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# Self-assembly of supramolecular coordination polymers constructed from AgCN and bipodal spacers

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#### ABSTRACT

The syntheses and crystal structures of novel supramolecular coordination polymers (SCPs) of AgCN with bipodal ligands; 4,4'-bipyridine (bpy), *trans*-1,2-bis(4-pyridyl)ethylene (tbpe) and 1,2-bis(4-pyridyl)eth-ane (bpe) are reported. The syntheses were affected in H<sub>2</sub>O/acetonitrile/NH<sub>3</sub> media at room temperature. SCP [(AgCN)<sub>2</sub> · bpy] (1) is monoclinic and crystallizes in the space group  $P2_1/c$ , a = 9.0565(4) Å, b = 16.0063(8) Å, c = 9.1361(4) Å,  $\beta = 110.51^{\circ}$  and Z = 4. SCP [(AgCN)<sub>3</sub> · (tbpe)<sub>2</sub> · H<sub>2</sub>O] (2) is triclinic and crystallizes in the space group  $P\overline{1}$ , a = 9.8427(4) Å, b = 10.3596(4) Å, c = 14.0864(6) Å,  $\alpha = 98.873^{\circ}$ ,  $\beta = 101.739^{\circ}$ ,  $\gamma = 95.506^{\circ}$  and Z = 2. SCP [(AgCN)<sub>4</sub> · bpe] (3) is monoclinic and crystallizes in the space group  $P2_1/c$ , a = 10.1872(5) Å, b = 9.1610(5) Å, c = 14.4862(6) Å,  $\beta = 130.00(18)^{\circ}$  and Z = 2. The 3D-topol-gies of **1–3** resulted from the bridging action of the bipodal ligands and the argentophilic interactions as well as extensive H-bonding and  $\pi$ - $\pi$  stacking.

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#### 1. Introduction

Supramolecular chemistry is concerned with preparing assemblies of molecules using a combination of secondary chemical interactions rather than covalent bonding. The comparatively simple molecules used in these assembles are driven to spontaneously self-assemble, and then hold together, via such non-covalent interactions as hydrogen bonds, metal-ligand coordination interactions and  $\pi$ - $\pi$  stacking. The underlying self assembly has long been known: Fischer's lock-and-key theory of enzyme activity may be considered as their foundation store because it recognized the central role of shape and geometry in molecular interactions [1]. In fact, self-assembly processes are vital to biosynthesis in nature because they allow large complicated structures to form quickly.

Silver(I) is good candidate as a soft acid favoring coordination to soft bases such as ligands containing halogens, sulfur and nitrogen atoms. Many scientists have exploited the coordination flexibility of silver(I) in the construction of a large number of coordination polymers exhibiting interesting structural diversity [2,3]. On the other hand, although cyanide is a potential bridging ligand, its silver(I) coordination polymer not yet well documented [4,5]. Detailed structural information on AgCN was unavailable until the appearance of a report on its vibrational spectroscopy and the determination of the crystal structure using powder neutron diffraction data [6]. The AgCN structure is composed of the packing of parallel, linear (AgCN)<sub> $\infty$ </sub> chains in accordance with the *R3 m* 

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space group symmetry, and all the inter-chain Ag-Ag separations exceed 3.88 Å. Also, only a few examples of silver(I) pseudo-halide coordination polymers with nitrogen bases have been previously reported [5,7]. In an attempt to encourage the self-assembly of phases of high dimensionality from silver(I) cyanide, bipyridine (bpy), trans-bis(4-pyridyl)ethylene (tbpe) and 1,2-bis(4-pyridyl)ethane (bpe) have been used. It was felt that the potential of multiple coordination sites in ambidentate ligands would allow the linkage of metal centers through the organodiimine bridges. In addition to such chaining, it was supposed that the bpy, tbpe and bpe ligands would not be constrained to a planar conformation and subsequently allow for the interconnection of chains and propagation of the microstructure in two or three dimensions. Here we report the synthesis and structural characterization of [(AgCN)<sub>2</sub> · bpy] (1),  $[(AgCN)_3 \cdot (tbpe)_2 \cdot H_2O]$  (2) and  $[(AgCN)_4 \cdot bpe]$  (3) from the simple reaction of AgCN and the bpy, tbpe or bpe ligand in H<sub>2</sub>O/acetonitrile/NH<sub>3</sub> media at room temperature. Further, we report on the crystal packing effects, namely metal-ligand, Ag-Ag and ligand-ligand interactions, which may have an effect on the formation and stability of the SCPs 1-3.

#### 2. Experimental

All reagents were commercially available and were used as received. Microanalyses (C, H and N) were carried out with a Perkin Elmer 2400 automatic elemental analyzer. The IR spectra were recorded on a Bruker Vector 22 (Germany) spectrophotometer as KBr disks. Thermogravimetric analysis was carried out on a Shimadzu AT 50 thermal analyzer (under N<sub>2</sub> atmosphere).





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Electronic absorption spectra were measured on a Shimadzu (UV-310PC) spectrometer. Luminescence spectra were recorded using a Perkin Elmer (LS 50 B) spectrometer.

#### 2.1. Synthesis of $[(AgCN)_2 \cdot bpy](1)$

Seventy eight milligram (0.5 mmol) of bpy in 10 mL MeCN was added to 33 mg (0.25 mmol) of AgCN in 10 mL H<sub>2</sub>O. The resulting mixture was heated at about 70°, while concentrated ammonia solution was added dropwise with stirring until the solution became clear. Prismatic colorless crystals appeared after standing at room temperature for two weeks. The crystals were recovered by filtration, washed with H<sub>2</sub>O and dried in air (the yield was 65.5% with respect to AgCN).

