

Heterobimetallic Coordination Polymers Incorporating $[M(CN)_2]^-$ ($M = Cu, Ag$) and $[Ag_2(CN)_3]^-$ Units: Increasing Structural Dimensionality via $M-M'$ and $M \cdots NC$ Interactions

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A series of new heterometallic coordination polymers has been prepared from the reaction of metal–ligand cations and $KAg(CN)_2$ units. Many of these contain silver–silver (argentophilic) interactions, analogous to gold–gold interactions, which serve to increase supramolecular structural dimensionality. Compared to $[Au(CN)_2]^-$ analogues, these polymers display new trends specific to $[Ag(CN)_2]^-$, including the formation of $[Ag_2(CN)_3]^-$ and the presence of $Ag \cdots N$ interactions. $[Cu(en)_2][Ag_2(CN)_3][Ag(CN)_2]$ (**1**, en = ethylenediamine) forms 1-D chains of alternating $[Ag(CN)_2]^-$ and $[Ag_2(CN)_3]^-$ units via argentophilic interactions of 3.102(1) Å. These chains are connected into a 2-D array by strong cyano(N)–Ag interactions of 2.572(3) Å. $[Cu(dien)Ag(CN)_2][Ag_2(CN)_3][Ag(CN)_2]$ (**2**, dien = diethylenetriamine) forms a 1-D chain of alternating $[Cu(dien)]^{2+}$ and $[Ag(CN)_2]^-$ ions with the Cu(II) atoms connected in an apical/equatorial fashion. These chains are cross-linked by $[Ag_2(CN)_3]^-$ units via argentophilic interactions of 3.1718(8) Å and held weakly in a 3-D array by argentophilic interactions of 3.2889(5) Å between the $[Ag(CN)_2]^-$ in the 2-D array and the remaining free $[Ag(CN)_2]^-$. $[Ni(en)][Ni(CN)_4] \cdot 2.5H_2O$ (**4**) was identified as a byproduct in the reaction to prepare the previously reported $[Ni(en)_2Ag_2(CN)_3][Ag(CN)_2]$ (**3**). In $[Ni(tren)Ag(CN)_2][Ag(CN)_2]$ (**5**, tren = tris(2-aminoethyl)amine), $[Ni(tren)]^{2+}$ cations are linked in a *cis* fashion by $[Ag(CN)_2]^-$ anions to form a 1-D chain similar to the $[Au(CN)_2]^-$ analogue. $[Cu(en)Cu(CN)_2Ag(CN)_2]$ (**6**) is a trimetallic polymer consisting of interpenetrating (6,3) nets stabilized by d^{10} – d^{10} interactions between Cu(I)–Ag(I) (3.1000(4) Å). Weak antiferromagnetic coupling has been observed in **2**, and a slightly stronger exchange has been observed in **6**. The Ni(II) complexes, **4** and **5**, display weak antiferromagnetic interactions as indicated by their relatively larger *D* values compared to that of **3**. Magnetic measurements on isostructural $[Ni(tren)M(CN)_2][M(CN)_2]$ ($M = Ag, Au$) show that Ag(I) is a more efficient mediator of magnetic exchange as compared to Au(I). The formation of $[Ni(CN)_4]^{2-}$, $[Ag_2(CN)_3]^-$, and $[Cu(CN)_2]^-$ are all attributed to secondary reactions of the dissociation products of the labile $KAg(CN)_2$.

Introduction

The rational increase of structural dimensionality has become an important goal in the synthesis of functional materials via self-assembling building blocks.¹ Such highly dimensional systems possess the possibility of useful mag-

netic,² nonlinear optical,³ conducting,⁴ or porous⁵ properties. We have recently endeavored to build the crystal engineering “toolbox” through investigating metal–metal interactions as a means to increase dimensionality. Monovalent coinage metals have long demonstrated a remarkable degree of

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cluster-type aggregation despite the formally closed d^{10} electronic configuration.⁶ This aggregation has been termed “aurophilicity” in the case of Au–Au interactions^{6e} and has been supported theoretically by the relativistic stabilization of the 6s orbital.⁷ We successfully demonstrated that such interactions are viable design elements which can be used to increase dimensionality and influence the supramolecular structure of systems containing other metals in addition to gold.^{8,9} The strengths of these interactions have an order-of-magnitude comparable to that of hydrogen bonds,^{6,10} which are perhaps the most widely applied tool for the increase of dimensionality and control of supramolecular topology.¹¹

In a similar fashion, silver–silver (argentophilic) interactions could, in principle, impart the desired control of supramolecular structure and dimensionality. Although silver–silver interactions have been reported and calculated to be weaker than gold–gold interactions,^{8,12,13} many examples exist illustrating these interactions in both ligand-supported¹⁴ and ligand-unsupported systems.^{15–17} For the lighter congeners of the coinage metals, there has been much debate over the legitimacy of the (often ligand-supported) observed d^{10} – d^{10} interactions, though recent reports of ligand-un-

supported Ag(I)–Ag(I) interactions have led to the general acceptance of “argentophilicity”.^{15a}

Because of their ability to form strong bonds with transition metal cations, cyanometalate anions have been extensively used as building blocks in supramolecular coordination polymers.^{1d,18–19} Compared to the higher coordination counterparts (mostly octahedral)^{1d} of various transition metals, there has been considerably less investigation of two-coordinate, linear cyanometalate building blocks to construct coordination polymers.^{8,9,20–28} We have thus

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chosen to examine linear dicyanoargentate, $[Ag(CN)_2]^-$, to probe the utility of argentophilic interactions in increasing structural dimensionality.

In an effort to facilitate comparisons between gold(I) and silver(I), as we previously reported for $[Au(CN)_2]^-$,^{8,9} we have reacted a series of M(II)–amine complex cations with $K[Ag(CN)_2]$, controlling the number of open M(II) coordination sites through the use of different capping amine ligands. A variety of compounds resulted with a range of dimensionalities, (as was seen with the previous $[Au(CN)_2]^-$ studies) as well as new factors and influences on supra-molecular topology that are attributable uniquely to the incorporation of $[Ag(CN)_2]^-$.

Experimental Section

General Procedures and Physical Measurements. All manipulations were performed in air using purified solvents. The amine ligands ethylenediamine (en), diethylenetriamine (dien), tris-(2-aminoethyl)amine (tren), and all other reagents were obtained from commercial sources and used as received. IR spectra were obtained using a Thermo Nicolet Nexus 670 FT-IR spectrometer. Microanalyses (C, H, N) were performed at Simon Fraser University by Mr. Miki Yang.

Variable temperature magnetic susceptibility data were collected using a Quantum Design SQUID MPMS-5S magnetometer working down to 2 K at 1 T field strength. Samples were placed in a gelatin capsule and suspended in a clear plastic straw. All data was corrected for TIP, the diamagnetism of the sample holder, and the constituent atoms (by use of Pascal constants).²⁹

Synthetic Procedures. CAUTION: Although we have experienced no difficulties, perchlorate salts are potentially explosive and should only be used in small quantities and handled with care.

$[Cu(en)_2][Ag_2(CN)_3][Ag(CN)_2]$ (1). To a 5 mL aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.074 g, 0.2 mmol) was added a 2 mL aqueous solution of en (stock solution, 0.4 mmol). While stirring, a 5 mL aqueous solution of $KAg(CN)_2$ (0.080 g, 0.4 mmol) was added dropwise to this dark purple solution. The purple solution was then evaporated to half the volume and then covered and cooled overnight to yield a purple crystalline solid that was filtered and air-dried to give $[Cu(en)_2][Ag_2(CN)_3][Ag(CN)_2]$ (1). Yield: 0.045 g (53%). Anal. Calcd for $C_9H_{16}N_9Ag_3Cu$: C, 16.96; H, 2.53; N, 19.78. Found: C, 16.78; H, 2.46; N, 19.98. IR (KBr): 2156 (w ν CN), 2140 (ν CN), 2118 (s ν CN), 1581, 1455, 1317, 1268, 1084, 1026, 975, 696, 520 cm^{-1} . To obtain X-ray quality crystals, an H-shaped tube containing an aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.074 g, 0.2 mmol) and en (stock solution, 0.4 mmol) on one side and an aqueous solution of $KAg(CN)_2$ (0.080 g, 0.4 mmol) on the other side was prepared. Slow diffusion of the two reagents yielded dark purple single crystals of $[Cu(en)_2][Ag_2(CN)_3][Ag(CN)_2]$ (1) over several weeks, in low to moderate yield. The X-ray quality crystals had a comparable IR spectrum to the microcrystalline powder.

$[Cu(dien)Ag(CN)_2]_2[Ag_2(CN)_3][Ag(CN)_2]$ (2). To a 3 mL aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.140 g, 0.377 mmol) was added a 1 mL aqueous solution of dien (stock solution, 0.377 mmol). While stirring, a 3 mL aqueous solution of $KAg(CN)_2$ (0.150 g, 0.753 mmol) was added dropwise to this dark blue solution, resulting in an immediate blue precipitate, which was filtered and air-dried to give $[Cu(dien)Ag(CN)_2]_2[Ag_2(CN)_3][Ag(CN)_2]$ (2).

