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AgC(CN)$_3$-Based Coordination Polymers

Brendan F. Abrahams,[†] Stuart R. Batten,[*,‡] Bernard F. Hoskins,[†] and Richard Robson[†]

Schools of Chemistry, University of Melbourne, Victoria 3010, Australia, and Monash University, Victoria 3800, Australia

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Reaction of Ag(tcm), tcm = tricyanomethanide, C(CN)$_3^-$, with a range of terminal and bridging ligands results in formation of a series of new coordination polymers. Recrystallization of Ag(tcm) from acetonitrile generates Ag(tcm)(MeCN), which is composed of corrugated (6,3) sheets displaying two-fold 2D → 2D parallel interpenetration and is topologically identical to the parent Ag(tcm) structure. Ag(tcm)(L) species, L = 1,4-diazobicyclo-[2.2.2]-octane (dabco) or 4,4′-bipyridine (bipy), contain two interpenetrating 3D networks composed of 3-connecting (tcm) and 5-connecting (Ag) centers. The structure of Ag(tcm)(bpe), bpe = 1,2-bis(4-pyridyl)ethene, contains 1D ladderlike polymers connected by weak Ag–tcm interactions into two interpenetrating 3D nets. Ag(tcm)(Mepyz)$_{3/2}$, Mepyz = methylpyrazine, also contains 1D ladders, while Ag(tcm)(Me$_4$pyz)$_{1/2}$, Me$_4$pyz = tetramethylpyrazine, contains 2D sheets composed of Ag(tcm) 1D "tubes" linked by bridging Me$_4$pyz ligands. Ag(tcm)(hmt), hmt = hexamethylenetetramine, has a 3D network structure in which the hmt ligands are 3-connecting, the tcm anions are 2-connecting, and the silver atoms are 5-connecting. The topology is the same as displayed by Ag(tcm)(L), L = dabco or bipy.

Introduction

The crystal engineering of coordination polymers is presently a large and growing area of research.[1−3] Materials produced in this area have potential application in fields as diverse as molecule-based magnetism, nonlinear optics, and heterogeneous catalysis.

We have been examining the use of potentially trigonal-connecting ligands such as 1,3,5-tri(4-pyridyl)-2,4,6-triazine (tpt), dicyanamide (dca, N(CN)$_2^-$), and tricyanomethanide (tcm, C(CN)$_3^-$). The tpt ligand has been shown to form a number of high-symmetry 3D networks,[2,4] while the dca ligand forms rutile-like networks with octahedral transition metals which show long-range magnetic ordering.[5] Lee et al. have also reported coordination networks formed by a number of 3-connecting pyridyl- and nitrile-donor ligands.[6]

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[*] To whom correspondence should be addressed. E-mail: stuart.batten@sci.monash.edu.au. Fax: +61-3-9905-4606.

[†] University of Melbourne.

[‡] Monash University.

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The tcm anion has proved to be a versatile ligand for the construction of coordination polymers. Its anionic charge means that it usually plays the role of both bridging ligand and counterion, removing the requirement for the presence of other counterions. Doubly interpenetrating rutile-like networks are formed in the isomorphous series M(tcm)$_2$, M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg.[7] Single, self-penetrating networks are present in M(dca)(tcm), M = Co, Ni, Cu.[8] The networks are closely related to, but not identical to, the rutile network, and the Co and Ni compounds show long-range magnetic ordering. The structure of Cd(tcm)(B(OMe)$_4$)·*x*MeOH contains a complicated chiral 3D network with hexagonal symmetry.[9] In Hg$_2$(tcm)$_2$, the tcm ligand connects (Hg^I)$_2$ dimers into a 3D network.[10]

In all the described complexes, the tcm ligands are three-connecting. The ligand, however, can show a variety of coordination modes, and the nitrogen atoms can participate in hydrogen-bonding interactions as well as coordination bonds. The 3D network structure of (CH$_3$)$_2$Tl(tcm) contains μ_4 tcm ligands: two of the nitrogen atoms coordinate to a single metal atom each, while the third coordinates to two metal atoms simultaneously.[11] In [Cd(tcm)(hmt)(H$_2$O)](tcm), hmt = hexamethylenetetramine, half the tcm ligands are μ_3 while the other half are uncoordinated but hydrogen bond to a single water ligand each.[12] When hydrogen-bonding interactions are taken into account, 3D rutile-like networks are formed. The structures of M(tcm)$_2$(H$_2$O)$_2$·Me$_4$pyz, M = Co, Ni, Me$_4$pyz = tetramethylpyrazine, contain tcm ligands which coordinate to two metals and hydrogen bond to one water ligand each.[13] One-dimensional coordination polymers are formed which are connected via hydrogen-bonding interactions into a 3D net. Similarly, although not strictly a coordination polymer, the structure of (CH$_3$)$_3$Sn(tcm)(H$_2$O) contains tcm ligands which coordinate to one metal and hydrogen bond to two water ligands each; 2D (6,3) networks are formed.[14] The solvated species M(tcm)$_2$(EtOH)$_2$, M = Co, Ni, contain 2D (4,4) sheets of metal ions bridged by bidentate tcm ligands; the uncoordinated nitrile of the tcm hydrogen bonds to the alcohol ligands.[7] The structure of [Cu(tcm)(Hpz)$_4$](tcm), Hpz = pyrazole, contains 1D coordination chains; both μ_2 and uncoordinated tcm anions are present.[15] The structures of M(tcm)$_2$(2-methylimidazole)$_2$, M = Co, Cu, have metal ions bridged by μ_2 tcm anions into either 1D chains (Co) or 2D (4,4) sheets (Cu).[16] Finally, the structures of Cu(tcm)L, L = hmt, 4,4′-bipyridine (bipy), and Cu(tcm)(bpe)·1/4bpe·1/2MeCN, bpe = 1,2-bis(4-pyridyl)-ethene, all contain 2D (4,4) networks constructed using μ_2 tcm anions.[17] The structures of these selected tcm structures, along with the Ag(tcm)-derived structures described here and elsewhere,[18,19] are summarized in Table 1.

The results described here are a result of our interest in coordination polymers derived from Ag(tcm). The structure of Ag(tcm) was first reported by Konnert and Britton in 1966.[18] We recently reported an improved refinement of this structure, as well as two new compounds, Ag(tcm)(pyz), pyz = pyrazine, and Ag(tcm)(phz)$_{1/2}$, phz = phenazine.[19] The structure of Ag(tcm) consists of 2D (6,3) sheets in which the tcm anions each bind to three silver cations and the silver atoms in turn coordinate to three different tcm ligands each. The sheets show two-fold 2D → 2D parallel interpenetration.[2] The sheets are corrugated, and discrete layers are formed which each contain two interpenetrating sheets. The trigonal nodes of the net are the central carbon of the tcm anion and the silver cation. The corrugation of the sheets, which is crucial for the interpenetration, is due mainly to the pyramidal geometry of the silver atoms (the tcm anions are largely planar), with nonlinear CN−Ag angles also contributing.

The pyramidal geometry of the silver atoms led us to attempt to connect together sheets in adjoining layers by adding suitable bridging ligands to the reaction mixture. It was hoped that the bridging ligands would coordinate to the silver atoms, converting the silver coordination geometry from pyramidal to tetrahedral, and thus bridge the layers without disrupting the internal connectivity of the Ag(tcm) layers. When pyrazine (pyz) was added to the reaction, however, a new, unexpected structure type was discovered.[19] The structure of Ag(tcm)(pyz) contained 3D networks in which 5-coordinate, trigonal bipyramidal silver atoms were equatorially bridged by μ_3 tcm anions to form *planar* (6,3) sheets. These sheets were then bridged by apical pyz ligands into a 3D network, and the compound contained two such networks interpenetrating.

