

An anionic silver(I) column containing a novel asymmetric double cage with embedded acetylenediide and unprecedented μ_5 -ligation of the nitrate ion †

Quan-Ming Wang and Thomas C. W. Mak*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, P. R. China. E-mail: tcwmak@cuhk.edu.hk

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The new triple salt $(\text{PhCH}_2\text{NMe}_3)_4[\text{Ag}_{17}(\text{C}_2)_2(\text{CF}_3\text{CO}_2)_{16}(\text{NO}_3)(\text{H}_2\text{O})_4]$ (**1**) features an asymmetric silver(I) double cage constructed from the edge-sharing of a triangulated dodecahedron and a monocapped square antiprism, and an anionic columnar structure is generated with an unprecedented μ_5 -ligation mode of the nitrate ion.

We have demonstrated that three kinds of anions can be incorporated into a crystalline lattice to afford a silver(I) triple salt, for example $\text{Ag}_2\text{C}_2\cdot\text{AgF}\cdot 4\text{CF}_3\text{SO}_3\text{Ag}\cdot 2\text{L}$ ($\text{L} = \text{CH}_3\text{CN}$, $\text{C}_2\text{H}_5\text{CN}$),¹ $\text{AgCN}\cdot\text{AgF}\cdot 4\text{AgCF}_3\text{CO}_2\cdot 2\text{L}$ ($\text{L} = \text{CH}_3\text{CN}$, H_2O)² and $2\text{Ag}_2\text{C}_2\cdot 6\text{AgO}_2\text{CCF}_2\text{CF}_2\text{CO}_2\text{Ag}\cdot\text{AgNO}_3\cdot 12\text{H}_2\text{O}$.³ Recently, we have further developed our facile approach to construct anionic silver aggregates containing the acetylide dianion (C_2^{2-} , IUPAC name acetylenediide) as a component by introducing a quaternary ammonium cation into the synthetic procedure. With tetraethylammonium (Et_4N^+) as a structure-inducing agent, discrete anionic silver(I) clusters and polymeric structures have been successfully prepared and characterized.⁴ Subsequently, the benzyltrimethylammonium ion $[\text{PhCH}_2\text{NMe}_3]^+$ was chosen to integrate Ag_2C_2 and AgCF_3CO_2 components into a crystalline double salt to probe the influence caused by a bulky organic cation of different size and shape, with the anticipation that significant metal- π interactions might arise between silver(I) and the phenyl group of $[\text{PhCH}_2\text{NMe}_3]^+$.⁵

In previously reported double and multiple salts of silver acetylide, single polyhedral cages each containing an embedded C_2^{2-} species commonly occur, and some double cages have also been found. These double cages are composed of identical single cages sharing an edge or a face: for example, a centrosymmetric silver double cage with half of it in the shape of a dodecahedron in $\text{Ag}_2\text{C}_2\cdot 6\text{C}_2\text{F}_5\text{CO}_2\text{Ag}\cdot 2\text{C}_2\text{H}_5\text{CN}$, or a monocapped square antiprism in $\text{Ag}_2\text{C}_2\cdot 9\text{C}_2\text{F}_5\text{CO}_2\text{Ag}\cdot 3\text{MeCN}\cdot\text{H}_2\text{O}$.⁶ However, no double cage constructed from two kinds of silver polyhedra has been found so far. When benzyltrimethylammonium was introduced into the $\text{Ag}_2\text{C}_2/\text{AgCF}_3\text{CO}_2/\text{AgNO}_3$ system, a new triple salt $(\text{PhCH}_2\text{NMe}_3)_4[\text{Ag}_{17}(\text{C}_2)_2(\text{CF}_3\text{CO}_2)_{16}(\text{NO}_3)(\text{H}_2\text{O})_4]$ (**1**) containing an anionic silver(I) column constructed with three kinds of anions was isolated, in which an unprecedented asymmetric silver double cage was observed. ‡

As shown in Fig. 1, the double cage is generated from the edge-sharing of two types of polyhedra each encapsulating an acetylide dianion, namely a triangulated dodecahedron (cage A) and a monocapped square antiprism (cage B). This double cage possesses pseudo-*m* symmetry with the mirror plane passing through Ag4, Ag1, Ag2, Ag10, Ag11 and the carbon atoms of both C_2^{2-} species. In cage A, atom sets Ag1Ag2Ag10Ag11 and Ag12Ag13Ag14Ag15 are each coplanar within 0.019 and 0.027 Å, respectively, making a dihedral angle of 89.3°. This dodecahedron can be regarded as the fusion of two sets of tetrahedra: elongated Ag13Ag14Ag10Ag2 and flattened

