Inorg. Chem. **2003**, *42*, 3917–3924

Inorganic Chemistry
Article

$[Au(CN)_4]^-$ as a Supramolecular Building Block for Heterobimetallic Coordination Polymers

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Received February 11, 2003

A series of the first coordination polymers using the $[Au(CN)_4]^-$ anion as a building block has been prepared. The planar tetracyanoaurate anion uses one, two, or four cyano groups to bridge to Ni(II) or Cu(II) centers and exhibits weak Au(III)–N(cyano) interactions between anions. $Ni(en)_2[Au(CN)_4]_2\cdot H_2O$ (**1**, en = ethylenediamine) is a molecular compound with the two $[Au(CN)_4]^-$ anions coordinating in a trans orientation to Ni(II) without further cyanide coordination. $Cu(dien)[Au(CN)_4]_2$ (**2**, dien = diethylenetriamine) forms a similar molecular complex; however, the dimensionality is increased through weak intermolecular Au–N(cyano) interactions of 3.002(14) Å to form a 1-D zigzag chain. $Cu(en)_2[Au(CN)_4]_2$ (**3**) also forms a molecular complex similar to **1**, but with elongated axial bonds. The complex further aggregates through Au–N(cyano) interactions of 3.035(8) Å to form a 2-D array. In $[Cu(dmeda)_2Au(CN)_4][Au(CN)_4]$ (**4**, dmeda = *N*,*N*-dimethylethylenediamine) one $[Au(CN)_4]^-$ anion coordinates via two cis-N(cyano) donors to the axial sites of two Cu(II) centers to form a 1-D zigzag chain of alternating $[Cu(dmeda)_2]^{2+}$ and $[Au(CN)_2]^-$ units; the other $[Au(CN)_4]^-$ anion forms a 1-D chain via Au–N(cyano) interactions. In $[Cu(bipy)(H_2O)_2(Au(CN)_4)_{0.5}][Au(CN)_4]_{1.5}$ (**5**, bipy = 2,2′-bipyridine) one $[Au(CN)_4]^-$ anion uses all four cyano moieties to bridge four different Cu(II) centers, creating a 1-D chain.

Introduction

Square planar complexes are commonly formed by transition metal ions having a d^8 electron configuration, such as Pt(II), Pd(II), and Ni(II). Such planar complexes, especially those of platinum(II), can sometimes form metal−metal stacking interactions with metal−metal distances as low as 3.1 Å.[1,2] These d^8-d^8 interactions are thought to be associated with the energetic proximity and interactions of the $5d_{z^2}$ and the $6p_z$ orbitals.[2] We have previously illustrated the potential of using d^{10} metal−metal interactions to increase dimensionality in systems containing transition metal cations and Au(I) or Ag(I) cyanide anions.[3−6] Methods of rationally increasing dimensionality are an important focus in the field of supramolecular chemistry,[7,8] as highly dimensional systems have the potential to produce interesting and useful properties such as magnetism,[9] nonlinear optics,[10] conduction,[11] or porosity.[12]

Cyanometalate anions have been extensively used as design elements in supramolecular coordination systems

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10.1021/ic0341441 CCC: $25.00

where they can act as multidentate ligands, linking numerous metal centers together to form stable, high-dimensionality coordination polymers with transition metal cations.[8,13,14] Many studies have been done with square planar cyanometalates $[Pt(CN)_4]^{2-}$ and $[Ni(CN)_4]^{2-}$, indicating their usefulness in building multidimensional coordination polymers,[13,15−20] including the well-known Hofmann clathrates.[13,15] Despite this, the related $[Au(CN)_4]^-$ anion has received little attention in the field of supramolecular coordination chemistry. Au(III) is isoelectronic with Pt(II) and Pd(II) and thus also has the potential of displaying the aforementioned metal−metal stacking interactions. In light of these issues, we have endeavored to examine the ability of $[Au(CN)_4]^-$ to act as a building block to form heterobimetallic coordination polymers.

Experimental Section

General Procedures and Physical Measurements. All manipulations were performed in air using purified solvents. The $KAu(CN)_4$ salt, the amine ligands ethylenediamine (en), diethylenetriamine (dien), *N*,*N*-dimethylethylenediamine (dmeda), 2,2′-bipyridine (bipy), 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. Thermogravimetric analysis data were collected using a Shimadzu TGA-50 instrument in air atmosphere. 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. All data was corrected for TIP, the diamagnetism of the sample holder, and the constituent atoms (by use of Pascal constants).[21]

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.

$Ni(en)_2[Au(CN)_4]_2\cdot H_2O$ (1). To a 5 mL aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$ (0.032 g, 0.110 mmol) was added 0.015 mL of neat en (0.220 mmol) using a microsyringe. While stirring, a 5 mL aqueous solution of $KAu(CN)_4$ (0.075 g, 0.220 mmol) was added dropwise to this pale purple solution. The resulting solution was covered and left undisturbed. Over 2 months, pale purple, X-ray quality crystals of $Ni(en)_2[Au(CN)_4]_2\cdot H_2O$ (**1**) were deposited from the solution. Yield: 0.085 g (98%). Anal. Calcd for $C_{12}H_{18}N_{12}Au_2NiO$: C, 18.04; H, 2.27; N, 21.04. Found: C, 18.36; H, 2.20; N, 21.19. IR (KBr): 2214 (νCN), 2202 (νCN), 2190 (νCN), 2180 (w, νCN), 1600, 1462, 1384, 1320, 1284, 1272, 1089, 1023, 965, 699, 661, 531, 519, 415 cm^{-1}.

