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Construction of coordination polymers of cadmium(II) with mixed hexamethylenetetramine and terephthalate or thiocyanate ligands

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Abstract

Three new polymeric complexes $[Cd(hmt)(SCN)_2(H_2O)_2]_n$ (**1**), $[Cd_3(\mu_2\text{-hmt})_2(SCN)_6(H_2O)_2]_n$ (**2**), and $[Cd_2(hmt)_2(tp)_2(H_2O)_6]_n$ (**3**), [hmt = hexamethylenetetramine, tp = terephthalate] have been synthesized and characterized by single crystal X-ray diffraction. Both the compounds **1** and **2** are 1-D polymers where Cd units are linked by double end-to-end thiocyanate bridges but in **2** the chain is wider containing three cadmium atoms instead of one as found in **1**. In both compounds the coordination environment around cadmium atom is distorted octahedral. Compound **3** is a three-dimensional polymer having water-filled microporous channels. Both tp and hmt are μ_2-bridged. One of the acid groups of tp is coordinated in chelating bidentate and the other in monodentate fashion. Half of its Cd atoms are hexa-coordinated and the rest are hepta-coordinated. Thermogravimetric analysis and X-ray diffraction study of **3** show that its framework remains intact upon removal of water molecules. The flexibility of coordination number around cadmium atoms (six or seven) probably plays an important role in establishing the rigidity of the framework.

Keywords: Coordination polymers; Cadmium(II); Hexamethylenetetramine; Terephthalate; Thiocyanate

1. Introduction

The design and synthesis of supramolecular architectures analogous to important minerals such as zeolites using the principle of crystal engineering are of much current interest [1]. The crystal engineering of coordination polymers are usually achieved by using bi- or multidentate ligands to bind the metal centres. Two types of ligands, neutral organic e.g. 4,4′-bipyridine, pyrazine etc. [2–4] and anionic e.g. thiocyanate, azide [5–9], polyaromatic acids [10–13] etc. are used to synthesize one-, two- or three-dimensional polymers. Combination of these two types of ligands [14], though less frequently, has also been used to synthesize coordination polymers with variable cavities or channels. Among the anionic ligands, the terephthalate [15] and thiocyanate ions exhibit a variety of bridging abilities and have strong tendencies to form large, tightly bound metal cluster aggregates. The polycyclic tertiary amine, hexamethylenetetramine [16–19] is a potentially tetradentate neutral ligand but mostly coordinates to the meal centre in the bidentate fashion to produce several interesting polymers. The metal ion, Cd(II) is well suited for construction of such materials as its electronic configuration as well as size permits a wide variety of geometries and coordination numbers.

To explore the combination effects of neutral hmt and anionic thiocyanate or terephthalate ligands we synthesize coordination polymers of Cd(II) containing these ligands. Considering the variable coordination behaviour of hmt we changed the Cd(II): hmt ratio and found that two different 1-D polymers could be obtained in case of thiocyanate but only one type of 3-D polymer containing both hexa- and hepta- coordinated Cd(II) is obtained with tp, irrespective of the metal: hmt ratio. Reported herein are the details of the synthesis, crystal structure and other relevant physicochemical studies of these three polymers.

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2. Experimental

2.1. Materials and measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyser. The infrared spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. $Cd(OAc)_2 \cdot 2H_2O$, hexamethylenetetramine, and NH_4SCN were purchased from EMerck Germany and used as received. All other chemicals used were AR grade. The thermal analysis (TG-DTA) were carried out on a Metler Toledo TGA/SDTA 851 thermal analyser in a dynamic atmosphere of dinitrogen (flow rate: 30 cm^3 min^{-1}). The sample was heated in an alumina crucible at a rate of 10 °C min^{-1}.

2.2. Preparations

2.2.1. $[Cd(hmt)(SCN)_2(H_2O)_2]_n$ (**1**)

$Cd(OAc)_2 \cdot 2H_2O$ (1 g, 3.75 mmol) dissolved in methanol (10 cm^3) was added to a methanolic solution (10 cm^3) of NH_4SCN (0.571 g, 7.51 mmol) followed by methanolic solution (10 cm^3) of hmt (0.526 g, 3.75 mmol) with continuous stirring. The white precipitate which appeared immediately was filtered and dissolved in hot water. The solution was then left at room temperature. Colourless monocrystals suitable for X-ray determination were collected after 24 h. *Anal*. Calc. (%) for $C_8H_{12}CdN_6O_2S$: C, 23.95; H, 2.99; N, 20.96. Found: C, 23.87; H, 2.95; N, 20.95%.

2.2.2. $[Cd_3(\mu_2\text{-}hmt)_2(SCN)_6(H_2O)_2]_n$ (**2**)

It was prepared by the similar procedure as for **1** excepting $Cd(OAc)_2 \cdot 2H_2O$ (1 g, 3.75mmol), hmt (0.263 g, 1.87 mmole) NH_4SCN (0.571g 7.51 mmol) were taken in the molar ratio 1:0.5:2. *Anal*. Calc. (%) for $C_{20}H_{14}Cd_3N_{12}O_2S_6$: C, 24.39; H, 1.42; N, 17.07. Found: C, 24.37; H, 1.44; N, 17.05%.

