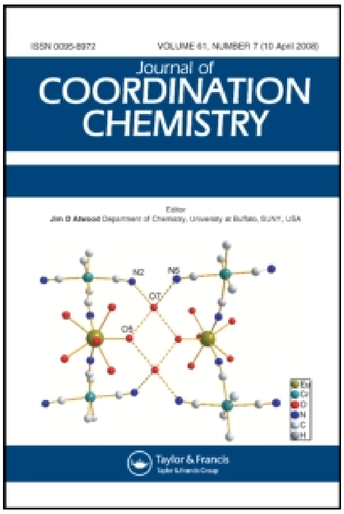

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Syntheses and structures of three coordination polymers based on 4-methylbenzenethiolates of Zn(II) and Cd(II) and bipyridine

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Syntheses and structures of three coordination polymers based on 4-methylbenzenethiolates of Zn(II) and Cd(II) and bipyridine

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Using 4-methylbenzenethiolates of Zn or Cd as precursors and 4,4′-bipyridine (4,4′-bpy) as bridges, we have synthesized three new Zn(II)/Cd(II) coordination polymers, $\{[Cd(4,4'\text{-bpy})_2(NCS)_2]\cdot 2(SC_6H_4CH_3\text{-}4)_2\}_n$ (**1**), $\{[Zn(4,4'\text{-bpy})(SC_6H_4CH_3\text{-}4)_2]\cdot DMF\}_n$ (**2**) and $\{[Zn(4,4'\text{-bpy})(SC_6H_4CH_3\text{-}4)_2]\cdot H_2O\cdot 0.5CH_3OH\}_n$ (**3**). Compound **1** is a 2-D sheet-like square polymer in which four 4,4′-bpy ligands and two isothiocyanate ligands complete the octahedral Cd(II) coordination sphere. Compounds **2** and **3** have similar coordination around Zn(II), but have different polymer structures. In **2**, Zn(II) centers are linked via a bidentate 4,4′-bipyridine to form 1-D twisted arched chains, which is a new structural type for Zn(II). Compound **3** has 1-D zigzag chains. The 2-D sheets in **1** and 1-D chains in **2** and **3** are assembled via intermolecular $C\text{–}H\cdots\pi$ and $C\text{–}H\cdots S$ interactions into 3-D supramolecular networks. $C\text{–}H\cdots S$ interactions are a vital factor in constructing the sulfur-containing coordination polymers. Different coordination modes and packing schemes in **1**–**3** show that the guest molecule has a critical influence on formation of polymers.

Keywords: Coordination polymer; Structure; Thiolate; Hydrogen bonding

1. Introduction

Considerable attention has been focused on design and synthesis of coordination polymeric networks with porous structures or open frameworks for intriguing structures, functional properties, and potential applications, such as in gas storage, molecular recognition, catalysis, and nonlinear optics [1]. Design and synthesis of Zn/Cd coordination polymers, particularly the frameworks based on bipyridines have been the topic of increasing interest [2]. As d^{10} metals, Zn^{2+} and Cd^{2+} form flexible coordination environments and their coordination geometry varies from tetrahedral to octahedral geometry [3]. 4,4′-Bipyridine and its derivatives have coordination versatility, forming 1-, 2-, and 3-D coordination networks. Coordination polymers based on Zn^{2+}/Cd^{2+} and bipyridine exhibit various structural topologies such as

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linear, zigzag chains, square grids, diamondoid, honeycomb, T-shaped, ladder, and brick wall and functional properties such as photoluminescent and nonlinear optical properties [4–8].

In constructing Zn/Cd-bipyridine polymers, sulfur-containing Zn/Cd salts such as dithiophosphates, dithiolates, and benzenethiolates react with bipyridine type ligands and their potential electrical and optical properties are of interest. For example, complexes of $[\{Zn(SPh)_2(4,4'\text{-bpy})\}_2\,\mu\text{-}4,4'\text{-bpy})]$ and $[\{Zn(SPh)_2\,\mu\text{-}4,4'\text{-bpy})\}_n]$ are potential candidates as "single-source" precursors for ZnS materials [9], while the mixed-ligand complexes of cadmium(II) dialkyldithiocarbamates with 1,10-phenanthroline, 2,2′-bipyridine, or 4,4′-bipyridine are promising precursors in the preparation of CdS films by chemical precipitation from the gas phase [10].

To further investigate properties and coordination structure of sulfur-containing polymers, we select 4-methylbenzenethiolates and 4,4-bipyridine (4,4′-bpy) as a co-ligand. The three new 1-D and 2-D Zn/Cd complexes of 4-methylbenzenethiolate and bipyridine are obtained from a similar synthetic system, namely $\{[Cd(4,4'\text{-bpy})_2(NCS)_2]\cdot 2(SC_6H_4CH_3\text{-}4)_2\}_n$ (**1**), $\{[Zn(4,4'\text{-bpy})(SC_6H_4CH_3\text{-}4)_2]\cdot DMF\}_n$ (**2**), and $\{[Zn\,(4,4'\text{-bpy})(SC_6H_4CH_3\text{-}4)_2]\cdot H_2O\cdot 0.5CH_3OH\}_n$ (**3**). The synthesis method, reactant composition, and guest molecules play a critical role in the formation of these compounds.

