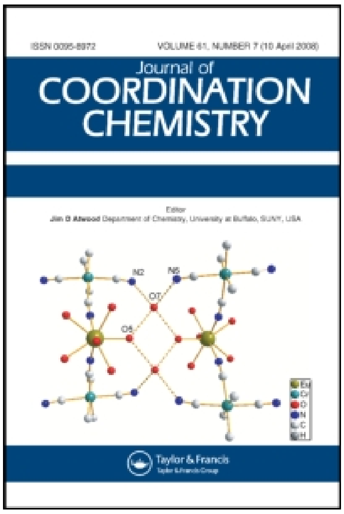

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Synthesis and structural characterization of two dimensional cadmium(II) coordination polymers

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Synthesis and structural characterization of two dimensional cadmium(II) coordination polymers

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Reactions of $Cd(NO_3)_2 \cdot 4H_2O$ with NH_4SCN, ppz (ppz = piperazine) and bpa (bpa = *bis*(4-pyridyl)ethane) in CH_3OH afforded the cavity-containing rectangular grids $\{Cd(SCN)_2(ppz)\}_n$ (**1**) and $\{Cd(NCS)_2(bpa)\}_n$ (**2**). The ppz ligand in **1** is coordinated to the metal through both nitrogen atoms to form the 1-D zig-zag chain structure and distorted $\{CdN_4S_2\}$ octahedral coordination geometry at each Cd center is completed by pairs of bidentate thiocyanato ligands. Complex **2** has the 2-D arrangement constructed through 1-D double μ(N,S) end-to-end bridging thiocyanato groups bridging Cd(II) chains interconnected through disordered bpa ligands.

Keywords: Coordination polymer; Cadmium; Thiocyanato; Bidentate nitrogen ligand; Sheet; Network; Zig-zag

1. Introduction

Effort has been devoted to self-assembly of organic and inorganic molecules in the solid state because it extends the range of new solids with desirable physical and chemical properties [1]. The range and variety of self-assembled inorganic structures relies on suitable metal–ligand interactions and hydrogen bonds, and the various types of polymeric structures include 1-D, 2-D and 3-D network structures [2]. Crystal engineering of coordination polymers with inner cavities or channels of desired size has been achieved recently by using suitable bidentate ligands. Investigations in this area have led to many materials of interesting structures with bidentate nitrogen ligands like pyrazine, piperazine and *bis*(pyridyl) ligands [3–5]. Charged ligands like thiocyanate are also used to bridge metal centres, giving complexes of analogous architectures with important physical properties such as supramolecular chemistry and molecular

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magnetism. The thiocyanate anion is a versatile ligand because it can act as a doubly bridging ligand or as a monodentate ligand by bonding solely through either its S or N [6]. The synthesis and structures of two new 2-D coordination polymeric networks of $\{Cd(SCN)_2(ppz)\}_n$ (**1**) and $\{Cd(NCS)_2(bpa)\}_n$ (**2**), form the subject of this report.

2. Experimental

2.1. *General procedures*

The IR spectra were recorded on a Bio-Rad FTs-7 spectrometer. Elemental analyses were obtained from a PE 2400 series II CHNS/O analyzer, PERKIN-ELMER CHN-2400 analyzer or HERAEUS VaruoEL analyzer.

2.2. *Starting material*

The reagents $Cd(NO_3)_2 \cdot 4H_2O$, ppz (ppz = piperazine), bpa (bpa = *bis*(4-pyridyl) ethane) and NH_4SCN were purchased from Aldrich Chemical Co. and used as received.

2.3. *Preparation of* $\{Cd(SCN_2(ppz)\}_n$ *(1)*

$Cd(NO_3)_2 \cdot 4H_2O$ (0.31 g, 1 mmol), NH_4SCN (0.15 g, 2 mmol) and ppz (0.086 g, 1 mmol) were placed in a flask containing 10 mL CH_3OH. The mixture was stirred at room temperature for 30 min to yield a white precipitate. The white solid was then filtered off and washed with CH_3OH and dried under vacuum. Yield for **1**: 0.25 g (80%). Anal. Calcd for $C_6H_{10}CdN_4S_2$: C, 22.90; H, 3.20; N, 17.80%. Found: C, 22.99; H, 3.10; N, 17.85%. IR (KBr disk): 3235(br), 2982(m), 2939(m), 2863(m), 2105(m), 1427(m), 1383(m), 1324(m), 1244(m), 1093(m), 1056(m), 1002(m), 867(m), 765(m), 625(m), 469(m). Colorless crystals suitable for X-ray diffraction were grown by slow diffusion of ppz in CH_3OH layered on the mixture of $Cd(NO_3)_2 \cdot 4H_2O$ and NH_4SCN in H_2O solution over 3 days.

