Effects of Direction of Bridging of Thiocyanato on the Dimension of Coordination Polymers: Synthesis, Characterization and Single-crystal X-ray Structure Determination of $[Cd(4,4'\text{-dm-}2,2'\text{-bpy})(NCS)_2]_n$ and $[Cd(4,4'\text{-dmo-}2,2'\text{-bpy})(NCS)_2]_n$ Coordination Polymers①

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ABSTRACT Two new cadmium(II)-thiocyanato coordination polymers with 4,4′-dimethyl-2,2′-bipyridine (4,4′-dm-2,2′-bpy) and 4,4′-dimethoxy-2,2′-bipyridine (4,4′-dmo-2,2′-bpy) as chelating ligands were synthesized and characterized by elemental analysis, IR and ^{1}H NMR spectroscopy and X-ray crystallography. Thermal properties were also studied as well. These complexes have formed as $[Cd(4,4'\text{-dm-}2,2'\text{-bpy})(NCS)_2]_n$ (**1**) and $[Cd(4,4'\text{-dmo-}2,2'\text{-bpy})(NCS)_2]_n$ (**2**). The coordination numbers of Cd^{II} in **1** and **2** are six (CdN_4S_2). Direction of bridging of thiocyanato anions in **1** and **2** created one- and two-dimensional coordination polymers, respectively. The supramolecular features in these complexes were guided and controlled by weak directional intermolecular interactions.

Keywords: 2,2′-bipyridine, cadmium(II), coordination polymer, weak interactions;
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1 INTRODUCTION

Construction of self-assembled coordination molecules and supramolecular entities[1] of varied nuclearities formed through control and manipulation of strong metal-ligand covalent bonds[2] and multiple weak non-covalent forces[3] is the center of attraction to the coordination chemists for the preparation of different varieties of functional materials[4]. Over the past few decades, mixed ligand self-assembly strategy has gradually become an effective approach, which is expected to fabricate frameworks with more diverse structural motifs compared to that using only one type of ligands[5–12]. However, controllable synthesis of coordination polymers with desired frameworks remains a great challenge to chemists. Therefore, the selection of special organic ligands with appropriate shape, flexibility and functionality together with metal ions is very important in the construction of target polymers[13, 14]. In addition, accurate control of the change of some external conditions (*e.g.*, template,

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solvents, temperature, counter ion, substitute group on the organic ligand and auxiliary ligand) in the self-assembly process is also very important[15, 16]. A series of variable frameworks have been successfully obtained *via* varying external conditions[17, 18]. Encouraged by the previous investigations, in this work, we selected 4,4′-dimethyl-2,2′-bipyridine and 4,4′-dimethoxy-2,2′-bipyridine as chelating ligands and versatile bridging modes of thiocyanato anions, which is supposed to make the structures of one- and two-dimensional coordination polymers.

2 EXPERIMENTAL

2. 1 Material and measurements

Cadmium(II) acetate dehydrate, potassium thiocyanate (Merck) and 4,4′-dimethyl-2,2′-bipyridine, 4,4′-dimethoxy-2,2′-bipyridine (Aldrich) were purchased and used as received. All chemicals were reagent graded and used without further purification. FT-IR spectra were collected on a Mattson 1000 spectrophotometer using KBr pellets in the range of 4000～450 cm^{-1}. Elemental analyses (CHN) were performed using a Carlo ERBA model EA 1108 analyzer, whereas the ^1H NMR spectra were obtained using a Bruker spectrometer at 250 MHz in [D6]DMSO. Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851e instrument.

