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Induced assembly of a catenated chain of edge-sharing silver(I) dodecahedra with embedded acetylide by silver(II)-tmc (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)

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In the mixed-valent complex $[Ag^{II}(tmc)(BF_4)][Ag^{I}_6(C_2)(CF_3CO_2)_5(H_2O)]\cdot H_2O$, a $[Ag^{II}(tmc)(BF_4)]^{+1}_{\infty}$ cationic column induces the assembly of a novel, anionic zigzag chain constructed from edge-sharing of silver(I) triangulated dodecahedra each enclosing a C_2^{2-} species.

Recent studies have furnished convincing spectroscopic and structural evidence for the existence of argentophilicity,[1–4] namely the d^{10}–d^{10} closed-shell attraction[5] that promotes the aggregation of silver(I) centers. Our efforts in this direction have yielded a series of novel double,[2] triple[3] and quadruple[4] salts containing Ag_2C_2 as a component, in which the C_2^{2-} species (commonly known as the acetylide dianion, IUPAC name acetylenediide) is fully encapsulated in a variety of silver polyhedra. In these silver acetylide-containing systems, bridging anionic ligands such as fluoride, nitrate, trifluoroacetate and triflate have been used to connect the $C_2@Ag_n$ (n = 6–9) units into layers and three-dimensional networks. A natural sequel is to investigate the effect of co-existing metal ions on the assembly of polyhedral silver(I) cages, and for this purpose we choose the macrocyclic *N*-donor ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tmc) for *in situ* generation of $[Ag^{II}(tmc)]$. A decided advantage of this strategy is to avoid the introduction of a different metal, which may cause complications such as competition with silver(I) for ligand binding or precipitation of undesirable products. Proceeding in this way, we have successfully isolated a novel, mixed-valent silver complex $[Ag^{II}(tmc)(BF_4)][Ag^{I}_6(C_2)(CF_3CO_2)_5(H_2O)]\cdot H_2O$ **1**, which represents the first example of an acetylide-containing, one-dimensional coordination polymer composed of edge-sharing $C_2@Ag_8$ cages.

Compound **1** was obtained by dissolving freshly prepared Ag_2C_2 in an aqueous solution of CF_3CO_2Ag and $AgBF_4$, to which tmc was then added.† The propensity of divalent silver to act as an oxidizing agent is well documented,[6] and this unusual oxidation state can be stabilized by macrocyclic ligands, especially aza-crowns and nitrogen heterocycles.[7] In the present instance, the addition of tmc led to disproportionation of silver(I) to give elemental silver and complexed silver(II). X-Ray structural analysis‡ indicated that the square planar $[Ag^{II}(tmc)]^{2+}$ cation (mean atomic deviation from least squares plane 0.06 Å) exhibits disorder, being a superposition of two distinct *RSSR* and *RSRS* configurations[8] in a 2 : 1 ratio. For *RSSR*, the four methyl groups of tmc are arranged in two pairs, one on each side of the AgN_4 plane [Fig. 1(a)]; this conformation is also designated as Type III for the possible stereoisomeric forms of tmc.[8] For *RSRS*, all four methyl groups lie on the same side of the AgN_4 plane, corresponding to the Type I conformation [Fig. 1(b)]. The Ag–N bond lengths in the range 2.180(8)–2.206(8) Å are in agreement with 2.195 Å found in $[Ag^{II}(tmc)](ClO_4)_2$.[9] Weak axial interactions of the d^9 silver(II) center, which is subjected to Jahn–Teller distortion, with adjacent BF_4^- ligands at Ag7–F1, 2.972 Å and Ag7–F2′ (1 + x, y, z), 2.934 Å serve to link the complexed Ag(II) cations into a $[Ag^{II}(tmc)(BF_4)]^{+1}_{\infty}$ column running parallel to the a axis [Fig. 2(a)]. The Ag–F distances fall within the range 2.60–3.02 Å for CF–Ag contacts in some silver(I) complexes containing fluorinated organic ligands.[10]

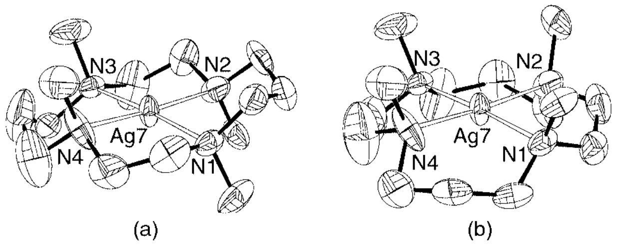

Fig. 1 Disordered $[Ag^{II}(tmc)]^{2+}$ cation involving superposition of two conformations of the tmc ligand: (a) Type III (*RSSR*) and (b) Type I (*RSRS*) in a ratio of 2 : 1. Both types share the same set of N atoms and two methyl groups. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): Ag7–N1 2.196(7), Ag7–N2 2.206(8), Ag7–N3 2.184(7), Ag(7)–N4 2.180(8).

