

Novel layer-type triple salts of silver(I), $\text{AgCN}\cdot\text{AgF}\cdot 4\text{AgCF}_3\text{CO}_2\cdot 2\text{L}$ ($\text{L} = \text{MeCN}$ or H_2O)[†]

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The novel silver(I) triple salts $\text{AgCN}\cdot\text{AgF}\cdot 4\text{AgCF}_3\text{CO}_2\cdot 2\text{L}$ ($\text{L} = \text{MeCN}$ or $2\text{H}_2\text{O}$) exhibit the same type of layer structure, in which $[\text{F@Ag}_6]$ units each representing a fluoride-centred octahedral silver cage are interconnected by $\mu_4\text{-}\kappa\text{C},\kappa\text{C}:\kappa\text{N},\kappa\text{N}$ -cyanide and $\mu_4\text{-O},\text{O}:\text{O}',\text{O}'$ -trifluoroacetato bridges.

Current interest in cyanide-bridged one-, two- and three-dimensional complexes is focused on not only their structural variety but also their unusual magnetic and electrical properties.¹ In contrast to the common usage of soluble $[\text{Ag}(\text{CN})_2]^-$ in the construction of coordination networks, we choose to combine AgCN with soluble silver salts to form crystalline double salts, anticipating that in such a silver-rich environment the cyanide ligand may display unusual bridging modes that lead to the formation of novel 2D or 3D coordination networks. This strategy has yielded a variety of silver(I) double salts of the general formula $m\text{AgY}\cdot n\text{AgZ}\cdot x\text{L}$ ($\text{Y}, \text{Z} = \text{anions}$; $\text{L} = \text{solvent molecule that may be present}$).^{2–5} Interestingly, when we attempted to synthesize double salts of the type $m\text{AgCN}\cdot n\text{AgCF}_3\text{CO}_2$, an unexpected product $\text{AgCN}\cdot\text{AgF}\cdot 4\text{AgCF}_3\text{CO}_2\cdot 2\text{MeCN}$ **1** was obtained and structurally characterized. Subsequently, another closely related triple salt $\text{AgCN}\cdot\text{AgF}\cdot 4\text{AgCF}_3\text{CO}_2\cdot 2\text{H}_2\text{O}$ **2** was accessible by a simple route.

Compound **1** was obtained by dissolving AgCN in an aqueous solution of $\text{CF}_3\text{CO}_2\text{Ag}$ and AgBF_4 in the presence of acetonitrile.[‡] Deliberate addition of AgBF_4 into the solution was intended to increase the Ag^+ concentration to the threshold that is necessary for dissolving AgCN . Although thermal decomposition of $\text{CF}_3\text{CO}_2\text{Ag}$ can release AgF ,⁶ AgBF_4 is more likely the source of F^- in the product. It has been demonstrated that, in some instances, decomposition of BF_4^- into F^- and BF_3 (presumably coordinated to ligand or solvent molecules) can occur in the reactions of transition metal (also including silver) tetrafluoroborate derivatives.⁷ Repeating the preparative procedure using AgF instead of AgBF_4 improved the yield of **1** and resulted in the formation of **2**.

Single crystal X-ray analysis[§] revealed that **1** has a layer structure, a portion of which is illustrated in Fig. 1. The F^- ion located at an inversion center is surrounded by six $\text{Ag}(\text{I})$ atoms in the form of a slightly elongated octahedron. The $\text{Ag}-\text{F}$ distances in the equatorial plane are almost the same at 2.4520(4) and 2.4490(4) Å, whereas the significantly longer axial distance of 2.5759(5) Å can be ascribed to the attachment of a terminal acetonitrile ligand to an axial $\text{Ag}(\text{I})$ atom. This $[\text{F@Ag}_6]$ octahedron may be compared with the regular one in rock salt-type AgF with $\text{Ag}-\text{F}$ 2.46 Å.⁸ In the 3D framework of $\text{Ag}_2\text{C}_2\cdot 8\text{AgF}$, in which the fluoride ions act as bridges between $[\text{C}_2\text{@Ag}_9]\text{Ag}$ moieties, the $\text{Ag}-\text{F}$ distances fall in the range 2.196(2)–2.571(2) Å.^{5c} It is noteworthy that there are very few examples of metal polyhedra enclosing a fluoride ion,^{9,10} and to our knowledge the $[\text{F@Ag}_6]$ octahedron occurs only in AgF and the present triple salts.