Yield: 0.108 g. Anal. Calcd for $C_{17}H_{26}N_{15}Ag_5Cu_2$: C, 18.45; H, 2.37; N, 18.98. Found: C, 18.14; H, 2.31; N, 18.77. IR (KBr): 2167 (ν CN), 2156 (s ν CN), 2137 (ν CN), 2134 (ν CN), 2120 (ν CN), 1460, 1254, 1130, 1077, 1056, 1019, 958, 528 cm^{-1} . The blue filtrate was covered and cooled to yield X-ray quality crystals of **2** after several days. Yield: 0.053 g (96% total yield). The crystals and powder had comparable IR spectra and elemental analysis. H-tube reactions also produced **2** with comparable elemental analysis and IR spectra.

$[Ni(en)_2Ag_2(CN)_3][Ag(CN)_2]$ (3) and $[Ni(en)][Ni(CN)_4] \cdot 2.5H_2O$ (4). The powder product of $[Ni(en)_2Ag_2(CN)_3][Ag(CN)_2]$ (3) was prepared in a fashion similar to that which was recently reported.²⁸ An improved synthesis and characterization is given here, along with that for the identified byproduct. To a 3 mL aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.110 g, 0.377 mmol) was added a 1 mL aqueous solution of en (stock solution, 0.753 mmol). While stirring, a 3 mL aqueous solution of $KAg(CN)_2$ (0.150 g, 0.753 mmol) was added dropwise to this purple solution, resulting in an immediate pink/purple precipitate, which was filtered and air-dried to give $[Ni(en)_2Ag_2(CN)_3][Ag(CN)_2]$ (3). Yield: 0.122 g (65%). Anal. Calcd for $C_9H_{16}N_9Ag_3Ni$ (3): C, 17.09; H, 2.55; N, 19.93. Found: C, 17.42; H, 2.56; N, 19.54. IR for **3** (KBr): 2159 (w ν CN), 2140 (s ν CN), 2123 (ν CN), 1582, 1462, 1384, 1329, 1276, 1132, 1023, 979, 661, 504 cm^{-1} . To acquire crystals, H-shaped tubes were prepared. After several weeks, along with a white precipitate (AgCN), dark pink $[Ni(en)_2Ag_2(CN)_3][Ag(CN)_2]$ (3) and pale pink $[Ni(en)][Ni(CN)_4] \cdot 2.5H_2O$ (4) crystals were identified and separated in low to moderate yields. The IR spectrum and elemental analysis for crystals of **3** were comparable to the powder data. Anal. Calcd for **4**, $C_6H_8N_6Ni_2 \cdot 2.5H_2O$: C, 22.07; H, 4.00; N, 25.73. Found: C, 21.97; H, 3.48; N, 24.93. IR for **4** (KBr): 2164 (s ν CN), 1602, 1384, 1097, 1035, 963, 672, 440 cm^{-1} . The rational preparation of **4** was also completed as follows: To a 3 mL aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.029 g, 0.1 mmol) was added an aqueous solution of en (stock solution, 0.1 mmol). While stirring, a 5 mL aqueous solution of $K_2Ni(CN)_4$ (0.024 g, 0.1 mmol) was added dropwise, resulting in an immediate pale purple precipitate. This solid was filtered and air-dried to give $[Ni(en)][Ni(CN)_4] \cdot 1.5H_2O$. Yield: 0.027 g (96%). The solid prepared in this fashion had a comparable IR spectrum to the crystals (4) prepared as previously described, despite having a slightly different amount of cocrystallized water. Anal. Calcd for $C_6H_8N_6Ni_2 \cdot 1.5H_2O$: C, 23.35; H, 3.59; N, 27.24. Found: C, 23.28; H, 4.14; N, 27.25.

$[Ni(tren)Ag(CN)_2][Ag(CN)_2]$ (5). To a 3 mL aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.029 g, 0.1 mmol) was added a solution of tren (stock solution, 0.1 mmol). While stirring, a 5 mL aqueous solution of $KAg(CN)_2$ (0.040 g, 0.2 mmol) was added dropwise to this pale purple solution, resulting in an immediate purple precipitate. This solid was filtered and air-dried to give $[Ni(tren)Ag(CN)_2][Ag(CN)_2]$ (5). Yield: 0.051 g (98%). Anal. Calcd for $C_{10}H_{18}N_8Ag_2Ni$: C, 22.89; H, 3.46; N, 21.35. Found: C, 22.80; H, 3.50; N, 21.17. IR (KBr): 2174 (s ν CN), 2139 (s ν CN), 1599, 1468, 1348, 1322, 1067, 1023, 993, 977, 882, 532, 468 cm^{-1} . Single crystals of **5** were prepared by slow diffusion of aqueous solutions of Ni/tren and $KAg(CN)_2$ in an H-shaped tube. The crystals and powder had comparable IR spectra.

$[Cu(en)Cu(CN)_2Ag(CN)_2]$ (6). An H-shaped tube containing a concentrated aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.070 g, 0.188 mmol) and en (concentrated stock solution, 0.188 mmol) on one side and an aqueous solution of $KAg(CN)_2$ (0.075 g, 0.376 mmol) on the other side was prepared. Slow diffusion of the two reagents into each other yielded X-ray quality, dark purple, single crystals of $[Cu(en)Cu(CN)_2Ag(CN)_2]$ (6) over several weeks. Yield: 0.019

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Table 1. Comparison of Cyanide (ν_{CN}) Absorptions (cm^{-1}) for Complexes **1–6** and Related Systems^a

complex	ν_{CN} absorption(s) (by type)			
	Ag-CN or Au-CN	Ag-CN-M or Au-CN-M	Ag-CN-Ag	other
K[Ag(CN) ₂] ⁴⁷	2139			
[Cu(en) ₂][Ag ₂ (CN) ₃][Ag(CN) ₂] (1)	2140	2156	2118	
[Cu(en) ₂ Ag(CN) ₂][Ag(CN) ₂] ¹⁷	2136 (broad)			
[Cu(dien)Ag(CN) ₂] ₂ [Ag ₂ (CN) ₃]-[Ag(CN) ₂] (2)	2137, 2134	2167, 2156	2120	
[Ni(en) ₂ Ag ₂ (CN) ₃][Ag(CN) ₂] (3)		2159, 2140	2123	
[Ni(en) ₂ Ag(CN) ₂][Ag(CN) ₂] ¹⁷	2136	2152		
[Ni(en)] [Ni(CN) ₄]·2.5H ₂ O (4)				2164
K ₂ [Ni(CN) ₄] ⁴⁸				2170
[Ni(tren)Ag(CN) ₂][Ag(CN) ₂] (5)	2139	2174		
[Ni(tren)Au(CN) ₂][Au(CN) ₂] ²⁴	2144	2179		
[Cu(en)Cu(CN) ₂ Ag(CN) ₂] (6)		2151, 2141		2127
K[Cu(CN) ₂] ⁴⁸				2115 ± 5

^a en = ethylenediamine, dien = diethylenetriamine, tren = tris(2-aminoethyl)amine.

Table 2. Summary of Crystallographic Data

	1 ^a	2 ^a	5 ^a	6 ^b
formula	C ₉ H ₁₆ N ₉ Ag ₃ Cu	C ₁₇ H ₂₆ N ₁₅ Ag ₃ Cu ₂	C ₁₀ H ₁₈ N ₈ Ag ₂ Ni	C ₆ H ₈ N ₆ AgCu ₂
fw	637.43	1106.92	524.75	399.13
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> , Å	6.6945(10)	6.9921(7)	7.9841(7)	8.0393(5)
<i>b</i> , Å	8.2741(13)	17.6629(17)	16.4951(15)	12.7741(6)
<i>c</i> , Å	9.0411(12)	12.5504(15)	13.9185(19)	11.0643(5)
α , deg	69.739(12)	90	90	90
β , deg	89.622(12)	90.714(8)	104.106(8)	94.264(4)
γ , deg	70.226(12)	90	90	90
<i>V</i> , Å ³	438.63(11)	1549.9(3)	1777.8(3)	1133.10(9)
<i>Z</i>	1	2	4	4
ρ_{calcd} , g/cm ³	2.413	2.372	1.961	2.339
μ , cm ⁻¹	44.8	44.5	32.2	54.01
<i>T</i> (K)	293	293	293	198
<i>R</i> , <i>R</i> _w (<i>I</i> > <i>x</i> σ (<i>I</i>)) ^{c,d}	0.021, 0.024 ^c	0.028, 0.021 ^c	0.029, 0.037 ^c	0.022, 0.034 ^d
<i>R</i> , <i>R</i> _w (all data)	0.030, 0.026			0.038, 0.069

^a Enraf-Nonius CAD-4 diffractometer, Mo K α radiation ($\lambda = 0.71069$ Å), graphite monochromator. ^b Rigaku/ADSC CCD diffractometer, detector swing angle -10.50° , aperture 94.0×94.0 mm² at a distance of 38.33 mm from the crystal, Mo K α radiation ($\lambda = 0.71069$ Å), graphite monochromator. ^c $x = 2.5$. Function minimized $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F_o) + 0.0001F_o^2$, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$. ^d $x = 3$. Function minimized $\sum w(|F_o^2 - F_c^2|)^2$ where $w^{-1} = \sigma^2(F_o^2)$, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$.

g (69%). Anal. Calcd for C₆H₈N₆AgCu: C, 18.06; H, 2.02; N, 21.06. Found: C, 18.20; H, 1.98; N, 20.80. IR (KBr): 2151 (ν_{CN}), 2141 (ν_{CN}), 2127 (ν_{CN}), 1578, 1458, 1311, 1275, 1088, 1041, 1009, 970, 873, 658, 515 cm⁻¹.

