



# Syntheses, structures and properties of two coordination polymers of Cadmium(II) pseudohalide containing an *in situ* generated bidentate Schiff base: Control of dimensionality by varying pseudohalides

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**Abstract.** Two neutral coordination polymers of Cadmium(II) pseudohalide of the type  $[\text{Cd}(\text{LL})(\mu_{1,5}\text{-dca})_2]_n$  (**1**) and  $[\text{Cd}(\text{LL})(\mu_{1,3}\text{-NCS})_2]_n$  (**2**) (LL = phenyl(pyridin-2-yl)methanimine and dca = dicyanamide) have been isolated using a 1:1:1:2 molar ratio of  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ , 2-aminopyridine (ap), 2-benzoylpyridine (bp) and  $\text{Na}(\text{dca})/\text{NH}_4\text{SCN}$  in alcoholic solvent at room temperature. X-ray structural study reveals that in the condensation reaction of ap and bp some degradation occurs in presence of the metal ion to afford an *in situ* generated bidentate Schiff base (LL) in the complexed form. Each Cadmium(II) center in both **1** and **2** adopts an octahedral geometry with a  $\text{CdN}_6$  chromophore in **1** and a  $\text{CdN}_4\text{S}_2$  chromophore in **2**. In **1**, each metal(II) center is connected to four other metal(II) centers through four different  $\mu_{1,5}\text{-dca}$  bridges affording a three-dimensional network structure, whereas each Cd(II) center in **2** is linked with neighbouring Cd(II) centers through bridged end-to-end (EE) thiocyanates to form a non-ending linear 1D zig-zag chain. Further, in crystalline state 1D chains in **2** are stabilized through weak intermolecular C-H...S hydrogen bond interaction promoting 2D sheet structure. Thermally stable compounds **1** and **2** show intraligand  $^1(\pi\text{-}\pi^*)$  fluorescence in DMF solution at room temperature.

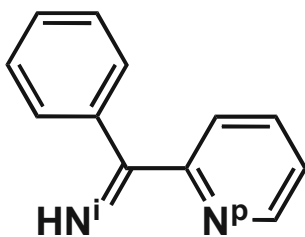
**Keywords.** Cadmium(II) coordination polymers; *in situ* generated Schiff base; dicyanamide/thiocyanate; X-ray structures; luminescence.

## 1. Introduction

Construction of different coordination molecules and supramolecular entities<sup>1–3</sup> through variation of ligand backbones and metal ion coordination environments has spawned immense interest in recent times. In this regard, Schiff base spacers and pseudohalide terminals/bridges are of great concern. Schiff bases<sup>4</sup> are used as organic spacers because of their ease of preparation, structural variety, varied denticity and subtle steric and/or electronic effects controlling molecular and crystalline architectures. In contrast, *in situ* unusual ligand

preparation<sup>5</sup> in presence of different metal ions, which are very much efficient for the isolation of stable veritable metal-organic frameworks (MOFs)<sup>6</sup> with exciting molecular properties, are rare. Dicyanamide (dca), a larger pseudohalide molecular ion-rod<sup>7,8</sup> is under active consideration as bridging unit due to versatile coordination motifs leading to interesting extended molecular and crystalline architectures coupled with tunable properties in metal bound states. Ambidentate thiocyanate<sup>9,10</sup> may act as terminal and/or bridging unit, and in the terminal mode it often participates in hydrogen bondings that influence supramolecular architectures.<sup>11</sup> Self-assembly<sup>12</sup> of the components is one of the efficient synthetic approaches to construct such entities

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**Scheme 1.** Framework of LL with  $N^I, N^P$  type backbone ( $N^I$  = imine N;  $N^P$  = pyridine N).

based on strong covalent bonds<sup>13</sup> and multiple lateral weak non-covalent forces.<sup>14</sup> Cadmium(II) compounds are of immense importance due to their structural varieties and electronic and optoelectronic properties.<sup>15–19</sup> This prompted us to study Cadmium(II) chemistry with *in situ* generated Schiff base [phenyl(pyridin-2-yl)methanimine (LL), Scheme 1] in conjunction with dca and thiocyanate as terminal and/or bridge unit. Successfully, we have isolated one 3D coordination polymer  $[Cd(LL)(\mu_{1,5} - dca)]_n$  (**1**) and one zigzag 1D coordination polymer  $[Cd(LL)(\mu_{1,3} - NCS)]_n$  (**2**) using a 1:1:1:2 molar ratio of  $CdCl_2 \cdot 6H_2O$ , 2-aminopyridine (ap), 2-benzoylpyridine (bp) and  $Na(dca)/NH_4SCN$  in alcoholic solvent at room temperature. The details of syntheses, spectroscopic results, X-ray structures and luminescence behavior of these compounds are described herein.

