Snowman-like silver alkynyl cluster consolidated by templating chloride and peripheral trifluoroacetates†

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A novel nonadecanuclear silver double cage was isolated, in which a square antiprism and a pentacapped pentagonal prism templated by a chloride ion share a tetragonal face to form a snowman-like cluster that is held together by bridging alkynyl groups and trifluoroacetates.

Chemical templates play an important role in the formation of supramolecular assemblies. The templating effects of cationic and neutral species have been widely studied, however, anionic templates have been much less developed in synthetic chemistry. Recently, anion-templated processes have attracted increasing attention, because the intrinsic properties (diffuse nature, pH sensitivity and relative high solvation free energy) of anions are not as critical as first thought.[1–4]

An important category of anion-templated synthesis is the construction of finite assemblies, and chloride has proven to effectively direct the formation of several metal–containing cycles and cages, such as the tetranuclear [12]mercuracarborad-4,[5] the pentadecanuclear complex $[Ln_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)]^{24+}$ and the nickel cage $[Ni_6(atu)_8Cl]^{3+}$ (atu = amidinothiourea).[6,7] Interestingly, Vilar, Mingos and co-workers reported novel halide-templated rhombohedral silver alkynyl cage compounds $[Ag_{14}(C{\equiv}CBu^t)_{12}X]^+$ (X = F, Cl, Br), which were obtained accidentally in the course of preparing a silver analogue of the gold(I) catenane $\{[AuC{\equiv}CBu^t]_6\}_2$.[8] Surprisingly, our attempt to prepare silver alkynyl oligomers with diamine capping agents led to the isolation of a novel double-caged cluster with silver atoms arranged in a snowman shape, in which the chloride is crucial for its formation. It represents a unique example of a chloride templated cage with fifteen silver atoms. Herein we report the synthesis and structures of a novel silver alkynyl complex $[Ag_{19}(C{\equiv}CBu^t)_{11}(CF_3CO_2)_7Cl]$ **1** and related complexes $[Ag_4(C{\equiv}CBu^t)(CF_3CO_2)_3(TMEDA)_2]_n$ **2**, $[Ag_{16}(C{\equiv}CBu^t)_8(CF_3CO_2)_8(MeOH)_3]_n$ **3**.

Reaction of $[AgC{\equiv}CBu^t]$ and CF_3CO_2Ag in the presence of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) led to the isolation of a white solid, which was dissolved in $MeOH\text{–}CHCl_3$ (1 : 1 v/v) to afford colorless crystals of **1** with concomitant fine needle-like microcrystalline solid **2**.‡ Complex **2** can be easily washed off with MeOH. Compound **1** was characterized by IR, NMR, elemental analysis and ESI-MS. An IR vibration band at 2008 cm^{-1} confirmed the presence of the C≡C group, and the band at 1675 cm^{-1} is assigned to CF_3CO_2 anion. Single-crystal X-ray structural analysis§ revealed that **1** is a neutral cluster consisting of 19 silver atoms consolidated by eleven alkynyl and seven trifluoroacetate (TFA) ligands along with one interstitial chloride ion (Fig. 1). Four TFA ligands bridge the upper rim of the silver skeleton, and the other three TFAs hold the middle part of the cluster.

The cluster skeleton is shown in Fig. 2(a), it lies on a mirror plane with the mirror passing through Ag3, Ag5, Ag10, Ag11 and Ag12. The skeleton is in the shape of a snowman, which comprises two silver cages, cage A (head) and cage B (body), sharing a square plane Ag3Ag4Ag5Ag4a. Cage A is relatively regular, which is in the shape of a square antiprism consisting of two sets of silver atoms Ag1Ag2Ag2aAg1a and Ag3Ag4Ag5Ag4a. Cage B is made up of fifteen silver atoms and is in the shape of a pentacapped pentagonal prism, *i.e.* the pentagonal prism consists of pentagons Ag4Ag6Ag8Ag9Ag7 and Ag4aAg6aAg8aAg9aAg7a with Ag5, Ag3, Ag11, Ag12 and Ag10 each capping one of the five tetragons. A structural feature is that this cage contains three types of