During the formation of coordination polymers, coordinative bonding is the primary interaction to sustain the network, but other supramolecular interactions such as hydrogen bonding and π–π stacking often play important roles to extend the coordinating network and direct the overall framework. The most common weak interactions, such as $C–H\cdots O$, $C–H\cdots N$, and $C–H\cdots\pi$ interactions, have been previously discussed [11–15], but $C–H\cdots S$ interactions have been paid less attention. Herein, we show that $C–H\cdots\pi$ and $C–H\cdots S$ interactions are vital factors for constructing and stabilizing sulfur-containing polymer networks.

2. Experimental

2.1. *General methods*

All reagents were purchased commercially and used without purification. The starting materials $Cd(SPhMe\text{-}4)_2$ and $Zn(SPhMe\text{-}4)_2$ were synthesized according to the literature procedure [16, 17]. Solvents were used as received without purification.

2.2. *Synthesis of $\{[Cd(4,4'\text{-bpy})_2(NCS)_2]\cdot 2(SC_6H_4CH_3\text{-}4)_2\}_n$ (1)*

Compound **1** was obtained as colorless plate-like crystals under solvothermal conditions. The detailed synthesis is as follows: 129 mg (0.36 mmol) of $Cd(SPhMe\text{-}4)_2$, 30 mg (0.4 mmol) of thiourea, 35 mg (0.18 mmol) of $4,4'\text{-bpy}\cdot 2H_2O$, 270 mg (15 mmol) of H_2O, and 1.67 g (40 mmol) of CH_3CN were mixed together in a 15 mL Teflon-lined stainless steel autoclave and stirred for 10 min. The vessel was sealed and heated at 150°C for 4 days. After cooling to room temperature, colorless crystals of **1** were obtained in 45% yield based on $Cd(SPhMe\text{-}4)_2$. Anal. Calcd for $C_{50}H_{44}CdN_6S_6$ (%): C, 58.08; H, 4.29; N, 8.13. Found: C, 57.47; H, 4.08; N, 8.13. IR (KBr, cm^{-1}): 3419m, 3207m, 2964m, 2921m, 2056vs, 1656m, 1602 s, 1562m, 1535m, 1489m, 1413 s, 1385 s, 1218m, 1164m, 1140m, 1072m, 1043w, 1009w, 945w, 910w, 858w, 806 s, 727w, 674w, 630 s, 569w, 507w, and 482w.

2.3. *Synthesis of* $\{[Zn(4,4'\text{-}bpy)(SC_6H_4CH_3\text{-}4)_2]\cdot DMF\}_n$ *(2)*

To prepare crystals of **2**, 175 mg (0.56 mmol) of Zn(SPhMe-4)$_2$ and 54 mg (0.28 mmol) of 4,4′-bpy · 2H$_2$O were dissolved in 4 g DMF to form a yellow solution. The solution was then layered with methanol (5 mL). After 4–6 weeks, yellow prismatic crystals were harvested. Yield: 45% [based on Zn(SPhMe-4)$_2$]. Anal. Calcd for $C_{27}H_{29}N_3OS_2Zn$ (%): C, 59.94; H, 5.40; N, 7.77. Found: C, 59.78; H, 5.44; N, 7.54. IR (KBr, cm^{-1}): 3435m, 3087w, 3060w, 3041w, 3008w, 2918w, 2860w, 1676vs, 1606s, 1535m, 1487s, 1442w, 1414m, 1385m, 1257w, 1213m, 1089s, 1066m, 1045w, 1012m, 809s, 729w, 636m, and 491m.

2.4. *Synthesis of* $\{[Zn(4,4'\text{-}bpy)(SC_6H_4CH_3\text{-}4)_2]\cdot H_2O\cdot 0.5CH_3OH\}_n$ *(3)*

To prepare crystals of **3**, 175 mg (0.56 mmol) of Zn(SPhMe-4)$_2$ and 54 mg (0.28 mmol) 4,4′-bpy · 2H$_2$O were dissolved in 6 g of a mixed DMF/CS$_2$ (weight ratio = 4 : 2) solvent to form a yellow solution. The solution was then layered with methanol (5 mL). After 4–6 weeks, yellow block crystals were obtained. Yield: 40% [based on Zn(SPhMe-4)$_2$]. Anal. Calcd for $C_{24.5}H_{26}N_2O_{1.5}S_2Zn$ (%): C, 58.62; H, 5.22; N, 5.58. Found: C, 58.49; H, 5.21; N, 5.63. IR (KBr, cm^{-1}): 3427m, 3090w, 3058w, 3038w, 3013w, 2965w, 2918w, 2858w, 1676vs, 1606s, 1535m, 1487s, 1413m, 1387m, 1319w, 1257w, 1213m, 1088s, 1066m, 1043m, 1012m, 809s, 728w, 636m, 576w, and 491m.

