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FULL PAPER

Flexibility in co-ordinative behaviour of *N*-(3-hydroxypropyl)-ethane-1,2-diamine toward cadmium(II) halides: syntheses, crystal structures and solid state thermal studies

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One new two-dimensional and two one-dimensional organic/inorganic composite coordination polymers have been synthesised by the reaction of cadmium(II) halides with *N*-(3-hydroxypropyl)ethane-1,2-diamine (L) and structurally characterised. $[Cd(L)Cl_2]_n$ (**1**) is a two-dimensional sheet which is built from intersecting zigzag chains and forms a honeycomb like (6,3) net where each octahedral cadmium is linked with two bridging chloride atoms, one pendant chloride atom, two chelated nitrogen atoms of L and an oxygen atom from a neighbouring ligand; each cadmium(II) acts as a branching centre. $[Cd(L)Br_2]_n$ (**2**) is a bromo bridged one-dimensional chain in which the non-chelated part of ligand L binds a neighbouring cadmium(II) centre resulting in an alternating array of four- and twelve-membered rings. $[Cd(L)I_2]_n$ (**3**) is an iodo bridged one-dimensional network of alternating octahedral (CdN_4I_2) and tetrahedral cadmium(II) (CdI_4) centres. Upon heating the complexes exhibit an irreversible endothermic phase transition [95–133 °C, $\Delta H = 29.5$ kJ mol^{-1} for (**1**); 83–128 °C, $\Delta H = 22.5$ kJ mol^{-1} for (**2**) and 91–128 °C, $\Delta H = 15.5$ kJ mol^{-1} for (**3**)] yielding transparent films of $CdLCl_2$ (**1a**), $CdLBr_2$ (**1b**) and $CdLI_2$ (**1c**) respectively. The derived species (**1a**, **1b** and **1c**) do not revert on keeping them in a humid atmosphere (relative humidity ≈ 60%) for several days but exhibit a glass transition upon heating.

Introduction

Coordination polymers of one-, two- and three-dimensional infinite frameworks involving cadmium(II) have been the subject of great interest in recent years owing to their potential application in catalysis, optical properties evolution, clathration *etc.*[1–5] The d^{10} configuration and softness of cadmium(II) permit a wide variety of geometries and coordination numbers. The coordination polymers of cadmium(II) have been exploited using organic ligands as well as anions *e.g.*, Cl^-, Br^-, I^-, SCN^-, N_3^-, $SeCN^-$ [6–15] *etc.* which are an essential part of the coordination polyhedra. The ligand, as well as the anions, are observed to control the structural diversity and stereochemistry of a cadmium(II) centre. Cannas *et al.*[16] reported the complexes of $CdCl_2$ with three triamines, bis(2-aminoethyl)amine (baa), bis(3-aminopropyl)amine (bpa) and (2-aminoethyl)(3-aminopropyl)amine (apa) and showed the influence of aliphatic chain length on molecular association. The ligand baa generates a polymeric species while bpa and apa produce dimeric complexes with *cis* and *trans* conformations respectively. However all the triamines act only as chelating agents and molecular association takes place due to the bridging chloride ion. The same research group published similar work[17,18] with $Cd(SCN)_2$ and proposed that $Cd(apa)(SCN)_2$ was a discrete five-coordinated species on the basis of the 0*kl* Weissenberg photograph.

On our way to explore polymeric cadmium(II) complexes we were able to isolate single crystals of $Cd(apa)(SCN)_2$ and the structural analysis revealed[11] a 2D polymeric species where each apa moiety acted as a chelating as well as a bridging ligand. This finding made us optimistic of obtaining some unique results from analogous triamines *e.g.*, baa and bpa *etc.* We reported unique three-dimensional complexes, $[Cd_3(L')_2(NCS)_6]_n \cdot nH_2O$ (L′ = baa[5] and bis(2-aminoethyl)methylamine,[12] mebaa) with two types of cadmium environment, one involving only N-donor atoms and the other only S-donor atoms, where baa and mebaa acted as chelating ligands only. In this context, we reasoned that the replacement of a propylenic arm with an ethylenic arm would result in a ligand which was no longer the right length to bond adjacent metal atoms, creating instead an environment for chelating the same metal. The foregoing facts suggest that a choice of ligand with ethylenic as well as propylenic moieties, *e.g.* the triamine apa, whereby donor atoms as well as anions may be varied would be an ideal way to generate novel polymeric species of cadmium(II). Based on this idea we have chosen the ligand *N*-(3-hydroxypropyl)ethane-1,2-diamine (L), which showed flexidentate (N–N/N–N–O)[19] as well as tetradentate (N–N–(μ)-OH)[20] behaviour, and anions Cl^-, Br^- and I^-, each of which have different sizes and potential bridging abilities, to react with cadmium(II) to obtain novel polymeric architectures. In the present work, we report the syntheses, single crystal X-ray structure determinations and solid state thermal properties of three polymeric architectures, $[Cd(L)Cl_2]_n$ (**1**), $[Cd(L)Br_2]_n$ (**2**) and $[Cd(L)I_2]_n$ (**3**) [L = *N*-(3-hydroxypropyl)ethane-1,2-diamine].