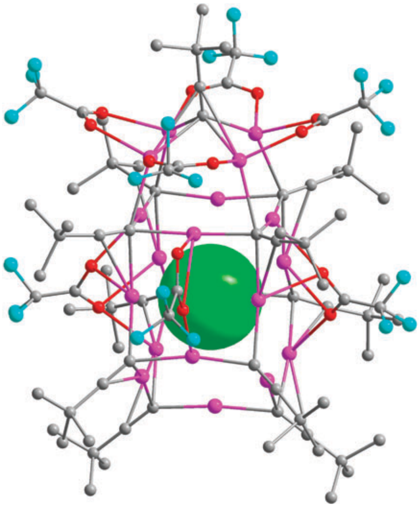

Fig. 1 The structure of the nonadecanuclear cluster $[Ag_{19}(C{\equiv}CBu^t)_{11}(CF_3CO_2)_7Cl]$ (**1**). The templating chloride is showed in space filling mode. Hydrogen atoms and Ag···Ag contacts have been omitted for clarity. Color legend: silver (purple), chlorine (green), carbon (grey), oxygen (red), fluorine (blue).

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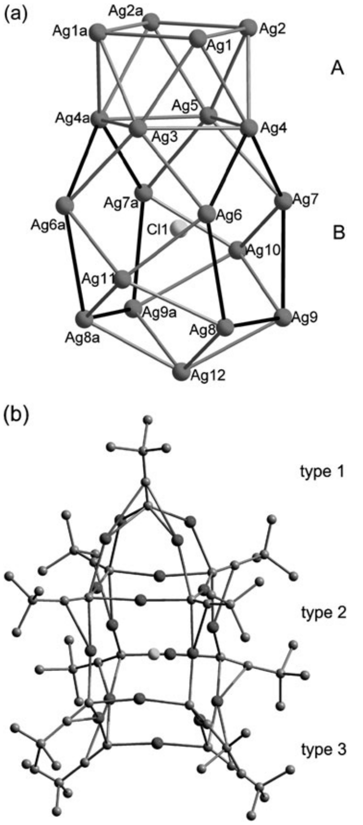

Fig. 2 (a) The snowman-like silver skeleton of **1** showing Ag···Ag contacts (<3.4 Å) with the two pentagons highlighted in dark bonds. Selected bond distances [Å]: Ag1···Ag1a, 3.008(3); Ag1···Ag2, 2.924(2); Ag1···Ag3, 2.912(3); Ag1···Ag4, 3.004(3); Ag2···Ag4, 2.985(3); Ag2···Ag5, 2.921(3); Ag2···Ag2a, 2.922(3); Ag3···Ag4, 3.043(3); Ag3···Ag6, 3.044(3); Ag4···Ag5, 2.963(3); Ag4···Ag6, 3.016(3); Ag4···Ag7, 3.116(3); Ag5···Ag7, 3.055(2); Ag6···Ag8, 3.313(3); Ag6···Ag11, 2.886(3); Ag7···Ag9, 3.094(3); Ag7···Ag10, 2.955(2); Ag8···Ag9, 3.023(3); Ag8···Ag11, 3.109(3); Ag9···Ag10, 3.187(3); Ag9···Ag12, 3.059(3). Symmetry code: (a) x, $-y + 1/2$, z. (b) Three types of binding modes of alkynyls in **1**, Ag···Ag contacts have been omitted for clarity.

polygons: triangle, tetragon and pentagon. The argentophilic Ag···Ag interactions range from 2.886(3) to 3.313(3) Å, which are significantly shorter than twice the van der Waals radius of the silver atom.[9]