2.5. *X-ray crystallography*

The crystal structures of **1**–**3** were determined on a Siemens (Bruker) SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K using the ω-scan technique. Cell parameters were obtained using SMART software and refined using SAINT [18] on all observed reflections. Data were collected using a narrow-frame method with scan width of 0.30° in ω and an exposure time of 10 s per frame. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS [19]. Structures were solved by direct methods using SHELXL-97 [20]. Positions of metals and their first coordination spheres were located from direct-method E-maps; other nonhydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogens were placed in calculated positions and refined as riding with a uniform value of U_{iso}. The crystallographic data and selected bond lengths and angles are listed in tables 1 and 2, respectively.

Table 1. Crystallographic data for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{50}H_{44}CdN_6S_6$	$C_{27}H_{29}N_3OS_2Zn$	$C_{49}H_{52}N_4O_3S_4Zn_2$
Formula weight	1033.67	541.02	1003.93
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P2₁/n*	*C2/c*	*C2/c*
Unit cell dimensions (Å, °)			
a	10.6409(11)	10.651(7)	31.9666(19)
b	15.6974(17)	19.543(13)	28.474(3)
c	14.8457(16)	26.171(17)	14.3397(17)
β	94.802(2)	91.213(3)	114.194(2)
Volume (Å^3), *Z*	2471.0(5), 2	5446(6), 8	11905.6(19), 8
Calculated density [(g cm^{-3})	1.389	1.320	1.120
F(000)	1060.0	2256	4176
Absorption coefficient (mm^{-1})	0.736	1.079	0.982
Reflections collected	13,217	14,737	32,112
Independent reflections	4853	5343	11,637
Data/restraints/parameters	276	311	668
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.053$, $wR_2 = 0.117$	$R_1 = 0.056$, $wR_2 = 0.128$	$R_1 = 0.058$, $wR_2 = 0.143$
R indices (all data)	$R_1 = 0.070$, $wR_2 = 0.122$	$R_1 = 0.081$, $wR_2 = 0.133$	$R_1 = 0.090$, $wR_2 = 0.152$
Goodness-of-fit on F^2	1.058	1.040	1.068
Largest difference peak and hole (e Å^{-3})	0.32 and −0.96	0.30 and −1.36	0.26 and −0.83

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.[a]

1			
Cd1–N1	2.384(3)	Cd1–N2^{i}	2.378(3)
Cd1–N3	2.303(4)	S2–S3	2.007(2)
N3–C25–S1	179.1(4)	N3–Cd1–N2^{i}	88.72(1)
N3–Cd1–N1	91.03(1)	N2^{i}–Cd1–N1	94.05(1)
C15–S2–S3	106.37(1)	C22–S3–S2	104.39(1)
2			
N1–Zn1	2.122(3)	N2–Zn1	2.083(3)
S1–Zn1	2.2799(15)	S2–Zn1	2.3026(16)
N2–Zn1–N1	97.55(13)	N2–Zn1–S1	105.15(10)
N1–Zn1–S1	100.22(10)	N2–Zn1–S2	104.79(11)
N1–Zn1–S2	114.41(10)	S1–Zn1–S2	129.95(5)
3			
N1–Zn1	2.091(2)	N2–Zn2	2.154(3)
N3–Zn1	2.128(2)	N4–Zn3	2.0820(19)
S1–Zn1	2.2495(8)	S2–Zn1	2.2505(7)
S3–Zn2	2.2533(8)	S4–Zn3	2.2571(7)
N1–Zn1–N3	94.20(9)	N1–Zn1–S1	104.46(6)
N3–Zn1–S1	110.02(6)	N1–Zn1–S2	111.33(6)
N3–Zn1–S2	105.56(6)	S1–Zn1–S2	126.56(3)
N2^{i}–Zn2–N2	94.74(16)	N2–Zn2–S3^{i}	110.87(7)
N2–Zn2–S3	104.57(7)	S3–Zn2–S3^{i}	126.68(5)
N4^{ii}–Zn3–N4	94.08(11)	S4^{ii}–Zn3–S4	126.28(4)
N4–Zn3–S4^{ii}	110.47(5)	N4–Zn3–S4	105.42(5)

[a] Symmetry transformations for **1**: (i) $-0.5+x$, $0.5-y$, $-0.5+z$; for **3**: (i) $-x$, y, $0.5-z$; (ii) $1-x$, y, $0.5-z$.

