含 2-(2-吡啶胺基)吡嗪配位基配位高分化合物合成與結構之研究

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Abstract

The reaction of $Cd(NO_3)_2 \cdot 6H_2O$ with NH_4SCN and dpa (dpa = 2, 2′-dipyridylamine) in CH_3OH afforded the complex $[Cd(SCN)_2(dpa)]_n$, **1**, while reaction of $Cd(NO_3)_2 \cdot 6H_2O$ 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 $Cd(NO_3)_2 \cdot 6H_2O$ 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 and thermal spectra have been recorded and their structures have been determined. Complex **1** shows the 1-D polymeric double stranded chains by the bridging thiocyanato groups. The double stranded linear chains in **1** have 8 membered rings and close-pack to form the 3-D structures through C-H···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 N and one S atom from the two bridging and one monodentate NCS^- ligands, which forms the 1-D polymeric helical chain, respectively. Complex **3** shows the 3-D supramolecular structures by weak S···S interactions among the 2-D ionic sheets to contain each Cd 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 ligand.

Keyword: Coordination polymer, Cadmium, Thiocyanato, Sheet, Network, Zig-zag, Helical

1. Introduction

Recently, great effort has been devoted to the 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 bondings, 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 cannels of desired sized has been achieved recently by using suitable bidentate ligand. Investigations in this area have led to many materials of interesting structures with rigid ligands like pyrazine and 4,4′-bipyridine [3-4]. Charge ligands like thiocyanate is also used to bridge metal centres, which gives complexes of anomalous architectures with important physiical properties such as supramolecular chemistry and molecular magnetism. The thiocyanate anion is versatile bridging ligands as they 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 of $[Cd(SCN)_2(dpa)]_n$, **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. General procedures

The IR spectra were recorded on a Bio-Rad FTs-7 spectrometer. Thermogravimetric analysis (TGA) were conducted on a SDT 2960 using a heating rate of 10°C/min. Differential scanning calorimetry (DSC) measurements were carried on a Dupon DSC Q-10.

2.2. Starting Material

The reagent $Cd(NO_3)_2{\cdot}4H_2O$, 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 receivied.

2.3. 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 (0.17g, 1mmol) 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 then 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.

2.4. 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 (pca = 2,2'-dipicolylamine) (0.20g, 1mmol) 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 then 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: $C_{14}H_{13}CdN_5S_2$. 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.

2.5. 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 then 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), 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 ^{o}C on a Bruker AXS P4 diffractometer and that complex **3** was collected at 25 ^{o}C on a Siemens CCD diffractometer, which were equipped with a graphite-monochromated Mo Ka ($\lambda\alpha$ = 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 copper atom, 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 R1 = 0.0325, wR2 = 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 R1 = 0.0489, wR2 = 0.1101 for **2** and R1 = 0.0157, wR2 = 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 $Cd(NO_3)_2 \cdot 6H_2O$ 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 spectrums for **1** - **3** show the 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 we two ν_{CS} bands [8-10]. The IR spectrum for **3** also displays the characteristic bands of the bridging D_{2h} oxalate groups which are a strong band near 1605 cm^{-1} for $\nu_{asCO,}$ 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. Fig. 1(a) shows the local coordination of the cadmium center in **1**. Selected bond distances and angles are 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 form two pyridyl grourps of dpa ligand, two *cis* nitrogen and *cis* two sulfur atoms from the four differently bridging coordinated 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 being in good agreement with previous reports. Both NCS$^-$ ligands are linear, with angles at the cadmium center of 179.4(2)^{o} of N(1)-C(1)-S(1) and 177.6(2)^{o} of N(2)-C(2)-S(2), respectively. The Cd···Cd distance in the molecular chain is 6.006 Å that was separated by two bridging NCS$^-$ ligands as shown in Fig. 1(b) . The dpa ligand is coordination cadmium center in a bidentate fashion, with two terminal pyridine nitrogen atoms coordination, 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^o in complex **1**.

