0.61: 0.39 Mg_2Li_2:Li_4 ratio had unit cell dimensions, $a = 16.832(5)$, $b = 16.828(9)$, $c = 15.728(5)$ Å, $\beta = 118.45(2)^\circ$). For **2**, $C_{24}H_{72}Mg_2Na_2N_4O_{1.32}Si_8$; ($0.7 \times 0.4 \times 0.4$ mm^3), triclinic, $P\bar{1}$, $a = 10.778(2)$, $b = 12.695(4)$, $c = 8.8511(14)$ Å, $\alpha = 108.03(2)$, $\beta = 99.49(2)$, $\gamma = 95.21(2)^\circ$, $V = 1122.8$ (5) Å^3, $\rho_{calcd} = 1.120$ g cm^{-3}, $\mu = 0.310$ mm^{-1}; $2\theta_{max} = 58^\circ$, 6266 data measured, 5966 unique, $R_m = 0.020$. H atoms and the peroxide O were refined isotropically and all other atoms anisotropically. Final refinement with 5100 observations ($I > 2\sigma(I)$) on F with Texsan.[12] $R = 0.0295$, $R_w = 0.0426$, GOF = 1.573, max/min residual electron density = 0.457/ − 0.330. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, as supplementary publications no. CCDC-101597 and 101598. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ. (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Novel Cyanide Coordination Models in Layer-Type Hydrated Double Salts of AgCN and AgF**

Guo-Cong Guo and Thomas C. W. Mak*

Dedicated to Professor James Trotter on the occasion of his 65th birthday

The chemistry of cyanide-bridged compounds has undergone quite spectacular advances in the last decade, especially in regard to one-, two-, and three-dimensional complexes that exhibit unusual magnetic and electrical properties.[1] Furthermore, the syntheses of oligonuclear cyanide-bridged complexes and investigation of the electronic interactions between their metal centers have been pursued by several research groups.[2] Recently another incentive to study bimetallic cyano complexes has emerged from finding that the enzyme cytochrome c oxidase is poisoned by cyanide.[3] During the course of our current study on the bonding interaction between the acetylenediide anion, C_2^{2-}, and silver(I) ions in various double salts of silver acetylide with other soluble silver salts,[4] we also explored the possibility of stabilizing the related isoelectronic diatomic species CN^- by coordination to multiple silver(I) sites in a crystalline environment. Herein we report two new double salts, $3\,AgCN \cdot 2\,AgF \cdot 3\,H_2O$ (**1**) and $AgCN \cdot 2\,AgF \cdot 3\,H_2O$ (**2**), which exhibit novel layer-type structures and bonding interaction between the cyanide anion and adjacent silver ions.

The coordination modes of the cyanide group in their metal complexes show considerable diversity (Figure 1). By far the two most commonly observed modes are the terminal

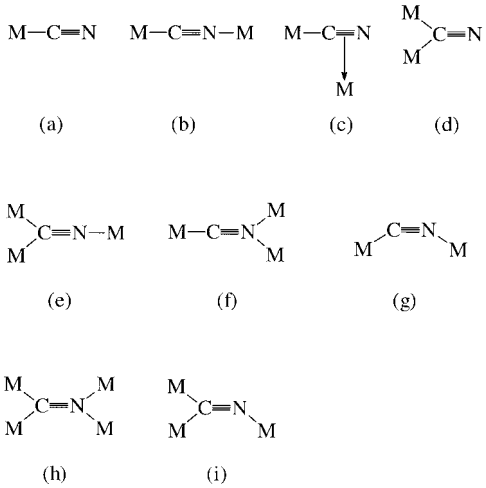

Figure 1. Coordination modes of the cyanide ion.

C-bound mode (a) and the linear-bridged arrangement (b), which are based on the well-known fact that the cyanide ion possesses a donor electron pair at both its C and N terminals.[5] Modes (c) – (g) are much less common,[6] and to our knowledge modes (h) and (i) are found for the first time in compound **1**.