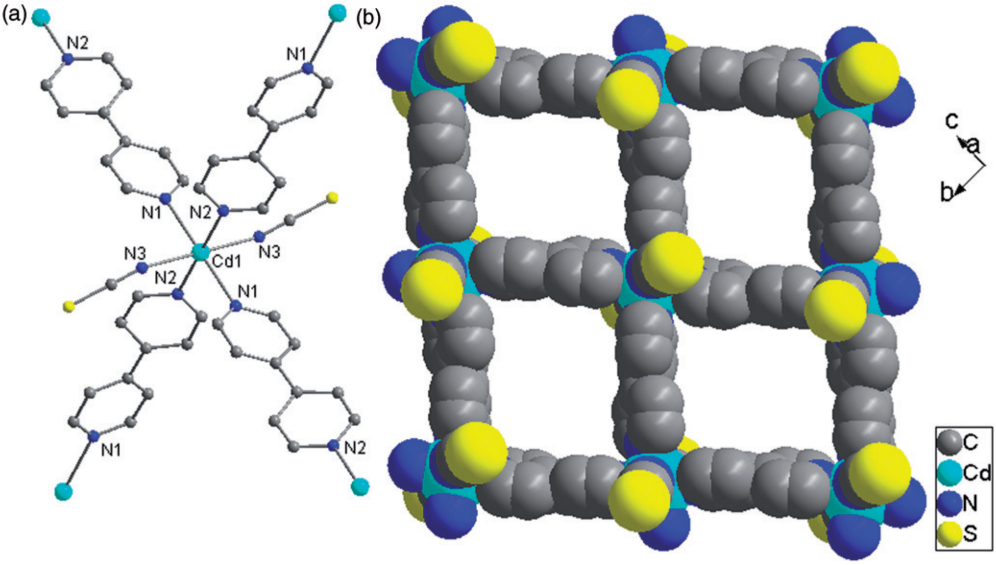

Figure 1. (a) Coordination environment of Cd and (b) 2-D grid networks in **1**. Hydrogen atoms and filling agents are omitted for clarity.

3. Results and discussion

3.1. *Description of crystal structure* $\{[Cd(4,4'\text{-}bpy)_2(NCS)_2]\cdot 2(SC_6H_4CH_3\text{-}4)_2\}_n$ *(1)*

X-ray structure analysis shows that **1** crystallizes in the monoclinic space group $P2_1/n$ with one six-coordinate Cd(II) center, four 4,4′-bpy ligands, and two monodentate isothiocyanates in the asymmetric structural unit. As shown in figure 1, Cd(II), sitting on an inversion center, is in a compressed octahedral geometry with four 4,4′-bpy ligands coordinated at equatorial positions (the Cd–N bond distances range from 2.378(3) to 2.384(3) Å), and two isothiocyanates coordinated axially through nitrogen (the Cd–N bond distance is 2.303(4) Å). The 4,4′-bpy is slightly distorted with a dihedral angle between two pyridine rings of 25.9°, while the –NCS group is almost linear with an N–C–S angle of 179.1(4)°. Connections between Cd and –NCS are bent with a C25–N3–Cd1 angle of 155.5°. Each Cd(II) links four neighboring Cd(II) centers via four bridging 4,4′-bpy, forming a 2-D noninterpenetrative grid network along the crystallographic *bc* plane (figure 1).

The square nets are stacked parallel along the *a* direction through weak interactions to construct a 3-D layer network with square channels. The square channels are slightly distorted with the N1–Cd1–N2 angles of 85.9(1)° and 94.0(1)° and ca 11.8 × 11.8 Å in diameter. The channel is filled by chair-like disulfide $(SC_6H_4CH_3\text{-}4)_2$ molecules, which twist around the 4,4′-bpy ligands via hydrogen bonding interactions. The guest disulfide and isothiocyanate were produced *in situ* from 4-methylbenzenethiolate and CH_3CN, respectively. Isothiocyanate replaced the 4-methylbenzenethiolate on Cd in **1**, indicating that 4-methylbenzenethiolate has weaker coordination ability than isothiocyanate.

The structure of **1** is different from the previously reported complex $[Cd(4,4'\text{-bpy})(SCN)_2]_n$ [21] of similar composition. In the latter, two kinds of chains cross with each

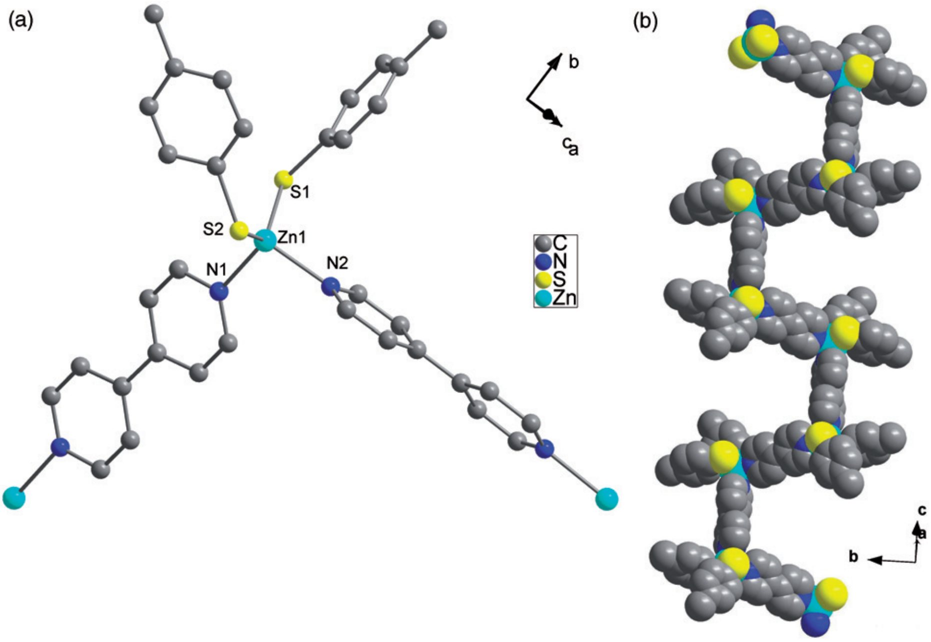

Figure 2. (a) Coordination environment of Zn and (b) 1-D twisted-arch chain in **2**. Hydrogen atoms and the filling solvent molecules are omitted for clarity.

other to construct a 2-D sheet. This structure difference may result from the different synthesis, i.e. hydrothermal condition and room temperature diffusion.

