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Synthesis and crystal structures of three novel coordination polymers constructed from Ag(I) thiocyanate and nitrogen donor ligands

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1. Introduction

In recent years there has been considerable interest in the development of the rational synthetic routes to coordination polymers by self assembly due to their potential applications in the areas such as magnetism, nonlinear optics, electronics, catalysis and molecular topologies such as honeycomb, brick wall, grid, ladder, herringbone diamondoid polycatenanes and polyrotaxanes [1–5]. Self-assembly is heavily influenced by many factors such as the solvent systems [6], template [7,8], pH value of the solution [8] and counter ions [9]. Therefore, much work is required to extend knowledge of the relevant structural types and establish proper synthetic strategies leading to the desired species. So far, considerable attention has been paid to synthesis and characterization of adducts of silver(I) pseudo-halides with nitrogen bases [10–17]. On the other hand, polytopic ligands incorporating multiple oligopyridine metal-binding domains are important components in the development of metallosupramolecular chemistry [18,19]. The importance of these components comes from the fact that they can be used in material science and as double helical supramolecular array which is an attractive geometric motif in nature [20]. However, little research has been reported on the complexes of pseudo-halogen species in particular the thiocyanate ion with bidentate nitrogen ligands [14-17]. With its ambidextrous character the thiocyanate anion is expected to show a rich variety of coordination modes. The elements acting as hard Lewis acid form mainly thiocyanate-N complexes (isothiocyanate) while the electron rich metal acting as soft Lewis acid usually form thiocyanate-S-complexes. The M-S

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ABSTRACT

Three supramolecular coordination polymers (SCPs) [(AgSCN)₂L] {L = 4,4'-bipyridine (bpy) (1), *trans*-1,2bis(4-pyridyl)ethylene (tbpe) (2) and phenazine (phenz) (3)} have been synthesized and structurally characterized by single-crystal X-ray diffraction. Synthesis was affected in H₂O/acetonitrile/NH₃ media at room temperature. The bpy, tbpe and phenz bipodal ligands adopt different conformations which would affect the skeleton of the (AgSCN)_n building blocks that allow the interconnection of the (AgSCN)_n fragments and propagation of the network structure in three dimensions. Supramolecular interactions such as hydrogen-bonding, argentophilic interaction and π - π stacking play an important role in the assembly of these coordination polymers.

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bond length is usually longer than the M-N bonds while the M-N-C angle is approximately linear and the M-S-C is bent which in agreement with the mesomeric structure of the thiocyanate group [21]. Silver(I) is good candidate as a soft acid favoring coordination to soft bases such as ligands containing sulfur and nitrogen atoms. The simple silver(I) thiocyanate salt was suggested to have a chain structure [22], however its adducts with pyridine and other ligands have been shown to be mono- and di-meric complexes [23,24], as well as one- and two-dimensional networks containing AgSCN fragments as building blocks [25]. In this report the reactions of the ternary system; thiocyanate as a potential bridging ligand, rigid linear or angular bipodal ligands, e.g. phenz, bpy, tbpe and AgNO₃ are utilized to obtain high dimensional supramolecular coordination AgSCN polymers with unique topologies. Argentophilic interaction and formation of the minicycle Ag₂S₂ motif should result in assemblies of the 3D-networks.

2. Experimental

2.1. Materials and general methods

All the reagents for the syntheses were commercially available and employed without further purification. Elemental analysis was performed with a Perkin–Elmer 2400 automatic elemental analyzer. The IR spectra were recorded on a Brucker Vector 22 Spectrophotometer as KBr discs. Thermogravimetric analysis was carried out on a Shimadzu AT 50 thermal analyzer (under N₂ atmosphere). Electronic absorption spectra were measured on Shimadzu (UV-310PC) spectrometer. Luminescence spectra were carried out using Perkin–Elmer (LS 50 B) spectrometer.



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The SCPs **1–3**, were prepared by the same procedure under the same conditions. A solution of 85 mg (0.5 mmol) of AgNO₃ in 10 mL H₂O was being added at room temperature to the mixture of (0.5 mmol) of the bipodal ligand; L, in 10 mL MeCN and of 48 mg (0.5 mmol) of KSCN in 10 mL H₂O. White turbidity appeared then after concentrated ammonia solution was added to the hot mixture dropwise with stirring till clearness. The mixture was filtered off and the filtrate was left to stand for some days. Prismatic colorless crystals of **1** appeared after two weeks. After filtration, subsequent washing with small portions of water and MeCN and overnight drying, about 109 mg of [(AgSCN)₂ · bpy] 1 were obtained. Anal. Calc. for 1 (C12H8N4S2Ag2): C, 29.50; H, 1.63; N, 11.47. Found: C, 29.32; H, 1.60; N, 11.55%. IR (KBr, cm⁻¹): 3045w, 2117s, 2090s, 1597s, 1528m, 1409s, 1372m, 1214m, 1067m, 799s, 622s, 562m, 508s, 452w and 431w. Also, brown prismatic crystals of $[(AgSCN)_2 \cdot (tbpe)]$, **2**, were formed after two weeks and filtered off then after washed with small portions of water and MeCN and dried overnight. Ninety-six milligrams of 2

