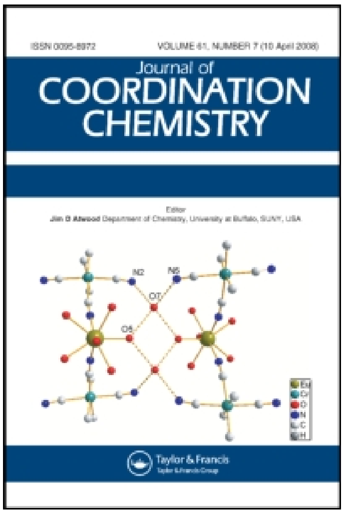

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and structural characterization of three new cadmium(II) coordination polymers containing thiocyanato and pyridyl ligands

Maw-Cherng Suen[a]; Ju-Chun Wang[b]
[a] Department of Textile Science, Nanya Institute of Technology, Jhongli, R.O.C, Taiwan [b] Department of Chemistry, Soochow University, Taipei, R.O.C, Taiwan

To cite this Article Suen, Maw-Cherng and Wang, Ju-Chun(2007) 'Synthesis and structural characterization of three new cadmium(II) coordination polymers containing thiocyanato and pyridyl ligands', Journal of Coordination Chemistry, 60: 3, 257 — 268

To link to this Article: DOI: 10.1080/00958970600873315

URL: http://dx.doi.org/10.1080/00958970600873315

Journal of Coordination Chemistry
Vol. 60, No. 3, 10 February 2007, 2007, 257–268

Taylor & Francis
Taylor & Francis Group

Synthesis and structural characterization of three new cadmium(II) coordination polymers containing thiocyanato and pyridyl ligands

MAW-CHERNG SUEN*† and JU-CHUN WANG‡

†Department of Textile Science, Nanya Institute of Technology, Jhongli, Taiwan, R.O.C
‡Department of Chemistry, Soochow University, Taipei, Taiwan, R.O.C

(*Received 16 December 2005; in final form 4 April 2006*)

The reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with NH_4SCN and dpa (dpa = 2,2′-dipyridylamine) in CH_3OH afforded the complex $[Cd(SCN)_2(dpa)]_n$ (**1**), while reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with NH_4SCN and pca (pca = 2,2′-dipicolylamine) in CH_3OH gave complexes of the type $[Cd(SCN)_2(pca)]_n$ (**2**). The reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with NH_4SCN, H_2ox (H_2ox = oxalic acid) and amp (amp = 2-aminopyridine) in CH_3OH gave complexes of the type $\{[Cd(NCS)_2(ox)](Hamp)_2\}_n$ (**3**). Their IR spectra have been recorded and their structures determined. Complex **1** shows 1-D polymeric double-stranded chains with bridging thiocyanato groups. The double-stranded linear chains in **1** have eight-membered rings and close-pack to form the 3-D structures through C–H$\cdots$S hydrogen bonding and π–π interactions. In the pseudo {CdN5S} octahedral complex **2**, the nitrogen containing ligands occupy amine and pyridyl groups of the *fac*-pca ligand and two nitrogen atoms and one sulfur atom from the two bridging and one monodentate NCS^- ligands, forming the 1-D polymeric helical chain. Complex **3** shows a 3-D supramolecular structure by weak S$\cdots$S interactions among the 2-D ionic sheets to contain each cadmium octahedrally coordinated by two *cis* sulfur atoms, two *cis* nitrogen atoms from four μ(N,S) bridging thiocyanato groups and two oxygen atoms from the chelating oxalate ligands.

Keywords: Coordination polymer; Cadmium; Thiocyanato; Sheet; Network; Zig-zag; Helical

1. Introduction

Great 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 that can be constructed relies on suitable metal-ligand interactions and hydrogen bonding, and the various types of polymeric structures include 1-D, 2-D and 3-D network structures [2]. The crystal engineering of coordination polymers with inner cavities or channels of desired sized has been achieved recently by using suitable bidentate ligands. Investigations in this area have led to many materials of interesting structures with rigid ligands like pyrazine and 4,4′-bipyridine [3–4]. The thiocyanate

---

*Corresponding author. Email: sun@nanya.edu.tw

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970600873315

anion is a versatile bridging ligand as it can link a metal centre either end-to-end or end-on, both possibilities being structurally characterized for transition metal complexes [5]. The synthesis and structures of three new coordination polymers, $[Cd(SCN)_2(dpa)]_n$ (**1**), $[Cd(SCN)_2(pca)]_n$ (**2**) and $\{[Cd(NCS)_2(ox)](Hamp)_2\}_n$ (**3**), form the subject of this report.

2. Experimental

2.1. *Starting material*

The reagents $Cd(NO_3)_2 \cdot 4H_2O$, NH_4SCN, dpa (dpa = 2,2′-dipyridineamine), pca (pca = 2,2′-dipicolylamine), H_2ox (H_2ox = oxalic acid) and amp (amp = 2-aminopyridine) were purchased from Aldrich Chemical Co. and used as received.

2.2. *Preparation of $[Cd(SCN)_2(dpa)]_n$ (1)*

$Cd(NO_3)_2 \cdot 4H_2O$ (0.31 g, 1 mmol), NH_4SCN (0.15 g, 2 mmol) and dpa (0.17 g, 1 mmol) were placed in a flask containing 10 mL CH_3OH. The mixture was stirred at room tempature 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**: 0.33 g (83%). Anal. Calcd for $C_{12}H_9CdN_5S_2$: C, 36.05; H, 2.27; N, 17.52%. Found: C, 36.01; H, 2.23; N, 17.82%. IR (KBr disk): 3308(br), 2115(m), 1626(m), 1584(m), 1525(m), 1470(m), 1433(m), 1417(m), 1384(m), 1347(m), 1271(m), 1228(m), 1162(m), 1060(m), 1007(m), 902(m), 775(m), 603(m), 521(m). Colorless crystals suitable for X-ray diffraction were grown by slow diffusion of dpa 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.