2.4. *Preparation of* $\{Cd(NCS)_2(bpa)_2\}_n$ *(2)*

$Cd(NO_3)_2 \cdot 4H_2O$ (0.31 g, 1 mmol), NH_4SCN (0.15 g, 2 mmol), and bpa (0.18 g, 1 mmol) were placed in a flask containing 10 mL CH_3OH. The mixture was stirred at room temperature for 30 min to yield a white precipitate. The white solid was then filtered off and washed with CH_3OH and dried under vacuum. Yield for **2**: 0.35 g (85%). Anal. Calcd for $C_{14}H_{12}CdN_4S_2$: C, 34.15; H, 5.73; N, 14.48%. Found: C, 34.02; H, 5.75; N, 14.54%. IR(KBr disk): 3501(br), 2933(m), 2864(m), 2097(m), 1560(m), 1500(m), 1454(m), 1427(m), 1383(m), 1223(m), 1070(m), 1015(m), 943(m), 828(m), 771(s), 543(m), 467(m). Colorless crystals suitable for X-ray diffraction were grown by slow diffusion of the mixture of bpa in CH_3OH layered on the mixture of $Cd(NO_3)_2 \cdot 4H_2O$ and NH_4SCN in H_2O solution over a week.

3. X-ray crystallography

The diffraction data for complexes **1** were collected at 25°C on a Siemens CCD diffractometer and that for **2** at 25°C on a Bruker AXS P4 diffractometer, equipped with graphite-monochromated Mo-Kα (K$\alpha = 0.71073$ Å) radiation. Data reduction was carried out by standard methods with the use of well-established computational procedures [7]. The structure factors were obtained after Lorentz and polarization correction. The positions of some of the heavier atoms, including the copper atom, were located by direct methods. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements [8]. The final residuals of the final refinement were $R_1 = 0.0265$, $wR_2 = 0.0688$ for **1**. The crystallographic procedures for **2** were similar to those for **1** and the final residuals of the final refinement were $R_1 = 0.0325$, $wR_2 = 0.0800$ for **2**. Basic information pertaining to crystal parameters and structure refinement is summarized in table 1.

Table 1. Crystal data for **1**–**2**.

	1	**2**
Formula	$C_6H_{10}CdN_4S_2$	$C_{11}H_{22}CdN_4S$
Fw	314.70	354.79
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	6.016(3)	21.385(3)
b (Å)	6.788(3)	5.7738(8)
c (Å)	7.310(4)	16.288(2)
α (°)	64.984(4)	90
β (°)	75.339(5)	123.34(5)
γ (°)	70.045(5)	90
V (Å^3)	252.1(2)	1680.2(4)
Z	1	4
D_{Calcd} (g cm^{-3})	2.073	1.403
$F(000)$	154	720
Cryst size (mm)	$0.16 \times 0.20 \times 0.40$	$0.20 \times 0.20 \times 0.02$
μ (Mo-Kα) (mm^{-1})	2.538	1.421
Data collcn. Instrum.	CCD	$P4$
Radiation monochromated in incident beam, λ(Mo-Kα) (Å)	0.71073	0.71073
Range (2θ) for data collection (°)	$6.20 \le 2\theta \le 56.62$	$4.56 \le 2\theta \le 50.08$
Temp. (°C)	25	25
Limiting indices	$-5 \le h \le 8$, $-8 \le k \le 9$, $-7 \le l \le 9$	$-25 \le h \le 25$, $-5 \le k \le 6$, $-19 \le l \le 19$
Reflections collected	1663	4955
Independent reflections	1189 [R(int) = 0.0473]	1481 [R(int) = 0.0195]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1189/0/82	1481/0/93
Quality-of-fit indicator[c]	1.072	1.077
Final R indices $[I > 2\sigma(I)]$[a,b]	$R_1 = 0.0265$, $wR_2 = 0.0668$	$R_1 = 0.0325$, $wR_2 = 0.0800$
R indices (all data)	$R_1 = 0.0295$, $wR_2 = 0.0675$	$R_1 = 0.0377$, $wR_2 = 0.0836$
Largest diff. peak & hole (e Å^{-3})	0.715 and –1.214	0.812 and –0.503

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (ap)^2 + (bp)]$, $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. $a = 0.041$, $b = 0.2244$ for **1**; $a = 0.0353$, $b = 8.70$ for **2**.

