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2-D Interwoven and 3-D 5-fold Interpenetrating Silver(I) Complexes of 1-(Isocyanidomethyl)-1*H*-benzotriazole and 1,3-Bis(dicyanomethylidene)indan

Ichiro Ino, Jian Chu Zhong, Megumu Munakata,* Takayoshi Kuroda-Sowa,
Masahiko Maekawa, Yusaku Suenaga, and Yoshinobu Kitamori

Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

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This paper presents novel and distinctive organosilver polymers with intriguing structure motifs, constructed from iodoacetonitrile (L^1), 1-(isocyanidomethyl)-1*H*-benzotriazole (L^2), 1,3-bis(dicyanomethylidene)indan (L^3), and silver(I) salts, respectively. Treatment of L^1 with $AgClO_4$ generated $[Ag(L^1)(ClO_4)]_n$ (**1**), whose X-ray determination revealed a 2-D wavy sheet structure with square grids. Reaction of L^2 with $AgPF_6$ gave rise to a novel 2-D wavy interwoven network, $\{[Ag(L^2)(PO_2F_2)_{0.5}](PF_6)_{0.5}\}_n$ (**2**). The complex $[Ag_2(L^3)_2]_n$ (**3**) obtained by reaction of $AgClO_4$ with L^3 can be regarded as unprecedented 3-D 5-fold interpenetrating nets with columnar aromatic stacks and indicates semiconductive behavior. The IR, ESR spectroscopic results, conductivities, and structural features of the complexes are discussed, respectively. The present findings may provide insight into the coordination versatility of silver(I) and polynitrile ligands and an inspiration for the self-assembly of novel supramolecular networks with multifunctional ligands. Crystal data: **1**, $C_2H_2AgINClO_4$, orthorhombic, $Pca2_1$ (No. 29), $a = 14.503(1)$ Å, $b = 5.104(2)$ Å, $c = 10.2019(9)$ Å, $Z = 4$; **2**, $C_8H_6AgN_4PF_4O$, orthorhombic, $Pnna$ (No. 52), $a = 12.2705(3)$ Å, $b = 21.150(1)$ Å, $c = 10.040(1)$ Å, $Z = 8$; **3**, $C_{30}H_{10}Ag_2N_8$, triclinic, $P\bar{1}$ (No. 2), $a = 14.920(2)$ Å, $b = 11.896(2)$ Å, $c = 7.400(4)$ Å, $\alpha = 86.55(2)°$, $\beta = 80.87(2)°$, $\gamma = 74.47(1)°$, $Z = 2$.

Introduction

The synthesis and design of supramolecular coordination polymeric networks, constructed from multifunctional ligands and transition metals, has been a field of rapid growth and received considerable attention in recent years.[1,2] Of these ligands for building up supramolecular frameworks, TCNX analogous compounds such as TCNQ, TCNB, TCNP, and TCNE, and halocarbons RX, where R represents an alkyl or aryl group, are of great interest respectively, principally because the former show variable hapticity,[3−5] ability to form charge-transfer derivatives,[4,6] propensity to construct infinite networks,[2c,7−13] facile reduction to radical anions or dianions,[4,5,14,15] interesting magnetic properties[4,5,16] and ability to produce donor−acceptor complexes,[17] while the latter are very weak bases which coordinate to transition metal centers in variable modes and R−X bonds can be easily broken by nucleophilic attack.[18] In spite of these achievements, examples of TCNX derivatives and tailored halocarbonitrile species as multidentate ligands for constructing coordination polymeric networks are rare.

The self-assembly of molecules into supramolecular networks takes advantage of coordination bonds, hydrogen bonds, $\pi-\pi$ stacking interactions, S−S contacts, and metal−metal contacts in modern supramolecular chemistry; hence, it is difficult to accurately predict the self-assembling structures of supramolecular networks in advance. However, taking inspiration from the biological examples which present the organization of simple units into a broad range of sophisticated and beautiful structures

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* Author to whom correspondence should be addressed. E-mail: munakata@chem.kindai.ac.jp.

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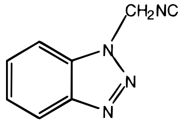
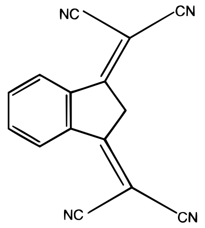
with complex and wonderful efficient function, many chemists have been attracted by the deliberate design and control of self-assembling infinite coordination networks via selecting the chemical structure of ligands.[1c,2c,e−g,7a,10,19,20a] Among some notable examples of deliberately designing supramolecular structures, the construction of square grid networks is a successful paradigm, with selection of a rodlike ligand and a metal with an octahedral coordination environment to form a variety of structures.[1a,20] Silver(I) exhibits labile coordination modes, such as linear, trigonal, tetrahedral, pentagonal, square-pyramidal, and even octahedral fashions; therefore, the self-assembly of silver(I) with ligands, especially polyhapto ligands, can give rise to a variety of novel network structures.[1a,21] As a part of our continuing interest in silver(I) polymeric complexes with unique features and variable coordination fashions as well as in consequence of the paucity of silver(I) supramolecular networks constructed from TCNX derivatives and tailored halocarbonitriles as ligands, we report here three unique silver(I) coordination polymers with interwoven and interpenetrated networks in which silver(I) ions are coordinated to iodoacetonitrile (L^1), 1-(isocyanidomethyl)-1*H*-benzotriazole (L^2), and 1,3-bis(dicyanomethylidene)indan (L^3), respectively, in different modes.