Anal. Calcd for **1** ( $C_{12}H_8N_4Ag_2$ ): C, 33.96; H, 1.88; N, 13.20. Found: C, 33.56; H, 1.79; N, 13.46. IR (KBr, cm<sup>-1</sup>): 3048 ( $\nu_{CH}$ ), 2135 ( $\nu_{C=N}$ ), 1594 ( $\nu_{C=N}$ ), 1529, 1481 ( $\nu_{C=C}$ ), 1404, 1317 ( $\delta_{CH}$ ), 1218, 1063, 995, 803, 726, 618, 571, 471.

#### 2.2. Synthesis of $[(AgCN)_3 \cdot (tbpe)_2 \cdot H_2O]$ (2)

Ninety one milligram (0.5 mmol) of tbpe in 10 mL MeCN was added to 33 mg (0.5 mmol) of KCN in 5 mL H<sub>2</sub>O. The resulting mixture was added to 85 mg (0.5 mmol) of AgNO<sub>3</sub> in 10 mL H<sub>2</sub>O. Concentrated ammonia solution was added dropwise with stirring to the previous mixture until the solution became clear. Yellow needle crystals appeared after standing at room temperature for two weeks. The crystals were recovered by filtration, washed with H<sub>2</sub>O and dried in air (the yield was 85.6% with respect to AgNO<sub>3</sub>).

Anal. Calc. for **2** ( $C_{27}H_{22}N_7OAg_3$ ): C, 41.32; H, 2.80; N, 12.49. Found: C, 41.21; H, 2.37; N, 11.47%. IR (KBr, cm<sup>-1</sup>): 3440 ( $\nu_{H_{2}O}$ ), 3046 ( $\nu_{CH}$ ), 2117 ( $\nu_{C=N}$ ), 1601 ( $\nu_{C=N}$ ), 1555, 1498 ( $\nu_{C=C}$ ), 1421, 1349 ( $\delta_{CH}$ ), 1219, 1067, 971, 826, 669, 550, 468.

#### 2.3. Synthesis of $[(AgCN)_4 \cdot bpe]$ (3)

Ninety two milligram (0.5 mmol) of bpe in 10 mL MeCN was added to 33 mg (0.5 mmol) of KCN in 10 mL H<sub>2</sub>O. The resulting mixture was added to 85 mg (0.5 mmol) of AgNO<sub>3</sub> in 10 mL H<sub>2</sub>O and then concentrated ammonia solution was added dropwise with stirring to the previous mixture until the solution became clear. A colorless polycrystalline precipitate appeared after standing at room temperature for two weeks. The precipitate was recovered by filtration, washed with H<sub>2</sub>O and dried in air (the yield was 70% with respect to AgNO<sub>3</sub>).

Anal. Calc. for **3** ( $C_{16}H_{12}N_6Ag_4$ ): C, 26.69; H, 1.66; N, 11.67. Found: C, 27.10; H, 1.59; N, 11.44%. IR (KBr, cm<sup>-1</sup>): 3060, 2938, 2861 ( $v_{CH}$ ), 2130, 2160 ( $v_{C=N}$ ), 1600 ( $v_{C=N}$ ), 1558, 1492, ( $v_{C=C}$ ), 1453, 1416, 1339 ( $\delta_{CH}$ ), 1210, 1070, 830, 722, 610, 570 and 469.

#### 2.4. X-ray structural determination

Structural measurements for SCPs 1-3 were performed on a Kappa CCd Enraf Nonius FR 90 four cycle geniometer with graphite monochromatic Mo K $\alpha$  radiation {[ $\lambda$  Mo K $\alpha$ ] = 0.71073 Å} at 25 ± 2 °C. All the structures were resolved using direct-methods and all of the non-hydrogen atoms were located from the initial solution or from subsequent electron density difference maps during the initial stages of the refinement. After locating all of the non-hydrogen atoms in each structure the models were refined against  $F^2$ , first using isotropic and finally using anisotropic thermal displacement parameters. The positions of the hydrogen atoms were then calculated and refined isotropically, and then the final cycle of refinements was performed. The cyano groups of all structures were ordered unless otherwise stated. Crystallographic data for **1–3** are summarized in Table 1. Selected bond distances and bond

#### Table 1

Crystal data and structure refinement parameters of the SCPs 1-3.

	1	2	3
Empirical formula	C <sub>12</sub> H <sub>8</sub> N <sub>4</sub> Ag <sub>2</sub>	C <sub>27</sub> H <sub>22</sub> N <sub>7</sub> OAg <sub>3</sub>	C16H12N6Ag
Formula weight	423.944	784.101	719.794
T (K)	298	298	298
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P1	$P2_1/c$
a (Å)	9.0565 (4)	9.8431 (4)	10.1872 (5)
b (Å)	16.0063 (8)	10.3592 (4)	9.1610 (5)
c (Å)	9.1361 (4)	14.0880 (6)	14.4862 (6)
α (°)	90.00	98.873 (2)	90.00
β(°)	110.516 (3)	101.739 (2)	130.0 (18)
γ (°)	90.00	95.506 (3)	90.00
V (Å <sup>3</sup> )	1240.38 (10)	1377.54 (10)	974.01 (8)
Ζ	4	2	2
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	3.14	2.14	3.97
Calculated density (Mg $m^{-3}$ )	2.270	1.818	2.454
Goodness-of-fit on F <sup>2</sup>	2.014	2.127	1.704
F(000)	808	730	676
R indices [I>3 $\sigma$ (I)] $R_1/wR_2$	0.035/0.072	0.039/0.078	0.033/0.076
R indices (all data)	0.121/0.094	0.081-0.087	0.077/0.084
R <sub>int</sub>	0.031	0.028	0.033
Data/restraints/parameters	1370/0/163	3452/0/343	1049/0/113

Table 2	2
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Selected bond distances (Å) and bond angles (°) for SCP 1.

