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Anion-controlled assembly of layer-type structures in double and triple salts of silver cyanide

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Abstract

Three new polymeric silver cyanide complexes $AgCN\cdot AgF\cdot 4AgCF_3CO_2\cdot 2CH_3CH_2CN$ (**3**), $AgCN\cdot AgCF_3CF_2CO_2$ (**4**) and $AgCN\cdot 2AgCF_3SO_3\cdot H_2O$ (**5**) have been obtained by dissolving AgCN in an aqueous solution of AgX ($X = CF_3CO_2$, $C_2F_5CO_2$ or CF_3SO_3) and $AgBF_4$, and their layer-type crystal structures determined by X-ray crystallography. In the silver-rich environments, all the co-existing ancillary anions display unusual coordination modes: μ_4-O,O,O′,O′-trifluoroacetate and pentafluoropropionate and μ_4-$\eta^1\kappa$O:$\eta^1\kappa$O′:$\eta^1\kappa^2$O″-triflate. The cyanide ion functions as a μ_3-$\eta^1\kappa^2$C:$\eta^1\kappa$N bridge in the construction of an unprecedented chain-like $[Ag_2(CN)]_\infty$ motif in **4**.

Keywords: Cyanide; Pentafluoropropionate; Triflate; Trifluoroacetate; Silver

1. Introduction

Transition metal cyanide chemistry has undergone remarkable advances over the past decade, and a variety of cyanide-bridged compounds exhibiting polymeric and oligomeric structures have been prepared [1,2]. The $[Ag(CN)_2]^-$ moiety is a versatile rod-shaped building block for the construction of coordination polymers. However, AgCN is hardly used because its insolubility in common solvent presents serious difficulty in preparation and characterization of the intended products. Taking advantage of the fact that AgCN can be dissolved in a concentrated aqueous solution of a soluble silver salt, we have synthesized and characterized several double salts that possess two-dimensional network ($3AgCN\cdot 2AgF\cdot 3H_2O$ and $AgCN\cdot 2AgF\cdot 3H_2O$) [3] and linear polymeric ($AgCN\cdot 2AgNO_3$, $AgCN\cdot 2AgClO_4\cdot 2H_2O$) [4,5] structures.

Expanding our systematic study on the formation of silver cyanide coordination networks, we decided to explore the effect of larger anions bearing a hydrophobic group, such as trifluoroacetate (CF_3CO_2), pentafluoropropionate ($C_2F_5CO_2$) and triflate (CF_3SO_3). Recently, we reported two novel layer-type triple salts of silver(I) formulated as $AgCN\cdot AgF\cdot 4AgCF_3CO_2\cdot 2L$ ($L = CH_3CN$ **1**, H_2O **2**) [6]. Herein, we describe the isolation and characterization of three anion-controlled layer-type cyanide compounds $AgCN\cdot AgF\cdot 4AgCF_3CO_2\cdot 2CH_3CH_2CN$ (**3**), $AgCN\cdot AgCF_3CF_2CO_2$ (**4**) and $AgCN\cdot 2AgCF_3SO_3\cdot H_2O$ (**5**). In the silver-rich environment that exists in these compounds, both cyanide and carboxylate ions display rare coordination modes, and the $[Ag_2(CN)]_\infty$ motif in **4** is unprecedented.

2. Experimental

2.1. Materials

AgCN (BDH, 98.5%), AgF (ACROS, 99%), $AgCF_3CO_2$ (ACROS, 98%), $AgC_2F_5CO_2$ (Aldrich, 99+%), $AgCF_3SO_3$ (ACROS, 98%) and $AgBF_4$ (Aldrich, 99%) were used as purchased without further purifications. Infrared spectra were recorded with a

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Nicolet Impact 420 FT IR spectrometer using KBr pellets.

2.2. Synthesis of $AgCN \cdot AgF \cdot 4AgCF_3CO_2 \cdot 2CH_3CH_2CN$ (**3**)

2.2.1. Method (a)

AgCN was added to 1 ml of a concentrated aqueous solution of $AgCF_3CO_2$ and $AgBF_4$ (molar ratio ~1:1) in a plastic beaker with stirring until saturated. The excess amount of AgCN was filtered off, and a few drops of C_2H_5CN were added to the filtrate (note: excess C_2H_5CN 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 **3** were obtained in approximately 10% yield after several days.