The desired aim of bridging the doubly interpenetrating layers of Ag(tcm) was finally achieved using the more bulky ligand phenazine (phz).[19] The layers in Ag(tcm)(phz)$_{1/2}$ are bridged in such a way that two separate interpenetrating 3D networks are formed. This "malleability" of the Ag(tcm) substructure which allows it to form a variety of network types depending on the coligand used led us to investigate a

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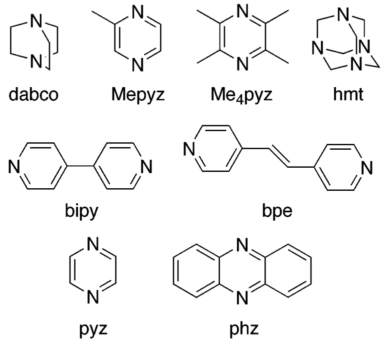
Table 1. Summary of the Structures of the Ag(tcm) Derivatives and Other Selected tcm Structures

compd	structure	ref
Ag(tcm)	two interpenetrating 2D (6,3) nets	18, 19
Ag(tcm)(MeCN)	two interpenetrating 2D (6,3) nets	this work
Ag(tcm)(phz)$_{1/2}$	two interpenetrating 3D nets containing tetrahedral Ag	19
Ag(tcm)(pyz)	two interpenetrating 3D nets containing 5-coordinate Ag, μ_3 tcm, and μ_2 pyz	19
Ag(tcm)(dabco)	two interpenetrating 3D nets containing 5-coordinate Ag, μ_3 tcm, and μ_2 dabco	this work
Ag(tcm)(bipy)	two interpenetrating 3D nets containing 5-coordinate Ag, μ_3 tcm, and μ_2 bipy	this work
Ag(tcm)(bpe)	1D ladders connected by weak Ag−tcm interactions into two interpenetrating 3D nets	this work
Ag(tcm)(Mepyz)$_{3/2}$	1D ladders	this work
Ag(tcm)(Me$_4$pyz)$_{1/2}$	2D sheets composed of 1D Ag(tcm) “tubes” bridged by Me$_4$pyz	this work
Ag(tcm)(hmt)	two interpenetrating 3D nets containing 5-coordinate Ag, μ_2 tcm, and μ_3 hmt	this work
Cu(tcm)(hmt)	interdigitated 2D (4,4) sheets	17
Cu(tcm)(bipy)	interpenetrating 2D (4,4) sheets	17
Cu(tcm)(bpe)·1/4(bpe) ·1/2MeCN	2D (4,4) sheets with intercalated bpe and MeCN molecules	17
M(tcm)$_2$, M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg	two interpenetrating 3D rutile nets	7
M(dca)(tcm), M = Co, Ni, Cu	self-penetrating 3D net	8
Cd(tcm)(B(OMe)$_4$)·*x*MeOH	chiral 3D net	9
[Cd(tcm)(hmt)(H$_2$O)](tcm)	rutile network if hydrogen bonding taken into account	12
M(tcm)$_2$(H$_2$O)$_2$·Me$_4$pyz, M = Co, Ni	1D chains connected by hydrogen bonding into a 3D net	13
M(tcm)$_2$(EtOH)$_2$, M = Co, Ni	2D (4,4) sheets	7b
[Cu(tcm)(pyrazole)$_4$](tcm)	1D chains	15
Co(tcm)$_2$(2-methylimidazole)$_2$	1D chains	16a
Cu(tcm)$_2$(2-methylimidazole)$_2$	2D (4,4) sheets	16b
Hg$_2$(tcm)$_2$	3D net	10
Me$_2$Tl(tcm)	3D net	11
Me$_2$Sn(tcm)(H$_2$O)	2D (6,3) sheets if hydrogen bonding taken into account	14

Chart 1



series of different coligands. The results of this investigation are presented here. The coligands used are acetonitrile (MeCN), 1,4-diazobicyclo-[2.2.2]-octane (dabco), 4,4′-bipyridine (bipy), 1,2-bis(4-pyridyl)ethene (bpe), methylpyrazine (Mepyz), tetramethylpyrazine (Me$_4$pyz), and hexamethylenetetramine (hmt) (Chart 1).

Experimental Section

Syntheses. All chemicals were used as supplied from commercial sources, except Ag(tcm), which was prepared using the previously published procedure.[18]

Ag(tcm)(MeCN). Ag(tcm) (75 mg, 0.38 mmol) was dissolved in 12 mL of hot acetonitrile, and the solution was allowed to cool. Colorless, solvent-sensitive needles of Ag(tcm)(MeCN) (40.1 mg, 0.17 mmol, 45%) crystallized as the solution cooled. Anal. Calcd for $AgC_6H_3N_4$: C, 30.15; N, 23.45; H, 1.27. Found: C, 24.56; N, 21.90; H, 0.00. Analysis indicated complete loss of MeCN (Anal. Calcd for AgC_4N_3: C, 24.27; N, 21.23; H, 0.00).

Ag(tcm)(dabco). Combination of Ag(tcm) (75 mg, 0.38 mmol) in 15 mL of acetonitrile and dabco (43 mg, 0.38 mmol) in 5 mL of acetonitrile gave colorless needles of Ag(tcm)(dabco) (99 mg, 0.32 mmol, 84%). IR (KBr, cm^{-1}): 550, 802, 912, 1000, 1054, 1230, 1260, 1320, 1364, 1452, 2160, 2800, 2890, 2950. Anal. Calcd for $AgC_{10}H_{12}N_5$: C, 38.72; N, 22.59; H, 3.91. Found: C, 38.78; N, 22.77; H, 4.05.

Ag(tcm)(bipy). Combination of Ag(tcm) (75 mg, 0.38 mmol) in 15 mL of acetonitrile and 4,4′-bipyridine (59 mg, 0.38 mmol) in 5 mL of acetonitrile gave colorless rods of Ag(tcm)(bipy) (117 mg, 0.33 mmol, 87%). IR (KBr, cm^{-1}): 482, 560, 608, 630, 674, 726, 810, 1004, 1040, 1064, 1097, 1216, 1230, 1258, 1320, 1336, 1427, 1484, 1530, 1600, 1624, 2150, 2165, 2210, 2450, 2800, 3040, 3070. Anal. Calcd for $AgC_{14}H_8N_5$: C, 47.48; N, 19.78; H, 2.28. Found: C, 47.64; N, 20.08; H: 2.00.

Ag(tcm)(bpe). Combination of Ag(tcm) (75 mg, 0.38 mmol) in 15 mL of hot acetonitrile and 1,2-bis(4-pyridyl)ethene (69 mg, 0.38 mmol) in 10 mL of hot acetonitrile gave fine white needles of Ag(tcm)(bpe) (112 mg, 0.29 mmol, 76%). IR (KBr, cm^{-1}): 548, 558, 824, 966, 1015, 1065, 1202, 1214, 1245, 1295, 1422, 1500, 1603, 2150, 2900. Anal. Calcd for $AgC_{16}H_{10}N_5$: C, 50.54; N, 18.43; H, 2.66. Found: C, 50.67; N, 18.79; H, 2.23.

Ag(tcm)(Mepyz)$_{3/2}$. Ag(tcm) (100 mg, 0.51 mmol) was dissolved in 5 mL of methylpyrazine, 20 mL of ethanol was added and the reaction kept at 4 °C for 3 days, producing colorless crystals of Ag(tcm)(Mepyz)$_{3/2}$ (77 mg, 0.23 mmol, 45%). IR (KBr, cm^{-1}): 406,