The most striking feature in complex **1** shows that the molecular chains are interlinked into a two-dimensional structure through extensive C-H···S (H···S = 2.801 Å and ∠ C-H···S = 178.9^o) 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 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 molecular through C-H···S hydrogen bonding and π - π stackings to form a three-dimensional structures, as shown in Fig. 1(c). There are two *cis* thiocyanate sulfurs and two *cis* thiocyanate nitrogens with two *cis* pyridine nitrogens in structure **1** which differently from the complex $[Cd(SCN)_2(dpa)_2]$ [13] shows a new unequivalent coordination of two SCN^- and a layered structure built by the types of C-H···S and N-H···S hydrogen bondings 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 are 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 $Cd(SCN)_2$ chain in **1**.

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

The structure of **2** was solved in the space group Pbca. Fig. 2(a) shows the local coordination of the cadmium center in **2**, while Fig. 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 the bond angles only deviates slightly from 90 or 180^o. The cadmium metal center adopts a distorted octahedral geometry of five nitrogen atoms and one sulfur atom. Three N atoms are form the *fac*-tridentated pca ligand, and two N and one S atom from the two bridging and one monodentate NCS^- ligands. The five bond lengths of Cd-N observed from 2.273(6) to 2.392(6) Å are clearly shorter than Cd-S distance of 2.756(2) Å being in good agreenent with previos 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 in the molecule contains a sort of intraligand dihedral angle between two pyridyl rings with angles of 91 ^{o}. Fig. 2(b) shows that complex **2** is a coordination polymer of $\{Cd(SCN)_2(pca)\}_n$, forming 1-D helical chain. Both NCS^- ligands are linear, with angles at the Cd center of 177.0(7) ^{o} for S(1)-C(1)-N(1) and 173.3(9) ^{o} for S(2)-C(2)-N(2), respectively. The Cd···Cd distance in the molecular chain is 6.415 Å. Fig. 3(c) shows the packing of the helical chains in **2**, viewing down the b-axis.

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

The structure of **3** was solved in the space group P1. Fig. 3(a) shows the local coordination of the cadmium center in **3**, while Fig. 3(b) shows its two-dimensional anionic frameworks 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 coordination geometry with the bond angles only deviates slightly from 90 or 180^o. In the distorted octahedral anionic frameworks $[Cd(SCN)_2(ox)]^{2-}$, the *cis*-oxygen atoms containing oxalate ligands, two *cis* nitrogen and *cis* two sulfur atoms from the four differently bridging coordinated NCS$^-$ ligands, which shows that the Cd(II) centers adopt a {CdN2O2S2} octahedral coordination geometry, respectively. The two bond lengths of Cd-N observed from 2.2519(15) to 2.3588(16) Å are clearly shorter than Cd-S distance of 2.6318(5) or 2.7138(6) Å being in good agreement with previous reports. The tetradentate bridging oxalates chelate to the cadmium centers (Cd-O = 2.3227(11) or 2.3457(11) Å) with different carboxyl groups forming the five-membered rings. The 2-D $[Cd(SCN)_2(ox)]^{2-}$ nets show 24-membered rings containing the nano-honeycomb pores (10.74 × 10.67 Å^2), which from in six cadmium atoms, four SCN- bridging ligands and two tetradentate bridging oxalates. The Cd···Cd distances in the molecular chain is 5.81 and 5.97 Å that were separated by bridging NCS$^-$ ligands as shown in Fig. 3(c) with the solid line, and the Cd···Cd distance in the net that was separated by bridging oxalate groups is 10.67 Å with the dashed solid line, respectively. The structure of **3** consist protonated 2-aminopyridine cationic molecules (Hamp) to fill to the full the anionic nets with the 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 Fig. 3(d). Complex **3** also shows the 3-D supramolecular structures by weak S···S interactions (3.609 Å) among the 2-D ionic sheets. The S---S distances of complexes **3** which is 3.609 Å, is shorter than twice the van der Waals radius of sulfur (3.7 Å).