X-ray Crystallographic Analysis. [Cu(en)₂][Ag₂(CN)₃]-[Ag(CN)₂] (**1**), [Cu(dien)Ag(CN)₂]₂[Ag₂(CN)₃][Ag(CN)₂] (**2**), and [Ni(tren)Ag(CN)₂][Ag(CN)₂] (**5**). Crystallographic data for all structures are collected in Table 2. All crystals were mounted on glass fibers using epoxy adhesive. Crystal descriptions for each compound are as follows: **1** was a purple prism having dimensions $0.29 \times 0.19 \times 0.12$ mm³; **2** was a blue plate having dimensions $0.15 \times 0.12 \times 0.05$ mm³; **5** was a purple prism having dimensions $0.31 \times 0.25 \times 0.25$ mm³. The following data ranges were recorded with the diffractometer control program DIFRAC³⁰ and an Enraf Nonius CAD4F diffractometer: **1**, $4^\circ \leq 2\theta \leq 55^\circ$; **2**, $4^\circ \leq 2\theta \leq 55^\circ$; **5**, $4^\circ \leq 2\theta \leq 60^\circ$. The data were corrected by integration for the effects of absorption with the following transmission ranges: **1**, 0.4837–0.6533; **2**, 0.6255–0.8192; **5**, 0.4249–0.5568. Data reduction for all compounds included corrections for Lorentz and polarization effects. Final unit-cell dimensions were determined on the basis of the following well-centered reflections: **1**, 40 reflections with range $40^\circ \leq 2\theta \leq 52^\circ$; **2**, 58 reflections with range $40^\circ \leq 2\theta \leq 46^\circ$; **5**, 72 reflections with range $44^\circ \leq 2\theta \leq 54^\circ$.

For all compounds, coordinates and anisotropic displacement parameters for the non-hydrogen atoms were refined. Hydrogen atoms were placed in calculated positions (d C–H 0.95 Å; d N–H 0.93 Å), and their coordinate shifts were linked with those of the respective carbon or nitrogen atoms during refinement. Isotropic thermal parameters for the hydrogen atoms were initially assigned proportionately to the equivalent isotropic thermal parameters of their respective carbon or nitrogen atoms. Subsequently, the isotropic thermal parameters for the C–H hydrogen atoms were constrained to have identical shifts during refinement, as were those N–H hydrogen atoms. An extinction parameter³¹ was included in the final cycles of full-matrix least-squares refinement of **1** and **5**. The final refinements, using observed data ($I_o \geq 2.5\sigma(I_o)$), included the following: **1**, 106 parameters for 1690 data; **2**, 185 parameters for 1824 data; **5**, 196 parameters for 3123 data. Selected bond lengths and angles for **1**, **2**, and **5** are found in Tables 3, 4, and 5, respectively.

The programs used for all absorption corrections, data reduction, and structure solutions of **1**, **2**, and **5** were from the NRCVAX Crystal Structure System.³² The structures were refined using CRYSTALS.³³ Diagrams were made using Ortep-3.³⁴ Complex scattering factors for neutral atoms³⁵ were used in the calculation of structure factors.

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[Cu(en)Cu(CN)₂Ag(CN)₂] (6). A blue block crystal of **6** having dimensions of $0.50 \times 0.50 \times 0.35 \text{ mm}^3$ was mounted on a glass fiber and measured on a Rigaku/ADSC CCD diffractometer. Data were collected in 0.50° oscillations with 12 s exposures to a maximum 2θ value of 60.1° . A sweep of data was done using ϕ oscillations from 0.0° to 190.0° at $\chi = -90^\circ$, and a second sweep was performed using ω oscillations between -19.0° and 23.0° at $\chi = -90^\circ$. The final unit-cell parameters were obtained by least-squares on the setting angles for 7354 reflections with $2\theta = 6.0\text{--}60.1^\circ$. The data (10288 data collected, 3031 unique; $R_{\text{int}} = 0.031$) were processed and corrected for Lorentz and polarization effects and absorption (minimal/maximal transmission 0.5730–1.0000).³⁶

The structure was solved by heavy-atom methods (PATY)³⁷ and expanded using Fourier techniques (data/parameter ratio: 21.44). Full-matrix least-squares refinement was conducted with all non-hydrogen atoms anisotropic; hydrogen atoms were refined isotropically. Final $R_1 = 0.038$, $wR_2 = 0.069$, $GOF = 1.10$ on all data, and $R_1 = 0.022$, $wR_2 = 0.034$ on 2551 observed reflections ($I > 3\sigma(I)$). Selected bond lengths and angles are found in Table 6. Diagrams were made using Ortep-3.³⁴

Results

Synthesis. The reaction (eq 1) of an aqueous solution of metal compound ($\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) containing 1 or 2 equiv of capping amine ligand with an aqueous solution of 2 equiv of $\text{KAg}(\text{CN})_2$ produced a variety of different coordination polymers.



The capping amine ligand(s) can occupy two (one equivalent of en), three (dien), or four coordination sites (tren, 2 equivalents of en) on the metal center, thus leaving progressively fewer sites available for coordination of $[\text{Ag}(\text{CN})_2]^-$. The crystal structures of the complexes described in following paragraphs show a variety of supramolecular geometries that are influenced strongly by d^{10} metal–metal interactions and cyano(N)–metal interactions.

Structural Studies. **[Cu(en)₂][Ag₂(CN)₃][Ag(CN)₂] (1).** Crystals of **1** were formed upon slow diffusion of an aqueous solution of 1 equiv of $[\text{Cu}(\text{en})_2]^{2+}$ and 2 equiv of $[\text{Ag}(\text{CN})_2]^-$ in an H-shaped tube. The X-ray crystal structure of **1** revealed a one-dimensional (1-D) zigzag chain, propagating in the [010] direction, of $[\text{Ag}_2(\text{CN})_3]^-$ and $[\text{Ag}(\text{CN})_2]^-$ units connected via argentophilic interactions (Figure 1). The Ag(1)–Ag(2) bond length is 3.102(1) Å, which is significantly lower than 3.44 Å, the sum of the van der Waals radii of two Ag(I) centers.³⁸ This argentophilic

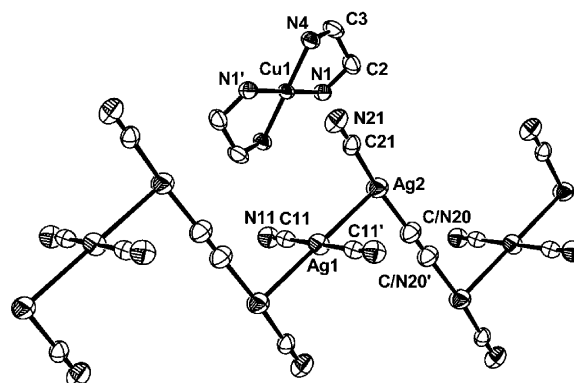


Figure 1. Extended structure of $[\text{Cu}(\text{en})_2][\text{Ag}_2(\text{CN})_3][\text{Ag}(\text{CN})_2]$ (**1**) showing only the 1-D chain (ORTEP, 50% ellipsoids).

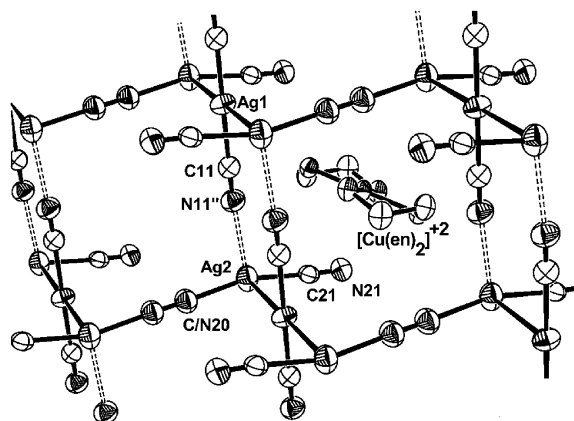


Figure 2. Extended structure of $[\text{Cu}(\text{en})_2][\text{Ag}_2(\text{CN})_3][\text{Ag}(\text{CN})_2]$ (**1**) showing the 2-D network propagated by $\text{Ag} \cdots \text{N}$ interactions. Only one $[\text{Cu}(\text{en})_2]^{2+}$ cation is shown for clarity (ORTEP, 50% ellipsoids).