Table 1

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

	1	2	3
Empirical formula	$C_{12}H_8Ag_2N_4S_2$	$C_{14}H_{10}Ag_2N_4S_2$	$C_{14}H_8Ag_2N_4S_2$
Formula weight	488.072	514.110	512.114
Temperature (K)	298	298	298
Crystal system	monoclinic	triclinic	monoclinic
Space group	C_2/c	ΡĪ	$P2_1/c$
a (Å)	18.3525 (7)	5.9315 (2)	4.1453 (2)
b (Å)	6.2310 (3)	7.3747 (3)	20.6722 (9)
c (Å)	12.1581 (4)	9.6990 (4)	9.3478 (4)
α (°)	90.00	99.676 (2)	90.00
β (°)	99.836 (3)	106.843 (2)	110.00(18)
γ (°)	90.00	97.072 (2)	90.00
V (Å ³)	1369.89 (10)	393.59 (3)	760.36 (6)
Ζ	4	1	2
μ(Mo Kα) (mm ⁻¹)	3.16	2.75	2.85
R ₁	0.044	0.029	0.033
wR ₂	0.212	0.060	0.079
R _{int}	0.024	0.022	0.026
Data/restraints/parameters	925/0/91	1251/0/100	1085/0/106
Calculated density (mg/m ³)	2.367	2.169	2.237
Goodness-of-fit on F ²	2.506	1.026	1.316

Table 2

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

Ag1-S2	2.7742 (6)	S2-N15	2.797 (2)
Ag1–S2 ^a	3.0637 (6)	S2-C14	1.660 (2)
Ag1–N8	2.247 (2)	C14-N15	1.138(2)
Ag1–N15 ^b	2.158 (2)	Ag1–Ag1 ^a	3.2431 (5)
Ag1 ^a –S2	3.3939(6)		
S2–Ag1–S2 ^a	92.95 (2)	Ag1-S2-C14	103.06 (7)
S2–Ag1–N8	99.45 (4)	Ag1 ^a -S2-N15	94.34 (4)
S2–Ag1–N15 ^b	98.98 (5)	Ag1 ^a -S2-C14	94.73 (6)
S2 ^a –Ag1–N8	88.88 (4)	Ag1-N8-C10	153.18 (9)
S2 ^a –Ag1–N15 ^b	91.53 (4)	Ag1-N8-C12	145.15 (9)
N8–Ag1–N15 ^b	161.52 (7)	Ag1-N8-C9	125.21 (12)
Ag1–S2–Ag1 ^a	87.05 (2)	Ag1-N8-C11	170.53 (8)
Ag1-S2-N15	103.30 (4)	Ag1-N8-C13	116.99 (13)
Ag1 ^c –N15–S2	172.81 (9)	S2-C14-N15	178.9 (2)
Ag1 ^c –N15–C14	172.2 (2)		
Interlayer H-bonding			
S2–H9 ^a	2.8667 (5)		
S2–H13 ^a	3.0163 (4)		
N15-H13 ^d	2.657 (2)		
C14–H13 ^d	2.907 (2)		

Symmetry codes: (a) 1/2 - x, 1/2 - y, -z; (b) x, -y, z - 1/2; (c) x, -y, 1/2 + z; (d) 1/2 - x, -1/2 - y, -z.

were obtained. *Anal.* Calc. for **2** ($C_{14}H_{10}N_4S_2Ag_2$): C, 32.67; H, 1.94; N, 10.89. Found: C, 32.63; H, 1.97; N, 10.75%. IR (KBr, cm⁻¹): 3047w, 2925w, 2862w, 2099s, 1599m, 1419s, 1319m, 1295m, 1250m, 1207m, 980s, 827s, 754s, 552s, 448m. Brown needle crystals of **3** were formed after one week and filtered off then after washed with small portions of water and MeCN and dried overnight. Sixty-two milligrams of [(AgSCN)₂ · phenz], **3**, were obtained. *Anal.* Calc. for **3** ($C_{14}H_8N_4S_2Ag_2$): C, 32.80; H, 1.56; N, 10.93. Found: C, 32.64; H, 1.55; N, 11.09%. IR (KBr, cm⁻¹): 3048w, 3006w, 2867w, 2131s, 1513s, 1466m, 1432m, 1360m, 1119m, 905m, 823m, 748s, 654m, 594m, 439m.

