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A novel organometallic columnar complex containing endohedral silver(I)–ethynediyl binding and exterior silver(I)–aromatic interaction†

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Unprecedented η^3 π-donor behavior of the benzyltrimethylammonium ion is observed in the polymeric silver(I) complex $[(PhCH_2NMe_3)Ag_7(C_2)(CF_3CO_2)_6]_n$ that comprises a columnar backbone constructed from the fusion of Ag_8 square antiprisms each enclosing an acetylide dianion.

The history of silver–aromatic binding can be traced to the 1920s when Hill described complexes formed between aromatic moieties and silver(I).[1] Nearly three decades later, the first crystal structure of a silver–aromatic complex $C_6H_6{\cdot}AgClO_4$ was reported.[2] Subsequently, a series of systematic studies was carried out by Amma and coworkerson silver(I)–aromatic complexes.[3] Recent renaissance in the investigation of silver complexes containing polycyclic aromatics has shown that the latter can stabilize unusual organosilver molecular systems.[4] In these silver–aromatic adducts, arenes usually function as neutral π donors to exhibit the η^2 coordination mode.

In our studies on multiple salts of silver, we conducted an exploration on structural diversity by incorporating hydrophobic organic cations into silver acetylide systems, thus favoring the formation of anionic silver aggregates through the attainment of overall charge balance. With tetraethylammonium (Et_4N^+) as a structure-inducing agent, discrete silver(I) clusters and polymeric structures have been successfully prepared, showing that this strategy is indeed practical.[5] In the present work, the benzyltrimethylammonium ion (Me_3BzN^+) was chosen to integrate Ag_2C_2 and $AgCF_3CO_2$ components into a crystalline complex. This study not only probed the influence caused by a quaternary ammonium ion of different size and shape, but was also prompted by the envision that significant interaction might arise between silver(I) and the phenyl group of Me_3BzN^+, notwithstanding the positive charge on the organic cation.

Gratifyingly, such anticipation has been realized with the isolation of the novel polymeric silver complex $[(PhCH_2NMe_3)Ag_7(C_2)(CF_3CO_2)_6]_n$ (**1**). There are a large number of complexes in which quaternary ammonium containing an aryl substituent functions as a simple counter-cation;[6] however, the cationic π-donor role of a quaternary arylammonium is observed for the first time.

Complex **1** was isolated by dissolving Ag_2C_2 in an aqueous solution of $AgCF_3CO_2$ and $AgBF_4$ followed by the addition of $[PhCH_2NMe_3]F$.‡ The deployment of $AgBF_4$ favors the dissolving of silver acetylide and the crystallization of the product, as found in previous silver acetylide systems.[7] While a high concentration of silver(I) is a requisite for dissolving silver acetylide, it also might be a driving force for the interaction between Me_3BzN^+ and silver(I).

Single crystal X-ray analysis§ revealed **1** to be a column-like silver(I) complex. Its building unit is a square-antiprismatic silver cluster as shown in Fig. 1. The least-squares deviations of the two square planes Ag1Ag2Ag3Ag4 and Ag1aAg5Ag3bAg6 are 0.0547 and 0.1552 Å, respectively; these two squares make a dihedral angle of 13.1°. A C_2^{2-} species is enclosed in the silver polyhedron and stabilized by six σ bonds and two π bonding interactions with its vertices (Fig. 1). The bond length C1–C2 1.203(8) indicates that the acetylide dianion retains the triple bond character of acetylene, and the silver–carbon bond lengths vary in a wide range from 2.100(6) Å for Ag6–C2 to 2.729(5) Å for Ag1a–C1, which are in agreement with our previous finding.[8] An additional silver atom Ag7 is attached to Ag2 of the silver polyhedron through the bridging of three carboxylates. This kind of silver polyhedra share edges of type Ag1···Ag1a and Ag3···Ag3b, whose midpoints lie on consecutive inversion centers to generate a chain running along the *a* direction (Fig. 2).

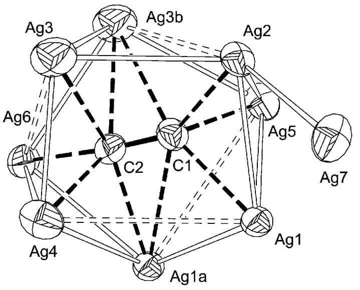

Fig. 1 The basic unit of $[(PhCH_2NMe_3)Ag_7(C_2)(CF_3CO_2)_6]_n$ (**1**) comprising a Ag_8 square antiprism with an attached silver atom (50% ellipsoids shown). The Ag···Ag distances lie in the range 2.8076(9)–3.2835(8) Å, and those longer than 3.4 Å (twice the van der Waals radius of silver) are represented by broken open lines. Selected bond distances (Å): C1–C2 1.203(8), C1–Ag1 2.303(6), C1–Ag2 2.194(5), C1–Ag5 2.304(6), C1–Ag1a 2.729(5), C1–Ag3b 2.660(6), C2–Ag3 2.611(6), C2–Ag4 2.295(6), C2–Ag6 2.100(6), C2–Ag1a 2.449(5), C2–Ag3b 2.541(6). Symmetry code: (a) $1 - x, -y, -z$; (b) $-x, -y, -z$.

