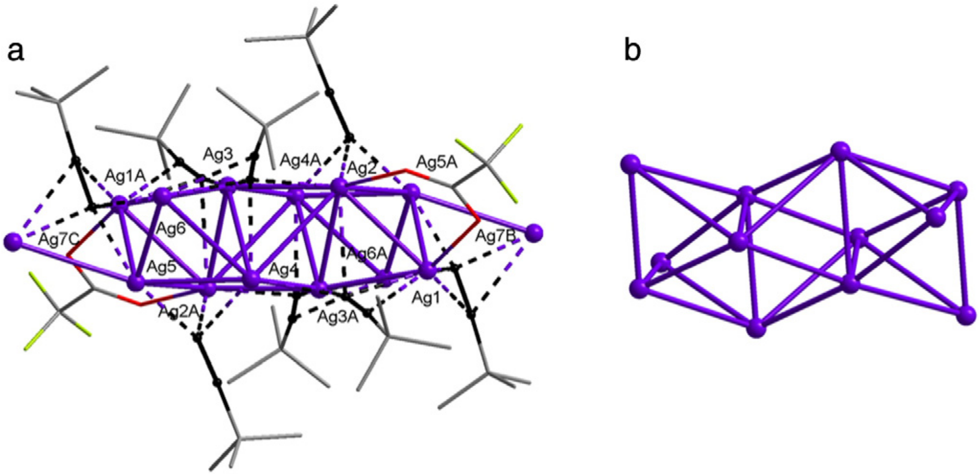

Fig. 2. (a) The centrosymmetric $[Ag_{14}(C{\equiv}C^tBu)_8(CF_3CO_2)_2]^{4+}$ cluster skeleton in complex **1**. H atoms are omitted for clarity. The carbon atoms of the ethynide group are represented as small black balls, and their bonds to silver atoms are indicated by broken lines. Atoms Ag7B and Ag7C are symmetry equivalents of Ag7. (b) Perspective view of the center Ag_{12} portion in $[Ag_{14}(C{\equiv}C^tBu)_8(CF_3CO_2)_2]^{4+}$ cluster skeleton. Color codes: Ag, violet; C, gray; O, red; and F, lime. Ag1···Ag5A = 2.899(2), Ag1···Ag3A = 2.985(2), Ag1···Ag2 = 3.076(2), Ag2···Ag3 = 2.945(2), Ag2···Ag3A = 3.064(3), Ag2···Ag5A = 3.115(3), Ag2···Ag4 = 3.317(2), Ag3···Ag4 = 2.983(2), Ag3···Ag4A = 2.995(2), Ag3···Ag6 = 3.278(3), Ag4···Ag5 = 3.000(2), Ag4···Ag6 = 3.231(2), Ag5···Ag6 = 2.938(3), Ag5···Ag7B = 3.325(2). Symmetry codes: A 1 − *x*, −*y*, −*z*; B −1 + *x*, *y*, *z*; and C 2−*x*, −*y*, −*z*.

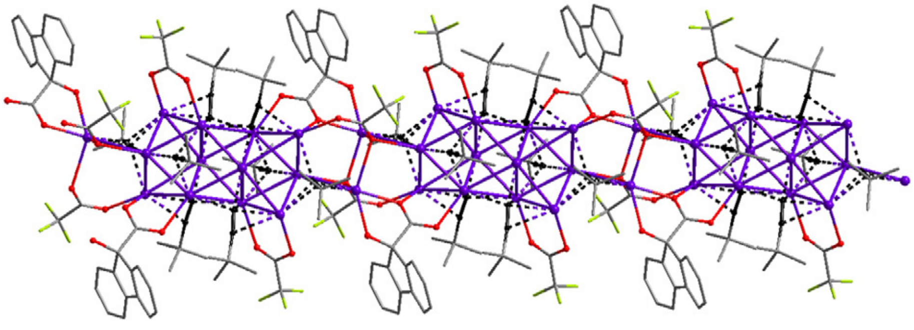

Fig. 3. Coordination polymeric chain in complex **1**. Each C≡C triple bond is represented by a bold rod. The Ag – C bonds are indicated by broken lines. All hydrogen atoms and methanol molecules have been omitted for clarity. Color codes: Ag, violet; C, gray; O, red; and F, lime.