2.2.2. Method (b)

Method (b) is the same as (a) with $AgBF_4$ replaced by AgF, and **3** was obtained in a significantly improved yield of ~40%. IR (KBr pellet) (cm^{-1}): 2139w, 1682vs, 1651sh, 1433m, 1207vs, 1134vs, 829s, 804s, 724s, 518w.

2.3. Synthesis of $AgCN \cdot AgCF_3CF_2CO_2$ (**4**)

The preparation procedure was similar to that of **1**, using $AgC_2F_5CO_2$ instead of $AgCF_3CO_2$. AgCN was added to 1 ml of a concentrated aqueous solution of $AgC_2F_5CO_2$ and $AgBF_4$ (molar ratio ~1:1) in a plastic beaker with stirring until saturated. The excess amount of AgCN was filtered off, and the resulting solution was placed in a desiccator charged with P_2O_5. Colorless plates of **4** were obtained in ~30% yield after several days. IR (KBr pellet) (cm^{-1}): 2139m, 1682vs, 1409m, 1326s, 1215s,1164s, 1083s, 1030s, 820m, 733m, 522w.

2.4. Synthesis of $AgCN \cdot 2AgCF_3SO_3 \cdot H_2O$ (**5**)

The preparation procedure of **4** was repeated using $AgCF_3SO_3$ instead of $AgC_2F_5CO_2$. Colorless needles of **5** were obtained in ~40% yield after several days. IR (KBr pellet) (cm^{-1}): 2140m, 1623s, 1274sh, 1250vs, 1173vs, 1083w, 1034vs, 764m, 651s, 579m, 521m.

All three compounds decomposed readily in common solvents such as water, ethanol and acetonitrile.

2.5. X-ray crystallography

Colorless crystals mounted inside Lindemann glass capillaries were used for data collection at 293K on a Bruker SMART 1000 CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) from a sealed-tube generator. Data collection and reduction were performed using SMART and SAINT software [7], with frames of oscillation range 0.3° in the θ range $2° < \theta < 28°$. An empirical absorption correction was applied using SADABS program [8]. All structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using the SHELXTL program pakage [9]. In **3**, the cyanide ion is disordered over an inversion center. However, in **4** and **5** the C and N atoms of the cyanide group could be identified unambiguously from their thermal parameters, and also by comparing the refinement with that of an alternative model in which these atoms were interchanged. The crystallographic data for **3**–**5** are summarized in Table 1, and selected bond distances and angles for **3**–**5** are listed in Table 2.

3. Results and discussion

Compound **3**–**5** were obtained by dissolving AgCN in an aqueous solution of AgX ($X = CF_3CO_2$, $C_2F_5CO_2$ or CF_3SO_3) and $AgBF_4$. The addition of $AgBF_4$ was based on the premise that it can provide a sufficiently high concentration of silver(I) ions requisite for dissolving AgCN. In such a situation, $AgBF_4$ both promotes the dissolution of AgCN and induces the crystallization of the double salts. Moreover, in the case of **3**, $AgBF_4$ acts as the precursor of AgF, and hence the resulting product is a triple salt rather than a double salt. Compound **3** can also be prepared by using AgF instead of $AgBF_4$ with improved yield. However, our attempt to isolate a double salt of AgCN and $AgCF_3CO_2$ was unsuccessful.

