

Two new hexacoordinated coordination polymers of cadmium(II) containing bridging units only: Syntheses, structures and molecular properties

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Abstract. The syntheses, characterizations and structures of a neutral 2D coordination polymer [Cd(bnzd)(NCS)₂]_n (**1**) and a polycationic 3D coordination polymer isolated as perchlorate salt [Cd(bnzd)₃]_n(ClO₄)_{2n} (**2**) (bnzd = benzidine) are described. X-ray structural analyses reveal that each hexacoordinated cadmium(II) center in **1** adopts a distorted octahedral geometry with a CdN₄S₂ chromophore bound by two N atoms of two different bnzd units and two N and two S atoms of symmetric doubly bridged end-to-end NCS⁻ units extended in a 2D sheet. Six N atoms of six different bridged bnzd units are bonded to each cadmium(II) in **2** in a non-ended fashion affording a 3D network structure. In the crystalline state, each 2D sheet structure in **1** is further stabilized by $\pi \cdots \pi$ interaction which in turn affords a 3D network structure through multiple intermolecular N-H \cdots S hydrogen bonds. On the other hand, the 3D network structure in **2** is stabilized by weak intermolecular N-H \cdots O hydrogen bonds and C-H \cdots π interactions. Bnzd, **1** and **2** display intraligand ¹(π - π^*) fluorescence in DMF solution at room temperature.

Keywords. Cadmium(II); coordination polymers; benzidine; thiocyanate; X-ray structures; luminescence.

1. Introduction

The isolation of coordination polymers¹ and supramolecular frameworks² based upon strong covalent bonds³ and weak non-covalent forces⁴ is an area of current interest due to fabrication of new functional materials^{5–12} such as catalysts,⁵ magnetic materials,⁶ conducting materials,⁷ porous materials,⁸ luminous materials,⁹ non-linear optical materials,¹⁰ chemical sensors¹¹ and for molecular recognition.¹² Judicious choice¹³ of suitable organic ligands with different denticities, polyatomic bridges with multiple connectors and metal templates gives rise to a diverse range of molecular and crystalline architectures.^{14,15} One-pot synthesis¹⁶ using the building units is an efficient approach to afford such metal-organic frameworks (MOFs).¹⁷ Thiocyanate^{18–20} has attracted much attention since it results in interesting extended architectures and related properties in metal bound states. Recently, we are active^{21–23} in the preparation of functional MOFs through variation of ligand frameworks and metal coordination environments. Polynuclear cadmium(II) compounds^{23–25} have received much attention due to electronic and optoelectronic

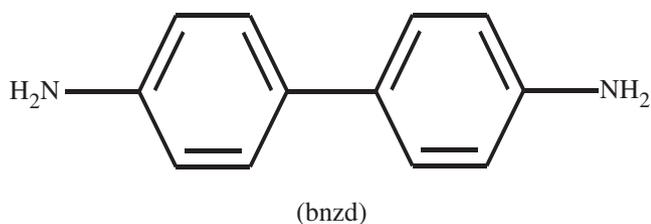
properties.^{26,27} Coordination chemistry of benzidine (bnzd, Scheme 1) is relatively less explored.^{28,29} This work stems from our interest to isolate coordination polymers and polymer-based supramolecular entities with photoluminescent behaviour. In the present endeavor, we have isolated and X-ray crystallographically characterized two new polynuclear cadmium(II) compounds of the composition [Cd(bnzd)(NCS)₂]_n (**1**) and [Cd(bnzd)₃]_n(ClO₄)_{2n} (**2**) through use of the 4d member Group 12 metal ion, cadmium(II), in combination with inorganic (NCS⁻) and organic (bnzd) bridging ligands.