The trifluoroacetato ligand usually acts as a μ_2 -bridge in its metal complexes,^{11a} and the μ_3 -coordination mode is much less

common.^{11b} In contrast, each trifluoroacetato ligand in **1** functions in an asymmetric $\mu_4\text{-O},\text{O}:\text{O},\text{O}'$ mode [$\text{Ag}(1)-\text{O}(4)$ 2.455(4), $\text{Ag}(3)-\text{O}(4)$ 2.562(4) Å, $\text{Ag}(2)-\text{O}(3)$ 2.458(4), $\text{Ag}(3')-\text{O}(3)$ 2.537(3) Å], with its carboxylato group bridging an edge of a $[\text{F@Ag}_6]$ octahedron while linking the vertices of two adjacent octahedra (see Fig. 1). Compound **1** thus provides the first example of a trifluoroacetato ligand coordinated to four metal centers, although several carboxylato complexes (especially oxalates) containing a μ_4 -carboxylato group have been reported.¹²

The four equatorial $\text{Ag}(\text{I})$ atoms of each $[\text{F@Ag}_6]$ octahedron are connected to neighboring octahedra through bridging cyanide ligands to generate a 2D $\{[\text{F@Ag}_6(\text{CN})]^{4+}\}_\infty$ coordination network, as shown in Fig. 2. This linkage pattern is different from those in the double salts $\text{Ag}_2\text{C}_2\cdot 2\text{AgClO}_4\cdot 2\text{H}_2\text{O}$ ^{5a} and $\text{Ag}_2\text{C}_2\cdot \text{AgNO}_3$,^{5b} in which the $[\text{C}_2\text{@Ag}_6]$ octahedra share vertices or edges to generate a 2D or 3D network, respectively. The cyanide ion is disordered about a $\bar{1}$ site, and is modeled by atom C1 with an assigned site-occupancy factor of $(6+7)/(6\times 2) = 1.083$ [$\text{Ag}1-\text{C}1$ 2.232(5) and $\text{Ag}2-\text{C}1$ 2.234(5)]. The cyanide ligand with C–N bond length 1.108(9) Å bridges four $[\text{F@Ag}_6]$ octahedra in a rare $\mu_4\text{-}\kappa\text{C},\kappa\text{C}:\kappa\text{N},\kappa\text{N}$ ligating mode, the only precedent being found in $3\text{AgCN}\cdot 2\text{AgF}\cdot 3\text{H}_2\text{O}$,² in which bent Ag_2F_2 and triangular $[\text{Ag}_3(\text{H}_2\text{O})_3]$ units are interconnected by μ_4 - and μ_3 -cyanide groups.

The 2D network lies in the (100) plane, and the acetonitrile ligands and hydrophobic tails of trifluoroacetato groups are accommodated in the interlayer region with a layer-to-layer separation of $a\sin\beta = 13.90$ Å.

The layer structure of **2** is formally derived from that of **1** with each acetonitrile ligand replaced by a smaller aqua ligand. The $[\text{F@Ag}_6]$ octahedron in **2** exhibits some distortion in the equatorial plane with $\text{Ag}-\text{F}$ bond lengths of 2.371(3), 2.379(3), 2.464(3) and 2.484(3) Å, whereas the axial $\text{Ag}-\text{F}$ distances are 2.585(3) and 2.589(3) Å. The more condensed packing of layers