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 successfully accomplished. Structure $\{Cd(SCN)_2(dpa)\}_n$, **1**, shows the 1-D chain containing each cadmium octahedrally coordinated by two bridging thiocyanato groups and the other two sites are 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** consists of molecular through C-H···S hydrogen bonding and π - π stackings to form a three-dimensional structures. The complex **2** shows the 1-D coordination polymeric helical chain structure, which contains one *fac*-pca ligand, two bridging and one mono-dentate SCN groups. Complex **3** shows the 3-D supramolecular structures by weak S···S interactions, N-H---O hydrogen bondings and π - π stackings among the molecules to contain each Cd octahedrally coordinated from four μ(N,S) bridging thiocyanato groups and two oxygen atoms from the chelating oxalate ligands.

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

formula	$C_{12}H_9CdN_5S_2$	$C_{14}H_{13}CdN_5S_2$	$C_8H_7CdN_4O_2S_2$
fw	399.76	427.81	367.70
crystal system	Monoclinic	Orthorhombic	Triclinic
space group	$P2_1/c$	Pbca	P1
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
cryst size, mm	0.20× 0.40× 0.40	1.00 × 0.40 × 0.30	0.10 × 0.20 × 0.20
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),Å)	0.71073	0.71073	0.71073
range(2θ) for data collection,deg	$4.56 \leq 2\theta \leq 50.08$	$5.10 \leq 2\theta \leq 49.98$	$4.98 \leq 2\theta \leq 56.72$
temp.°C	25	25	25
limiting indices	$-25 \leq h \leq 25$, $-5 \leq k \leq 6$, $-19 \leq l \leq 19$	$0 \leq h \leq 10$, $0 \leq k \leq 13$, $0 \leq l \leq 37$	$-11 \leq h \leq 11$, $-12 \leq k \leq 11$, $-12 \leq l \leq 12$

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 > 2σ(I)] [a,b]	R1 = 0.0325, wR2 = 0.0800	R1 = 0.0489, wR2 = 0.1101	R1 = 0.0157, wR2 = 0.0397
R indices (all data)	R1 = 0.0377, wR2 = 0.0836	R1 = 0.0646, wR2 = 0.1201	R1 = 0.0174, wR2 = 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

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[a] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. $w = 1 / [\sigma^2(F_o^2) + (ap)^2 + (bp)]$, $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)] / 3$. 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 = $[\Sigma w(|F_o^2| - |F_c^2|)^2 / N_{observed} - N_{parameters}]]^{1/2}$

Table 2. Selected Bond Distances (Å) and Angles (°) for [Cd(SCN)$_2$(dpa)]$_n$, **1**.

Distances

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)

Angles

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.

Table 3. Selected Bond Distances (Å) and Angles (°) for [Cd(SCN)$_2$(pca)]$_n$, **2**.

Distances

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)

Angles

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.

Table 4. Selected Bond Distances (Å) and Angles (°) for {[Cd(NCS)$_2$(ox)](Hamp)$_2$}$_n$, **3**.