There is a templating anion inside cage B, which is identified as a chloride based on the elemental analytic data and the fact that chloroform was used as one of the solvents in the preparation. The identity of this interstitial atom was also confirmed indirectly by ESI-MS experiments carried out in methanol solution. Although no molecular-ion peak of **1** was found, a strong peak at 2518.1 with isotopic pattern exactly matching that of $[Ag_{14}(C{\equiv}CBu^t)_{12}Cl]^+$ was clearly observed (see ESI†).[10] This suggests that **1** is labile in the ionization process leading to the generation of the more stable species $[Ag_{14}(C{\equiv}CBu^t)_{12}Cl]^+$. Although no chloride ion was included in the starting materials, it could be derived from $CHCl_3$ as similarly indicated in other reports.[11] The Ag···Cl distances fall in the range from 2.940 (Cl1···Ag7) to 3.847 Å (Cl1···Ag12), which is significantly longer than the conventional silver–chloride bond lengths (*ca.* 2.6 Å). Most Ag···Cl distances are also longer than those found in $[Ag_{14}(C{\equiv}CBu^t)_{12}Cl]BF_4$ (3.116–3.297 Å), because cage B (Cl@Ag_{15}) has one more silver atom than the rhombohedral cage Cl@Ag_{14}.[8]

As shown in Fig. 2(b), there are 11 alkynyl ligands in this cluster, which can be classified into three types. One alkynyl ligand (type 1) holds the upper four silver atoms in μ_4-η^1,η^1,η^2,η^2 mode. Four alkynyls of type 2 adopt μ_4-η^1,η^1,η^1,η^2 bridging mode to make connections around the neck of the 'snowman' skeleton; Six alkynyl ligands of type 3 function as μ_3-η^1,η^1,η^2 capping agents on the six triangles around the bottom of cage B.

The *tert*-butyl groups of alkynyls showed only a singlet at 1.36 ppm in the ^{1}H NMR spectrum (see ESI†), which did not corroborate the solid structure (three types of ligation modes of $Bu^tC{\equiv}C$ ligands). This suggests that **1** might be unstable in solution.

The presence of TMEDA was found in **2**, which has a chain structure consisting of butterfly-like tetrasilver units as shown in Fig. 3. The dihedral angle of the wings Ag1Ag2Ag3 and Ag1Ag4Ag3 is 59.5°. One $Bu^tC{\equiv}C$ ligand bridges four silver atoms in μ_4-η^1,η^1,η^1,η^2 mode along with the argentophilic interactions in the range of 2.8055(4)–3.3035(4) Å. Ag1 and Ag3 each are chelated by one TMEDA, which leaves Ag2 and Ag4 open for connection to the neighbouring units through TFA ligands.

Although TMEDA was not incorporated in **1**, it is evident that TMEDA also plays a role in the formation of **1**. Repeating the same synthetic procedure for **1** in the absence of TMEDA led to the isolation of a silver compound with a columnar structure $[Ag_{16}(C{\equiv}CBu^t)_8(CF_3CO_2)_8(MeOH)_3]_n$ **3**. As illustrated in Fig. 4, alkynyl, TFA and methanol ligands are coordinated to silver atoms and wrap the column up. It is plausible that TMEDA favors the cleavage of chloride from chloroform, which templates the formation of the cage complex

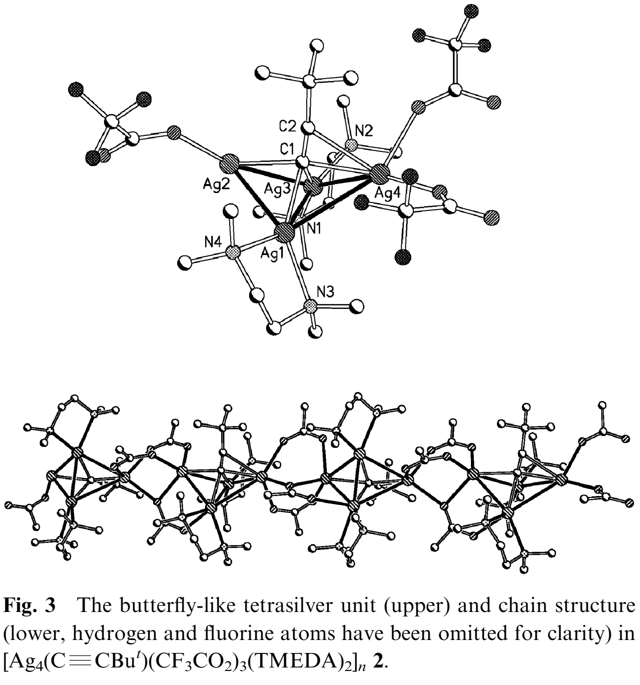

Fig. 3 The butterfly-like tetrasilver unit (upper) and chain structure (lower, hydrogen and fluorine atoms have been omitted for clarity) in $[Ag_4(C{\equiv}CBu^t)(CF_3CO_2)_3(TMEDA)_2]_n$ **2**.