$Cu(dien)[Au(CN)_4)]_2$ (2). To a 2 mL aqueous solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.030 g, 0.075 mmol) was added a 1 mL stock solution (0.075 M) of dien. While stirring, a 3 mL aqueous solution of $KAu(CN)_4$ (0.051 g, 0.150 mmol) was added dropwise to this dark blue solution. The resulting solution was covered and left undisturbed to yield X-ray quality, purple crystals of $Cu(dien)[Au(CN)_4]_2$ (**2**) over several weeks. Yield: 0.047 g (81%). Anal. Calcd for $C_{12}H_{13}N_{11}Au_2Cu$: C, 18.75; H, 1.70; N, 20.04. Found: C, 18.58; H, 1.69; N, 19.83. IR (KBr): 2241 (νCN), 2219 (νCN), 2189 (νCN), 1585, 1317, 1142, 1092, 1028, 974, 653, 526, 419 cm^{-1}.

$Cu(en)_2[Au(CN)_4]_2$ (3). To a 3 mL aqueous solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.028 g, 0.075 mmol) was added a 1 mL stock solution (0.150 M) of en. While stirring, a 3 mL aqueous solution of $KAu(CN)_4$ (0.051 g, 0.150 mmol) was added dropwise to this purple solution. The resulting solution was covered and left undisturbed to yield X-ray quality, purple crystals of $Cu(en)_2[Au(CN)_4]_2$ (**3**) over several weeks. Yield: 0.043 g (84%). Anal. Calcd for $C_{12}H_{16}N_{12}Au_2Cu$: C, 18.34; H, 2.05; N, 21.39. Found: C, 18.15; H, 2.05; N, 21.22. IR (KBr): 2187 (νCN), 2180 (νCN), 1589, 1462, 1315, 1084, 1037, 973, 702, 533, 413 cm^{-1}.

$[Cu(dmeda)_2Au(CN)_4][Au(CN)_4]$ (4). To a 3 mL aqueous solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.041 g, 0.110 mmol) was added a 2 mL stock solution (0.110 M) of dmeda. While stirring, a 3 mL aqueous solution of $KAu(CN)_4$ (0.075 g, 0.220 mmol) was added dropwise to this purple solution. An immediate purple precipitate of $[Cu(dmeda)_2Au(CN)_4][Au(CN)_4]$ (**4**) formed. The remaining filtrate was left to evaporate slowly for several days to yield X-ray quality, purple crystals of **4**. Yield: 0.076 g (94%). The powder and crystals had comparable IR spectra and elemental analyses. Anal. Calcd for $C_{16}H_{24}N_{12}Au_2Cu$: C, 22.83; H, 2.87; N, 19.96. Found: C, 22.63; H, 2.85; N, 19.78. IR (KBr): 2190 (νCN), 3302, 3245, 3160, 3023, 2986, 2944, 1598, 1478, 1468, 1462, 1444, 1291, 1190, 1151, 1124, 1062, 1033, 1004, 937, 893, 781, 669, 461, 421, 417 cm^{-1}.

$[Cu(bipy)(H_2O)_2(Au(CN)_4)_{0.5}][Au(CN)_4]_{1.5}$ (5). To a 4 mL aqueous solution of an excess of $Cu(ClO_4)_2\cdot 6H_2O$ (0.054 g, 0.147 mmol) was added a 4 mL methanolic solution of bipy (0.011 g, 0.074 mmol). While stirring, a 4 mL aqueous solution of $KAu(CN)_4$ (0.050 g, 0.147 mmol) was added dropwise to this blue solution. The solution was covered and cooled for 4 days, then left to evaporate slowly at room temperature over several weeks to yield X-ray quality crystals of $[Cu(bipy)(H_2O)_2(Au(CN)_4)_{0.5}][Au(CN)_4]_{1.5}$ (**5**). Yield: 0.061 g (97% based on Au). Anal. Calcd for $C_{18}H_{12}N_{10}Au_2CuO_2$: C, 25.20; H, 1.41; N, 16.33. Found: C, 25.19; H, 1.39; N, 16.25. IR (KBr): 3515, 3277 (broad), 3117, 3091, 3083, 2263 (νCN), 2198 (νCN), 2187 (νCN), 1612, 1605, 1567, 1501, 1475, 1444, 1315, 1254, 1152, 1106, 1037, 777, 731, 650, 531, 430, 415, 405 cm^{-1}.

X-ray Crystallographic Analysis. Crystallographic data for all structures are collected in Table 1. All crystals were mounted on glass fibers using epoxy adhesive. Using the diffractometer control program DIFRAC[22] and an Enraf Nonius CAD4F diffractometer, data ranges, as indicated in the crystallographic information file

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Table 1. Summary of Crystallographic Data[a]

	1	**2**	**3**	**4**	**5**
formula	$C_{12}H_{18}N_{12}Au_2NiO$	$C_{12}H_{13}N_{11}Au_2Cu$	$C_{12}H_{16}N_{12}Au_2Cu$	$C_{16}H_{24}N_{12}Au_2Cu$	$C_{18}H_{12}N_{10}Au_2CuO_2$
fw	798.98	768.79	785.82	841.95	857.84
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	*Pnam* (No. 62)	$P\bar{1}$ (No. 2)
a, Å	8.372(1)	7.5489(9)	6.688(1)	8.9325(12)	7.5006(9)
b, Å	9.844(1)	15.3231(19)	7.6961(9)	15.7920(21)	12.0252(18)
c, Å	14.819(3)	17.7943(19)	20.273(3)	18.362(4)	14.2116(17)
α, deg	73.00(2)	90	90	90	73.878(11)
β, deg	77.16(2)	95.474(8)	97.044(14)	90	89.642(11)
γ, deg	68.90(1)	90	90	90	73.102(11)
V, $Å^3$	1080.26	2048.9(4)	1038.80	2590.1	1174.39
Z	2	4	2	4	2
ρ_{calc}, g/cm^3	2.456	2.492	2.520	2.159	2.426
μ, cm^{-1}	144	153	151	121	134
T (K)	293	293	293	293	293
R, R_w ($I > 2.5\sigma(I)$)[b]	0.022, 0.029	0.034, 0.033	0.030, 0.037	0.035, 0.044	0.024, 0.027

[a] Enraf-Nonius CAD-4 diffractometer, Mo Kα radiation ($\lambda = 0.71069$ Å), graphite monochromator. [b] Function minimized $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F_o) + 0.0001F_o^2$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

(CIF), were recorded. The data were corrected empirically for the effects of absorption and data reduction for all compounds included corrections for Lorentz and polarization effects.