[c] Quality-of-fit $= [\Sigma w(|F_o^2| - |F_c^2|)^2/N_{\text{observed}} - N_{\text{parameters}}]^{1/2}$.

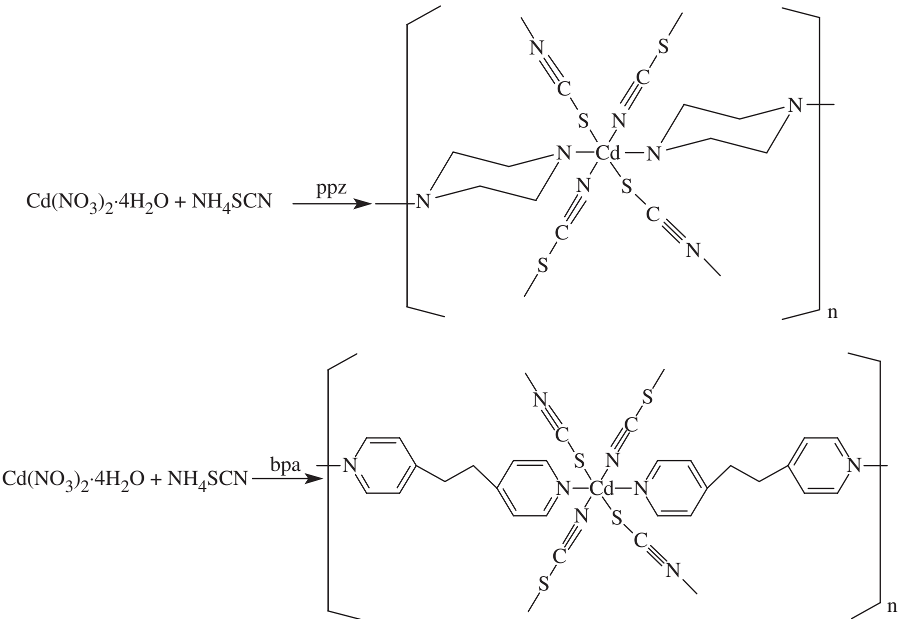
4. Results and discussion

4.1. *Synthesis*

Reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with ppz (ppz = piperazine), bpa (bpa = *bis*(4-pyridyl)ethane) and NH_4SCN in CH_3OH afforded the complexes $\{Cd(SCN)_2(ppz)\}_n$ (**1**) and $\{Cd(NCS)_2(bpa)\}_n$ (**2**), respectively. The reaction pathways are shown in scheme 1. Their structures have been determined by spectroscopic methods and by X-ray crystallography. The IR spectra for **1** and **2** show the very strong and sharp bands at 2088, 2105 and 2097 cm^{-1} due to the ν_{CN} stretching mode, in addition to medium to strong bands at 760–780 cm^{-1} related to ν_{CS} of the thiocyanato anions. Bridging thiocyanato groups are expected to exhibit two ν_{CN} bands above and below 2000 cm^{-1} as well as two ν_{CS} bands [9–11].

4.2. *Structure of* $\{Cd(SCN)_2(ppz)\}_n$ *(1)*

The structure of **1** was solved in the space group $P\bar{1}$. Figure 1(a) shows the local coordination of the cadmium center in **1**. Selected bond distances and angles are listed in table 2. The cadmium adopts a distorted octahedral geometry of four nitrogen atoms and two *trans*-sulfur atoms. The *trans*-N atoms form the ppz ligands (Cd(1)–N(1) = 2.380(2), N(1)–Cd(1)–N(1A) = 180.0°), and two pairs of N and S atoms from the bridging bidentate NCS^- ligands (S(1)–Cd(1)–S(1A) = 180.0°, N(2)–Cd(1)–N(2A) = 180.0°). The four Cd–N bond distances ranging from 2.354(3) to 2.380(2) Å are clearly shorter than Cd–S distance of 2.7517(11) Å in good agreement with previous reports. The connection between Cd(II) and NCS^- groups are bent with a Cd(1A)–N(2)–C(3) angle of 164.1(3)°. The neutral ppz ligands are bonded to the metal center