$I-CH_2-CN$

L^1



L^2



L^3

Experimental Section

General Methods. Preparations and manipulations were carried out under an argon atmosphere by using the conventional Schlenk techniques. All chemicals were reagent grade and used as supplied without further purification. Solvents were dried and distilled by standard methods before use. Iodoacetonitrile and 1-(isocyanidomethyl)-1*H*-benzotriazole, silver perchlorate, and silver hexafluorophosphorate were purchased from Aldrich. 1,3-Bis(dicyanomethylidene)indan was purchased from TCI. IR spectra were measured as KBr disks on a JASCO FT/IR-8000 spectrometer. ESR spectra were obtained on a JEOL JES-TE200ESR spectrometer.

The measurements of electric conductivity were made by a conventional two-probe technique at room temperature with compacted pellets. A plastic cylinder, whose diameter is 3 mm, is filled with the powder sample of a complex, the two copper probes press the sample from the two ends of the cylinder, and the resistance of the compacted pellet for the complex is recorded until its value becomes constant. In order to avoid the reaction of Ag(I) with copper generating metal silver, the ends of the copper probes were covered with a layer of silver metal.

SAFETY NOTE. *Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should be handled with great caution.*

Synthesis of $[Ag(L^1)(ClO_4)]_n$ (1). $AgClO_4\cdot H_2O$ (89.0 mg, 0.4 mmol) and iodoacetonitrile (66.8 mg, 0.4 mmol) were dissolved in 10 mL of benzene at room temperature, and the resultant colorless solution was introduced to a 7 mm glass tube and was layered with *n*-pentane. The glass tube, sealed under argon, was left standing at room temperature for 7 days in the dark; colorless plate crystals of **1** were obtained. Anal. Calcd for $C_2H_2AgINClO_4$: C, 6.42; H, 0.54; N, 3.74. Found: C, 6.13; H, 0.60; N, 3.50. Main IR bands (cm^{-1}): 2017 (w), 1103 (s).

Synthesis of $\{[Ag(L^2)(PO_2F_2)_{0.5}](PF_6)_{0.5}\}_n$ (2). To 10 mL of acetone were added $AgPF_6$ (75.8 mg, 0.3 mmol) and 1-(isocyanidomethyl)-1*H*-benzotriazole (47.4 mg, 0.3 mmol). After stirring for a while, the resultant yellow solution was transferred to a 7 mm glass tube under argon and covered by *n*-pentane slowly. Then, the glass tube was sealed and kept at room temperature in the dark. After standing for 7 days, yellow brick crystals suitable for X-ray analysis, corresponding to **2**, were isolated. Anal. Calcd for $C_8H_6AgN_4PF_4O$: C, 24.07; H, 1.55; N, 14.40. Found: C, 24.53; H, 1.57; N, 13.81. Main IR bands (cm^{-1}): 2185 (m), 1497−1143 (m), 837 (s).

Synthesis of $[Ag_2(L^3)_2]_n$ (3). This compound was obtained by an indirect method. $AgClO_4\cdot H_2O$ (22.5 mg, 0.1 mmol) and 1,3-bis(dicyanomethylidene)indan (24.2 mg, 0.1 mmol) were dissolved in 10 mL of methanol, respectively. Then, the resultant solution of $AgClO_4$ was first transferred into one compartment of an h-shape glass tube; in turn, the solution of 1,3-bis(dicyanomethylidene)indan was introduced to another compartment of the h-shape tube and ethanol was added to the h tube with bridging of the two solutions. The glass tube, sealed under argon, was allowed to stand for 1 month; gold plate crystals suitable for X-ray determination were collected. Anal. Calcd for $C_{30}H_{10}Ag_2N_8$: C, 51.61; H, 1.44; N, 16.05. Found: C, 49.16; H, 1.57; N, 15.6. Main IR bands (cm^{-1}): 2199 (m), 1604−1183 (m).

X-ray Crystallography. The single-crystal X-ray analyses for all complexes in this paper were carried out at room temperature on a Rigaku AFC-7R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation and a rotating anode generator ($\lambda(K\alpha) = 0.71069$ Å). For **1** and **2**, the collection of three representative reflections, measured at every 150 reflections, showed no significant changes in intensities, while for complex **3**, the standard reflections decreased during the data collection. Thus, a linear correction factor was applied to the data for complex **3**. An empirical absorption correction based on azimuthal scans of several reflections was applied to all three complexes. Intensities were obtained from continuous $\omega - 2\theta$ scans, and all data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods followed by subsequent Fourier-difference calculation and refined by full-matrix least-squares analysis on F^2, using the TEXSAN package. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms for all three complexes were introduced in their calculated positions; they were included, but not refined in the refinement. Details of the X-ray determinations and crystal data are summarized in Table 1; selected bond distances and bond angles are given in Table 2.