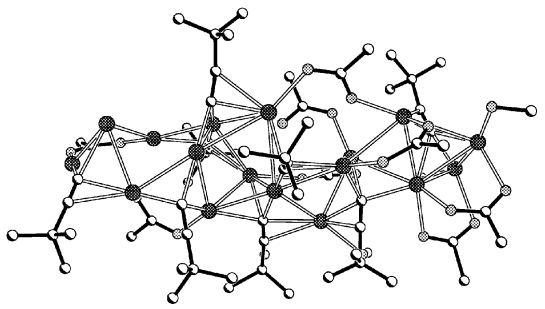

Fig. 4 The side view of the columnar structure of $[\text{Ag}_{16}(\text{C}{\equiv}\text{CBu}^t)_8(\text{CF}_3\text{CO}_2)_8(\text{MeOH})_3]_n$ **3**. Hydrogen and fluorine atoms have been omitted for clarity.

1. In the case of **2** or **3**, no choride ions were incorporated, and no cage compounds formed. Further experiments trying to improve the yield of **1** by adding $[\text{Bu}^n{}_4\text{N}]\text{Cl}$ or HCl as a chloride source were not successful. The slow release of a chloride from CHCl_3 could be important for the crystallization of **1** *via* avoiding the competing formation of AgCl. Amine mediated C–Cl bond cleavage of chloroform has been known in a trinuclear copper(II) complex,[12] but TMEDA was not active. A different process might be involved in the present case. In addition, it is noted that in the case of rhombohedral complexes $[\text{Ag}_{14}(\text{C}{\equiv}\text{CBu}^t)_{12}\text{X}]^+$, Abu-Salah *et al.* found that a similar rhombohedral structure $[\text{Ag}_{14}(\text{C}{\equiv}\text{CBu}^t)_{12}](\text{BF}_4)_2$ could be obtained without halide templates.[13]

Attempts to prepare the analogous bromide cage complex of **1** by using CHBr_3 were not successful, which always led to the formation of a dark intractable solid.

In summary, the present study underlines the importance of anion templation in synthetic chemistry. Alkynyl ligands are versatile for construction of high nuclearity silver clusters with the assistance of interstitial chloride and peripheral trifluoroacetates. Further work on the templating effect of various anions is underway.

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Notes and references

‡ *Synthesis* of **1**: $\text{AgC}{\equiv}\text{CBu}^t$ (0.0573 g, 0.30 mmol) was dissolved in a methanol–ethanol mixture (6 mL, 1 : 1 v/v) containing AgCF_3CO_2 (0.1333 g, 0.61 mmol) under ultrasonication. After adding TMEDA (0.0704 g, 0.61 mmol), the resulting solution was kept under stirring for 0.5 h, a white suspension was formed. Evaporation of the solvent under reduced pressure gave a white solid, which was then dissolved in 6 mL methanol–trichloromethane (1 : 1, v/v). Slow evaporation of the clear solution afforded colorless block-like crystals **1** with concomitant fine needle-like microcrystalline solid **2**. After washing off the needle-like microcrystalline **2** with methanol, **1** was obtained in 16.9% yield. Calc. (%) for $\text{Ag}_{19}\text{C}_{80}\text{F}_{21}\text{H}_{99}\text{O}_{14}\text{Cl}$: C, 25.50; H, 2.65; found: C, 25.61; H, 2.66; IR (KBr, ν/cm^{-1}): 2008 (C≡C), 1675 (CF_3COO^-); ^1H NMR (400 MHz, CD_3CN): δ 1.36 ppm (s, CCH_3); ESI-MS: *m*/*z*: 2518.1 $[\text{Ag}_{14}(\text{C}{\equiv}\text{CBu}^t)_{12}\text{Cl}]^+$, 2472 $[\text{Ag}_{13}(\text{C}{\equiv}\text{CBu}^t)_9(\text{CF}_3\text{CO}_2)_3]^+$, 1053.0 $[\text{Ag}_6(\text{C}{\equiv}\text{CBu}^t)_5]^+$. Compound **2** can also be obtained as a pure phase in the following procedure.