2.2.3. $[Cd_2(hmt)_2(tp)_2(H_2O)_6]_n$ (**3**)

$Cd(OAC)_2 \cdot 2H_2O$ (1 g, 3.75 mmole) dissolved in water (10 cm^3) was added to aqueous solution of hmt (0.263 g, 1.87 mmol) followed by aqueous solution (100 cm^3) of Na_2tp (0.789 g, 3.75 mmol). The colourless solution was filtered and left to evaporate at room temperature. Colourless crystals suitable for X-ray determination were collected after several weeks. *Anal*. Calc. (%) for $C_{28}H_{44}Cd_2N_8O_{14}$: C, 36.68; H, 4.67; N, 11.89. Found: C, 36.67; H, 4.66; N, 11.87%.

2.3. Crystal structure determination

Data for all three crystals were measured with Mo Kα radiation ($\lambda = 0.71073$ Å) using the MAR research Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [20]. The structures were solved using direct methods with the SHELX-86 program [21]. The non-hydrogen atoms were refined with anisotropic thermal parameters in all cases. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Absorption corrections were carried out using the DIFABS program [22]. The structures were then refined to convergence on F^2 using SHELXL [23]. All calculations were carried out using SHELXS-86, SHELXL-93, PLATTON-99, ZORTEP programs. Selected crystallographic data of three complexes are summarized in Table 1 while selected bond lengths and bond angles of the crystals are presented in Tables 2–4.

3. Results and discussion

Compounds **1** and **2** are prepared by varying the hmt concentration keeping other constituents constant. Interestingly, it has been observed that when the cadmium:hmt molar ratio is varied between 1:0.25–1:0.75 compound **2** is obtained as revealed by C, H, N, thermal and X-ray powder diffraction analysis whereas when the Cd:hmt molar ratio is maintained in the range 1:1–1:2 complex **1** is obtained. On the other hand, complex **3** is the only product in the concentration ranges of cadmium:hmt = 1:0.2–1:2.

3.1. IR spectra

The position of the IR-bands corresponding to the stretching frequency of the thiocyanate group and tp group can be used for characterisation of the mode of coordination to the metal. The ν(CN) of a bridging thiocyanate is usually found to be around 2100 cm^{-1}. Both for compound **1** and **2** the stretching frequency occur as a single peak at 2080 and 2096 cm^{-1} respectively, indicating the presence of end-to-end NCS bridges. The IR spectra of **3** show that the $\nu_{as}(CO_2)$) and $\nu_s(CO_2)$ appear at 1569 and 1388 cm^{-1} as very strong single peaks. The splitting between the bands is 181 cm^{-1}. Although two types of coordination modes of a tp ligands, (chelating bidentate and monodentate) are present in this complex, no splitting of $\nu_s(CO_2)$ or $\nu_{as}(CO_2)$ was observed unlike other tp complexes [15a,24].

3.2. Description of the crystal structures

The structure determination of complex **1** reveals that the cadmium(II) atoms are bridged by end-to-end thiocyanato ligand with the occurrence of a 1-D

Table 1
Crystal data and structure refinement for the structures

Compound	**1**	**2**	**3**
Empirical formula	$C_8H_{16}CdN_6O_2S_2$	$C_{18}H_{28}Cd_3N_{14}O_2S_6$	$C_{28}H_{44}Cd_2N_8O_{14}$
Formula weight	404.79	1002.10	941.51
Crystal system	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbca*
a (Å)	6.011(11)	5.936(8)	17.38(2)
b (Å)	10.041(14)	8.980(14)	17.37(2)
c (Å)	12.959(14)	15.84(2)	22.91(3)
α (°)	67.76(1)	101.33(1)	(90)
β (°)	75.51(1)	95.88(1)	(90)
γ (°)	76.43(1)	101.50(1)	(90)
V (Å^3)	692	802	6915
Z	2	1	4
μ_{calc} (Mg m^{-3})	1.942	2.007	1.809
Collected reflections (R_{int})	3966/0.1502	5046/0.0695	12803/0.0638
Unique data/restraints/parameters	2410/0/173	2851/0/197	4630/24/506
Final R indices [$I > 2\sigma(I)$]			
R_1	0.0898	0.0759	0.0494
wR_2	0.2270	0.1501	0.1223
R indices (all data)			
R_1	0.0931	0.857	0.0768
wR_2	0.2376	0.1586	0.1352
Max, min peak (e Å^{-3})	2.170, −1.205	3.551, −0.884	0.774, 0.915

polymeric infinite chain. A ZORTEP drawing of the chain with atom labelling scheme is shown in Fig. 1. In the coordination chain each cadmium(II) is attached with the four bridging thiocyanato ligands, one hmt ligand and water molecule in a distorted octahedral environment with CdN_3S_2O chromophore. The two nitrogen atoms (N1, N2) [Cd1–N1, 2.301(8) Å; Cd1–N2, 2.319(8) Å] and two symmetry related sulfur atoms (S1*, S2*) [Cd1–S1*, 2.768(3) Å; Cd1–S2*, 2.718(3) Å] from the four bridging thiocyanate ligands form the equatorial plane around the each Cd1 centre. The *trans* axial sites are occupied by the nitrogen atom (N11) [Cd1–N11, 2.379(7) Å] from the pendent hmt ligand and the oxygen atom (O20) [Cd1–O20; 2.325(7) Å] of the water molecule. The degrees of distortion from the ideal octahedral geometry are reflected in cisoid and transoid angels, which are all within 9° of ideal values. The deviation of the Cd1 atom from the mean plane formed by the four equatorial atoms (N1, N2, S1*, S2*) is about 0.146 Å and the deviation of N1 and S2* deviates from above and below the mean plane respectively by 0.053 Å. The nearest neighbour Cd···Cd distance within the chain is 6.011 Å. In addition in the asymmetric unit, there is a water molecule O(10) which forms hydrogen bonds with N(16) ($1-x$, $-1-y$, $-z$) at 2.79 Å and O(20) at 2.78 Å and O(20) ($-x$, $-y-1$, $-z$) at 2.75 Å.