interaction can be compared to the 2.889 Å distance of the Ag–Ag bonds in metallic silver and many silver(I) oxides.³⁹ The $[\text{Ag}(\text{CN})_2]^-$ moieties retain their expected linear geometry ($\text{C}(11)\text{--Ag}(1)\text{--C}(11)' = 180.00^\circ$ by symmetry, where $' \equiv -x, 1 - y, -z$) due to the balanced effect of two Ag–Ag interactions in opposing positions. The $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Ag}_2(\text{CN})_3]^-$ fragments are oriented nearly orthogonally with respect to each other ($\text{C}(21)\text{--Ag}(2)\text{--Ag}(1)\text{--C}(11)' = 81.7^\circ$), as has been observed in other $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Ag}_2(\text{CN})_3]^-$ systems.^{16–17,20–21c}

Cyano-N(11)··Ag(2) interactions connect these 1-D zigzag chains into a two-dimensional (2-D) array (Figure 2). The Ag(2)–N(11)'' (where $'' \equiv 1 - x, -y, -z$) bond distance of 2.572(3) Å is well below the sum of the van der Waals radii (3.27 Å)³⁸ and within the range of other Ag–N bonds (2.085–2.979 Å) reported in the literature.^{40,41} The $[\text{Ag}_2(\text{CN})_3]^-$ unit is distorted from linearity ($\text{C}(21)\text{--Ag}(2)\text{--C/N}(20) = 163.59(13)^\circ$) because of the Ag–N interaction. There have been very few studies where the binding of silver atoms by the nitrogen atoms of $[\text{Ag}(\text{CN})_2]^-$ units has been observed.^{28,41} Furthermore, this is only the second reported structure where a $[\text{Ag}(\text{CN})_2]^-$ nitrogen generates a strong Ag–N interaction in a nonlinear fashion ($\text{N}(11)\text{--Ag}(2)\text{--C/N}(20) = 96.06(11)^\circ$). The first, recently reported, structure

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with such an interaction was $[\text{Ni}(\text{en})_2\text{Ag}_2(\text{CN})_3][\text{Ag}(\text{CN})_2]$, which showed similar nonlinearity ($\text{N}-\text{Ag}-\text{C}/\text{N} = 95.2(2)^\circ$) and a slightly stronger interaction ($\text{Ag}-\text{N} = 2.415(4) \text{ \AA}$).²⁸

The $[\text{Cu}(\text{en})_2]^{2+}$ cation is not strongly coordinated to the 2-D array (Figure 1). There are, however, weak interactions ($\text{Cu}(1)-\text{N}(21) = 2.657(3) \text{ \AA}$) between the copper(II) center and the free cyano(N) atoms of the $[\text{Ag}_2(\text{CN})_3]^-$ units. As a result, the 2-D array is held weakly (via these interactions) in a three-dimensional (3-D) network.

There are significant differences between the structure of **1** and the previously reported structure of $[\text{Cu}(\text{en})_2\text{Ag}(\text{CN})_2][\text{Ag}(\text{CN})_2]$.^{21b} This complex, containing no $[\text{Ag}_2(\text{CN})_3]^-$ units, forms a 1-D chain of $[\text{Cu}(\text{en})_2]^{2+}$ and bridging $[\text{Ag}(\text{CN})_2]^-$ units with a $\text{Cu}-\text{N}$ bond of $2.569(4) \text{ \AA}$, a stronger interaction than that observed in **1**. In $[\text{Cu}(\text{en})_2\text{Ag}(\text{CN})_2][\text{Ag}(\text{CN})_2]$, the $\text{Ag}-\text{Ag}$ interaction between the bridging $[\text{Ag}(\text{CN})_2]^-$ and the free $[\text{Ag}(\text{CN})_2]^-$ is $3.1580(5) \text{ \AA}$, creating a 2-D array. This argentophilic interaction is slightly weaker than that observed in **1**. Finally, $[\text{Cu}(\text{en})_2\text{Ag}(\text{CN})_2][\text{Ag}(\text{CN})_2]$ displays no $\text{Ag}\cdots\text{N}$ interactions.

[Cu(dien)Ag(CN)₂]₂[Ag₂(CN)₃][Ag(CN)₂ (2). Crystals of **2** were formed upon slow evaporation of an aqueous mixture of 2 equiv of $[\text{Ag}(\text{CN})_2]^-$ and 1 equiv of $[\text{Cu}(\text{dien})]^{2+}$. The X-ray structure of **2** shows that the $[\text{Cu}(\text{dien})]^{2+}$ cations are each connected to two $[\text{Ag}(\text{CN})_2]^-$ units; thus, each copper(II) is five-coordinate (Figure 3). The copper center adopts a distorted square pyramidal coordination such that one $[\text{Ag}(\text{CN})_2]^-$ moiety is coordinated equatorially ($\text{Cu}(1)-\text{N}(11) = 1.984(5) \text{ \AA}$), one is coordinated apically ($\text{Cu}(1)-\text{N}(12)' = 2.166(5) \text{ \AA}$, where $' \equiv -x + 1/2, y - 1/2, -z + 1/2$), and the final three equatorial sites are occupied by the three nitrogens of the dien ligand. The apical $\text{Cu}-\text{N}$ bond is slightly stronger as compared with previously reported distorted copper complexes ($\text{Cu}-\text{N}$ apical = $2.2-2.7 \text{ \AA}$).^{21a-c,42-43} The $[\text{Ag}(\text{CN})_2]^-$ fragments bridge apical/equatorial sites between $[\text{Cu}(\text{dien})]^{2+}$ cations to form a 1-D zigzag chain (Figure 3) in the $[010]$ direction.

Zigzag chains of alternating $[\text{M}(\text{ligand})]^{2+}$ and $[\text{M}(\text{CN})_2]^-$ units have been observed for both $[\text{Au}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_2]^-$

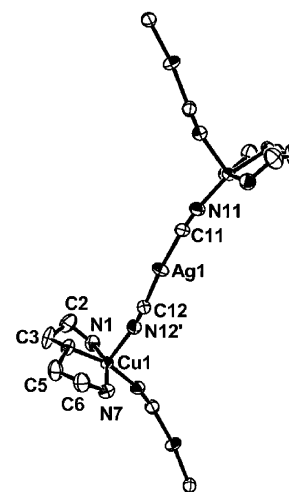


Figure 3. Extended structure of $[\text{Cu}(\text{dien})\text{Ag}(\text{CN})_2]_2[\text{Ag}_2(\text{CN})_3][\text{Ag}(\text{CN})_2]$ (**2**) showing only the 1-D chain (ORTEP, 50% ellipsoids).

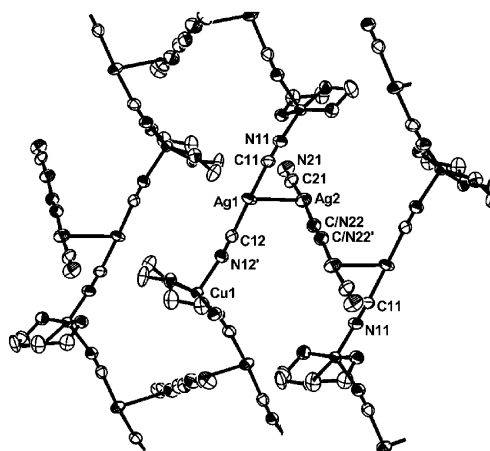


Figure 4. Extended structure of $[\text{Cu}(\text{dien})\text{Ag}(\text{CN})_2]_2[\text{Ag}_2(\text{CN})_3][\text{Ag}(\text{CN})_2]$ (**2**) showing the 2-D network propagated through argentophilic interactions (ORTEP, 50% ellipsoids).

Table 3. Selected Bond Lengths (\AA) and Angles ($^\circ$) for $[\text{Cu}(\text{en})_2][\text{Ag}_2(\text{CN})_3][\text{Ag}(\text{CN})_2]$ (**1**)

$\text{Ag}(1)-\text{C}(11)$	2.046(3)	$\text{Ag}(2)-\text{C}(21)$	2.071(4)
$\text{Ag}(2)-\text{C}/\text{N}(20)$	2.085(4)	$\text{C}/\text{N}(20)-\text{C}/\text{N}(20)'$	1.129(8)
$\text{N}(11)-\text{C}(11)$	1.125(4)	$\text{N}(21)-\text{C}(21)$	1.110(6)
$\text{Cu}(1)-\text{N}(1)$	1.998(3)	$\text{Cu}(1)-\text{N}(4)$	2.0162(21)
$\text{Ag}(1)-\text{Ag}(2)$	3.102(1)	$\text{Ag}(2)-\text{N}(11)'$	2.572(3)

$\text{C}(21)-\text{Ag}(2)-\text{C}/\text{N}(20)$	163.59(13)	$\text{C}/\text{N}(20)'\text{-C}/\text{N}(20)-\text{Ag}(2)$	178.3(3)
$\text{N}(1)-\text{Cu}(1)-\text{N}(4)$	84.50(11)	$\text{N}(11)'\text{-Ag}(2)-\text{C}/\text{N}(20)$	96.06(11)

^a Symmetry transformations: $' \equiv -x, 1 - y, -z$; $'' \equiv 1 - x, -y, -z$.

complexes.^{8,20} Unlike **2**, the dicyanoaurate analogue, $\text{Cu}(\text{dien})[\text{Au}(\text{CN})_2]_2$, does not display such chains.⁸ Instead, $[\text{Au}(\text{CN})_2]^-$ moieties are coordinated to $[\text{Cu}(\text{dien})]^{2+}$ cations at one end only, leaving the other cyano(N) free. The resulting molecular $\text{Cu}(\text{dien})[\text{Au}(\text{CN})_2]_2$ units are then connected through $\text{Au}-\text{Au}$ interactions.