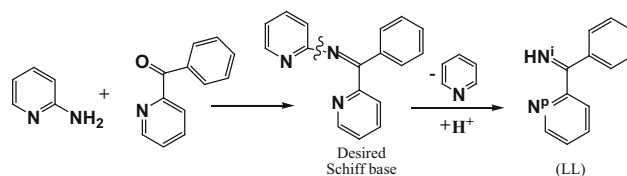
## 2. Experimental

### 2.1 Materials

High purity 2-aminopyridine (SRL, India), 2-benzoylpyridine (Lancaster, UK), Cadmium(II) chloride monohydrate (SRL, India), sodium dicyanamide (Lancaster, UK) and ammonium thiocyanate (E. Merck, India) were purchased and used as received. The synthetic reactions and work-up were done in open air at room temperature. All other chemicals and solvents used were analytical reagent (AR) grade.

### 2.2 Physical measurements

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs,  $4000\text{--}400\text{ cm}^{-1}$ ) were recorded using a Perkin-Elmer FTIR model RX1 spectrometer. Thermal studies were made with a Perkin-Elmer Diamond TG/DTA analyzer heated from  $30\text{--}800\text{ }^\circ\text{C}$  under nitrogen atmosphere. Ground state absorption spectra were measured with a Jasco model V-530 UV-Vis



**Scheme 2.** Probable steps of the *in situ* reaction to afford LL.

spectrophotometer. Fluorescence measurements were done using a Fluorescence Spectrophotometer F-7000.

### 2.3 Syntheses of the *in situ* ligand (LL) and complexes

**2.3a *In situ* generation of LL:** Structural analysis of compounds **1** and **2** reveals the presence of a bidentate Schiff base (LL). It may be assumed that in the condensation reaction of 2-aminopyridine (ap) and 2-benzoylpyridine (bp), some degradation process<sup>5,20</sup> occurs in presence of Cadmium(II) to result in this tailored Schiff base (LL). A possible path may be portrayed (Scheme 2) in which elimination of the pyridine ring followed by protonation presumably occurs.

**2.3b  $[Cd(LL)(\mu_{1,5} - dca)]_n$  (**1**):** To a  $CdCl_2 \cdot H_2O$  (0.201 g, 1 mmol) solution in MeOH (10 mL), 2-aminopyridine (0.094 g, 1 mmol) and 2-benzoylpyridine (0.183 g, 1 mmol) dissolved each in the same solvent (10 mL) were added drop wise. A solution of  $Na(dca)$  (0.178 g, 2 mmol) in the same solvent (10 mL) was added drop wise to this solution mixture. After filtration through a fine glass frit, the supernatant light reddish-orange solution was kept in air for slow evaporation. After three days, deposited yellow crystals of **1** were separated by filtration and dried *in vacuo* over silica gel indicator. Yield: 0.298 g (72%). Anal. Calc. for  $C_{16}H_{10}N_8Cd$  (**1**): C, 45.0; H, 2.4; N, 26.3%. Found: C, 44.8; H, 2.3; N, 26.2%. IR (KBr,  $cm^{-1}$ ):  $\nu(C=N)$  1639, 1594;  $\nu_{as} + \nu_s(C \equiv N)$  2289;  $\nu_{as}(C \equiv N)$  2239;  $\nu_s(C \equiv N)$  2167;  $\nu_{as}(C-N)$  1346;  $\nu_s(C-N)$  952;  $\nu(N-H)$  3456. UV-Vis ( $\lambda_{max}$ , nm): 272.

**2.3c  $[Cd(LL)(\mu_{1,3} - NCS)]_n$  (**2**):**  $CdCl_2 \cdot H_2O$  (0.201 g, 1 mmol) dissolved in methanol (10 mL) was allowed to react with a solution mixture of 2-aminopyridine (0.094 g, 1 mmol) and 2-benzoylpyridine (0.183 g, 1 mmol) in the same solvent (15 mL) followed by the addition of  $NH_4SCN$  (0.152 g, 2 mmol) in methanol (10 mL). The final solution was left undisturbed in open air for slow evaporation. The yellow microcrystals of **2** were collected as described in **1**. Yield: 0.534 g (65%). Anal. Calc. for  $C_{28}H_{20}N_8S_4Cd_2$  (**2**): C, 41.0; H, 2.5; N, 13.6%. Found: C, 40.8; H, 2.4; N, 13.5%. IR (KBr,  $cm^{-1}$ ):  $\nu(C=N)$  1631, 1592;  $\nu(N=C=S)$  2108;  $\nu(C-S)$  770;  $\nu(N-H)$  3450. UV-Vis ( $\lambda_{max}$ , nm): 267.