Results and Discussion

2-D Sheet Structure of $[Ag(L^1)(ClO_4)]_n$ (1). X-ray crystallography has indicated that complex **1** is made up of two-dimensional infinite wavy sheets, a perspective view of **1** together with the atom-numbering scheme being shown in Figure 1a. For complex **1**, silver(I) exhibits a distorted tetrahedral coordination sphere, being surrounded by one iodine atom and one nitrogen atom of a cyano group from two different iodoacetonitrile molecules, while the two remaining coordination sites are completed by two oxygen atoms from two different perchlorate ions. In this structure, each ligand, iodoacetonitrile, links two silver(I) ions to form one-dimensional wavy chains and the neighboring chains are further bridged by perchlorate ions to generate a two-dimensional wavy sheet with cavities similar to a square grid, the waves propagating down the *a* axis

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Table 1. Crystallographic Data for Complexes **1**−**3**

	1	**2**	**3**
formula	$C_2H_2AgINClO_4$	$C_8H_6AgN_4PF_4O$	$C_{30}H_{10}Ag_2N_8$
fw	374.27	389.00	698.20
space group	$Pca2_1$ (No. 29)	*Pnna* (No. 52)	$P\bar{1}$ (No. 2)
a,Å	14.503(1)	12.2705(3)	14.920(2)
b,Å	5.104(2)	21.150(1)	11.896(2)
c,Å	10.2019(9)	10.040(1)	7.400(4)
α, deg			86.55(2)
β, deg			80.87(2)
γ, deg			74.47(1)
V, Å^3	755.2(3)	2605.6(6)	1249.2(6)
Z	4	8	2
temp, °C	22	22	23
λ(Mo Kα), Å	0.71069	0.71069	0.71069
ρ, g/cm^3	3.292	1.983	1.856
μ, cm^{-1}	70.61	17.10	16.01
R^a	0.046	0.092	0.051
$R_w{}^b$	0.159	0.177	0.154

^{a} $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $[\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma(F_o{}^2)^2]^{1/2}$.

Table 2. Selected Bond Distances(Å) and Angles(deg) for Complexes **1**−**3**

Complex **1**			
Ag(1)−I(1)	2.743(2)	Ag(1)−O(2)	2.53(1)
Ag(1)−N(1)	2.22(1)	I(1)−C(2)	2.15(1)
Ag(1)−O(1)	2.65(1)	N(1)−C(1)	1.11(2)
Ag(1)−I(1)−C(2)	99.5(4)	O(1)−Ag(1)−N(1)	85.6(5)
I(1)−Ag(1)−O(1)	119.1(3)	O(2)−Ag(1)−N(1)	95.0(6)
I(1)−Ag(1)−O(2)	98.1(4)	Ag(1)−N(1)−C(1)	147(1)
I(1)−Ag(1)−N(1)	154.0(3)	N(1)−C(1)−C(2)	177(1)
O(1)−Ag(1)−O(2)	78.0(4)	I(1)−C(2)−C(1)	108.4(8)
Complex **2**			
Ag(1)−C(8)	2.081(7)	C(8)−N(4)	1.113(7)
Ag(1)−N(1)	2.193(4)	Ag(1)−O(1)	2.389(5)
O(1)−Ag(1)−C(8)	99.7(2)	N(1)−Ag(1)−C(8)	164.0(2)
O(1)−Ag(1)−N(1)	96.3(2)	Ag(1)−C(8)−N(4)	167.5(5)
Complex **3**			
Ag(1)−N(1)	2.126(4)	N(3)−C(14)	1.116(8)
Ag(2)−N(3)	2.427(6)	N(4)−C(15)	1.137(7)
Ag(2)−N(6)	2.280(4)	N(5)−C(26)	1.130(6)
Ag(3)−N(5)	2.138(4)	N(6)−C(27)	1.144(6)
Ag(4)−N(7)	2.182(4)	N(7)−C(29)	1.152(6)
N(1)−C(11)	1141(6)	N(8)−C(30)	1.150(6)
N(2)−C(12)	1.140(7)		
N(1)−Ag(1)−N(1*)	180	N(5)−Ag(3)−N(5*)	180
N(3)−Ag(2)−N(3*)	180	N(7)−Ag(4)−N(7*)	180
N(6)−Ag(2)−N(6*)	180	Ag(1)−N(1)−C(11)	175.1(5)
N(3)−Ag(2)−N(6)	84.1(2)	Ag(2)−N(3)−C(14)	164.7(6)
N(3*)−Ag(2)−N(6*)	84.1(2)	Ag(2)−N(6)−C(27)	175.3(5)
N(3)−Ag(2)−N(6*)	95.9(2)	Ag(3)−N(5)−C(26)	171.6(5)
N(3*)−Ag(2)−N(6)	95.9(2)	Ag(4)−N(7)−C(29)	162.5(5)

and perchlorate ions being alternatively above and beneath the wavy sheet (Figure 1). Compared with the silver(I)−iodocarbon complexes formerly prepared from the reaction of some silver(I) salts and simple diiodocarbons,[21a,b] the Ag−I bond length here has a value of 2.743(2) Å, slightly shorter than those observed in the reported complexes (2.812−3.144 Å), while the C−I bond distance (2.15(1) Å) and the Ag−I−C bond angle (99.54(1)°) fall within the ranges 2.11−2.18 Å and 85.4−104.2° reported for bond length and for bond angle, respectively. The Ag−N bond distance (2.22 Å) and C≡N bond length (1.11 Å) are also within the limits reported (2.18−2.33 and 1.07-1.15 Å).[22] Only the Ag−N≡C angle (147°) becomes smaller than the range of 166−176° reported previously.[22]