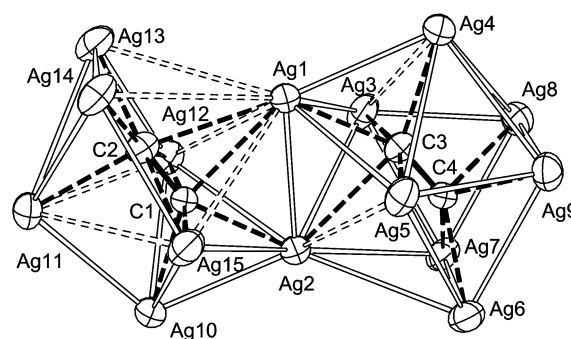


Fig. 1 Asymmetric double cage unit $(\text{C}_2)_2@Ag_{15}$ composed of a triangulated dodecahedron (left cage) and a monocapped square antiprism (right cage). The thermal ellipsoids are drawn at the 35% probability level. The observed $\text{Ag}\cdots\text{Ag}$ distances lie between 2.8273(9) and 3.3640(8) Å, and those longer than 3.4 Å are represented by broken open lines. Selected bond distances (Å): C1–C2, 1.235(9); C1–Ag1, 2.573(7); C1–Ag2, 2.223(7); C1–Ag10, 2.229(7); C1–Ag12, 2.359(8); C1–Ag15, 2.349(8); C2–Ag1, 2.645(8); C2–Ag12, 2.614(8); C2–Ag13, 2.189(7); C2–Ag14, 2.211(8); C2–Ag15, 2.638(8); C3–C4, 1.212(9); C3–Ag1, 2.241(7); C3–Ag2, 2.649(7); C3–Ag3, 2.448(8); C3–Ag4, 2.233(7); C3–Ag5, 2.422(8); C4–Ag6, 2.280(7); C4–Ag7, 2.264(8); C4–Ag8, 2.336(7); C4–Ag9, 2.317(7).

Ag11Ag1Ag12Ag15. A C_2^{2-} species is accommodated in the silver cage, which has mainly π interactions with the silver(I) atoms in the latter set with $\text{Ag}-\text{C}$ bond distances in the range 2.349(8)–2.649(7) Å; the C1–Ag11 distance of 2.760(5) Å is too long to be taken into account. On the other hand, shorter $\text{Ag}-\text{C}$ bond lengths ranging from 2.189(7) to 2.229(7) Å are found for the three-center-two-electron ($3c-2e$) systems C1Ag2Ag10 and C2Ag13Ag14, which are longer than typical $\text{Ag}-\text{C}$ σ bonds (e.g. 2.087(3) and 2.108(6) Å in $\text{Ag}_2\text{C}_2\cdot 2\text{AgClO}_4\cdot 2\text{H}_2\text{O}$).⁷

Cage B is best described as a monocapped square antiprism. The silver atoms of the upper square Ag2Ag3Ag4Ag5 are almost coplanar with a least-squares plane deviation of 0.173 Å, and the bottom square Ag6Ag7Ag8Ag9 is coplanar within 0.007 Å. These two squares are nearly parallel to each other, making a dihedral angle of 4.8°. Atom Ag1 caps face Ag2–Ag3Ag4Ag5. The encapsulated C_2^{2-} species has its molecular axis oriented approximately parallel to the triangular face Ag4Ag8Ag9, with $\text{Ag}-\text{C}$ distances in the range 2.233(7)–2.649(7) Å. This is similar to the situation in $\text{Ag}_2\text{C}_2\cdot 9\text{C}_2\text{F}_5\text{CO}_2\text{Ag}\cdot 3\text{MeCN}\cdot\text{H}_2\text{O}$ where C_2^{2-} is bound to all nine silver atoms of the polyhedral cage,⁸ but different from that of the Ag_9 single cage in $\text{Ag}_2\text{C}_2\cdot 8\text{AgF}$ where the C–C bond runs parallel to the bottom face and C_2^{2-} is linked to only eight silver atoms.⁹ Cage A and B share edge Ag1 \cdots Ag2 to form an asymmetric double cage, which is found for the first time.