2.2. X-ray structural determination

Structural measurements for the SCPs **1–3** were performed on a Kappa CCd Enraf Nonius FR 90 four cycle geniometer with graphite monochromatic Mo K α radiation {[λ Mo K α] = 0.71073 Å} at 25 ± 2 °C. All structures were resolved using direct-methods and

Table 3	
Selected bond distances (Å) and bond ang	les (°) for the SCP 2.

Ag1-S2 Ag1-S2ª	2.7534 (8)	S2-H6	2.9547 (7) 1 154 (3)
A =1 N2	2.7722(0)	C10-N5	1.154 (5)
Ag1-N3	2.248 (2)	S2-C10	1.652 (3)
Ag1–N5	2.173 (3)	Ag1–Ag1ª	3.3638 (6)
CD 4 4 CD3	105.00 (0)	1 13 03 010	00.57 (10)
52–Ag1–52"	105.00 (2)	Ag1°-52-C10	98.57 (10)
S2–Ag1–N3	103.72 (6)	Ag1–N3–C4	173.91 (12)
S2–Ag1–N5	100.08 (7)	Ag1-N3-C7	154.34 (14)
S2 ^a –Ag1–N3	95.27 (6)	Ag1-N3-C8	145.69 (12)
S2 ^a –Ag1–N5	103.02 (8)	Ag1-N3-C9	125.3 (2)
N3–Ag1–N5	144.95 (10)	Ag1-N3-C11	117.5 (2)
Ag1–S2–Ag1ª	75.00 (2)	Ag1-N5-S2	155.98 (13)
Ag1–S2–N5	96.58 (6)	Ag1-N5-C10	155.6 (2)
Ag1-S2-C10	96.37 (10)	Ag1 ^a -S2-N5	98.91 (6)
S2-C10-N5	179.1(3)		
Hydrogen-bonding			
Inter-laver		Intra-laver	
S2_H6	29547(7)	N5_H11 ^c	2027(3)
52-110 co. Uzb	2.3347(7)		2.527(3)
52-H/ ⁵	3.0761 (7)	CIU-HII ^c	2.869 (3)
N5-H7 ^b	3.202 (7)		
N5-H6 ^b	3.292 (7)		
C10–H7 ^b	2.838 (3)		
	. ,		

Symmetry codes: (a) -*x*, -*y*, 1-*z*; (b) -*x*, -*y*, -*z*; (c) 1 - *x*, -*y*, 1 - *z*.

Table 4 Selected bond distances (Å) and bond angles (°) for the SCP 3.							
Ag1-S2 S2-C6	2.6020 (8)	Ag1-N11 ^a C6-N11	2.219 (3)				
Ag1-N4	2.438 (2)	Ag1–S2 ^a	2.5942 (8)				
S2-Ag1-S2 S2-Ag1-N4 S2-Ag1-N11 ^a S2-Ag1-N4 S2-Ag1-N11 ^a N4-Ag1-N11 ^a Ag1-S2-Ag1 Ag1-S2-C6 Ag1-S2-N11 S2-C6-N11	105.82 (3) 115.69 (5) 108.30 (7) 87.82 (5) 121.83 (7) 116.26 (9) 105.82 (3) 110.23 (10) 100.18 (6) 178.5 (3)	Ag1-N4-C3 Ag1-N4-C3 ^b Ag1-N4-N4 ^b Ag1-N4-C5 Ag1-N4-C8 Ag1-N4-C8 Ag1-N4-C9 Ag1 ^c -N11-S2 Ag1 ^c -N11-S2	122.1 (2) 150.78 (12) 179.2 (2) 90.95 (10) 120.4 (2) 152.51 (11) 89.49 (10) 176.83 (13) 177.7 (3)				
Hydrogen-bonding S2–H5 S2–H10 ^b C6–H7	2.84 (3) 2.97 (3) 3.037 (3)	N11-H7 N11-H9 ^c N11-H9 ^d	3.014 (3) 2.997 (3) 2.728 (3)				

Symmetry codes: (a) x - 1, 1/2 - y, z - 1/2; (b) -x, -y, 1 - z; (c) 1 + x, 1/2 - y, 1/2 + z; (d) 1 + x, 1/2 - y, 1/2 + z.

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 the final cycle of refinements was performed. The cyano groups of all structures were ordered. Crystallographic data for the SCPs **1–3** are summarized in Table 1. Selected bond distances and bond angles are given in Tables 2–4.