Table 2
Distances (Å) and angles (°) for **1**

Bond distances			
Cd(1)–N(1)	2.301(8)	O(20)–Cd(1)–N(11)	173.1(2)
Cd(1)–N(2)	2.319(8)	N(1)–Cd(1)–S(2)*	91.4(2)
Cd(1)–O(20)	2.325(7)	N(2)–Cd(1)–S(2)*	86.9(2)
Cd(1)–N(11)	2.379(7)	O(20)–Cd(1)–S(2)*	88.5(2)
Cd(1)–S(2)*	2.718(3)	N(11)–Cd(1)–S(2)*	98.3(2)
Cd(1)–S(1)*	2.768(3)	N(1)–Cd(1)–S(1)*	88.4(5)
Bond angles			
N(1)–Cd(1)–N(2)	175.1(2)	N(2)–Cd(1)–S(1)*	92.7(2)
N(1)–Cd(1)–O(20)	87.9(3)	O(20)–Cd(1)–S(1)*	83.2(2)
N(2)–Cd(1)–O(20)	87.6(3)	N(11)–Cd(1)–S(1)*	90.0(2)
N(1)–Cd(1)–N(11)	92.1(2)	S(2)*–Cd(1)–S(1)*	171.7(1)
N(2)–Cd(1)–N(11)	92.7(2)		

Symmetry codes: (a) $1+x$, y, z (b) $-1+x$, y, z.

The structure of complex **2** is made up of a 1-D neutral rectangular-grid like network of cadmium(II) bridged by the hmt and thiocyanate lying along the crystallographic a-axis. The most interesting feature of the structure is that the three parallel thiocyanate bridged chains are running which are connected by the hmt ligand forming the three leg rectangular grid-like structure. ZORTEP drawing of the 1-D chain with atom numbering scheme is shown in Fig. 2. In the coordination chain there are two unique cadmium atoms, Cd1 which is situated on a centre of symmetry and Cd2 in a general position and both the cadmium atoms are bonded to four bridging thiocyanates in a similar fashion to that found in complex **1**. The two nitrogen atoms (N3 and its symmetry related counter part N3*) [Cd1–N3, 2.273(7) Å] and the two sulfur atoms (S3 and its symmetry related counterpart S3*) [Cd1–S3, 2.742(6) Å] form the equatorial plane around each Cd1 and the *trans* axial positions are occupied by the two nitrogen atoms (N17, N17*) [Cd1–N17, 2.472(6) Å] from the two bridging hmt ligand. In case of Cd2, the equatorial positions occupied by the N2, N4, S2 and S4 [Cd2–N2,

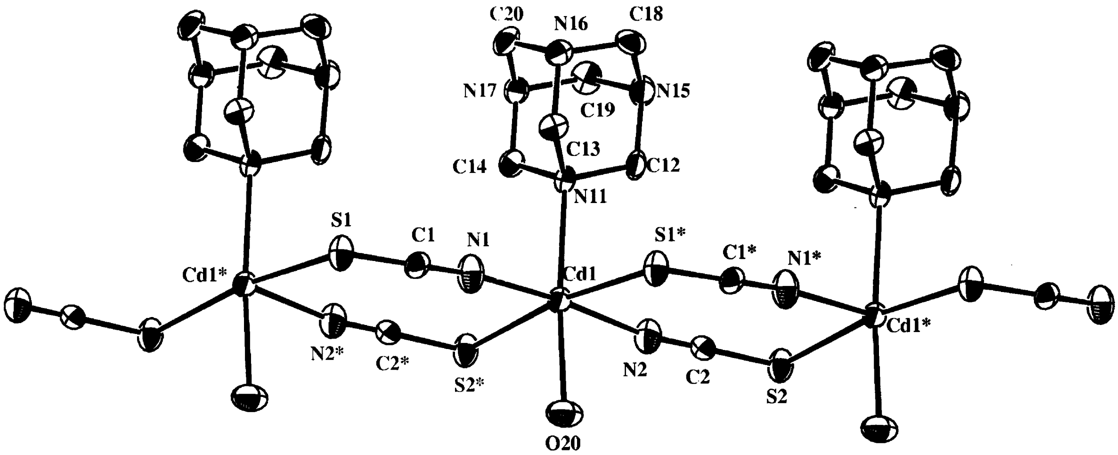

Fig. 1. ZORTEP plot of complex **1** with atom numbering scheme.