Ag1–C7	2.085 (3)	Ag1-Ag2 <sup>d</sup>	3.2550 (4)
Ag1–N5 <sup>a</sup>	2.570 (2)	Ag2-N6	2.249 (2)
Ag1–C8 <sup>b</sup>	2.080 (3)	Ag2–N3	2.129 (3)
Ag2-N4	2.387 (3)	N4-C8	1.127 (4)
C7-N3	1.124 (4)		
C7–Ag1–N5 <sup>a</sup>	91.26 (9)	Ag1 <sup>c-</sup> N5-C13	127.0 (2)
C7–Ag1–C8 <sup>b</sup>	164.85 (11)	Ag1 <sup>c-</sup> N5-C12	117.2 (2)
N5 <sup>a-</sup> Ag1–C8 <sup>b</sup>	103.39 (9)	Ag2-N4-C8	161.7 (3)
N4-Ag2-N6	94.86 (9)	Ag2-N6-C16	125.9 (2)
N4–Ag2–N3	110.43 (9)	Ag2-N6-C14	173.80 (11)
N6-Ag2-N3	151.13 (10)	Ag2-N6-C15	154.03 (13)
Ag1–C7–N3	163.3 (3)	Ag2-N6-C18	146.26 (13)
Ag1 <sup>c-</sup> N5-C9	154.10 (14)	Ag2-N6-C17	117.6 (2)
Ag1 <sup>c-</sup> N5-C10	170.35 (13)	Ag2-N3-C7	166.0 (3)
Ag1 <sup>c-</sup> N5–C11	144.60 (13)		
Hydrogen bonding			
Intra-layer H-bonding		Inter-layer H-bonding	
C7-H16 <sup>e</sup>	2.989 (3)	C8-H15	3.065 (3)
C7-H15 <sup>e</sup>	2.840 (3)	N3-H18 <sup>f</sup>	2.978 (3)
C7-H13 <sup>a</sup>	3.047 (3)		
N4-H13 <sup>a</sup>	2.895 (3)		
N4-H17	2.583 (3)		
N3-H16 <sup>e</sup>	2.841 (3)		
C8-H9 <sup>a</sup>	2.923 (3)		
N3-H13 <sup>a</sup>	3.031 (3)		
C17-H12 <sup>e</sup>	3.056 (3)		
C8-H17	3.033 (3)		

Symmetry codes:  ${}^{a}x - 1, 1/2 - y, 1/2+z; {}^{b}-1 - x, 1/2+y, 3/2 - z; {}^{c}1+x, 1/2 - y, z - 1/2; {}^{d}-1 - x, -y, 1 - z; {}^{e}-x, -y, 1 - z; {}^{f}x, 1/2 - y, 1/2 + z.$ 

angles are given in Tables 2–4. The C9 atom and N11 atom of the two bridging cyanide groups in **3** were located at inversion centers and were modeled as disordered over a pair of sites of equal occupancy. The disorder of these cyano groups in the asymmetric unit of **3** reflects the observation that  $R_w$  remains constant upon adopting a C atom or N atom at these sites.

#### 3. Results and discussion

The novel SCPs **1–3** exhibit variable stoichiometries. The molar ratios of AgCN:L are 2:1 for **1**, 3:2 for **2** and 4:1 for **3** in MeCN/H<sub>2</sub>O/NH<sub>3</sub> solution. It seems that self-assembly of either authentic or in situ prepared AgCN and the bipodal ligand takes place at the appropriate stoichiometry required by the extended framework

Table 3			
Selected bond distan	ces (Å) and bond	angles (°) for	SCP 2.