2.3. *Preparation of $[Cd(SCN)_2(pca)]_n$ (2)*

$Cd(NO_3)_2 \cdot 4H_2O$ (0.31 g, 1 mmol), NH_4SCN (0.15 g, 2 mmol) and pca (0.20 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**: 0.33 g (78%). Anal. Calcd for $C_{14}H_{13}CdN_5S_2$: C, 39.30; H, 3.06; N, 16.37%. Found: C, 38.99; H, 3.00; N, 16.37%. IR (KBr disk): 3203(br), 2090(m), 2065(m), 1628(m), 1582(m), 1529(m), 1471(m), 1418(m), 1362(m), 1270(m), 1230(m), 1153(m), 1004(m), 905(m), 864(m), 770(s), 700(m), 638(m), 600(s), 527(m). Colorless crystals suitable for X-ray diffraction were grown by slow diffusion of pca 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 $\{[Cd(NCS)_2(ox)](Ham)_2\}_n$ (3)*

$Cd(NO_3)_2 \cdot 4H_2O$ (0.31 g, 1 mmol), NH_4SCN (0.15 g, 2 mmol), H_2ox (0.09 g, 1 mmol) and amp (0.19 g, 2 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 **3**: 0.27 g (75%). Anal. Calcd for $C_8H_7CdN_4O_2S_2$: C, 26.13; H, 1.92; N, 15.24%. Found: C, 26.33; H, 1.90; N, 15.33%. IR(KBr disk): 3345(br), 2102(m), 1670(m), 1641(m), 1605(m), 1482(m), 1384(m), 1347(m), 1313(m), 792(m), 777(m), 766(m), 517(m). Colorless crystals suitable for X-ray diffraction were grown by slow diffusion of the mixture of ox and amp 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** and **2** were collected at 25°C on a Bruker AXS P4 diffractometer and that of complex **3** was collected at 25°C on a Siemens CCD diffractometer, both of which were equipped with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. Data reduction was carried out by standard methods with the use of well-established computational procedures [6]. The structure factors were obtained after Lorentz and polarization correction. The positions of some of the heavier atoms, including the cadmium, were located by the direct method. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements [7]. The final residuals of the final refinement were $R_1 = 0.0325$, $wR_2 = 0.0800$ for **1**. The crystallographic procedures for **2** and **3** were similar to those for **1** and the final residuals of the final refinement were $R_1 = 0.0489$, $wR_2 = 0.1101$ for **2** and $R_1 = 0.0157$, $wR_2 = 0.0397$ for **3**. Basic information pertaining to crystal parameters and structure refinement is summarized in table 1.

4. Results and discussion

4.1. *Synthesis and spectroscopic studies*

The reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with dpa (dpa = 2,2′-dipyridineamine), pca (pca = 2,2′-dipicolylamine), H_2ox (H_2ox = oxalic acid) and amp (amp = 2-aminopyridine) and NH_4SCN in CH_3OH afforded the complexes $[Cd(SCN)_2(dpa)]_n$ (**1**), $[Cd(SCN)_2(pca)]_n$ (**2**) and $\{[Cd(NCS)_2(ox)](Hamp)_2\}_n$ (**3**), respectively. Their structures have been determined by spectroscopic methods and by X-ray crystallography. The IR spectra for **1**–**3** show very strong and sharp bands at 2115, 2090 and 2102 cm^{-1} due to the ν_{CN} 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 [8–10]. The IR spectrum for **3** also displays the characteristic bands of the bridging D_{2h} oxalate groups with a strong band near 1605 cm^{-1} for ν_{asCO}, a doublet in the 1350–1340 cm^{-1} for ν_{syCO} and a band near 792 cm^{-1} for δ_{OCO} [11–12].

4.2. *Structure of $[Cd(SCN)_2(dpa)]_n$ (1)*

The structure of **1** was solved in the space group $P2_1/c$. Figure 1(a) shows the local coordination of the cadmium center in **1**. Selected bond distances and angles are

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

Formula	$C_{12}H_9CdN_5S_2$	$C_{14}H_{13}CdN_5S_2$	$C_8H_7CdN_4O_2S_2$
Formula weight	399.76	427.81	367.70
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$Pbca$	$P\bar{1}$
a (Å)	7.3566(7)	9.0572(7)	8.9872(14)
b (Å)	18.006(2)	11.195(3)	9.1559(14)
c (Å)	10.9432(8)	31.898(2)	9.2538(14)
α (°)	90	90	112.213(2)
β (°)	100.629(5)	90	108.439(2)
γ (°)	90	90	97.480(2)
V (Å^3)	1427.7(2)	3234.3(8)	641.14(17)
Z	4	8	2
D_{calc} (g cm^{-3})	1.864	1.757	1.905
$F(000)$	784	1696	358
μ(Mo-Kα), (mm^{-1})	1.421	1.611	2.023
Data collcn. Instrum.	Bruker AXS P4	Bruker AXS P4	Siemens CCD
Radiation monochromated in incident beam (λ(Mo-Kα))	0.71073	0.71073	0.71073
Range (2θ) for data collection (°)	$4.56 \le 2\theta \le 50.08$	$5.10 \le 2\theta \le 49.98$	$4.98 \le 2\theta \le 56.72$
Temp. (°C)	25	25	25
Limiting indices	$-25 \le h \le 25$, $-5 \le k \le 6$, $-19 \le l \le 19$	$0 \le h \le 10$, $0 \le k \le 13$, $0 \le l \le 37$	$-11 \le h \le 11$, $-12 \le k \le 11$, $-12 \le l \le 12$
Reflections collected	4955	2810	7288
Independent reflections	1481 [R(int) = 0.0195]	2810 [R(int) = 0.0000]	3073 [R(int) = 0.0176]
Refinement method	Full-matrix Least-squares on F^2	Full-matrix Least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1481/0/93	2810/0/199	3073/0/183
Quality-of-fit indicator[c]	1.077	1.232	1.066
Final R indices [$I > 2\sigma(I)$][a,b]	$R_1 = 0.0325$, $wR_2 = 0.0800$	$R_1 = 0.0489$, $wR_2 = 0.1101$	$R_1 = 0.0157$, $wR_2 = 0.0397$
R indices (all data)	$R_1 = 0.0377$, $wR_2 = 0.0836$	$R_1 = 0.0646$, $wR_2 = 0.1201$	$R_1 = 0.0174$, $wR_2 = 0.0409$
Largest diff. peak and hole e (Å^3)	0.812 and −0.503	1.147 and −0.560	0.499 and −0.374