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Experimental

Materials

High purity *N*-(3-hydroxypropyl)ethane-1,2-diamine (L) was purchased from TCI, Japan and cadmium(II) chloride, cadmium(II) bromide tetrahydrate and cadmium(II) iodide were purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals were of AR grade.

Syntheses of $[Cd(L)Cl_2]_n$ (1), $[Cd(L)Br_2]_n$ (2) and $[Cd(L)I_2]_n$ (3)

The complex **1** was synthesised by adding an ethanolic solution (5 ml) of L (1 mmol, 0.118 g) to a solution of cadmium(II) chloride (1 mmol, 0.183 g) dissolved in ethanol–water (9 : 1) mixture (10 ml). The resulting solution was stirred for 30 min and filtered. The filtrate was kept in a $CaCl_2$ desiccator. After a few days suitable single crystals were obtained for X-ray diffraction study, yield: 85%. Anal. found: C, 19.88; H, 4.63; N, 9.28, Cd, 37.28. Calc. for $C_5H_{14}CdCl_2N_2O$: C, 19.89; H, 4.64; N, 9.28; Cd, 37.27%.

Complexes **2** and **3** were synthesised by following the above method using cadmium(II) bromide tetrahydrate and cadmium(II) iodide respectively instead of cadmium(II) chloride. Yield : 83%. Anal. found: C, 15.35; H, 3.58; N, 7.18; Cd, 28.85. Calc. for $C_5H_{14}N_2CdBr_2O$: C, 15.36; H, 3.58; N, 7.17; Cd, 28.80% for complex **2**. Yield: 80%. Anal. found: C, 12.38; H, 2.87; N, 5.77; Cd, 23.28. Calc. for $C_5H_{14}N_2CdI_2O$: C, 12.38; H, 2.89; N, 5.78; Cd, 23.20% for complex **3**.

Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer and cadmium(II) content was estimated gravimetrically.[21] The IR spectrum (4000–400 cm^{-1}) and far-IR spectrum (400–50 cm^{-1}) were taken using Nicolet Magna-IR 750 series-II and FTIR Bomen DA 8.3 spectrometers respectively. The thermal analyses (TG-DTA) were carried out using a Shimadzu DT-30 thermal analyzer under a flow of nitrogen (flow rate 30 ml min^{-1}). The enthalpy changes of phase transitions were calculated by means of a Perkin-Elmer DSC-7 differential scanning calorimeter using indium metal as a calibrant. X-Ray diffraction patterns were obtained at 25 °C using a Seifert XRD-3000P instrument, where the source of X-rays was Cu radiation (30 kV/30 mA); the primary slits were 3 mm/soller/2 mm and the secondary slits soller/0.2 mm.

Crystallographic data collection and refinement

The X-ray single crystal data for compound **1** was collected on an Enraf-Nonius CAD4 four-circle automatic diffractometer while single crystals of compounds **2** and **3** were mounted on a Siemens P4 diffractometer equipped with a graphite monochromator. The crystallographic data, conditions for the intensity data collection and some features of the structure refinements are listed in Table 1. For **1** Cu-K_α radiation (λ = 1.5418 Å) was applied, while Mo-K_α (λ = 0.71073 Å) was used for **2** and **3** using ω–2θ scan mode. The unit cell parameters and crystal orientation matrices were determined from automatic centring of 25 reflections for **1** and **2** and 32 reflections for **3**. The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction[22] based on ψ-scans was also applied for all cases. A total of 2186, 1812 and 2671 reflections were measured and 2011, 1682 and 1613 reflections were assumed observed applying the condition $I > 2\sigma(I)$ for complexes **1**, **2** and **3** respectively. All the structures were solved by Patterson methods and followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on F^2 were carried out using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located from the difference map for complexes **1** and **3** and for complex **2** they were constrained to ride on the respective carbon or nitrogen atoms with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of their parent atom. Complex neutral scattering factors[23] were used throughout for all cases. The refinement converged to residual indices R = 0.0581 and wR = 0.1447; R = 0.0346 and wR = 0.0871; R = 0.0394 and wR = 0.0887 for complexes **1**, **2** and **3** respectively. The maximum and minimum peaks in the final difference Fourier syntheses were 2.37 and −4.20 e $Å^{-3}$ for **1**; 0.93 and −2.08 e $Å^{-3}$ for **2** and 0.75 and −0.67 e $Å^{-3}$ for **3** within ≈1 Å distance around the heavy atoms having no chemical significance, and arise mainly due to series termination error. All calculations were carried out using SHELXS 86,[24] SHELXL 97,[25] PLATON 99[26] and ORTEP-3[27] programs. Selected bond lengths and angles are given in Tables 2, 3 and 4 for complexes **1**, **2** and **3** respectively. H-Bonding parameters are displayed in Table 5 for complexes **1**, **2** and **3** respectively.