2. 2 Crystallography

The crystal structures of the title compounds were determined from single crystals. These were mounted on an Agilent Super Nova providing Mo$K\alpha$ radiation (λ = 0.71073 Å) at 123 K. Absorption was corrected in both cases by multi-scans[19]. The crystal structures were solved using SIR2004[20] and refined with SHELXL-2014[21]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. Selected bond lengths and bond angles of **1** and **2** are listed in Table 1.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

1					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)–N(3)	2.2695(18)	Cd(1)–N(2)	2.343(2)	Cd(1)–S(1)	2.6382(6)
Cd(1)–N(4)	2.314(2)	Cd(1)–N(1)	2.3542(18)	Cd(1)–S(2)	2.8242(6)
Angle	(°)	Angle	(°)	Angle	(°)
N(3)–Cd(1)–N(4)	90.84(7)	N(2)–Cd(1)–N(1)	70.12(6)	N(3)–Cd(1)–S(2)	91.93(5)
N(3)–Cd(1)–N(2)	91.80(7)	N(3)–Cd(1)–S(1)	102.29(6)	N(4)–Cd(1)–S(2)	176.08(5)
N(4)–Cd(1)–N(2)	98.04(7)	N(4)–Cd(1)–S(1)	94.78(5)	N(2)–Cd(1)–S(2)	84.65(5)
N(3)–Cd(1)–N(1)	161.88(8)	N(2)–Cd(1)–S(1)	160.79(5)	N(1)–Cd(1)–S(2)	87.69(5)
N(4)–Cd(1)–N(1)	90.54(7)	N(1)–Cd(1)–S(1)	95.60(5)	S(1)–Cd(1)–S(2)	81.92(2)
2					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)–N(4)	2.2803(16)	Cd(1)–N(2)	2.3476(15)	Cd(1)–S(1)	2.6865(5)
Cd(1)–N(3)	2.3387(16)	Cd(1)–N(1)	2.3498(15)	Cd(1)–S(2)^i	2.7946(5)
Angle	(°)	Angle	(°)	Angle	(°)
N(4)–Cd(1)–N(3)	88.53(6)	N(2)–Cd(1)–N(1)	69.43(5)	N(4)–Cd(1)–S(2)^i	93.82(4)
N(4)–Cd(1)–N(2)	157.82(5)	N(4)–Cd(1)–S(1)	104.05(4)	N(3)–Cd(1)–S(2)^i	171.99(4)
N(3)–Cd(1)–N(2)	96.14(6)	N(3)–Cd(1)–S(1)	88.67(4)	N(2)–Cd(1)–S(2)^i	84.55(4)
N(4)–Cd(1)–N(1)	88.80(5)	N(2)–Cd(1)–S(1)	97.75(4)	N(1)–Cd(1)–S(2)^i	95.74(4)
N(3)–Cd(1)–N(1)	91.96(5)	N(1)–Cd(1)–S(1)	167.16(4)	S(1)–Cd(1)–S(2)^i	83.339(14)

Symmetry transformation: i:–x+1/2, y+1/2, –z+1/2

The crystal data of **1**: $C_{14}H_{12}CdN_4S_2$, M_r = 412.80, triclinic, $P\bar{1}$, a = 8.1429(4), b = 10.3070(6), c = 10.5524(5) Å, α = 84.090(4), β = 72.211(4), γ = 69.900(5)°, V = 791.94(8) $Å^3$, Z = 2, ρ_c = 1.731 $g\cdot cm^{-3}$, Mo$K\alpha$ radiation (λ = 0.71073 Å), graphite monochromator, $3.89 \leqslant \theta \leqslant 32.23°$, $-11 \leqslant h \leqslant 11$, –14

$\leqslant k \leqslant 13$, $-15 \leqslant l \leqslant 15$, 7430 reflections measured, of which 5033 were symmetrically independent (4441 reflections with $I > 2\sigma(I)$), R_{int} = 0.0339, 192 parameters, 0 restraints, $R(F)$ = 0.032 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.074 (all data), S = 1.037.

The crystal data of **2**: $C_{14}H_{12}CdN_4O_2S_2$, M_r = 444.80, monoclinic, $P2_1/n$, a = 11.0212(2), b = 10.0730(1), c = 15.1162(2) Å, β = 108.843(2)°, V = 1588.21(4) Å^3, Z = 4, ρ_c = 1.860 g cm^{-3}, Mo$K\alpha$ radiation (λ = 0.71073 Å), graphite monochromator, $3.49 \leqslant \theta \leqslant 32.49°$, $-16 \leqslant h \leqslant 15$, $-15 \leqslant k \leqslant 15$, $-16 \leqslant l \leqslant 22$, 14200 reflections measured, of which 5272 were symmetrically independent (4565 reflections with $I > 2\sigma(I)$), R_{int} = 0.0295, 210 parameters, 0 restraints, $R(F)$ = 0.025 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.054 (all data), S = 1.031.