For all compounds, coordinates and anisotropic displacement parameters for the non-hydrogen atoms were refined. The hydrogen atoms on carbon and nitrogen atoms in all complexes 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. Most of these hydrogen atoms were observed in Fourier difference maps, in positions that differed little from the idealized ones ultimately preferred. Isotropic thermal parameters for these 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 hydrogen atoms of CH, CH_2, CH_3, or NH_2 groups were, respectively, constrained to have identical shifts during refinement. For the water molecule in **1**, hydrogen atoms were positioned geometrically using hydrogen-bonding contacts and refined with isotropic thermal parameters constrained to be equivalent. For the water molecules in **5**, hydrogen atoms were found from the Fourier difference map and initially refined against soft bond distance restraints. However, in the final cycles of refinement, these hydrogen atoms were constrained to ride on their respective oxygen atoms and with a single refined isotropic temperature factor. An extinction parameter[23] was included in the final cycles of full-matrix least-squares refinement of **1**−**5**. The final refinements, using observed data ($I_o \geq 2.5\sigma(I_o)$), included **1** = 260 parameters for 3655 data; **2** = 238 parameters for 2148 data; **3** = 127 parameters for 1472 data; **4** = 155 parameters for 1829 data; and **5** = 304 parameters for 3015 data. Selected bond lengths and angles for all compounds are found in Tables 2−6.

The programs used for all absorption corrections, data reduction, and structure solutions of **1**−**5** were from the *NRCVAX* Crystal Structure System.[24] The structures were refined using CRYSTALS.[25] Diagrams were made using Ortep-3.[26] Complex scattering factors for neutral atoms[27] were used in the calculation of structure factors.

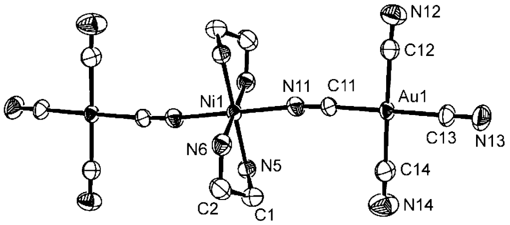

Figure 1. Molecular structure of $Ni(en)_2[Au(CN)_4]_2 \cdot H_2O$ (**1**). Water and hydrogen atoms have been omitted for clarity (ORTEP, 50% ellipsoids).

Results

Synthesis and Structural Studies. $Ni(en)_2[Au(CN)_4]_2 \cdot H_2O$ (1). Crystals of **1** formed from an aqueous solution containing $[Ni(en)_2]^{2+}$ and $2[Au(CN)_4]^-$. The IR data shows four νCN bands at 2214, 2202, 2190, and 2180 cm^{-1}. These bands, when compared to the νCN band of $KAu(CN)_4$ at 2189 cm^{-1},[28] suggest a combination of both transition metal bound (bridging) and nonbridging cyanides, given that the IR bands of bridging cyanides shift to higher energy values.[13] Similar shifted νCN bands were observed in our previous studies with $Au(CN)_2^-$ (νCN band shifts from 2141 cm^{-1} to between 2143 and 2209 cm^{-1}) and $Ag(CN)_2^-$ (νCN band shifts from 2139 cm^{-1} to between 2140 and 2174 cm^{-1}).[3−6] The X-ray crystal structure of **1** (Figure 1) reveals that the two $[Au(CN)_4]^-$ anions are bound in a trans fashion to the octahedral Ni(II) center (Ni(1)−N(11) = 2.129(5) Å). The slightly distorted octahedral geometry is completed by two mutually trans en ligands. Although the asymmetric unit contains two half-molecules of $Ni(en)_2[Au(CN)_4]_2$ (each sitting on a center of inversion), the structural parameters are essentially identical for both.

One equivalent of water is also found in the unit cell of the crystal structure. The thermogravimetric analysis data shows weight loss corresponding to the loss of 1 equiv of

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Ni(en)_2[Au(CN)_4]_2 \cdot H_2O$ (**1**)

Au(1)−C(11)	1.977(6)	Au(1)−C(12)	1.997(6)
Au(1)−C(13)	1.985(6)	Au(1)−C(14)	1.993(6)
Ni(1)−N(11)	2.129(5)	Ni(1)−N(6)	2.099(5)
Ni(1)−N(5)	2.086(5)		
C(11)−Au(1)−C(13)	179.5(2)	N(5)−Ni(1)−N(6)	82.7(2)
N(5)−Ni(1)−N(11)	88.95(19)	N(6)−Ni(1)−N(11)	89.8(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Cu(dien)[Au(CN)_4]_2$ (**2**)

Au(1)−C(11)	1.995(15)	Au(1)−C(12)	1.988(17)
Au(1)−C(13)	1.973(16)	Au(1)−C(14)	2.011(19)
Au(2)−C(21)	1.995(14)	Au(2)−C(22)	1.958(18)
Au(2)−C(23)	2.025(17)	Au(2)−C(24)	1.953(17)
Cu(1)−N(11)	1.977(12)	Cu(1)−N(21)	2.225(13)
Cu(1)−N(5)	1.994(11)	Cu(1)−N(6)	1.983(14)
Cu(1)−N(7)	1.984(11)	Au(1)−N(22)′[a]	3.002(14)
C(11)−Au(1)−C(13)	179.0(6)	C(21)−Au(2)−C(23)	178.7(6)
N(11)−Cu(1)−N(21)	99.1(5)	N(11)−Cu(1)−N(5)	93.9(5)
N(11)−Cu(1)−N(6)	94.6(6)	N(21)−Cu(1)−N(5)	97.7(5)
N(21)−Cu(1)−N(6)	96.1(5)	N(5)−Cu(1)−N(6)	162.4(6)
N(7)−Cu(1)−N(11)	167.7(5)	N(7)−Cu(1)−N(21)	93.3(5)
N(5)−Cu(1)−N(7)	84.0(5)	N(6)−Cu(1)−N(7)	84.3(5)
Cu(1)−N(11)−C(11)	168.2(12)	Cu(1)−N(21)−C(21)	166.6(13)

[a] Symmetry transformations: (′) $x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2$.