The crystal structure of AgCN, which has been determined by powder neutron diffraction, is composed

Table 1
Crystal data for compounds **3**–**5**

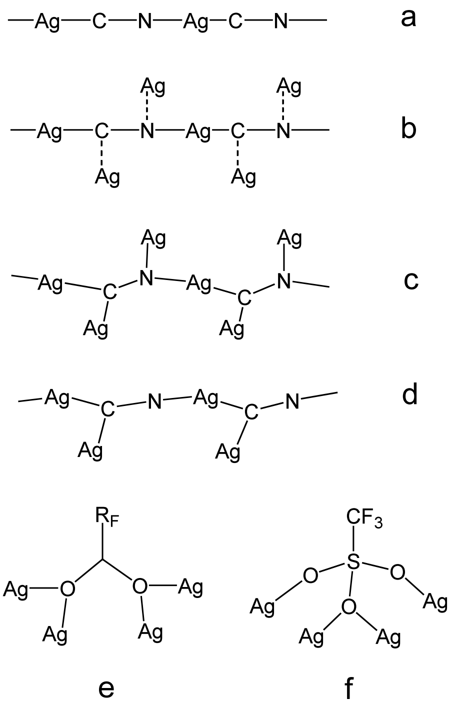
	3	**4**	**5**
Empirical formula	$C_{15}H_{10}Ag_6F_{13}N_3O_8$	$C_4Ag_2F_5NO_2$	$C_3H_2Ag_3F_6NO_7S_2$
Fw	1254.48	404.79	665.79
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	14.417(8)	11.825(8)	5.317(1)
b (Å)	9.9921(5)	5.349(3)	15.917(4)
c (Å)	9.9897(5)	13.399(9)	16.801(4)
β (°)	97.034(1)	109.58(3)	95.387(5)
V (Å^3)	1248.2(1)	798.6(9)	1415.7(6)
Z	2	4	4
μ (Mo Kα) (cm^{-1})	41.63	49.63	45.03
R_1 ($I > 2\sigma(I)$)	0.0271	0.0534	0.0388
wR_2 (all data)	0.0686	0.1237	0.0974
Data ($I > 2\sigma(I)$)	3010	1503	2468
Data/parameters	3455/206	1881/128	3459/199

Table 2
Selected bond distances (Å) and angles (°) for complexes **3**–**5**

*Complex **3***			
Bond lengths			
Ag(1)–Ag(2)	2.8807(4)	Ag(2)–O(1)	2.444(3)
Ag(1)–F(1)	2.4495(3)	Ag(3a)–O(1)	2.610(3)
Ag(2b)–F(1)	2.4500(3)	Ag(2)–O(3)	2.469(3)
Ag(3)–F(1)	2.5787(3)	Ag(3c)–O(3)	2.529(3)
Ag(1)–C(1)	2.240(4)	Ag(1)–O(4)	2.457(3)
Ag(2)–C(1)	2.233(4)	Ag(3)–O(4)	2.585(3)
Ag(1)–O(2)	2.444(3)	Ag(3)–N(1)	2.254(5)
Ag(3d)–O(2)	2.539(3)	C(1)–C(1e)	1.097(7)
Bond angles			
C(1e)–C(1)–Ag(1)	138.9(5)	C(1e)–C(1)–Ag(2)	140.9(5)
Ag(2)–C(1)–Ag(1)	80.2(1)		
*Complex **4***			
Bond lengths			
Ag(1)–C(1a)	2.136(6)	Ag(2)–O(1a)	2.319(4)
Ag(1)–N(1)	2.179(5)	Ag(2)–O(2)	2.336(5)
Ag(1)–O(1b)	2.474(4)	Ag(2)–O(2c)	2.434(5)
Ag(1)–Ag(2)	2.770(2)	Ag(2)–Ag(2d)	3.328(2)
Ag(2)–C(1a)	2.302(7)	C(1)–N(1)	1.125(8)
Bond angles			
N(1)–C(1)–Ag(1e)	158.5(6)	Ag(1e)–C(1)–Ag(2e)	77.1(2)
N(1)–C(1)–Ag(2e)	123.8(6)	C(1)–N(1)–Ag(1)	177.9(6)
*Complex **5***			
Bond lengths			
Ag(1)–C(1a)	2.119(5)	Ag(2)–O(22a)	2.506(5)
Ag(1)–N(1)	2.173(4)	Ag(2)–N(1)	2.559(5)
Ag(1)–O(13)	2.519(4)	Ag(3)–C(1a)	2.190(5)
Ag(1)–Ag(3)	2.7645(8)	Ag(3)–O(1W)	2.332(4)
Ag(2)–O(23)	2.378(6)	Ag(3)–O(12b)	2.401(5)
Ag(2)–O(11c)	2.461(4)	Ag(3)–O(11d)	2.433(5)
Ag(2)–O(1We)	2.489(5)	C(1)–N(1)	1.122(7)
Bond angles			
N(1)–C(1)–Ag(1c)	151.9(5)	C(1)–N(1)–Ag(1)	168.2(5)
N(1)–C(1)–Ag(3c)	128.2(4)	C(1)–N(1)–Ag(2)	98.8(4)
Ag(1c)–C(1)–Ag(3c)	79.8(2)	Ag(1)–N(1)–Ag(2)	92.8(2)