The layer-type structure of **1** can be regarded as constructed from two basic building blocks, namely a nonlinear dimeric Ag_2F_2 unit and the first edge-bridged triangular silver(I) cluster core $[Ag_3(\mu\text{-}CN)_3(H_2O)_3]$ (Figure 2). The Ag – Ag distances, which range from 2.8110(8) to 2.9189(8) Å in the Ag_3 cluster, are comparable to the interatomic contact of 2.89 Å in silver metal,[7] and hence suggestive of the existence of weak interactions of the same order of magnitude. The Ag–Ag distance of 2.7484(9) Å in the Ag_2F_2 unit (Ag–F 2.316(4) – 2.422(4) Å) is significantly shorter than those in the Ag_3 cluster. To our knowledge the μ_4-$\eta^1\kappa C$:$\eta^1\kappa N$ and bent μ_3-$\eta^1\kappa C$:$\eta^1\kappa N$ coordination modes observed for the cyanide group, as well as their coexistence in the same complex, are both unprecedented. Each of the two independent μ_3-cyanide groups is symmetrically bridged to an edge of the Ag_3 triangle through its N terminal and also bonded to one Ag atom of an adjacent Ag_2F_2 unit through its C terminal. The μ_4-cyanide group bridges an edge of the Ag_3 triangle through its N

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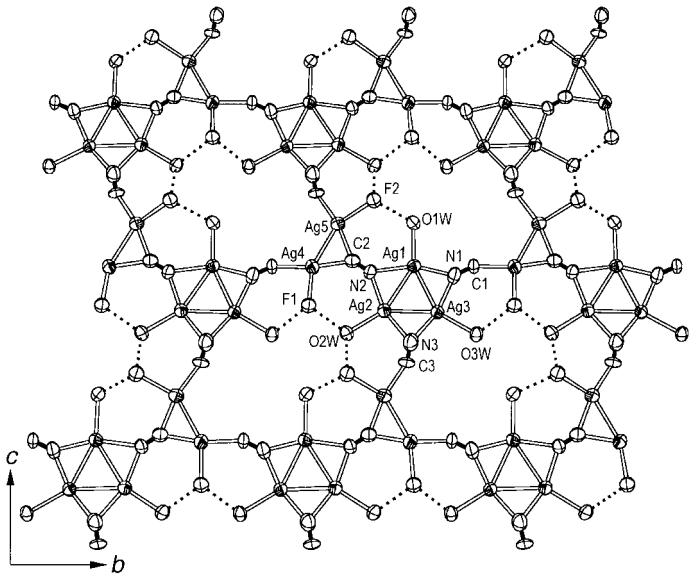

Figure 2. Layer structure of $3AgCN \cdot 2AgF \cdot 3H_2O$ viewed along the *a* direction. The thermal ellipsoids are drawn at the 50% probability level. The dotted lines represent hydrogen bonds in the layer. Selected bond lengths [Å] and angles [°]: Ag1–Ag3 2.8111(4), Ag1–Ag2 2.9195(4), Ag2–Ag3 2.8132(4), Ag1–N1 2.198(3), Ag1–N2 2.356(3), Ag1–O1W 2.384(2), Ag2–N3 2.236(3), Ag2–N2 2.256(2), Ag2–O2W 2.363(2), Ag3–N1 2.191(2), Ag3–N3 2.208(3), Ag3–O3W 2.389(2), Ag4–C1^{i} 2.161(3), Ag4–C2 2.173(4), Ag5–C3^{ii} 2.140(3), Ag5–C2 2.171(3), C1–N1 1.160(4), C2–N2 1.129(4), C3–N3 1.128(4); N1-C1-Ag4^{iii} 152.9(2), N2-C2-Ag5 143.2(3), N2-C2-Ag4 138.3(2), C2-N2-Ag2 140.9(2), C2-N2-Ag1 140.1(2), N3-C3-Ag5^{iv} 157.5(3). Symmetry codes: i: $x, y-1, z$; ii: $x-1, -y-1/2, z-1/2$; iii: $x, y+1, z$; iv: $x+1, -y-1/2, z+1/2$.