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

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (ap)^2 + (bp)]$, $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. $a = 0.1874$, $b = 0.0000$ for **1**; $a = 0.000$, $b = 0.9054$ for **2**; $a = 0.0268$, $b = 5.5388$ for **3**.

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

listed in table 2. The cadmium metal center adopts a distorted octahedral geometry of four nitrogen atoms and two sulfur atoms. Four nitrogen atoms are from two pyridyl groups of dpa, two *cis* nitrogen and *cis* two sulfur atoms from the four different NCS^- ligands. The four bond lengths of Cd–N observed from 2.321(2) to 2.3603(19) Å are clearly shorter than Cd–S distance of 2.6560(7) or 2.8445(7) Å in good agreement with previous reports. Both NCS^- ligands are linear, with angles at the cadmium center of 179.4(2)° of N(1)–C(1)–S(1) and 177.6(2)° of N(2)–C(2)–S(2). The Cd $\cdots$ Cd distance in the molecular chain is 6.006 Å, separated by two bridging NCS^- ligands as shown in figure 1(b). The dpa ligand is coordinated to cadmium center in a bidentate fashion, with two terminal pyridine nitrogen atoms, i.e. in a *cis*-N conformation, and amine group nitrogen atoms are not coordinated. The bidentate dpa ligand in each molecule is not flat, but twisted around the central C–N bonds, with dihedral angles between the planes of two pyridine rings of 32° in complex **1**.