3. Results and discussion

3.1. Crystal structures

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

The ORTEP plot of the novel SCP **1** shows one half of the chemical formula; Fig. 1a, while the formula unit contains two crystallographically identical silver atoms, two thiocyanate ligands and one byy ligand. Each silver atom is bound to one S atom and one N atom of two thiocyanate ligands and one N atom of byy ligand forming distorted trigonal planar geometry with N8–Ag1–N15



Fig. 1. (a) An ORTEP view of the asymmetric unit of the SCP 1. (b)View of the ribbon structure of the SCP 1 along the b-axis; H-atoms are omitted for clarity.



Fig. 2. View of the 3D-structure of the SCP 1 along the *b*-axis showing the crossing of the 2D-layers.



Fig. 3. View of the 3D-structure of the SCP 1 along the c-axis showing the Ag-Ag, Ag-S interactions and hydrogen-bonding.

angle equals to 161.52°, Table 2 and Fig. 1b. The thiocyanate ligand acts as μ_2 -1,3-ligand connecting the silver atoms, Ag1-N15 = 2.158 Å, Ag1-S2 = 2.774 Å, which are in the range of the reported values [10,14]. On the other hand, the AgNC angle is nearly linear, while AgSC angle is nearly perpendicular; Table 2. The AgSCN building blocks create infinite parallel zig-zag chains with S2-Ag1-N15 = 98.99° and Ag1-S2-C14 = 103.06°. These zig-zag chains are bridged by the bpy bipodal ligand forming extended vertical 2D-ribbons along the *b*-axis, Fig. 1b. In this case, a polygon consisting of $[(Ag_4(SCN)_2(bpy)_2]$, of dimensions of 6.096 Å × 16.632 Å, is recognized as a typical fragment of **1**. These polygons are arranged in unique way that one pyridyl ring of the bpy ligand in one polygon is parallel to another pyridyl ring of bpy in the adjacent polygon with a separation distance of 3.74 Å suggesting the presence of weak but not negligible stacking interactions, between the pyridine rings, as well as Ag $-\pi$ interaction between the silver(I) ion and the neighboring pyridyl ring; 3.695 Å; Fig. 1b. It is worth mentioned here that one pyridyl ring in each bpy ligand is tilted out of the plane defined by the other bpy ring by an angle of 43.93°. Alternatively, these ribbons can be considered as infinite non-interpenetrating 2D-layers that cross each other along the baxis via the AgSCN fragments, Fig. 2. On the other hand, each ribbon can be considered as a compressed spring along the c-axis creating a unique shape, Fig. 3.

The ribbons are arranged parallel in unique way where one layer connect two ribbons above and two ribbons below by Ag-Ag interactions; Ag-Ag = 3.242 Å and by H-bonds between H-atoms of the pyridyl rings in one layer and thiocyanate groups in the neighboring layers; H-S = 2.867 and 3.016 Å, C-H = 2.907 Å and N-H = 2.657 Å, as well as considerable contacts between Ag atoms and S2 atoms in the adjacent layers Ag-S2^a = 3.0627 and 3.393 Å forming 3D-network structure; Fig. 3. The Ag-Ag and Ag-S2 contacts cause pyramidalisation of Ag(1) sites.



Fig. 4. (a) An ORTEP plot of the asymmetric unit of the SCP **2**. (b) The basic building block of the SCP **2**; H-atoms are omitted for clarity.



Fig. 5. (a) Stair-case-like ribbon of the SCP 2 along the *a*-axis. (b) View of the 2D-layer of the SCP 2 along the *b*-axis; H-atoms are omitted for clarity.



Fig. 6. View of the layer stacking of the SCP **2** along the *a*-axis showing H-bonding and π - π stacking.



Fig. 7. (a) An ORTEP plot the asymmetric unit of the SCP **3**. (b) The basic building block of the SCP **3**; H-atoms are omitted for clarity.