CCDC reference numbers 174453–174455.

See http://www.rsc.org/suppdata/dt/b1/b105984j/ for crystallographic data in CIF or other electronic format.

Results and discussion

IR spectroscopy

The IR spectral band positions of the complexes **1**, **2** and **3** are presented in Table 6. In the free ligand L ν(O–H) and ν(N–H) bands (not shown in Table 6) overlap and a very strong and broad band is obtained in the region of 3500–3100 cm^{-1}. The broadness of the band is likely to be due to extensive hydrogen bonding in the free ligand. The ν(N–H) bands in all the complexes are sharp and shifted to lower wavenumber in comparison to the free ligand suggesting coordination of the ethylenediamine part of the ligand. Complexes **1** and **2** show strong and sharp bands at 3349 and 3392 cm^{-1} respectively which correspond to ν(O–H). The sharpness and shifting of the bands to lower wavenumber suggest the coordination of the O–H part of the ligand. On the other hand, complex **3** shows a very strong and sharp ν(O–H) band at 3495 cm^{-1} which hints that the hydroxy group is not coordinated to the cadmium(II) centre. All the complexes show a number of strong ν(C–H) bands at *ca.* 2850–2950 cm^{-1} but profiles of ν(C–H) spectral bands for complexes **1** and **2** differ from those for complex **3** suggesting a difference in conformation of the propylenic part of ligand L. The molecular compositions of all complexes, as revealed from elemental analyses, suggest the presence of Cd–X (X = Cl^-, Br^- and I^-) bonds. In order to assign the Cd–X bonds spectral analyses at the far-IR region have been performed.[6–7,28] Complex **1** shows bands at 272 and 176 cm^{-1} assigned to ν_t(Cd–Cl) and ν_b(Cd–Cl), respectively. These bands are shifted to 160 and 125 cm^{-1} in $[Cd(L)Br_2]_n$ (**2**) and to 159 and 138 cm^{-1} in $[Cd(L)I_2]_n$ (**3**). The shift is related to the mass of the halogens, as expected.[29]

Structural description of $[Cd(L)Cl_2]_n$ 1

The structure determination reveals that complex **1** has the stoichiometry $Cd(L)Cl_2$ with the occurrence of a two-dimensional infinite sheet which is built from intersecting zigzag chains lying on the crystallographic *bc*-plane. An ORTEP drawing with the atom numbering scheme showing a portion of the layer structure is shown in Fig. 1 where each cadmium atom acts as a centre of branching. The most interesting feature of the structure is that the ethylenic part of the ligand is chelated to form a five-membered ring but the propylenic arm is engaged in bonding with the adjacent cadmium centre as a non-chelating end, *i.e.*, the propylenic arm acts as a spacer between two adjacent cadmium centres. Thus each cadmium centre is linked with the three different nearest cadmium centres *via* chloride

Table 1 Crystal data and structure refinement for complexes **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_5H_{14}CdCl_2N_2O$	$C_5H_{14}Br_2CdN_2O$	$C_5H_{14}CdI_2N_2O$
Formula weight	301.49	390.39	484.39
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
a/Å	8.0338(9)	9.113(3)	14.0470(10)
b/Å	9.4550(1)	7.187(3)	10.6900(10)
c/Å	13.122(4)	16.420(5)	15.965(3)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Crystal size/mm^{-1}	0.53 × 0.60 × 0.75	0.13 × 0.21 × 0.26	0.21 × 0.32 × 0.39
β/°	95.97(2)	106.03(3)	94.510(10)
T/K	293	293	293
Z	4	4	8
V/Å^3	991.3(3)	1033.6(7)	2389.9(5)
λ/Å	Cu-K$_\alpha$ 1.5418	Mo-K$_\alpha$ 0.71073	Mo-K$_\alpha$ 0.71073
$D_{\mathrm{calc.}}$/g cm^{-3}	2.020	2.509	2.693
μ/mm^{-1}	Cu-K$_\alpha$ 22.229	Mo-K$_\alpha$ 9.798	Mo-K$_\alpha$ 6.955
θ_{range}/°	5.5–74.9	2.3–25.0	2.4–25.0
Total data	2186	1812	2671
F(000)	592	736	1760
Observed data [$I > 2\sigma(I)$]	2011	1682	1613
R	0.0581	0.0346	0.0394
wR	0.1447	0.0871	0.0887