The chains in **2** are cross-linked via $\text{Ag}(1)-\text{Ag}(2)$ interactions of $3.1718(8) \text{ \AA}$ to $[\text{Ag}_2(\text{CN})_3]^-$ units, thus creating a 2-D array in the (101) plane (Figure 4). A distortion from linearity is observed for both the $[\text{Ag}_2(\text{CN})_3]^-$ units and the $[\text{Ag}(\text{CN})_2]^-$ moieties ($\text{C}(21)-\text{Ag}(2)-\text{C}/\text{N}(22) = 172.0(2)^\circ$ and $\text{C}(12)-\text{Ag}(1)-\text{C}(11) = 169.3(2)^\circ$), which could be due to the presence of argentophilic interactions. Such distortions

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Cu(dien)Ag(CN)_2]_2[Ag_2(CN)_3][Ag(CN)_2]$ (**2**)

Cu(1)–N(1)	2.008(5)	Cu(1)–N(4)	2.016(4)
Cu(1)–N(7)	2.011(5)	Cu(1)–N(12)' ^a	2.166(5)
Cu(1)–N(11)	1.984(5)	Ag(1)–C(12)	2.068(6)
Ag(1)–C(11)	2.050(6)	Ag(2)–C/N(22)	2.064(5)
Ag(2)–C(21)	2.041(7)	Ag(1)–Ag(3)	3.2889(5)
Ag(1)–Ag(2)	3.1718(8)	Ag(3)–C(31)	2.066(7)
C/N(22)–C/N(22)''	1.139(9)		
N(12)'–Cu(1)–N(11)	101.95(18)	N(12)'–Cu(1)–N(7)	98.46(18)
N(12)'–Cu(1)–N(4)	93.95(19)	N(12)'–Cu(1)–N(1)	100.51(19)
N(7)–Cu(1)–N(4)	83.74(19)	N(7)–Cu(1)–N(11)	90.81(19)
N(4)–Cu(1)–N(11)	163.8(2)	N(4)–Cu(1)–N(1)	83.85(19)
N(7)–Cu(1)–N(1)	157.96(19)	N(11)–Cu(1)–N(1)	96.13(19)
Ag(2)–Ag(1)–C(11)	69.58(16)	Ag(3)–Ag(1)–C(11)	116.62(16)
Ag(2)–Ag(1)–C(12)	103.06(16)	Ag(3)–Ag(1)–C(12)	72.13(16)
C(11)–Ag(1)–C(12)	169.3(2)	Ag(2)–Ag(1)–Ag(3)	103.742(17)
Ag(1)–Ag(2)–C/N(22)	78.16(16)	Ag(1)–Ag(2)–C(21)	101.21(17)
C/N(22)–Ag(2)–C(21)	172.0(2)	Ag(1)–Ag(3)–C(31)	67.87(18)

^a Symmetry transformations: ' $\equiv -x + 1/2, y - 1/2, -z + 1/2$; '' $\equiv 1 - x, 1 - y, -z$.

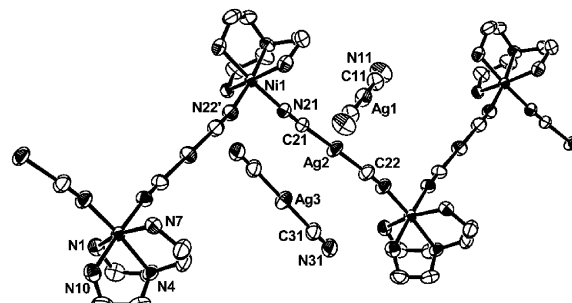
have been recently calculated in aurophilic $[Au(CN)_2]^-$ dimers.²⁵ In contrast to **1**, $[Ag(CN)_2]^-$ forms an interaction with only one $[Ag_2(CN)_3]^-$ unit.

The 2-D planes are connected into a weakly held 3-D array via further argentophilic interactions of 3.2889(5) Å between silver atoms in the $[Ag(CN)_2]^-$ units of the two-dimensional array (Ag(1)) and the remaining $1/2$ equiv of free $[Ag(CN)_2]^-$ (Ag(3)) (3-D array not shown). As a result, argentophilic interactions have increased the dimensionality of **2** from one to three and can thus be viewed, like gold–gold interactions, as a tool with which to increase structural dimensionality.^{8,9}

The reaction to produce the analogous complex with Ni(II) yields a purple precipitate with an IR showing ν_{CN} bands of 2160 (broad), 2140, 2135, and 2123 cm^{-1} , similar to **2**. Although this might suggest an analogous structure, suitable crystals could not be obtained.

[Ni(en)₂Ag₂(CN)₃][Ag(CN)₂] (3**) and [Ni(en)][Ni(CN)₄] \cdot 2.5H₂O (**4**).** Crystals of both $[Ni(en)_2Ag_2(CN)_3][Ag(CN)_2]$ (**3**) and $[Ni(en)][Ni(CN)_4]\cdot 2.5H_2O$ (**4**) were obtained through an H-tube experiment. The X-ray structure of **3** has been previously reported,²⁸ although there was no discussion of the formation of the $[Ni(CN)_4]^{2-}$ byproduct (**4**). The Ag–N bond in **3** is similar to that observed in **1**, in that it is a nonlinear bond between a cyano(N) and silver atom (C/N–Ag–N = 95.2(2)°), but is slightly stronger (Ag–N = 2.415(4) Å) than that observed in **1**.²⁸

No discussion has been reported regarding the structural impact of the increased length of the $[Ag_2(CN)_3]^-$ unit as compared to the $[Ag(CN)_2]^-$ unit.²⁸ The structure of **3** can be compared to the previously reported $[Ni(tn)_2][Ag(CN)_2]_2$ (tn = 1,3-diaminopropane).^{21a} Even though only one carbon atom has been added to the chelate backbone, in $[Ni(tn)_2][Ag(CN)_2]_2$, 1-D chains of alternating $[M(L)_2]^{2+}$ and $[Ag(CN)_2]^-$ do not form; rather, only a trimetallic molecule of $Ni(tn)_2(\mu-NC-Ag-CN)_2$ is observed.^{21a} This suggests that the increased length of the $[Ag_2(CN)_3]^-$ unit (approximately 11.6 Å vs 6.3 Å for the $[Ag(CN)_2]^-$ unit) is sufficient to allow for linear propagation in an axial fashion. There are also no Ag–N bonds in $[Ni(tn)_2][Ag(CN)_2]_2$ that

**Figure 5.** Extended structure of $[Ni(tren)Ag(CN)_2][Ag(CN)_2]$ (**5**) (ORTEP, 50% ellipsoids).

increase dimensionality; the only increase in dimensionality results from Ag–Ag interactions of 3.2627(3) Å, which generate a 1-D chain. These comparisons suggest that the incorporation of $[Ag_2(CN)_3]^-$ units can serve to enhance dimensionality, as the increased length may allow for coordination between units that could be sterically hindered if connected by $[Ag(CN)_2]^-$ units.

From the crystals of $[Ni(en)][Ni(CN)_4]\cdot 2.5H_2O$ (**4**) that were obtained from the same H-tube experiment that yielded **3**, only a crude crystal structure was obtained, which served to confirm the identity of the compound and provide a general picture of the resulting complex. Each octahedral nickel center is capped by en, and the remaining four sites are occupied by $[Ni(CN)_4]^{2-}$ units, which then bridge to three other nickel centers; related compounds such as $[Cd(en)Ni(CN)_4]$ have been reported.²⁷ This builds a 3-D structure with cavities throughout that are filled with 2.5 equiv of water. Further studies are currently being conducted with **4**, and related compounds.

[Ni(tren)Ag(CN)₂][Ag(CN)₂] (5**).** Crystals of **5** were obtained through an H-tube diffusion method. The resulting crystal structure is virtually isostructural to the previously reported gold analogue.²⁴ In both cases, $[Ni(tren)]^{2+}$ cations are linked in a *cis* fashion by $[M(CN)_2]^-$ units to form a 1-D zigzag chain in the [010] direction (Figure 5). The Ni(II) adopts an octahedral geometry in both cases. It was observed in $[Ni(tren)Au(CN)_2][Au(CN)_2]$ that the two cyano(N)–Ni distances varied slightly in bond lengths (2.05(2) Å vs 2.12(1) Å),²⁴ and this was also observed in **5** (Ni(1)–N(22)' = 2.039(3) Å and Ni(1)–N(21) = 2.098(3) Å, where ' $\equiv -x + 1/2, y + 1/2, -z + 3/2$). The $[M(CN)_2]^-$ moieties in both structures were linear.

In $[Ni(tren)Au(CN)_2][Au(CN)_2]$, the gold–gold distances were 3.5963(8) Å and 3.5932(8) Å.²⁴ In the Ag(I) equivalent (**5**), the silver–silver distances are 3.5607(6) Å (Ag(1)–Ag(2)) and 3.7125(6) Å (Ag(2)–Ag(3)). In both cases, these long distances suggest that there are no significant metallophilic interactions present, and both structures remain 1-D.