2. Experimental

2.1 Materials

High purity benzidine (SRL, India), ammonium thiocyanate (E. Merck, India), cadmium(II) acetate dihydrate (SRL, India) were purchased and used as received. Cadmium perchlorate hexahydrate was prepared by treatment of cadmium carbonate (E. Merck, India) with perchloric acid (E. Merck, India) followed by slow evaporation on steam-bath, filtration through a fine glass-frit, and preservation in a desiccator containing

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Scheme 1. Framework of benzidine.

concentrated sulfuric acid (E. Merck, India) for subsequent use. All other chemicals and solvents used were AR grade. The synthetic reactions and work-up were done in open air at room temperature.

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, 4000–400 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 30–800°C under nitrogen atmosphere. Ground state absorptions were measured with a Jasco model V-530 UV-Vis spectrophotometer. Fluorescence measurements were done using a Hitachi Fluorescence Spectrofluorimeter F-4500.

2.3 Syntheses of the complexes

2.3a $[\text{Cd}(\text{bnzd})(\text{NCS})_2]_n(\mathbf{1})$: Bnzd (0.184 g, 1 mmol) in methanol-acetonitrile (9:1) mixture (20 mL) was added slowly to a $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.266 g, 1 mmol) solution in methanol (10 mL). NH_4NCS (0.152 g, 2 mmol) in methanol (10 mL) was added dropwise to this solution mixture. After filtration through a fine glass frit, the supernatant yellowish-brown solution was kept in air for slow evaporation. Yellowish-brown crystals of **1** that deposited within a couple of days were collected by filtration and dried *in vacuo* over silica gel indicator. Yield: 0.289 g (70%). Anal. Calc. for $\text{C}_{14}\text{H}_{12}\text{CdN}_4\text{S}_2$ (**1**): C, 40.7; H, 2.9; N, 13.6%. Found: C, 40.9; H, 2.9; N, 13.7%. IR (KBr, cm^{-1}): $\nu(\text{N-H})$ 3325, 3244, 3147; $\nu(\text{C-H})$ 2914, 2856; $\nu(\text{N=C=S})$ 2114; $\nu(\text{C-S})$ 810; $\nu(\text{C=N})$ 1612; $\nu(\text{C=C})$ 1585. UV-Vis ($\lambda_{\text{max}}/\text{nm}$): 297.

2.3b $[\text{Cd}(\text{bnzd})_3]_n(\text{ClO}_4)_{2n}(\mathbf{2})$: $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.419 g, 1 mmol) in methanol (10 mL) was added

slowly to a solution of bnzd (0.553 g, 3 mmol) in methanol-acetonitrile (3:1) mixture (20 mL). After filtration through a fine glass frit, the supernatant yellowish-brown solution was kept in air for slow evaporation. Brown crystals of **2** that deposited within a week were collected by filtration and dried *in vacuo* over silica gel indicator. Yield: 0.605 g (70%). Anal. Calc. for $\text{C}_{36}\text{H}_{36}\text{CdCl}_2\text{N}_6\text{O}_8$ (**2**): C, 50.0; H, 4.2; N, 9.7%. Found: C, 50.2; H, 4.3; N, 9.8%. IR (KBr, cm^{-1}): $\nu(\text{N-H})$ 3321, 3241, 3151; $\nu(\text{C-H})$ 2965, 2920; $\nu(\text{C=C})$ 1578; $\nu_{\text{as}}(\text{C-N})$ 1344, 1324; $\nu_{\text{s}}(\text{C-N})$ 916; $\nu(\text{ClO}_4)$ 1104, 624. UV-Vis ($\lambda_{\text{max}}/\text{nm}$): 296.