		()		()				
Ag1–Ag2 <sup>a</sup>		3.04	15 (5)	Ag2	-N33		2.40	09 (3)
Ag1–N4		2.49	6 (3)	Ag2	-N34	2.48	87 (4)	
Ag1-C31		2.076 (4)		Ag3	-N25		2.21	11 (4)
Ag1-C32		2.07	8 (4)	Ag3	-C26		2.06	62 (5)
Ag2-N30		2.33	0(3)	Ag3	-N33		2.71	16 (4)
Ag2-N18		2.29	4 (3)	Ag3	-N34		2.59	90 (5)
Ag2 <sup>a-</sup> Ag1-N4		117.	.89 (8)	Ag2	-N30-	C14	170	0.1 (2)
Ag2 <sup>a-</sup> Ag1-C31		74.3	9 (11)	Ag2	-N30-	C12	130	.0 (3)
Ag2 <sup>a-</sup> Ag1-C32		95.2	6 (11)	Ag2	-N30-	C13	158	.3 (2)
N4-Ag1-C31		96.8	0 (14)	Ag2	-N30-	C15	141	.8 (2)
N4-Ag1-C32		99.8	3 (14)	Ag2	-N30-	C16	114	.0 (3)
C31-Ag1-C32		163	.2 (2)	Ag2	-N18-	C22	176	5.8 (2)
Ag1 <sup>a-</sup> Ag2-N30	)	89.2	2 (8)	Ag2	-N18-	C21	148	.9 (2)
Ag1 <sup>a-</sup> Ag2-N18	5	74.8	4 (8)	Ag2	-N18-	C29	120	0.1 (2)
Ag1 <sup>a-</sup> Ag2-N33	;	138	.25 (9)	Ag2	-N18-	C23	151	.8 (2)
Ag1 <sup>a-</sup> Ag2-N34	Ļ	130	.54 (10)	Ag2	-N18-	C19	123	.7 (3)
N30-Ag2-N18		164	.01 (12)	Ag3	-N25-	C24	170	0.2 (2)
N30-Ag2-N33		93.5	6 (12)	Ag3	-N25-	C40	149	.4 (2)
N30-Ag2-N34		90.5	5 (13)	Ag3	-N25-	C38	120	.4 (3)
N18-Ag2-N33		99.1	8 (12)	Ag3	-N25-	C39	148	.5 (2)
N18-Ag2-N34		98.78 (13)		Ag3-N25-C37			122	.3 (3)
N33-Ag2-N34		91.12 (14)		Ag1-C31-N33			172	.3 (4)
N25-Ag3-C26		158.9 (2)		Ag2-N33-Ag3			92.5	56 (12)
N25-Ag3-N33		83.78 (13)		Ag2-N33-C31			148	3.6 (3)
N25-Ag3-N34		86.52 (14)		Ag3-N33-C31			118	3.0 (3)
C26-Ag3-N33		109.8 (2)		Ag1-C32-N34			176	5.8 (4)
C26-Ag3-N34		110.7 (2)		Ag2-N34-Ag3			93.8	37 (13)
N33-Ag3-N34		82.38 (11)		Ag2-N34-C32			132	.8 (4)
Ag1-N4-C9		172.	.6 (2)	Ag3-N34-C32			132	.5 (4)
Ag1-N4-C6		118.4 (3)		Ag3-C26-N27			176	i.0 (5)
Ag1-N4-C5		124	.6 (3)	Ag1-N4-C8			152	.6 (2)
Ag1-N4-C7		146	.8 (2)	U				
Intra-laver H-l	onds	1	Nater H-bonds			Inter-laver I	H-bor	nds
C31-H6	2.878 (4)	(	7–H35A	2.710	(4)	C37-H37 <sup>c</sup>	3.0	061 (4)
C31-H37	2 982 (4)	(	15-H35B	3 0 3 7	(4)	C26-H13	3 (	)53 (5)
N33-H16	3 008 (4)	1	N27-H35A	2,809	(5)			(-)
N34-H16	2,952 (4)	1	N27-H35B	2,839	(5)			
N34-H38	2,862 (5)	1	N27-H35B <sup>b</sup>	2.847	(4)			
N27-H13	2,945 (6)	. (	)35-H11	2,770	(4)			
C26-H16	2,955 (5)	Ċ	035-H17 <sup>b</sup>	2,735	(4)			
N30-H29 <sup>c</sup>	2.812 (3)	(	)35-H7	2.689	(4)			
C12-H19 <sup>b</sup>	3 045 (4)	(	)35-H15	2,490	(4)			
C17-H23 <sup>b</sup>	2.865(4)	,		2.150	(-)			
C14-H23 <sup>b</sup>	2,729(4)							
C. I 1123	2.725 (4)							

Symmetry codes:  ${}^{a}1 - x, -y, 1 - z; {}^{b}-x, -y, -z; {}^{c}1 - x, -y, -z.$ 

#### Table 4

Selected bond distances (	Å)	and	bond	angles	(°)	) for	SCP	3
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1-2 64	2 021 (2)	4.1.4.2	2.0505 (4)
Ag2–C4	3.031 (3)	Ag1-Ag2	3.0565 (4)
Ag2–C9	2.060 (4)	Ag1–N3	2.253 (3)
Ag2-N11	2.068 (3)	Ag1–C4	2.064 (4)
Ag1–N8 <sup>a</sup>	2.301 (4)		
Ag2–Ag1–N3	125.84 (7)	Ag1-C4-N8	177.9 (3)
Ag2–Ag1–C4	69.52 (9)	Ag1 <sup>a-</sup> N8-C4	152.0 (3)
Ag2–Ag1–N8 <sup>a</sup>	71.35 (7)	Ag2–C9–C9 <sup>b</sup>	178.1 (5)
N3-Ag1-C4	139.58 (11)	Ag2-N11-N11 <sup>c</sup>	176.8 (5)
N3–Ag1–N8 <sup>a</sup>	96.94 (11)	Ag1-N3-C5	122.6 (2)
C4–Ag1–N8 <sup>a</sup>	123.10 (12)	Ag1-N3-C7	121.6 (2)
C9-Ag2-N11	165.58 (14)		
Hvdrogen bonding			
C6-H5 <sup>d</sup>	2,918 (3)		
C7 1112d	2.064(2)		
С/-піз	5.004 (5)		
N8-H7ª	2.813 (3)		

Symmetry codes: a-x,1/2+y,-1/2-z; b-x,-y,-1-z; c1-x,-y,-z; d1-x,1/2+y,1/2-z.

structure to adopt enough space demanded by the bipodal bridging ligand. The increased ratio of AgCN as the size specificity of the bridging ligand is increased can be considered as an essential requirement for the construction of unique  $(AgCN)_n$  building blocks which create extended networks suitable for accommodat-

ing such long bridging ligands. In addition, these ligands behave as non-rigid spacers which are capable of displaying a variety of conformations. SCPs **1–3**, which are prepared at room temperature, can be also considered as unprecedented SCPs that may be compared with those prepared by hydrothermal reactions, described for  $[(CuCN)_2, \mu$ -L] with L = bpy and tbpe [8] and  $(CuCN)_2$  [ $(CuCN)_2(\mu$ -4,4'-bpy)] [9]. Hydrothermal reactions, in spite of being exploited to prepare numerous SCPs, afford mostly the formation of mixtures of undesirable materials. The present procedure, in spite of being surprisingly simple, affords the formation of precipitates of **1–3** which consist exclusively of one discrete species and never of mixtures of different assemblies.