Symmetry codes: for **3** (a) $-x, y-1/2, -z+1/2$; (b) $x, -y+1/2, z-1/2$; (c) $x, -y+1/2, z+1/2$; (d) $-x, -y+1, -z$; (e) $-x, -y, -z$; for **4** (a) $x, y+1, z$; (b) $x, -y-3/2, z-1/2$; (c) $-x+2, -y-1, -z+1$; (d) $-x+2, -y, -z+1$; (e) $x, y-1, z$; for **5** (a) $x-1, y, z$; (b) $-x-1/2, y-1/2, -z+3/2$; (c) $x+1, y, z$; (d) $-x-3/2, y-1/2, -z+3/2$; (e) $-x-1/2, y+1/2, -z+3/2$.

of a packing of parallel linear $[\mathrm{AgCN}]_\infty$ chains (Scheme 1(a)) with inter-chain Ag···Ag separations exceeding 3.88 Å [10a]. Recently, total neutron diffraction at 10 K has yielded accurate bond lengths, Ag–C = Ag–N = 2.06 Å and C–N = 1.16 Å, for the disordered crystalline solid AgCN [10b]. In AgCN·2AgNO$_3$, the structure also consists of each (Scheme 1(b)). In AgCN·2AgClO$_4$·2H$_2$O, the $[\mathrm{AgCN}]_\infty$ chain is significantly distorted from linearity and the cyanide ligand is asymmetrically bonded to four silver atoms (Scheme 1(c)), resulting in a μ_4-$\eta^1\kappa^2$C:$\eta^1\kappa^2$N coordination mode which was first found in 3AgCN·2AgF·3H$_2$O [3]. It was reported that in the 1:2 adduct of silver(I) cyanide with triphenylstibine, the AgCN chain also displays a kinky distortion due to steric repulsion of the bulky SbPh$_3$ ligand [11]. There are also infinite AgCN backbones in the structures of **4** (Scheme 1(d)) and **5** (Scheme 1(c)). However, no chain structure exists in **3** with the incorporation of fluoride ions.



Scheme 1.

Single crystal X-ray analysis revealed that compound **3** is structurally analogous to **1** and **2**, with EtCN replacing MeCN in **1** or aqua molecule in **2**. The fluoride, cyanide and trifluoroacetate anions connect silver centers to construct a layer structure, a portion of which is illustrated in Fig. 1. The F$^-$ ion located at an inversion center is surrounded by six Ag(I) atoms in the form of a slightly elongated octahedron. The Ag–F distances in the equatorial plane are almost the same at 2.4495(3) and 2.4500(3) Å, whereas the significantly longer axial distance of 2.5787(3) Å can be ascribed to the attachment of a terminal propionitrile ligand to an axial Ag(I) atom. This [F@Ag$_6$] octahedron may be compared with the regular one in rock salt-like AgF with Ag–F = 2.46 Å [12]. It is noteworthy that there are very few examples of metal polyhedra containing an encapsulated fluoride ion [13], and thus far the [F@Ag$_6$] octahedron occurs only in AgF and triple salts **1**–**3**.