3.1.2. Crystal structure of $[(AgSCN)_2 \cdot tbpe](2)$

The crystal structure of 2 consists of silver(I) thiocyanate and tbpe fragments in a 2:1 molar ratio creating a three-dimensional network formulated as ∞^3 [(AgSCN)₂ · tbpe] $\equiv \infty^3$ [Ag₂(μ_3 -SCN)₂(μ tbpe)]. The asymmetric unit of **2** consists of only one Ag(I) ion, one SCN group and half of the tbpe ligand, Fig. 4a. Each Ag(I) ion is pseudo-tetrahedrally four-coordinated by a tbpe nitrogen atom; Ag1-N3 = 2.248 Å, two thiocyanate sulfur atoms Ag1-S2 = 2.753 Å, $Ag1-S2^{a} = 2.772$ Å and one nitrogen atom of another thiocyanate ligand; Ag1-N5 = 2.173 Å, with the bond angles at the silver atom in the range of 95.27–144.95°; Fig. 4b, Table 3. The extended structure of **2** consists of infinite parallel AgSCN zig-zag chains bonded at the sulfur atom; Ag1–S2–C10 = 96.37° and contains the unusual bifurcated cyanide fragment which exhibits bent AgCN angle, where Ag1-N5-C10 = 155.6°; Table 3. Each two close parallel AgSCN zigzag chains are connected via two silver atoms and two sulfur atoms forming an array of fused polymer rings containing the unique quadro minicycle (Ag_2S_2) motif, in addition to the usual hexagonal rings of Ag₂(SCN)₂ with dimensions of 3.776 Å \times 5.577 Å; Fig. 4b. These fused rings create stair-case like ∞^{1} [Ag₂(SCN)₂] ribbons in which the minicycle (Ag_2S_2) motif represents the steps along the *a*-axis, Fig. 5a. The S–S distance in the minicycle is equal to 4.383 Å while the Ag-Ag distance is equal to 3.364 Å which is shorter than the sum of the van der Waals radii of two silver atoms (3.44 Å [26]),



Fig. 8. (a) View of the parallel zig-zag (AgSCN)_n chains showing the hexagonal Ag₃(SCN)₃ rings. (b) 3D-dimensional structure of the SCP **3** along the *a*-axis. H-atoms are omitted for clarity.

Table 5		
Absorption and emission ba	oands for bpy, tbpe,	phenz and the SCPs 1-3.

	Ligand			SCP			
	λ_{abs} (nm)	Assignment	$\lambda_{\rm em} (\rm nm)$		λ_{abs} (nm)	Assignment	$\lambda_{\rm em} ({\rm nm})$
bpy	218	${}^{1}L_{a} \gets {}^{1}A$	400	1	219	${}^{1}L_{a} \gets {}^{1}A$	430
	278	${}^{1}L_{b} \leftarrow {}^{1}A$	452		278	${}^{1}L_{b} \leftarrow {}^{1}A$	450
	390	$n-\pi^*$	481		345	CT	487
			516				528
			660				
tbpe	232	${}^{1}L_{a} \leftarrow {}^{1}A$	390	2	214	${}^{1}L_{a} \leftarrow {}^{1}A$	425
•	265	${}^{1}L_{b} \leftarrow {}^{1}A$	478		272	${}^{1}L_{b} \leftarrow {}^{1}A$	450
	325	$\pi - \pi^*$	529		352 b	CT	490
	450	$n-\pi^*$					519
							543
phenz	220	${}^{1}C_{b} \leftarrow {}^{1}A$	390	3	218	${}^{1}C_{b} \leftarrow {}^{1}A$	428
<u></u>	275	${}^{1}B_{b} \leftarrow {}^{1}A$	464		252	${}^{1}B_{b} \leftarrow {}^{1}A$	493
	340	${}^{1}L_{a} \leftarrow {}^{1}A$	490		366	${}^{1}L_{a} \leftarrow {}^{1}A$	528
	394		522		412	${}^{1}L_{b} \leftarrow {}^{1}A$	583
	414	${}^{1}L_{b} \leftarrow {}^{1}A$			442	СТ	
	510	$n-\pi^*$					

* b, broad.

indicating argentophilic interaction. The bifurcated silver-SCN fragment can be considered as a consequence of the formation of the minicycle (Ag_2S_2) motif which represents the essential building block in the structure of **2**.

These infinite parallel stair-case-like ribbons are arranged in a quasi-parallel fashion in the cell and separated by a distance of 13.606 Å. They are bridged by the tbpe ligands via silver atoms along the diagonal of the unit cell, forming infinite two-dimensional layered structure; Fig. 5b. In this case, one tbpe is directed to the space of the hexagonal ring $Ag_2(SCN)_2$ and the ethylenic moiety locates toward the quadro minicycle (Ag₂S₂) motif while the other pyridyl ring is directed to the next hexagonal ring in the adjacent stair-case chain. The bridging tbpe molecules are arranged in a parallel way with a distance between two successive tbpe ligands equal to 5.932 Å forming distorted polygon structure consisting of $[Ag_4(SCN)_2(tbpe)_2]$ with dimensions of 5.415 Å \times 18.348 Å. It is interesting that the network structure of 2 consists of adjacent parallel infinite 2D-layers which are all related by translation in the *a*-axis direction in the solid state, being stacked in an ... AAAA... fashion to build up the three-dimensional structure with the inter-layer separation of about 6.5 Å; Fig. 6. The 3D-network structure of **2** is stabilized by extensive $\pi - \pi$ stacking between the pyridyl rings, 3.360 Å, as well as hydrogen bonds between H-atoms of the ethylenic group and the sulfur atoms, 2.955 Å, and between the H-atom of the pyridyl rings and C10 of the thiocyanate group, 2.838 Å; see Table 3.