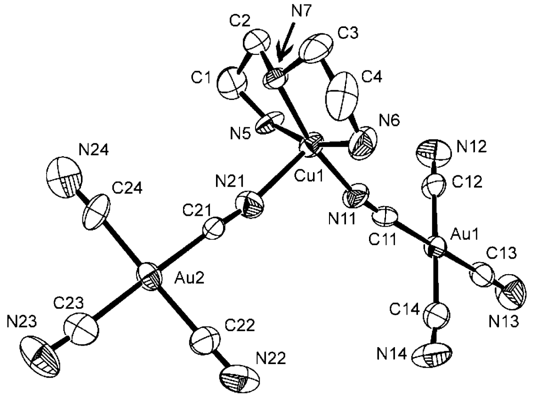

Figure 2. Molecular structure of $Cu(dien)[Au(CN)_4]_2$ (**2**). Hydrogen atoms have been omitted for clarity (ORTEP, 50% ellipsoids).

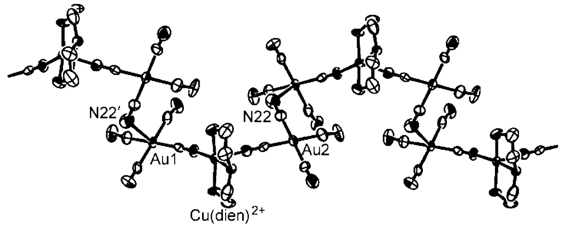

Figure 3. Extended structure of $Cu(dien)[Au(CN)_4]_2$ (**2**) showing the 1-D network propagated through Au(III)−N interactions. Hydrogen atoms have been omitted for clarity (ORTEP, 50% ellipsoids).

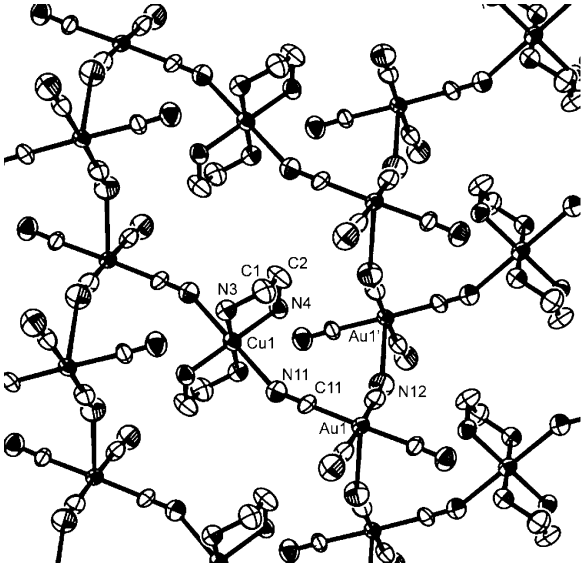

Figure 4. Extended structure of $Cu(en)_2[Au(CN)_4]_2$ (**3**). Hydrogen atoms have been omitted for clarity (ORTEP, 50% ellipsoids).

water between 115 and 185 °C (observed weight loss, 1.80%; calculated, 2.25%). The complex is then stable until 240 °C, after which it begins to undergo a complex series of decompositions yielding NiO and Au at 435 °C (observed weight loss, 38.5%; calculated, 39.1%). The water molecule serves to weakly connect the $Ni(en)_2[Au(CN)_4]_2$ units into a three-dimensional system through hydrogen bonding (O−N distances: 3.206(8), 2.925(8) Å). There are also additional hydrogen bonds between many of the amino hydrogen and N(cyano) atoms (N(H)−NC distances: 3.169−3.323 Å). All hydrogen bonding is very weak and thus is not shown.

$Cu(dien)[Au(CN)_4]_2$ (2). Crystals of **2** formed from an aqueous solution containing $[Cu(dien)]^{2+}$ and $2[Au(CN)_4]^-$. The IR data, showing three νCN bands at 2241, 2219, and 2189 cm^{-1}, suggests that there is a combination of bridging and nonbridging cyanide groups present. The crystal structure confirms that two $[Au(CN)_4]^-$ ions are bound to a Cu(II) center through N(cyano) atoms. The Cu(II) center adopts a distorted square pyramidal geometry (Figure 2), where one $[Au(CN)_4]^-$ unit is bound to the basal site (Cu(1)−N(11) = 1.977(12) Å) and the other is bound to the elongated apical site (Cu(1)−N(21) = 2.225(13) Å). The remaining three basal sites are occupied by the dien ligand.

Each $Cu(dien)[Au(CN)_4]_2$ complex is connected by weak intermolecular Au(III)−N(cyano) interactions (Au(1)−N(22)′ = 3.002(14) Å), resulting in a 1-D chain (Figure 3). This is the first reported Au(III)−N interaction where N interacts in an apical, intermolecular fashion with a square planar Au(III), making it weakly 5-coordinate. There are also weak hydrogen bonds (not shown) between amino hydrogen and N(cyano) atoms (N(H)−NC distances = 3.106−3.379 Å).

$Cu(en)_2[Au(CN)_4]_2$ (3). Crystals of **3** formed from an aqueous solution containing $[Cu(en)_2]^{2+}$ and $2[Au(CN)_4]^-$. The IR data shows two νCN bands at 2187 and 2180 cm^{-1}. The crystal structure indicates that the $[Au(CN)_4]^-$ ions are coordinated to the Jahn−Teller distorted axial sites of the octahedral Cu(II) center (Cu(1)−N(11) = 2.548(9) Å) (Figure 4). This axial bond length is significantly longer than that seen in **1**. The axial bond length in **3** is on the weaker end of the reported distorted Cu(II) complexes in the literature (which range from 2.2 to 2.7 Å),[19,29] thus explaining the lack of blue shift of the νCN band in the IR spectrum for the N-bound cyanide. The equatorial sites of the Cu(II) are occupied by the two en ligands.