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Cd1–Cl2	2.5246(12)	Cd1–Cl3	2.6416(12)
Cd1–N1	2.353(4)	Cd1–N2	2.386(4)
Cd1–O*	2.451(3)	Cd1–Cl3*	2.6410(13)
Cl2–Cd1–Cl3	99.14(4)	Cl2–Cd1–N1	172.91(10)
Cl2–Cd1–N2	98.28(9)	Cl2–Cd1–O*	91.99(7)
Cl2–Cd1–Cl3*	94.78(4)	Cl3–Cd1–N1	86.96(10)
Cl3–Cd1–N2	95.44(10)	Cl3–Cd1–O*	166.84(7)
Cl3–Cd1–Cl3*	89.29(4)	N1–Cd1–N2	77.42(13)
O*–Cd1–N1	82.43(12)	Cl3*–Cd1–N1	88.87(10)
O*–Cd1–N2	89.84(11)	Cl3*–Cd1–N2	165.20(9)
Cl3*–Cd1–O*	82.76(7)		

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Cd–Br1	2.7971(14)	Cd–Br2	2.6733(14)
Cd–N1	2.483(6)	Cd–N2	2.435(5)
Cd–Br1*	2.7842(14)	Cd–O*	2.477(4)
Br1–Cd–Br2	93.25(4)	Br1–Cd–N1	83.18(12)
Br1–Cd–N2	152.56(12)	Br1–Cd–Br1*	95.31(4)
Br1–Cd–O*	92.21(11)	Br2–Cd–N1	175.42(12)
Br2–Cd–N2	110.11(12)	Br1*–Cd–Br2	94.72(4)
Br2–Cd–O*	85.30(11)	N1–Cd–N2	72.66(17)
Br1*–Cd–N1	88.48(13)	O*–Cd–N1	91.96(16)
Br1*–Cd–N2	96.83(12)	O*–Cd–N2	76.16(16)
Br1*–Cd–O*	172.47(11)	Cd–Br1–Cd*	84.69(4)

Table 4 Selected bond lengths (Å) and angles (°) for complex **3**

Cd1–N1	2.241(8)	Cd1–N2	2.406(7)
Cd1–I1	3.2469(9)	Cd2–I1	2.8001(10)
Cd2–I2	2.7477(10)		
Cd1–I1–Cd2	106.49(2)	I1–Cd1–N1	92.3(2)
I1–Cd1–N2	89.62(18)	I1–Cd1–I1*	180.00
I1–Cd1–N1*	87.7(2)	I1–Cd1–N2*	90.38(18)
N1–Cd1–N2	77.8(3)	I1*–Cd1–N1	87.7(2)
N1–Cd1–N1*	180.00	N1–Cd1–N2*	102.2(3)
I1*–Cd1–N2	90.38(18)	N1*–Cd1–N2	102.2(3)
N2–Cd1–N2*	180.00	I1*–Cd1–N1*	92.3(2)
I1*–Cd1–N2*	89.62(18)	N1*–Cd1–N2*	77.8(3)
I1–Cd2–I2	106.76(2)	I1–Cd2–I1*	104.28(4)
I1–Cd2–I2*	110.17(2)	I1*–Cd2–I2	110.17(2)
I2–Cd2–I2*	117.90(4)	I1*–Cd2–I2*	106.76(2)