2.295(7) Å; Cd2–N4, 2.269(7) Å; Cd2–S2, 2.799(3) Å; Cd2–S4, 2.687(3) Å] from the four bridging thiocyanate ligands and the *trans* axial positions are occupied by N11 [Cd2–N11, 2.461(6) Å] from the hmt and O100 [Cd2–O100, 2.359(7) Å] of the water molecule. Around the Cd1 atom the cisoid angles are in the range 87.56(19)°–92.44(19)° and the transoid angles are 180° and Cd1 atom perfectly sits with the equatorial plane without any deviation. Deviation of Cd2 from the mean plane formed by the four equatorial atoms is about 0.080 Å while N2, N4 atoms and S2, S4 atoms sits above and below the equatorial plane by 0.015 Å respectively. The degree of distortion of Cd2 from the ideal octahedral geometry was reflected in the cisoid, 83.32(18)°–95.22(18)° and transoid angles, 172.5(2)°–175.99(6)°. The Cd1···Cd1 and Cd2···Cd2 distances in the thiocyanato bridged part is 5.94 Å and the Cd1···Cd2 distances through the hmt linkage is 6.44 Å. The Cd–S–C and Cd–N–C angles in the bridged part are consistent with those found in previously reported cadmium thiocyanato bridged complexes. [N···O 2.797 Å] hydrogen bonds arise from the interaction of the hmt N of one 1-D chain with the H of coordinated water molecules of adjacent 1-D chain and vice versa. This H-bonded double linkage joining adjacent 1-D chain creates 2-D network with a porous cavity propagating along a-axis (Fig. 3).

The structure determination reveals that the complex **3** is a 3-D-coordination polymer bridged through both

Table 3
Distances (Å) and angles (°) for **2**

Bond distances			
Cd(1)–N(3)	2.274(7)	N(2)–Cd(2)–O(100)	85.5(2)
Cd(1)–N(17)	2.466(6)	N(4)–Cd(2)–N(11)	86.2(2)
Cd(1)–S(3)	2.742(4)	N(2)–Cd(2)–N(11)	96.8(2)
Cd(2)–N(4)	2.278(7)	O(100)–Cd(2)–N(11)	172.5(2)
Cd(2)–O(100)	2.358(7)	N(4)–Cd(2)–S(4)	88.5(2)
Cd(2)–N(2)	2.297(7)	N(2)–Cd(2)–S(4)	95.2(2)
Cd(2)–N(11)	2.463(6)	O(100)–Cd(2)–S(4)	92.8(2)
Cd(2)–S(4)	2.690(3)	N(11)–Cd(2)–S(4)	94.14(14)
Cd(2)–S(2)	2.800(3)	N(4)–Cd(2)–S(2)	90.7(2)
Bond angles			
N(3)–Cd(1)–S(3)	87.8(2)	N(2)–Cd(2)–S(2)	85.3(2)
N(17)–Cd(1)–S(3)	91.77(11)	O(100)–Cd(2)–S(2)	83.3(2)
N(3)–Cd(1)–N(17)	92.45(19)	N(11)–Cd(2)–S(2)	89.73(14)
N(4)–Cd(2)–N(2)	175.0(2)	S(4)–Cd(2)–S(2)	175.99(6)
N(4)–Cd(2)–O(100)	91.0(3)		

Symmetry codes: (a) 1.5−*x*, *y*−0.5, *z*. (b) *x*, 0.5−*y*, *z*−0.5. (c) 1.5−*x*, 1−*y*, *z*−0.5.

Table 4
Distance (Å) and angles (°) for **3**

Bond distances			
Cd(1)–O(71)*	2.236(6)	O(71)*–Cd(1)–N(45)*	94.9(2)
Cd(1)–O(20)	2.322(6)	O(20)–Cd(1)–N(45)*	89.8(2)
Cd(1)–N(45)*	2.371(6)	O(71)*–Cd(1)–O(20)	80.1(2)
Cd(1)–O(82)	2.389(6)	O(51)*–Cd(2)–O(59)	152.5(3)
Cd(1)–N(18)	2.391(6)	O(51)*–Cd(2)–O(30)	84.4(2)
Cd(1)–O(81)	2.554(5)	O(59)–Cd(2)–O(30)	122.0(2)
Cd(2)–O(10)	2.418(5)	O(51)*–Cd(2)–N(11)	87.8(2)
Cd(2)–N(41)	2.437(7)	O(59)–Cd(2)–N(11)	95.2(2)
Cd(2)–O(58)	2.642(6)	O(30)–Cd(2)–N(11)	97.7(2)
Cd(2)–O(51)*	2.252(6)	O(51)*–Cd(2)–O(10)	78.5(2)
Cd(2)–O(59)	2.281(5)	O(59)–Cd(2)–O(10)	74.7(2)
Cd(2)–O(30)	2.343(5)	O(30)–Cd(2)–O(10)	162.7(2)
Cd(2)–N(11)	2.408(7)	N(11)–Cd(2)–O(10)	84.4(2)
O(20)–Cd(1)–N(18)	111.5(2)	O(51)*–Cd(2)–N(41)	89.0(2)
Bond angles			
N(45)*–Cd(1)–N(18)	158.5(2)	O(59)–Cd(2)–N(41)	87.5(2)
O(82)–Cd(1)–N(18)	89.3(2)	O(30)–Cd(2)–N(41)	82.3(2)
O(71)*–Cd(1)–O(81)	149.4(2)	N(11)–Cd(2)–N(41)	176.7(2)
O(20)–Cd(1)–O(81)	130.3(2)	O(10)–Cd(2)–N(41)	94.5(2)
N(45)*–Cd(1)–O(81)	83.3(2)	O(51)*–Cd(2)–O(58)	154.8(2)
O(82)–Cd(1)–O(81)	52.4(2)	O(59)–Cd(2)–O(58)	52.6(2)
N(18)–Cd(1)–O(81)	81.0(2)	O(30)–Cd(2)–O(58)	72.0(2)
O(20)–Cd(1)–O(82)	79.0(2)	N(11)–Cd(2)–O(58)	86.7(2)
N(45)*–Cd(1)–O(82)	92.6(2)	O(10)–Cd(2)–O(58)	125.3(2)
O(71)*–Cd(1)–N(18)	91.2(2)	N(41)–Cd(2)–O(58)	96.4(2)
O(71)*–Cd(1)–O(82)	157.7(2)		