2. 3 Preparation of [Cd(4,4′-dm-2,2′-bpy)(NCS)$_2$]$_n$ (1)

4,4′-Dimethyl-2,2′-bipyridine (0.092 g, 0.5 mmol) was placed in one of the arms of a branched tube[22], and cadmium(II) acetate dihydrate (0.134 g, 0.5 mmol) and potassium thiocyanate (0.097 g, 1 mmol) were placed in the other arm. Methanol and water in a ratio of (2:2) were carefully added to fill both arms. The tube was then sealed and the ligand-containing arm was immersed in a bath at 60 ℃ while the other was maintained at ambient temperature. After 1 day, crystals that were deposited in the cooler arm were filtered off, washed with the mother liquid and dried in air, yield: 65%. Analysis found: C, 40.65; H, 2.82; N, 13.89%. Calculated for $C_{14}H_{12}CdN_4S_2$: C, 40.70; H, 2.91; N, 13.56%. IR (cm^{-1}) selected bands: 670 (s), 830 (s, C–H), 1055(s), 1224(s) 1369, 1485, 1560 (s, aromatic ring), 2090, 2120 (vs, thiocyanate), 2895(w, C-H aliphatic), 3046(w, C–H aromatic). ^{1}H NMR (DMSO, δ): 2.47 (s, 6H), 7.3～7.5 (d, 2H), 8.2～8.4 (s, 2H), 8.5～8.7 (d, 2H). ^{13}C NMR (DMSO, δ): 21.26, 122.55, 123.44, 125.87, 149.33, 149.49, 155.10.

2. 4 Preparation of [Cd(4,4′-dmo-2,2′-bpy)(NCS)$_2$]$_n$ (2)

Complex **2** was synthesized in the same way as complex **1** using 4,4′-dimethoxy-2,2′-bipyridine in place of 4,4′-dimethyl-2,2′-bipyridine, yield: 68%. Analysis found: C, 31.33; H, 2.45; N, 7.59%. Calculated for $C_{15}H_{15}N_3O_2PbS$: C, 31.01; H, 2.58; N, 7.24%. IR (cm^{-1}) selected bands: 655 (s), 833 (vs, C–H), 1041(s), 1161(s), 1242(s), 1346(s) 1445(s, acetate), 1473, 1527(s, aromatic ring), 1600 (s, acetate), 2085, 2125(vs, thiocyanate), 2875(w, C–H aliphatic), 3030(w, C–H aromatic). ^{1}H NMR (DMSO, δ): 8.51 (d, 2H), 7.92 (S, 2H), 7.04 (d, 2H), 3.59 (s, 6H) ppm. ^{13}C NMR (DMSO, δ): 55.89, 116.79, 121.19, 127.26, 150.93, 157.17, 161.58, ppm.