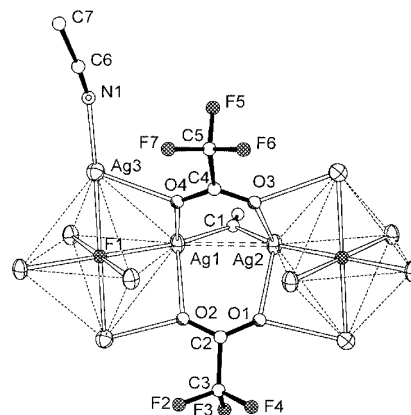


Fig. 1 A portion of the layer structure of $\text{AgCN}\cdot\text{AgF}\cdot 4\text{AgCF}_3\text{CO}_2\cdot 2\text{MeCN}$ **1** with labeling of atoms in the independent unit. $\text{Ag}(\text{I})$ atoms are drawn as 30% thermal ellipsoids and the remaining atoms are differentiated by size and shading. The edges of each Ag_6 octahedron, which lie in the range 3.463–3.562 Å, are outlined by dotted lines. The $\text{Ag}1\cdots\text{Ag}2$ distance is 2.8835(8) Å.

[†] Dedicated to the memory of Professor George Alan Jeffrey (1915–2000).

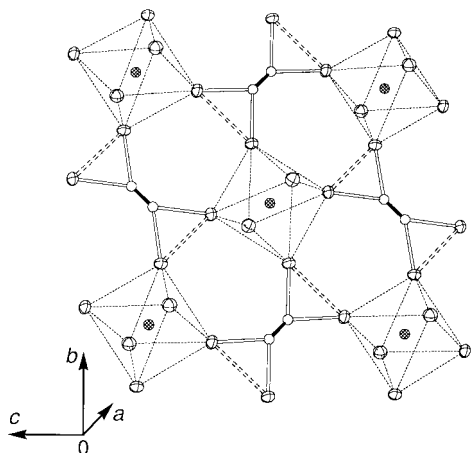


Fig. 2 A two-dimensional $\{[(F@Ag_6)(CN)]^{4+}\}_\infty$ network in **1**.

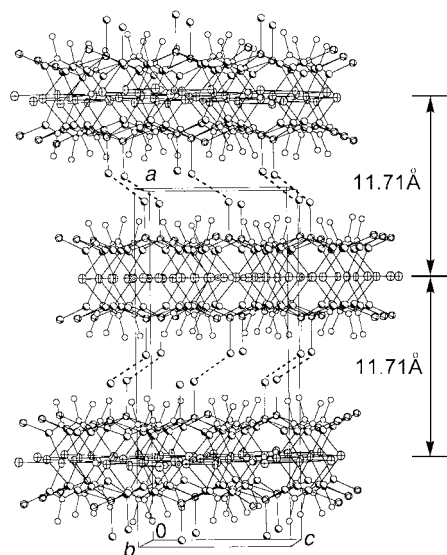


Fig. 3 Crystal structure of $AgCN \cdot AgF \cdot 4AgCF_3CO_2 \cdot 2H_2O$ **2** viewed approximately in the b direction. Hydrogen bonds between aqua ligands of adjacent layers are represented by broken lines. All F atoms have been omitted for clarity.

in **2** yields an interlayer separation of $(asin\beta)/2 = 11.71 \text{ \AA}$, shorter by *ca.* 2.1 \AA than that in **1**. Adjacent layers are related by a 2_1 axis along the b direction, which leads to the ABAB... packing shown in Fig. 3 This is different from the case in **1**, where the layers are related by lattice translation a . The outstretched aqua ligands of adjacent layers in **2** form weak hydrogen bonds of the type $O1w \cdots O1w' = 3.020$ and $O2w \cdots O2w' = 3.027 \text{ \AA}$ in successive interlayer regions, linkings the layers into a 3D network. This kind of packing may account for equatorial distortion of the $[F@Ag_6]$ unit in **2**, in contrast to that in **1**.