Symmetry codes: (a) 1.5−*x*, *y*−0.5, *z*. (b) *x*, 0.5−*y*, *z*−0.5. (c) 1.5−*x*, 1−*y*, *z*−0.5.

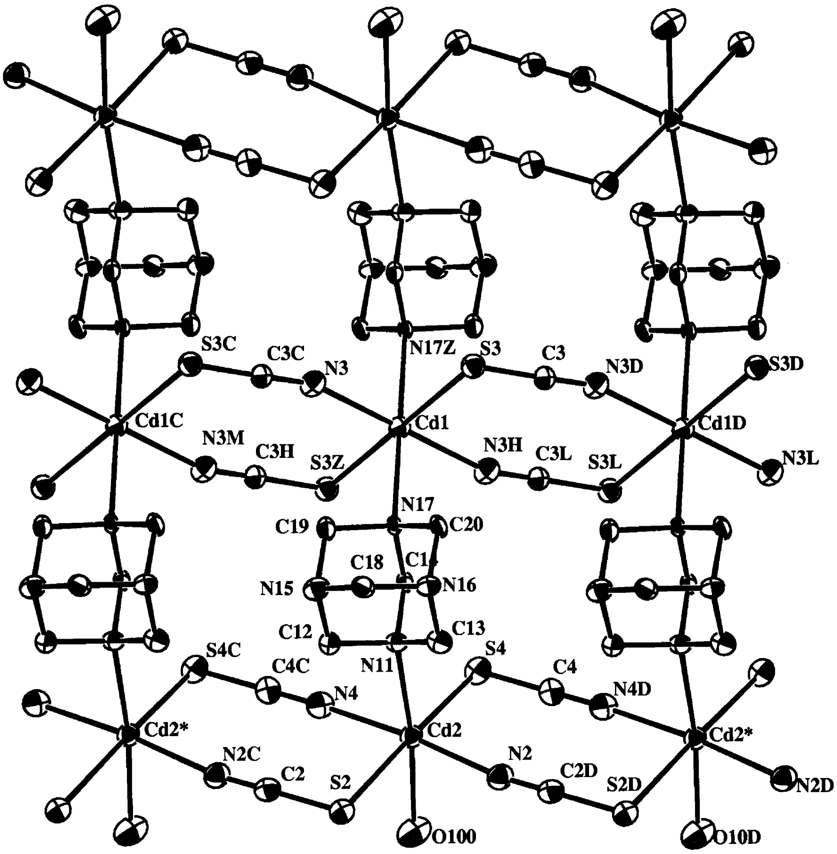

Fig. 2. ZORTEP plot of complex **2** with atom labelling scheme.

the terephthalate and hmt ligand. The ZORTEP drawing of the asymmetric unit with the atom numbering scheme is shown in Fig. 4. There are two unique cadmium atoms in the asymmetric unit with different coordination environment, one is hexagonal (Cd1) and the other is pentagonal bipyramidal (Cd2). In the 3-D network there are two chains of Cd1 and Cd2 atoms, bridged by hmt, which makes the polymeric structure unique. The local environment around Cd1 can best be described as highly distorted octahedral with one bidentate chelating carboxylate, one monodentate carboxylate from the two tp and one water molecule in the equatorial plane and the two nitrogen atoms from the two hmt ligand are ligated in the *trans* axial positions. The equatorial, Cd1–O bond lengths are in the range, 2.236(6)°–2.554(5) Å and the axial Cd1–N are 2.371(6)°–2.391(6) Å. The degrees of distortion of Cd1 can be observed in the cisoid, 52.42(17)°–94.88(18)° and transoid angles, 149.4(2)°–158.53(18)°. Of the two water molecules (O10, O30) and the two tp ligand, one is bidentate chelate and another is monodentate form the equatorial plane and the axial positions are occupied by the two nitrogen atom from the two hmt ligands. The Cd2–O and Cd2–N bond lengths are in the range 2.252(6)–2.642(6) Å and 2.408(7)–2.437(7) Å respectively. The deviations of Cd1 and Cd2 from the mean plane are about 0.003 and 0.006 Å respectively. The contrast between the two coordination geometries around Cd1 and Cd2 is due to the fact that the distances of the non-bonded oxygen atom (O52*) from Cd2 is much larger [Cd2–O53*, 3.54(1) Å] than the corresponding distance of O73* from Cd1 [Cd1–O73*, 3.06(1) Å]. The latter close contact blocks the position for a additional water molecule for the pentagonal bipyramidal arrangement. It can be seen from a perspective view down the *c*-axis that the tpt coordination chain of Cd1 is perpendicular to the tpt chain of Cd2, and both the chains are linked by the flexible hmt ligand, resulting in the formation of a regular three dimensional rectangular grid like network with the channel dimensions 4.3 × 4.1 Å (Fig. 5). The channels contain the solvent water molecules. The void space along the Z-axis is about 183 Å^3, which is 2.7% of the unit cell volume. Cd1···Cd1 and Cd2···Cd2 distance through tp linkage is 11.46 Å and Cd1···Cd2 distance through the hmt linkage is about 6.34 Å. To the best of our knowledge this is the first example in which there are two regular octahedral and trigononal bipyramidal cadmium(II) chains of tp linkage through the rigid hmt ligand which is the responsible for the construction of the 3-D network.