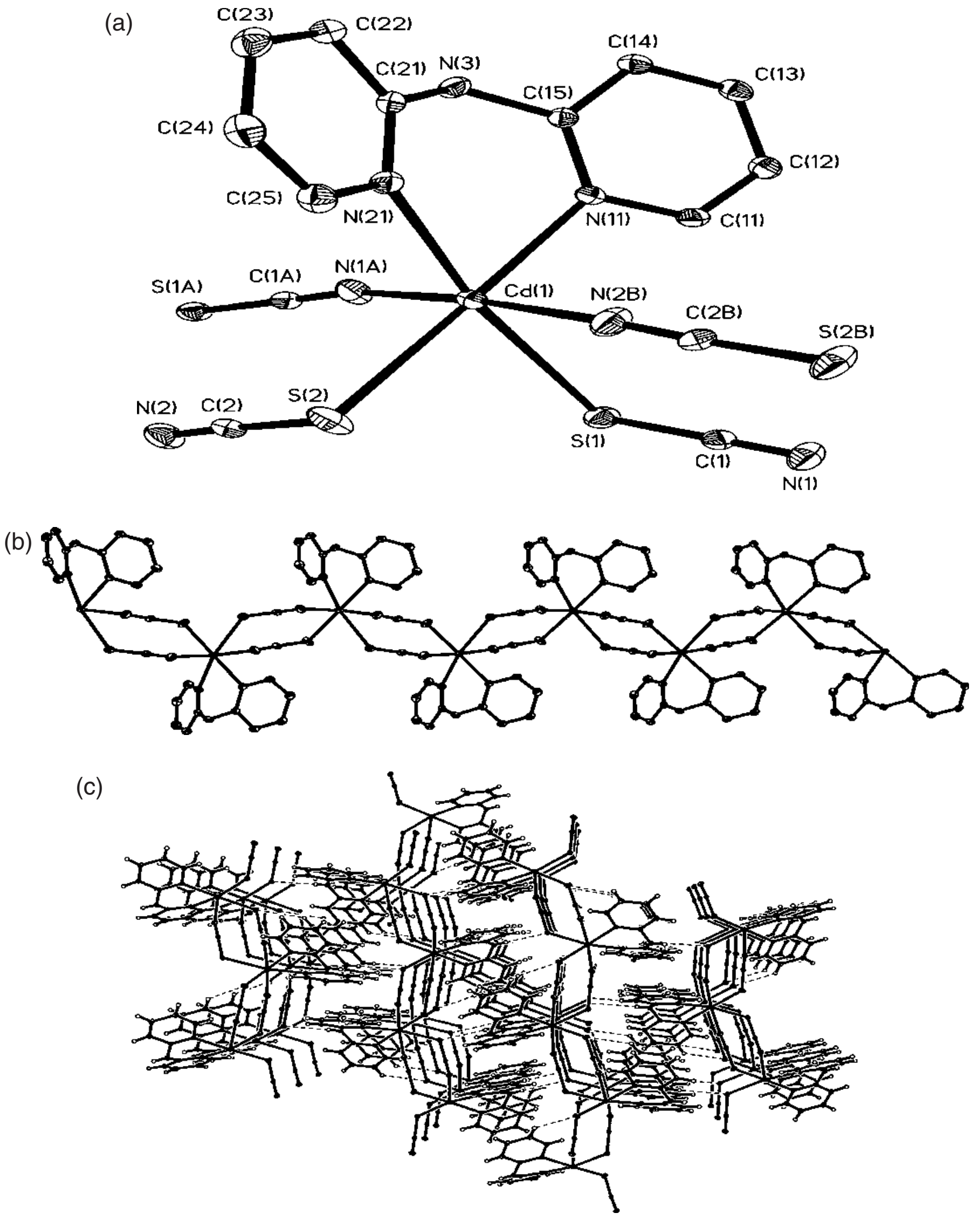

Figure 1. (a) An ORTEP drawing showing the local coordination of Cd in **1**. (b) An ORTEP diagram showing the infinite one-dimensional chains. (c) Packing diagram of **1** showing the channel-type chains which are linked by the C–H $\cdots$ S interactions.

The most striking feature in complex **1** shows that the molecular chains are interlinked into a two-dimensional structure through extensive C–H $\cdots$ S (H $\cdots$ S = 2.801 Å and ∠C–H $\cdots$ S = 178.9°) hydrogen bonding intermolecular hydrogen bonding interactions between C–H groups of the pyridyl rings and the sulfur atoms of the thiocyanate groups. The molecular chains are further linked to each other through

Table 2. Selected bond distances (Å) and angles (°) for $[Cd(SCN)_2(dpa)]_n$ (**1**).

Cd(1)–N(1A)	2.321(2)	Cd(1)–N(2B)	2.325(2)
Cd(1)–N(11)	2.3344(17)	Cd(1)–N(21)	2.3603(19)
Cd(1)–S(2)	2.6560(7)	Cd(1)–S(1)	2.8445(7)
N(1A)–Cd(1)–N(2B)	174.90(8)	N(1A)–Cd(1)–N(11)	90.84(7)
N(2B)–Cd(1)–N(11)	91.77(8)	N(1A)–Cd(1)–N(21)	98.80(8)
N(2B)–Cd(1)–N(21)	85.97(7)	N(11)–Cd(1)–N(21)	80.08(6)
N(1A)–Cd(1)–S(2)	94.19(5)	N(2B)–Cd(1)–S(2)	83.52(7)
N(11)–Cd(1)–S(2)	173.68(5)	N(21)–Cd(1)–S(2)	95.35(5)
N(1A)–Cd(1)–S(1)	87.81(6)	N(2B)–Cd(1)–S(1)	87.67(6)
N(11)–Cd(1)–S(1)	93.15(5)	N(21)–Cd(1)–S(1)	170.55(5)
S(2)–Cd(1)–S(1)	90.87(3)	N(2)–C(2)–S(2)	177.6(2)
N(1)–C(1)–S(1)	179.4(2)		

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

aromatic π–π stackings to form an infinite three-dimensional network. The inter planar distances between the pyridyl rings is 3.88 Å. The structure of $\{Cd(SCN)_2(dpa)\}_n$ (**1**) consists of C–H ⋯ S hydrogen bonding and π–π stackings to form a three-dimensional structure, as shown in figure 1(c). There are two *cis* thiocyanate sulfurs and two *cis* thiocyanate nitrogens with two *cis* pyridine nitrogens in structure **1** which differ from $[Cd(SCN)_2(dpa)_2]$ [13] showing a new unequivalent coordination of two SCN^- ligand and a layered structure built by C–H ⋯ S and N–H ⋯ S hydrogen bonding and weak π–π interactions. Structure **1** was similar to the complex $[Cd(3,5\text{-dmp})_2(N_3)_2]_n$ (3,5-dmp = 3,5-dimethylpyridine, N_3 = the anion of azide) [14] which shows the 1-D chain containing each cadmium octahedrally coordinated by two double μ(1,3)-bridging azides and the other two sites occupied by two pyridine ligands in a *cis*-arrangement. The Cd ⋯ Cd distances in the $Cd(N_3)_2$ eight membered chains are 5.142(2) and 5.152(2) Å shorter than the 6.006 Å of the $Cd(SCN)_2$ chain in **1**.

4.3. *Structure of* $[Cd(SCN)_2(pca)]_n$ *(2)*

The structure of **2** was solved in the space group *Pbca*. Figure 2(a) shows the local coordination of the cadmium center in **2**, while figure 2(b) shows its one-dimensional helical chains consisting of cadmium(II) ions and bridging SCN^- ligands. Selected bond distances and angles are listed in table 3. The cadmium metal center adopts a slightly distorted octahedral coordination geometry with bond angles only deviating slightly from 90 or 180°. The cadmium metal center adopts a distorted octahedral geometry of five nitrogen atoms and one sulfur atom. Three N atoms are from the *fac*-tridentate pca ligand, and two nitrogen atoms and one sulfur atom from the two bridging and one monodentate NCS^- ligands. The five Cd–N bond lengths from 2.273(6) to 2.392(6) Å are clearly shorter than the Cd–S distance of 2.756(2) Å in good agreement with previous reports. The neutral pca ligands are chelated to the metal center through one amine nitrogen atom and two adjacent pyridine nitrogen atoms, resulting in two five-membered rings. Each of the two pca's in the molecule contains a sort of intraligand dihedral angle between two pyridyl rings with angles of 91°. Figure 2(b) shows that complex **2** is a coordination polymer of $\{Cd(SCN)_2(pca)\}_n$, forming a 1-D helical chain. Both NCS^- ligands are linear, with angles at the Cd center of 177.0(7)° for S(1)–C(1)–N(1) and 173.3(9)° for S(2)–C(2)–N(2). The Cd ⋯ Cd distance in the molecular