The crystal structure of **3** also displays weak intermolecular Au(III)−N interactions of 3.035(8) Å. These interactions are similar to, but slightly weaker than those observed in **2**. A

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Cu(en)_2[Au(CN)_4]_2$ (**3**)

Au(1)−C(11)	1.995(9)	Au(1)−C(12)	1.975(9)
Au(1)−C(13)	1.986(9)	Au(1)−C(14)	1.990(9)
Cu(1)−N(11)′[a]	2.548(9)	Cu(1)−N(3)	2.010(7)
Cu(1)−N(4)	2.015(7)	Au(1)−N(12)″	3.035(8)
C(11)−Au(1)−C(13)	178.6(3)	N(11)′−Cu(1)−N(3)	93.5(3)
N(11)′−Cu(1)−N(4)	88.5(3)	N(3)−Cu(1)−N(4)	84.3(3)

[a] Symmetry transformations: (′) $x, y - 1, z$; (″) $-x + 1, y - {}^1/_2, -z + {}^5/_2$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[Cu(dmeda)_2Au(CN)_4][Au(CN)_4]$ (**4**)

Au(2)−C(21)	2.007(11)	Au(2)−C(22)	1.958(12)
Cu(1)−N(1)	2.100(8)	Cu(1)−N(2)	1.985(8)
Cu(1)−N(21)′[a]	2.724(10)	Au(1)−C(11)	1.999(10)
Au(1)−C(12)	2.001(15)	Au(1)−C(13)	2.002(13)
Au(1)−N(12)″	2.963(13)		
C(12)−Au(1)−C(13)	175.9(5)	C(21)−Au(2)−C(22)	89.8(5)
Au(1)−C(12)−N(12)	175.1(14)	N(1)−Cu(1)−N(2)	84.6(3)
N(1)−Cu(1)−N(21)′	85.8(3)	N(2)−Cu(1)−N(21)′	86.5(3)

[a] Symmetry transformations: (′) $x - {}^1/_2, -y + {}^3/_2, z$; (′) $-x + {}^1/_2, -y + {}^1/_2, z$.

key difference between **2** and **3** is that, in **3**, every $[Au(CN)_4]^-$ unit forms two Au−N interactions by acting as a donor via N(12) for one interaction and an acceptor via Au(1) for another, resulting in a 2-D sheet (Figure 4). This contrasts with the 1-D chain found in **2** (Figure 3) that does not propagate in two dimensions because $[Au(CN)_4]^-$ units only participate in one such interaction, through *either* the Au(1) *or* N(22) atoms.

The structure of **3** also differs from the analogous Ni(II) compound **1**. The Ni analogue does not display Au(III)−N interactions, possibly due to steric hindrances, as the M−N(cyano) bond lengths are significantly shorter in **1**. Hydrogen-bonding interactions involving the water molecule in **1** may also compete with the weak intermolecular Au−N interactions.

Weak hydrogen bonding between amino hydrogen and N(cyano) atoms is also present in **3** (N(H)−NC distances: 3.121(11)−3.395(12) Å).

$[Cu(dmeda)_2Au(CN)_4][Au(CN)_4]$ (4). Crystals of **4** formed upon slow evaporation of a very dilute aqueous solution containing $[Cu(dmeda)_2]^{2+}$ and $2[Au(CN)_4]^-$. One νCN band at 2190 cm^{-1} is present. The crystal structure reveals a distorted octahedral Cu(II) center with two equatorially bound dmeda ligands and elongated N(cyano) axial coordination of $[Au(CN)_4]^-$ (Figure 5). Although this weak coordination (Cu(1)′−N(21) = 2.724(10) Å) does not produce a blue-shifted νCN band in the IR spectrum, it serves to build a 1-D cationic zigzag chain of alternating $[Cu(dmeda)]^{2+}$ and $[Au(CN)_4]^-$ ions where two cyanides on $[Au(CN)_4]^-$ are coordinated to separate $[Cu(dmeda)]^{2+}$ units in a cis fashion. Despite the weak cyanide ligation, it is chemically significant: an immediate precipitation of the insoluble polymer **4** occurs whereas the previous reactions (not producing cyanometalate-bridged polymeric products) do not immediately precipitate.

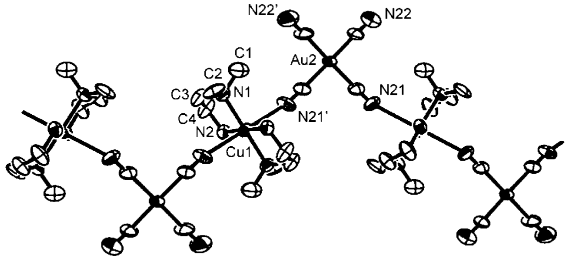

Figure 5. Extended structure of the cation $[Cu(dmeda)_2Au(CN)_4]^+$ in $[Cu(dmeda)_2Au(CN)_4][Au(CN)_4]$ (**4**). Hydrogen atoms have been omitted for clarity (ORTEP, 50% ellipsoids).

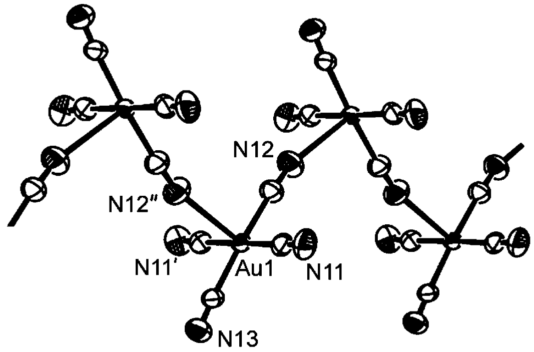

Figure 6. Extended structure of the $[Au(CN)_4]^-$ chain in $[Cu(dmeda)_2Au(CN)_4][Au(CN)_4]$ (**4**) (ORTEP, 50% ellipsoids).