terminal in an asymmetrical manner, but is symmetrically bound to both metal atoms of the Ag_2F_2 unit through its C terminal. As seen from Figure 2, the $[Ag_3(\mu\text{-}CN)_3(H_2O)_3]$ clusters constitute a regular hexagonal array that is interconnected differently by the Ag_2F_2 units. It is worthy of note that all silver atoms, bridged cyanide groups, and terminal aqua ligands are nearly coplanar, resulting in a supraconjugated π system based on the frontier orbitals of Ag and O atoms and the cyanide groups. All fluoro ligands lie out of the mean plane of each layer on the same side, such that type F1 and F2 atoms are hydrogen-bonded to aqua ligands of type O1W and O3W, respectively, of an adjacent layer, thereby generating a double layer of thickness 3.16 Å (Figure 3). The separation between double layers is 2.53 Å.

The layer structure in **2** features a pseudo-cubane cluster with a void Ag position $[Ag_3F(H_2O)_3]$, which is unprecedented despite the fact that incomplete-cubane structures are commonly found in early transition metal chalcogenides.[8] The clusters are directly linked through corner silver(I) atoms of type Ag1 and Ag2 with a Ag – Ag distance of 2.7700(9) Å to generate zigzag chains at $y \approx 0$ running parallel to the *c* direction (Figure 4). Each μ_3-$\eta^1\kappa C$:$\eta^1\kappa N$-cyanide group is bound to the third Ag3 atom of a pseudo-cubane cluster through its N terminal and asymetrically bridges a Ag – Ag bond of an adjacent chain at $y \approx 1$ through its C terminal, resulting in the formation of a corrugated layer whose mean plane lies normal to the *b* axis. The crystal structure of **2** comprises a stack of layers, in which the aqua ligands form

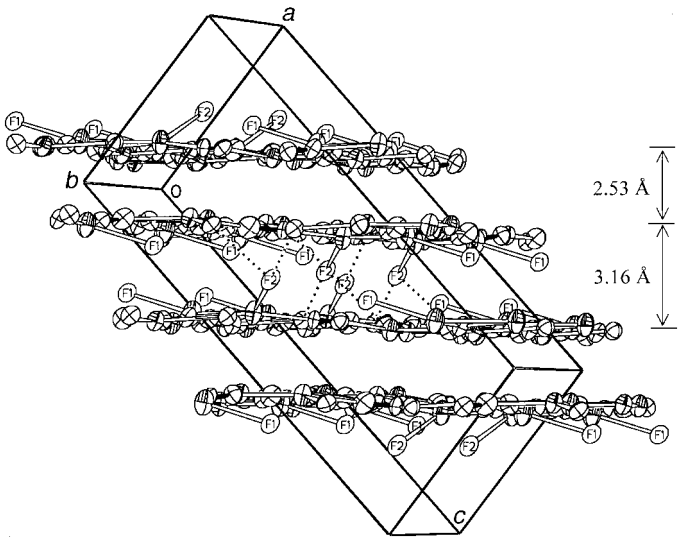

Figure 3. Crystal structure of $3AgCN \cdot 2AgF \cdot 3H_2O$. Hydrogen bonds between adjacent layers are represented by dotted lines.