Induced by the presence of such a cationic column, a parallel polymeric anionic chain [Fig. 2(b)] is assembled from the Ag(I), C_2^{2-} and $CF_3CO_2^-$ species. The building block of its backbone is an unprecedented triangulated dodecahedron as shown in Fig. 3. Atom sets Ag1–Ag2–Ag3–Ag4 and Ag5–Ag5a–Ag6–Ag6b are each coplanar within 0.088 and 0.109 Å, respectively, making a dihedral angle of 80.2°. This dodecahedron can be regarded as the fusion of two sets of tetrahedra, elongated Ag2–Ag3–Ag5a–Ag6 and flattened Ag1–Ag4–Ag5–Ag6b. The C_2^{2-} species retains its triple bond character with C–C bond length 1.17(1) Å. In contrast, much longer C–C bond distances are found for interstitial C_2 units in organometallic compounds, such as 1.39(2) Å in $[Co_9(C_2)(CO)_{19}]^{2-}$ and 1.48(2) Å in

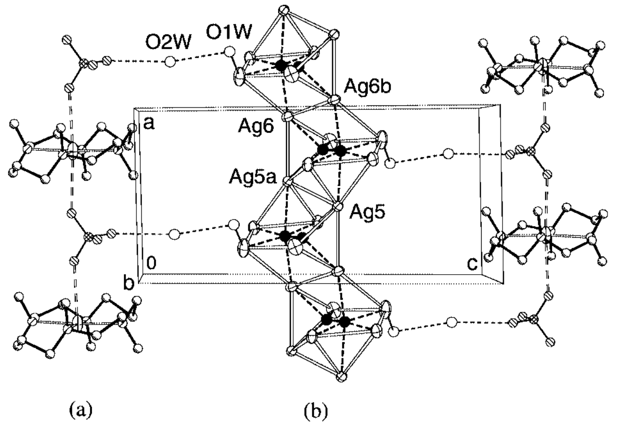

Fig. 2 Crystal structure of **1**. Hydrogen bonds are shown as dashed lines, and trifluoroacetate ligands have been omitted for clarity. (a) A column-like $[Ag^{II}(tmc)(BF_4)]^{+1}_{\infty}$ cationic column. The disordered $[Ag^{II}(tmc)]^{2+}$ cation is represented by its major configuration, and the weak axial Ag^{II}···F interactions are shown by dashed open lines. (b) Polymeric $[Ag^{I}_6(C_2)(CF_3CO_2)_5(H_2O)]^{-1}_{\infty}$ zigzag chain formed from edge-sharing of silver dodecahedra. The mid-points of the Ag5–Ag5a and Ag6–Ag6b bonds are located at inversion centers.

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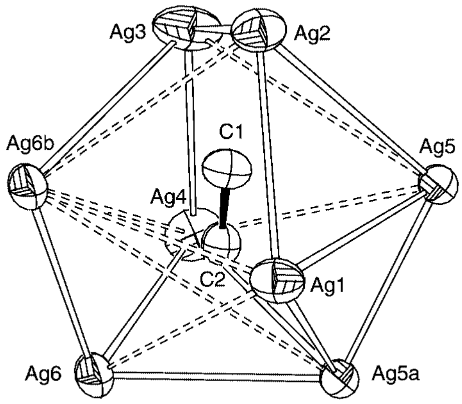

Fig. 3 Silver(I) triangulated dodecahedron with an encapsulated C_2^{2-} anion. Ag···Ag distances longer than 3.4 Å (twice the van der Waals radius of silver) are represented by broken open lines. Thermal ellipsoids are drawn at the 30% probability level. Symmetry codes: (a) $-x + 1, -y + 1, -z + 1$; (b) $-x + 2, -y + 1, -z + 1$.