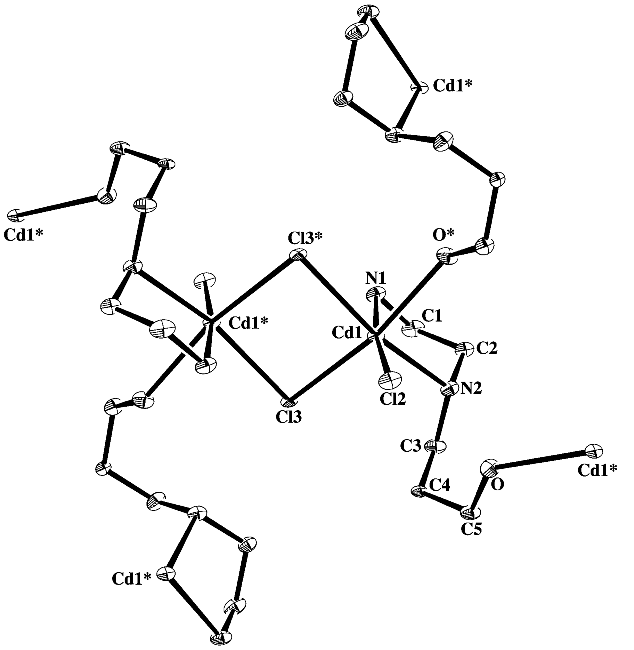

Fig. 1 ORTEP diagram of $[Cd(L)Cl_2]_n$ **1** showing a portion of the 2D sheet with the atom labeling scheme showing 50% probability thermal elipsoids for all non-hydrogen atoms.

atoms and oxygen atoms of non-chelated arms of the ligands L to form a honeycomb like (6,3) polymeric net[30] (Fig. 2). The geometry around each cadmium atom is best described as a pseudo octahedron with a CdN_2Cl_3O chromophore. The two nitrogen atoms (N1, N2) [Cd1–N1, 2.353(4) Å; Cd1–N2, 2.386(4) Å] of the hydroxyamine ligand (L) and two chloride atoms, one symmetry related bridging (Cl3*) [Cd1–Cl3, 2.6410(13) Å] and the other pendant arm (Cl2) [Cd1–Cl2, 2.5246(12) Å] define the basal plane around each cadmium atom. The *trans* axial positions of the octahedron are occupied by another bridging chloride atom (Cl3) [Cd1–Cl3, 2.6416(12) Å] and the symmetry related oxygen atom (O*) [Cd1–O*, 2.451(3) Å] from the non-chelated portion of the ligand L. The degrees of distortion from an ideal octahedral geometry are reflected in the *cisoid* [82.43(12)–99.14(4)°] and *transoid* angles [165.20(9)–172.91(10)°]. The equatorial atom sets exhibit small deviations from planarity and each cadmium atom is shifted above the basal plane by 0.131 Å. The bridging angle Cd1–Cl3–Cd1* of 90.71(4)° is comparable to that in similar systems. Other bond lengths and angles in the ligand are close to the expected values. The pendant (Cl2) and bridging (Cl3) chloride atoms and oxygen atom (O*) of the ligand L show

Table 5 Hydrogen bonds (Å, °) for complexes **1**, **2** and **3**

D–H ··· A	D–H	H ··· A	D ··· A	D–H ··· A
Complex **1**				
O–H ··· Cl2	0.930(4)	2.222(3)	3.150(3)	174.8(3)
N1–H1B ··· $Cl2^{(i)}$	0.900(5)	2.622(4)	3.476(4)	158.6(4)
N2–H2 ··· O	0.910(5)	2.466(5)	3.054(5)	122.6(4)
N2–H2 ··· $Cl3^{(ii)}$	0.910(5)	2.622(4)	3.463(4)	154.1(4)
Complex **2**				
N1–H1A ··· $Br2^{(i)}$	0.90	2.9014	3.777(6)	164.66
N1–H1B ··· $Br2^{(ii)}$	0.90	2.5893	3.470(6)	168.30
O–H1O ··· Br2	0.93	2.4162	3.342(4)	174.16
N2–H2 ··· O	0.91	2.5291	3.118(7)	122.81
N2–H2 ··· $Br2^{(iii)}$	0.91	2.6973	3.534(5)	153.22
Complex **3**				
O–H ··· I2	0.820(13)	2.929(10)	3.619(10)	143.2(11)
N1–H1A ··· $O^{(i)}$	0.900(12)	2.009(13)	2.908(13)	177.8(9)
N1–H1B ··· $I2^{(ii)}$	0.900(11)	3.027(8)	3.842(8)	151.5(9)

Symmetry codes. For **1**: (i) = $-x, -1/2 + y, 3/2 - z$; (ii) $x, 1/2 - y, -1/2 + z$. For **2**: (i) $1 - x, -y, -z$; (ii) $x, 1 + y, z$; (iii) $-x, -y, -z$. For **3**: (i) $1/2 + x, -1/2 + y, z$; (ii) $-x, -y, 1 - z$.