The present work describes the first structural characterization of novel silver(I) triple salts of the type $lAgX \cdot mAgY \cdot nAgZ \cdot xL$, in which octahedral $\{F@Ag_6\}$ units are consolidated by $\mu_4\text{-}\kappa C, \kappa C: \kappa N, \kappa N$ -cyanide and $\mu\text{-}O, O: O', O'$ -carboxylato groups. Notably, the propensity of all three anions to attain their highest ligation numbers,^{4a} along with argentophilicity [attractive interaction between silver(I) atoms to form aggregates],^{2,13} provide the driving force to assemble the robust $\{[(F@Ag_6)(CN)(CF_3CO_2)_2]\}_\infty$ layer from its components.

Dissolving $AgCN$ in a concentrated silver salt solution may lead to the formation of some $[Ag_n(CN)]^{(n-1)+}$ species, which is comparable to the complexation of CuI to yield $[Cu_4]^{3-}$. The self-assembly of such polynuclear species to generate a 2D network in **1** and **2** is envisaged to be a complex process in which the fluoride ion draws six $Ag(I)$ atoms together, the cyanide ion bridges the resulting $[F@Ag_6]$ octahedra, and the trifluoroacetato ligand further stabilizes the octahedra while

providing for charge balance. The terminally coordinated, neutral ligand L plays a secondary role as either acetonitrile or aqua ligand can be attached to each layer with little effect on its structural integrity. Extension of this work by inserting other solvent molecules such as fumaronitrile or succinonitrile between the layers is in progress.

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Notes and references

‡ *Synthesis*: $AgCN$ 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. The excess amount of $AgCN$ was filtered off, and a few drops of MeCN were added to the filtrate. (Note: excess MeCN would lead to deposition of $AgCN$ as a white precipitate.) The resulting solution was placed in a desiccator charged with P_2O_5 . Colorless plate-like crystals of **1** were obtained in *ca.* 10 yield after several days.

Using AgF instead of $AgBF_4$ in the above preparation produced colorless plate-like crystals of **1** in *ca.* 20% yield as the first crop, and a second crop of colorless block-like crystals of **2** was obtained in *ca.* 40% yield. Both complexes are light-sensitive and decompose readily in common solvents such as water, methanol and acetonitrile. IR (KBr pellet)/ cm^{-1} : 2138w, 1682vs, 1434m, 1208vs, 1135vs, 839s, 804s, 724s, 518vw for **1**; 2139w, 1682vs, 1433m, 1135vs, 839s, 804s, 724s, 518vw for **2**.

§ *Crystal data*: compound **1**: $C_{13}H_6Ag_6F_{13}N_3O_8$, $M = 1226.43$, monoclinic, space group $P2_1/c$ (no. 14), $a = 14.484(1)$, $b = 10.0013(7)$, $c = 9.9918(7) \text{ \AA}$, $\beta = 106.259(2)^\circ$, $V = 1389.5(2) \text{ \AA}^3$, $Z = 2$, $D_c = 2.931 \text{ Mg m}^{-3}$, $F(000) = 1136$, $\mu(Mo-K\alpha) = 4.275 \text{ mm}^{-1}$. 9031 reflections measured, 3346 unique ($R_{int} = 0.0448$), final $R1 = 0.0343$, $wR2 = 0.0809$ for 2584 independent reflections [$I > 2\sigma(I)$].

Compound **2**: $C_9H_4Ag_6F_{13}NO_{10}$, $M = 1180.35$, monoclinic, space group $P2_1/c$, $a = 23.446(2)$, $b = 9.9378(7)$, $c = 9.8962(7) \text{ \AA}$, $\beta = 90.002(2)^\circ$, $V = 2305.8(3) \text{ \AA}^3$, $Z = 4$, $D_c = 3.400 \text{ Mg m}^{-3}$, $F(000) = 2176$, $\mu(Mo-K\alpha) = 5.149 \text{ mm}^{-1}$. 17536 reflections measured, 6532 unique ($R_{int} = 0.0399$), final $R1 = 0.0385$, $wR2 = 0.0867$ for 3986 independent 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 $3 < \theta < 28^\circ$ for **1** and $3 < \theta < 30^\circ$ for **2**.

CCDC 182/1691. See <http://www.rsc.org/suppdata/cc/b0/b003821k/> for crystallographic files in .cif format.

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