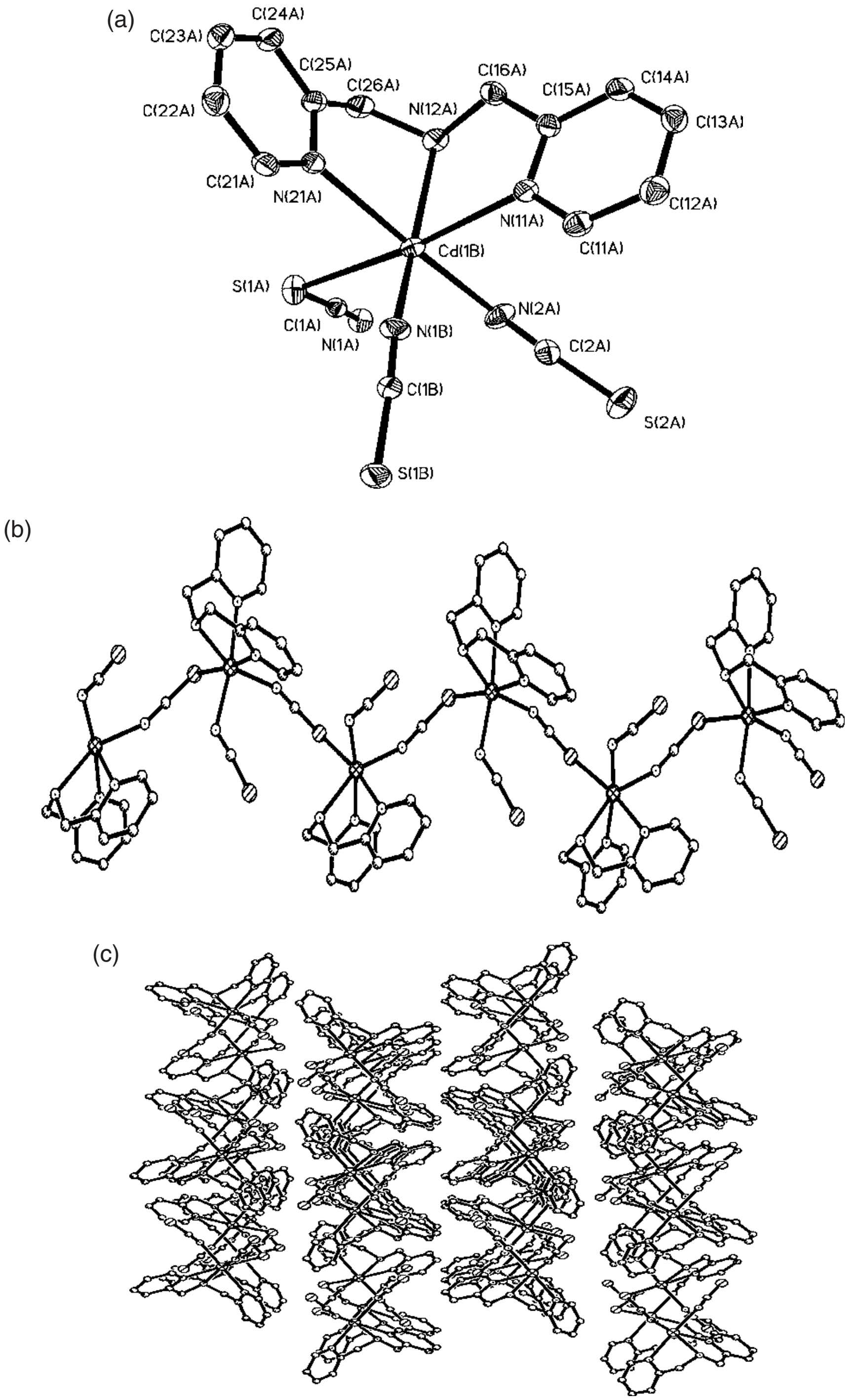

Figure 2. (a) An ORTEP drawing showing the local coordination of Cd in **2**. (b) An ORTEP diagram showing the one-dimensional helical chains. (c) View down the b-axis showing the packing of the chains in **2**.

Table 3. Selected bond distances (Å) and angles (°) for $[Cd(SCN)_2(pca)]_n$ (**2**).

Cd(1)–N(1)	2.273(6)	Cd(1)–N(2)	2.314(8)
Cd(1)–N(12)	2.368(7)	Cd(1)–N(11)	2.376(6)
Cd(1)–N(21)	2.392(6)	Cd(1)–S(1A)	2.756(2)
N(1)–Cd(1)–N(2)	94.8(3)	N(1)–Cd(1)–N(12)	156.0(2)
N(2)–Cd(1)–N(12)	100.8(3)	N(1)–Cd(1)–N(11)	90.6(2)
N(2)–Cd(1)–N(11)	87.7(2)	N(12)–Cd(1)–N(11)	72.1(2)
N(1)–Cd(1)–N(21)	93.2(2)	N(2)–Cd(1)–N(21)	171.6(2)
N(12)–Cd(1)–N(21)	72.5(2)	N(11)–Cd(1)–N(21)	94.9(2)
N(1)–Cd(1)–S(1A)	98.92(19)	N(2)–Cd(1)–S(1A)	93.02(19)
N(12)–Cd(1)–S(1A)	98.31(17)	N(11)–Cd(1)–S(1A)	170.36(17)
N(21)–Cd(1)–S(1A)	83.11(15)	N(1)–C(1)–S(1)	177.0(7)
N(2)–C(2)–S(2)	173.3(9)		

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

chain is 6.415 Å. Figure 3(c) shows the packing of the helical chains in **2**, viewed down the b-axis.