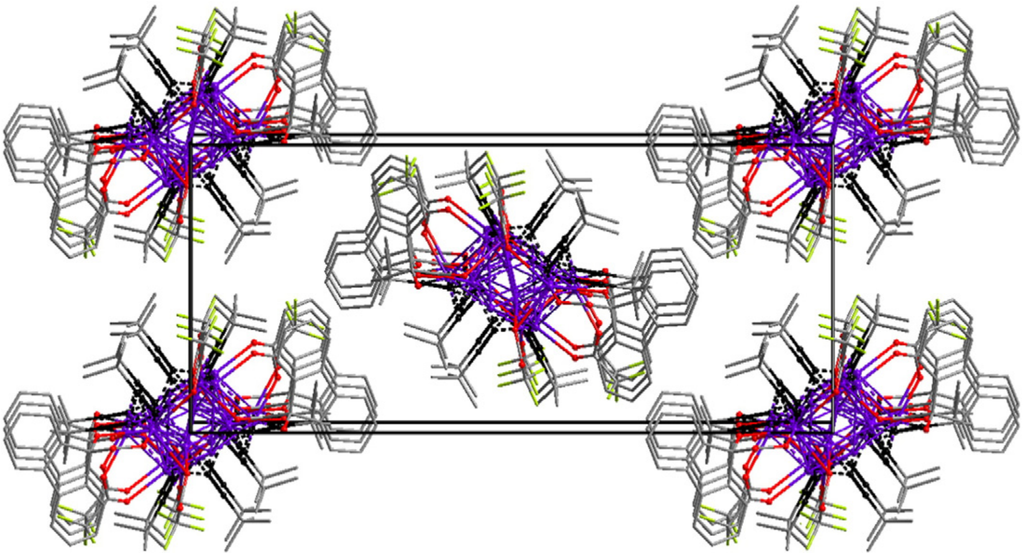

Fig. 4. Packing of coordination polymeric chains in the crystal structure of **1** viewed parallel to the *a* axis. All methanol molecules have been omitted for clarity. Color codes: Ag, violet; C, gray; O, red; and F, lime.

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Appendix A. Supplementary material

CCDC 907576 contains the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2013.02.019.

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[33] HL (0.023 g, 0.010 mmol) was dissolved in CH_3OH (4 mL). Then $^tBuC{\equiv}CAg$ (0.095 g, 0.500 mmol) and $AgCF_3CO_2$ (0.022 g, 0.100 mmol) were added under stirring. After 30 min, a clear solution was collected by filtration. Slow evaporation of the clear solution afforded colorless prismatic crystals **1** in *ca*. 16%. Elemental analysis (%) calcd for $C_{43}H_{49}Ag_7F_6O_8$: C 33.04, H 3.16; found: C 33.35, H 3.31; selected IR data (KBr): 2005 ($C{\equiv}C$).

[34] Crystallographic data. Complex **1**: monoclinic, $a = 13.625(1)$, $b = 29.180(3)$, $c = 13.767(1)$ Å, $\beta = 111.262(1)$ $V = 5101(8)$ Å^3, $T = 293$ K, space group $P2_1/c$, $Z = 4$, $\lambda = 0.71073$ Å, $\rho = 2.034\ \mathrm{cm}^{-3}$, $\mu(\mathrm{Mo_{K\alpha}}) = 2.699\ \mathrm{mm}^{-1}$, $R_1 = 0.0462$, $wR_2 = 0.1366$ for $I > 2\sigma(I)$, GOF = 1.117. Crystal data were collected on a Bruker Smart Apex II CCD diffractometer with Mo–Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program [36] within WINGX [37].

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