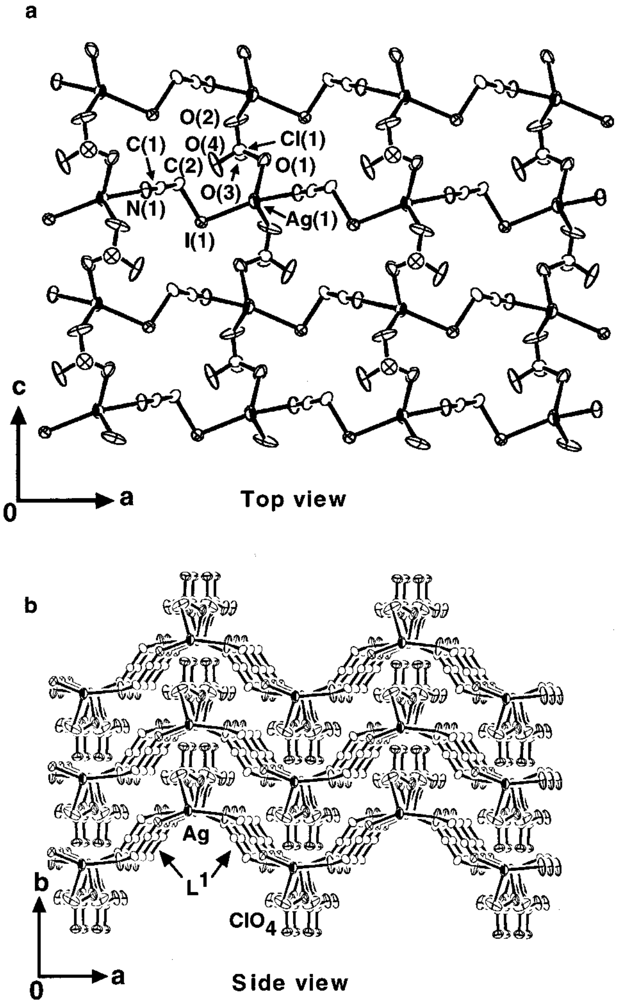

Figure 1. Perspective view of the 2-D wavy structure in **1**: (a) top view and (b) side view, showing 50% thermal ellipsoid.

2-D Interwoven Structure of $\{[Ag(L^2)(PO_2F_2)_{0.5}](PF_6)_{0.5}\}_n$ (2). An ORTEP drawing together with the atom-numbering scheme, corresponding to **2**, is given in Figure 2a. The silver(I) in **2** adopts a distorted trigonal coordination geometry in which it is coordinated by one nitrogen atom of a triazole and one carbon atom of an isocyanide group from two distinct L^2 molecules; the third coordination site is occupied by an oxygen atom of $PO_2F_2{}^-$ formed by hydrolysis of $PF_6{}^-$.[23] The measurement of the structure for complex **2** in the crystalline state reveals that the ligand, L^2, bridges two silver atoms to form 1-D wavy pattern chains which are further alternatively interwoven like warp and woof to generate a clothlike 2-D sheet, and the L^2 molecules of warp and weft chains are oriented with respect to each other in an orthogonal mode (Figure 2a and Figure 3). The interwoven sheet consists of square grid cavities in which $PO_2F_2{}^-$ ions are intercalated. There is no interaction between the sheets because of $PF_6{}^-$ ions existing between these layers (Figure 4). The selected bond lengths and angles are listed in Table 2. The Ag−C (2.081(7) Å) and N≡C (1.113(7) Å) bond distances and Ag−C≡N bond angle (167.5(5)°) are close to the data reported, with the ranges 2.059(4)−2.19(2) Å for the Ag−C bond, 1.089−1.16(13) Å for the N≡C bond, and

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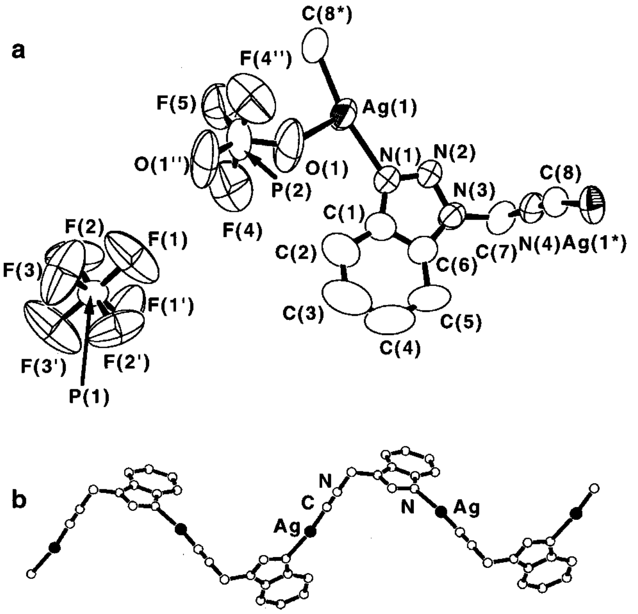

Figure 2. ORTEP view of the structure (showing 50% thermal ellipsoid) and chain framework of **2**.