3.1.3. Crystal structure of $[(AgSCN)_2 \cdot phenz]$ (3)

The reaction of in situ prepared AgSCN with phenazine in aqueous ammonical solution affords the brown needle crystals ∞^{3} [(AgSCN)₂ · phenz], **3**. The crystal structure of **3** confirms the assignment of 2:1 stoichiometry for the silver(I) thiocyanate phenazine complex while the asymmetric unit of 3 comprises half of the formula unit, Fig. 7a. The asymmetric unit consists of one type of silver(I) which is four-coordinated assuming distorted tetrahedral geometry with angles in the range of 87.82–121.83°; Table 4. The silver site is coordinated to two sulfur atoms: Ag-S = 2.594 and 2.602 Å, a nitrogen atom of the thiocyanate ligand; Ag-N = 2.219 Å and nitrogen atom of the phenazine ligand; Ag-N = 2.438 Å, Fig. 7b. In this case, two silver atoms are bridged almost symmetrically by the S atom of the μ_3 -1,1,3-SCN ligand. The structure of **3** is best described as AgSCN infinite chains which significantly perturbed at S atom to assume zig-zag conformation arranged parallelly to the crystallographic *c*-axis, Fig. 8a. The angles of the thiocyanate ligand are almost linear while the Ag1–S2–C6 acquires bent conformation, 110.80°; Table 4. These parallel zig-zag chains are bridged by the sulfur atoms where each S atom connects two silver atoms, one from its own chain and the other silver atom is from the adjacent chain, creating 2D-sheet containing fused hexagonal rings, 4.145 Å × 7.194 Å, that adopt chair conformation leading to the formation of corrugated layers consisting of Ag₃(SCN)₃ fragments, Fig. 8a. These hexagonal rings are interwoven along the *b*-axis.

The 2D-sheets of $(AgSCN)_n$ are further linked by the planar phenazine ligands creating distorted polygons consisting of $[Ag_6(SCN)_4(phenz)_2]$ with enough space to accommodate the phenyl rings of the phenazine ligand forming 3D-network structure. It is worth noting here that the phenazine ligands as well as the thiocyanate bridges are completely parallel assuming weak stacking interactions; 3.618 Å, while hydrogen bonds with S2; 2.84 and 2.97 Å, and the CN unit; 2.728–3.014 Å; Table 4, as well as short contacts between silver atom and carbon atoms of phenz and SCN ligands, 3.347 and 3.339 Å, lead to further stabilization of the 3D-network of **3**, Fig. 8b.



Fig. 9. Emission Spectra of the SCPs **1–3**; (λ_{ex} is 300 nm for **1**, 270 nm for **2** and 300 nm for **3**).

Table 6	
Thermogravimetric analysis data of the SCPs 1–3.	

Compound	First step			Second step			Third step			Residue		
	Transition temperature (°C)	$\Delta m\%$ observed (calculated)	Assignment (%)	Transition temperature (°C)	∆m% observed (calculated)	Assignment (%)	Transition temperature (°C)	$\Delta m\%$ observed (calculated)	Assignment (%)	Formation temperature (°C)	∆m% observed (calculated)	Assignment (%)
1 2 3	180–250 200–300 150–250	32.5 (31.9) 35.5 (35.4) 35.5 (35.6)	1 bpy 1 tbpe 1 phenz	380–480 350–450 270–350	6.5 (6.5) 6.0 (6.22) 6.4 (6.19)	1 S 1 S 1 S	500–750 480–750 400–750	10.5 (10.5) 10.5 (10.1) 10.0 (10.0)	1 (CN) ₂ 1 (CN) ₂ 1 (CN) ₂	750 750 750	50.5 (50.7) 47.5 (48.1) 48.0 (48.0)	Ag ₂ S Ag ₂ S Ag ₂ S

Table 7

Geometry of the thiocyanate group in the SCPs 1-3.

Angle (°)/bond (Å)	1	2	3
Ag–N–C	172.2	155.6	177.7
Ag–S–C	103.6-94.73	96.37-98.53	110.23-100.17
S-C-N	178.9	179.1	178.5
S-C	1.660	1.652	1.652
C–N	1.138	1.154	1.150