The four equatorial Ag(I) atoms of each [F@Ag$_6$] octahedron are connected to neighboring octahedra through bridging cyanide ligands to generate a 2D $\{[(\mathrm{F@Ag_6})(\mathrm{CN})(\mathrm{C_2H_5CN})_2]^{4+}\}_\infty$ coordination network, as shown in Fig. 2. The cyanide ligand with C–N bond length 1.109(6) Å bridges four [F@Ag$_6$] octahedra in a rare μ_4-$\kappa C,\kappa C{:}\kappa N,\kappa N$ ligating mode. This coordination mode only occurs in a few silver-rich

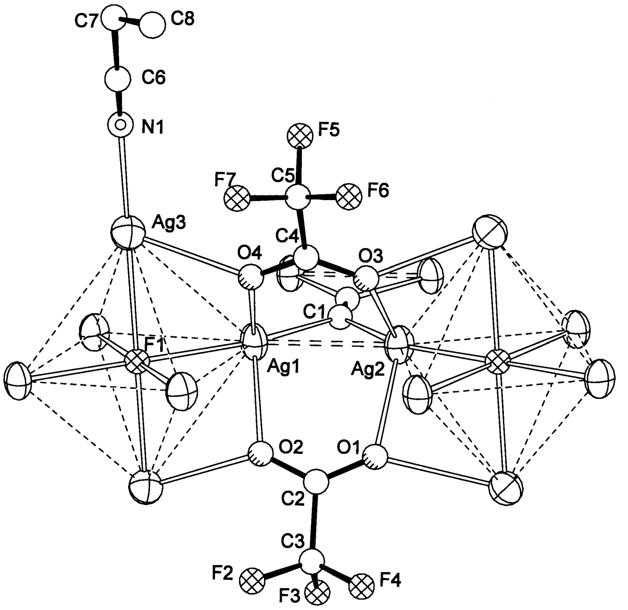


Fig. 1. A portion of the layer structure of $AgCNAgF4AgCF_3CO_22C_2H_5CN$ (**3**) with labeling of atoms in the independent unit. Ag(I) atoms are drawn as 50% thermal ellipsoids and the remaining atoms are shown as spheres and differentiated by size and shading. The edges of each Ag_6 octahedron are outlined by dotted lines. C1 = 1/2C + 1/2N.

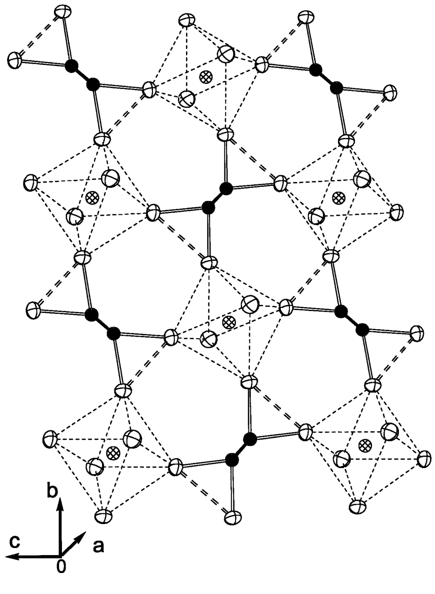


Fig. 2. Two-dimensional $\{[(F@Ag_6)(CN)(C_2H_5CN)_2]^{4+}\}_\infty$ network in **3**. Octahedra represent ($F@Ag_6$) units. The disordered cyanide ions, represented by black circles, are located at inversion centers.

complexes: $3AgCN2AgF \cdot 3H_2O$,[3] $AgCN \cdot 2AgClO_4 \cdot 2H_2O$,[4] and $2Ag_2C_23AgCN15CF_3CO_2Ag2AgBF_4 \cdot 9H_2O$ [14].

The 2D network lies in the (100) plane, and the propionitrile ligands and hydrophobic tails of trifluoroacetato groups are accommodated in the interlayer region. Adjacent layers are related by lattice translation *a*, which is similar to the case in **1**. This is different from the case in **2**, where adjacent layers are related by a 2_1 axis along the *b* direction, which leads to the ABAB type of packing. The outstretched aqua ligands of adjacent layers in **2** form weak hydrogen bonds at 3.020 and 3.027 Å in successive interlayer regions, linking the layers into a 3D network. This kind of packing accounts for equatorial distortion of the [$F@Ag_6$] unit in **2**, where the equatorial Ag–F bond lengths are divided into shorter 2.371(3), 2.379(3) and longer 2.464(3) and 2.484(3) Å.