Table 6 Infrared frequencies (cm^{-1}) for complexes **1**, **2** and **3**

Compound	ν(O–H)	ν(N–H)	ν(C–H)	δ(N–H)	ν_t (Cd–X)	ν_b (Cd–X)
$[Cd(L)Cl_2]_n$ **1**	3349	3275 3250	2950 2940 2908 2864	1468 1446	272	176
$[Cd(L)Br_2]_n$ **2**	3392 3324	3276 3265	2958 2941 2885 2880	1467 1450	160	125
$[Cd(L)I_2]_n$ **3**	3495	3288 3218 3142	2934 2875	1452 1444	159	138

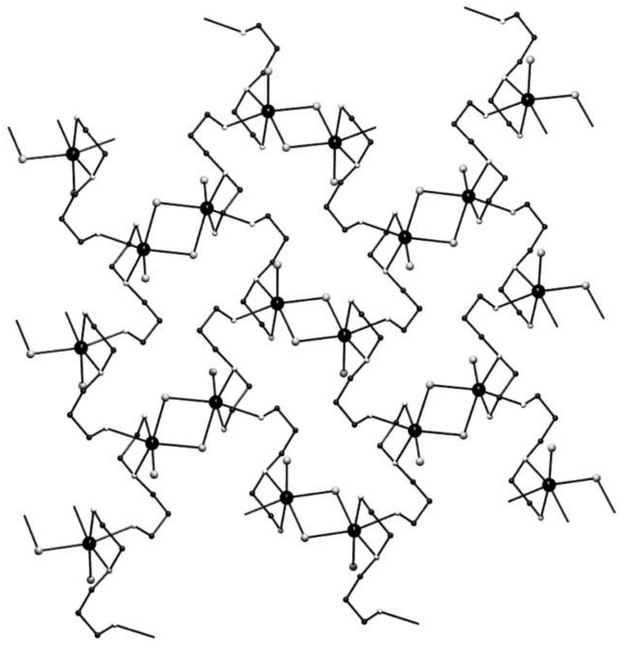

Fig. 2 Honeycomb like 2D (6,3) polymeric net of $[Cd(L)Cl_2]_n$ **1**.

intramolecular H-bonding interactions (Table 5). In the coordination chain the shortest Cd ··· Cd separation in the chloro bridged and propylenic arm bridged part is 3.759 Å and 5.810 Å respectively. From this point it is to be noted that between two adjacent cadmium centres simultaneous bridging through the propylenic arm of the ligand and the chloride atom is not possible as the length is not compatible with the bridged Cd1–Cl3–Cd1* length. As a result a two-dimensional branched polymeric sheet is formed which makes the structure unique.

Structural description of $[Cd(L)Br_2]_n$ 2

The structure determination reveals that complex **2** is an infinite one-dimensional coordination chain of cadmium(II) alternately bridged by a bromide atom and hydroxyamine ligand (L). An ORTEP view along the crystallographic *a*-direction, with the atom numbering scheme of the coordination chain, is shown in Fig. 3. The ethylenic part of the ligand L forms a five-membered ring around each cadmium and the propylenic arm is used as a

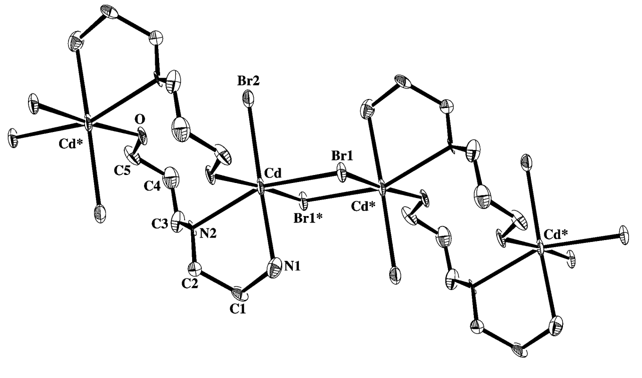

Fig. 3 ORTEP diagram of the 1D chain in $[Cd(L)Br_2]_n$ **2** with the atom labeling scheme showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

non-chelated end to bridge another adjacent cadmium centre. Thus each cadmium atom possesses a distorted octahedral geometry with a CdN_2Br_3O chromophore. Two bromide atoms, one from the bridging part (Br1) [Cd–Br1, 2.7971(14) Å] and another from the terminal part (Br2) [Cd–Br2, 2.6733(14) Å] together with two nitrogen atoms (N1, N2) [Cd–N1, 2.483(6); Cd–N2, 2.435(5) Å] from the chelated portion of the ligand form an equatorial plane around each cadmium centre. The apical positions of the octahedron are occupied by one symmetry related bromide atom (Br1*) and the symmetry related oxygen atom (O*) [Cd–O*, 2.477(4) Å] from the non-chelated portion of the hydroxyamine ligand (L). The degrees of distortion from an ideal octahedral geometry are reflected in the *cisoid* [76.16(16)–110.11(12)°] and *transoid* angles [152.56(12)–175.42(12)°]. The deviation of each cadmium atom from the mean plane formed by the four equatorial atoms is 0.186 Å and the maximum deviation of N1 below the mean plane among all the equatorial nitrogen atoms is 0.141 Å.