### 2.4 X-ray crystallography

Diffraction data of the single crystals of **1** and **2** were collected at 296 K on a Bruker SMART APEX II CCD area-detector

**Table 1.** Crystallographic data and structure refinement in **1** and **2**.

Compound	<b>1</b>	<b>2</b>
Formula	C <sub>16</sub> H <sub>10</sub> N <sub>8</sub> Cd	C <sub>28</sub> H <sub>20</sub> N <sub>8</sub> S <sub>4</sub> Cd <sub>2</sub>
Formula weight	426.74	821.55
Crystal system	Orthorhombic	Triclinic
Space group	P2(1)2(1)2(1)	P1
<i>a</i> (Å)	9.2634(17)	8.7798(3)
<i>b</i> (Å)	12.852(2)	9.3608(3)
<i>c</i> (Å)	14.426(3)	10.4566(3)
$\alpha$ (°)	90.00	85.665(2)
$\beta$ (°)	90.00	72.194(2)
$\gamma$ (°)	90.00	73.465(2)
<i>V</i> (Å <sup>3</sup> )	1717.5(6)	784.32(4)
$\lambda$ (Å)	0.71073	0.71073
$\rho_{\text{calcd}}$ (gm cm <sup>-3</sup> )	1.658	1.710
<i>Z</i>	4	1
<i>T</i> (K)	296(2)	296(2)
$\mu$ (mm <sup>-1</sup> )	1.288	1.652
<i>F</i> (000)	848	397
Crystal size (mm <sup>3</sup> )	0.17 × 0.15 × 0.12	0.15 × 0.13 × 0.11
$\theta$ ranges (°)	3.17 to 27.10	2.27 to 27.21
<i>h</i> / <i>k</i> / <i>l</i>	-11, 11/-11, 16/-16, 18	-11, 11/-11, 11/-13, 13
Reflections collected	9557	11801
Data/restraints/parameters	3662/0/226	6044/0/379
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.978	0.847
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0459	0.0344
<i>R</i> indices (all data)	0.0772	0.0475
Largest peak and hole (eÅ <sup>-3</sup> )	0.462 and -0.537	0.604 and -0.599

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ,  $\text{calcd } w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ ;  $x = 0.0418$  (for **1**),  $0.1000$  (for **2**), and  $y = 0.0000$  (for **1**),  $0.0000$  (for **2**); where  $P = (F_o^2 + 2F_c^2)/3$ .

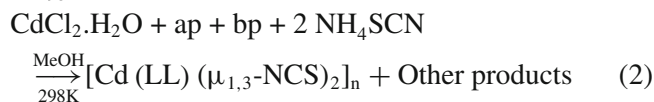
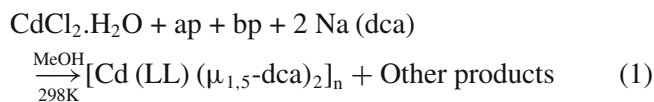
diffractometer using graphite monochromated Mo-K $\alpha$  radiation (0.71073 Å). The unit cell parameters were obtained from SAINT<sup>21</sup> and absorption corrections were performed with SADABS.<sup>22</sup> The structures were solved by direct methods and refined by full-matrix least-squares method based on  $|F|^2$  using SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed in calculated positions after checking their positions in the difference map. All calculations were carried out using SHELXL-97,<sup>23</sup> SHELXTL,<sup>24</sup> PLATON,<sup>25</sup> and Mercury 3.3<sup>26</sup> programs. A summary of the crystallographic data and structure determination parameters for both complexes is given in Table 1.

### 3. Results and Discussion

#### 3.1 Synthesis and formulation

Two neutral hexacoordinated coordination polymers **1** and **2** of different dimensionalities were obtained through one-pot synthesis using 1:1:1:2 molar ratio of