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

The electronic absorption spectra of the ligands and the SCPs 1-**3** were measured in the solid state at room temperature as reflectance spectra. The absorption spectra of the SCPs 1-3 display, generally, the absorption bands of ligands in addition to the CT bands. Thus, investigating the absorption spectra of the bpy and tbpe ligands reveals that the spectra display mainly three absorption bands at 218–232 nm (${}^{1}L_{a} \leftarrow {}^{1}A$), 265–278 nm (${}^{1}L_{b} \leftarrow {}^{1}A$), and 325 nm $(\pi - \pi^*)$, in addition to a band at 390–450 nm $(n - \pi^*)$, Table 5. On the other hand, the spectrum of phenazine shows several bands at 220, 275, 340, 394, 414, 510 nm; Table 5. It is a matter of fact that replacement of the methine group in anthracene by nitrogen atom in phenazine ligand results in relatively little changes in the spectrum of phenazine. This is especially true due to the fact that the replacement of N for CH of anthracene occurs at positions that it does not seriously affect the symmetry of anthracene. Thus, the phenz and anthracene are isoelectronic. In spite of the fact that transition $({}^{1}C_{b} \leftarrow {}^{1}A)$ in anthracene is forbidden the $({}^{1}C_{b} \leftarrow {}^{1}A)$ band in phenz is observed at 220 nm which is surprisingly intense for a forbidden transition [27]. The band at 270 nm exhibits red shift than ${}^{1}B_{b} \leftarrow {}^{1}A$ band of anthracene [27]. The bands at 340 and 394 nm should be assigned to ${}^{1}L_{a} \leftarrow {}^{1}A$ transition, whereas the band of phenz at 414 nm should be assigned to ${}^{1}L_{b} \leftarrow {}^{1}A$ transition. The relatively low intensity band at the long wavelength side is assigned to $n-\pi^{T}$ transition. The bands due to $n-\pi^{T}$ transitions disappear in the spectra of SCPs **1–3** due to participation of the bipodal ligands in the coordination sphere of silver(I) ions. The absorption spectra of the SCPs 1-3 exhibit an additional broad band at 345, 352 and 442 nm, respectively, corresponding to metal-to-ligand charge transfer (MLCT) where the charge is transferred from the silver(I) center to the unoccupied π -orbital of the ligand.

The emission spectra of the SCPs **1–3**, Fig. 9, together with the emission spectra of their ligands were measured using the same excitation wavelength in each case. The emission spectra of the bipodal ligands display structural bands, Table 5, which correspond to the lowest (π, π^*) and close lying (n, π^*) states. On the other hand, the emission spectra of the SCPs **1–3** display structural peaks of the bipodal ligands as well as additional bands which may assigned to MLCT or metal-centered transitions of the type $4d^{10} \rightarrow 4d^9$ 5s¹ and $4d^{10} \rightarrow 4d^9$ 5p¹ on the silver(I) center. The emission spectra of the SCPs **1–3** exhibit red shift compared to those of the corresponding ligands.

3.3. Thermogravimetric analysis of the SCPs 1-3

The SCPs **1–3** are thermally stable until 150–200 °C, then after they start decomposition with the loss of ligand in the temperature range 150–300 °C, Table 6. The second decomposition step involves removal of one sulfur atom in the temperature rang 350– 480 °C, for the SCP **1** and **2** and at 270–360 °C for the SCP **3**. The third step occurs at slow rate and over relatively large temperature range, 400–750 °C, where two cyanide groups are lost as cyanogen, Table 6. Finally above 750 °C the residue is obtained which is coincident with the silver sulfide. The relatively high temperature at which the SCN groups are released supporting the bridging capability of this group forming stable (AgSCN)_n chains.

4. Conclusions

The general features of the structure of the SCPs 1-3 are the formation of AgSCN-L adducts in a 2:1 molar ratio forming 3Dnetworks containing the AgSCN building blocks connected via μ_2 -1,3-SCN in **1** and μ_3 -1,1,3-SCN in **2** and **3**. These AgSCN building blocks form zig-zag AgSCN chains which are bridged by the bipodal ligands creating polygons consisting of $[Ag_4(SCN)_2(L)_2]$; L = bpy or tbpe, and $[Ag_6(SCN)_4(phenz)_2]$. However, the parallel zig-zag chains assume different modes of interaction where in 1 they are bridged by Ag–Ag bonding interactions, in 2 via the formation of quaro minicycle Ag₂S₂ motif with weaker Ag-Ag interaction and in 3 by S atoms creating hexagonal rings which adopt chair conformation without any interaction between the silver atoms. The mode of bridging depends on the nature of the bipodal ligand, whereas the longest bipodal ligand tbpe; 9.412 Å, acquire wide space in the network structure of **2** which should be achieved by the formation of the minicycle motif and the bifurcated AgNC fragment which assumes quasi-linear fashion in 1; 172.2° while it is almost linear in 2; 177.7°. In the same direction, the AgSCN zig-zag chains are more puckered in 2 than in 1 and 3; Table 7. The S-C-N fragment tends to be linear in all cases, whereas the Ag-N-C-S fragment is quasi-linear in 1 and 3 but nonlinear in 2. On the other hand, the Ag-S distances in 1 and 2 are longer than that in molecular AgSCN (2.648 Å) [22], while they assume shorter distance in **3**. Thus, using bipodal ligands which would not be constrained to a planar conformation like bpy and tbpe which exhibit the two pyridyl rings in two parallel planes separated by ethylenic bond or the bulky planar phenazine ligand, would change the shape and geometry of the $(AgSCN)_n$ chains and allow the interconnection of chains and propagation of the microstructure in three dimensions.