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 diffractometer using graphite monochromated Mo-K α radiation (0.71073 Å). The unit cell parameters were obtained from SAINT³⁰ and absorption corrections were performed with SADABS.³¹ 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, SHELXTL,³² PLATON,³³ Diamond³⁴ and Mercury 3.3³⁵ 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

One-pot syntheses of the building components in appropriate molar ratios (1:1:2 for **1** and 1:3 for **2**) in methanol-acetonitrile solvent mixture at room temperature afforded a hexacoordinated 2D coordination polymer $[\text{Cd}(\text{bnzd})(\text{NCS})_2]_n$ (**1**) and a 3D coordination polymer $[\text{Cd}(\text{bnzd})_3]_n(\text{ClO}_4)_{2n}$ (**2**). 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:

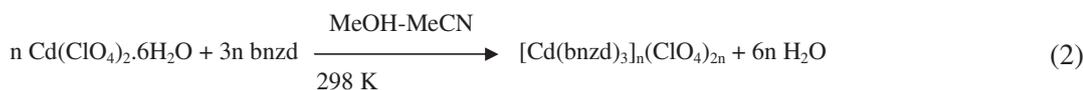
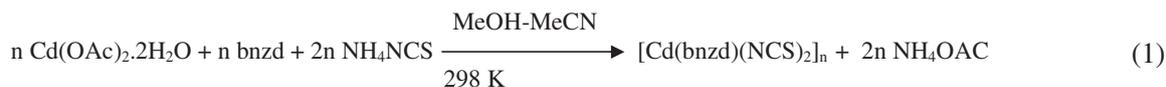


Table 1. Crystallographic data for **1** and **2**.

Compound	1	2
Chemical formula	C ₁₄ H ₁₂ CdN ₄ S ₂	C ₃₆ H ₃₆ CdCl ₂ N ₆ O ₈
Formula mass	412.83	864.01
Crystal system	Triclinic	Rhombohedral
Space group	P-1	R-3c
<i>a</i> /Å	6.0444(4)	9.5015(3)
<i>b</i> /Å	6.5440(5)	9.5015(3)
<i>c</i> /Å	10.4117(5)	65.063(3)
α°	106.940(4)	90
β°	95.623(4)	90
γ°	97.824(5)	120
<i>V</i> /Å ³	386.15(4)	5086.9(3)
λ /Å	0.71073	0.71073
ρ_{calcd} /g cm ⁻³	1.775	1.692
<i>Z</i>	1	6
T/K	296(2)	296(2)
μ (mm ⁻¹)	1.681	0.867
<i>F</i> (000)	204	2640
Crystal size (mm ³)	0.12×0.12×0.10	0.11×0.15×0.19
θ ranges (°)	3.304 to 24.643	1.88 to 28.49
<i>h</i> / <i>k</i> / <i>l</i>	-7, 5/-7,4/-12,12	-12, 9/-10,12/-86,65
Reflections collected	1644	8867
Independent reflections	1232	1439
Data/restraints/parameters	1232/23/97	1439/0/81
<i>R</i> _{int}	0.018	0.023
Final <i>R</i> 1 values [<i>I</i> >2 σ (<i>I</i>)]	0.0345	0.0261
Final w <i>R</i> (<i>F</i> ²) values [<i>I</i> >2 σ (<i>I</i>)]	0.0746	0.0952
Final <i>R</i> 1 values (all data)	0.0385	0.0348
Final w <i>R</i> (<i>F</i> ²) values (all data)	0.0772	0.1149
Goodness of fit on <i>F</i> ²	1.017	0.942
Largest peak and hole (eÅ ⁻³)	0.359 and -0.466	0.621 and -0.717

Weighting scheme: $R = \frac{\sum ||F_0| - |F_c||}{\sum |F_0|}$, $wR = \frac{[\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)]^{1/2}}{\text{calc. } w = 1/[\sigma^2(F_0^2) + (0.0379P)^2 + 0.4207P]}$ (**1**) and $\text{calc. } w = 1/[\sigma^2(F_0^2) + (0.1000P)^2 + 0.0000P]}$ (**2**) where $P = (F_0^2 + 2F_c^2)/3$.

The air-stable and moisture-insensitive compounds **1** and **2** are insoluble in methanol, ethanol, dichloromethane and acetonitrile but moderately soluble in warm dimethylformamide.