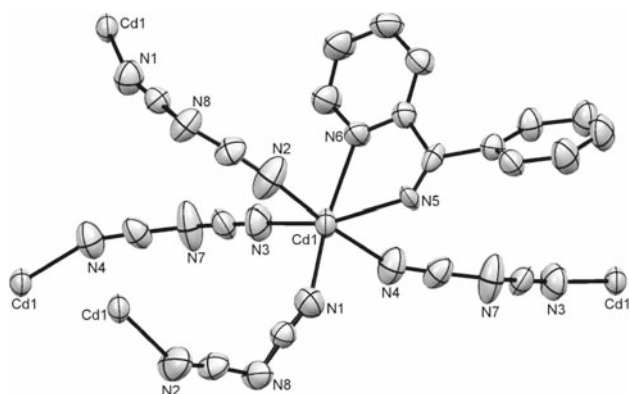
Cadmium(II) chloride monohydrate, 2-aminopyridine, 2-benzoylpyridine and sodium dicyanamide/ammonium thiocyanate in methanolic solutions at room temperature. The reactions were reproducible, as were evident from repetitive microanalytical and spectral results. The reproducibility reflects an inherent tendency towards the formation of **1** and **2**. The reactions are summarized in Eqs. 1 and 2:



The moisture-insensitive compounds are stable over long periods of time in powdery or crystalline state and are soluble in dimethylformamide (DMF) and dimethylsulphoxide (DMSO). In DMF solutions, **1** and **2** behave as non-electrolyte as reflected from their low conductivity value ( $\sim 5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ).

### 3.2 Spectroscopic features

In the IR spectrum,  $\nu(\text{C}=\text{N})$  stretching frequencies of the metal-bound Schiff base<sup>27</sup> in compounds **1** and **2** are observable at  $\sim 1630$  and  $\sim 1590 \text{ cm}^{-1}$ . Compound **1** shows strong  $\nu_s(\text{C} \equiv \text{N})$  absorption at  $2167 \text{ cm}^{-1}$  and two weak to medium  $\nu_{as}(\text{C} \equiv \text{N})$  and  $\nu_{as} + \nu_s(\text{C} \equiv \text{N})$  absorptions at  $2239$  and  $2289 \text{ cm}^{-1}$ , respectively; the shift of frequency values as compared to those of free dca ( $2179$ ,  $2232$  and  $2286 \text{ cm}^{-1}$ ) is presumably due to bridging ( $\mu_{1,5}$ ) coordination of dca.<sup>7</sup> Bands corresponding to  $\nu_{as}(\text{C}-\text{N})$  and  $\nu_s(\text{C}-\text{N})$  stretching vibrations of dca are found at  $1346 \text{ cm}^{-1}$  and at  $952 \text{ cm}^{-1}$ , respectively. The  $\nu(\text{N}=\text{C}=\text{S})$  stretching frequency is noticed at  $2108 \text{ cm}^{-1}$  and  $\nu(\text{C}-\text{S})$  frequency is seen at  $770 \text{ cm}^{-1}$  for **2**. A strong band at  $\sim 3450 \text{ cm}^{-1}$  assignable to  $\nu(\text{NH})$

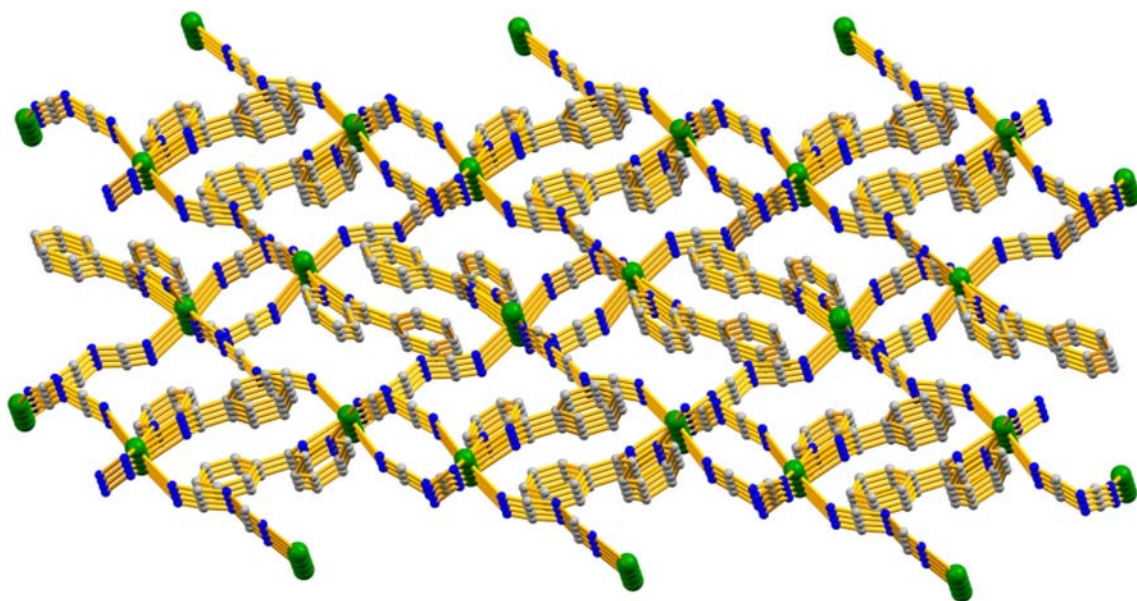


**Figure 1.** An ORTEP diagram of the fundamental coordination unit of 3D coordination polymer **1** with 40% probability level of the ellipsoid.

stretching vibration of ligand (LL) is observed in both the compounds. The bands at  $272$  and  $267 \text{ nm}$  in UV-Vis spectra respectively in compounds **1** and **2** may be assigned to a ligand based charge transfer transition.