3.2. *Description of crystal structures* $\{[Zn(4,4'\text{-}bpy)(SC_6H_4CH_3\text{-}4)_2]\cdot DMF\}_n$ *(2) and* $\{[Zn(4,4'\text{-}bpy)(SC_6H_4CH_3\text{-}4)_2]\cdot H_2O\cdot 0.5CH_3OH\}_n$ *(3)*

Both **2** and **3** crystallize in the monoclinic space group *C2/c*, built from bridging 4,4′-bpy and terminal $SC_6H_4CH_3$-4 ligands. The coordination environments around zinc in **2** and **3** are very similar, but exhibit different polymeric structures. As shown in figures 2 and 3, Zn in both **2** and **3** has a slightly distorted tetrahedral coordination geometry through bonding to two nitrogens of two pyridines and two sulfurs from two 4-methylbenzenethiol. The bond angles around Zn(II) range from 97.55(13)° to 129.95(5)° in **2** and 94.08(11)° to 126.68(5)° in **3**. The Zn–S distances range from 2.2799(15) to 2.3026(16) Å in **2**, and 2.2495(8) to 2.2571(7) Å in **3**, while the Zn–N bond lengths range from 2.083(3) to 2.122(3) Å in **2** and 2.0820(19) to 2.154(3) Å in **3**. These angles and distances are similar to those found in related structures [5, 6, 9].

The difference between the two structural units is that the 4,4′-bpy ligands in **3** are coplanar (the dihedral angles between two pyridine rings range from 0.35° to 1.10°), while one of the 4,4′-bpy ligands in **2** is twisted with a dihedral angle between two pyridine ring of 26.3°. This difference results in different polymeric structures of **2** and **3**, as shown in figures 2(b) and 3(b). Complex **2** exhibits a 1-D arched chain along the *c*-axis. The twisted nonplanar 4,4′-bpy ligands in the chain cross each other

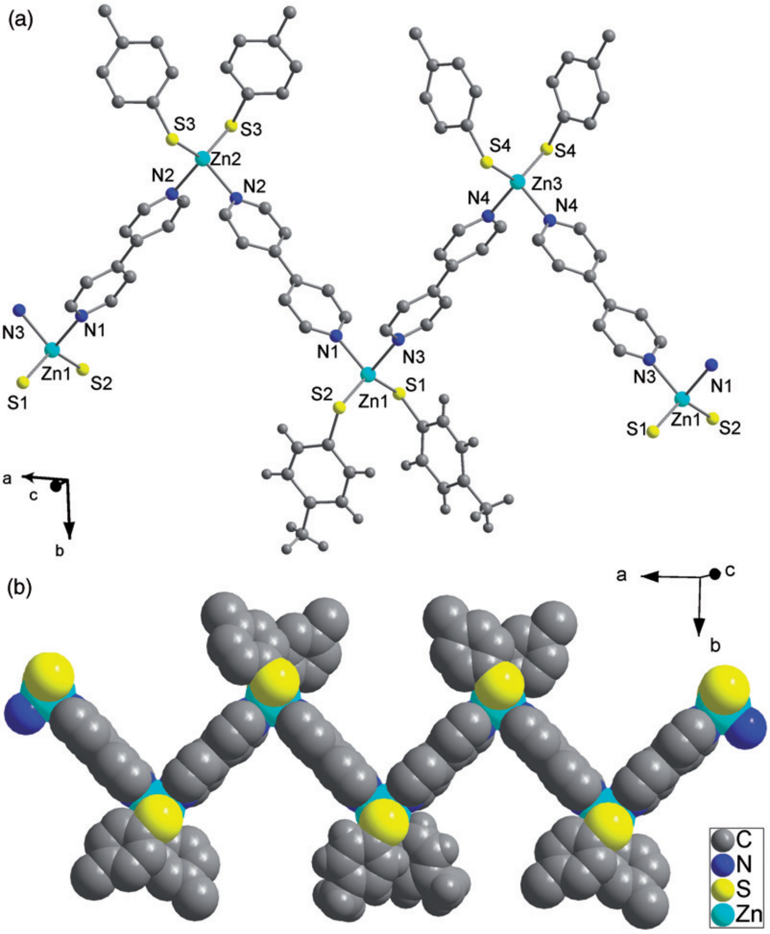

Figure 3. (a) Coordination environment of Zn and (b) 1-D zigzag chain in **3**. Hydrogen atoms and filling agents are omitted for clarity.

when viewed along the extension direction. Complex **3**, on the other hand, forms a 1-D zigzag chain along the *a*-axis. The 4,4′-bpy ligands in the chain are absolutely overlapped when viewed along the *a*-axis. At the same time, the chains in both **2** and **3** stack parallel to form a sheet, which further packs to form 3-D networks. The DMF in **2** and water and methanol in **3** fill the network as guests. The twisted-arch chain formed in **2** is a new polymeric structure of Zn(II) bipyridine complexes.