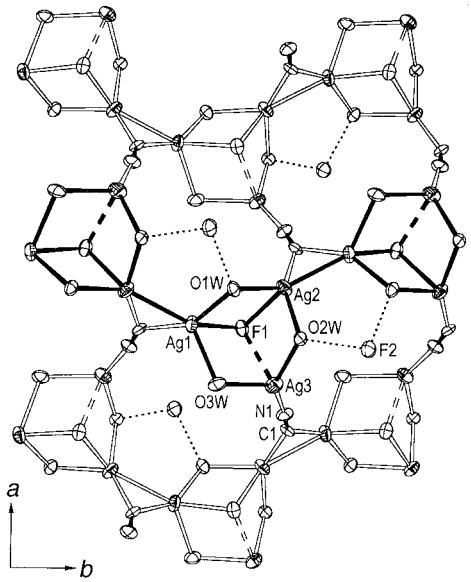

Figure 4. Layer structure of $AgCN \cdot 2AgF \cdot 3H_2O$ viewed along the *b* direction. The thermal ellipsoids are drawn at the 50% probability level. The cluster chains at $y \approx 0$ and $y \approx 1$ are differentiated by filled and open bond types. The broken lines represent the lengthened Ag–F distances, and the dotted lines represent hydrogen bonds. Selected bond lengths [Å] and angles [°]: Ag1–C1^{i} 2.226(6), Ag1–O1W 2.304(4), Ag1–O3W 2.462(4), Ag1–F1 2.471(3), Ag1–Ag2^{ii} 2.7700(9), Ag2–C1^{iii} 2.160(6), Ag2–O2W 2.318(4), Ag2–F1 2.443(4), Ag2–O1W 2.494(4), Ag2–Ag1^{iv} 2.7700(9), Ag3–N1 2.192(6), Ag3–O2W 2.349(4), Ag3–O3W 2.419(5), C1–N1 1.099(8); C1-N1-Ag3 173.6(5). Symmetry codes: i: $-x+1, -y+1, z-1/2$; ii: $-x+1/2, y, z-1/2$; iii: $x-1/2, -y+1, z$; iv: $-x+1/2, y, z+1/2$.

donor hydrogen bonds to the F atoms in adjacent layers, thus contributing to the stability of the solid-state structure.

Although compounds **1** and **2** were prepared under the same conditions, and crystal samples were obtained in different ways (see Experimental Section), there is no apparently simple mechanism for their structural interconversion. The cyanide group in transition metal cyanide compounds often exhibits head-to-tail disorder,[9] and O and F atoms are not easily differentiated in X-ray structure analysis. However, in **1**

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and **2** an ordered arrangement of the cyanide groups can be assigned on the basis of refinement of their anisotropic thermal parameters, and the fluoro and aqua ligands can be identified by consideration of their thermal ellipsoids as well as the scheme of hydrogen bonding. The measured bond lengths of the μ_3-$\eta^1\kappa C$:$\eta^1\kappa N$ and μ_4-$\eta^1\kappa C$:$\eta^1\kappa N$ cyanide groups in **1** and **2** are comparable to those found in cyano complexes.[6] Thus the cyanide anion in **1** and **2** retains its triple-bond character inherited from its parent AgCN; this, is analogous to the case for double salts of Ag_2C_2 with soluble silver salts.[4]

Hitherto the shortest Ag – Ag distance reported for any silver dicyanide salt of known crystal structure is 3.11 Å, which was found in $Tl[Ag(CN)_2]$.[10] In the intertwined double $(-Ag-SR-)_n$ -strand chain structure of crystalline (3-methylpentane-3-thiolato)silver, the closest contact between strands is Ag–Ag = 2.886(4) Å, which is interpreted as nonbonding.[11] In contrast, the much shorter Ag–Ag distances of 2.748 – 2.811 Å in **1** and **2** provide supporting evidence for the significance of *argentophilicity* in polynuclear compounds of silver(I),[10] which is a complementary logical extension of the well-established concept of aurophilicity for gold(I) complexes.[12] It is worthy of note that the Raman spectra of **1** and **2** exhibit strong cyano stretching absorptions at 2078 and 2080 cm^{-1}, respectively, which are comparable to that of free CN^- in solution (2080 cm^{-1}), but significantly lower than those found in $Tl[Ag(CN)_2]$ (2107, 2250 cm^{-1})[10] and other silver cyano complexes.[13] Generally, $\tilde{\nu}$(C≡N) of a terminal M–C≡N group shifts to a higher frequency if it forms a bridge of the M–C≡N–M′ type derived from σ coordination of the weakly antibonding nitrogen lone pair to a second metal center M′. Thus the red shift of $\tilde{\nu}$(C≡N) in **1** and **2** attest to the existence of strong metal →cyanide π-backbonding in these compounds.