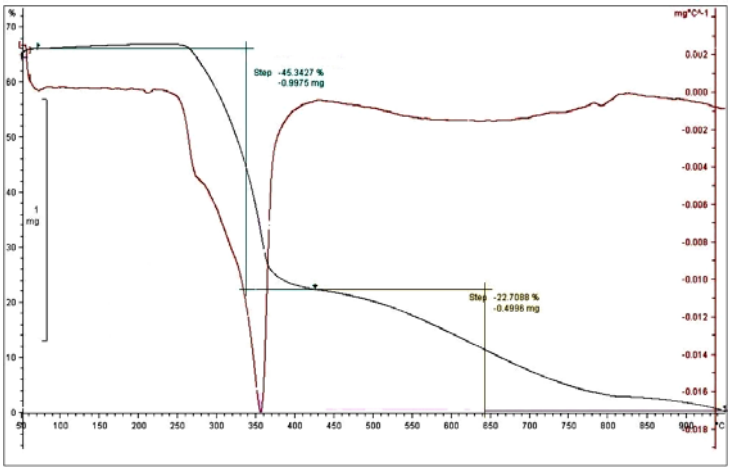
3 RESULTS AND DISCUSSION

3. 1 Spectroscopic studies

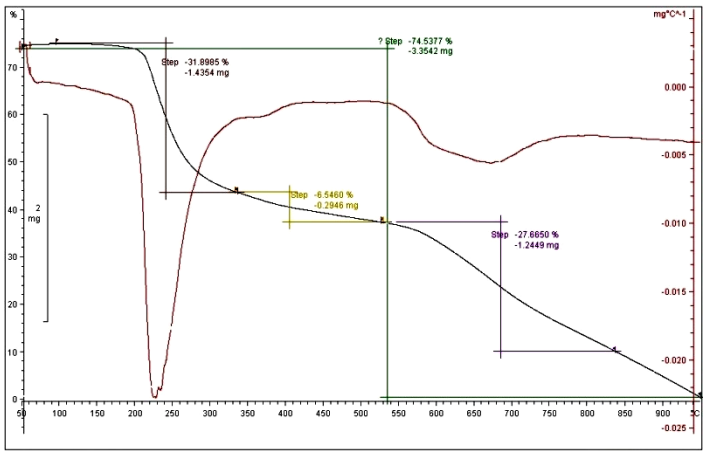
The reaction of Cd(II) acetate with 4,4′-dimethyl-2,2′-bipyridine (4,4′-dm-2,2′-bpy), 4,4′-dimethoxy-2,2′-bipyridine (4,4′-dmo-2,2′-bpy) and potassium thiocyanate yielded crystalline materials with formulas [Cd(4,4′-dm-2,2′-bpy)(NCS)$_2$]$_n$ (**1**) and [Cd(4,4′-dmo-2,2′-bpy)(NCS)$_2$]$_n$ (**2**). The IR spectra displayed characteristic absorption bands for the chelating ligands and thiocyanate anions. The relatively weaker absorption bands around 3046 and 3030 cm^{-1} are due to the C–H modes involving aromatic-ring hydrogen atoms of **1** and **2**, respectively. The C–H modes involving the aliphatic hydrogen atoms of 4,4′-dm-2,2′-bpy and 4,4′-dmo-2,2′-bpy are at 2895 and 2875 cm^{-1}, respectively. The absorption bands with variable intensity in the frequency range of 1400～1570 cm^{-1} are corresponding to the aromatic ring vibrations of the ligands. In **1**, the bands with nearly equal intensity at 2080～2125 cm^{-1} are attributed to the thiocyanate anions. These two absorption bands are expected to be the end-to-end bridging thiocyanates[23]. The ^{1}H NMR spectra of the DMSO solution of compounds **1** and **2** at 7.00～8.60 (aromatic protons) and 2.47, 3.59 (aliphatic protons) ppm had displayed four different protons of 4,4′-dimethyl-2,2′-bipyridine and 4,4′-dimethoxy-2,2′-bipyridine, respectively.

3. 2 Thermal studies

To evaluate the thermal behavior, thermal analyses of **1** and **2** were analyzed on polycrystalline samples under a nitrogen atmosphere from 30 to 900 ℃. In the TGA of **1** (Fig. 1a), the first significant weight loss of 45.34% from 270 to 360 ℃ corresponds to the departure of one coordinated 4,4′-dm-2,2′-bpy ligand (calcd.: 44.66%). The second mass loss occurring from 430 to 900 ℃ is 22.71%, assigned to the decomposition of thiocya- nate anions. Compound **2** is stable to 200 ℃. Subsequently, the decomposition occurs in two distinct stages. The first mass loss comes up to 38.45% from 200 to 530 ℃ and corresponds to the decomposition of 4,4′-dmo-2,2′-bpy ligand. The second mass loss occurring from 530 to 900 ℃ is 36.088% due to the complete removal of 4,4′- dmo-2,2′-bpy ligand and the thiocyanate anions (Fig. 1b). The mass loss calculations as well as micro- analyses (atomic absorption) of the solid residues suggest that the residue left as a final decomposition product of the complexes at around 900 ℃ is CdO with the total mass loss of 31.95% for **1** (Calc. 31.13 %) and 25.5% for **2** (Calc. 28.94%), respectively, which agrees well with the proposed structures. IR analysis of the final residue (at 900 ℃) revealed none of the characteristic absorption bands of the ligands of coordination polymers.