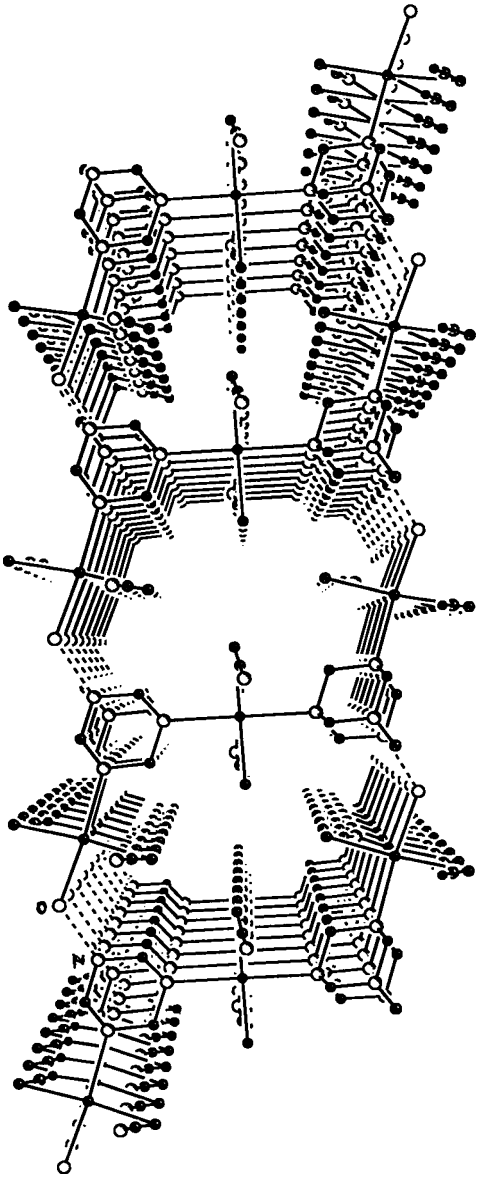

Fig. 3. View of complex **2** along *a*-axis showing H-bonding by dotted lines between adjacent chains.

3.3. Thermal analysis

Both the compounds **1** and **2** upon heating lose their water molecules in very similar pattern. The TG curve shows that the loss of water molecules for both the compounds occur in two steps; the first step starts at approximately 90 °C and completes at approximately 110 °C. The second step starts at approximately 140 °C and completes at 170 °C. The percentage of water loss indicates that almost half of the water molecules are lost in the first step and rest portion in the second step. The water molecules of both the compounds are lost if they are kept in the vacuum desiccators for several days. It is to be noted that once the water molecules are lost, the crystals break into powder which does not absorb any water molecules from the atmosphere (unlike compound **3**). Compound **3** upon heating loses its water molecules in three steps, which start at 70 °C and complete at 160 °C as is evident from the TG–DTG curve (Fig. 6). The observed weight loss corresponds to 6 molecules of water per formula unit. The crystals turn opaque on removal of water molecules but do not break into powder. This dehydrated species on exposure in open atmosphere for 2 h absorbs exactly 6 molecules of water per formula unit and no more water molecules was absorbed on keeping for a longer period. The water loss behaviour of rehydrated species as found in the TG–DTG curve is identical to that of the original sample. The X-ray powder diffraction pattern shows that these two species are identical. These observations clearly indicate that the framework integrity of **3** remains intact upon removal of the water molecules. The crystal structure of **3** shows the presence of channels occupied by guest water molecules. On removal of these guest molecules along with the coordinated water molecules should lead to a porous solid which maintains the structural integrity of the Cd-hexamine terephthalate network. In order to find if other solvents can be occupied in the channel as guest molecules, we dehydrated the compound at 150 °C and kept it overnight as a suspension in dry methanol and ethanol. The TG analysis of this compound after separation and drying shows the absence of any guest molecule. However if the methanol or ethanol contains water (1% or more), the dehydrated compound readily reverts to **3**. The above results indicate that only water can be accommodated as guest molecules in the channels of **3**. The size of the pores is calculated to be 183 Å^3 and seems to be large enough to accommodate MeOH or EtOH, working on the basis of 20 Å^3 per non-H atom. The selectivity is more likely to arise from the dimensions of the channels allowing access to these pores or from selective hydrogen bonding interactions. The stability of the framework structure in **3** is most likely due to the multidentate functionality of the terephthalate ion as well of the variable coordination number of the Cd(11). The pendent part of the monodentate carboxylate group of **3** is just needed to be coordinated in bidentate fashion to maintain a uniform coordination of six around Cd(11) in the dehydrated species.