The crystal structure of **4** also consists of a stacking of layers. As depicted in Fig. 3, the cyanide ligand acts as a μ_3-$\eta^1\kappa^2C{:}\eta^1\kappa N$ bridge to bind silver atoms to form a $[Ag_2CN]_\infty$ chain-like motif: silver(I) atoms of type Ag1 and the cyanide ligand construct a distorted linear AgCN chain (Ag1′–C1–N1, 158.5(6)°); C1–N1–Ag1, 177.9(6)°), and type Ag2 atoms are attached to this chain with Ag–C 2.302(7) Å. In the 2D complex $[Ag_6(CN)_2(tpmb)_3](NO_3)_4$ (tpmb = 1,2,4,5-tetrakis(pyrazol-1-ylmethyl)benzene) [15], the cyanide ion also functions as a μ_3-$\eta^1\kappa^2C{:}\eta^1\kappa N$ bridge, but is more bent (C–N–Ag, 166.0(4)°) than that in **4**. The $[Ag_2CN]_\infty$ motifs are linked by pentafluoropropionate ions to generate a channel-like building unit. Neighboring channels are then fused together via the carboxylate bridges to generate a layer-type structure. Adjacent layers are separated by 11 Å with the pentafluoroethyl groups occupying the interlayer region (Fig. 3).

There are two structural features in **4**: (i) there are examples of infinite chains of the type $[AgCN]_\infty$ and $[Ag_3CN]_\infty$ in the literature. However, there is no precedent of the $[Ag_2CN]_\infty$ motif, which is shown as type (d) in Scheme 1; (ii) monodentate or μ-*O*,*O′* ligation modes of the pentafloropropionate ion are known [16], but this is the first example of a μ_4-*O*,*O*,*O′*,*O′* pentafluoropropionate and such a binding mode is also rare among carboxylate complexes.

Single crystal X-ray analysis revealed that **5** has a 3D network structure made up of layers, as shown in Fig. 4. The cyanide ligand adopts a μ_4-$\eta^1\kappa^2C{:}\eta^1\kappa^2N$ coordination mode to bridge Ag atoms to form a $[Ag_3CN]_\infty$ chain. This motif is similar to type (c) in Scheme 1. Such chains are further linked by triflate and aqua ligands to construct a layer structure. There are two independent triflates: one (S1) acts as a μ_4-$\eta^1\kappa O{:}\eta^1\kappa O'{:}\eta^1\kappa^2 O''$ bridge between $[Ag_3CN]^{2+}$ chains, whereas the other (S2) functions as a double bridge in which two O atoms (O22 and O23) are coordinated to separate Ag atoms within the chain. In addition, the third (O21) is bound to aqua ligand (O1w) of an adjacent layer through hydrogen bonding (O21–O1w ($3/2+x$, $1/2-y$, $-1/2+z$), 2.722 Å). The layers are linked by such hydrogen bonds to form a 3D network as illustrated in Fig. 5. This is different from the case of $3AgCN \cdot 2AgF \cdot 3H_2O$ [3], where adjacent layers are hydrogen-bonded to generate