(a)



(b)

Fig. 1. TG curves of (a) 1 and (b) 2

3. 3 Crystal structures of 1 and 2

The single-crystal X-ray diffraction analysis reveals that compounds **1** and **2** were crystallized in triclinic space group $P\bar{1}$ and monoclinic space group $P21/n$, respectively. The ORTEP diagrams of **1** and **2** are depicted in Figs. 2 and 3, respectively.

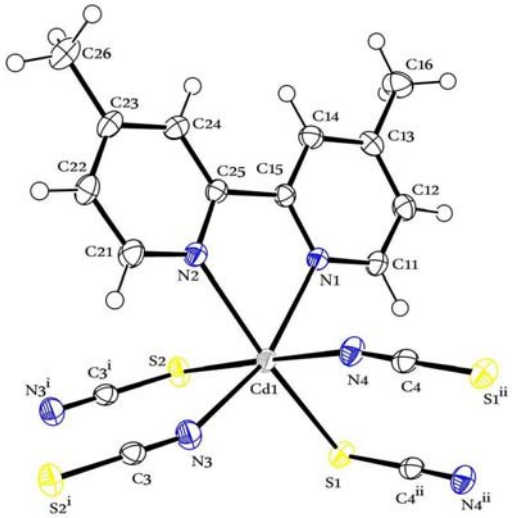


Fig. 2. ORTEP diagram of 1 at 50% probability thermal ellipsoids with atomic numbering scheme (Symmetry codes: *i*: 1–*x*, 1–*y*, –*z* and *ii*: 1–*x*, 1–*y*, 1–*z*)

Complex **1** forms one dimensional coordination polymers based on bridging thiocyanato and chelating 4,4′-dm-2,2′-bpy ligands. The cadmium atoms are coordinated in a distorted octahedral fashion by two nitrogen atoms from a 4,4′-dm-2,2′-bpy ligand, two *cis* NCS-nitrogen atoms from two thiocyanato anions and two *cis* SCN-sulfur atoms from the other two thiocyanato anions. Four SCN ligands bridge between three symmetry-related cadmium atoms. The Cd–S and Cd–N of thiocyanate bond lengths are 2.6382(6), 2.8242(6) Å and 2.2695(18), 2.314(2) Å, respectively, which are similar to those in the closely related compounds[24]. The most interesting structural feature of complex **1** is that each thiocyanate group acts as a bidentate bridging ligand and links two Cd(II) centers together, resulting in the formation of a 1D network structure. The two bidentate bridging thiocyanate ligands, which link the two Cd(II) ions, form two centrosymmentric eight-membered $Cd_2(SCN)_2$ rings with the Cd···Cd separations of 5.854(2) and 5.827(2) Å. The corresponding N–C–S bonds are almost linear (179.23(2)°, 178.70(3)°) whereas the Cd–S–C and Cd–N–C linkages are rather bent (Cd–S–C = 95.89(8)°, 99.07(9)°; Cd–N–C 157.37°, 164.66°), similar to those in literatures[25].

The asymmetric unit of **2** consists of one cadmium(II) cation, two thiocyanato anions and one 4,4′-dmo-2,2′-bpy ligand, all of which are located in the general positions. Each cadmium(II) cation is coordinated by two N- and two S-bonded thiocyanate anions as well as one 4,4′-dmo-2,2′-bpy ligand into a slightly distorted octahedral geometry (Fig. 3). The CdN_4S_2 distances fall in the range of 2.2803(16)～2.7946(5) Å with angles around the cadmium(II) cation of 83.34(1)° to 104.05(4)° and 157.82(5)° to 171.99(4)° (Table 2). In the crystal structure dimeric units are present, in which the metal cations are linked by pairs of μ-1,3-bridging thiocyanato anions whereas two units are connected by pairs of thiocyanato anions into chains. These dimers are linked into chains by single anionic ligands, which are further connected into layers (2D network) by additional thiocyanato anions (Fig. 4). This structural motif is common and observed in a number of similar compounds[26, 27]. The 4,4′-dmo-2,2′-bpy ligands only act as a bidentate ligand. As mentioned above, this compound was obtained by serendipity and can not be prepared in larger amounts as a phase pure material. The two bidentate bridging thiocyanate ligands link two Cd(II) ions, forming two centrosymmentric eight-membered $Cd_2(SCN)_2$ and twenty four-membered $Cd_6(SCN)_6$ rings with the Cd···Cd separations of 6.065(2) and 6.003(2) Å. The corresponding N–C–S bonds are almost linear (N(4)–C(4)–S(2) = 179.95°, N(3)–