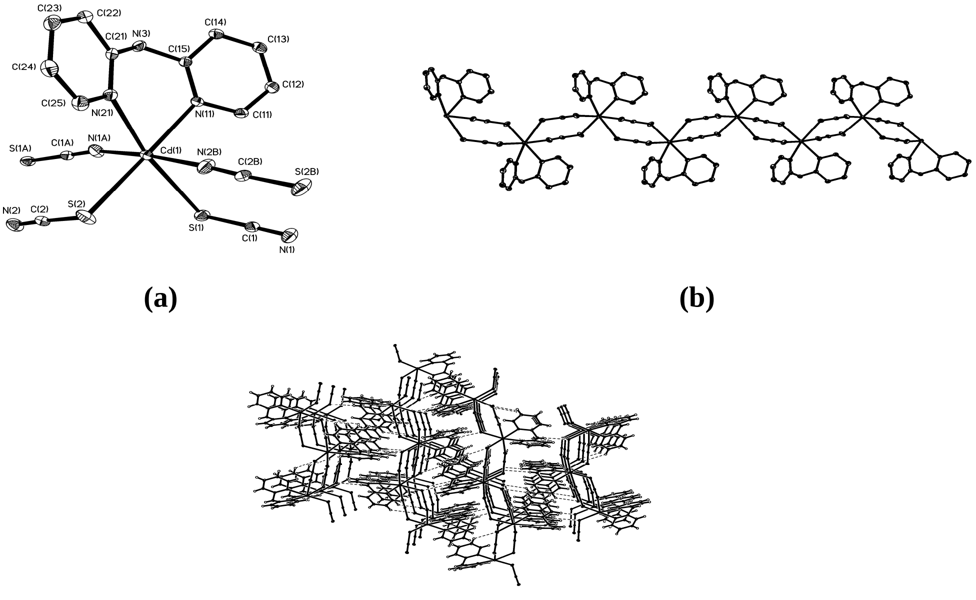
Distances

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)

Angles

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(2A)-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(2A)-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)		

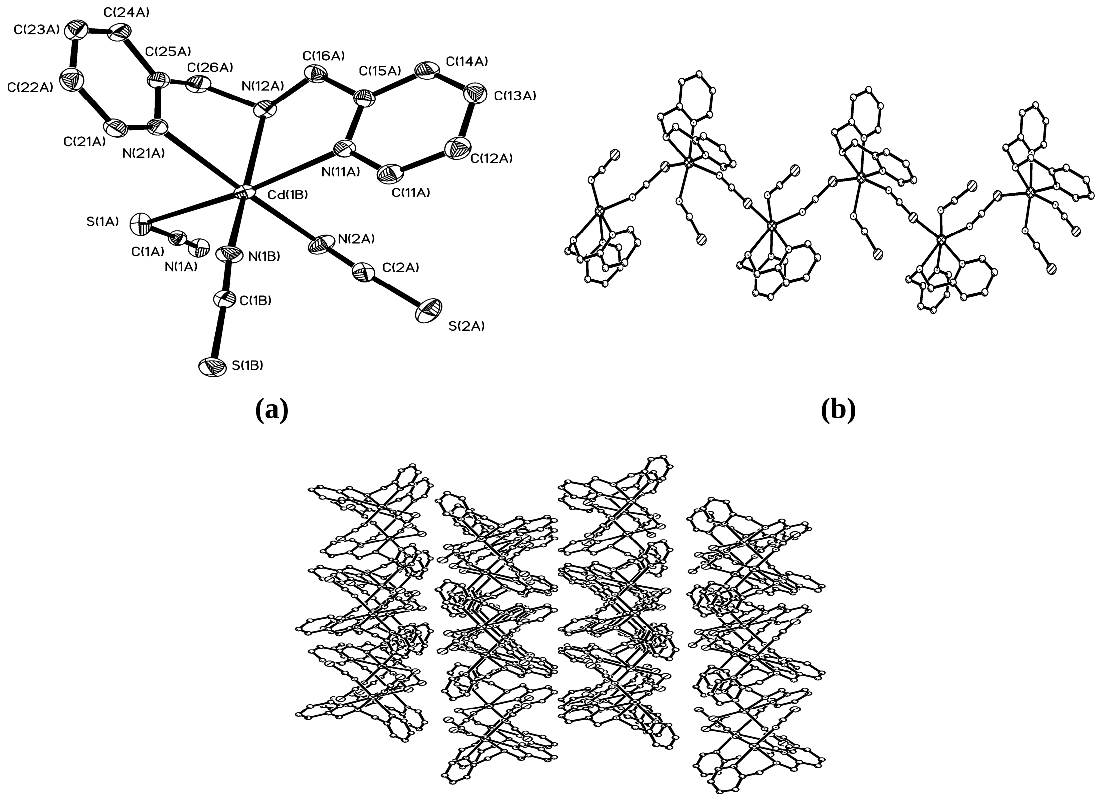
Symmetry transformations used to generate equivalent atoms:
(A) : -x, -y+1, -z+1; (B) : -x, -y+2, -z+1; (C) : -x+1, -y+2, -z+2.