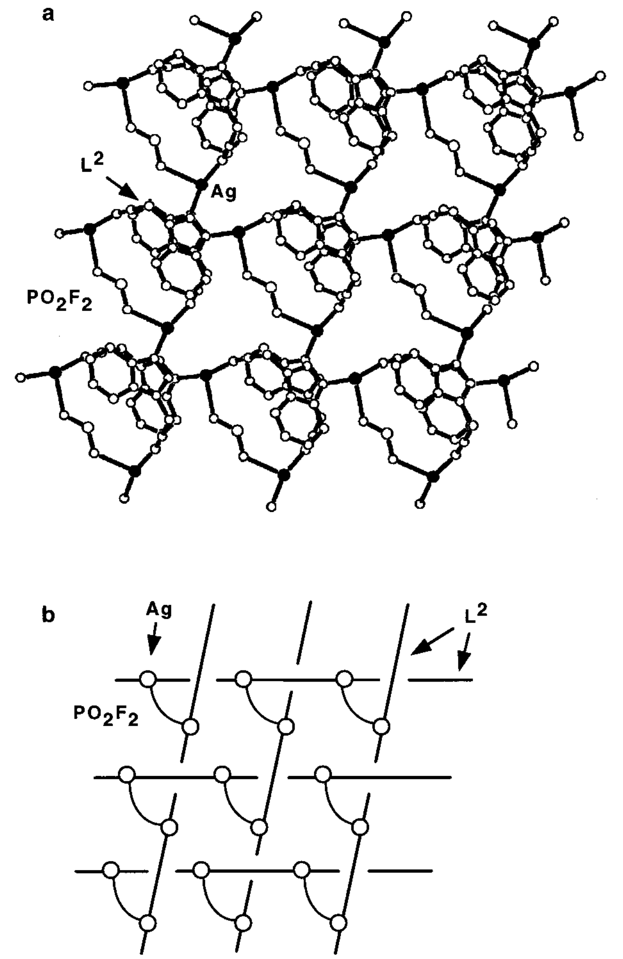

Figure 3. Perspective view of the interwoven network in **2** where PF$_6^-$ of the counteranions are deleted and PO$_2$F$_2^-$ are presented by PO$_2$: (a) top view and (b) schematic view of the interwoven structure.

160.8(9)−173.7(4)° for the $\mathrm{Ag{-}C{\equiv}N}$ bond angle, respectively.[24,25a] The Ag−N bond distance has a value of 2.193(4) Å, shorter than the ranges reported (2.236(6)−2.245(7) and 2.349(3)−2.390(3) Å)[23a,25a] and close to those observed in bis(benzotriazole) silver(I) nitrate.[25b]

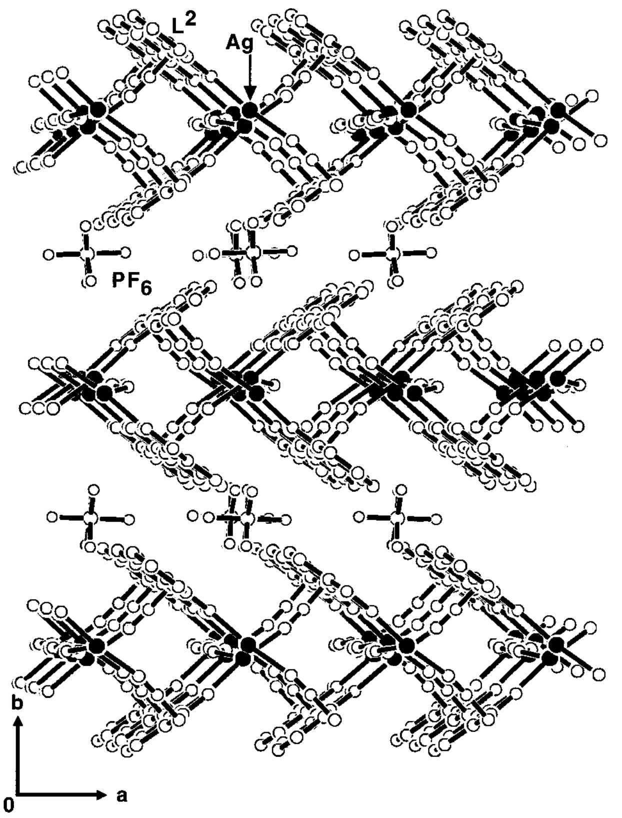

Figure 4. Side view of the network in **2** along the *c* axis.

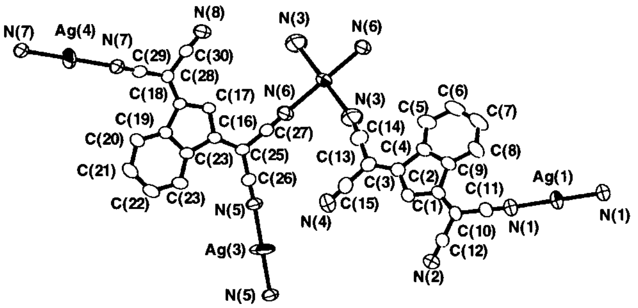

Figure 5. ORTEP view of the structure of **3**, showing 50% thermal ellipsoids.

3-D 5-fold Interpenetrating Structure of [Ag$_2$(L^3)$_2$]$_n$ (3). X-ray crystal structure determination displays that the structure of **3** is made up of unique and intricate 5-fold interpenetrating 3-D nets. The molecular ORTEP drawing of **3** together with the atom-numbering scheme is depicted in Figure 5. Four crystallographically independent silver atoms exist in the structure, and all are located on inversion centers; three of them, i.e., Ag(1), Ag(3), and Ag(4), adopt a linear coordination mode where they are biconnected by two cyano group nitrogen atoms from two different L^3 molecules, respectively, while Ag(2) has a rare coordination geometry in which the silver atom is surrounded by four cyano groups from four different L^3 molecules in a square planar coordination sphere (Figure 6). L^3 is not neutral in complex **3**, but monoanionic from charge balance. It is interesting that the ligands also possess two different bridging fashions in which one interacts with three

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(24) (a) Perreault, D.; Drouin, M.; Michel, A.; Harvey, P. D. *Inorg. Chem.* **1993**, *32*, 1903. (b) Fortin, D.; Drouin, M.; Harvey, P. D.; Herring, F. G.; Summers, D. A.; Thompson, R. C. *Inorg. Chem.* **1999**, *38*, 1253.