Supported by carboxylato bridges, silver atoms of type Ag7 are connected to the silver column with Ag2···Ag7 3.2506(8) Å, slightly shorter than twice the van der Waals radius of silver of 3.4 Å. Each Ag7 is exteriorly coordinated by one Me_3BzN^+, and the binding mode is displayed in Fig. 3. Atom Ag7 lies almost directly above C03 of the phenyl ring with bond angles Ag7–C03–C02, 88.5(5)° and Ag7–C03–C04, 92.9(5)° and distances Ag7–C03 2.468, Ag7–C02 2.784 and Ag7–C04 2.878 Å. Since these three Ag–C distances are below the upper limit of 2.92 Å for effective π interaction between silver(I) and an aryl carbon atom, the coordination mode can be regarded as η^3. A precedent exhibiting even stronger η^3–π interaction has been found in $[Ag(GaCl_4){\cdot}\{(p\text{-}C_6H_4CH_2CH_2)_2\}]$ with Ag–C distances of 2.431(7), 2.642(8) and 2.661(8) Å.[9] Such an asymmetric interaction mode is in accord with the structural feature of η^2-arene coordination observed by Griffith and

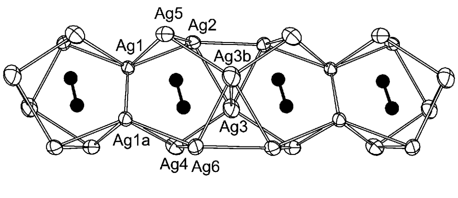

Fig. 2 Square-antiprismatic silver cages sharing edges of type Ag1···Ag1a and Ag3···Ag3b alternately to generate an infinite chain running along the *a* direction. Only short Ag···Ag distances are shown.

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† In memory of Dr. Daniel Y. Chang.

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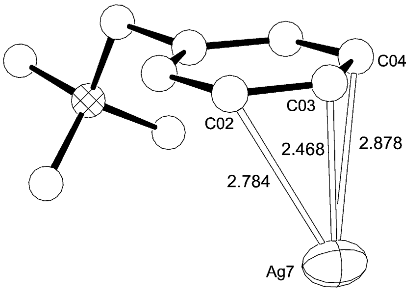

Fig. 3 η^3-Coordination of the phenyl group of the benzyltrimethylammonium ion to silver(I).

Amma, despite the difference in denticity.[10] While the binding between silver(I) and neutral aromatics commonly occurs, a similar interaction between silver(I) and an aryl group of quaternary ammonium is unprecedented. In addition, it is noteworthy that two types of silver–carbon interactions occur in **1**, namely endohedral silver(I)–ethynediyl binding within a polyhedron and exterior silver(I)–aromatic interaction (Fig. 4).

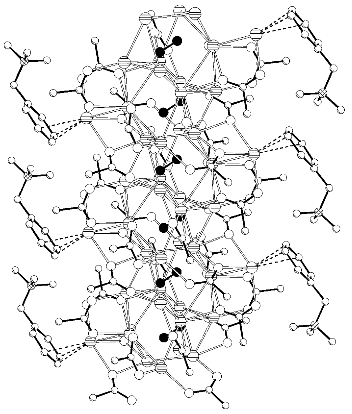

Fig. 4 Infinite silver(I) column in **1** containing endohedral silver(I)–ethynediyl and exterior Ag(I)–aromatic interactions. F atoms have been omitted for clarity, and only short Ag···Ag distances are shown. Black circles represent C_2^{2-} species; cross-hatched, nitrogen.

Notably, Me_3BzN^+ is attached to the silver column as an exterior π-donor ligand carrying one positive charge instead of being just a counter-cation, thereby making the whole silver column neutral. This differs from previous examples of anionic silver columnar complexes generated with counter-cations.[11] The additional π-ligation presented by Me_3BzN^+ influences the assembly process of silver(I), trifluroacetate and acetylide dianion, leading to the formation of a one-dimensional complex exhibiting uninterrupted silver(I)–silver(I) contacts. Other quaternary ammonium ions containing aryl groups, especially asymmetric ones, are worthy of further exploration.

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Notes and references

‡ **CAUTION**: thoroughly dried Ag_2C_2 detonates easily upon mechanical shock or heating, and only a small quantity should be used in any chemical reaction. Ag_2C_2 was prepared as described previously,[12] and excess amounts can be disposed in alkaline solution.[13]

Synthesis of **1**: $AgCF_3CO_2$ (2 mmol) and $AgBF_4$ (4 mmol) were dissolved in 1 mL water in a plastic beaker, then about 0.5 g moist Ag_2C_2 was added with stirring in the air until saturation was attained (5–10 min). The excess amount of Ag_2C_2 was filtered off, and 85 mg $[PhCH_2NMe_3]F$ were added to the filtrate. The resulting precipitates were removed by filtration, and the filtrate was placed in a desiccator charged with P_2O_5. Pale yellow prismatic crystals of **1** were isolated in *ca.* 20% yield after several days. The compound is stable in air and can be kept for months without decomposition when stored in the dark. Anal. Calc.: C, 18.10; H, 0.98; N, 0.83. Found: C, 17.93; H, 1.00; N, 0.87%. Mp ~ 110 °C (decomp.).

§ *Crystal data* for **1**: $C_{24}H_{16}Ag_7F_{18}O_{12}$, $M = 1607.47$, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.647(2)$, $b = 18.708(3)$, $c = 23.258(4)$ Å, $\beta = 100.049(3)$, $V = 3704(1)$Å^3, $Z = 4$, $D_c = 2.882$ Mg m^{-3}, $F(000) = 3016$, μ(Mo-Kα) $= 3.773$ mm^{-1}. 24840 reflections measured, 8964 unique ($R_{\mathrm{int}} = 0.0360$), final $R1 = 0.0429$, $wR2 = 0.1143$ for 6599 observed reflections $[I > 2\sigma(I)]$. Data collection was performed at 293 K on a Bruker SMART 1000 CCD diffractometer using frames of oscillation range 0.3°, with $1 < \theta < 28°$. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2. CCDC 192176. See http://www.rsc.org/suppdata/cc/b2/b208298e/ for crystallographic data in CIF or other electronic format.

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