Complexes **2** and **3** were synthesized under almost the same conditions except that CS_2 was added during formation of **3**. The structure-directing effect of CS_2 on self-assembly of polymer **3** is not clear, but results in different guest molecules in the product, inducing the different structures. The reactant composition of the synthesis system and the solvent molecule in the polymer play a critical role in formation of these polymer structures. Reported complexes [9] of $Zn(SPh)_2$ coordinated with 4,4′-bpy, having zigzag structure similar to **3**, also possess different stacking structures owing to the different occluded solvent molecules.

Table 3. Weak interactions in **1**–**3**; distances (Å) and angles (°).

Interaction (D–H···A)		D···A distance	H···A distance	∠D–H···A
1				
C–H···S	H20···S1	3.852(5)	2.99	155
	H21···S1	3.830(5)	2.98	153
C–H···π	H2···ring1 (C19–24)[a]	3.587(5)	2.76	149
	H7···ring1 (C19–24)	4.259(5)	3.40	154
	H18B···ring2 (C12–17)	4.161(5)	3.22	165
	H8···π (C25)	3.470(5)	2.88	122
2				
C–H···π	H2···ring1 (C11–16)	3.710(4)	2.91	145
	H4···ring1 (C11–16)	3.931(4)	3.11	149
	H7···ring2 (C18–23)	3.581(4)	2.72	155
	H17A···ring3 (C6–10,N2)	3.877(4)	3.36	116
C–H···S	H1···S1	3.484(5)	2.68	145
	H9···S2	3.632(5)	2.93	134
C–H···O	H5···O1	3.357(5)	2.64	134
3				
C–H···π	H38···ring1 (C1–6)	3.695(4)	2.88	147
	H35···ring2 (C25–30)	3.816(4)	2.96	153
	H18···ring3 (C42–47)	3.758(4)	2.92	152
C–H···S	H32···S1	3.562(3)	2.95	124
	H33···S1	3.562(3)	2.97	123
	H15···S2	3.501(3)	2.82	131
	H16···S2	3.549(4)	2.96	122
	H7A···S3	3.512(3)	2.79	133
	H40···S3	3.515(3)	2.89	126
	H41···S3	3.576(3)	2.98	124
	H23···S4	3.531(3)	2.90	127
	H24···S4	3.521(3)	2.95	121
O–H···π	H4X···ring4 (C20–24, N2)	3.341(4)	2.54	157
	H5Y···ring5 (C8–13)	4.513(4)	3.71	158
H···H	H50B···H44		2.17	
	H31B···H36		2.34	

[a] Ring1 (C19–24) means the centroid of the aromatic ring, which includes the atoms of C19, C20, C21, C22, C23, and C24; so do other rings.

3.3. *C–H···π and C–H···S weak interactions in the polymers*

The existence and structural importance of weak C–H···π and C–H···X (X = heteroatom) hydrogen bonding interactions in many molecular and polymeric compounds are well established [11–15]. The C–H···S hydrogen bonding interaction is particularly attractive because it has been proven to be very important in the formation of organic conducting and superconducting compounds [22, 23]. In **1**–**3**, C–H···π and C–H···S weak interactions are critical in stabilizing their low dimensional (1- and 2-D) frameworks. The weak interactions (bond lengths and angles) present in these complexes are listed in table 3.

In 2-D polymer **1**, the guest chair-like dimer $(SC_6H_4CH_3\text{-}4)_2$ is located in the square cavity, entangled around the 4,4′-bpy ligand (figure 4). It forms four weak interactions with the framework, i.e. two C–H···π interactions with the pyridine ring of 4,4′-bpy and two C–H···S interactions with –NCS, and one C–H···π interaction with another guest molecule. The C–H···X (X = π, S) distances range from 2.76 to 3.40 Å. Interactions of H7···ring1, H2···ring1 and H21···S1 are between the guest molecule

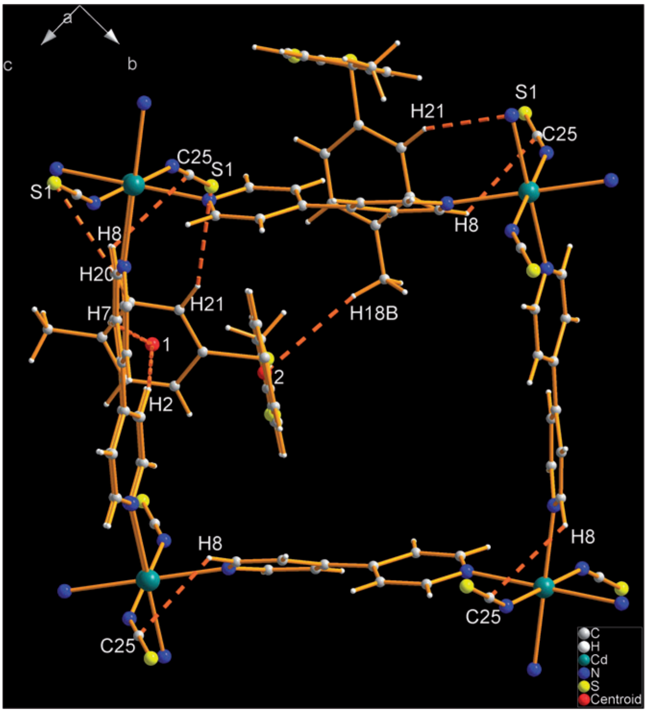

Figure 4. C–H···π and C–H···S interactions in **1**.