### 3.3 Molecular and crystal structures

**3.3a**  $[\text{Cd}(\text{LL})(\mu_{1,5}-\text{dca})_2]_n(\mathbf{1})$ : A perspective view of the fundamental unit with the atom labeling scheme and 3D network structure of the coordination polymer **1** are shown in Figures 1 and 2, respectively. Selected bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) may be found in Table 2. Each Cadmium(II) center (Figure 1) in the polymeric framework adopts an octahedral geometry with a  $\text{CdN}_6$  chromophore ligated through  $\text{N}^{\text{p}}$  ( $\text{N}6$ ) and  $\text{N}^{\text{i}}$  ( $\text{N}5$ ) atoms ( $\text{N}^{\text{p}}$  = pyridine N;  $\text{N}^{\text{i}}$  = imine N) of bidentate Schiff base (LL) and four nitrile N atoms ( $\text{N}1$ ,  $\text{N}2$ ,  $\text{N}3$  and  $\text{N}4$ ) of four different dca units. The equatorial positions are occupied by the two nitrile N atoms ( $\text{N}1$  and  $\text{N}3$ ) of two different  $\mu_{1,5}$ -bridged dca units and two N atoms ( $\text{N}5$  and  $\text{N}6$ ) of the bidentate blocker and the other two nitrile N atoms ( $\text{N}2$  and  $\text{N}4$ ) of two different  $\mu_{1,5}$ -bridged dca units are placed at the axial positions. Distortion from the ideal octahedral geometry is due to the asymmetric nature of the bound bidentate Schiff base and the deviations of the refine angles ( $90^\circ/180^\circ$ ) formed at the metal center. The degree of distortion from an ideal octahedral geometry is reflected in the equatorial [ $68.17(18)^\circ - 102.3(3)^\circ$ ] and the axial [ $160.5(2)^\circ - 173.0(3)^\circ$ ] bond angles. The  $\text{Cd1}-\text{N}_{\text{dca}}$  distances lie in the range  $2.238(7)$ - $2.315(7) \text{ \AA}$ , whereas  $\text{Cd1}-\text{N}(\text{LL})$  distances are in the range of



**Figure 2.** A Mercury view of 3D network structure in **1**.



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

Bond distance (Å)			
<b>1</b>			
Cd1-N1	2.238(7)	Cd1-N4	2.315(7)
Cd1-N2	2.295(7)	Cd1-N5	2.442(5)
Cd1-N3	2.270(7)	Cd1-N6	2.356(5)
<b>2</b>			
Cd1-N34	2.31(2)	Cd2-N33	2.224(16)
Cd1-N7	2.323(14)	Cd2-N37	2.329(13)
Cd1-N5	2.378(9)	Cd2-N4	2.389(12)
Cd1-N6	2.396(13)	Cd2-N3	2.434(13)
Cd1-S4	2.627(6)	Cd2-S2	2.621(5)
Cd1-S1	2.736(5)	Cd2-S3	2.745(6)