#### 3.1. Crystal Structures

#### 3.1.1. Crystal structure of $[(AgCN)_2 \cdot bpy](1)$

The asymmetric unit of **1** contains one fragment which consists of two silver atoms, two cyanide groups and one bpy molecule, Fig. 1a. The two silver atoms assume a distorted trigonal planar geometry where each is coordinated to two ordered cyanide groups and to the nitrogen atom of the bpy ligand. The two silver atoms are crystallographically different. Ag1 is strongly bonded to the cyanide groups, Ag1–C = 2.08 Å, but it is weakly coordinated to the bpy ligand, Ag1–N5 = 2.570 Å, which in spite of being weak is only slightly longer than those of previously reported silver complexes [5,7]. In this case the bpy ligand is at right angles to the C7–Ag1–C8 plane, N5–Ag1–C7 = 91.26°. On the other hand, whereas the Ag1–C distances are in the normal range, the bonds from the nitrogen atoms of the cyanide ligands to Ag2 are second-



**Fig. 1.** (a) ORTEP plot of the asymmetric unit of **1**. (b) Structure of the 2D-layer of **1** along the diagonal of the unit cell. H-atoms have been omitted for clarity.

ary with a much longer range of distances, Ag2-N = 2.129-2.387 Å, while the Ag2-N6(bpy) bond is relatively strong with a distance equals to 2.249 Å. The extended structure of **1** consists of infinite puckered 1D-AgCN chains exhibiting a wave-like structure with a separation distance between the successive chains of 5.8093 Å, Fig. 1b. The wave-like appearance of the individual [AgCN]<sub>∞</sub> chains results not only from the wide N(C)-Ag-C(N) angles at Ag1 and Ag2 (C7-Ag1-C8 = 164.85° and N3-Ag2-N4 = 110.43°) but also from the pronounced deviation from linearity for N3-C7-Ag1 = 163.3°, C7–N3–Ag2 = 166.0° and C8–N4–Ag2 = 161.7°. This deviation from linearity at the silver atoms in the  $[AgCN]_{\infty}$  chains is in order to allow the coordination of the silver ions with the bidentate organodiimine ligand. These puckered chains are connected in a unique way by the bpy ligand via the Ag1 and Ag2 atoms creating corrugated 2D-layers with two types of fused rectangular rings; the first one consists of Ag<sub>8</sub>(CN)<sub>6</sub>(bpy)<sub>2</sub> with dimensions of  $6.804 \times 23.39$  Å, while the second ring consists of  $Ag_4(CN)_2(bpy)_2$  with dimensions of  $6.526 \times 12.142$  Å, Fig. 1b. Analogous connectivity patterns in which infinite [CuCN]<sub>∞</sub> chains are bridged by bpy have also been reported for [(CuCN)<sub>2</sub>(µ-4,4'bpy)], [{CuCN( $\mu$ -4,4'-bpy)}·2( $\mu$ -4,4'-bpy)] [8,10] and (CuCN)<sub>2</sub>  $[(CuCN)_2(\mu-4,4'-bpy)]$  [9]. Interestingly, only one type of hexagonal ring,  $\{Cu_4(CN)_4(bpy)_2\}$ , exists in the sheets forming the lamellar structure of  $[(CuCN)_2(\mu-4,4'-bpy)]$ , which differs however from those realized in 1. Also, the layer's structure is stabilized by extensive H-bonding between the cyanide groups and hydrogen atoms of the bpy ligands, 2.583-3.056 Å, Table 2. The corrugated layers are arranged in parallel positions along the *b*-axis with a separation distance of almost 3.901 Å, creating channels, Fig. 2. These corrugated layers are interwoven along the *c*-axis causing stacking of the layers via interconnections of Ag-Ag interactions, Ag1-Ag2 = 3.2548 Å, meanwhile they are further packed by hydrogen bonding, N3–H18<sup>d</sup> = 2.975 Å and C8–H15 = 3.056 Å, and  $\pi$ – $\pi$ stacking, 3.120-3.379 Å, creating a novel 3D-network structure, Figs. 2 and 3. The Ag-Ag bonding interactions look like pillars between the layers. The argentophilic interaction as well as the close inter-layers Ag2-N5 and Ag1-N4 contacts of 3.120 and 3.236 Å. respectively, cause pyramidalisation of the silver atoms in such way that the angles of the planar trigonal geometry around the silver sites deviate significantly from 120° in spite of the sum of the angles being 360°, Table 2. Such behavior is also observed for Cu(I) in CuCN complexes [8].

#### 3.1.2. Crystal structure of $[(AgCN)_3 \cdot (tbpe)_2 \cdot H_2O]$ (2)

The reaction of the ternary system AgNO<sub>3</sub>, tbpe and KCN in H<sub>2</sub>O/ MeCN/NH<sub>3</sub> media affords yellow needle crystals of  $[Ag_3(CN)_3(\mu-tbpe)_2 \cdot H_2O]$ , (**2**). One molecule of **2** comprises the asymmetric unit of the structure which consists of two independent fragments containing three chemically and crystallographically different Ag(I)



Fig. 2. 3D-dimensional structure of 1 showing the argentophilic interaction. Hatoms have been omitted for clarity.