Complex 2 makes interesting comparisons with the complexes $[Cd(pca)_2](ClO_4)_2$, $[Cd(pca)(NCCH_3)(OH_2)(OClO_3)](ClO_4)\cdot(CH_3CN)$ and $Zn(pca)(SPh)_2$ (SPh = the anion of thiophenol) [15]. The complex $[Cd(pca)_2](ClO_4)_2$ was prepared by the reactions of $CdCl_2\cdot H_2O$ with $pca\cdot 3HCl\cdot H_2O$, NaOH and $LiClO_4$ in methanolic aqueous solution at *RT*. The coordination sphere of this two-fold axis complex is octahedron, with two *fac*-tridentate pca ligands and four pyridyl nitrogen atoms lying on the equatorial plane [15(a)]. The monocation complex $[Cd(pca)(NCCH_3)(OH_2)(OClO_3)](ClO_4)\cdot CH_3CN$ was synthesized by $Cd(ClO_4)_2\cdot 6H_2O$ with pca ligands in the CH_3CN aqueous solution. In the pseudo-octahedral monocation, the nitrogen-containing ligands occupy equatorial positions with amine and pyridyl groups of the *mer*-pca ligand and one $NCCH_3$, and the Cd(II) centers adopt a {CdN4O2} octahedral coordination geometry [15(b)]. $Zn(pca)(SPh)_2$ was obtained from $Zn(ClO_4)_2$, pca, and NaSPh in methanol. $Zn(pca)(SPh)_2$ is of the ZnN3S2 type in the nitrogen donors reliably occupy one equatorial and both axial positions of a trigonal bipyramid, which would then force the thiolate donors to fill the two remaining equatorial positions [15(c)]. Complex **2** is the first Cd coordination polymer containing tridentate pca ligands.

4.4. *Structure of* $\{[Cd(NCS)_2(ox)](Hamp)_2\}_n$ *(3)*

The structure of **3** was solved in the space group $P\bar{1}$. Figure 3(a) shows the local coordination of the cadmium center in **3**, while figure 3(b) shows its two-dimensional anionic framework consisting of cadmium(II) ions and bridging SCN^- and oxalate ligands. Selected bond distances and angles are listed in table 4. The cadmium metal center adopts a slightly distorted octahedral geometry with the bond angles only deviating slightly from 90 or 180°. In the distorted octahedral anionic frameworks $[Cd(SCN)_2(ox)]^{2-}$, the *cis*-oxygen atoms of oxalate, two *cis* nitrogen and two *cis* sulfur atoms from the four different NCS^- ligands, give a $\{CdN_2O_2S_2\}$ octahedral coordination geometry. The two Cd–N bond lengths observed 2.2519(15) and 2.3588(16) Å are clearly shorter than the Cd–S distance of 2.6318(5) or 2.7138(6) Å.

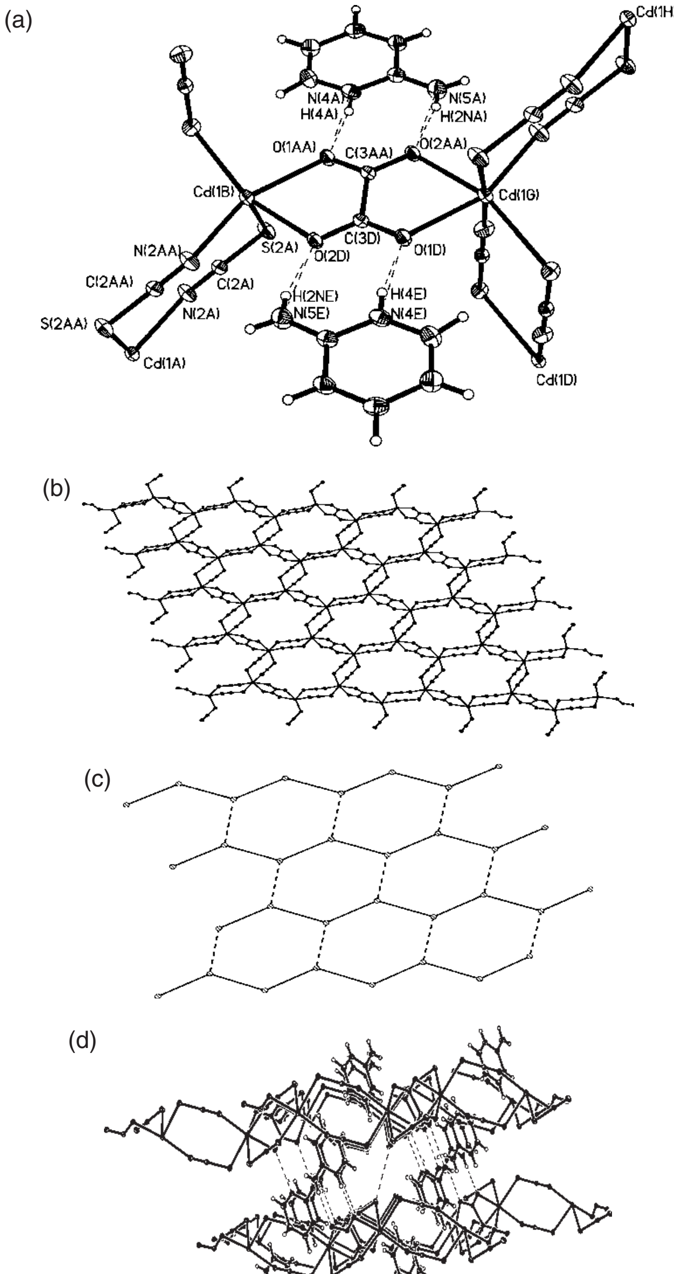

Figure 3. (a) An ORTEP drawing showing the local coordination of Cd in **3** and N–H—O hydrogen bondings among molecules. (b) The two-dimensional anionic frameworks in **3**. (c) Schematic drawing for complex **3**. The bridging NCS^- ligands with the solid line, and the oxalate groups with the dashed solid line, respectively. (d) Packing diagram for **4** showing the N–H—O and S—S interactions between the chains.