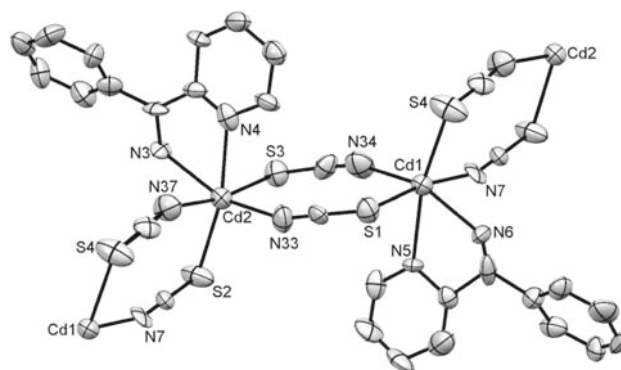
**Bond angle (°)**

<b>1</b>			
N1 Cd1 N3	102.3(3)	N4 Cd1 N6	92.2(3)
N1 Cd1 N2	89.2(3)	N1 Cd1 N5	96.8(2)
N3 Cd1 N2	91.2(3)	N3 Cd1 N5	160.5(2)
N1 Cd1 N4	91.4(3)	N2 Cd1 N5	92.8(2)
N3 Cd1 N4	95.5(3)	N4 Cd1 N5	80.2(2)
N2 Cd1 N4	173.0(3)	N6-Cd1-N5	68.17(18)
N1 Cd1 N6	163.7(2)	C15 N7 C14	124.6(8)
N3 Cd1 N6	93.2(2)	C12 N8 C13 <sup>iv</sup>	120.4(7)
N2 Cd1 N6	85.4(3)		
<b>2</b>			
N34 Cd1 N7	90.8(6)	N33 Cd2 N37	93.1(6)
N34 Cd1 N5	89.3(5)	N33 Cd2 N4	92.8(6)
N7 Cd1 N5	90.1(4)	N37 Cd2 N4	88.2(4)
N34 Cd1 N6	157.5(5)	N33 Cd2 N3	160.6(5)
N7 Cd1 N6	86.5(5)	N37 Cd2 N3	85.8(5)
N5 Cd1 N6	68.4(4)	N4 Cd2 N3	67.8(4)
N34 Cd1 S4	107.7(5)	N33 Cd2 S2	104.6(5)
N7 Cd1 S4	93.1(3)	N37 Cd2 S2	95.1(4)
N5 Cd1 S4	162.7(4)	N4 Cd2 S2	162.1(4)
N6 Cd1 S4	94.8(4)	N3 Cd2 S2	94.9(3)
N34 Cd1 S1	96.1(5)	N33 Cd2 S3	94.0(4)
N7 Cd1 S1	171.3(4)	N37 Cd2 S3	170.3(4)
N5 Cd1 S1	84.7(3)	N4 Cd2 S3	85.0(3)
N6 Cd1 S1	85.1(4)	N3 Cd2 S3	85.2(4)
S4 Cd1 S1	89.88(18)	S2 Cd2 S3	89.44(16)
N33 C1 S1	178.8(15)	N7 C44 S2	175.6(16)
N37 C47 S4	174.8(18)	N34 C3 S3	174.7(18)

Symmetry code: <sup>i</sup>  $-x, y, 1/2 - z$ ; <sup>ii</sup>  $3/2 - x, 1 - y, 1/2 + z$ ; <sup>iii</sup>  $1 - x, -1/2 + y, 1/2 - z$ ; <sup>iv</sup>  $-1/2 + x, 1/2 - y, -z$ .

2.356(5)-2.442(5) Å. The Cd···Cd separation across single  $\mu_{1,5}$  dca ranges from 7.257 to 8.755 Å. The structural analyses reveal **1** to comprise of a 3D network structure through  $\mu_{1,5}$ -bridging motif of four dca units (Figure 2). All the Cadmium(II) atom lies in an inversion center, and is connected to four other neighboring Cadmium(II) centers through four different  $\mu_{1,5}$ -dca bridges.

**3.3b**  $[Cd(LL)(NCS)_2]_n$  (**2**): An ORTEP diagram of the fundamental coordination unit of **2** with atom

**Figure 3.** An ORTEP diagram of fundamental molecular unit of **2** with 40% probability level of the ellipsoid.

numbering scheme is shown in Figure 3. Selected bond distances (Å) and bond angles (°) are listed in Table 2. Hydrogen bond interaction parameters are shown in Table 3. In compound **2**, the adjacent Cadmium(II) centers are connected by the bibridged end-to-end thiocyanate units to form an extended structure with a zigzag 1-D chain (Figure 4). Each Cadmium(II) center in this chain is surrounded by a  $CdN_4S_2$  chromophore with a distorted octahedral geometry. The coordination sites of the metal ion are fulfilled by two N atoms ( $N^i$  and  $N^p$ ) of chelated Schiff base (LL), two N atoms and two S atoms of bridging SCN ligand. The equatorial plane around Cd1 is made up with N5, N6 atoms of LL and N34, S4 atoms of SCN whereas N3, N4 atoms of LL and N33, S2 atoms of SCN comprise equatorial plane around Cd2 center. The axial sites are fulfilled by S1, N7 atoms (in Cd1) and S3, N37 atoms (in Cd2) of bridging SCN units. Cd1 and Cd2 deviate from the corresponding mean plane by 0.020 Å and 0.047 Å, respectively. The degree of distortion from ideal octahedral geometry is seen in *cisoid*-[67.8(4)-107.7(5)°] and *transoid*-[157.5(5)-171.3(4)°] bond angles. Average Cd···Cd separation through bibridged SCN ranges from 5.716 to 5.831 Å. The 1D chain in **2** self-assemble through cooperative intermolecular C-H···S hydrogen bond interactions giving rise to a 2D supramolecular sheet structure along crystallographic *bc* plane (Figure 5). The bridging sulfur atom (S3) is hydrogen bond acceptor whereas one C-H (H7) of aromatic benzene ring is the donor (C7-H7···S3<sup>v</sup>: 2.8700 Å, 139.00°; symmetry code:  $-1+x,y,z$ ).