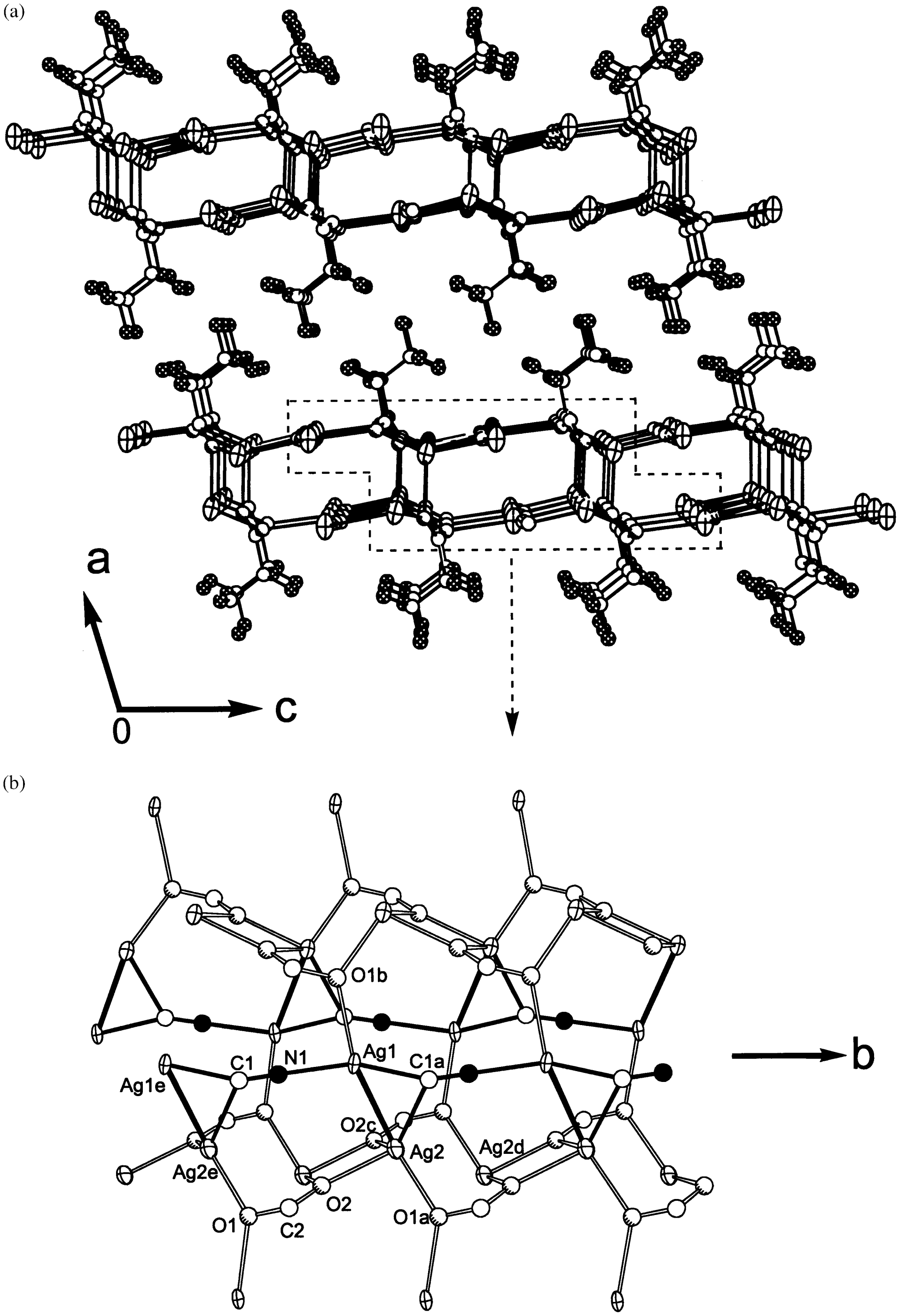


Fig. 3. (a) Layer structure in $AgCN \cdot AgCF_3CF_2CO_2$ (**4**). (b) The $[Ag_2CN]_\infty$ chain-like motif highlighted by solid lines; the CF_3CF_2 groups have been omitted for clarity.

a double layer. Besides **5**, there are only two other examples of a μ_4-triflate anion bonded to four metal centers, namely $[HgAg_2(mesityl)_2(CF_3SO_3)_2]_2$ [17] and $[Ag(3,3'\text{-dcpa})(CF_3SO_3)] \cdot C_6H_6$ (3,3′-dcpa = 3,3′-dicyanodiphenylacetylene) [18].

In compound **1**–**5**, the cyanide, tfa, pfp and triflate ligands are in silver-rich environments, and they all display unusual coordination modes (Scheme 1). The rod-like cyanide group has a pair of silver atoms attached to each end. The tfa and pfp ligands also are coordinated to four silver centers with each oxygen atom binding two silver atoms. In the case of one of the triflate ions, it bridges four silver atoms with one oxygen atoms bound to two silver atoms.