C(3)–S(1) = 176.69°), whereas the Cd–S–C and Cd–N–C linkages are rather bent (Cd(1)–S(2)–C(14) = 96.19°, Cd(1)–S(1)–C(3) = 103.82°, Cd(1)–N(4)–C(4) = 168.70°, Cd(1)–N(3)–C(3) = 154.67°) and they are similar to those for the reported compounds[24].

Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°)

D–H···A	d(H···A)	d(D···A)	∠DHA
1			
C(22)–H(22)···N(4)[a]	2.623	3.506(2)	154.91
C(16)–H(16C)···N3[b]	2.735	3.615(2)	149.59
C(24)–H(24)···S2[b]	2.902	3.782(2)	154.53
C(26)–H(26A)···π [a]	2.860	3.605(2)	137.26
π-π stacking (slipped edge-to-edge)		3.488	
π-π stacking (slipped edge-to-edge)		3.561	
Symmetry codes: (a) 2–*x*, 1–*y*, –*z*; (b) 1+*x*, –1+*y*, *z*, –*z*			
2			
C(12)–H12···O2[c]	2.568	3.256(3)	130.38
C(16)–H16A···N3[d]	2.675	3.436(3)	134.72
C(14)–H14···N3[d]	2.810	3.710(3)	158.52
C(21)–H21···S2[c]	2.871	3.736(2)	151.96
C(26)–H26B···S2[e]	2.946	3.661(3)	130.64
C(26)–H(26[a])···π[f]	2.883	3.505(2)	122.18
π-π stacking (slipped face-to-face)		3.411	
Symmetry codes: (c) *x*, –1+*y*, *z*; (d) –*x*, –*y*, 1–*z*; (e) –1+*x*, 1+*y*, *z*; (f) –1/2–*x*, –1/2+*y*, 1/2–*z*			