3.4. Fluorescence properties

The room temperature fluorescence spectra of terepthalic acid and its cadmium complex in the solid state are shown in Fig. 7(a) and (b) respectively. It is found from the figure that the terepthalic acid shows a strong emission band at 441 nm when excited at the strongest absorption band ($\lambda_{\text{ex}} = 350$ nm). On the contrary the cadmium complex shows very weak emission at 420 nm on 350 nm excitation (Fig. 7(b)). It is evident from some

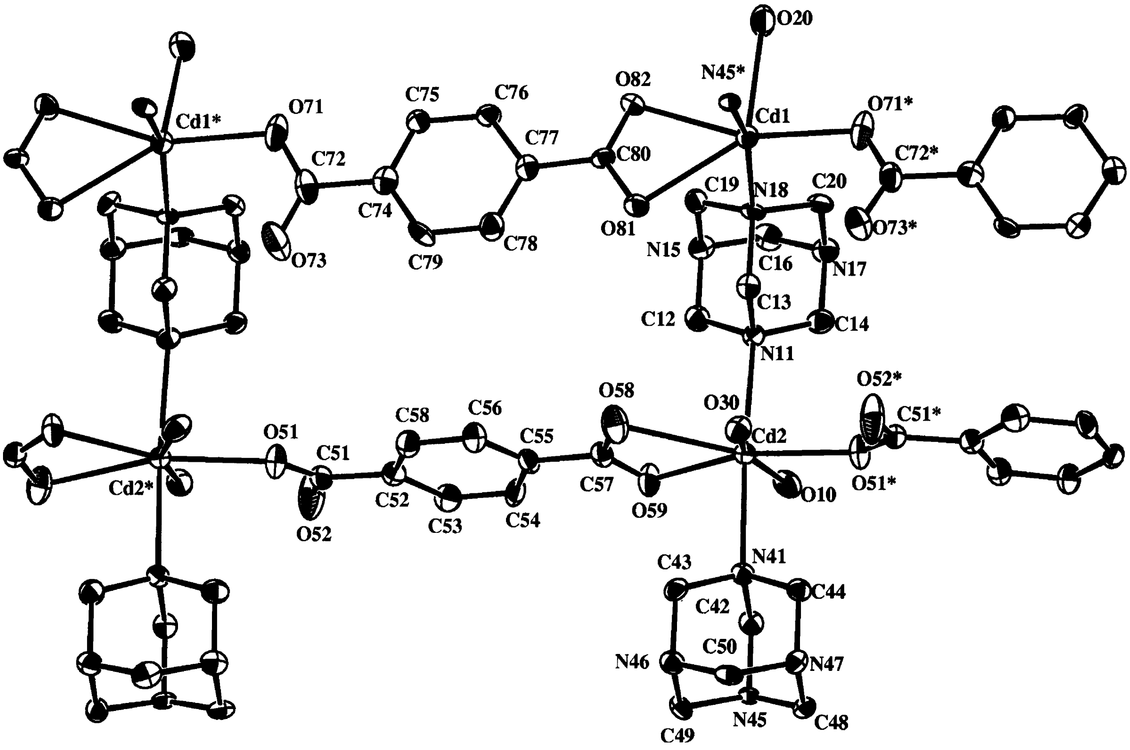

Fig. 4. ZORTEP view of complex **3** showing the coordination around metal atoms.