Table 4. Selected bond distances (Å) and angles (°) for $\{[Cd(NCS)_2(ox)](Hamp)2\}_n$ (**3**).

Cd(1)–N(2)	2.2519(15)	Cd(1)–O(2A)	2.3227(11)
Cd(1)–O(1)	2.3457(11)	Cd(1)–N(1B)	2.3588(16)
Cd(1)–S(1)	2.6318(5)	Cd(1)–S(2C)	2.7138(6)
N(2)–Cd(1)–O(2A)	89.11(6)	N(2)–Cd(1)–O(1)	158.10(6)
O(2A)–Cd(1)–O(1)	70.64(4)	N(2)–Cd(1)–N(1B)	91.26(6)
O(2A)–Cd(1)–N(1B)	80.06(5)	O(1)–Cd(1)–N(1B)	93.26(6)
N(2)–Cd(1)–S(1)	107.26(5)	O(2 16)–Cd(1)–S(1)	161.65(3)
O(1)–Cd(1)–S(1)	94.08(3)	N(1B)–Cd(1)–S(1)	91.07(4)
N(2)–Cd(1)–S(2C)	93.43(4)	O(2 16)–Cd(1)–S(2C)	98.27(4)
O(1)–Cd(1)–S(2C)	81.75(3)	N(1B)–Cd(1)–S(2C)	175.00(5)
S(1)–Cd(1)–S(2C)	89.192(17)	N(1)–C(1)–S(1)	178.61(16)
N(2)–C(2)–S(2)	178.98(16)		

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

The tetradentate bridging oxalates chelate to the cadmium centers (Cd–O = 2.3227(11) or 2.3457(11) Å) with different carboxyl groups forming five-membered rings. The 2-D $[Cd(SCN)_2(ox)]^{2-}$ networks show 24-membered rings containing nano-honeycomb pores (10.74 × 10.67 $Å^2$), composed of six cadmium atoms, four SCN- bridging ligands and two tetradentate bridging oxalates. The Cd ⋯ Cd distances in the molecular chain are 5.81 and 5.97 Å, separated by bridging NCS^- ligands as shown in figure 3(c) with the solid line, and the Cd ⋯ Cd distance that was separated by bridging oxalate groups is 10.67 Å with the dashed solid line. The structure of **3** consists of protonated 2-aminopyridine cationic molecules (Hamp) with N–H—O hydrogen bondings (H–O = 2.009–2.163 Å, ∠N–H—O = 166.8–167.2°) and π–π stackings (3.624 Å) as shown in figure 3(d). Complex **3** also shows the 3-D supramolecular structure by weak S ⋯ S interactions (3.609 Å) among the 2-D ionic sheets. The S–S distances of **3** which is 3.609 Å, is shorter than twice the van der Waals radius of sulfur (3.7 Å). The S–S interaction has been observed in several compounds, such as $[4,4'\text{-bipyH}_2][M(NCS)_4]$ ($M = Mn^{2+}$, Co^{2+} or Zn^{2+}; 4,4′-bipy = 4,4′-bipyridine) [16], Cu_2Cl_4L (L = 2, 5-bis (2-pyridylmethylsufanylmethyl)pyrazine) [17] and $[Hg_2(C_5H_4S_5)_2Cl_4]_n$ ($C_5H_4S_5$ = 4, 5-ethylenedithio-1,3-dithiole-2-thione) [18].

5. Conclusions

The synthesis and structures of three complexes $[Cd(SCN)_2(dpa)]_n$ (**1**), $[Cd(SCN)_2(pca)]_n$ (**2**) and $\{[Cd(NCS)_2(ox)](Hamp)_2\}_n$ (**3**) have been determined. $\{Cd(SCN)_2(dpa)\}_n$ (**1**), shows a 1-D chain containing each cadmium octahedrally coordinated by two bridging thiocyanato groups and the other two sites occupied by two pyridine groups of dpa ligands in a *cis*-arrangement. The Cd ⋯ Cd distance in the $Cd(SCN)_2$ eight-membered chains is 6.006 Å. The structure of **1** has C–H ⋯ S hydrogen bonding and π–π stackings to form a three-dimensional structure. Complex **2** shows a 1-D helical chain structure, with one *fac*-pca ligand, two bridging and one monodentate SCN groups. Complex **3** shows a 3-D supramolecular structure by weak S ⋯ S interactions, N–H—O hydrogen bonding and π–π stackings among the molecules of each octahedrally coordinated Cd from four μ(N,S) bridging thiocyanato groups and two oxygen atoms from the chelating oxalate ligands.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 256014-256016. 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 or Email: deposit@ccdc.cam.ac.uk)

Acknowledgments

We thank the National Science Council of the Republic of China for support.

References

[1] (a) G.R. Desiraju. *Angew. Chem., Int. Ed. Engl.*, **34**, 2311 (1995); (b) G.R. Desiraju. *Chem. Commun.*, **16**, 1475 (1997); (c) J.M. Lehn. *Supramolecular Chemistry*, VCH, Weinheim (1995).