### 3.4 Thermal studies

Thermogravimetric analyses (TG) were made between 30 and 800 °C in a static atmosphere of nitrogen to examine thermal stabilities of the coordination polymers **1** and **2**. The TG curve (Figure S1) of **1** indicates that it is

stable up to 135 °C at which temperature decomposition commences and takes place gradually in the temperature range 135–550 °C corresponding to the weight loss (observed, 73% and calculated, 74.8%) of two dca units

**Table 3.** Non-covalent force parameters for **2**.

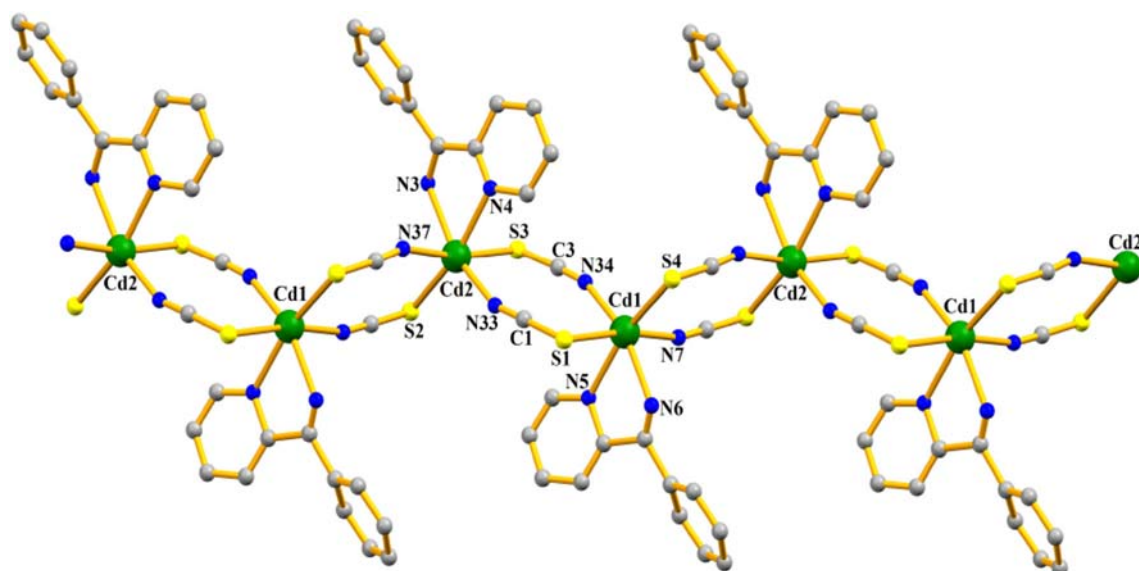
Hydrogen bond interaction parameters (Å, °)				
D-H...A	D-H	H...A	D...A	D-H...A
C7-H7...S3 <sup>v</sup>	0.9300	2.8700	3.619(19)	139.00

Symmetry code: <sup>v</sup> = 1 + x, y, z.