The most striking feature of the structure of **2** in comparison to **1** is that the non-chelated part of the each hydroxyamine ligand, *i.e.*, the propylenic arm, simultaneously binds two adjacent cadmium centres to form a twelve-membered ring. As a result a two-dimensional sheet like **1** is not formed in **2**. This leads to an array of alternating four- and twelve-membered rings making the overall molecular structure unique. The intra- and inter-molecular H-bonding interactions stabilise the overall conformations and polymeric network (Table 5). The intra-chain Cd ··· Cd separation in the bromo bridge region is 3.7583 Å and in the propylenic arm part it is 5.4786 Å.

Structural description of $[Cd(L)I_2]_n$ 3

The molecular structure of complex **3**, with the atom numbering scheme, is shown in Fig. 4. The structure determination reveals that the polymer has stoichiometry $Cd(L)I_2$ with a one-dimensional infinite co-ordination polymer lying along the *c*-axis. In the polymeric chain there is an alternating array of octahedral and tetrahedral cadmium centres. The geometry around Cd1 is distorted octahedral with a CdN_4I_2 chromophore and the geometry around Cd2 is distorted tetrahedral with a CdI_4 chromophore. The two nitrogen atoms (N1, N2) and symmetry related counterparts N1*, N2* [Cd1–N1, 2.241(8) Å; Cd1–N2, 2.406(7) Å] from the two hydroxyamine ligands define the equatorial plane around Cd1. The apical positions of the octahedron are occupied by bridging I1 and symmetry related I1* atoms [Cd1–I1, 3.2469(9) Å] from the two neighbouring tetrahedral cadmium centres. Each Cd1 atom sits perfectly in the equatorial plane and the equatorial atoms do not show any deviation from the mean plane. Each tetrahedral Cd2 centre is attached to the two neighbouring octahedral Cd1 through an iodide bridge (I1) [Cd2–I1, 2.8001(10) Å] and the other two iodide atoms are pendant arms [Cd2–I2, 2.7477(10) Å]. The degrees of distortion of Cd1 from the ideal octahedral geometry are reflected in the *cisoid* angles [77.8(3)–102.2(3)°] and of Cd2 from the ideal tetrahedral geometry by [104.28(4)–117.90(4)°]. It is interesting to note that in this system the ethylenic part of the ligand L is chelated to Cd1 and the propylenic part is the pendant arm. The bridging angle [Cd1–I1–Cd2, 106.49(2)°] is much higher in comparison to complexes **1** and **2** which may be due to the large size of the iodide atom resulting in a single bridge. The Cd1–N2 distance observed is considerably larger than the Cd1–N1 distance. This enhancement is due to the greater steric crowding at N2 by the pendant propylenic arm and the strong electron withdrawing group (–OH) attached at the end of the propylenic arm of the ligand (L). The intra- and inter-molecular H-bonding stabilise the overall conformation and the polymeric network of **3** (Table 5). In the chain the closest separation between the octahedral Cd1 and tetrahedral Cd2 is 4.8521 Å. The formation of a one-dimensional alternating octahedral and tetrahedral arrangement is due to the large size and greater softness of the iodide atoms compared to the other halogens studied. The octahedral Cd1 centre is sp^3d^2 hybridised while the tetrahedral Cd2 centre is sp^3 hybridised. This accounts for the more electronegative Cd2 centre compared to Cd1, allowing Cd2 to bind the larger and more soft iodide atoms.

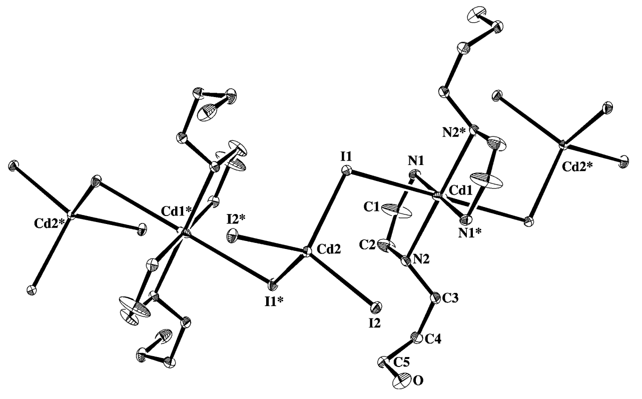

Fig. 4 ORTEP diagram of the alternate octahedral and tetrahedral 1D chain in $[Cd(L)I_2]_n$ **3** with the atom labeling scheme showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