and 4,4′-bpy and –NCS in one 2-D sheet, and the interaction of H18B···ring2 is formed between two guest molecules. These weak interactions cause the guest molecules to align around the 4,4′-bpy in the matrix. Weak C–H8···π(C25) interaction exists between the pyridine of 4,4′-bpy and π system in –NCS group, which coordinates to the same Cd [24]. The 2-D sheets link via the H20···S1 interactions between the guest molecule in one sheet and the –NCS group in another to form a 3-D network.

In **2** and **3**, the presence of different guest molecules and resulting hydrogen bonding interactions account for their different structure packing. As shown in figures 5 and 6, 1-D chains in both **2** and **3** are linked through intermolecular weak interactions to form 2-D sheets. These weak interactions in **2** include H4···ring1 (C11–16), H2···ring1, and H17A···ring3 (C6–10, N2) C–H···π weak interactions with distances of 3.11, 2.91 and 3.36 Å, respectively, and C–H···S interaction with a H1···S1 distance of 2.68 Å. Weak C–H···O hydrogen bonding interactions, with a bond length of 2.64 Å, exist between O1 of DMF and H5 of 4,4′-bpy in the framework. In **3**, 1-D chains are linked by H7A···S3 interactions (2.79 Å). The 2-D sheets in both structures stack through inter-layer weak interactions to construct a 3-D network. In **2**, the inter-layer interactions include H7···ring2 (C18–23) and S2···H9 interactions, while for **3** they are C–H···S interactions such as H32···S1, H15···S2, H40···S3, H23···S4 and C–H···π interactions of H38···ring1 (C1–6), H35···ring2 (C25–30) and H18···ring3 (C42–47) (table 3). Polymer **3** exhibits two kinds of unusual noncovalent O–H···π interactions and intermolecular H···H contacts. The O–H···π interactions occur between the guest molecules and the framework, i.e. H4O···ring4 (C20–24, N2) and

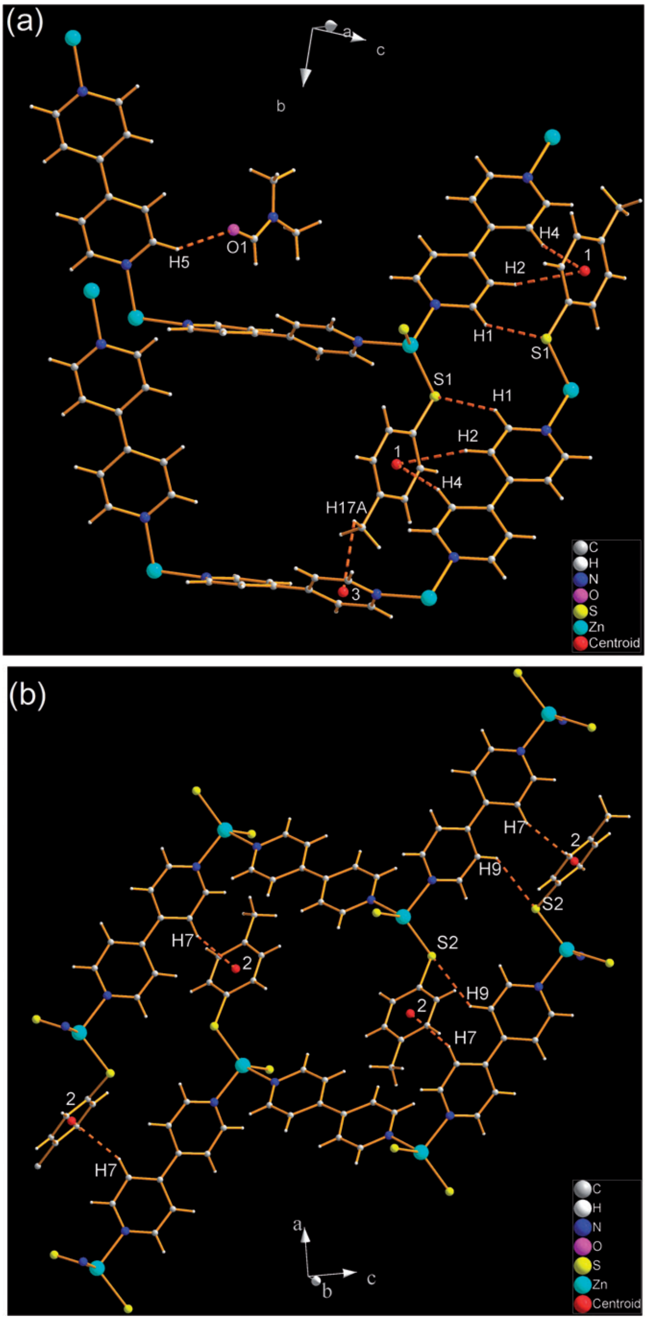

Figure 5. Intra- (a) and inter-layer (b) weak interactions in **2**.