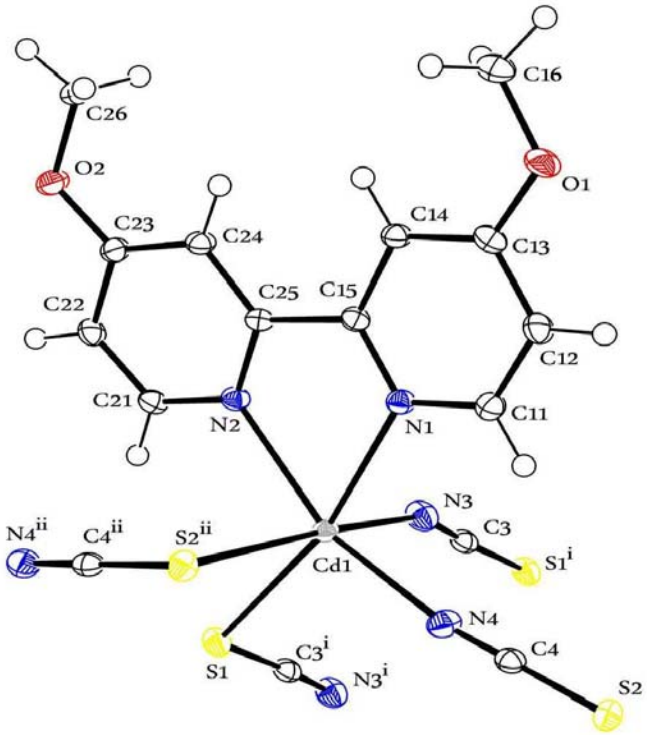
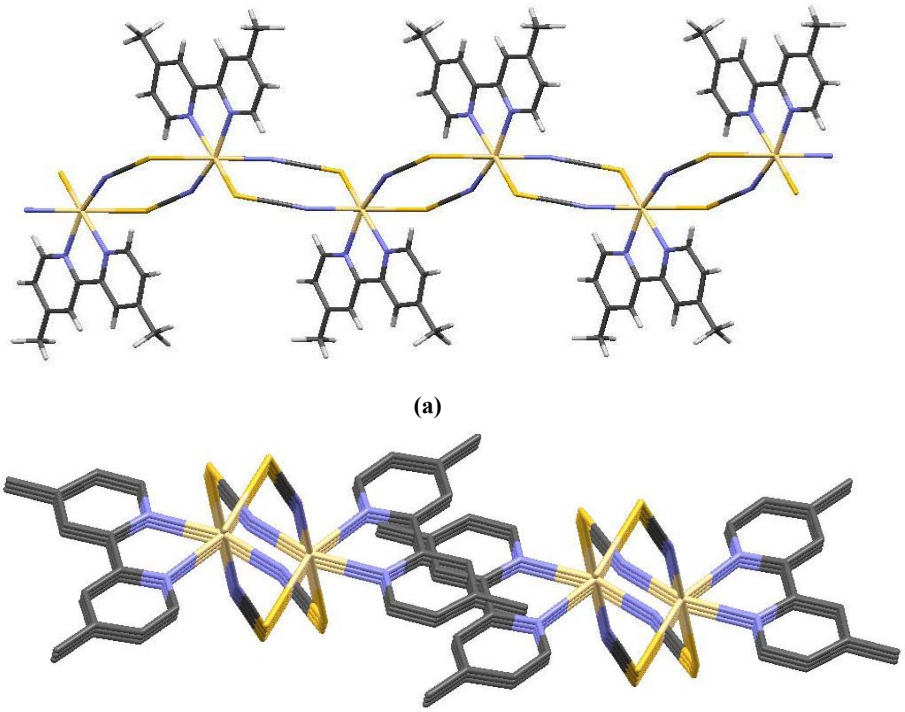


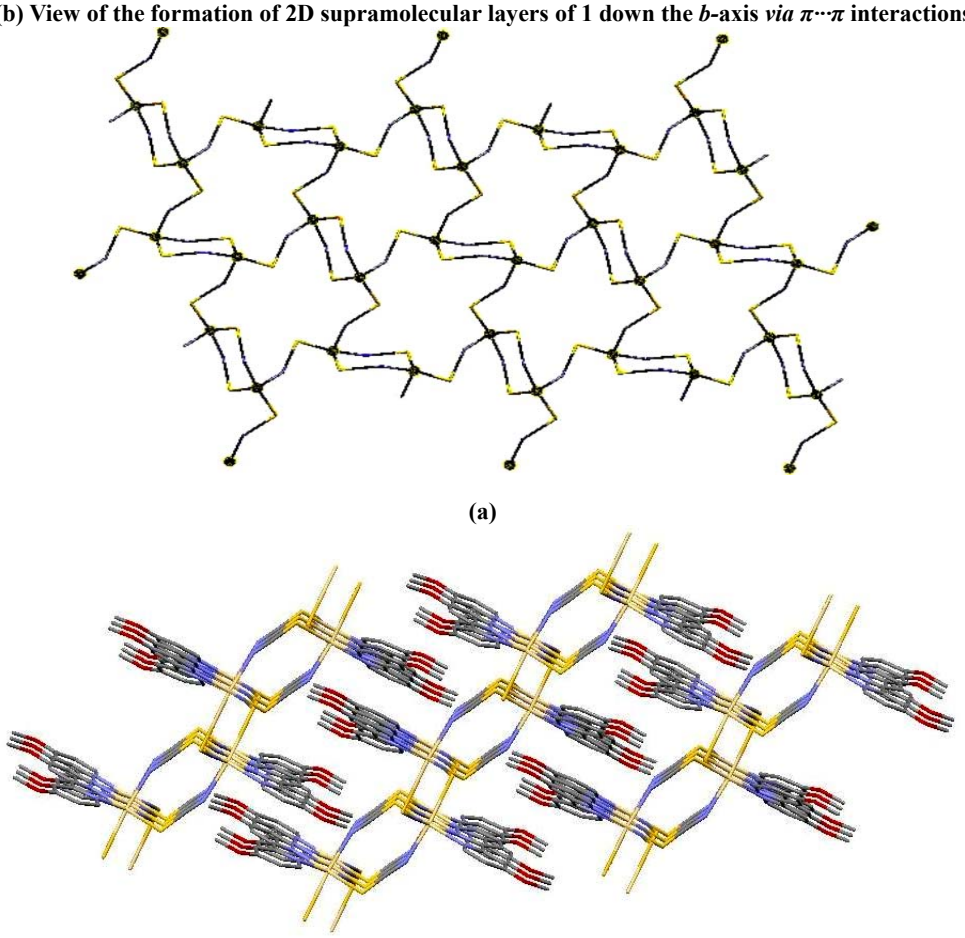
Fig. 3. ORTEP diagram of 2 at 50% probability thermal ellipsoids with atomic numbering scheme (Symmetry codes: *i*: 1–*x*, –*y*, 1–*z* and *ii*: 1/2–*x*, 1/2+*y*, 1/2–*z*)