(a) **(b)**

(c)

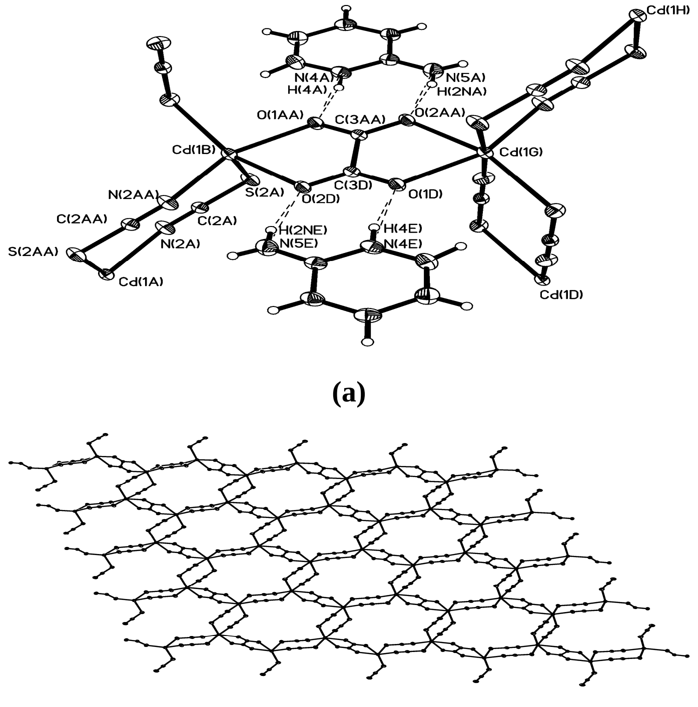
Figure 1. (a) An ORTEP drawing showing the local coordination of Cd in **1**(b) An ORTEP diagram showing the infinite one-dimensional chains.(c) Packing diagram of **1** showing the channel-type chains which are linked by the C-H···S interactions.



(a) **(b)**

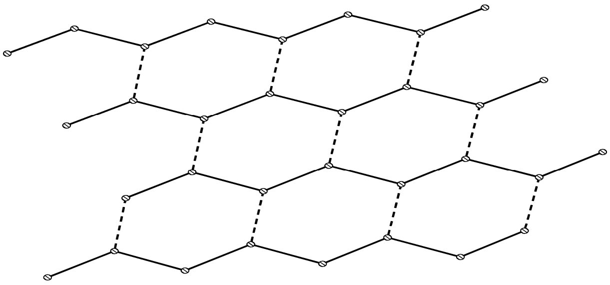
(c)

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**.

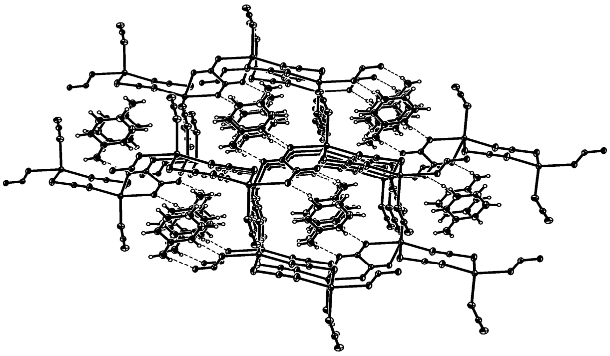


(a)

(b)



(c)



(d)

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 interactions between the cations and the anions