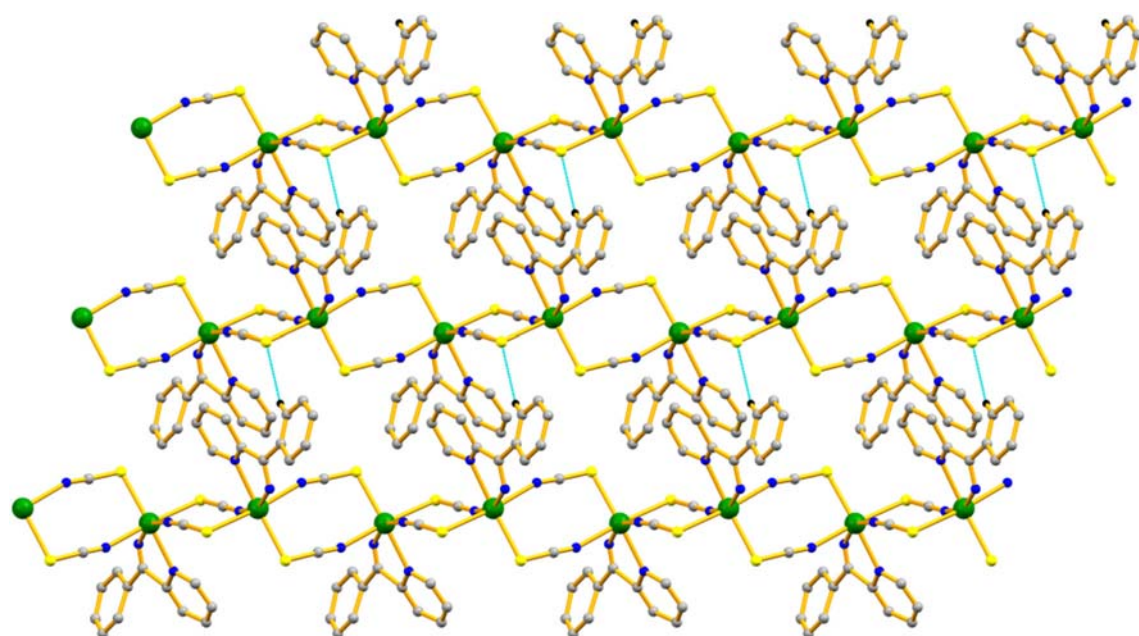
and one ligand (LL) unit per formula unit. The TG curve (Figure S2) of **2** shows that this compound is stable up to 180 °C and its decomposition takes place gradually in the temperature range 180–660 °C corresponding to the weight loss (observed, 60% and expected, 63.2%) of two NCS<sup>-</sup> units and one ligand (LL) unit per formula unit.

### 3.5 Fluorescence studies

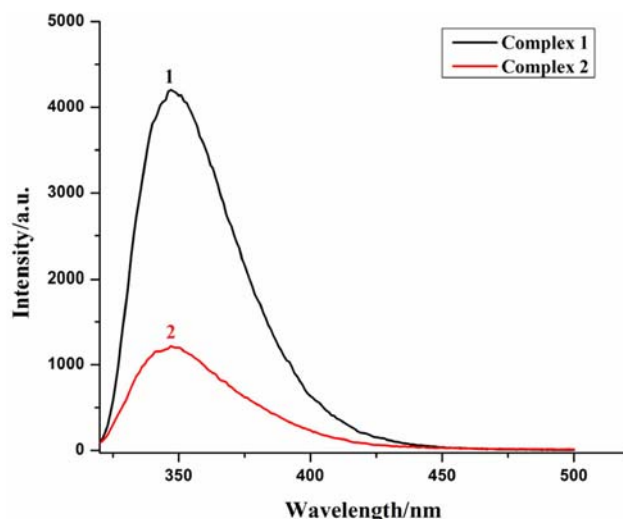
Light yellow-orange DMF solutions of compounds **1** and **2** showed strong absorption at 272 and 267



**Figure 4.** A segmented 1D zigzag chain in **2** along crystallographic *ab*-plane.



**Figure 5.** 2D sheet structure in **2** formed through C-H...S hydrogen bonds.



**Figure 6.** Fluorescence spectra of compounds **1** and **2** in DMF at 298 K (Excitation wavelength: 280 nm).

nm, respectively, presumably due to ligand-based transition.<sup>28</sup> Upon photoexcitation at the corresponding absorption band in DMF solutions, **1** and **2** exhibit broad fluorescent emission centered at 347 nm due to the intraligand  $^1(\pi - \pi^*)$  transition (Figure 6). The compound **1** showed more intense photoluminescence compared to compound **2** presumably due to greater conformational rigidity of the ligand (LL) upon coordination.

#### 4. Conclusions

In summary, two uncharged coordination polymers of Cadmium(II) pseudohalide in combination with a bidentate Schiff base were isolated and characterized by X-ray crystallography. The compounds **1** and **2** have different molecular architectures of different dimensionalities just by incorporating varied pseudohalides. Weak intermolecular C-H...S hydrogen bond interactions in **2** are seen promoting the 1D chains to a 2D sheet structure. The coordination polymers are thermally stable, luminous materials. This work on such compounds illustrates the versatile approach towards construction of uncharged luminous metal-organic frameworks (MOFs), which have spawned great interest<sup>15–19,29</sup> by different research groups towards isolation and application as electronic and optoelectronic materials with varied MOFs.

#### Supplementary Information (SI)

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic data center

No. 1452048 (**1**) and 1452049 (**2**). Copy of this information can be obtained, free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Thermal behavior of compounds **1** and **2** (Figures S1 and S2, respectively) are shown in Supplementary Information, available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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