3.2 Spectroscopic features

In IR spectra of **1** and **2**, three peaks at ~3320, ~3240 and ~3150 cm⁻¹ are observed assignable to $\nu(\text{NH})$ stretching vibrations of the -NH₂ groups of bnzd.^{23a} Complex **1** shows an intense peak at 2114 cm⁻¹ corresponding to $\nu(\text{NCS})$. In **2**, $\nu(\text{ClO}_4)$ stretches are found at 1104 and 624 cm⁻¹. X-ray study corroborates this hypothesis and defines the molecular structure and crystalline architecture. The electronic spectra of the complexes **1** and **2** in DMF solution exhibit strong absorptions at ~300 nm presumably due to ligand-based transition.³⁶

3.3 Molecular and crystal structures

3.3a $[\text{Cd}(\text{bnzd})(\text{NCS})_2]_n$ (**1**): An ORTEP diagram of the fundamental coordination unit of **1** with atom numbering scheme is shown in Figure 1. Selected bond distances (Å) and bond angles (°) are listed in Table 2. Hydrogen bond and $\pi \cdots \pi$ interaction parameters are shown in Tables 3 and 4, respectively. The coordination polyhedron around each cadmium(II) center in the polymeric framework is best described as a distorted octahedron with a CdN₄S₂ chromophore. Cadmium(II) is located on a crystallographic inversion center and one half of the monomeric unit is symmetrical to the other half. The coordination includes two amine N (N1 and N1^c) atoms of two different bnzd bridging units, two N (N2 and N2^c) atoms and two S (S1^a and S1^b) atoms of two thiocyanate units in symmetric doubly bridged end-to-end fashion [symmetry codes: ^a1+x, y, z;

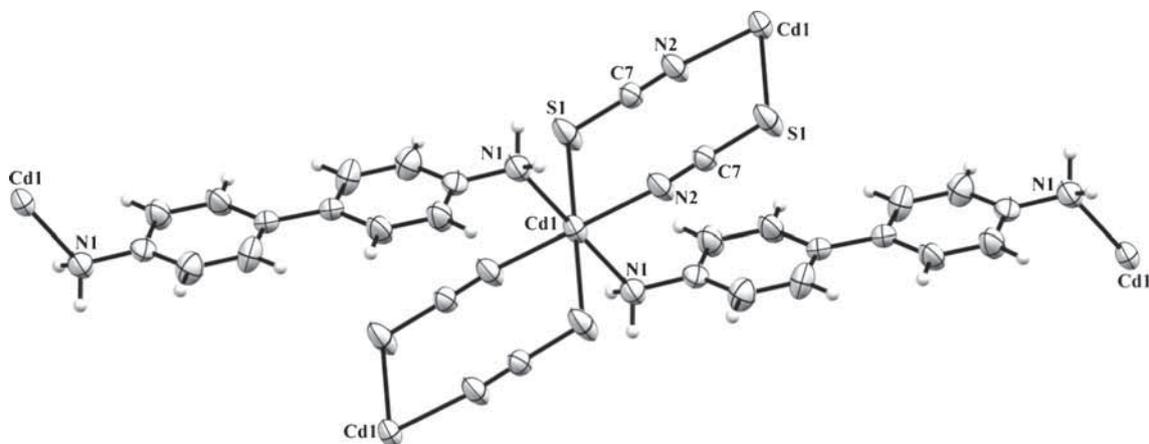


Figure 1. An ORTEP diagram of the fundamental coordination unit of 2D polymer **1** with 50% probability level of the ellipsoid.