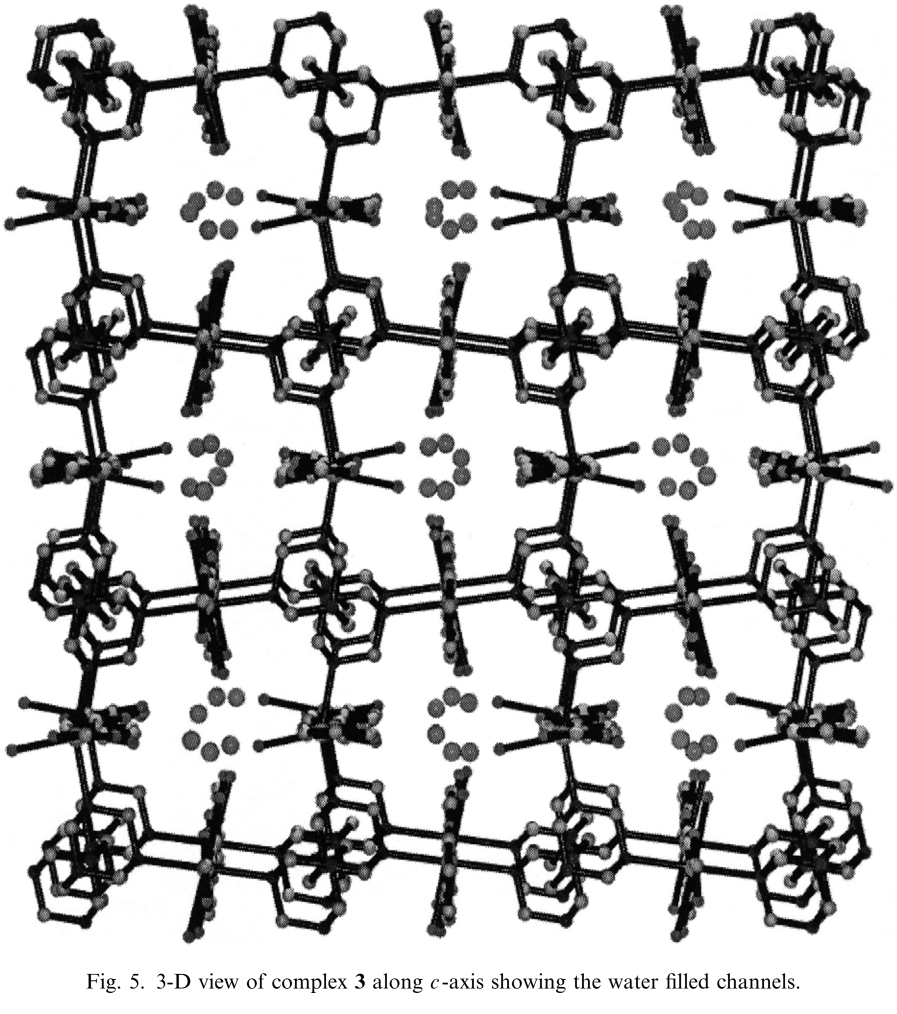

Fig. 5. 3-D view of complex **3** along c-axis showing the water filled channels.

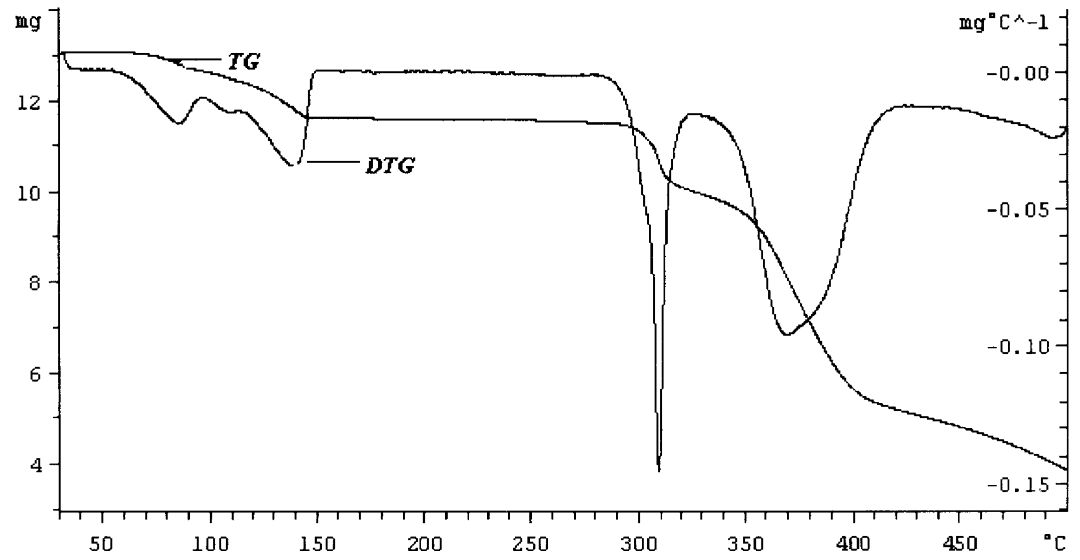

Fig. 6. TG–DTG curve of complex **3** (sample mass: 13.0250 mg).

reported case that complex formation sometimes increases the fluorescence intensity due to reduction of symmetry of the ligand or charge transfer emission (MLCT or LMCT emission). In the present case quenching of fluorescence on complex formation could be due to metal quenching.

4. Conclusion

In this work, we reported two 1-D polymers of the formula $[Cd(hmt)(SCN)_2(H_2O)_2]_n$ (**1**) and $[Cd_3(\mu_2\text{-}hmt)_2(SCN)_6(H_2O)_2]_n$ (**2**) with double end-to-end thiocyanate bridges formed by varying the hexamine ratio and a noninterpenetrating rigid 3-D coordination framework with $[Cd_2(hmt)_2(tp)_2(H_2O)_6]$ as building blocks whose novelty lies in two different hexa and hepta coordinated Cd environment in the same structural motif bridged by hexamine and terephthalate to form hydrophilic channels where guest water molecules reside.

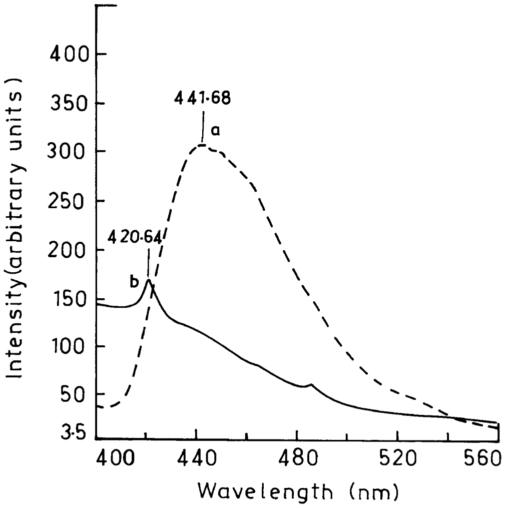

Fig. 7. Solid-state fluorescent emission spectra of complex **3** at room temperature.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 190884–190886 for complexes **1**–**3** respectively. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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