H5O$\cdots$ring5 (C8–13) interactions with distances of 2.54 and 3.71 Å, respectively. The intermolecular H$\cdots$H contacts include H44$\cdots$H50B interaction with a distance of 2.17 Å and H36$\cdots$H31C interaction with a distance of 2.34 Å, similar to reported values [25].

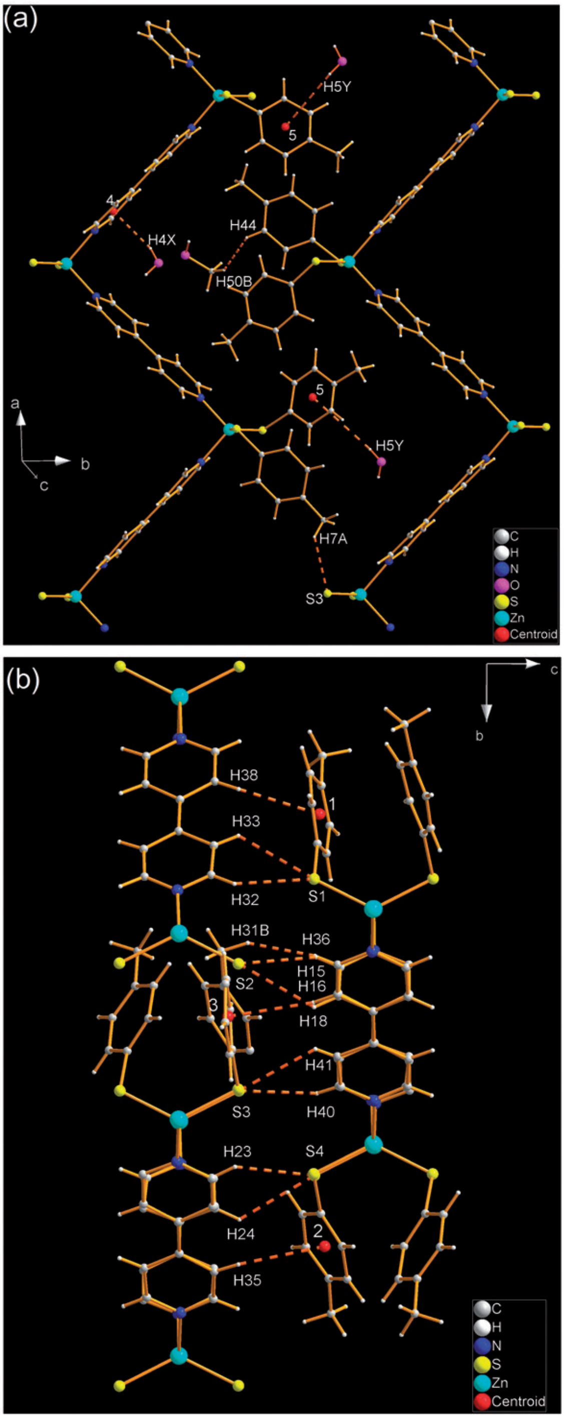

Figure 6. Intra- (a) and inter-layer (b) weak interactions in **3**.

4. Conclusions

Three new coordination polymers, $\{[Cd(4,4'\text{-bpy})_2(NCS)_2]\cdot 2(SC_6H_4CH_3\text{-}4)_2\}_n$ (**1**), $\{[Zn(4,4'\text{-bpy})(SC_6H_4CH_3\text{-}4)_2]\cdot DMF\}_n$ (**2**), and $\{[Zn(4,4'\text{-bpy})(SC_6H_4CH_3\text{-}4)_2]\cdot H_2O$ $0.5CH_3OH\}_n$ (**3**), were prepared based on the self-assembly of Zn(II)/Cd(II) 4-methylbenzenethiolates with 4,4′-bpy. Their structures are built upon 4,4′-bpy and 4-methylbenzenethiol, but with different coordination modes and structural topologies. **1** is a 2-D square-grid sheet-like polymer; **2** and **3** are 1-D twisted, arched, and zigzag chain-like polymers, respectively. In all compounds, 4,4′-bpy is bidentate bridging. 4-Methylbenzenethiolate has two different effects in self-assembly of these polymers, a space-filling agent in **1** and a terminal monodentate ligand in **2** and **3**. The structural difference in these compounds can be attributed to the presence of different guest molecules in the networks and the weak interactions between the guest molecule and the framework, as demonstrated by the presence of various $C–H\cdots\pi$, $C–H\cdots S$ interactions and unusual $C–H\cdots C$, $O–H\cdots\pi$, and $H\cdots H$ interactions.

Supplementary materials

CCDC 716274–716276 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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