Table 2. Crystallographic Data

	Ag(tcm)(MeCN)	Ag(tcm)(dabco)	Ag(tcm)(bipy)	Ag(tcm)(bpe)	Ag(tcm)-(Mepyz)$_{3/2}$	Ag(tcm)-(Me$_4$pyz)$_{1/2}$	Ag(tcm)(hmt)
formula	$AgC_6H_3N_4$	$AgC_{10}H_{12}N_5$	$AgC_{14}H_8N_5$	$AgC_{16}H_{10}N_5$	$AgC_{11.5}H_9N_6$	$AgC_8H_6N_4$	$AgC_6H_3N_4$
M	238.99	310.12	354.13	380.16	339.12	266.04	338.14
cryst syst	orthorhombic	hexagonal	monoclinic	triclinic	triclinic	triclinic	orthorhombic
space group	*Pbcm*	$P6_3/mmc$	*C*2/*c*	$P\bar{1}$	*P*1	$P\bar{1}$	*Pnma*
a/Å	5.961(1)	9.369(2)	7.353(2)	10.217(3)	7.8182(2)	7.197(2)	16.6204(3)
b/Å	17.493(3)	9.369(2)	17.082(5)	11.546(3)	8.2681(3)	8.110(1)	6.5616(1)
c/Å	8.049(2)	7.129(1)	10.332(2)	13.552(4)	10.3971(2)	8.757(2)	10.2480(2)
α/deg	90	90	90	74.01(2)	102.723(2)	88.16(2)	90
β/deg	90	90	100.73(1)	76.02(3)	93.550(2)	69.99(2)	90
γ/deg	90	120	90	77.92(2)	90.317(2)	72.61(2)	90
U/Å^3	839.3(3)	541.9(2)	1275.0(6)	1473.7(7)	654.20(3)	456.9(2)	1117.61(3)
Z	4	2	4	4	2	2	4
D_c/g cm^{-3}	1.891	1.900	1.845	1.713	1.722	1.934	2.010
μ(Mo Kα)/mm^{-1}	2.340	1.838	1.576	1.370	1.533	2.160	1.797
data collected	1301	2644	1927	6131	10688	3247	8276
unique data (R_{int})	791 (0.0965)	329 (0.0292)	1465 (0.0289)	5178 (0.0385)	6757 (0.028)	2652 (0.0089)	1079 (0.0306)
final R1, wR2							
[$I > 2\sigma(I)$]	0.0665, 0.1435	0.0381, 0.0786	0.0268, 0.0629	0.0973, 0.1623	0.0316, 0.0888	0.0224, 0.0583	0.0221, 0.0456
(all data)	0.1123, 0.1581	0.0547, 0.0837	0.0371, 0.0681	0.2157, 0.1922	0.0395, 0.1015	0.0252, 0.0592	0.0230, 0.0468

467, 563, 745, 630, 980, 1025, 1062, 1155, 1178, 1244, 1304, 1399, 1441, 1476, 1524, 1584, 2175, 2344, 2372, 2497, 2831, 3056. Anal. Calcd for $AgC_{11.5}H_9N_6$: C, 40.73; N, 24.78; H, 2.68. Found: C, 30.60; N, 22.78; H, 0.82. Analysis on two separate samples was consistent with decomposition and loss of Mepyz in air (Anal. Calcd for Ag(tcm)(Mepyz)$_{0.4}$: C, 30.59; N, 22.59; H, 1.03).

Ag(tcm)(Me$_4$pyz)$_{1/2}$. Combination of Ag(tcm) (75 mg, 0.38 mmol) in 15 mL of acetonitrile and tetramethylpyrazine (26 mg, 0.19 mmol) in 5 mL of acetonitrile gave large clear, colorless crystals of Ag(tcm)(Me$_4$pyz)$_{1/2}$ (17 mg, 0.064 mmol, 17%) after one week. IR (KBr, cm^{-1}): 484, 562, 684, 816, 994, 1176, 1220, 1238, 1248, 1277, 1358, 1412, 2165, 2190, 2230, 2490, 2820, 2910. Anal. Calcd for $AgC_8H_6N_4$: C, 36.11; N, 21.06; H, 2.28. Found: C, 36.41; N, 21.25; H, 1.94.

Ag(tcm)(hmt). Ag(tcm) (75 mg, 0.38 mmol) was dissolved in a combined mixture of water (5 mL) and 25% aqueous ammonia (5 mL) and added to an aqueous solution (5 mL) of hexamethylenetetramine (53 mg, 0.38 mmol). The solution was left open to the atmosphere, allowing slow loss of ammonia from solution. Clear, colorless crystals were filtered off after 4 days (67 mg, 0.20 mmol, 53%). IR (KBr, cm^{-1}): 500, 515, 552, 667, 692, 780, 807, 826, 924, 990, 1007, 1018, 1056, 1228, 1239, 1374, 1382, 1459, 2172, 2958. Anal. Calcd for $AgC_{10}H_{12}N_3$: C, 35.52; N, 29.00; H, 3.58. Found: C, 35.56; N, 29.03; H, 3.39.

X-ray Structural Analyses. Crystal data for the compounds reported here are given in Table 2. The data were collected using Enraf-Nonius CAD4-F (MeCN, dabco, bpe, and Me$_4$pyz structures), CAD4-MachS (bipy), or Nonius KappaCCD (Mepyz, hmt) diffractometers. Solutions were obtained by direct methods (SHELXS 97)[20] followed by successive Fourier-difference methods and refined by full-matrix least-squares on F_{obs}^2 (SHELXL 97).[20] Absorption corrections and extinction coefficients were applied to all structures except the bpe, Mepyz, and hmt structures; absorption corrections only were applied to the bpe data.

The dabco structure showed disorder of the dabco ligand over two positions related by an approximate 60° rotation about the N···N axis. The two positions were initially allowed to refine their site occupancy factors (with their sum adding to full occupancy), but for the final refinements, their site occupation factors were fixed close to the values they refined to, giving a 60:40 ratio between the two positions. Due to this disorder, this was the only structure in which hydrogen atoms were not included in the model. In all other structures, hydrogen atoms were assigned to geometric positions but not refined.

Due to the weak nature of the bpe data, only the silver atoms were refined anisotropically in this structure. In all other structures, all non-hydrogen atoms were refined anisotropically. The Mepyz structure was refined as a racemic twin in the *P*1 space group (final Flack[21] parameter 0.44(4)); close inspection of the structure indicated it is truly noncentrosymmetric, due to the asymmetry of the Mepyz ligand. Imposition of a center of symmetry to this structure would require the methyl group of the bridging Mepyz ligand to be disordered over two sites. This disorder is eliminated by refinement in *P*1.

Results and Discussion

Given the polymeric structure of Ag(tcm), it was surprising to find it was soluble in acetonitrile. This solubility, however, provided simple reaction conditions in which a series of new compounds containing Ag(tcm) could be synthesized with relative ease and without the possible complications of counterions. Suitable crystals for crystallographic studies were also obtained readily. Indeed, all the compounds described here (except Ag(tcm)(Mepyz)$_{3/2}$ and Ag(tcm)(hmt)) were obtained from the reaction of acetonitrile solutions of Ag(tcm) and coligand.

Ag(tcm)(MeCN). Simple recrystallization of Ag(tcm) from acetonitrile produces colorless crystals of Ag(tcm)(MeCN) which are sensitive to solvent loss. The compound contains puckered, doubly interpenetrating (6,3) sheets (Figure 1) showing 2D → 2D parallel interpenetration.[2] The interpenetration topology is identical to that seen in Ag(tcm). The silver atoms, however, are tetrahedral, with acetonitrile ligands occupying the fourth coordination sites (Figure 2). The layers of interpenetrating sheets stack in such a way that there are two distinct, alternating antiparallel orientations of the layers (Figure 2). This allows the acetonitrile ligands on each silver to point into the space between the layers in

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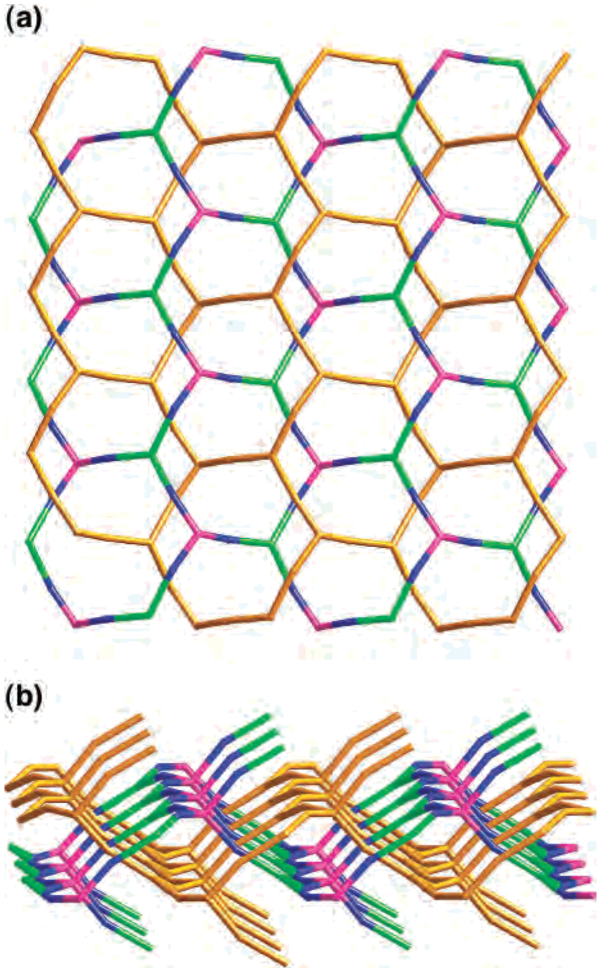