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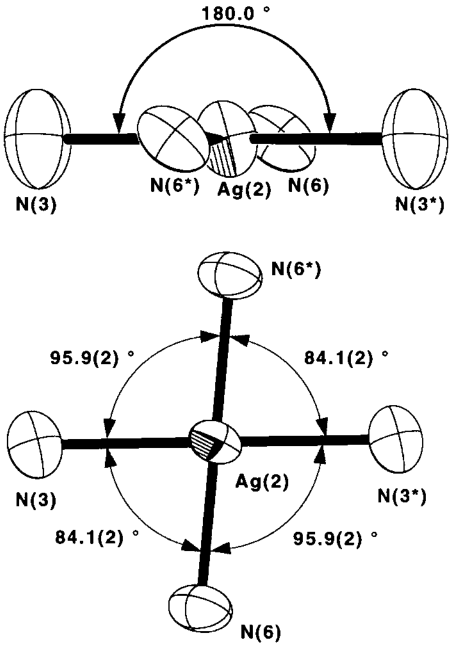

Figure 6. Square planar coordination of silver(I) in **3**, showing 50% thermal ellipsoids.

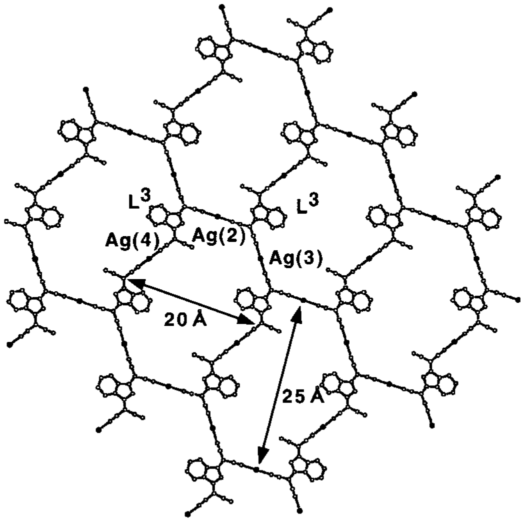

Figure 7. Top view of 2-D sheet structure for **3**.

different silver atoms, via three cyano groups, to give rise to a 2-D sheet with 52-membered rings (20 Å × 25 Å), each ring consisting of six silver atoms and six L^3 molecules (Figure 7), and the other links two silver atoms, further connecting two 2-D sheets via $-$L^3$-$Ag$-$L^3$-$ to form a 3-D network (Figure 8). The 3-D networks interpenetrate each other in quintuple mode, and the 5-fold interpenetrating results in columnar aromatic stacks of the benzene moieties from L^3 molecules (Figure 9). The separations between stacking benzene moieties are alternatively 3.35 and 3.52 Å, indicating $\pi-\pi$ interactions[8,23a,b,26] and similar to [Cu(dmtpn)$_2$](ClO$_4$)(THF) with 3.37 and 3.51 Å.[19] The Ag$-$N bond distances range from 2.126(4) to 2.427(6) Å, within the limits reported in complexes with polynitriles and silver(I).[8a,11a,22] All N$-$Ag$-$N angles formed by two face to face nitrogen atoms are 180°.

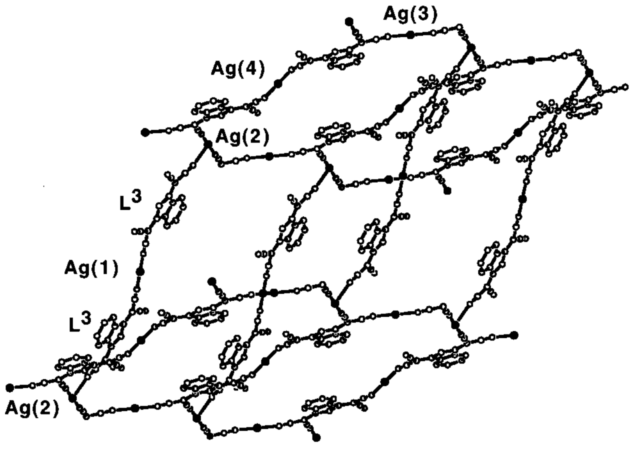

Figure 8. View of a single 3-D network in **3**.

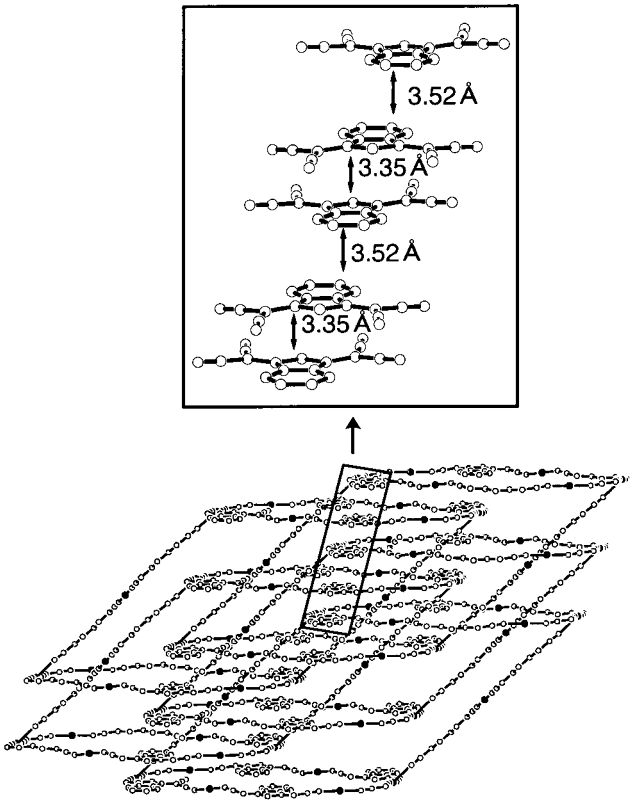

Figure 9. 5-fold interpenetrating structure of **3** with intermolecular $\pi-\pi$ interactions.