The remaining equivalent of $[Au(CN)_4]^-$ is unbound to any Cu center, but does form Au(III)−N interactions with adjacent free $[Au(CN)_4]^-$ units, generating an anionic 1-D zigzag chain that runs perpendicular to the $[Cu(dmeda)_2Au(CN)_4]^+$ chain (Figure 6). The Au(1)−N(12)″ distance of 2.963(13) is significantly shorter than the Au(III)−N interactions in **2** and **3**.

$[Cu(bipy)(H_2O)_2(Au(CN)_4)_{0.5}][Au(CN)_4]_{1.5}$ (5). Crystals of **5** were obtained through slow evaporation of an aqueous/methanolic solution containing 1 equiv of bipy, 2 equiv of $[Au(CN)_4]^-$, and an excess of Cu(II). The IR data shows three νCN bands at 2203, 2198, and 2187 cm^{-1}, consistent with a combination of bridging and nonbridging $[Au(CN)_4]^-$ units. The crystal structure shows a 1-D "criss-crossed" chain where one $[Au(CN)_4]^-$ unit is bound to four Cu(II) centers (Figure 7). Each Cu(II) center has two such $[Au(CN)_4]^-$ units bound in a cis fashion, resulting in a connectivity to five other Cu(II) centers and thus 1-D propagation.

The $[Au(CN)_4]^-$ units occupy both an equatorial (Cu(1)−N(12)′ = 1.973(6) Å) and an axial site (Cu(1)−N(11) = 2.359(6) Å) of the distorted octahedral Cu(II) center. This difference in coordinated bond lengths likely results in the two distinct blue-shifted νCN bands observed in the IR spectrum. The remaining three equatorial sites on the Cu(II) center are occupied by the bipy ligand (Cu(1)−N(1) =

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Table 6. Selected Bond Lengths (Å) and Angles (deg) for $[Cu(bipy)(H_2O)_2(Au(CN)_4)_{0.5}][Au(CN)_4]_{1.5}$ (**5**)

Au(1)−C(11)	1.997(7)	Au(1)−C(12)	1.988(7)
Au(2)−C(21)	1.996(9)	Au(2)−C(22)	2.019(8)
Au(2)−C(23)	1.985(8)	Au(2)−C(24)	1.978(8)
Au(3)−C(31)	1.991(9)	Au(3)−C(32)	2.00(1)
Cu(1)−N(1)	1.981(6)	Cu(1)−N(2)	2.001(5)
Cu(1)−N(11)	2.359(6)	Cu(1)−N(12)′[a]	1.973(6)
Cu(1)−O(1)	2.026(5)	Cu(1)−O(2)	2.475(6)
C(11)−Au(1)−C(12)	91.8(3)	C(22)−Au(2)−C(24)	176.0(3)
C(31)−Au(3)−C(32)	88.4(4)	O(1)−Cu(1)−O(2)	91.53(19)
O(1)−Cu(1)−N(1)	95.8(2)	O(2)−Cu(1)−N(1)	91.5(2)
O(1)−Cu(1)−N(2)	176.6(2)	O(2)−Cu(1)−N(2)	86.5(2)
N(1)−Cu(1)−N(2)	81.6(2)	O(1)−Cu(1)−N(11)	84.7(2)
O(2)−Cu(1)−N(11)	174.7(2)	N(1)−Cu(1)−N(11)	92.6(2)
N(2)−Cu(1)−N(11)	97.4(2)	O(1)−Cu(1)−N(12)′	87.8(2)
O(2)−Cu(1)−N(12)′	84.3(2)	N(1)−Cu(1)−N(12)′	174.6(2)
N(2)−Cu(1)−N(12)′	94.7(2)	N(11)−Cu(1)−N(12)′	91.7(2)

[a] Symmetry transformations: (′) $x - 1, y, z$.

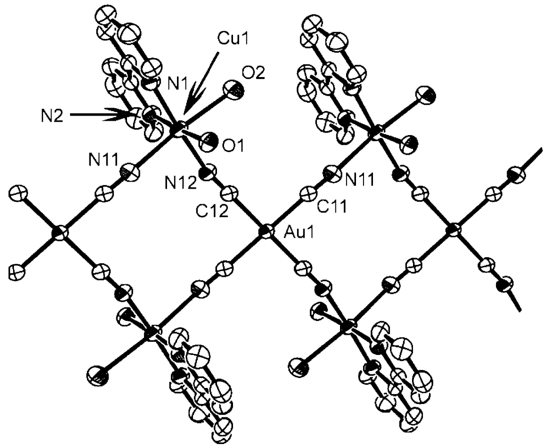

Figure 7. Extended structure of $[Cu(bipy)(H_2O)_2(Au(CN)_4)_{0.5}][Au(CN)_4]_{1.5}$ (**5**) showing only the 1-D chain of $[Cu(bipy)(H_2O)_2(Au(CN)_4)_{0.5}]^{1.5+}$. Hydrogen atoms have been omitted for clarity (ORTEP, 50% ellipsoids).

1.981(6) Å and Cu(1)−N(2) = 2.001(5) Å) and a bound water molecule (Cu(1)−O(1) = 2.026(5) Å), with the final elongated axial site occupied by the other equivalent of water (Cu(1)−O(2) = 2.475(6) Å).

The remaining equivalents of $[Au(CN)_4]^-$ form a linear trimeric anionic cluster via a Au(III)−N interaction of 3.052(9) Å, similar to that seen in **4** and comparable in length to that seen in **2** and **3**. However, unlike in **4**, the interaction does not propagate.

Both the coordinated water molecules and the bipy ligands serve to increase dimensionality through weak hydrogen bonds and π-interactions, respectively. The structure is thus loosely held in a three-dimensional array (not shown).