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

Parameters		1		2
Bond distances	Cd1-S1 ^a	2.7483(14)	Cd1-N1	2.4403(16)
	Cd1-S1 ^b	2.7483(14)	Cd1-N1 ^d	2.4402(16)
	Cd1-N1	2.346(4)	Cd1-N1 ^e	2.4402(16)
	Cd1-N1 ^c	2.346(4)	Cd1-N1 ^f	2.4402(16)
	Cd1-N2	2.308(4)	Cd1-N1 ^g	2.4402(16)
	Cd1-N2 ^c	2.308(4)	Cd1-N1 ^h	2.4402(16)
Bond angles	N1-Cd1-N2	86.56(14)	N1-Cd1-N1 ^d	96.56(5)
	N1-Cd1-N1 ^c	180.00	N1-Cd1-N1 ^e	96.56(5)
	N1-Cd1-N2 ^c	93.44(14)	N1-Cd1-N1 ^f	180.0
	N2-Cd1-N2 ^c	180.00	N1-Cd1-N1 ^g	83.44(5)
	N1 ^c -Cd1-N2	93.44(14)	N1-Cd1-N1 ^h	83.44(5)
	N1 ^e -Cd1-N2 ^c	86.56(14)	N ^d -Cd1-N1 ^e	96.56(5)
	S1 ^a -Cd1-N1	93.82(10)	N1 ^d -Cd1-N1 ^f	83.44(5)
	S1 ^a -Cd1-N2	88.76(11)	N1 ^d -Cd1-N1 ^g	180.00(6)
	S1 ^a -Cd1-N1 ^c	86.18(10)	N1 ^d -Cd1-N1 ^h	83.44(5)
	S1 ^a -Cd1-N2 ^c	91.24(11)	N1 ^e -Cd1-N1 ^f	83.44(5)
	S1 ^a -Cd1-S1 ^b	180.00	N1 ^e -Cd1-N1 ^g	83.44(5)
	S1 ^b -Cd1-N1	86.18(10)	N1 ^e -Cd1-N1 ^h	180.00(8)
	S1 ^b -Cd1-N2	91.24(11)	N1 ^f -Cd1-N1 ^g	96.56(5)
	S1 ^b -Cd1-N1 ^c	93.82(10)	N1 ^f -Cd1-N1 ^h	96.56(5)
	S1 ^b -Cd1-N2 ^c	88.76(11)	N1 ^g -Cd1-N1 ^h	96.56(5)
S1-C7-N2	178.5(4)			

Symmetry code: ^a1+x,y,z; ^b1-x,1-y,2-z; ^c2-x,1-y,2-z; ^d2-y,1+x-y,z; ^e1-x+y,2-x,z; ^f2-x,2-y,-z; ^gy,1-x+y,-z; ^h1+x-y,x,-z.

Table 3. Hydrogen bond and C-H... π interaction parameters for **1** and **2**.

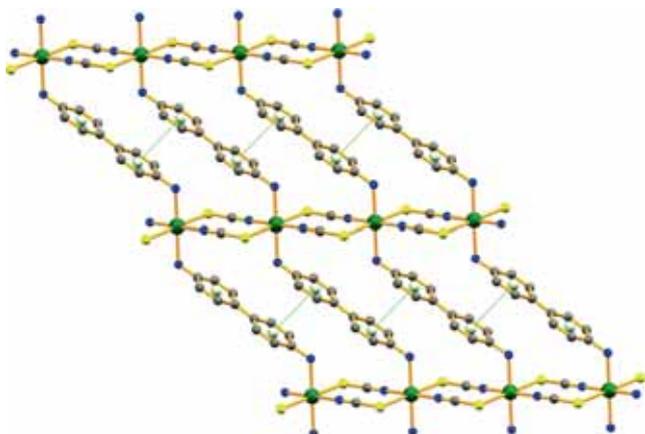
Compound	Hydrogen bond (Å, °)				
1	D-H...A	D-H	H...A	D...A	D-H...A
	N1-H1A...S1	0.9700	2.5700	3.523(4)	169.00
2	Hydrogen bond and C-H... π interaction (Å, °)				
	N1-H1A...O1	0.9000	2.4600	3.235(4)	144.00
	N1-H1A...O1 ^h	0.9000	2.3300	3.217(3)	167.00
	C3-H3...Cg(1)	0.9300	2.8300	3.588(18)	139.00

Symmetry code: ^h1+x-y,x,-z; Cg(1) = C(1)→C(2)→C(3)→C(4)→C(5)→C(6).