Figure 1. (a) Two interpenetrating Ag(tcm) (6,3) nets in Ag(tcm)(MeCN) displaying 2D → 2D parallel interpenetration. For clarity, the acetonitrile ligands are omitted. (b) The same two interpenetrating nets viewed side-on and with the acetonitrile ligands added (hydrogens omitted for clarity). In the multicolored network, Ag is depicted in pink, carbon green, and nitrogen blue.

an interdigitating fashion. This feature of the structure is reminiscent of the structure of [9-oxo-indolo[1,2-*a*]pyridinium][Cu(SCN)$_2$],[22] which contains (6,3) sheets with terminal SCN ligands directed into the intersheet regions above and below the sheets. It is also closely related to the structure of Ag(AcTCNE), AcTCNE = 1,1,2,2-tetracyanopentan-4-one-1-ide, which contains layers of doubly interpenetrating (6,3) sheets which show the same interpenetration topology as Ag(tcm)(MeCN).[23] Pendant sections of the 3-connecting anionic nitrile ligand are directed into the interlayer regions of the structure. The structures of [Cu(L)(MeCN)]BF$_4$.MeCN·1/2H$_2$O, L = 2,6-bis(3-pyridyloxy)pyrazine,[24] and Cu(dca)(MeCN)[25] also contain (6,3) sheets composed of 3-connecting ligands and 3-connecting, tetrahedral metals with pendant acetonitrile ligands. A number of Ag−hmt coordination

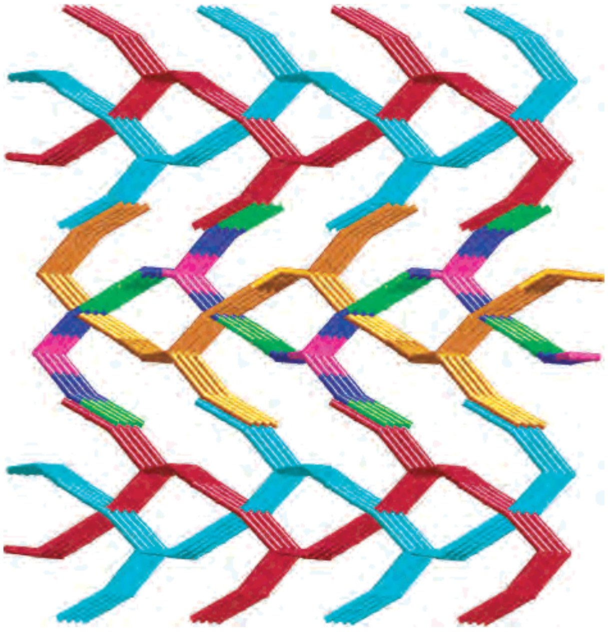

Figure 2. The interdigitation and antiparallel orientation of adjoining layers of doubly interpenetrating in Ag(tcm)(MeCN).

polymers also contain puckered (6,3) networks with tetrahedral metal ions and pendant ligands that are either monodentate or bridging to the next layer (giving topologies similar or identical to that seen in Ag(tcm)(phz)$_{1/2}$).[26]

Although the layers in Ag(tcm)(MeCN) are similar those to Ag(tcm), they stack differently, with there only being one orientation in the latter structure. The presence of the acetonitrile ligands also causes an increased separation between the layers. Due to the translation or rotation of adjacent layers, it is best to use the distance between equivalent silver atoms in *every second* layer to illustrate the increased separation. This distance is 10.147(2) Å for Ag(tcm) (the unit cell length *b*) and 17.499(3) Å for Ag(tcm)(MeCN) (also the *b* cell length). This raises the possibility of replacing the acetonitrile ligand with other, longer ligands, such as long chain alkyl or aryl nitriles, thus forcing the Ag(tcm) layers even further apart. This would be reminiscent of the intercalation of various species into clays and other layered materials forcing apart the layers to produce microporous materials.[27] Similar approaches have also been used for Hoffman clathrates.[28]

As expected, the N−Ag−N angles in Ag(tcm)(MeCN) are considerably closer to true tetrahedral angles (N−Ag−N =

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98.8(6)−115.3 (3)°) than those in Ag(tcm). The tcm angles and bond lengths, and Ag−N(tcm) bond lengths (Ag−N = 2.22(1), 2.22(2) Å) are consistent with those seen in Ag(tcm). The Ag−N(MeCN) bond length (2.40(2) Å) and internal MeCN geometry is also consistent with similar structures.[29]

Ag(tcm)(dabco). The structure of Ag(tcm)(dabco) is topologically identical to the previously reported Ag(tcm)(pyz).[19] It consists of single, planar, hexagonal Ag(tcm) sheets bridged by dabco ligands. All atoms within each hexagonal sheet lie on a mirror plane, with the central carbons of the tcm anions and the silver atoms lying on sites of *m*2 symmetry. With the nitrile carbons and nitrogens of the tcm positioned on sites of *mm*2 symmetry, the sheets have completely regular hexagonal geometry. The dabco ligands connect the sheets into a 3D network by coordinating to the axial positions of the 5-coordinate, trigonal bipyramidal silver atoms. Two such frameworks interpenetrate such that the dabco bridges of one framework pass through the centers of the hexagonal rings in the sheets of the second framework (Figure 3). The network thus consists of equal numbers of 3- and 5-connecting centers and has the Schäfli symbol (6^3)(6^9.8). Networks containing 5-connecting centers are rare, with only a few having been reported.[19,30]

The dabco ligands are disordered over two positions, with the second position related to the first by an approximately 60° rotation around the N···N axis of the dabco. This second position is less populated (40%) than the first (60%), possibly because in the second position the carbons of the dabco are much closer to the nitrile atoms of the tcm anions in the sheets above and below it. The more populated position has the dabco in a more sterically comfortable position, and only this position is shown in Figure 3. Nonetheless, the very long Ag−N(tcm) interactions (2.873(7) Å) are likely to be a consequence of the steric interactions between the tcm and dabco ligands.

The Ag−N(dabco) bond is considerably shorter (2.266(4) Å), and an alternative description of the structure would be in terms of Ag(dabco) 1D chains with weakly associated tcm anions. However, the close relationship to the pyz structure indicates that the description in terms of 5-coordinate silver atoms is useful. Indeed, it is of interest to compare the two structures more closely. In Ag(tcm)(pyz), the Ag−N(tcm) bond lengths (2.333(5)−2.538(6) Å) are considerably shorter than in Ag(tcm)(dabco) and are comparable to the Ag−N(pyz) bond length (2.363(4) Å).[19] In this compound, however, the (6,3) Ag(tcm) sheets are considerably distorted (although still planar) by the penetration of the pyz ligands of each net through the hexagonal rings of the other. This and the lack of 3-fold symmetry in the bridging ligand result in the loss of the 3-fold symmetry of the silver atoms and the central carbon atoms of the anions present in the dabco structure.

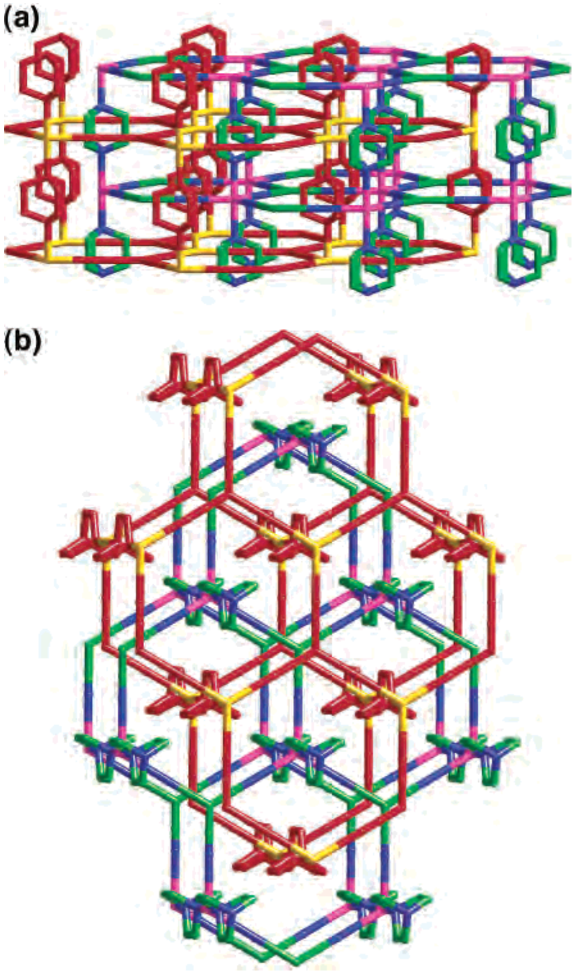

Figure 3. The two interpenetrating 3D nets in the structure of Ag(tcm)(dabco) viewed from two alternative angles. For clarity, only one orientation of the disordered dabco ligand is shown. In the multicolored network, the silver atoms are depicted in pink, carbon green, and nitrogen blue, while in the predominantly red network the metal atoms are depicted in yellow.