Scheme 1. Reaction pathways for **1–2.**

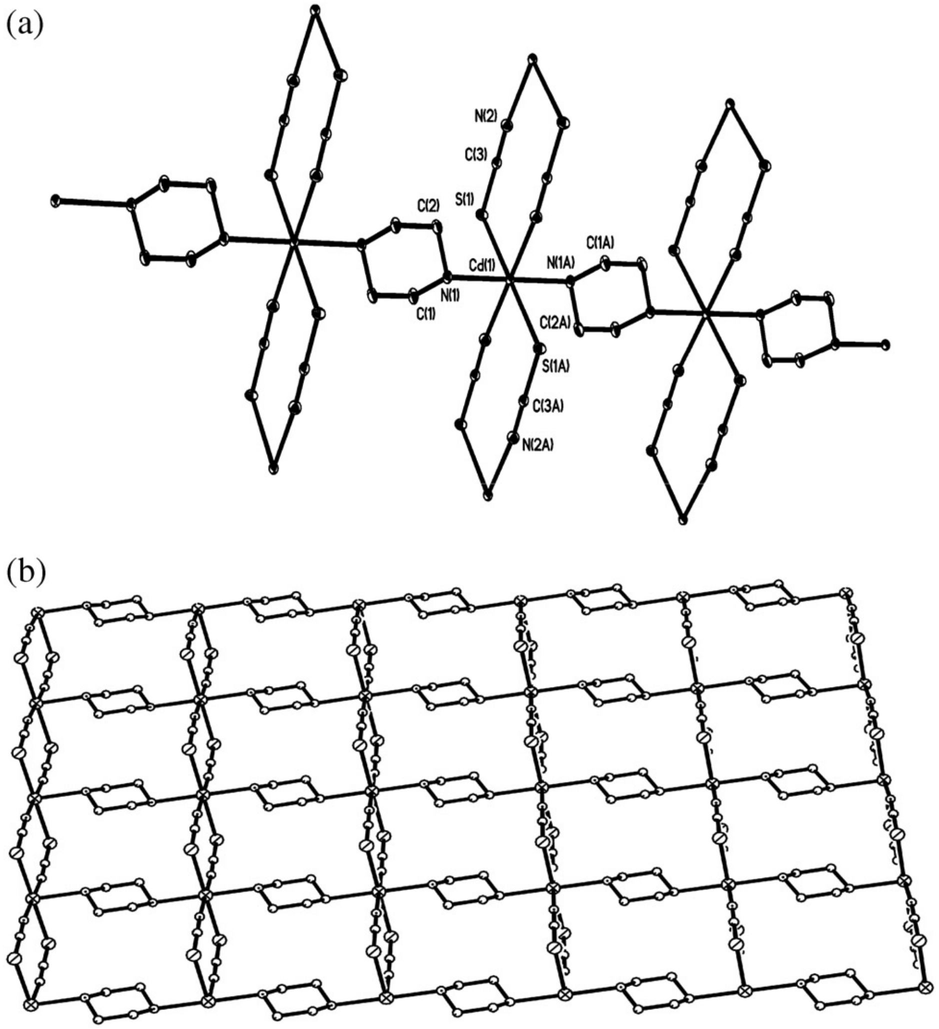


Figure 1. (a) An ORTEP drawing showing the local coordination of Cd in **1**. (b) An ORTEP diagram showing the two-dimensional rectangular grid.

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

Cd(1)–N(2A)	2.354(3)	Cd(1)–N(1)	2.380(2)
Cd(1)–S(1)	2.7517(11)		
N(2A)–Cd(1)–N(2A)	180.0	N(2A)–Cd(1)–N(1)	89.57(10)
N(2A)–Cd(1)–N(1)	90.43(10)	N(2A)–Cd(1)–N(1A)	90.43(10)
N(1)–Cd(1)–S(1)	90.69(7)	N(1A)–Cd(1)–S(1)	89.31(7)
S(1)–Cd(1)–S(1A)	180.0	N(2)–C(3)–S(1)	178.1(3)

Symmetry transformations used to generate equivalent atoms: (A): $-x+2$, $-y$, $-z$.

through two neutral amine nitrogen atoms, forming one-dimensional linear Cd–ppz–Cd chains consisting of cadmium(II) ions and bridging ppz ligands. The 2-D grid structure of **1** can be regarded as double bridging chains involving thiocyanato ligands. The ppz ligand is bidentate to the metal through the two amine nitrogen atoms, while two NCS^- ligands bridge Cd(II) atoms in a bidentate bonding mode through their S and N atoms. Figuer 1(b) shows that **1** is a coordination polymer of $\{Cd(SCN)_2(ppz)\}_n$, forming 2-D rectangular grids. Both NCS^- ligands are linear, with angles at the Cd center of 178.1(3)° for S(1)–C(1)–N(1). The Cd $\cdots$ Cd distance in the Cd–ppz–Cd chain is 7.582 Å and the Cd $\cdots$ Cd separation in the Cd–$(NCS)_2$–Cd chain is 6.016 Å.