IR, ESR, and Conductivity Studies. The IR spectra of all three complexes and their free ligands were recorded in the region 4000$-$400 cm^{-1} on KBr disks. For complex **1**, a strong ν(C≡N) stretching frequency of 2243 cm^{-1} was observed in free ligand (L^1), while the infrared spectrum of **1** exhibits a weak absorption peak for the nitrile group at 2017 cm^{-1} which is red-shifted relative to the band for the nitrile group of the free ligand. The resultant phenomena imply that an interaction between the nitrile group and silver(I) takes place. In addition, complex **1** gives a broad strong absorption of ν(OCl) at 1103 cm^{-1}, confirming the presence of perchlorate ion in the compound. For complex **2**, a weak interaction between the isocyano group and silver(I) takes place owing to the band of the ν(N≡C) stretching vibration being blue-shifted from 2141 to 2185 cm^{-1}, whereas the observed broad absorption at 837 cm^{-1} confirms the incorporation of the PF$_6^-$ ion into the compound. The coordination of silver(I) ions to the nitrile groups

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of L^3 in **3** can be also seen by comparing its $\nu(C{\equiv}N)$ and $\nu(C{=}C)$ stretching frequencies with those of free ligand L^3, here the $\nu(C{\equiv}N)$ stretching vibration frequency being slightly red-shifted from 2228 to 2199 cm^{-1} and $\nu(C{=}C)$ showing obvious changes.

The roomtemperature conductivities for complexes **1**−**3** were measured. Complexes **1** and **2** are insulators, whereas complex **3** gives an electric conductivity $\sigma = 2.4 \times 10^{-4}$ S cm^{-1} owing to existing columnar aromatic $\pi-\pi$ stacks, similar to that observed in Ag(TCNQ) ($\sigma = 3.6 \times 10^{-4}$ S cm^{-1}).[8a] No ESR signal for complexes **1** and **2** was observed. In complex **3**, an ESR signal attributable to organic radicals was observed with low spin density, but no ESR signal attributable to silver(II) was observed because of the low sensitivity and concentration.

Molecular Structure Features. The three polymeric networks reported here display novel and interesting structure features. Complex **1** consists of extended neutral molecular frames with 2-D wavy sheets, while complexes **2** and **3** were constructed from cationic units with 2-D interwoven wavy layers and 3-D 5-fold interpenetrating networks, respectively.

As is well-known, iodine atom is a weak base. Some simple monoiodocarbons react with silver(I) salts to generate immediately AgI precipitate.[21b] To our surprise, upon the opposite ends of these tailored monoiodocarbons being substituted by cyano groups, the coordination of monoiodocarbons to silver(I) ions came true. Interestingly, comparing L^2 with 2,1,3-benzothiadiazole (btd) which was employed as a ligand to react with silver(I) salts, in spite of both ligands being bidentates and similar in structure, the former leads to a 2-D interwoven sheet structure owing to extending an isocyanidomethyl functional group from the nitrogen atom of benzotriazole of L^2, however, the latter only gives a 1-D slightly bent linear chain$\{[Ag(btd)](ClO_4)\}_n$.[23a] The phenomena demonstrate that the selection of the chemical structure for multifuntional ligands plays an important role in the self-assembly of supramolecular networks.

The 2-D interwoven wavy network of complex **2** is a rare and distinct structure. If one neglects the Ag−OPO−Ag bridges, it consists of 1-D zigzag chains which give warp and woof sheets. To our knowledge, only one similar structure, $[IAuP(C_6H_5)_2(CH_2)_6P(C_6H_5)_2AuI]_n$,[27] was reported, where the infinite chains being woven as warp and woof are connected by weak metal−metal contacts, while the infinite chains in complex **2** are linked by coordination bonds between silver(I) ions and nitrogen/carbon atoms from different functional groups of L^2. Thus, some differences exist between both structures in Nature. This interwoven network is different from the usual 2-D interpenetrating ones, because it is woven by 1-D chains instead of 2-D nets and there do not exist “real” knots. Therefore, in order to disentangle these interwoven networks, it is not necessary to break any link in the networks.[1c] On the other hand, taking into account the above bridges one obtains a unique case of a single triconnected 2-D layer which appears self-entangled. From the topological point of view, it can be assigned to a net with $(8^2,10)$ topology by considering the three shortest circuits starting and ending at each metal center, namely, with the ratio of octagons to decagons being 2:1 for Ag(I) ions.[28]