The reaction to produce the analogous Cu(II) complex yielded an immediate light blue precipitate in low yield with IR ν_{CN} bands at 2166 and 2140 cm^{-1} , similar to **5**. Single crystals could not be obtained.

[Cu(en)Cu(CN)₂Ag(CN)₂] (6**).** Crystals of **6** were obtained in moderate yield through an H-tube diffusion method; repeated attempts to prepare **6** via other methods led to

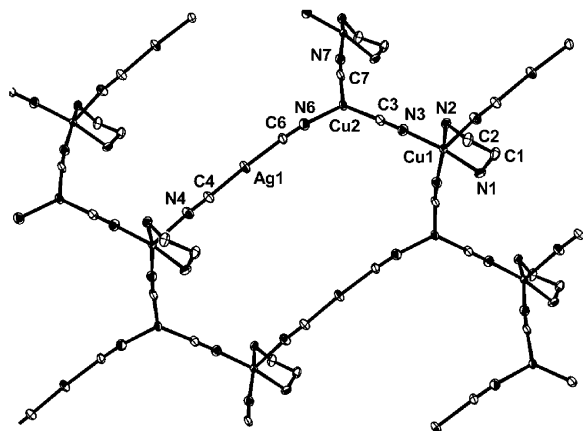


Figure 6. Extended structure of $[\text{Cu}(\text{en})\text{Cu}(\text{CN})_2\text{Ag}(\text{CN})_2]$ (**6**) showing only the 2-D net (ORTEP, 50% ellipsoids).

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Ni}(\text{tren})\text{Ag}(\text{CN})_2][\text{Ag}(\text{CN})_2]$ (**5**)

Ag(1)–C(11)	2.046(4)	Ag(3)–C(31)	2.056(4)
Ag(2)–C(21)	2.046(3)	Ag(2)–C(22)	2.049(4)
Ni(1)–N(1)	2.123(3)	Ni(1)–N(4)	2.106(3)
Ni(1)–N(7)	2.093(3)	Ni(1)–N(10)	2.112(3)
Ni(1)–N(21)	2.098(3)	Ni(1)–N(22) ^a	2.039(3)
C(21)–Ag(2)–C(22)	179.31(15)		
N(1)–Ni(1)–N(4)	82.11(12)	N(1)–Ni(1)–N(7)	83.18(11)
N(1)–Ni(1)–N(10)	91.96(12)	N(4)–Ni(1)–N(10)	82.88(12)
N(7)–Ni(1)–N(10)	93.58(11)	Ni(1)–Ni(1)–N(21)	85.93(12)
N(4)–Ni(1)–N(21)	93.59(12)	N(7)–Ni(1)–N(21)	87.59(11)
N(10)–Ni(1)–N(21)	176.12(12)	N(1)–Ni(1)–N(22) ^a	99.49(13)
N(4)–Ni(1)–N(22) ^a	172.85(12)	N(7)–Ni(1)–N(22) ^a	96.03(12)
N(10)–Ni(1)–N(22) ^a	90.09(12)	N(21)–Ni(1)–N(22) ^a	93.48(12)
Ni(1)–N(21)–C(21)	174.4(3)	Ni(1)–N(22) ^a –C(22) ^a	170.6(3)

^a Symmetry transformations: $' \equiv -x + 1/2, y + 1/2, -z + 3/2$.

complex mixtures. The resulting X-ray structure reveals a five-coordinate, distorted square pyramidal copper(II) center, with equatorial sites occupied by en ($\text{Cu}(1)\text{--N}(1) = 2.030(2)$ Å and $\text{Cu}(1)\text{--N}(2) = 2.036(2)$ Å) and $[\text{Cu}(\text{CN})_2]^-$ units ($\text{Cu}(1)\text{--N}(3) = 1.984(2)$ Å and $\text{Cu}(1)\text{--N}(7) = 1.989(2)$ Å) and the apical site coordinated by a $[\text{Ag}(\text{CN})_2]^-$ moiety ($\text{Cu}(1)\text{--N}(4) = 2.211(2)$ Å) (Figure 6).

Each $[\text{Cu}(\text{CN})_2]^-$ moiety bridges two $[\text{Cu}(\text{en})]^{2+}$ cations. This trigonal ($\text{C}(3)''\text{--Cu}(2)\text{--C}(7) = 126.1(1)^\circ$ where $'' \equiv 1/2 + x, 1/2 - y, -1/2 + z$) Cu(I) center is three-coordinate by virtue of cyano(N) coordination from a $[\text{Ag}(\text{CN})_2]^-$ unit ($\text{Cu}(2)\text{--N}(6) = 1.975(2)$ Å). This linear Ag(I) fragment then bridges to another $[\text{Cu}(\text{en})]^{2+}$ cation. The end result is a coordinately bonded, 2-D array of closed elongated hexagons (Figure 6), which can be described as an infinite (6,3) net.⁴⁴ This (6,3) net is comparable to that seen in **3**, but in **3**, there is further propagation of these nets via argentophilic interactions.²⁸

Although the nets in **6** do not possess interactions extending them into infinite 3-D networks, the apparent free volume in the structure is filled by a second, interpenetrating (6,3) net (Figure 7). The interpenetration occurs in a parallel fashion, and the layers are connected and stabilized by $\text{Cu}(2)\text{--Ag}(1)$ interactions of 3.1000(4) Å. This is an unusual

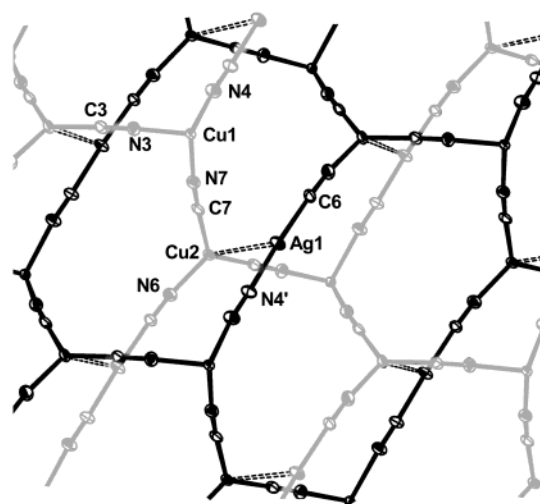


Figure 7. Extended structure of $[\text{Cu}(\text{en})\text{Cu}(\text{CN})_2\text{Ag}(\text{CN})_2]$ (**6**) showing two interpenetrating 2-D nets stabilized by Cu–Ag interactions (3.1000(4) Å, dotted lines) (ORTEP, 50% ellipsoids and en ligand removed for clarity).

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Cu}(\text{en})\text{Cu}(\text{CN})_2\text{Ag}(\text{CN})_2]$ (**6**)

Ag(1)–C(4) ^a	2.062(2)	Ag(1)–C(6)	2.073(2)
Cu(1)–N(1)	2.030(2)	Cu(1)–N(2)	2.036(2)
Cu(1)–N(3)	1.984(2)	Cu(1)–N(4)	2.211(2)
Cu(1)–N(7)	1.989(2)	Cu(2)–N(6)	1.975(2)
Cu(2)–C(3)''	1.923(2)	Cu(2)–C(7)	1.926(2)
Ag(1)–Cu(2)	3.1000(4)		
N(1)–Cu(1)–N(2)	83.48(8)	N(1)–Cu(1)–N(3)	167.82(9)
N(1)–Cu(1)–N(4)	90.82(9)	N(1)–Cu(1)–N(7)	90.21(8)
N(2)–Cu(1)–N(3)	91.33(8)	N(2)–Cu(1)–N(4)	93.92(8)
N(2)–Cu(1)–N(7)	163.13(8)	N(3)–Cu(1)–N(4)	100.56(9)
N(3)–Cu(1)–N(7)	91.70(9)	N(4)–Cu(1)–N(7)	101.83(8)
C(4) ^a –Ag(1)–C(6)	175.0(1)	N(6)–Cu(2)–C(3)''	117.5(1)
N(6)–Cu(2)–C(7)	116.35(9)	C(3)''–Cu(2)–C(7)	126.1(1)

^a Symmetry transformations: $' \equiv 1 + x, y, z;$ $'' \equiv 1/2 + x, 1/2 - y, -1/2 + z$.

example of metalphilic $d^{10}\text{--}d^{10}$ interactions between Cu(I) and Ag(I). The only previously reported Cu(I)–Ag(I) interactions are in constrained cluster complexes, with concomitantly lower Cu(I)–Ag(I) distances (2.67–3.07 Å).⁴⁵ A related structure, $\text{Cu}(\text{NH})_3(\text{py})\text{Ag}_{3-x}\text{Cu}_x(\text{CN})_5$, has a similar general framework and interpenetration, but the Cu(I) and Ag(I) sites are disordered because of partial replacement of Ag(I) for Cu(I).⁴⁶ The metalphilic interactions (2.791(3) and 2.641(1) Å) in this case are between adjacent trigonal centers (as opposed to trigonal and linear centers in **6**) and are supported by partially bridging CN-ligands, thus accounting for their strength compared with that of **6**. The disorder present in this previously reported structure, however, precludes any further meaningful discussion of metalphilic interactions.