Ag(tcm)(bipy). Ag(tcm)(bipy) has the same topology as Ag(tcm)(pyz) and Ag(tcm)(dabco): two interpenetrating 3,5-connected networks (Figure 4). The increase in ligand length from pyz and dabco to bipy, however, results in considerable distortion of these nets. The bipy ligands bridge between the sheets at an angle of approximately 70°, bringing the sheets closer together than they would otherwise be and increasing the packing efficiency of the networks (Figure 5). The narrow part of the bipy bridge where one pyridine moiety joins the other also allows the ligand the steric maneuverability to pass through the second framework's sheets at varying angles, a feature not possessed by the pyrazine or dabco bridges.

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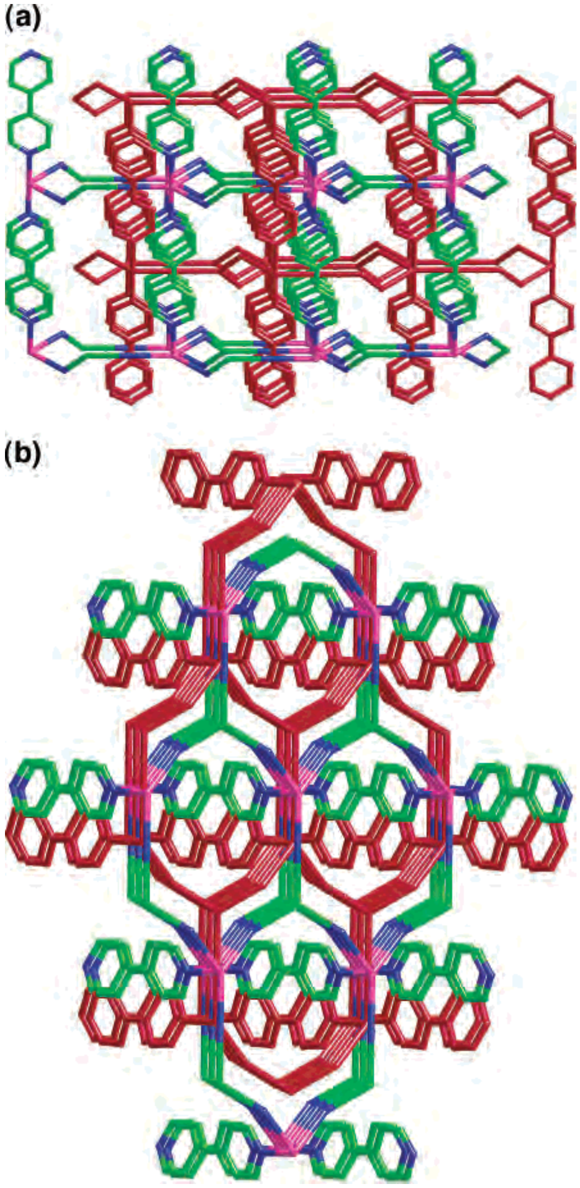

Figure 4. The two interpenetrating 3D nets in the structure of Ag(tcm)(bipy) viewed from two alternative angles. In the multicolored network, the silver atoms are depicted in pink, carbon green, and nitrogen blue.

This "collapsing" of the networks results in the movement of one sheet relative to the other on each end of the bipy bridge, such that a ring in the top sheet is now directly over the equivalent of its *neighbor* in the bottom sheet. Another consequence of the angle at which the bipy bridges is a change in the relative position of the interpenetrating networks to each other. One net is translated relative to the other such that the trigonal carbons of both no longer lie on a line perpendicular to the sheets, as seen in the two related structures. The trigonal carbons of the second sheet now lie halfway between the trigonal carbons of the first when the structure is viewed perpendicular to the sheets (Figure 4).

The angular bridging of the bipy ligands also results in the Ag(tcm) sheets themselves no longer being planar. Instead, two of the three tcm cyanides are pushed out of the plane (one up and one down), so that the silver can partially preserve its trigonal bipyramidal geometry. Most of the angular distortion needed to achieve this is contained in the angle around one of the tcm nitrogens (CN−Ag = 133.3(3)°). The bipy bridges are twisted around the carbon−carbon bond joining the two pyridine halves, and all ligand bond lengths and angles are as expected. As for Ag(tcm)(dabco), the Ag−N(tcm) bond lengths (2.737(3), 2.813(3) Å) are rather long, while the Ag−N(bipy) bond (2.214(2) Å) is a much stronger interaction.

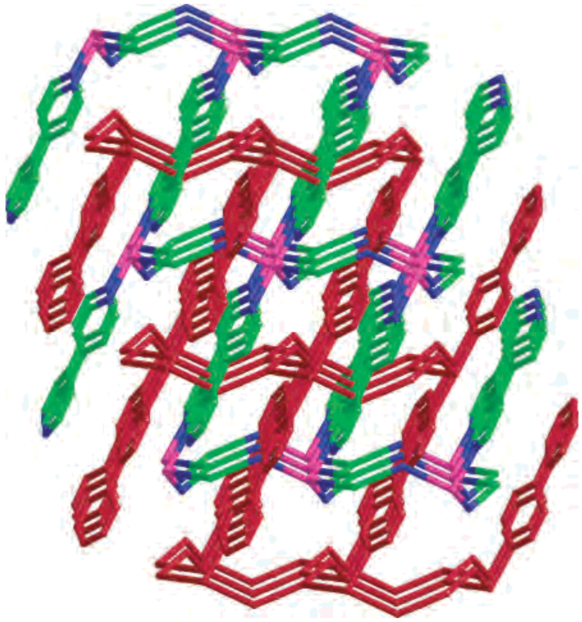

Figure 5. The "collapse" of the two interpenetrating networks in Ag(tcm)(bipy) that increases the crystal packing efficiency in the structure.

An interesting feature of these three related structures is the decrease in space group symmetry from hexagonal (dabco) to orthorhombic (pyz) to monoclinic (bipy) as the framework becomes more and more distorted from the hexagonal "ideal".

Ag(tcm)(bpe). Given the "collapse" of the bipy framework due to the longer bridge length, it was of interest to see what would happen if we increased the bridge length even further. Reaction of 1,2-bis(4-pyridyl)ethene and Ag(tcm) in acetonitrile gave colorless needles of Ag(tcm)(bpe); however, the structure was found to be unrelated to those previously discussed. The asymmetric unit consists of two unique Ag atoms (Ag1 and Ag2), two unique bpe ligands (which we will call "bpe1" and "bpe2"), and two unique tcm anions ("tcm1" and "tcm2"). The structure contains linear chains of silvers connected by bpe ligands. There are two crystallographically unique chains, one containing Ag1 and bpe1, the other containing Ag2 and bpe2. The Ag−N distances (Ag−N = 2.179(10)−2.209(12) Å) are consistent with the distances seen in the polymeric chain structure of Ag(L)(ClO_4), L = 1,2-bis(2-pyridyl)ethene (2.158(3) and 2.166(3) Å).[31] These chains are connected in pairs by weakly bonded μ_2 tcm1 anions (Ag−N = 2.62(2), 2.63(2) Å) to form ladderlike motifs (Figure 6). The rungs of the ladders are formed by the tcm1 anions, while the sides consist of one Ag1/bpe1 chain and one Ag2/bpe2 chain.