Synthesis of **2**: AgC_2Bu^t (0.0179 g, 0.09 mmol) was dissolved in 3 mL methanol containing AgCF_3COO (0.0625 g, 0.28 mmol) under ultrasonication. To the resulting solution TMEDA (0.0220 g, 0.189 mmol) was added with stirring, and a white suspension was formed after 0.5 h. Evaporation of the solvent under reduced pressure gave a white solid, which was then dissolved in 5 mL methanol. Setting the clear solution in 4 °C afforded the product as pure colorless crystals. Yield: 41.95% (0.0430 g). Calc. (%) for $\text{Ag}_8\text{C}_{48}\text{F}_{18}\text{H}_{82}\text{O}_{12}\text{N}_8$: C, 26.59; H, 3.81; N, 5.17; found: C, 26.97; H, 3.84; N, 5.11. IR (KBr, ν/cm^{-1}): 2005 (C≡C), 1677 (CF_3COO^-).

Synthesis of **3**: AgC_2Bu^t (0.0645 g, 0.34 mmol) was added in a mixture of 4 mL methanol and 4 mL ethanol containing AgCF_3COO (0.15 g, 0.68 mmol) under ultrasonication, and a clear solution was obtained after *ca.* 2 min. After the solvent was removed under reduced pressure, the solid residue was dissolved in 6 mL methanol–dichloromethane (1 : 1, v/v). Slow evaporation of the solution afforded **3** as colorless crystals. Yield: 52.45% (0.0750 g). Calc. (%) for $\text{Ag}_{16}\text{C}_{64}\text{F}_{24}\text{H}_{72}\text{O}_{16}$: C, 23.44; H, 2.21; found: C, 23.32; H, 2.10. IR (KBr, ν/cm^{-1}): 2008 (C≡C), 1674 (CF_3COO^-).

§ *Crystal data* for **1**, $[\text{C}_{80}\text{H}_{99}\text{O}_{14}\text{F}_{21}\text{ClAg}_{19}]$, M = 3768.57, monoclinic, $P2_1/m$, a = 14.5411(6), b = 27.478(1), c = 15.0210(6) Å, β = 115.516(5)°, V = 5416.3(4) Å^3, Z = 2, T = 173 K, 19 722 reflections measured, 8478 unique (R_{int} = 0.0521), final R_1 = 0.1000, wR_2 = 0.2662 for 5837 observed reflections [$I > 2\sigma(I)$].

Crystal data for **2**, $[\text{C}_{24}\text{H}_{41}\text{O}_6\text{F}_9\text{N}_4\text{Ag}_4]$, M = 1084.09, monoclinic, $P2_1/n$, a = 14.3857(1), b = 18.6977(2), c = 14.7257(1) Å, β = 111.674(1)°, V = 3680.88(5) Å^3, Z = 4, T = 173 K, 16 774 reflections measured, 5727 unique (R_{int} = 0.0274), final R_1 = 0.0223, wR_2 = 0.0464 for 5837 observed reflections [$I > 2\sigma(I)$].

Crystal data for **3**, $[\text{C}_{67}\text{H}_{81}\text{O}_{19}\text{F}_{24}\text{Ag}_{16}]$, M = 3372.24, triclinic, $P\bar{1}$, a = 14.0190(7), b = 15.9616(9), c = 23.660(1) Å, α = 70.585(5), β = 80.663(4), γ = 74.957(5)°, V = 5416.3(4) Å^3, Z = 2, T = 173 K, 51 503 reflections measured, 25895 unique (R_{int} = 0.0882), final R_1 = 0.1212, wR_2 = 0.3908 for 9286 observed reflections [$I > 2\sigma(I)$].

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