The nitrate ion functions as a μ_5 -bridge to link directly an edge of cage B, a vertex of neighboring cage A and two additional atoms (Ag16 and Ag17) to generate a columnar structure $[\text{Ag}_{17}(\text{C}_2)_2(\text{CF}_3\text{CO}_2)_{16}(\text{NO}_3)(\text{H}_2\text{O})_4]^{4-}$ (Fig. 2). Atoms Ag16 and Ag17 are each coordinated by oxygen atoms from one nitrate, two carboxylate, and two aqua ligands in a square-

† Dedicated to Professor Khi-Rui Tsai (also known as Cai Qirui) on the occasion of his 89th birthday.

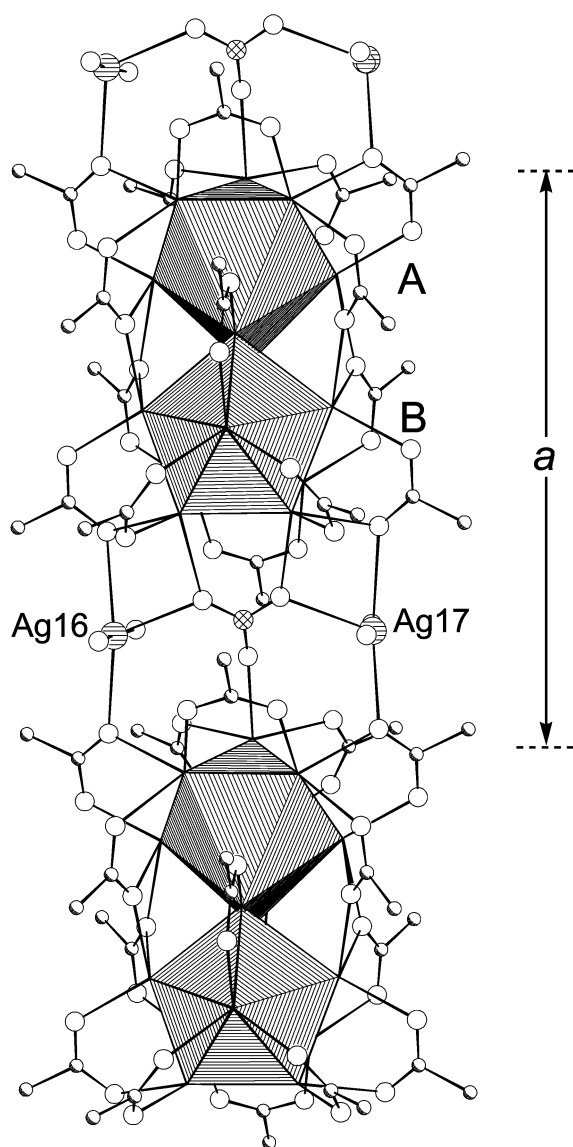
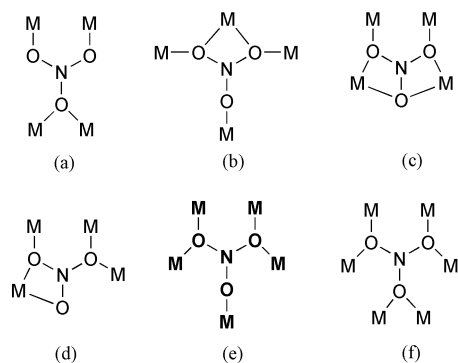


Fig. 2 A portion of the silver column constructed from $(C_2)_2@Ag_{15}$ polyhedra connected by nitrate and trifluoroacetato bridges. Large hatched circle, Ag; open circle, O; cross-hatched circle, N; side-hatched, C. Fluorine atoms have been omitted for clarity.

pyramidal geometry. Silver atoms Ag8'Ag9'Ag11Ag16Ag17 and the nitrate ion are almost coplanar with a least-squares plane deviation of 0.102 Å, and all five Ag–O bond lengths lie between 2.401(7) and 2.529(8) Å. The nitrate ion is known to display various bridging modes in connecting up to four metal centers, and the reported μ_4 -coordination modes are shown in Scheme 1 (a)–(d).¹⁰ There is also an example in which it exhibits