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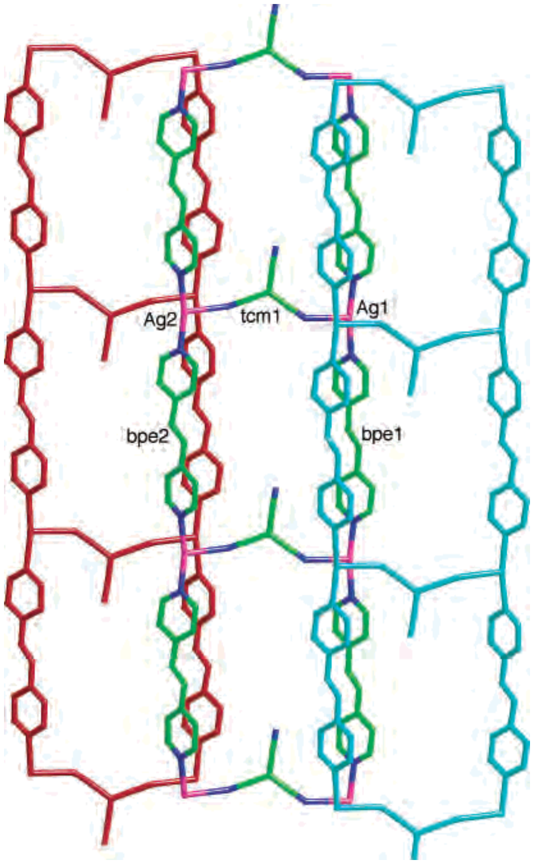

Figure 6. Three adjoining 1D ladders in the structure of Ag(tcm)(bpe). The weaker Ag−tcm interactions are not shown here, and in the central ladder, the silver atoms are depicted in pink, carbon green, and nitrogen dark blue.

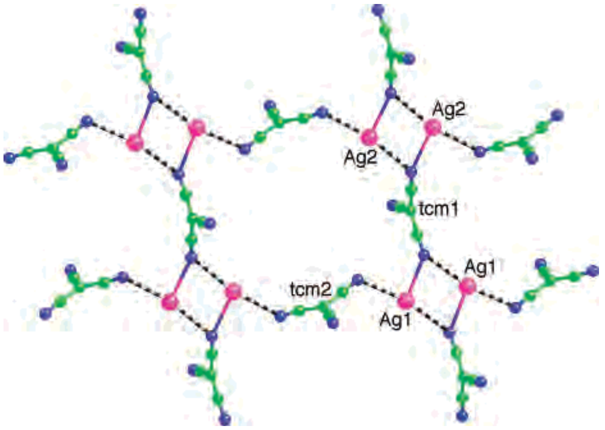

Figure 7. The Ag/tcm sheet substructure in Ag(tcm)(bpe), with weak Ag−tcm interactions depicted by dashed bonds (see main text). For clarity, the bpe ligands are omitted, and the silver atoms are depicted in pink, carbon green, and nitrogen blue.

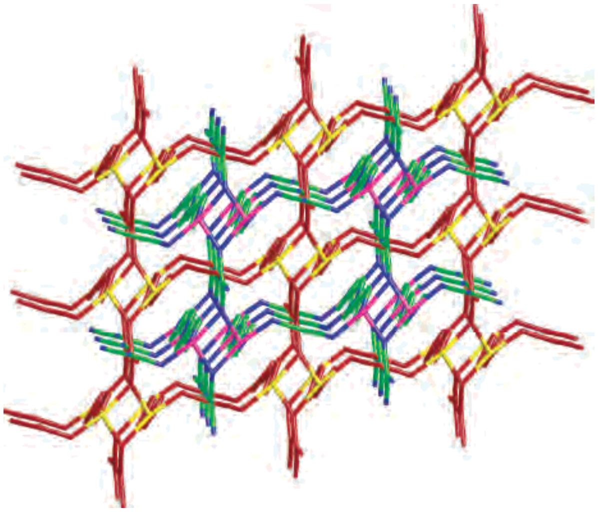

Figure 8. The two interpenetrating networks in Ag(tcm)(bpe) that are generated if the weak Ag−tcm interactions are assigned as bonds. In the predominantly red network, the silver atoms are depicted in yellow; in the multicolored network, the colors are as before.

These ladders are further interconnected to one another via a complicated series of very weak interactions between the tcm anions and the silver atoms. These interactions occur in sheets perpendicular to the direction of the chains. One such sheet is shown in Figure 7. The silver atoms occur in two similar pairs (Ag1 and Ag1^{I}; Ag2 and Ag2^{II}) in which the two silver atoms are related in a centrosymmetric fashion. The two Ag atoms in each pair also belong to adjoining ladders. The two inequivalent tcm molecules bridge these pairs in very different ways. The tcm1 anions, which form the ladderlike motifs, also have a longer interaction with the other silver atom in the pair (Ag−N = 3.01(2), 2.94(2) Å), which is represented as a dashed bond in Figure 7. These interactions bring the silver atoms into close contact (Ag1···Ag1^{I} = 3.409(3) Å, Ag2···Ag2^{II} = 3.373(3) Å). This also in turn brings the bpe ligands which are coordinated to these silvers (Figure 6) into close contact, such that there are $\pi-\pi$ interactions between them (although the pyridyl rings of adjacent ligands are not strictly parallel, the closest non-hydrogen contacts are 3.425 Å for the (bpe1)$_2$ pair, and 3.261 Å for the (bpe2)$_2$ pair).

The silver pairs are also connected to each other via weak interactions with the second type of tcm (tcm2). These interactions (Ag−N = 2.83(2), 2.91(2) Å) are again shown as dashed bonds in Figure 7.

The overall effect of these interactions is to form sheets of rectangles in which the vertices are the alternating inequivalent Ag pairs, and the edges are formed by the tcm anions. The sheets are connected to neighboring sheets by pairs of the Ag(bpe) chains shown in Figure 6, giving a three-dimensional framework which can be related to α-Po if the Ag$_2$ pairs are treated as nodes and the two bpe ligands bridging between each pair are treated as a single link. Two such frameworks interpenetrate, as shown in Figure 8. The interpenetration is such that the weakly interacting tcm2 anions associated with one net lie within the windows formed by the ladders of the other net, and vice versa.

It should be emphasized that many of these Ag···N interactions, although nontrivial (i.e., less than the sum of the van der Waals radii (3.27 Å)), are weak. Similar interactions of tcm with metal centers, however, are seen in the structure of (CH$_3$)$_2$Tl(tcm),[11] in which one of the tcm nitrogens bridges between two Tl atoms at a distance of 2.91(1) Å to each. All angles and bond lengths of the tcm and bpe ligands are as expected.

The reasons why the use of the bpe ligand did not produce either the bipy or phz structure types discussed earlier are

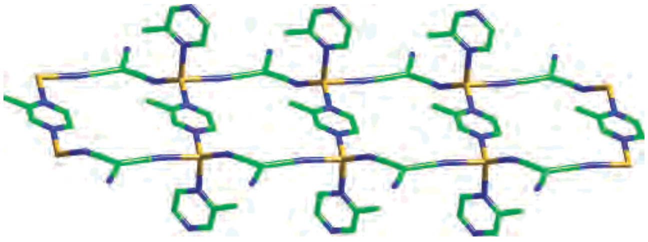

Figure 9. The 1D ladderlike polymer Ag(tcm)(Mepyz)$_{3/2}$. The silver atoms are depicted in yellow, carbon green, and nitrogen blue.

unclear; however, a number of relevant observations can be made. The length of the bpe bridge would result in a large separation between the layers of doubly interpenetrating sheets in the phz structure type, most likely giving a less efficient packing than that seen in the structure actually formed by bpe. The structure actually formed also allows $\pi-\pi$ interactions between pairs of bpe chains, something not possible in the bipy type structures based on linked planar hexagonal nets.