**Fig. 3.** 3D-structure of **1** along the *c*-axis showing the interwoven layers. H-atoms have been omitted for clarity.

atoms, Fig. 4a. The Ag(I) atoms are coordinated to ordered cyanide groups in a unique way representing the main building blocks of the structure of 2. These building blocks form parallel ribbons connected by the tbpe ligands via silver atoms, Fig. 4b. Ag2 and Ag3 atoms are coordinated in tetrahedral fashion, while Ag1 atom exhibits a distorted planar trigonal configuration. Ag1 is strongly coordinated to two cyanide groups, Ag1-C31 = 2.076 Å, Ag1-C32 = 2.078 Å, and one nitrogen atom of the tbpe ligand, Ag1–N4 = 2.496 Å. The angles of the trigonal configuration at Ag1 assume a large deviation from the ideal value of 120° causing substantial pyramidal distortion which results essentially from the strong argentophilic interaction between Ag1 and Ag2. Table 3. The Ag2 atom exhibits a tetrahedral configuration via coordination to two cyanide groups and two tbpe ligands. On the other hand, the Ag3 atom assumes a strong coordination to the nitrogen atom of the tbpe ligand, Ag3–N25 = 2.211 Å, and to one cyanide group, Ag3–C26 = 2.062 Å, while it is weakly coordinated to the other cyanide groups that complete the distorted tetrahedral surroundings, Ag3–N33 = 2.716 Å, Ag3–N34 = 2.590 Å. The tetrahedral geometry around Ag3 is more distorted than that around Ag2 in consequence of the small chelate angles of 82.38° and 91.120°. In this case, two cyanide groups are asymmetrically bonded to three silver atoms, resulting in the µ<sub>3</sub>\_CN coordination mode forming a quadro minicycle  $[Ag_2(\mu_3-CN)_2]$  motif, Fig. 5, similar to that found in the prototype CuCN coordination polymers [11].

Alternatively, the  $(AgCN)_{\infty}$  building blocks create unusual parallel infinite ribbons which consist of fused hexagonal rings,  $Ag_4(CN)_2$ , with two double edge sides of the quadro minicyle  $[Ag_2(\mu_3-CN)_2]$ motifs, Figs. 4b and 5. Surprisingly, the ribbons contain free terminal cyanide unit at Ag3, Ag3–C26–N27 = 176.0°. Four cyanide angles exhibit significant deviation from linearity, Ag2–N34–C32 = 132.8°, Ag2–N33–C31 = 148.6°, Ag3–N33–C31 = 118.0°, Ag3–N34–C32 = 132.5°, while the other Ag1–CN bonds are nearly linear, Table 3. The cyanide ligands turn out to be free of any disordered. **2** is the first example containing the minicycle  $[Ag_2(\mu_3-CN)_2]$  motif, thus a comparison to CuCN complexes containing a similar type of the unusual minicycle  $[Cu_2(\mu_3-CN)_2]$  motif is particularly pertinent. The minicycle  $[Cu_2(\mu_3-CN)_2]$  motif is now realized as being the basic building block of an increasing number of 2D or 3D supramolecular assemblies [11,12]. The unusual character of the  $[Cu_2(\mu_3-CN)_2]$  motif



Fig. 4. (a) ORTEP plot of the asymmetric unit of 2. (b) Structure of the layer of 2 along the *b*-axis showing the parallel ribbons. H-atoms have been omitted for clarity.



**Fig. 5.** View of the  $(AgCN)_n$  ribbon showing the minicyclic  $[Ag_2(\mu_3-CN)_2]$  motif along the *c*-axis.

comes from the fact that the carbon atoms bridge two copper atoms while the nitrogen atoms coordinate to one copper atom. In contrast, the nitrogen atoms in the  $[Ag_2(\mu_3-CN)_2]$  motif act as  $\mu_2$ -bridges, as should be expected. However, while the bifurcation of cyanide groups is no longer unusual, it greatly exceeds that in CuCN SCPs [12], while the Ag–N distances are not equal leading to the formation of a distorted rhombus with the sum of the internal angles being quite close to 360°, scheme 1. The bifurcated cyanide ligands can

be considered as a consequence of the formation of the quadro minicycle  $[Ag_2(\mu_3-CN)_2]$  motifs. Also, the  $(AgCN)_{\infty}$  building blocks create a cluster-like structure consisting of three silver atoms exhibiting a strong Ag1–Ag2 interaction with a distance of 3.0145 Å and a weak Ag2–Ag3 interaction with a distance of 3.715 Å. Examples of weak Ag–Ag interactions with intermetallic distances from 3.40 to 3.724 Å are known [13]. The parallel ribbons are connected in a unique way by the tbpe molecules. One set of three nearly parallel tbpe



Scheme 1. Distorted [Ag<sub>2</sub>(µ<sub>3</sub>-CN)<sub>2</sub>] rhombus in 2.

ligands, with separation distances of 3.617–3.81 Å, and one tbpe ligand lying at right angles to the other ligands and to the plane defined by the  $(AgCN)_n$  ribbon connect these ribbons in an alternate

manner along the *a*-axis forming layers, Fig. 6. These layers contain polygons with dimensions of  $9.843 \times 14.602$  Å. On the other hand, one type of the tbpe molecules fill the space of the hexagonal rings along the *c*-axis, alternatively one being vertical while the other one is horizontal, Fig. 7. The second type of tbpe ligands intermingle around both sides of the ribbon in horizontal positions while the terminal cyanide groups are directed to the space between the layers which form the 3D-network structure of 2, Figs. 6 and 7. The structure of the layer is also stabilized by a wide range of intra-layer hydrogen bonding between the cyanide groups and the H-atoms of the pyridyl rings, 2.729-3.045 Å, Table 3. These parallel layers exhibit large channels in which water molecules thread, acting as guest molecules. The water molecules play an essential role in connecting the layers as they thread along the sides of the layers, H-bonding with the terminal cyanide groups belonging to one layer, tbpe ligand in the same layer and with the terminal cyanide groups of the adiacent layer, Table 3 and Fig. 6. This was further confirmed by TGA as SCP 2 starts decomposition by the loss of water molecules between 120 and 160 °C. The layers close packing was also achieved by weak but not negligible inter-layer hydrogen bonding, C37-H37<sup>d</sup> = 3.061 Å and C26–H13 = 3.053 Å, as well as  $\pi - \pi$  stacking interactions between the pyridyl ring of tbpe from one layer and the ethylenic group from the adjacent layer, C10–C7 = 3.394 Å.