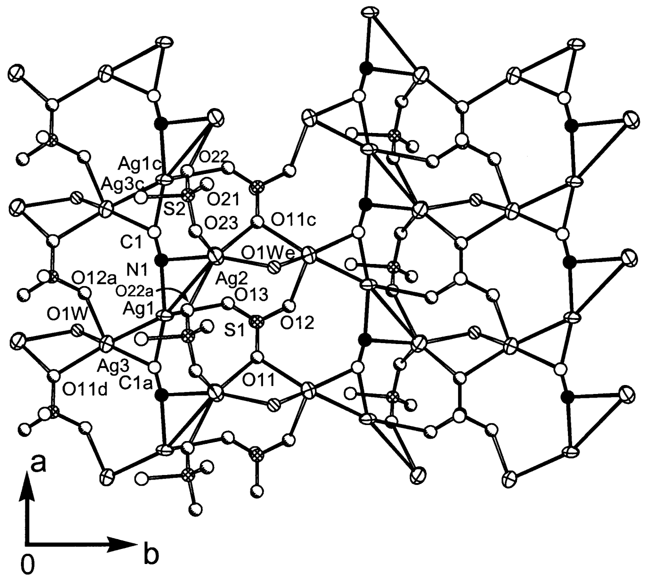


Fig. 4. Triflate (μ_4 (S1) and μ_2 (S2)) and aqua ligands connect the $[Ag_3CN]_\infty$ chains (highlighted by solid lines) to generate the layer structure in $AgCN \cdot 2AgCF_3SO_3 \cdot H_2O$ (**5**). Ag(I) atoms are drawn as 50% thermal ellipsoids and the remaining atoms are shown as spheres and differentiated by shading. The F atoms have been omitted for clarity.

4. Conclusions

The present work has demonstrated that AgCN can be used as a synthetic precursor in the construction of a variety of polymeric coordination networks. The resulting structures are affected by the ancillary anions, so that distinct layer-type architectures are found in compound **3**–**5**. In particular, all the co-existing anions display unusual coordination modes in the silver-rich environments.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Centre, CCDC reference number 158201–158203. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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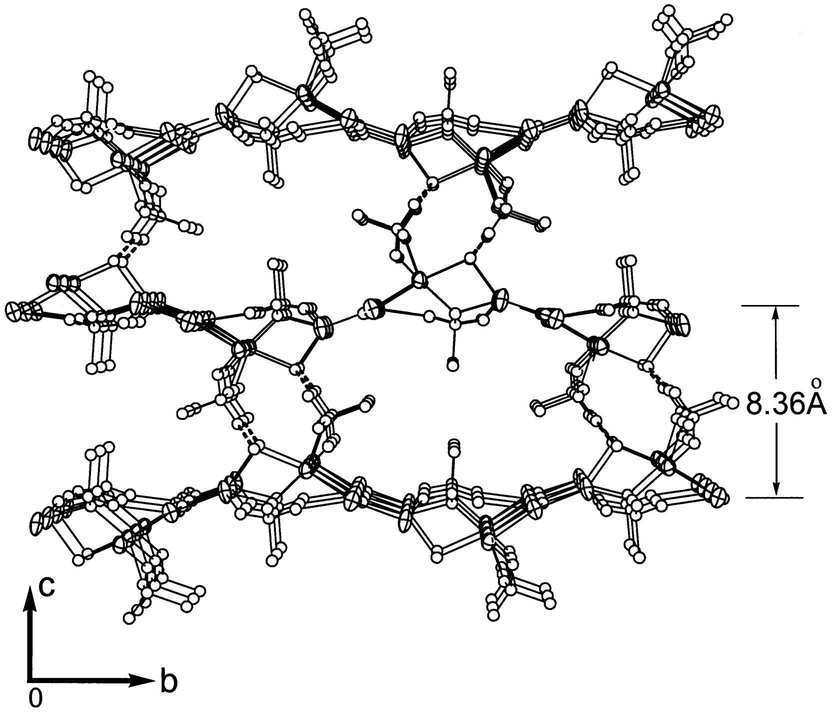

Fig. 5. Crystal structure of **5** made up of layers linked by hydrogen bonds. Hydrogen bonds between triflates and aqua ligands are represented by broken lines.

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