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Infrared Spectral Studies. For all complexes, the IR spectra are invaluable in understanding the structure on the basis of the different possible environments of the cyanide moieties, as outlined later. The ν_{CN} bands in the IR spectra of each complex are collected in Table 1 for comparison.

Unbound Terminal Cyanides of $[Ag(CN)_2]^-$ and $[Ag_2(CN)_3]^-$. Structures **1**, **2**, and **5** contain unbound cyano-(N) moieties and thus exhibit bands close to the 2139 cm^{-1} band of $KAg(CN)_2$.⁴⁷ Both the terminal cyanides of $[Ag(CN)_2]^-$ and $[Ag_2(CN)_3]^-$ exhibit stretches in the same region, and thus, their differentiation on this basis is not possible.

Transition Metal...Silver Bridging Cyanides of $[Ag(CN)_2]^-$ and $[Ag_2(CN)_3]^-$. The blue-shifted bands (relative to free $[Ag(CN)_2]^-$) observed in **1**, **2**, **3**, and **6** originate from bridging cyanides, and the extent of the shift relates to the strength of the bond.¹⁸ In **1**, **2**, and **6**, the blue-shifted bands are attributed to bridging $[Ag(CN)_2]^-$. In **3**, the only ν_{CN} stretching frequency that is unaccounted for is 2140 cm^{-1} , a value that suggests a terminal cyanide, though there is no unbound cyanide present in the structure. This stretching frequency is thus attributed to the bridging cyanide units of the $[Ag_2(CN)_3]^-$ moieties, which do not bridge in any other observed structure. It is possible that this stretching frequency remains relatively unaltered as compared to the terminal stretching frequencies because of a combination of a blue-shift effect (from the CN- σ donation from the antibonding orbital) and a red-shift effect (discussed later).¹⁸

Central Bridging Cyanides of $Ag_2(CN)_3$. The lowest of the observed ν_{CN} bands (in **1**, **2**, and **3**) have not been observed in previous $[Ag(CN)_2]^-$ studies.^{17,21} IR investigations of $[Ag_2(CN)_3]^-$ have not been conducted because of the inability to isolate this complex as a pure solid; the few reported $[Ag_2(CN)_3]^-$ -containing coordination polymers did not present IR data.²² We suggest that this band is attributable to the bridging central cyanide moiety in $[Ag_2(CN)_3]^-$; its red shift relative to $[Ag(CN)_2]^-$ may result from π -back-bonding from each silver atom into this CN bond. Although CN is generally a weak π -acceptor, red shifts for bridging cyanides have been reported where the π -back-bonding influence dominates.¹⁸

Other Transition Metal Cyanide Bands. In **4**, the only cyanide stretch observed is 2164 cm^{-1} , which is consistent with the cyanide stretch found in $K_2Ni(CN)_4$ (2170 cm^{-1}).⁴⁸ Although, in most cases, a blue shift is observed with cyanide bridging, π -back-bonding may play a larger role in this structure.⁴⁹ Similarly, in **6**, a bridging cyanide resonance at 2127 cm^{-1} can be compared to the value for $KCu(CN)_2$ of $2115 \pm 5\text{ cm}^{-1}$.⁴⁸

Magnetic Properties. The product of the magnetic susceptibility with temperature, $\chi_M T$, for **1** at 300 K was determined to be $0.39\text{ cm}^3\text{ K mol}^{-1}$, consistent with the presence of an $S = 1/2$, Cu(II) center. No significant magnetic

interactions are expected in this system as the $[Cu(en)_2]^{2+}$ ions are structurally isolated from each other, according to the X-ray structure.

For complexes **2–6**, the temperature (T) dependence of the molar magnetic susceptibilities (χ_M) was measured from 2 to 300 K, and the data were examined for the presence of magnetic interactions. For $[Cu(dien)Ag(CN)_2]_2[Ag_2(CN)_3][Ag(CN)_2]$ (**2**), $\chi_M T = 0.47\text{ cm}^3\text{ K mol}^{-1}$ at 300 K and is temperature independent until 25 K, at which point $\chi_M T$ drops to $0.43\text{ cm}^3\text{ K mol}^{-1}$ at 2 K. The data can be fit to the Curie–Weiss law with $\theta = -0.17\text{ K}$, consistent with weak antiferromagnetic coupling between Cu(II) centers. This magnetic interaction is likely mediated by bridging $[Ag(CN)_2]^-$ units, which bridge Cu(II) centers in an apical/equatorial fashion to yield a 1-D coordinately bonded chain; the distance between Cu(II) centers is 10.541 \AA . An exchange coupling constant of $J = -0.18\text{ cm}^{-1}$ with $g = 2.24$ is obtained from the model for a 1-D Heisenberg chain of $S = 1/2$ centers.⁵⁰ Although the diamagnetic Ag(I) ion is mediating magnetic exchange in this system, the long distance between magnetic centers mitigates against strong exchange in this system. Silver(I) ions have been reported to be mediators of magnetic exchange, particularly between organic radical ligands.⁵¹ In addition, the observation of antiferromagnetic interactions in this system, as opposed to the ferromagnetic interactions usually observed in apical/equatorial Cu(II)-chain systems,^{52a} can be attributed to the N(12)–Cu(1)–N(11) bond angle of $101.95(18)^\circ$ versus the 90° angle required for the strict orthogonality that generates ferromagnetic coupling; in the related $Cu(tmeda)[Au(CN)_2]_2$, a N–Cu–N angle of $89.3(4)^\circ$ in an axial/equatorial chain yielded a significant ferromagnetic interaction mediated by the Au(I) centers.^{9a}

In $[Cu(en)Cu(CN)_2Ag(CN)_2]$ (**6**), from a magnetic point of view, a similar 1-D coordinately bonded chain of Cu(II) centers is present and is bridged by nonlinear $[Cu^I(CN)_2]^-$ units. It is assumed that the Cu(I)–Ag(I) interactions and the chain-cross-linking $[Ag(CN)_2]^-$ units do not significantly contribute to the magnetic behavior of **6**. In this case, $\chi_M T = 0.39\text{ cm}^3\text{ K mol}^{-1}$ at 300 K and, starting from 15 K, drops to $0.26\text{ cm}^3\text{ K mol}^{-1}$ at 2 K. The data can be fit with the Curie–Weiss law with $\theta = -0.83\text{ K}$, and the same 1-D chain model can be applied for **2** with $J = -0.88\text{ cm}^{-1}$ and $g = 2.05$. The substantially larger exchange interaction for this Cu(I)-mediated system (vs **2**) can be rationalized by the short Cu–N bond lengths ($<2\text{ \AA}$) that propagate the chain compared to a longer $2.166(5)\text{ \AA}$ Cu–N(12)' apical bond length in **2**. In addition, the chain structure of **6** has an equatorial/equatorial arrangement, which produces the observed antiferromagnetic exchange.^{52b} The previously reported magnetic studies involving diamagnetic copper(I)

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centers have all contained orthogonal magnetic orbitals; therefore, the magnetic exchange interactions have been ferromagnetic.^{51,53}

The investigation of weak magnetic interactions in the Ni(II) complexes is complicated by the presence of the zero-field splitting (zfs) of octahedral Ni(II) ions. [Ni(en)₂Ag₂(CN)₃][Ag(CN)₂] (**3**), which contains an eight-atom [Ag₂(CN)₃][−] bridge between Ni(II) centers, is a good representation of isolated octahedral Ni(II) centers with which to compare to our later structures. For **3**, $\chi_M T = 1.15 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K and decreases to $1.00 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The data for **4** and **5** show the same general trends. The data for **3** can be fitted²⁹ using the zfs parameter $D = 2.8 \text{ cm}^{-1}$ with $g = 2.23$; these are reasonable values for magnetically dilute $S = 1$ Ni(II) centers.⁵⁴ In contrast, the magnetic susceptibility data for [Ni(en)][Ni(CN)₄]·2.5H₂O (**4**) can be fitted using the same isolated-Ni(II) model to yield $D = 5.0 \text{ cm}^{-1}$. In this procedure, g was fixed at 2.23 to allow for a meaningful comparison of D values between systems; the coordination spheres of **3**, **4**, and **5** are very similar, and thus, this is an acceptable approximation. The significantly larger value of D for **4** than that for **3** implies that Ni(II)-mediated magnetic interactions are operative in this system. The addition of a molecular-field parameter yields an improved fit for **4**, but this overparametrization of a weak interaction does not lead to significant conclusions.²⁹

Similarly, the variable temperature magnetic susceptibility data for [Ni(tren)Ag(CN)₂][Ag(CN)₂] (**5**) can be fit using $D = 4.6 \text{ cm}^{-1}$ with $g = 2.23$. Weak antiferromagnetic interactions within the 1-D chain of Ni(II) centers, mediated by [Ag(CN)₂][−] bridges, are indicated by the larger value of D compared to **3**; again, the quantification of this weak interaction would be ambiguous. However, to compare the relative abilities of Ag(I) and Au(I) to mediate magnetic exchange, the variable temperature magnetic susceptibility for the isostructural [Ni(tren)Au(CN)₂][Au(CN)₂] complex²⁴ was measured. In this case, using the same methodology, $D = 3.1 \text{ cm}^{-1}$ with $g = 2.23$. On the basis of the reasonable assumption that the D values for these two completely isostructural compounds should be the same in the absence of any coupling interactions, this result suggests that Ag(I) is a better mediator of magnetic exchange as compared to Au(I).