[2] (a) A.J. Blake, N.R. Champness, P. Hubberstey, W.-S. Li, M.A. Withersby, M. Schröder. *Coord. Chem. Rev.*, **183**, 117 (1999); (b) S. Muthu, J.H.K. Yip, J.J. Vittal. *J. Chem. Soc. Dalton Trans.*, 4561 (2002); (c) S.R. Batten, R. Robson. *Angew. Chem., Int.*, **37**, 1460 (1998).

[3] (a) O. Kahn. *Molecular Magnetism, a Supramolecular Function*, Kluwer, Dordrecht (1996); (b) M. Gannas, G. Carta, A. Christini, G. Marongiu. *J. Chem. Soc., Dalton Trans*, 300 (1976); (c) Von G. Thiele, D. Messer, Z. Anorg. *Allgem. Chem.*, **24**, 421 (1976).

[4] (a) L.R. Groneveled, G. Vos, C. Verschoor, J. Reedijk. *J. Chem. Soc., Chem. Commun.*, **11**, 620 (1982); (b) M. Cannas, G. Carta, A. Christini, G. Marongiu. *Inorg. Chem.*, **16**, 228 (1977); (c) M. Taniguchi, M. Shimoi, A. Ouchi. *Bull. Chem. Soc. Jpn.*, **60**, 1321 (1987).

[5] (a) I.S. Ahuja, A. Grag. *J. Inorg. Nucl. Chem.*, **34**, 1929 (1972); (b) M. Taniguchi, M. Shimoi, A. Ouchi. *Bull. Chem. Soc. Jpn.*, **59**, 2299 (1986); (c) R.G. Goel, W.P. Henry, M.J. Olivier, A.L. Beauchamp. *Inorg. Chem.* **20**, 3924 (1981).

[6] SMART/SAINT/ASTRO. *Release 4.03, Siemens Energy & Automation, Inc.*, Madison, Wisconsin, USA (1995).

[7] M. Sheldrick. '*SHELXTL PLUS, Release 4.1', Siemens Analytical X-ray Instruments Inc.*, Karlsruche, Germany (1991).

[8] M.A.S. Goher, F.A. Mautner, A.K. Hafez, M.A.M. Abu-Youssef, G. Gspan, A.M.-A. Dadr. *Polyhedron*, **22**, 975 (2003).

[9] (a) P.C.H. Mitchell, R.J.P. Williams. *J. Chem. Soc.*, 1912 (1960); (b) A. Tramer. *J. Chem. Phys.*, **59**, 232 (1962); (c) J. Lewin, R.S. Nyholm, P.N. Smith. *J. Chem. Soc.*, 4590 (1961).

[10] (a) R.J.H. Clark, C.S. Williams. *Spectrochim. Acta.*, **22**, 1081 (1966); (b) A. Subatini, I. Bertini. *Inorg. Chem.*, **4**, 959 (1965); (c) M. Aslam, W.H.S. Assai. *Inorg. Nucl. Chem. Lett.*, **7**, 96 (1971); (d) M.A.S. Goher. *Coll. Czech, Chem. Commun.*, **42**, 1478 (1977).

[11] (a) F.L. Floch, J.S. Pala, J.E. Guerchais. *Bull. Soc. Chim. Fr.*, **1–2**, 120 (1975); (b) Y. Pei, Y. Journaux, O. Kahn. *Inorg. Chem.*, **28**, 100 (1989); (c) F. Bérézovsky, S. Triki, J.S. Pala, E. Coronado, C.J. Gómez-García, J.R. Galán-Mascarós. *Synth. Met.*, **102**, 1753 (1999).

[12] (a) F. Bérézovsky, S. Triki, J.S. Pala, A.A. Hajem, P. Molinié. *Inorg. Chem. Acta.*, **284**, 8 (1999); (b) F. Bérézovsky, S. Triki, J.S. Pala, E. Coronado, C.J. Gómez-García, P. Molinié, J.M. Clemente, A. Riou. *Inorg. Chem.*, **39**, 3771 (2000); (c) F. Bérézovsky, S. Triki, J.S. Pala, M.-T. Garland. *Inorg. Chem. Acta.*, **308**, 31 (2000).

[13] H. Zhu, M. Ströbele, Z. Yu, Z. Wang, H-J. Meyer, X. You. *Inorg. Chem. Commun.*, **4**, 577 (2001).

[14] M.A.S. Goher, F.A. Mautner, A.K. Hafez, M.A.M. Abu-Youssef, C. Gspan, A.M.-A. Badr. *Polyhedron*, **23**, 975 (2003).

[15] (a) J. Glerup, P.A. Goodson, D.J. Hodgson, K. Michelsen, K. M. Nielsen, H. Weihe. *Inorg. Chem.*, **31**, 4611 (1992); (b) D.C. Beout, S.W. Stokes. *Inorg. Chem.*, **38**, 1126 (1999); (c) U. Brand, R. Burth, H. Vahrenkamp. *Inorg. Chem.*, **35**, 1083 (1996).

[16] H.-J. Chen, L.-Z. Zhang, Z.-G. Cai, G. Yang, X.-M. Chen. *J. Chem. Soc., Dalton Trans.*, 2463 (2000).

[17] P.L. Caradoc-Davies, D.H. Gregory, L.R. Hanton, J.M. Turnbull. *J. Chem. Soc., Dalton Trans.*, 1574 (2002).

[18] Q.-H. Wang, D.-L. Long, J.-S. Huang. *Polyhedron*, **17**, 3665 (1998).