The 3-D 5-fold interpenetrating nets of complex **3** also exhibit some intriguing features. From the viewpoint of topology, the compound **3** can be visualized as 3-D interpenetrating nets with three- and four-connected nodes in which the Ag(2) ions are tetraconnected centers and the ligands on 2-D layers triconnected centers, respectively, while the 2-D sheets of the network can be described as deforming hexagon nets (6,3) in which each L^3 bridges three silver(I) ions and two of the six sides are distorted owing to asymmetrical coordination of L^3. However, in a strict topological sense, the 2-D layers are formed by eight-membered circuits owing to the two Ag(2) ions also acting as nodes of the net. Hence, we can describe the topological type of single 3-D (3,4)-connected net for **3** as an $(8^3)_2(8,{}^5 10)$ net, meaning that the shortest circuits starting and ending on each center are three octagons for the triconnected ligands and five octagons and one decagon for tetraconnected Ag(2) ions, and the ratio of triconnected centers to tetraconnected ones is 2:1.[28] Compared with the 3-D interpenetrating networks with two types of nodes, reported previously, such as $[Cd(bipy)_2\{Ag(CN)_2\}_2]$ (two-interpenetrating with three- and six-nodes),[29] [Ag(tcm)(Dabco)] (two-interpenetrating with three- and five-nodes),[1c] and $[Ag_2Si(p\text{-}C_6H_4CN)_4]$ (four-interpenetrating with three- and four-nodes),[30] it is worth mentioning that only two of the six metal centers on the 2-D layer of the network in **3** participate in the construction of the connected nodes, whereas in the reported networks each metal center on 2-D layers takes part in the formation of nodes. In other words, other silver ions on the layer of **3**, such as Ag(3) and Ag(4), which do not occupy nodes of the net and only act as simple spacers to link two polydentate ligands, form so-called metallic synthons (ligand−metal−ligand).[2e,f] In fact, Ag(2) can be regarded as both a connected node for all of the net and a spacer for the layer of the net, while Ag(1) is also employed as a simple spacer to connect the layers of the network. Thus, here we call the network of complex **3** a quasi-network based on polydentate ligands (as centers) and metallic synthons. The networks exclusively constructed by ligand centers and metallic synthons are rare in a strict sense. The most important feature of the design of the supramolecular networked materials via using metallic synthons lies in the network topologies being controlled only by organic donor units.[2f] Another feature of these networks formed from metallic synthons is that the frameworks synthesized in this way possess larger cavities or channels for possible application in separation processes and catalysis. Generally, the degree of interpenetration in a diamond-like structure is intensively related to the bridged metal−metal distance, namely, the size of cavities or rings in the network.[31] Hence, the higher degree of interpenetration in **3** can be attributed to the larger circles formed via using metallic synthons in the network. On the other hand, another most important feature of complex **3** can be assigned to the square planar coordination sphere of Ag(2). As is well-known, silver(I) generally adopts linear, trigonal, tetrahedral, and octahedral coordination geometry. The square planar coordination of silver(I) like complex **3** was only described in $[Ag(4\text{-}cnpy)_2](BF_4)$ (cnpy = 4-cyanopyridine)[32] and $[Ag(C_{10}H_7)]_n$ ($C_{10}H_7$ = 1,1,2,4,5,5-hexacyano-3-azapenta-1,4-dienide).[33] The silver(I) in the former complex is linearly bonded to two nitrogen atoms (py) [average Ag−N(py) 2.175 Å, N(py)−Ag−N(py) 173.4(3)°] and weakly linked by two nitrogen atoms (cn) [Ag−N(cn)

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2.71(1), 3.06(1) Å] of other ligands to afford a distorted square planar coordination, while the latter silver(I) adopts a pseudo square planar coordination with being connected by four different organic ligands [Ag−N 2.32(1), 2.30(1) Å] and, meanwhile, very weakly interacting with two nitrogen atoms of neighbor planes [Ag−N 3.36(1) Å]. However, Ag(2) reported here is linked symmetrically by N(3), N(3*) and N(6), N(6*) (Figure 6), giving a N(3)−Ag(2)−N(3*) angle of 180°, a N(6)−Ag(2)−N(6*) angle of 180°, a N(3)−Ag bond distance of 2.427(6) Å, and a N(6)−Ag distance of 2.280(4) Å, respectively. Thus, this case is a real square planar coordination geometry of silver(I). In addition, it is noteworthy that L^3 adopts a rare μ_3 and a usual μ_2 bridging mode to lead to 3-D interpenetrating nets with columnar $\pi-\pi$ stacks. On the other hand, in the coordination of TCNQ to silver(I) and copper(I) in a μ_4 fashion, only neighboring TCNQ molecules are rotated 90° relative to each other to form the columnar aromatic stacks.[8] As far as we know, very often TCNQ and TCNE behave as tetradentate as well as bidentate ligands. The phenomenon of L^3 acting as a tridentate ligand might be due to the steric factor of the ligand, directly resulting in the formation of larger 52-membered rings. As mentioned above, complex **3** exhibits unprecedented quintuple interpenetrating nets with three- and four-connected nodes and $\pi-\pi$ stacks.

Conclusion

Several novel and distinct silver coordination networks have been synthesized via using different nitrogen- and/or iodine-containing multidentate ligands in this work. The polymeric species described here demonstrate that the coordination versatility of silver(I) and polynitrile ligands and the selection of chemical structure for multidentate ligands play important roles in the self-assembly of silver(I) complex networks with unprecedented topologies and potential useful properties. Complex **2** is constructed from cationic infinite chains with a 2-D interwoven structure, while complex **3** consists of cationic frameworks with 3-D quintuple interpenetrating networks. It is believed that the preliminary results obtained here provide an inspiration to future rational design of novel architectures, especially for the design of interpenetrating networks. TCNX species and other polynitriles constitute an important class of multifunctional and multidentate ligands, and the coordination of these species to transition metals often gives rise to some novel networks with potential useful properties owing to their versatile coordination fashions and the ability of charge transfer.[34] Thus, further research on the coordination of polynitrile ligands to transition metals holds the promise of providing novel supramolecular functional materials.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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