Similar 1-D chains have been observed in a related $[Ni(CN)_4]^{2-}$ complex, $[\{Cu_2(medpt)_2Ni(CN)_4\}(ClO_4)_2 \cdot 2.5H_2O]$ (medpt = bis(3-aminopropyl)methylamine), whereby $[Ni(CN)_4]^{2-}$ anions coordinate through all four cyanides to form a “criss-crossed” 1-D chain of connected square pyramidal Cu(II) cations.[17] The analogous $[Pt(CN)_4]^{2-}$ complex with $[Cu(bipy)]^{2+}$ does not form such “criss-crossed” chains, but instead forms either a discrete supramolecular square via cis coordination of two cyanometalates in the case of $[\{Cu(bipy)(H_2O)Pt(CN)_4\}_2] \cdot 2H_2O$,[30] or an infinite 1-D chain with trans cyanide coordination in the case of $Cu(bipy)Pt(CN)_4$.[18] In both cases, $[Pt(CN)_4]^{2-}$ bridging occurs through only two cyanides, rather than four as seen in **5**.

Magnetic Properties. For complexes **3**−**5** 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.

The product of the magnetic susceptibility with temperature, $\chi_M T$, for **3** at 300 K was determined to be 0.48 cm^3 K mol^{-1}, consistent with the presence of an $S = {}^1/_2$ Cu(II) center. In **3**, the $[Cu(dien)]^{2+}$ units are essentially isolated from each other according to the X-ray structure, except for the presence of intermolecular Au(III)−N interactions. This pathway is too long for significant magnetic interactions to occur (and the Cu−N bond is quite long at 2.548(9) Å); thus, as expected, $\chi_M T$ is observed to be virtually temperature independent, exhibiting only a very slight decrease (to 0.46 cm^3 K mol^{-1}) below 25 K.

In both **4** and **5**, shorter Cu−Cu interaction pathways are present. In $[Cu(dmeda)_2Au(CN)_4][Au(CN)_4]$ (**4**), the Cu(II) centers are connected through very weakly coordinated (Cu−N = 2.724(10) Å) axial sites in an orthogonal fashion. For **4**, poor overlap associated with this long bond effectively severs the pathway for magnetic exchange, as previously observed,[3,5] yielding an essentially temperature independent $\chi_M T$ vs T graph until 5 K, at which point $\chi_M T$ drops from 0.47 to 0.35 cm^3 K mol^{-1} at 2 K.

For **5**, $\chi_M T = 0.40$ cm^3 K mol^{-1} at 300 K and is temperature independent until 25 K, at which point $\chi_M T$ drops to 0.29 cm^3 K mol^{-1} at 2 K. The data can be fit to the Curie−Weiss law with $\theta = -0.40$ K, consistent with weak antiferromagnetic coupling between the Cu(II) centers. The X-ray structure of $[Cu(bipy)(H_2O)_2(Au(CN)_4)_{0.5}][Au(CN)_4]_{1.5}$ (**5**) shows several magnetic exchange pathways between Cu(II) centers that must be considered; each has a through-bond Cu−Cu distance of approximately 10 Å. Each Cu(II) center has two linear pathways, one through elongated axial/axial bonding (Cu−N(11) = 2.359(6) Å) and one through equatorial/equatorial bonding (Cu−N(12) = 1.973(6) Å). Each Cu(II) center also has four axial/equatorial pathways (through a combination of Cu−N(11) and Cu−N(12) bonds). The orthogonal axial/equatorial pathways are known to generate ferromagnetic coupling,[31] whereas the equatorial/equatorial and axial/axial pathways generate antiferromagnetic coupling.[32] The observed weak coupling is likely a combination of the antiferromagnetic and ferromagnetic coupling pathways. Of these, the equatorial/equatorial pathway yields the strongest orbital overlap, as all other pathways utilize the elongated Cu−N(11) axial bond. Due to the complexity of possible magnetic pathways and the overall weak magnetic interaction, this data was not further analyzed.

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Discussion

Although the use of cyanometalate anions as building blocks in the formation of coordination polymers has been well-documented (especially octahedral cyanometalates),[8,13,14] the $[Au(CN)_4]^-$ unit has never previously been used as such a building block. Systems **4** and **5** are the first examples of $[Au(CN)_4]^-$-based coordination, where polymer formation is a result of multiple cyanide bridging (2-cis and 4) through the anionic building block. Similar coordination polymers have been formed with other related anions, such as $[Ni(CN)_4]^{2-}$ and $[Pt(CN)_4]^{2-}$.[13,15−18] Also, the $[Au(CN)_4]^-$-based systems are quite different from previously studied $[Au(CN)_2]^-$-based polymers,[3−5] as would be expected given the change in oxidation state and geometry (from linear to square planar).

In general, the formation of cyanometalate-containing coordination polymers and their dimensionality depend on the type of capping ligand and number of open coordination sites that exist on the cation.[3−6] This dependence, however, does not appear to be a strong factor in $[Au(CN)_4]^-$-based systems. Although **1**, **2**, and **3** all have either two or three available coordination sites (hence the possibility for increasing dimensionality via cyanometalate bridging), in all cases the $[Au(CN)_4]^-$ unit coordinates through one cyanide only, resulting in molecular systems (excluding Au(III)−N or hydrogen-bonding interactions). This contrasts with systems such as $[Ni(en)_2Ag_2(CN)_3][Ag(CN)_2]$,[6,33] $[Cu(dien)Ag(CN)_2]_2$-$[Ag_2(CN)_3][Ag(CN)_2]$,[6] and $[Cu(en)_2Au(CN)_2][Au(CN)_2]$,[3] all of which show similar transition metal coordination spheres, but show increased dimensionality through bridging cyanometalates. This bridging coordination *is* seen in **4** and **5**, which still each contain two open coordination sites at the Cu(II) cation, suggesting that there are more important factors at play. One key factor is likely the decreased basicity of Au(III) vs both Au(I) cyanometalates and $[M(CN)_4]^{2-}$ which would decrease the propensity of the cyanometalate to coordinate to another metal center, and hence decrease the likelihood of bridging cyanides. Although the square planar $[Au(CN)_4]^-$ has increased steric bulk as compared to a linear Au(I) cyanometalate, this is likely not causing decreased bridging, as many $[Pt(CN)_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ bridging polymers have been reported.[13,15−20]