Experimental Section

AgCN was added to 2 mL of a concentrated aqueous solution of AgF (about 40%) in a plastic vessel with stirring until saturated. The excess amount of AgCN was filtered off, and the solution was divided into two equal parts. One part was placed in a desiccator charged with P_2O_5, and a good crop of colorless crystals of **1** was obtained after several days. The other part was put into a furnace kept at 50 °C, and a good crop of colorless crystals of **2** was obtained in the course of two days. Both compounds were obtained in satisfactory yields that normally exceed 50%. The crystals can be kept indefinitely when immersed in a concentrated aqueous solution of silver(I) ions, but are easily decomposed by common solvents such as water, methanol, and THF. After selecting a good sample of **2** for storage and X-ray analysis, the solution containing the remaining crystals was exposed to air, and the crystals redissolved in about two days. The solution was then transferred to a desiccator charged with P_2O_5, and crystals of **1** appeared after several days. Solid-state Raman absorption spectra (Renishaw System 2000 Raman Image Microscope): $\tilde{\nu}$ = 3622(m), 2078(s), 1329(w), 1061(m) cm^{-1} for **1** and 2080(s), 1334(vw), 1041(m), 888(vw) 811(vw) cm^{-1} for **2**.

Crystal structure data for **1**: Colorless plate, Rigaku RAXIS IIC diffractometer, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), 1968 unique reflections, 1657 of which with $I > 2\sigma(I)$ were considered as observed. $P2_1/c$ (No. 14), $Z = 4$, ρ_{calcd} = 4.122 g cm^{-3}, a = 6.944(1), b = 10.752(1), c = 15.638(1) Å, β = 101.69(1)°, V = 1143.3(2) $Å^3$, μ = 84.31 cm^{-1}, $R1$ = 0.0501, GOF = 1.069.

Crystal structure data for **2**: Colorless prism, Siemens P4/PC diffractometer, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), 1241 unique reflections, 732 of which with $I > 2\sigma(I)$ were considered as observed. $Pca2_1$ (No. 29), $Z = 4$, ρ_{calcd} = 3.925 g cm^{-3}, a = 13.946(3), b = 4.522(2), c = 11.853(3) Å, V = 747.5(4) $Å^3$, μ = 77.67 cm^{-1}, $R1$ = 0.0605, GOF = 1.121. The structures of **1** and **2** were solved by direct methods (SHELXS-86) and refined by full-matrix least squares on F^2 using the Siemens SHELXTL-93 (PC Version) package of crystallographic software. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344, Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-408712 and CSD-408713.

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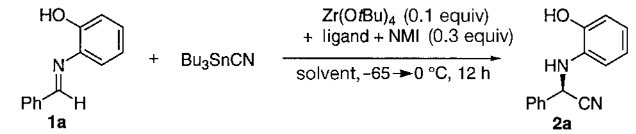
Catalytic, Enantioselective Synthesis of α-Aminonitriles with a Novel Zirconium Catalyst**

Haruro Ishitani, Susumu Komiyama, and Shū Kobayashi*

α-Aminonitriles are useful intermediates for the synthesis of amino acids[1] and nitrogen heterocycles such as thiadiazoles and imidazoles.[2] The Strecker reactions of aldimines with cyanides provide one of the most efficient methods for the preparation of α-aminonitriles,[3] and several diastereoselective approaches for the synthesis of optically active α-aminonitriles have been reported.[4] In 1996 Lipton et al. reported the first catalytic enantioselective Strecker-type reactions with use of a dipeptide ligand as catalyst.[5] Although efficient catalytic reactions provide α-aminonitriles derived from benzaldehyde derivatives in high enantioselectivities, low selectivities were observed in the reactions of aldimines derived from aliphatic and heterocyclic aldehydes.[6] Here we report chiral zirconium-catalyzed Strecker reactions of aldimines with tributyltin cyanide (Bu_3SnCN), which provide various types of α-aminonitriles in high yields and with high enantioselectivities.

