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Letter

A mixed-valent silver(I, II) complex containing a self-assembled silver(I) cluster dimer with encapsulated acetylide dianion†

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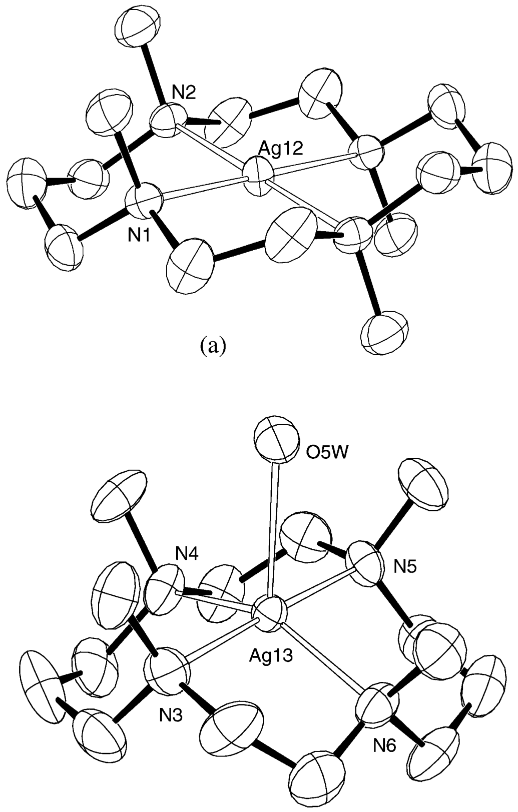
A new mixed-valent silver complex $[Ag^{II}(tmc)][Ag^{II}(tmc)(H_2O)]_2 \cdot [Ag^{I}_{11}(C_2)(CF_3CO_2)_{12}(H_2O)_4]_2$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) was synthesized by adding tmc to a concentrated aqueous solution of silver trifluoroacetate containing dissolved silver acetylide. Single-crystal X-ray analysis revealed that the resulting $[Ag^{II}(tmc)]^{2+}$ and $[Ag^{II}(tmc)(H_2O)]^{2+}$ complex cations induce the self-assembly of a centrosymmetric anionic cluster dimer from the Ag(I), C_2^{2-} and $CF_3CO_2^-$ species. A new type of cluster core $[C_2@Ag_8]Ag$ was observed, which takes the form of a bicapped trigonal prism with a pendant silver atom attached to one edge.

A large number of mixed-valent systems[1] have been studied in the decades since the structure of the first man-made example, Prussian Blue, was elucidated over 30 years ago.[2] Despite the fact that compounds such as Ag_2F(0, I), AgO(I, III) and $Ag(Ag_6O_8)NO_3$(I, III) are known, mixed-valent silver complexes are rarely reported in the literature mainly due to the powerful oxidizing nature of silver in higher oxidation states. Our recent study on the chemistry of silver acetylide (Ag_2C_2) has demonstrated that Ag(I) and Ag(II) co-exist in the complex $[Ag^{II}(tmc)(BF_4)][Ag^{I}_6(C_2)(CF_3CO_2)_5(H_2O)] \cdot H_2O$ (tmc = 1,4,8,-11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), and an infinite $[Ag^{II}(tmc)(BF_4)]_{\infty}^{+1}$ cationic column induces the assembly of an anionic zigzag chain constructed from edge-sharing of silver(I) triangulated dodecahedra each enclosing a C_2^{2-} species.[3] It is of interest to establish the generality of the generation of this kind of mixed-valent complex *via* disproportionation of silver(I) in the presence of a nitrogen macrocycle. In addition, we would like to investigate the effect of disruption of the cationic column on the assembly process. Herein we report the synthesis and crystal structure of the new complex $[Ag^{II}(tmc)]\ [Ag^{II}(tmc)(H_2O)]_2\ [Ag^{I}_{11}(C_2)(CF_3CO_2)_{12}(H_2O)_4]_2$, **1**.