Ag(tcm)(Mepyz)$_{3/2}$. Given the difference in the structures formed by reaction of the closely related pyz and phz ligands with Ag(tcm),[19] we decided to explore a number of other sterically hindered pyrazine derivatives. Dissolution of Ag(tcm) in methylpyrazine followed by addition of ethanol and cooling gave large colorless crystals of Ag(tcm)(Mepyz)$_{3/2}$. The asymmetric unit of the structure contains two silver atoms (Ag1 and Ag2), two tcm anions ("tcm1" and "tcm2"), and three Mepyz ligands ("Mepyz1", "Mepyz2", and "Mepyz3"). The overall structure consists of ladderlike 1D polymers (Figure 9), closely related to a number of other reported ladderlike 1D polymers containing tetrahedral metals and terminal ligands on the periphery.[6b,25,32] Unlike Ag(tcm)(bpe), however, the sides of the ladders consist of two unique Ag(tcm) chains (one Ag1/tcm1 chain and one Ag2/tcm2 chain; Ag$-$N = 2.172(8)$-$2.334(9) Å), while the rungs of the ladders consist of bridging Mepyz1 ligands (Ag$-$N = 2.328(9), 2.369(9) Å). The tetrahedral geometry of the silver atoms is completed by monodentate Mepyz ligands (Mepyz2 and Mepyz3; Ag$-$N = 2.352(8), 2.411(9) Å), such that all the monodentate Mepyz ligands are directed above the ladder on one side of the ladder, and below the ladder on the other side. Thus, zigzag Mepyz$-$Ag$-$Mepyz$-$Ag$-$Mepyz moieties are generated which are bridged by the tcm anions, which lie roughly coplanar to the central Ag$-$Mepyz$-$Ag substructure, to produce the ladders. The most significant interladder supramolecular interactions are between a methyl group and an uncoordinated pyrazine nitrogen (H$\cdots$N = 2.460 Å, C$-$H$\cdots$N = 155°), and between a pyridyl hydrogen and an uncoordinated tcm nitrogen (H$\cdots$N = 2.580 Å, C$-$H$\cdots$N = 126°).

Ag(tcm)(Me$_4$pyz)$_{1/2}$. The structure of Ag(tcm)(Me$_4$pyz)$_{1/2}$ was also found to be unrelated to those seen earlier. It consists of "rectangular tubes" of Ag(tcm), which lie parallel to the *y* axis, bridged by Me$_4$pyz ligands (Figure 10). The "tubes" are composed of two Ag(tcm) chains in which the silver atoms are bridged by two-coordinate tcm anions (Ag$-$N = 2.295(2), 2.257(2) Å). The two chains are then connected to each other via bonds from the tcm nitrogen atoms not involved in the intrachain bonding to the silver atoms of the other chain (Ag$-$N = 2.647(3) Å). These nitrogen atoms bond to the silver atoms with a CN$-$Ag angle of 101.6(l)°, and the bridging Me$_4$pyz ligands (Ag$-$N = 2.283(2) Å) complete the tetrahedral geometry of the silver cations. The Me$_4$pyz bridges result in sheets being formed, which stack along the *x* axis (Figure 10). The sheets pack closely, with 12 different interactions between the sheets being less than 3.5 Å, the smallest being 3.145(3) Å (N4$\cdots$C5).

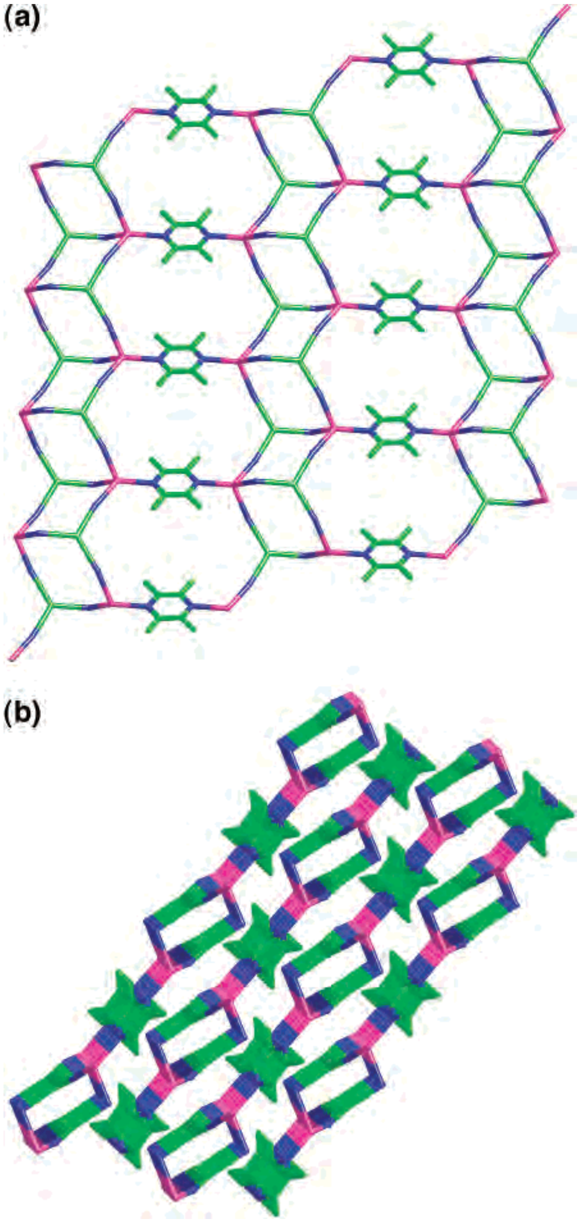

Figure 10. (a) A single sheet in the structure of Ag(tcm)(Me$_4$pyz)$_{1/2}$. (b) Stacking of the sheets along the *x* axis. Note the tubelike Ag(tcm) substructure formed. Silver atoms are depicted in pink, carbon green, and nitrogen blue.

Ag(tcm)(hmt). Unlike most of the other non-tcm ligands discussed here, hexamethylenetetramine (hmt) is not a linear

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[32] (a) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Chem. Commun.* **1999**, 449. (b) Blake, A. J.; Champness, N. R.; Khlobystov, A.; Lemenovskii, D. A.; Li, W.-S.; Schroder, M. *Chem. Commun.* **1997**, 2027.

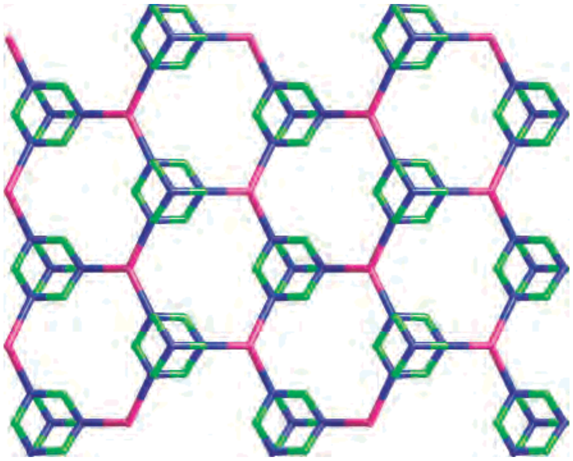

Figure 11. The (6,3) sheet substructure in Ag(tcm)(hmt) formed by the silver atoms (pink) and the hmt ligands (carbon in green, nitrogen blue).

pyridyl-donor bridge, but rather, it has the potential to coordinate to up to four Ag atoms in a tetrahedral fashion, has no aromatic functional groups to potentially participate in π-stacking interactions, and has a more spherical rather than "slablike" steric profile. Given these differences from the previously used ligands, and the extensive Ag−hmt coordination polymer chemistry already reported,[26,33,34] it was of interest to see what the effect of using such a different coligand would have on the $Ag(tcm)(L)_x$ structures.

Colorless crystals of Ag(tcm)(hmt) were obtained by dissolving Ag(tcm) and hmt in an aqueous ammonia solution and then allowing the solution to lose ammonia to the atmosphere over a number of days. The structure contains five-coordinate silver atoms, μ_3 bridging hmt ligands, and μ_2 bridging tcm anions. The hmt ligands bridge the silver atoms (Ag−N = 2.363(3), 2 × 2.399(2) Å) into puckered (6,3) sheets in which both the Ag and hmt moieties act as 3-connecting nodes, as shown in Figure 11. This is a common structural motif seen in Ag−hmt structures.[26,33] These (6,3) sheets are then bridged through the five-coordinate Ag atoms to the adjoining sheets via the 2-connecting tcm anions (Ag−N = 2.556(3), 2.619(3) Å) to generate a single 3D network (Figure 12). The resultant network has the same topology as Ag(tcm)(L), L = pyz, dabco, bipy. The roles of ligands, however, are reversed: this time, the coligand is acting as the 3-connecting ligand in the (6,3) sheets, and the tcm anion is acting as the 2-connecting intersheet bridge. This is also the first reported Ag−hmt coordination polymer to contain 5-coordinate Ag centers.