#### 3.1.3. Crystal structure of $[(AgCN)_4 \cdot bpe]$ (3)

Half of the formula unit comprises the asymmetric unit of the structure of **3**, which contains two crystallographically different silver atoms, two cyanide groups and half of a bpe molecule, Fig. 8. Ag1 is coordinated to two ordered cyanide groups and to the nitrogen atom of the bpe ligand. Ag1 assumes a distorted trigo-



Fig. 6. View of packing of 2 along the *a*-axis showing H-bonding through water molecules.



Fig. 7. View of one layer of 2 along the *c*-axis. H-atoms have been omitted for clarity.

nal planar geometry with the sum of bond angles equal to  $360^\circ$ , Table 4. The substantial pyramidal distortion of the essentially trigonal planar coordination sphere results mainly from the argentophilic interaction between Ag1 and Ag2, Table 4. Ag2 is coordinated to two disordered cyanide groups where it adopts a quasi-linear geometry, N(C)-Ag2-N(C) =  $165.58^\circ$ . This loss of linearity results from close Ag1-Ag2 and Ag2...C4 (3.031 Å) contacts.

The structure of **3** consists of two types of  $(AgCN)_n$  chains, Fig. 9a and b. The first type, which runs in the ac-plane, is nearly linear and is composed of  $\{Ag2-CN\}_n$  fragments. The second type,



Fig. 8. ORTEP plot of the asymmetric unit of 3.

that runs along the *b*-axis, consists of corrugated chains of  $\{Ag1CN\}_n$  and exhibits a wave-like structure with a separation distance between the chains of 11.132 Å. These chains are interconnected by the bpe ligands creating a 3D-network structure, while the two types of  $(AgCN)_n$  chains are interconnected by the argentophilic interaction, Fig. 10. On the other hand, the 3D-structure is stabilized by extensive  $\pi$ - $\pi$  stacking between the cyanide groups at both of the silver atoms and the pyridyl rings, 3.03 and 3.756 Å, and H-bonding between hydrogen atoms of the pyridyl rings and the cyanide groups at the silver atoms, 2.813, 3.159, 2.975 and 3.228 Å. The directions of propagation of the two chains are perpendicular to each other along the *a*-axis, Fig. 9b. The planes of the pyridyl rings are completely parallel in each set of the spacer ligands along the *b*-axis, while in the ac-plane each two sets of the spacer bpe ligands are interwoven in different conformations to accommodate a box-like structure of dimensions 9.161 × 11.132 Å, of intersecting  $(AgCN)_n$  chains, Fig. 11.

#### 3.2. Electronic absorption spectra and emission spectra of SCPs 1-3

The electronic absorption spectra of SCPs **1–3** display, generally, the absorption bands of the bipodal ligands in addition to the CT bands, Table 5. The bands due to  $n-\pi^*$  transitions of the bipodal ligands disappear in the spectra of SCPs **1–3** due to the participation of the bipodal ligands in the coordination sphere of the silver(I) ions. The absorption spectra of SCPs **1** and **2** exhibit an additional broad band at 301–350 nm, respectively, corresponding to



Fig. 9. (a) View of the basic building block of 3. H-atoms have been omitted for clarity. (b) View of the connection of (AgCN)<sub>n</sub> chains in 3 to form a 3D-network, neglecting the bpe ligand.



Fig. 10. View of the 3D-framework of 3 showing the argentophilic interaction. Hatoms have been omitted for clarity.

metalto-ligand charge transfer (MLCT), where the charge is transferred from the silver(I) center to the unoccupied  $\pi$ -orbital of the ligand. The emission spectra of the SCPs **1–3** together with the emission spectra of the bipodal ligands were measured in the solid state at room temperature and using the same excitation wavelength in each case, Fig. 12, Table 5. The emission spectra of the bipodal ligands display structural bands which correspond to the lowest ( $\pi$ – $\pi^*$ ) and close lying (n– $\pi^*$ ) states. On the other hand, the emission spectra of SCPs **1–3** display the structural bands of the bipodal ligands as well as additional bands at 600–640 nm, 584–624 nm and 600 nm, respectively. These bands may be attributed to MLCT or metal centered transitions of the type 4d<sup>10</sup>  $\rightarrow$  4d<sup>9</sup> 5s<sup>1</sup> and 4d<sup>10</sup>  $\rightarrow$  4d<sup>9</sup> 5p<sup>1</sup> on the silver(I) center. The emission spectra of SCPs **1–3** exhibit a slight red shift compared to those of the corresponding ligands, whereas the intensities of the bands of SCPs **2** and **3** increase significantly from those of the ligands.

#### 3.3. Thermogravimetric analysis of SCPs 1-3

The thermal decomposition bahaviour of SCPs **1–3** show broad similarity, but they are not identical, Table 6. They show the usual trend of similar early reported compounds [14]. Firstly dehydration occurs, followed by loss of the bipodal ligand and finally removal of the inorganic anions. After complete thermolysis the calculated and observed percentages of the residues are coincident with metallic silver. The loss of water molecules at 120–160 °C, for SCP **2**, confirms the involvement of the water molecules in hydrogen bonding with the cyanide groups, as depicted in the crystal structure (vide supra). The cyanide groups are lost in the form of cyanogen molecules at relatively high temperatures, indicating the bridging capability of the cyanide groups forming stable (AgCN)<sub>n</sub> frameworks.