$[Rh_{12}(C_2)(CO)_{25}]$.[11,12] The present C_2^{2-} ion has σ-type interactions with all seven silver(I) atoms at Ag–C = 2.172(8)–2.497(9) Å. The Ag···Ag distances lie in the range 2.818–3.366(1) Å, which is suggestive of significant argentophilic interactions.[1–4] The dodecahedra share edges of the type Ag5–Ag5a and Ag6–Ag6b to generate a chain-like structure [Fig. 2(b)]. An alternative description is that the silver atoms of type Ag5 and Ag6 construct a nearly planar zigzag chain with type Ag1, Ag2, Ag3 and Ag4 silver atoms hitched to it through the binding of C_2^{2-} anions. The aqua ligand O1W is coordinated to Ag3 at 2.426(7) Å, while one μ_3 and four μ_2 trifluoroacetate ligands chelate Ag···Ag edges or act as bridges between silver polyhedra. The Ag–O bond distances are in the range 2.208(7)–2.546(6) Å. The crystal structure of **1** is composed of a parallel packing of $[Ag^I_6(C_2)(CF_3CO_2)_5(H_2O)]^{-1}_{\infty}$ anionic zigzag chains and $[Ag^{II}(tmc)(BF_4)]^{+1}_{\infty}$ cationic columns, with lattice water molecule O2W forming hydrogen bonds with O1W and a F atom of the tetrafluoroborate group (Fig. 2).

The silver polyhedra with embedded C_2^{2-} that have been found so far are all single cages except for the face-sharing double cage in the quadruple salt $2Ag_2C_2 \cdot 3AgCN \cdot 15CF_3CO_2Ag \cdot 2AgBF_4 \cdot 9H_2O$.[4] The single cages are either connected by bridging ligands or directly linked through vertex sharing into two- or three-dimensional networks. Compound **1** represents the first example of a chain-like structure constructed from edge-sharing $C_2@Ag_8$ polyhedra.

Metal–macrocyclic complexes have been employed as templating agents in the synthesis of inorganic polymers and oligomers, two recent examples being the utilization of crown-ether complexes for generating one- and two-dimensional cadmium–thiocyanate coordination solids[13] and thio-crown-ether complexes for extended polyiodide networks.[14] Very recently, crown ethers have been used to isolate discrete clusters containing a $C_2@Ag_7$ unit in our laboratory.[15] In the present work, the unique capability of the tetraaza macrocyclic ligand to generate and stabilize a higher oxidation state of silver was exploited, and the resulting Ag(II)–tmc complex then utilized as a template to induce the formation of the $C_2@Ag_8$ dodecahedra and their inter-linkage into a silver(I) polymeric zigzag chain. Further investigation of the structural diversity of silver acetylide-containing systems and the role played by various metal–macrocycle templates is in progress.

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Notes and references

† Ag_2C_2 was prepared as described previously.[2] **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.

Synthesis of **1**: Ag_2C_2 was added to 1 mL of a concentrated aqueous solution of $AgCF_3CO_2$ and $AgBF_4$ (molar ratio *ca.* 1 : 1) in a plastic beaker with stirring until saturated. Excess Ag_2C_2 was filtered off, and 45 mg of tmc were added to the filtrate. The colorless solution turned rapidly to dark red along with the precipitation of black metallic silver, which was removed by filtration. The red filtrate was allowed to stand without disturbance, and dark-red block-like crystals of **1** were obtained in *ca.* 40% yield after several days. Compound **1** is relatively stable in the dark but readily decomposes in common solvents such as water and ethanol.

‡ *Crystal data* for **1**: $C_{26}H_{36}Ag_7F_{19}N_4O_{12}$, M = 1723.49, triclinic, space group $P\bar{1}$ (no. 2), a = 8.1641(3), b = 16.9942(7), c = 17.4266(8) Å, α = 71.826(1), β = 89.518(1), γ = 85.287(1)°, V = 2289.1(2) Å^3, Z = 2, D_c = 2.501 Mg m^{-3}, $F(000)$ = 1642, μ(Mo-Kα) = 3.066 mm^{-1}; 15581 reflections measured, 10862 unique (R_{int} = 0.0244), final $R1$ = 0.055, $wR2$ = 0.143 for 6130 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 2.5° < θ < 28°.

CCDC 153551. See http://www.rsc.org/suppdata/cc/b009765i/ for crystallographic data in .cif or other electronic format.

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