Complex **1** was obtained by adding tmc ligand to a concentrated aqueous solution of silver trifluoroacetate containing dissolved silver acetylide. The tmc ligand readily induces disproportionation of Ag(I) to elemental silver and Ag(II), and the higher oxidation state is stabilized by formation of the $[Ag^{II}(tmc)]^{2+}$ complex cation. X-Ray structure analysis revealed that there are two crystallographically distinguishable tmc ligands in the unit cell: one located at an inversion center with the RSSR (Type III) configuration while the other is in the RSRS (Type I) form.[4] An ORTEP drawing of these two kinds of $[Ag^{II}(tmc)]$ cations is illustrated in Fig. 1. For the RSSR cation shown in Fig. 1(a), four N atoms and Ag12 are strictly co-planar as Ag12 is located at an inversion center. But for the RSRS cation shown in Fig. 1(b), four N atoms and Ag13 are folded into two planes, N3N4N5Ag13 (deviation 0.015 Å) and N3N6N5Ag13 (deviation 0.016 Å), making a dihedral angle of 26.0°, due to coordination of an additional axial aqua ligand (Ag13–O5W: 2.684 Å). The Ag–N bond lengths in the range 2.185(5)–2.224(7) Å are in agreement with the 2.195 Å found in $[Ag^{II}(tmc)](ClO_4)_2$.[5]



(a)

(b)

Fig. 1 (a) RSSR (Type III) $[Ag^{II}(tmc)]^{2+}$ cation at a site of symmetry $\bar{1}$. Selected bond lengths (Å): Ag12–N1, 2.187(5); Ag12–N2, 2.185(5). (b) Aqua ligated RSRS (Type I) $[Ag^{II}(tmc)]^{2+}$ cation. Selected bond lengths (Å): Ag13–N3, 2.195(6); Ag13–N4, 2.194(7); Ag13–N5, 2.193(6); Ag13–N6, 2.224(7); Ag13–O5W, 2.684. Thermal ellipsoids are drawn at the 30% probability level.

The presence of divalent silver has been confirmed by the ESR spectrum of compound **1**, which elicits a distinct signal ($g = 2.05$) due to the d^9 electronic configuration of silver(II).

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† In memory of Dr Richard K. McMullan (1929–2002).

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Interestingly, overall charge balance with respect to the silver(II) complex cations is provided not by a simple counterion but by a novel silver(I) cluster dimer $\{[Ag^{I}_{11}(C_2)(CF_3CO_2)_{12}(H_2O)_4]_2\}^{6-}$. The basic polyhedral unit of this cluster anion is shown in Fig. 2, which can be described as a bicapped trigonal prism with one additional silver atom (Ag9) attached to one edge. This is a new kind of $C_2@Ag_8$ single cage, although a similar bicapped trigonal prism has been found in $2Ag_2C_2 \cdot 3AgCN \cdot 15CF_3CO_2Ag \cdot 2AgBF_4 \cdot 9H_2O$ where two such prisms share a triangular face to give a double cage.[6] In the present case, the trigonal prism comprises two triangles, Ag1Ag2Ag3 and Ag4Ag5Ag6, while Ag7 and Ag8 each caps a rectangular face. The mean deviation of the atoms constituting the three rectangular faces of the trigonal prism lies in the range 0.046–0.195 Å. A pendant atom Ag9 is attached to an edge of the trigonal prism with bond distances of Ag2···Ag9 = 3.0654(9) and Ag5···Ag9 = 3.0897(9) Å. The silver cage $[C_2@Ag_9]Ag$ in $Ag_2C_2 \cdot 8AgF$ also contains a pendant silver atom, but it is attached to one vertex (the capping atom) of a monocapped square antiprism with an Ag···Ag distance of 3.0632(5) Å.[7] These two types of silver cages with encapsulated C_2^{2-} species represent the only known examples that carry a pendant silver atom. The lengths of the edges of the $[C_2@Ag_8]Ag$ cage in **1** lie in the range of 2.8693(7)–3.3236(7) Å (within twice the van der Waals radius of the silver atom), except for three considerably longer ones at Ag1···Ag4 = 4.156, Ag2···Ag3 = 3.683 and Ag5···Ag6 = 3.689 Å. This is suggestive of the significance of argentophilicity,[8] namely the d^{10}-d^{10} closed-shell attraction[9] that promotes the aggregation of silver(I) centers.