Still, increases in dimensionality through intermolecular Au(III)−N interactions are observed in $[Au(CN)_4]^-$ systems. These are the first reported Au−N interactions whereby a nitrogen atom interacts at the apical site of a square planar Au(III) molecule in an intermolecular fashion (i.e., without the aid of chelation). This interaction serves to increase the dimensionality of heterobimetallic systems (**2** and **3**) and also generates chains of associated $[Au(CN)_4]^-$ anions (**4** and **5**). It is uncommon for Au(III) atoms to display coordination environments other than square planar, though a few higher coordination geometries do exist.[34] In such cases, very elongated apical M−ligand bond lengths are observed, such as seen in many examples with Cl in the apical position, where Au−Cl distances range between 2.911(2) and 3.223(3) Å.[35] A more comparable intermolecular interaction has been observed between square planar Au(III) and an oxygen donor where Au−O = 3.010(4) Å.[36] When such interactions are sterically enforced by the presence of a relatively rigid multidentate ligand, Au−N distances become significantly shorter, such as observed in many Au-amine complexes where the Au−N distances range from 2.58(1) to 2.839(5) Å.[37−39] These examples are considered to be more intramolecular in nature, as they are assisted by the coordination of one part of a multidentate ligand to a square planar site of Au(III). Without further literature examples of Au(III)−N *intermolecular* interactions, it becomes difficult to comment on its strength. The Au−N interaction distances (ranging from 2.963(13) to 3.052(9) Å) can be compared to the sum of the van der Waals radii (3.12−3.27 Å).[40]

With Cu(II), Jahn−Teller distortion results in very different coordination polymers as compared to the equivalent Ni(II) systems. This is evident in comparing the similar complexes $M(en)_2[Au(CN)_4]_2$ (**1**, M = Ni; **3**, M = Cu). In both cases, the $[Au(CN)_4]^-$ unit is coordinated in a trans fashion, but in **3** the M−N(cyano) distances are significantly longer (2.548(9) Å) as compared to **1** (2.129(5) and 2.116(5) Å). In **3**, the molecular unit is thus significantly longer than in **1**, allowing room for Au(III)−N interactions between molecular units, which does not occur in **1**. Even though **1** has a water molecule within the unit cell, which could interfere with potential interactions, a similar comparison can also be made between **3** and **4**, which differ only in two additional methyl groups on the ligand in **4** and do not contain the complication of interstitial water. There is a difference in coordination lengths between the two systems: the axial Cu−N(cyano) bond length is 2.724(10) Å in **4**, compared to 2.548(9) Å in **3**. This elongation of the molecular unit in **4** may be providing the space required for the $[Au(CN)_4]^-$ unit to further coordinate another Cu(II) center without steric hindrances, as **4** is able to form a cyano-bridged polymer, whereas **3** is not. These observations suggests that the longer the molecular unit, the stronger the propensity to form additional bridging interactions.

The $[Au(CN)_4]^-$ unit in **1**−**5** has been observed to bridge through one cyanide, two cyanides (cis), or all four cyanides.

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Although the steric profile of the ligands may influence the number of briding cyanides possible, another consideration is that both the hydrogen bonding and Au(III)−N interactions may be influencing the formation of cyano bridges to the metal centers. This interplay of intermolecular (hydrogen bonding) and intramolecular (cyanide coordination) interactions has been a topic of recent interest. In comparing the discrete square complex of $[Pt(CN)_4Cu(bipy)(H_2O)]_2{\cdot}2H_2O$ to the polymeric 1-D chain of $[Pt(CN)_4Cu(bipy)]$, it has been suggested that the square complex results from the stabilization imparted by hydrogen bonding to the terminal cyanide moieties such that these stabilizing hydrogen bonds compete with the cyano coordination and formation of the polymeric form.[41] This has similarly been the suggestion for the differences between $[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$[41] and the Hofmann clathrate system $[Pt(CN)_4Cu(NH_3)_2]_n{\cdot}2n$G ($G$ = guest molecule).[42] The former complex, which bridges through only one cyanide of the $[Pt(CN)_4]^{2-}$ unit, contains four NH_3 ligands and an extensive network of intermolecular interactions, whereas the latter PtCu Hoffmann clathrate contains only two NH_3 ligands and bridges through all four cyanides.

No d^8-d^8 stacking interactions were observed in our systems, despite the fact that $[Au(CN)_4]^-$ is isoelectronic and isostructural to $[Pt(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$. Although this might suggest that there are significant electronic differences between the Au(III) and Pt(II)/Pd(II) cyano complexes, the similarities between the aforementioned PtCu Hofmann clathrate and $[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$ complexes suggest that competition from intermolecular interactions and cyano bridging might affect stacking, as the clathrate shows no d^8-d^8 stacking, whereas the latter complex shows Pt−Pt interactions of 3.675 Å.[41,42] The choice of the ancillary ligands used may also exclude the possibility of stacking interactions−we are currently examining the effects of complex cation size and ligand choice and are working to minimize possible interfering interactions.

Conclusions

The first supramolecular coordination polymers containing $[Au(CN)_4]^-$ have been prepared, indicating that $[Au(CN)_4]^-$ may serve as a useful building block in the preparation of coordination polymers. Through multiple cyanide bridging, it can increase dimensionality of a molecular unit to a 1-D polymer, and via weak intermolecular Au(III)−N interactions, $[Au(CN)_4]^-$ can also increase dimensionality up to two dimensions.

Acknowledgment. Financial support from NSERC of Canada and the World Gold Council GROW program are gratefully acknowledged.

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

IC0341441

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