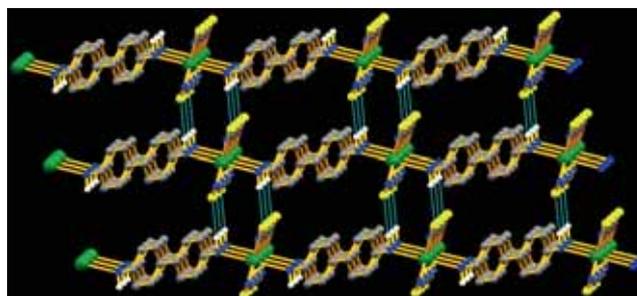
Table 4. $\pi \cdots \pi$ interaction parameter for **1**.

$\pi \cdots \pi$ interactions (\AA , $^\circ$)				
Ring-ring Cg(1)-Cg(1) ⁱ	Cg-Cg distance 3.685(3)	Dihedral angle (i, j) 0.00	Perpendicular distances between baricenters (i, j) 3.407(2)	Slippage 1.404

Symmetry code: ⁱ2-x, -y, 1-z; Cg(1) = C(1)→C(2)→C(3)→C(4)→C(5)→C(6).

**Figure 2.** 2D sheet structure in **1** stabilized by $\pi \cdots \pi$ interaction parallel to the *bc*-plane.

^b1-x, 1-y, 2-z; ^c2-x, 1-y, 2-z]. Two nitrile N (N2 and N2^c) atoms of bnzd and two S (S1^a and S1^b) atoms of two double $\mu_{1,3}$ bridged NCS⁻ define the equatorial plane whereas two amine N (N1 and N1^c) atoms of two different bnzd bridges occupy the axial positions. The axial Cd-N distance [2.346 \AA] is to some extent greater than the equatorial Cd-N distance [2.308 \AA] which is in line with the distorted coordination geometry. The sum of the equatorial bond angles (91.24 $^\circ$, 91.24 $^\circ$, 88.76 $^\circ$ and 88.76 $^\circ$) is exactly 360 $^\circ$ indicating all the equatorial N atoms along with Cd1 are in a least-squares plane. Double $\mu_{1,3}$ NCS⁻ bridges connect the neighboring cadmium(II) centers in the 2D polymer along *b*-axis forming eight-membered Cd-(NCS)₂-Cd loops with a rectangular conformation. A net (4,4) topology of the 2D polymer parallel to the *bc* plane can be conceived by connecting each cadmium(II) center of 1D chain along *b*-axis formed by two double $\mu_{1,3}$ NCS⁻ with binucleating, end-to-end bridging bnzd along *c*-axis. Cd \cdots Cd separation across double $\mu_{1,3}$ NCS⁻ bridge is shorter (6.044 \AA) than that (13.083 \AA) through bnzd, as expected. This 2D sheet structure is further stabilized by $\pi \cdots \pi$ interactions (Figure 2). 2D polymeric units lying parallel to the *bc* plane are associated by weak intermolecular hydrogen bonds (N1-H1A \cdots S1, 2.57 \AA , 169 $^\circ$) involving the S atom (S1) of NCS⁻ and H atom (H1A) of amine N (N1) of bnzd in the successive polymeric sheets along the *a*-axis affording

**Figure 3.** 3D network structure in **1** formed through intermolecular N-H \cdots S hydrogen bonds.

a 3D network structure (Figure 3). The specific orientation of the bnzd unit in a sheet towards the NCS⁻ of its adjacent sheet is responsible for the formation of such a superstructure through multiple non-covalent interactions.