(a)

(b)

Fig. 4. (a) Fragment of the (one-dimensional) coordination polymer of 1 with atom numbering scheme; (b) View of the formation of 2D supramolecular layers of 1 down the *b*-axis *via* π···π interactions



(a)

(b)

Fig. 5. (a) Perspective view of the thiocyanato 2D network of 2 along the *c* axis. The co-ligands are omitted for clarity; (b) View of the formation of 3D supramolecular layers of 2 down the *b*-axis *via* π···π interactions

Intermolecular, intramolecular and π-π stacking interactions are observed in **1** and **2**, responsible for the crystal packing of coordination polymers. An inspection of the data of compounds for weak directional intermolecular interactions by the programs PLATON and MERCURY, which were used for calculating the supramolecular interactions, reveals C–H···O[28], C–H···N[29] and C–H···S[30] inter- actions, and π-π stacking[31] (Table 2). The packing diagram of **1** and **2** exhibits 2*D* and 3*D* self- assembled structure through π-π stacking inter- actions (slipped face-to-face) with distances between the pyridine rings to be 3.488, 3.561 Å for **1** and 3.411 Å for **2**, which are remarkably shorter than those for normal π-π stacking interactions[32]. In addition to the π-π stacking in 3D supramolecular networks, C–H···O, C–H···N and C–H···S interac- tions are found in **1** and **2**. These are substantially shorter than the vander-Waals distances of 2.72 Å for H···O, 2.75 Å for H···N and 3.00 Å for the H···S distance (Table 2, Fig. 4)[33]. Recent structural study of the cadmium(II) complexes has provided a useful comparison with complexes **1** and **2**. Lengths of Cd–N bonds are similar to those for the reported cadmium(II) structures of 5,5′-dm-2,2′-bpy li- gands[34, 35]. The different substitutes on 2,2′-bpy result in interesting intermolecular interactions in the structures **1** and **2**. These values suggest relatively stronger interactions within this class of weak non-covalent contacts. The recent interactions cause to form hybrid multi-dimensional frameworks in **1** and **2**.

4 CONCLUSION

To summarize, two Cd(II) coordination polymers with a 4,4′-dimethyl-2,2′-bipyridine or 4,4′-dimethoxy-2,2′-bipyridine ligand and thiocyanate anions have been prepared under similar conditions. Direction of bridging of thiocyanato anions in **1** and **2** created one- and two-dimensional coordination polymers. These polymeric complexes have provided new structural examples of metallosupramolecular architectures. Ongoing studies will be aimed at more coordination assemblies of such versatile organic ligands and other metal centers, which may exhibit interesting structures and desired properties.

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