Thermal property

Upon heating the complexes $[Cd(L)X_2]_n$ [X = Cl (**1**)/Br (**2**)/I (**3**)] exhibit an irreversible endothermic phase transition [95–133 °C, $\Delta H = 29.5$ kJ mol^{-1} for (**1**); 83–128 °C, $\Delta H = 22.5$ kJ mol^{-1} for (**2**) and 91–128 °C, $\Delta H = 15.5$ kJ mol^{-1} for (**3**)] yielding transparent films of $CdLCl_2$ (**1a**), $CdLBr_2$ (**1b**) and $CdLI_2$ (**1c**) respectively (Fig. 5). **1a**, **1b** and **1c** do not revert on keeping in a humid atmosphere (relative humidity ≈ 60%) for several days. X-Ray powder pattern studies of each pair of complexes (*e.g.*, **1** and **1a**) indicate that the transitions are due to a crystalline ⟶ amorphous state transition. The amorphous materials do not revert even on keeping them at liquid nitrogen temperature but they exhibit a glass transition [**1a**–**1b** ($T_g = 14.4$ °C); **2a**–**2b** ($T_g = 10.9$ °C); **3a**–**3b** ($T_g = 2.5$ °C)] upon heating as is evident from the differential scanning calorimetric study (Fig. 6). Such behaviour probably occurs due to a rigid to flexible polymeric transformation.

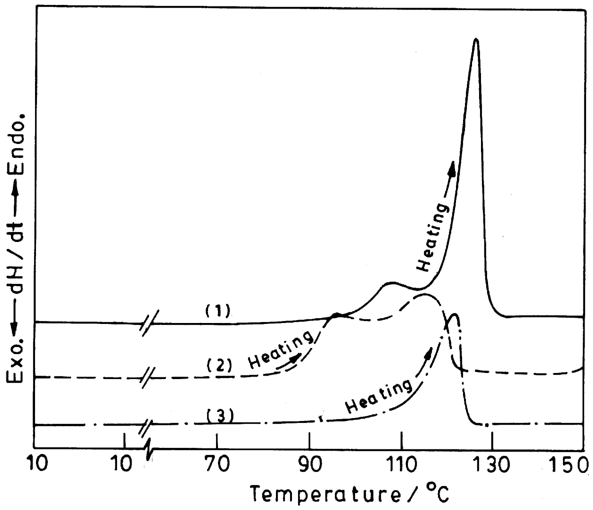

Fig. 5 DSC curves of $[Cd(L)Cl_2]_n$ **1** (—; sample mass, 9.24 mg); $[Cd(L)Br_2]_n$ **2** (----; sample mass, 9.32 mg) and $[Cd(L)I_2]_n$ **3** (–·–·–·–; sample mass, 13.45 mg).

Concluding remarks

Here we have shown the structural variation which can be obtained in cadmium halogen complexes using a linear chain

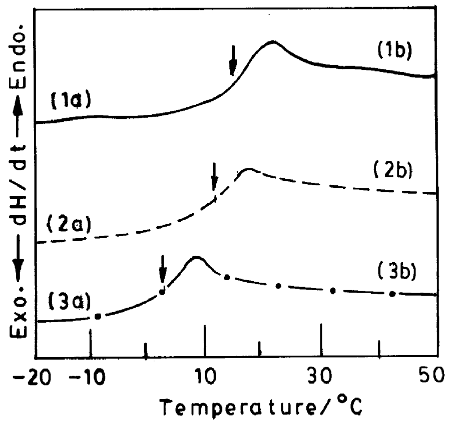

Fig. 6 DSC curves of $CdLCl_2$ (**1a**) (—), $CdLBr_2$ (**2a**) (----) and $CdLI_2$ (**3a**) (–•–•–•–).

flexible hydroxyamine ligand and the same synthetic procedure for each halogen. Cadmium metal is well suited for this as its d^{10} configuration permits a wide variety of geometries and coordination numbers. Systematic structural changes in the $[Cd(L)X_2]_n$ complexes can be attributed to steric factors associated with the increasing size of the bridging halides down the series, and to electronic factors associated with the increasing softness of the heavier halogens. In this paper the coordinative flexibility of the hydroxyamine ligand is well demonstrated and this is observed due to the unsymmetrical nature, *i.e.*, the ethylenic and propylenic part, of the ligand. By using the appropriate metal ions it is possible to force the amine to act in an unusual way, giving rise to compounds which present uncommon and unpredictable structures. The capability of the propylenic part to act as a spacer, compared to the ethylenic part, is favoured by the lower stability of six-membered chelate rings compared to five-membered ones.

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