3.3b $[\text{Cd}(\text{bnzd})_3]_n(\text{ClO}_4)_{2n}$ (**2**): A perspective view of the fundamental unit with the atom labeling scheme of the coordination polymer **2** is shown in Figure 4. Selected bond distances (\AA) and bond angles ($^\circ$) may be found in Table 2 and hydrogen bond and C-H \cdots π interaction parameters, in Table 3. In individual polycationic $[\text{Cd}(\text{bnzd})_3]_n^{2n+}$ species, the coordination environment around each cadmium(II) is a distorted octahedron with a CdN₆ chromophore. The coordination includes six amine N atoms (N1, N1^d, N1^e, N1^f, N1^g and N1^h; symmetry codes: ^d 2-y, 1+x-y, z; ^e 1-x+y, 2-x, z; ^f 2-x, 2-y, -z; ^g y, 1-x+y, -z and ^h +x-y, x, -z) of six different didentate bnzd bridges. The *cisoid* [83.44(5) $^\circ$ –96.56(5) $^\circ$] and *transoid* [180.00(8) $^\circ$] angles around each cadmium(II) center are in consonance with distortion from an idealized octahedron. The bridges are symmetric as is evident from similar Cd-N distances [Cd1-N1 2.4413(17) \AA]. An increase in Cd-N(bnzd) distance from **1** (2.346 \AA) to **2** (2.441 \AA) may presumably be due to steric crowding present in this binary coordination polymer arising from the steric interaction of *ortho* hydrogens of the six bnzd units around the metal(II) center. In the ternary complex **1**, the presence of the didentate bridging ligand NCS⁻ on the molecular plane and the housing of the two bnzd unit on axial position alleviates such steric crowding and thereby reducing

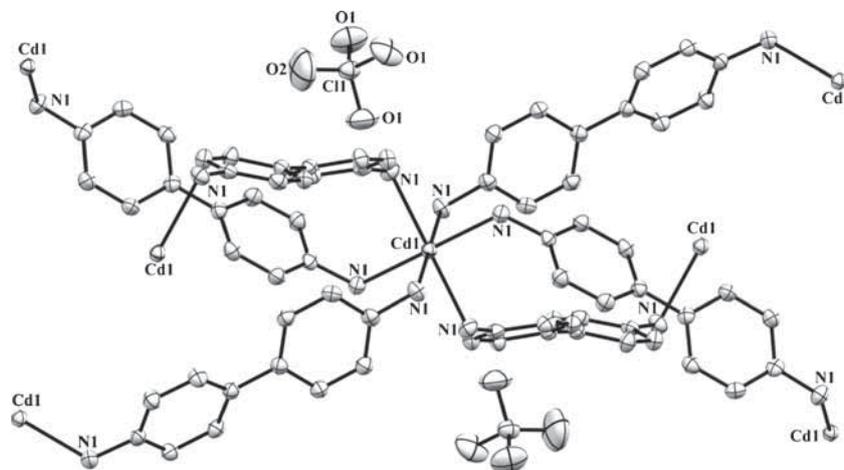


Figure 4. An ORTEP diagram of the fundamental coordination unit of 3D polymer **2** with 50% probability level of the ellipsoid.

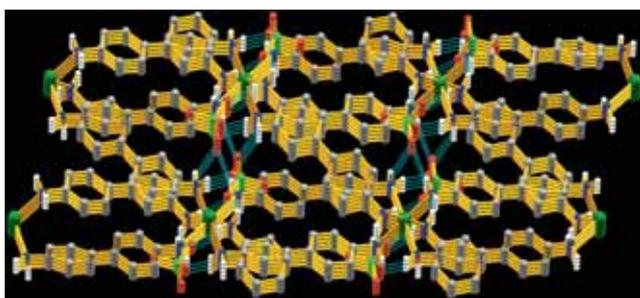


Figure 5. 3D network structure in **2** stabilized by intermolecular N-H...O hydrogen bonds.