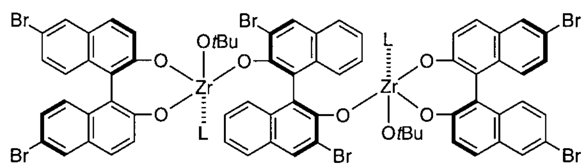
Recently, we reported the first catalytic enantioselective Mannich[7] and aza-Diels–Alder reactions[8] with a chiral zirconium catalyst. In these reactions, the zirconium catalyst effectively activates aldimines, which leads to efficient catalytic processes. We then used a zirconium catalyst in asymmetric Strecker reactions. In the presence of a zirconium catalyst (10 mol%) that was prepared from $Zr(OtBu)_4$, (*R*)-6,6′-dibromo-1,1′-bi-2-naphthol ((*R*)-6-Br-BINOL, 2 equiv),[9] and *N*-methylimidazole (NMI, 3 equiv), aldimine **1a** was treated with Bu_3SnCN[10] in dichloromethane at −45 °C. The reaction proceeded smoothly to afford the corresponding α-aminonitrile in 70% yield with 55% *ee*. After several reaction conditions were examined, the best results (92% yield, 91% *ee*) were obtained when the reaction was carried out in benzene/toluene (1/1) with use of a chiral zirconium catalyst prepared from $Zr(OtBu)_4$ (1 equiv), (*R*)-6-Br-BINOL (1 equiv), (*R*)-3,3′-dibromo-1,1′-bi-2-naphthol ((*R*)-3-Br-BINOL),[11] and NMI (3 equiv; Table 1). Use of other solvents resulted in a slight decrease in selectivity. The free hydroxyl group of the aldimine was important for obtaining both high yield and high selectivity.[7] When the aldimine prepared from aniline or 2-methoxyaniline was used under the same reaction conditions, the corresponding α-aminonitrile derivatives were obtained in much lower yields and with lower enantioselectivities (aniline: 29% yield, 1% *ee*; 2-methoxyaniline: 45% yield, 5% *ee*).

Table 1. Influence of ligands and solvents.



Ligand (equiv)	Solvent	Yield [%]	*ee* [%]
(*R*)-6-Br-BINOL (0.2)	CH_2Cl_2	70	55
(*R*)-6-Br-BINOL (0.2)	toluene/benzene (1/1)	72	69
(*R*)-6-Br-BINOL (0.1) + (*R*)-3-Br-BINOL (0.1)	toluene/benzene (1/1)	92	91
(*R*)-6-Br-BINOL (0.1) + (*R*)-3-Br-BINOL (0.1)	toluene	93	86
(*R*)-6-Br-BINOL (0.1) + (*R*)-3-Br-BINOL (0.1)	toluene/C_2H_5CN (1/1)	91	86
(*R*)-6-Br-BINOL (0.1) + (*R*)-3-Br-BINOL (0.1)	benzene/CH_2Cl_2 (1/1)	97	83
(*R*)-6-Br-BINOL (0.1) + (*R*)-3-Br-BINOL (0.1)	CH_2Cl_2	85	71

It was interesting that use of a mixture of (*R*)-6-Br-BINOL and (*R*)-3-Br-BINOL gave the best results. We then carefully examined the structure of the zirconium catalyst, and it was indicated from NMR studies that the zirconium binuclear complex **3** was formed under the reaction conditions (Scheme 1). Complex **3** consists of two zirconium centers, two (*R*)-6-Br-BINOL and two NMI units, and one (*R*)-3-Br-BINOL unit. The structure of this composition is very stable



Scheme 1. Structure of the chiral zirconium catalyst **3** (L = NMI).

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