Appendix A. Supplementary data

CCDC 682261–682263 contain the supplementary crystallographic data for SCPs **1–3**. 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.2009.01.005.

- [12] G.A. Bowmaker, Effendy, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 358 (2005) 4307.
- [13] M. Amirnasr, A.D. Khalaji, L.R. Falvello, T. Soler, Polyhedron 25 (2006) 1967.
- [14] F.B. Stocker, D. Britton, V.G. Young Jr., Inorg. Chem. 39 (2000) 3479.
- [15] C.-X. Ren, H.-L. Zhu, G. Yang, X.-M. Chen, J. Chem. Soc., Dalton Trans. (2001) 85.
 [16] T. Pretech, H. Hartl, Learn, Chim. Acta 258 (2005) 1170.
- [16] T. Pretsch, H. Hartl, Inorg. Chim. Acta 358 (2005) 1179.
- [17] A.A. Isab, M.I.M. Wazeer, M. Fettouhi, B.A. Al-Maythalony, A.R. Al-Arfaj, N.O. Al-Zamil, Inorg. Chim. Acta 360 (2007) 3719.
- [18] E.C. Constable, C.E. Housecroft, B.M. Kariuki, N. Kelly, C.B. Smith, Inorg. Chem. Commun. 5 (2002) 199.
- [19] R.S. Rarig Jr., J. Zubieta, Inorg. Chim. Acta 319 (2001) 235.
- [20] W.-H. Sun, T. Zhang, L. Wang, Y. Chen, R. Froehlich, J. Organomet. Chem. 689 (2004) 43. and references therein.
- [21] H. Krautscheid, N. Emig, N. Klaassen, P. Seringer, J. Chem. Soc., Dalton Trans. (1998) 3071.
- [22] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th Ed., Wily-Interscience, Singapore, 1988. pp. 940–941 (Chapter 18).
- [23] G.A. Bowmaker, Effendy, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1998) 2123. and reference therein.
- [24] C. Stockheim, K. Wieghardt, B. Nuber, J. Weiss, U. Flöurke, H.-J. Haupt, J. Chem. Soc., Dalton Trans. (1991) 1487.
- [25] J.-D. Lin, Z.-H. Li, J.-R. Li, S.-W. Du, Polyhedron 26 (2007) 107.
- [26] A. Bondi, J. Phys. Chem. 68 (1964) 441.
- [27] E.S. Stern, C.J. Timmons, Electronic Absorption Spectroscopy in Organic Chemistry, Edward Arnold Publishers Ltd., London, 1970. p. 113 (Chapter 6).

References

- J.W. Steed, D.R. Turner, K.J. Wallace, Core Concepts in Supramolecular Chemistry and Nanochemistry, John Wiley and Sons Ltd., 2007.
- [2] H.-F. Zhu, J. Fan, T.-a. Okamura, W.-Y. Sun, N. Ueyama, Cryst. Growth Des. 5 (2005) 289. and references therein.
- [3] M. Munakata, L.P. Wu, T. Kuroda-Sowa, Adv. Inorg. Chem. 46 (1999) 173.
- [4] F.-C. Liu, Y.-F. Zeng, J.-P. Zhao, B.-W. Hu, X.-H. Bu, J. Ribas, J. Cano, Inorg. Chem. 46 (2007) 1520.
- [5] Y. Song, Y. Xu, T.-W. Wang, Z.-X. Wang, X.-Z. You, J. Mol. Struct. 796 (2006) 36.
- [6] R. Robson, B.F. Abrahams, S.R. Batten, R.W. Gable, B.F. Hoskins, J. Lieu, Supramolecular architecture, in: T. Bein (Ed.), ACS, Washington, DC, 1992, p. 256.
- [7] H. Gudbjartson, K. Biradha, K.M. Poirier, M.J. Zaworotko, J. Am. Chem. Soc. 121 (1999) 2599.
- [8] M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen, S.W. Ng, Inorg. Chem. 37 (1998) 2645.
- [9] H.-L. Zhu, Y.-X. Tong, X.-M. Chen, J. Chem. Soc., Dalton Trans. (2000) 4182.
- [10] N.K. Mills, A.H. White, J. Chem. Soc., Dalton Trans. (1984) 229.
- [11] C. Pettinari, Polyhedron 20 (2001) 2755.