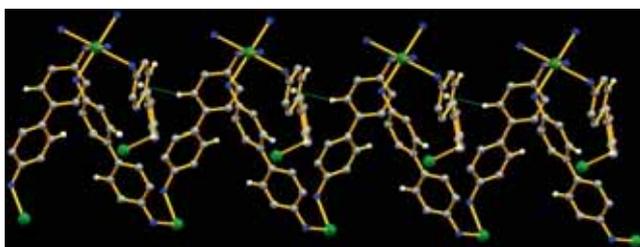


Figure 6. 3D network structure in **2** stabilized by C-H... π interactions.

the Cd-N(bnzd) distance substantially and closer to Cd-N(thiocyanate) distance (2.308 Å). Each fundamental unit of cadmium(II) is connected with six different cadmium(II) centers through bnzd bridges in non-ending fashion affording a 3D network structure. The Cd...Cd separation across the bnzd bridge is 12.153 Å. In the crystalline state, the 3D network is stabilized by intermolecular H-bonds (N1-H1A...O1 and N1-H1B...O1) involving the O atom (O1) of ClO₄⁻ ion and H atoms (H1A and H1B) of amine N (N1) of bnzd units (Figure 5) and C-H... π interactions (C3-H3...Cg(1)) (Figure 6).

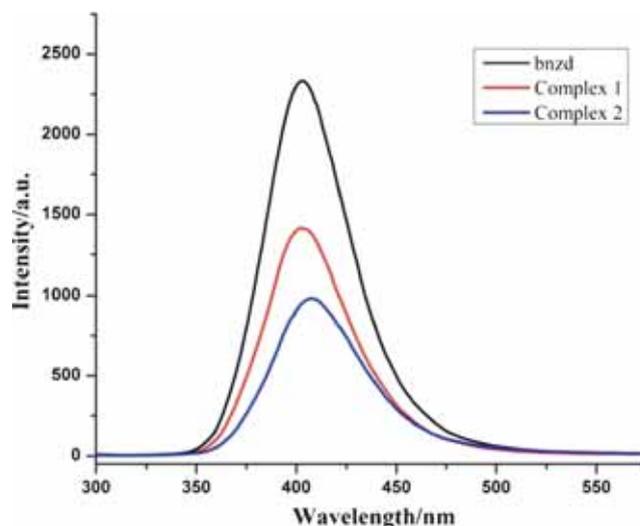


Figure 7. Fluorescence spectra of free bnzd, **1** and **2** in DMF solutions at 298 K.

3.4 Thermal studies

To examine thermal stabilities of **1** and **2**, thermogravimetric analyses (TG) were made between 30°C and 800°C in a static atmosphere of nitrogen. The TG curve (Figure S1) of **1** indicates that it is stable up to 214°C at which temperature decomposition commences and its decomposition takes place gradually in the temperature range 214–568°C corresponding to the weight loss (observed, 63.2% and calculated, 72.8%) of two NCS⁻ ions and one bnzd unit per formula unit. The TG curve (Figure S2) of **2** shows that the compound is stable up to 210°C and its decomposition takes place gradually in the temperature range 210–540°C corresponding to the weight loss (observed, 83.2% and expected, 87.0%) of three bnzd units and two perchlorate ions per formula unit.

3.5 Fluorescence studies

Light brown DMF solutions of free bnzd, **1** and **2** show strong absorption at 253, 297 and 296 nm, respectively, presumably due to ligand-based transition.³⁶ Upon photoexcitation at the corresponding absorption band in DMF solution, free bnzd exhibits a broad fluorescent emission centered at 402 nm; the corresponding cadmium(II) complexes **1** and **2** show less intense photoluminescence³⁷ with the main emission at the same position as that of free bnzd unit itself due to the intraligand $^1(\pi-\pi^*)$ transition (Figure 7). The less intensity in case of these coordination compounds may be attributed to heavy ion effect.

4. Conclusions

In summary, two coordination polymers of cadmium(II) are isolated using bridging units only. The 2D polymer **1** is a neutral one with two types of bridging ligands and 3D polycationic polymer **2** contains one kind of bridging unit. The two coordination polymers with different metal-organic frameworks (MOFs) afford different crystalline architectures through varied multiple weak non-covalent forces. These are thermally stable and behave as luminous materials.

Supplementary Information (SI)

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic data center No. 1409173 (**1**) and 1409172 (**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.

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