Complex **1** exhibits interesting comparisons with complexes containing ppz ligands [12,13]. The Co(II) center takes unusual compressed trigonal–bipyramidal coordination in mononuclear $[Co(Hppz)_2Cl_3] \cdot Cl \cdot H_2O$ and multiple hydrogen-bonding interactions extend this structure into a 3-D supramolecular network [12a]. The ppz ligand in $[Zn(NCS)_2(ppz)]_n$ is coordinated to Zn(II) centers through both N atoms to form a 1-D zigzag chain structure and the distorted tetrahedral coordination geometry at each metal center is completed by a pair of N-bonded SCN^- groups [12b]. $[CoCl_2(ppz)]_n$ has an analogous 1-D zigzag chain structure containing terminal chloro ligands [12b]. The 2-D network of $[Cd_2(OAc)_3(ppz)(im)]_n$ (im = imidazolate) is a quaternary coordination polymer [12c]. The complexes $[M(ppz)(ox)]_n$ (M = Cu and Ni) consist of intersecting $[M(ox)]_n$ and $[M(ppz)]_n$ chains, resulting in layered structures with cavities 5.9848(14) × 6.4997(16) Å and 5.414(1) × 6.8678(3) Å, respectively [12d]. Complex **1** has the largest cavity (6.016 × 7.582 Å) in 2-D rectangular coordination polymer grids containing ppz ligands in comparison to $[M(ppz)(ox)]_n$ (M = Cu and Ni).

4.3. *Structure of* $\{Cd(NCS)_2(bpa)\}_n$ *(2)*

The structure of **2** was solved in the space group *C*2/*c*. The ORTEP diagram, Figure 2(a), shows local coordination of the cadmium center and the overlap drawing of the disordered bpa ligands. Figure 2(b) shows two-dimensional frameworks consisting of cadmium(II) and bridging SCN^- and bpa ligands. Selected bond distances and angles are listed in table 3. The cadmium adopts a slightly distorted octahedral coordination geometry with the bond angles deviating slightly from 90 or 180°. The *trans*-nitrogen atoms from bpa ligands (N(2)–Cd(1)–N(2C) = 180.0°), two *trans* nitrogen and two *trans* sulfur atoms from the four differently bridging NCS^- ligands (N(1A)–Cd(1)–N(1B) = 180.0° and S(1)–Cd(1)–S(1C) = 180.00°), show that Cd(II) adopts a {CdN4S2} octahedral coordination geometry. The two Cd–N bond distances from 2.321(4) to 2.353(3) Å are clearly shorter than Cd–S, 2.7520(12) Å in good agreement with previous reports. The bidentate bridging thiocyanato groups bond to the cadmium centers with N and S atoms forming eight-membered rings. The 2-D $[Cd(SCN)_2(bpa)]_n$ networks show 30-membered rings containing rectangular pores (5.774 × 14.019 $Å^2$), which contain four cadmium atoms, four SCN^- bridging ligands and two bidentate bridging bpa ligands. The bpa ligand in this complex adopts an *anti* conformation with dihedral angles of −180° (C(4)–C(7)–C(7B)–C(4B)). Complex **2** makes interesting comparisons with the 2-D rectangular grids [14] $[M(N_3)_2(bpa)]_n$ (M = Fe, Mn, Co, Ni; N_3 = azide), $\{[Cu(bpa)(SO_4)(H_2O)] \cdot H_2O\}_n$, $[M(adipate)(bpa)]_n$ (M = Co and Mn), $[Co(ox)(bpa)]_n$, $[Ag(bpa)(NO_3)]_n$ and the 1-D polymeric chain structures of $[M(NCO)_2(bpa)_2]_n$ (M = Co, Mn) and $[Pb(NSC)_2(bpa)]_n$ [15]. Complex **3**