Scheme 1

a face-on trihapto coordination mode to bind four mercury atoms arranged in the form of a square.¹¹ To the best of our knowledge, the μ_5 -ligation mode of Scheme 1(e) in the present complex is an entirely new pattern. It is one step closer to the idealized highest ligation number (HLN)¹² of six for the nitrate ion (Scheme 1(f)), by analogy to the μ_6 -carbonato group in the hexanuclear oxovanadium(IV) cluster $[(VO)_6(\mu_6-CO_3)(\mu-CO_3)_3(\mu-OH)_9]^{5-13}$ and some cyclic hexamolybdenum complexes.¹⁴

Apart from the nitrate ion, the trifluoroacetato ligands function as μ_2 - or μ_3 -bridges across Ag \cdots Ag edges or between silver atoms of polyhedra A and B (Fig. 2). The anionic silver columns are arranged in parallel packing along the *a* direction with the $[PhCH_2NMe_3]^+$ ions occupying the space between them. Each column has pseudo-*m* symmetry, but no silver–aromatic interaction is found in **1**, in contrast to the case in the double salt $[(PhCH_2NMe_3)Ag_7(C_2)(CF_3CO_2)_6]_n$.⁵

Our synthetic strategy is based on the premise that, under the influence of argentophilicity,^{6,15} namely the d^{10} – d^{10} closed-shell attraction¹⁶ that promotes the aggregation of silver(I) centers, Ag_2C_2 readily dissolves in a concentrated aqueous solution of a silver salt to generate polynuclear $[Ag_n(C_2)]^{(n-2)+}$ moieties. The present study shows that the assembly of such species is affected by co-existing anions ($CF_3CO_2^-$ and NO_3^-) and a bulky organic cation ($[PhCH_2NMe_3]^+$) to afford a crystal structure exhibiting a novel double cage composed of two distinctly different silver polyhedra each encapsulating an acetylide dianion. Moreover, in the silver-rich crystalline environment, the nitrate ion is induced to display a most unusual and unprecedented ligation mode. Further study on the synthesis of a variety of anionic silver acetylide aggregates by variation of the quaternary ammonium counter ions and co-existing anions is in progress.

Acknowledgements

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Notes and references

† Ag_2C_2 was prepared as described previously.⁶ **CAUTION:** thoroughly dried Ag_2C_2 detonates easily upon mechanical shock and heating, and only a small quantity should be used in any chemical reaction. Excess amounts can be disposed of in alkaline solution *via* slow decomposition. Complex **1** was prepared by adding excess Ag_2C_2 to 1 mL of an aqueous solution of $AgCF_3CO_2$ (2 mmol), 50 mg $AgNO_3$ and $AgBF_4$ (2 mmol) in a plastic beaker with stirring until saturated. The undissolved Ag_2C_2 was filtered off, and then 82 mg benzyltrimethylammonium fluoride dissolved in a minimum quantity of water were added to the filtrate. After removing a small amount of precipitate, the filtrate was placed in a desiccator charged with P_2O_5 . Colorless block-like crystals of **1** were obtained after several days in *ca.* 35% yield. Calcd. C, 20.63; H, 1.64; N, 1.58. Found. C, 20.73; H, 1.54; N, 1.38%.

Crystal data for **1**: $C_{76}H_{72}Ag_{17}F_{48}N_5O_{39}$, $M = 4425.18$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.4540(8)$, $b = 20.447(1)$, $c = 22.263(1)$ Å, $\alpha = 88.327(1)$, $\beta = 72.582(1)$, $\gamma = 83.788(1)^\circ$, $V = 6341.1(6)$ Å³, $Z = 2$, $D_c = 2.355$ Mg m⁻³, $T = 293$ K, $\mu = 2.746$ mm⁻¹. Half of the sixteen trifluoroacetate ligands exhibit two-fold orientational disorder of the CF_3 group. The carbon atoms of the four independent benzyltrimethylammonium cations were assigned isotropic temperature factors, whereas all other non-hydrogen atoms were treated as anisotropic. Hydrogen atoms of all benzyltrimethylammonium cations were introduced in their idealized positions and allowed to ride on their parent carbon atoms. With the use of appropriate inter-atomic distance restraints for the organic cations and anions, blocked full-matrix least-squares refinement on F^2 (29564 unique data, 1634 variables) converged to $R1 = 0.0610$ for 15843 observed reflections [$I > 2\sigma(I)$], $wR2 = 0.1990$ for all data. CCDC reference number 195237. See <http://www.rsc.org/suppdata/dt/b2/b210057f/> for crystallographic data in CIF or other electronic format.

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