Another notable feature of the structure is that the puckered nature of the (6,3) sheet substructure and the nonlinear shape of the tcm bridges mean that the tcm anions form stacks running parallel to *b* in which the anions alternate between two different orientations related by a 180° rotation about the stacking axis. The tcm anions within these stacks show quite close $\pi-\pi$ stacking interactions (interplanar distance = 3.281 Å (i.e., $b/2$); closest interatomic contact = 3.307 Å).

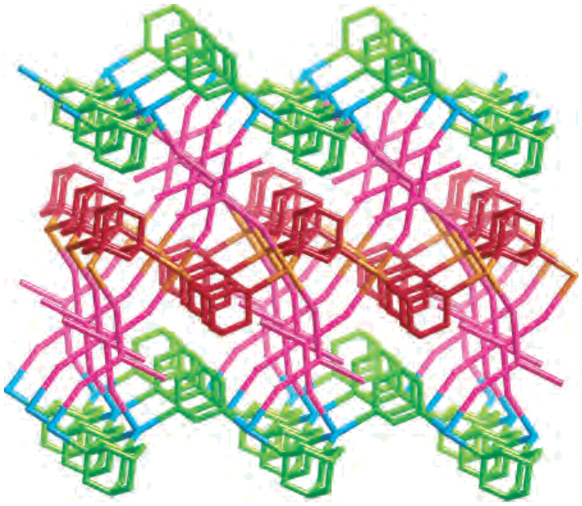

Figure 12. The 3D network of Ag(tcm)(hmt) formed by the bridging of the (6,3) sheets shown in Figure 11 by μ_2 tcm ligands. The tcm ligands are depicted in pink, while the Ag(hmt) sheets are shown in either orange (silver) and red (hmt), or blue (silver) and green (hmt).

General Discussion

The work described here and in our previous paper[19] shows that a rich variety of structures can be obtained from simple precursors, and with variation of only one reaction component. Subtle differences (length, steric bulk) have been shown to have a great effect on the network topology obtained.

Ag(tcm)(MeCN), obtained from the recrystallization of Ag(tcm) from acetonitrile, retains the doubly interpenetrating (6,3) sheet motif of the parent compound. Introduction of bridging ligands, however, has less predictable effects. Ag(tcm)(pyz) contains two interpenetrating 3,5-connected networks.[19] (6,3) Ag(tcm) sheets are still present; however, in this case they are planar and do not occur in interpenetrating pairs. Ag(tcm)(dabco) has an identical topology; however, in this structure the larger steric bulk of the dabco ligands results in quite long Ag−N(tcm) interactions. Ag(tcm)(bipy) also has the same topology, but the longer length of the bipy bridge results in the partial collapse of the network in order to maintain maximum packing efficiency. An even longer bridging ligand is used in Ag(tcm)(bpe); however, this results in a completely different structure based on pairs of Ag(bpe) chains bridged by tcm anions into a ladderlike motif. These ladders are then interconnected by weak Ag−tcm and $\pi-\pi$ interactions.

The doubly interpenetrating (6,3) sheet substructure of Ag(tcm) can be regenerated by using a bulky bridging ligand, as in $Ag(tcm)(phz)_{1/2}$.[19] This ligand disfavors the Ag(tcm)(pyz) structure for two reasons. Bulky ligands prefer lower metal coordination numbers (the silver is tetrahedral in $Ag(tcm)(phz)_{1/2}$ and trigonal bipyramidal in Ag(tcm)(pyz)),

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(33) (a) Michelet, A.; Viossat, B.; Khodadad, P.; Rodier, N. *Acta Crystallogr., Sect. B* **1981**, *37*, 2171. (b) Carlucci, L.; Ciani, G.; Gudenberg, D. W. v.; Proserpio, D. M.; Sironi, A. *Chem. Commun.* **1997**, 631.

(34) (a) Zheng, S.-L.; Tong, M.-T.; Yu, X.-L.; Chen, X.-M. *J. Chem. Soc., Dalton Trans.* **2001**, 586. (b) Zheng, S.-L.; Tong, M.-L.; Tan, S.-D.; Wang, Y.; Shi, J.-X.; Tong, Y.-X.; Lee, H. K.; Chen, X.-M. *Organometallics* **2001**, *20*, 5319. (c) Tong, M.-L.; Zheng, S.-L.; Chen, X.-M. *Chem. Commun.* **1999**, 561. (d) Bertelli, M.; Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Mater. Chem.* **1997**, *7*, 1271. (e) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Inorg. Chem.* **1997**, *36*, 1736. (f) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 12861. (g) Mak, T. C. W. *Inorg. Chim. Acta* **1984**, *84*, 19.

and the interpenetration of the two nets in Ag(tcm)(pyz) is such that the pyz bridging ligand of one net passes through $Ag_3(tcm)_3$ rings of the second; if the bridging ligand is too bulky to pass comfortably through this ring, then an alternative structure will be formed. This indeed was also the case when the sterically larger Mepyz and Me_4pyz ligands were used, although the structures formed were different from that formed with phz. $Ag(tcm)(Mepyz)_{3/2}$ formed a ladderlike motif, while $Ag(tcm)(Me_4pyz)_{1/2}$ formed sheets of Ag(tcm) "tubes" bridged by the Me_4pyz ligands. It is interesting to note that the relatively bulky ligands (phz, Mepyz, Me_4pyz) were the only ones to generate structures which did not have the general formula Ag(tcm)(L). Finally, the use of hmt, which, unlike the other bridging ligands used, can coordinate to more than two metal ions, gave a structure (Ag(tcm)(hmt)) which had the same topology as the Ag(tcm)(L), L = pyz, dabco, bipy, networks (although it was not interpenetrating). In this structure, however, the hmt acts as the 3-connecting ligand, generating the (6,3) sheets, and the tcm acts as the 2-connecting ligand bridging the sheets.

Three of the structures (dabco, bipy, and bpe) could easily be described in terms of AgL linear chains being the dominant structural motif, with weaker Ag−anion interactions also being present. Champness, Schröder, et al.[35] have extensively studied interchain interactions in such 1D structures, although only the bpe structure reported here has any significant interchain supramolecular interactions. The chains in this structure are arranged in pairs with offset face-to-face aromatic interactions and possibly weak Ag···Ag interactions being present.

The tcm anions show two main bonding modes in the structures in this series: μ_2 in the bpe, Mepyz, and hmt structures, and μ_3 in the parent Ag(tcm) structure and in the MeCN, pyz, dabco, bipy, phz, and Me_4pyz structures. Similarly, the silver shows two common coordination geometries: tetrahedral (Ag(tcm) and the MeCN, phz, Mepyz, and Me_4pyz structures) and trigonal bipyramidal (pyz, dabco, bipy, and hmt). In the bpe structure, however, the silver has T-shaped geometry, with weaker secondary Ag−tcm interactions, while the coordination geometry in both the dabco and bipy structures could also be described as linear with secondary weak Ag−tcm interactions generating the aforementioned trigonal bipyramidal geometry.

It is also worthwhile comparing the structures reported here with those obtained using the same bridging ligands and Cu^I, a metal ion which often shows similar coordination geometry preferences to Ag^I.[17] In contrast to the hmt, bipy, and bpe structures reported here, the structures of Cu(tcm)L, L = hmt, bipy, and Cu(tcm)(bpe)·1/4bpe·1/2MeCN all contain 2D (4,4) networks constructed using μ_2 ligands.

Conclusions

In conclusion, we have seen that a rich structural chemistry can be obtained from reaction of the versatile and structurally malleable Ag(tcm) precursor with various terminal and bridging ligands. Although some structural trends can be seen, the structures are still reasonably unpredictable despite the fact that only one reaction component (the bridging coligand) has been varied. Nonetheless, a number of interesting new coordination polymers have been produced, including rare examples of networks containing 5-connecting nodes.

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Supporting Information Available: Atom numbering diagrams and an X-ray crystallographic file in CIF format for the seven new structures reported here. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) (a) Khlobystov, A. N.; Blake, A. J.; Champness, N. R.; Lemenovskii, D. A.; Majouga, A. G.; Zyk, N. V.; Schröder, M. *Coord. Chem. Rev.* **2001**, *222*, 155. (b) Blake, A. J.; Baum, G.; Champness, N. R.; Chung, S. S. M.; Cooke, P. A.; Fenske, D.; Khlobystov, A. N.; Lemenovskii, D. A.; Li, W.-S.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4285. (c) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117.