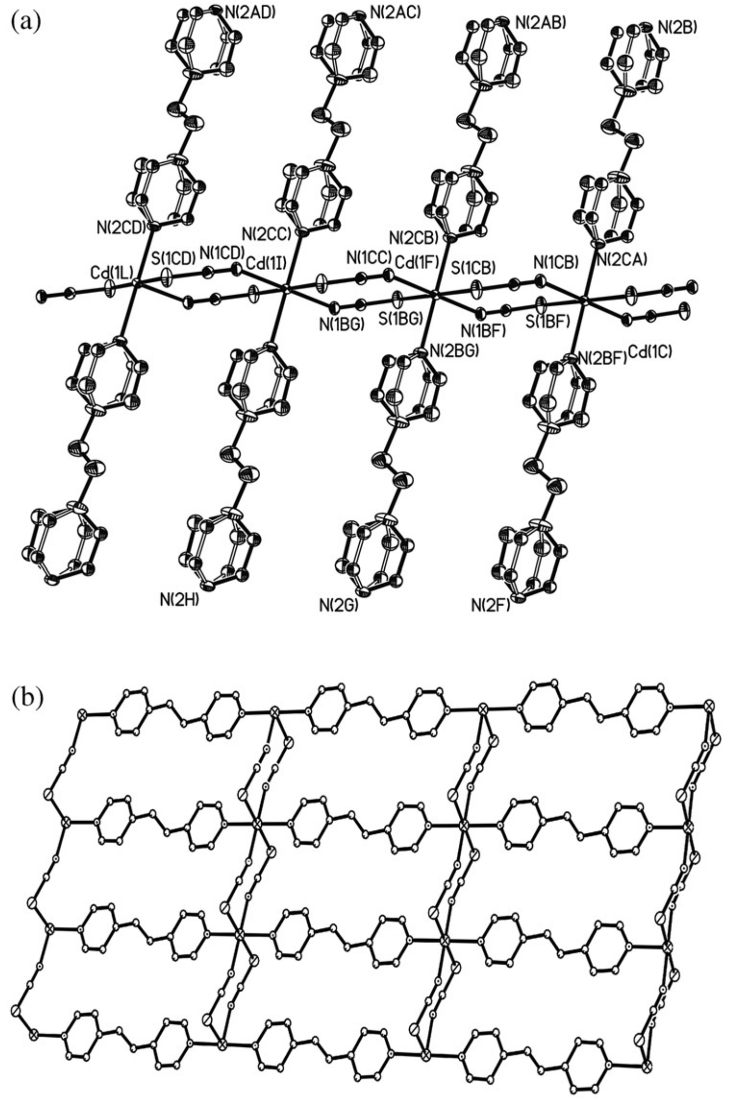


Figure 2. (a) An ORTEP drawing showing the local coordination of Cd in **2** and the overlap of the two disordered bpa ligands. (b) An ORTEP diagram showing the two-dimensional rectangular grid.

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Cd(1)–N(1A)	2.321(4)	Cd(1)–N(2)	2.353(3)
Cd(1)–S(1)	2.7520(12)		
N(1A)–Cd(1)–N(1B)	180.0	N(1A)–Cd(1)–N(2)	90.43(14)
N(1B)–Cd(1)–N(2)	89.57(14)	N(1A)–Cd(1)–N(2C)	89.57(14)
N(2)–Cd(1)–S(1)	88.30(10)	N(2C)–Cd(1)–S(1)	91.70(10)
S(1C)–Cd(1)–S(1)	180.00(6)	N(1)–C(1)–S(1)	178.6(4)

Symmetry transformations used to generate equivalent atoms: (A): $-x, -y+1, -z$; (B): $x, y+1, z$; (C): $-x, -y+2, -z$; (D): $x, y-1, z$.

was similar to the complexes $[M(N_3)_2(bpa)]_n$ (M = Fe, Mn, Co, Ni; N_3 = azide) with bridging N_3^- but all were 2-D rectangular grids. The 1-D complexes $[M(NCO)_2(bpa)_2]_n$ (M = Co, Mn) and $[Pb(NSC)_2(bpa)]_n$ are inter linked through CH–O or S–Pb interactions to form pseudo-network structures.

5. Conclusions

Syntheses and structures of rectangular grids $\{Cd(SCN)_2(ppz)\}_n$ (**1**) and $\{Cd(NCS)_2(bpa)\}_n$ (**2**) have been successfully accomplished. The complexes $\{Cd(NCS)_2(NN)\}_n$ (NN = ppz for **1** and bpa for **2**) consist of intersecting $[M(NCS)_2]_n$ and $[M(NN)]_n$ chains, resulting in layered structures with cavities 6.016 × 7.582 Å and 5.774 × 14.019 Å, respectively.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 600230–600231. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(0)-1223-336033; Email: deposit@ccdc.cam.ac.uk]

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