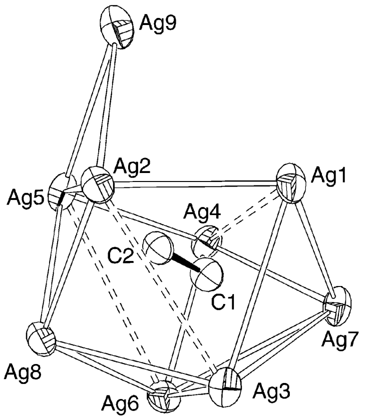

Fig. 2 Silver(I) bicapped trigonal prism with encapsulated C_2^{2-} anion and an extended arm (Ag9). In this $[C_2@Ag_8]Ag$ cluster core, Ag···Ag distances longer than 3.4 Å (twice the van der Waals radius of silver) are represented by broken open lines. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances Å: C1–C2 1.212(8), Ag1–C1 2.534(6), Ag3–C1 2.531(6), Ag4 –C1 2.242(6), Ag6–C1 2.285(6), Ag7–C1 2.202(6), Ag1–C2 2.410(6), Ag2–C2 2.138(6), Ag3–C2 2.563(6), Ag5–C2 2.380(6), Ag8–C2 2.309(6), Ag1···Ag2 3.0535(7), Ag1···Ag3 3.2758(8), Ag1···Ag7 2.9901(7), Ag2···Ag5 3.3236(7), Ag2···Ag8 2.8767(7), Ag2···Ag9 3.0654(9), Ag3···Ag6 2.9397(7), Ag3···Ag7 3.1807(7), Ag3···Ag8 2.9964(7), Ag4···Ag5 2.8693(7), Ag4···Ag6 2.8841(7), Ag4···Ag7 2.8832(6), Ag5···Ag8 2.9889(7), Ag5···Ag9 3.0897(9), Ag6···Ag7 3.1676(7), Ag6···Ag8 2.9721(7).

A C_2^{2-} species is accommodated in the bicapped trigonal prismatic Ag_8 cage and retains its triple bond character with a C–C bond length 1.212(8) Å. This is in accordance with the previous findings in a variety of $C_2@Ag_n$ cages,[10,11] but different from the case of interstitial C_2 units in organometallic compounds where much longer C–C bond distances are found, such as 1.39(2) Å in $[Co_9(C_2)(CO)_{19}]^{2-}$ and 1.48(2) Å in $[Rh_{12}(C_2)(CO)_{25}]$.[12,13]

There are two silver(I) atoms (Ag10 and Ag11) linked to this $[C_2@Ag_8]Ag$ system *via* carboxylate groups of the $CF_3CO_2^-$ ligands. A pair of aqua ligands of type O1W bridge two silver(I) atoms of type Ag10 to generate a centrosymmetric cluster dimer. Additional aqua ligands are terminally coordinated (O2W on Ag10, O3W and O4W on Ag11) to complete the tetrahedral coordination geometry around Ag10 and Ag11, giving rise to the supermolecular anion $[Ag^{I}_{11}(C_2)(CF_3CO_2)_{12}(H_2O)_4]_2^{6-}$ shown in Fig. 3. Intermolecular hydrogen bonds are formed between the aqua ligands on Ag11 and carboxylate groups of the neighboring cluster with bond distances O3W–O101 $(-1 + x, y, z)$ = 2.698 Å, O3W–O31 $(-1 + x, y, z)$ = 2.869 Å and O4W–O22 $(-1 + x, y, z)$ = 2.738 Å. A ladder-like structure is constructed through these hydrogen bonds along the *a* direction.

It is noteworthy that in $[Ag^{II}(tmc)(BF_4)][Ag^{I}_6(C_2)(CF_3CO_2)_5(H_2O)] \cdot H_2O$, the BF_4^- anions provide a weak axial linkage between adjacent $[Ag^{II}(tmc)]$ moieties to form a cationic column, inducing the assembly of a parallel polymeric anionic chain from the Ag(I), C_2^{2-} and $CF_3CO_2^-$ species.[3] In compound **1**, lacking the participation of BF_4^- ions, the Ag(II) cations do not line up in a one-dimensional array and instead a dimeric supermolecular Ag(I) cluster anion is generated.

The unique capability of tetraaza macrocyclic ligands such as tmc to generate and stabilize a higher oxidation state of silver[14] plays a key role in the formation of the present mixed-valent system. It is noteworthy that a quite different result was obtained when a crown ether was employed, which serves as a capping ligand directly coordinated to a vertex of the silver cage.[15]

This work has established the generality of the disproportionation reaction to incorporate both Ag(II) and Ag(I) in a crystalline complex. While Ag(II) ions are stabilized by tmc ligands to form complex cations, anionic clusters are assembled from the Ag(I), C_2^{2-} and $CF_3CO_2^-$ species.