Discussion

An examination of the structural trends displayed in the systems presented here yields an array of observations, some of which are consistent with our previous [Au(CN)₂][−] work, and some of which display trends specific to using [Ag(CN)₂][−] as a design element for enhancing structural dimensionality in heterometallic systems. As expected, the structures are dependent on both the number of available coordination sites on the metal (increasing available sites by altering the choice of capping ligand increases structural dimensionality) and

the metal identity. Thus, [Ag(CN)₂][−] reactions involving metal-tren and -dien cations resulted in immediate precipitates of polymeric products, whereas the reaction involving [Cu(en)₂]²⁺, with its Jahn–Teller weakened axial binding sites, did not. However, the analogous reaction with [Ni(en)₂]²⁺ yielded an immediate polymeric precipitate due to the lack of Jahn–Teller distortion in Ni(II) as compared with copper(II) centers.

The influence of argentophilic interactions on the structures of **1** and **2** is apparent, with Ag–Ag bonds ranging from 3.102(1) to 3.2889(5) Å. An increase in dimensionality from zero to one in [Cu(en)₂][Ag₂(CN)₃][Ag(CN)₂] (**1**) is assisted (in conjunction with Ag–N bonds) by Ag–Ag bonds. More significantly, dimensionality is increased from one to three in [Cu(dien)Ag(CN)₂]₂[Ag₂(CN)₃][Ag(CN)₂] (**2**) as a sole result of argentophilic interactions, demonstrating their use as a crystal engineering design element analogous to Au(I)–Au(I) interactions. Similarly, the weak heterometallic Cu(I)–Ag(I) interaction of 3.1000(4) Å in [Cu(en)Cu(CN)₂Ag(CN)₂] (**6**) also increases the structural dimensionality from two to three.

In addition, the formation of Ag–N interactions is also an important factor that has an impact on the overall structure of the [Ag(CN)₂][−]-containing polymers; Au–N bonds were not observed in [Au(CN)₂][−]-analogues.^{8,9} In the structures of both [Cu(en)₂][Ag₂(CN)₃][Ag(CN)₂] (**1**) and [Ni(en)₂Ag₂(CN)₃][Ag(CN)₂] (**3**), interactions between the cyano(N) of the [Ag(CN)₂][−] unit and the Ag of [Ag₂(CN)₃][−] were found. Note that, in every case, it is the Ag-atoms in a [Ag₂(CN)₃][−] unit that acts as acceptors. On this basis, the incorporation of the [Ag₂(CN)₃][−] unit also serves to increase structural dimensionality, through Ag–N interactions.

Clearly, when compared to the high-yield, straightforward reactions of metal–ligand cations with KAu(CN)₂, in which products that reflected the initial stoichiometries and reagents were obtained,^{8,9} the analogous reactions with KAg(CN)₂ are substantially more complex. In most cases, the [Ag(CN)₂][−] unit is not entirely preserved: new anionic units, including [Ag₂(CN)₃][−], [Ni(CN)₄]^{2−}, and [Cu(CN)₂][−], are formed and are incorporated into the supramolecular products. The key to explaining this difference in reactivity complexity lies in the lability of KAg(CN)₂ relative to KAu(CN)₂. The overall formation constant β_2 for KAu(CN)₂ is 10^{37} but a much lower $10^{20.44}$ for KAg(CN)₂.⁴⁸ The lability of KAg(CN)₂ was first observed in a comparison of the IR absorption studies of aqueous Au(I) and Ag(I) cyanide complexes;⁴⁷ this lability was also noted in the reactions of KAg(CN)₂ with organometallic cations [Cp(dppe)Fe]⁺ and [Cp(PPh₃)₂Ru]⁺, in which Ag–*iso*-cyanide coordination was invariably observed.⁵⁵ Significantly, a study of KAg(CN)₂ solutions in liquid ammonia using Raman spectroscopy suggested the dissociation of [Ag(CN)₂][−] into CN[−] and AgCN (eq 2).⁵⁶ In our systems, a variety of secondary reactions can then occur

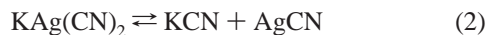
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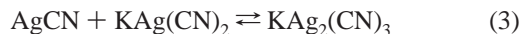
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between these products and the original reactants, resulting in the range of structures observed.



One common secondary reaction pathway is shown in eq 3: the formation of $[Ag_2(CN)_3]^-$ from the aggregation of in situ generated AgCN (eq 2) with $[Ag(CN)_2]^-$.⁵⁶



Though this $[Ag_2(CN)_3]^-$ unit has never been isolated for study, it has been identified in several crystal structures^{22,28} and is present in **1**, **2**, and **3**. The $[Ag_4(CN)_5]^-$ unit has also been reported (a further extension of the dissociation and aggregation process seen with $[Ag_2(CN)_3]^-$).⁵⁷ It is important to note that coordination polymers containing $[Ag(CN)_2]^-$ that do not incorporate the $[Ag_2(CN)_3]^-$ unit have been isolated.^{16,17,20,21,23,41a} It is difficult to compare these diverse systems, as they involve different ligands, use of ammonia for crystal formation, different solvents, and different metals. This might suggest that any of these factors may influence the incorporation of $[Ag(CN)_2]^-$ over $[Ag_2(CN)_3]^-$ into crystal structures. In previously reported $[Ag_2(CN)_3]^-$ -containing complexes,²² no attempt has been made to explain the mechanism of formation of this anion. It appears that because of the lability of $[Ag(CN)_2]^-$ in solution, the incorporation of either $[Ag(CN)_2]^-$ or a mix of $[Ag(CN)_2]^-$ and $[Ag_2(CN)_3]^-$ into the final polymer is a result of competition between the two moieties and their associated equilibria. This competition is influenced by the solvent medium, reagent concentrations, and the overall stability and solubility of the final product; we are continuing to probe these factors in a systematic fashion.

In the presence of $Ni(II)_{aq}$, another secondary reaction from the lability of $KAg(CN)_2$ becomes accessible. The free CN^- liberated via eq 2 can react with $Ni(II)_{aq}$ to yield the $[Ni(CN)_4]^{2-}$ unit. The large β_4 of $10^{30.2}$ drives the formation of this well-known cyanometalate building block;⁴⁸ its further reaction with available metal cations accounts for secondary products such as $[Ni(en)][Ni(CN)_4] \cdot 2.5H_2O$ (**4**). This reaction pathway is impeded by strongly complexing ligands such as tren; there is no evidence of formation of $[Ni(CN)_4]^{2-}$ moieties accompanying the synthesis of $Ni(tren)[Ag(CN)_2]_2$ (**5**). Many supramolecular assemblies are known that utilize the $[Ni(CN)_4]^{2-}$ unit in direct synthesis.^{27,43,58}

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Finally, if unligated $Cu(II)_{aq}$ is available, a secondary reaction with CN^- can occur: the reduction of Cu(II) to Cu(I) with the concomitant formation of cyanogen.⁵⁹ Further reaction of the Cu(I) with CN^- yields $[Cu(CN)_2]^-$ moieties. This Cu(I) product is another anionic building block that can form supramolecular structures. In conjunction with the available $[Ag(CN)_2]^-$ and remaining $[Cu(en)]^{2+}$, the mixed-valent, heterometallic coordination polymer **6**, with linear Ag(I), trigonal Cu(I), and square pyramidal Cu(II) centers, is formed. This reaction pathway is not observed when a higher denticity or concentration of amine ligand is present; amine ligands are known to suppress the reduction of Cu(II) by CN^- anion.⁵⁹ This third alternative pathway, along with the other two secondary reactions already described, illustrates the potential complexity of reactions involving the building block $[Ag(CN)_2]^-$. Other labile cyanometalate building blocks would likely present similar design challenges in supramolecular coordination polymer chemistry.

Conclusions

It has been illustrated that argentophilic interactions, like the previously examined aurophilic interactions, are a valuable tool with which to increase structural dimensionality in supramolecular systems. Furthermore, $[Ag(CN)_2]^-$ can also increase dimensionality through Ag–N interactions, though with less control than the argentophilic interactions. As compared to $[Au(CN)_2]^-$, the increased lability of $[Ag(CN)_2]^-$ results in a variety of complex equilibria and the formation of $[Ag_2(CN)_3]^-$, $[Ni(CN)_4]^{2-}$, and $[Cu(CN)_2]^-$.

Thus, the introduction of Ag(I) centers can be used as a design element in the synthesis of supramolecular structures, but care must be taken to avoid or control the possible lability equilibria associated with the use of $[Ag(CN)_2]^-$ as a building block.

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Supporting Information Available: Complete crystallographic data in CIF format for all four reported crystal structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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