#### 4. General discussion

The SCPs **1–3** illustrate the rich diversity of structures that can be achieved by variation of the spacer bipodal ligand. The length and the molecular conformation of the spacer ligands affect significantly the self-assembly of the  $(AgCN)_n$  building blocks to produce enough wide space to accommodate the spacer ligands via the formation of different rings and polygons. The bipodal ligands play the role of bridging the  $(AgCN)_n$  building blocks creating 2D-layers which are interwoven, 1 and 2, or intersecting, 3, to produce 3Dstructures via extensive H-bonding and  $\pi$ - $\pi$  stacking, as well as Ag $\cdots$  Ag interactions. The structures of **1** and **2** are completely different from those of the analogous  $[(Cu_2(CN)_2(u-4.4'-bpv)], 1']$  and  $[(CuCN)_2(\mu-tbpe)]$ , 2'. 1 exhibits an intervoven but non-interpenetrating open framework while 1' contains two identical non-intersecting but interpenetrating frameworks with a rhombic  $(Cu_2X_2)$ motif. In spite of both **2** and **2**' containing the minicycle  $(Cu_2X_2)$ and  $(Ag_2N_2)$  motifs, 2' contains large void spaces in the framework which results in interpenetration by a second independent framework, while **2** contains a cluster-like structure of  $(AgCN)_n$  ribbons which are connected in a unique way by the tbpe ligands creating



Fig. 11. View of the box-like structure in 3.

#### Table 5

Absorption and emission bands for bpy, tbpe, bpe and SCPs 1-3.

	Ligand			SCP			
	λabs (nm)	Assignment	λem (nm)		λabs (nm)	Assignment	λem (nm)
bpy	218 278 390	<sup>1</sup> L <sub>a</sub> <sup>1</sup> L <sub>b</sub> <i>n</i> -π <sup>*</sup>	400 452 481 516 660	1	220 255 301	<sup>1</sup> L <sub>a</sub> <sup>1</sup> L <sub>b</sub> CT	405 428 454 484 525 600 640
tbpe	232 265 325 450	${}^{1}L_{a}$ ${}^{1}L_{b}$ $n-\pi^{*}$ $n-\pi^{*}$	390 478 529	2	220 252 350	<sup>1</sup> La <sup>1</sup> L <sub>b</sub> CT	433 454 485 524 584 624b
bpe	201 258 315 392	<sup>1</sup> L <sub>a</sub> <sup>1</sup> L <sub>b</sub> <i>n</i> -π*	401 432 452 482 522 600	3	201 268	${}^{1}L_{a}$ ${}^{1}L_{b}$	405 425 444 487 527 600b

\* b = Broad.



**Fig. 12.** Emission Spectra of SCPs **1–3**; **1** (solid line), **2** (dashed line), **3** (doted line),  $(\lambda_{ex} \text{ is } 320 \text{ nm for } \mathbf{1}, 300 \text{ nm for } \mathbf{2} \text{ and } 270 \text{ nm for } \mathbf{3}).$ 

a non-interpenetrating 3D-network with terminal cyanide ligands and threaded water molecules. The unprecedented structure of **3** consists of intersecting  $(AgCN)_n$  chains forming a box-like structure with wide voids containing the interwoven bridging bpe ligands. In **1** and **2**, the Ag1–Ag2 and Ag1–N4 (in **1**) and Ag2–C4 (in **2**) contacts produce a distorted geometry at the silver sites. The coordination versatility of the silver atom is also in evidence as quasi-linear,

Table 6					
Thermogravimetric	analysis	data	for	SCPs	1-3.

[AgNC], distorted trigonal planar,  $[AgN_3]$ ,  $[AgC_2 N]$ ,  $[AgN_2C]$ , and tetrahedral  $[AgN_4]$ ,  $[AgN_3C]$  geometries have been observed, in addition to the influence of the argentophilic interaction on the distortion of the geometry around the silver sites.

#### 5. Conclusion

The results reinforce the observation that the cyanide group is an effective bridging ligand which can link together two or three silver centers,  $\mu_2$ -1,2-CN or  $\mu_3$ -1,2,2-CN. Ligand length and flexibility affect the AgCN–ligand ratio, where the proportion of the ligand decreases as the length and flexibility of the ligand increase. It is also clear that the organic ligands may be introduced as structural components of composite inorganic–organic materials and used, in addition to conventional and unconventional interactions, to propagate 3D-topologies.

#### Appendix A. Supplementary data

CCDC 682258, 682259 and 682260 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2008.12.053.

Comp.	First step			Second step			Third step			Residue		
	Trans. temp. (°C)	$\Delta$ m% obs. (cal.)	Assig. (%)	Trans. temp. (°C)	∆m% obs. (cal.)	Assig. (%)	Trans. temp. (°C)	$\Delta$ m% obs. (cal.)	Assig.	Form. Temp. (°C)	$\Delta$ m% obs. (cal.)	Assig. (%)
1	150-300	36.5 (36.8)	1 bpy	380-480	6.00 (6.13)	0.5 (CN) <sub>2</sub>	500-700	7.0 (6.13)	0.5 (CN) <sub>2</sub> %	700	50.5 (50.1)	2 Ag
2	120-160	2.19 (2.20)	1 H <sub>2</sub> O	170-360	45.84 (46.4)	2 tbpe	450-730	9.00 (9.9)	1.5 (CN) <sub>2</sub> %	750	42.9 (41.2)	3 Ag
3	150-300	26.1 (25.6)	1 bpe	320-600	13.8 (14.4)	2 (CN) <sub>2</sub>			· /2	620	60.1 (59.9)	4 Ag

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