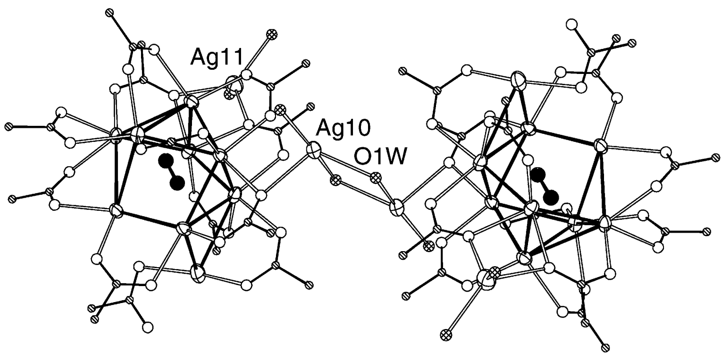

Fig. 3 Perspective view of the structure of the dimeric supermolecular anion in **1**. The silver(I) cages are highlighted by solid lines (only short Ag···Ag distances are shown). Aqua ligands are depicted in cross-hatched shading. The F atoms of the $CF_3CO_2^-$ ligands are omitted for clarity.

Experimental

Ag_2C_2 was prepared as described previously.[7] $AgCF_3CO_2$ (98%, ACROS) and tmc (99%, Aldrich) were used as purchased without further purification. Infrared spectrum was recorded on a Nicolet Impact 420 FT-IR spectrometer using KBr pellet over the range 4000–400 cm^{-1}. EPR spectrum (aqueous solution in capillary) was recorded at room temperature on a Bruker EMX X-band spectrometer equipped with an ER 4102ST TE_{102} rectangular cavity.

Preparation of $\{[Ag^{II}(tmc)]\,[Ag^{II}(tmc)(H_2O)]_2\}$-$\{[Ag^{I}_{11}(C_2)(CF_3CO_2)_{12}(H_2O)_4]_2\}$

Ag_2C_2 was added to an aqueous solution (1 ml) of $AgCF_3CO_2$ (442 mg, 2 mmol) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, and tmc (26 mg, 0.1 mmol) was added to the filtrate. The colorless solution turned rapidly dark red along with the precipitation of black metallic silver, which was removed by filtration. The filtrate was allowed to stand without disturbance, and dark-red prismatic crystals of **1** were obtained in *ca.* 70% yield (based on tmc) after several days. Compound **1** is relatively stable in the dark but readily decomposes in common solvents such as water and ethanol. Anal. calcd for $C_{94}H_{116}Ag_{25}F_{72}N_{12}O_{58}$: C, 17.6; H, 1.8; N, 2.6. Found: C, 16.9; H, 1.5; N, 2.3. IR (cm^{-1}): 1682(vs), 1651(sh), 1634(sh), 1472(w), 1434(m), 1208(vs), 1134(vs), 964(w), 839(s), 804(s), 724(s), 521(w).

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.

X-Ray crystallography

Data collection was performed at 293 K on a Bruker SMART 1000 CCD diffractometer using a 0.3° frames of oscillation range with $1.5° < \theta < 28°$. An empirical absorption correction was applied using the SADABS program.[16] The structure was solved by direct methods and all non-hydrogen atoms were anisotropically refined by full-matrix least-squares on F^2 using the SHELXTL program package.[17] Hydrogen atoms of the ligands were included with a riding mode, but no attempt was made to locate the H atoms of aqua molecules. The crystallographic data and structure refinement details are summarized in Table 1, and selected bond distances and angles are listed in captions for Fig. 1 and 2.

CCDC reference number 178881. See http://www.rsc.org/suppdata/nj/b2/b202709g/ for crystallographic data in CIF or other electronic format.

Table 1 Crystallographic data for **1**

Chemical formula	$C_{94}H_{116}Ag_{25}F_{72}N_{12}O_{58}$
Formula weight	6406.74
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	12.7452(6)
b/Å	13.4695(6)
c/Å	25.324(1)
α/°	87.885(1)
β/°	81.162(1)
γ/°	78.936(1)
U/Å^3	4215.8(3)
Z	1
T/°C	20
λ/Å	0.71073
μ(Mo-Kα)/cm^{-1}	29.88
Total reflect.	28 164
Unique reflect.	19 834
R_{int}	0.0208
$R_1{}^a$(obs. reflns)	0.0469
$wR_2{}^b$(all reflns)	0.1449

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma\,[w(F_o{}^2)^2]\}^{1/2}$.

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