DALTON
FULL PAPER

Synthesis and characterisation of infinite co-ordination networks from flexible dipyridyl ligands and cadmium salts†

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Crystallisation of flexible dipyridyl ligands with $Cd(NO_3)_2{\cdot}6H_2O$ or $CdSO_4{\cdot}6H_2O$ gives co-ordination networks of composition $[Cd(NO_3)_2(Py_2CH_2)_2]$ **1** [Py_2CH_2 = 1,1-bis(4-pyridyl)methane]; $[Cd_2(NO_3)_4(Py_2C_3H_6)_4(H_2O)]$ **2** [$Py_2C_3H_6$ = 1,3-bis(4-pyridyl)propane]; $[Cd_2(SO_4)_2(Py_2C_3H_6)_3(H_2O)_{2.7}]{\cdot}4.5H_2O$ **3**; $[Cd(NO_3)_2(Py_2C_4H_8)(H_2O)_2]$ **4** [$Py_2C_4H_8$ = 1,4-bis(4-pyridyl)butane]; $[Cd_2(NO_3)_4(Py_2C_5H_{10})_3(H_2O)]$ **5** [$Py_2C_5H_{10}$ = 1,5-bis(4-pyridyl)pentane] and $[Cd(NO_3)_2(Py_2C_6H_{12})_2]$ **6** [$Py_2C_6H_{12}$ = 1,6-bis(4-pyridyl)hexane]. The compounds were characterised by X-ray single crystal diffraction studies. In compounds **1**, **2**, **4** and **6** the cadmium ions are hexa-co-ordinate with a slightly distorted octahedral geometry. Compounds **3** and **5** both display examples of a less common hepta-co-ordinate cadmium ion geometry. Compounds **2**, **3** and **6** exhibit novel modes of interpenetration.

Introduction

The discovery of new co-ordination networks using the principles of crystal engineering provides an opportunity to explore assembly and structural diversity in the solid state.[1] An extensive literature on networks crystallised from different dipyridyl ligands[2] with various transition metal ions now exists. As well as the discovery of interesting infinite supramolecular architectures notable features include porosity and the structural support of void volume,[3] the formation of co-ordination networks that clathrate guest molecules and the influence of solvent upon structure,[4] the inclusion of novel molybdenum anions[5] and the use of dipyridyl ligands with hydrogen bond donor and acceptor functionality.[6] Here, we report our studies on the crystallisation of cadmium ions with bis(4-pyridyl) ligands that are connected by a flexible $(CH_2)_n$ linking group (n = 1, 3, 4, 5 or 6). The structure of $[Cd_2(NO_3)_4(Py_2C_2H_4)_3]$ [$Py_2C_2H_4$ = 1,2-bis(4-pyridyl)ethane, $n = 2$] formed from the missing ligand in the series, has been reported previously.[7] It consists of 1-D chains of cadmium ions bridged by two diet ligands forming a row of $(CdL)_2$ rings. The cadmium ions were bonded to three pyridine nitrogens forming a T-shape and two bidentate nitrate anions. The hepta-co-ordinate geometry[8] can be regarded as a distorted pentagonal bipyramid with two nitrate anions and a pyridyl group at the equatorial positions and two pyridyl groups at the apical positions. The ligands forming $(CdL)_2$ rings adopt a *cis* conformation while the bridging ligands adopt a *trans* conformation. The flexibility of the ligand was essential to form this particular structural motif. The occurrence of different networks in the solid state containing ligands that adopt different conformations is known as 'supramolecular isomerism'. However little is understood concerning the factors which determine ligand conformation(s) in a particular network and their influence upon the network structure. The solvent of crystallisation and guest clathration has been shown to give different networks with 1,2-bis(4-pyridyl)ethane. Apart from this study and a few others[9] little is known of the scope for long (n > 3) flexible dipyridyl ligands to form infinite co-ordination networks.

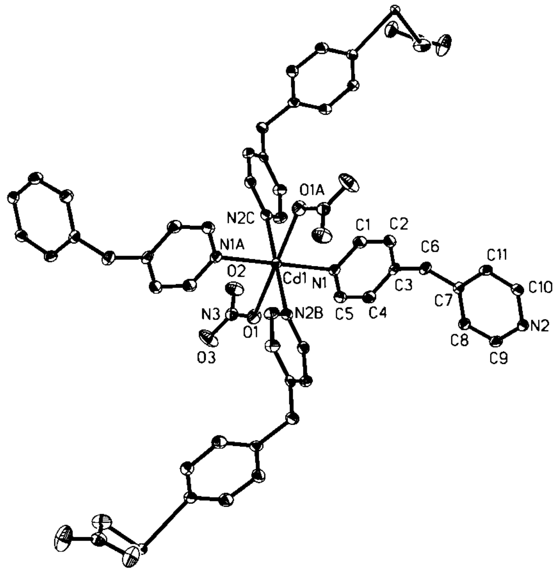

Fig. 1 Building block of structure **1** showing the atom numbering scheme and anisotropic displacement parameters.

Results and discussion

Crystal structure of $[Cd(NO_3)_2(Py_2CH_2)_2]$ 1

The co-ordination geometry in compound **1** is shown in Fig. 1. The molecular structure is a corrugated 2-D network with (4,4) topology.[10] The cadmium atoms, all of which are equivalent, serve as nodes and the ligands (L = Py_2CH_2) are rods (Fig. 2).

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† Electronic supplementary information (ESI) available: 1. Tables of hydrogen bonds for structures **2**–**4**. 2. Drawing showing disordered coordination sphere of Cd2 in structure **3**. 3. Refinement details for disordered ligands in structure **6**. 4. Two parallel interpenetrating (4,4) nets in **2** (*cf.* Fig. 6). 5. Three parallel interpenetrating (6,3) nets in **5** (*cf.* Fig. 15). 6. (a) Parallel arrangement of sheets in **1** and (b) channels in structure of **1** (view along [001]). 7. (a) One set of parallel (4,4) sheets in **6** and (b) inclination of two sets of sheets (NO_3 omitted for clarity). See http://www.rsc.org/suppdata/dt/b0/b002251i/

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Thus, the network is based upon squares $(CdL)_4$ formed from four ligands and four four-connected cadmium ions. These metallocylic rings are 40-membered. Since the cadmium atom is located at an inversion centre, the coordinating pyridyl ligands are co-planar in pairs. Both apical positions within the octahedral Cd co-ordination are adopted by a monodentate nitrate anion. The 2-D networks which extend perpendicular to the crystallographic *a*-axis are arranged in a parallel fashion forming stacks that contain a series of channels parallel to the *c*-axis (see ESI†).

Crystal structure of $[Cd_2(NO_3)_4(Py_2C_3H_6)_4(H_2O)]$ 2

The co-ordination geometry in compound **2** is shown in Fig. 3. The structure shown in Fig. 4 consists of an infinite 2-D square grid with (4,4) topology. There are two crystallographically independent cadmium ions both of which are octahedral but have a different co-ordination environment (Fig. 3). Cd1 is co-ordinated by four pyridine nitrogens in a square planar geometry, one monodentate nitrate ion and one water molecule. Two special positions are adopted by disordered nitrate molecules, neither of which co-ordinate Cd1. These anions are linked *via* hydrogen bonds to the water molecule attached to Cd1. Cd2 is co-ordinated by four pyridine nitrogens in an approximately square-planar fashion and two monodentate nitrate ions. In the co-ordination sphere about Cd1, and especially Cd2, there is significant departure from ideal planarity of the CdN_4 unit. Each molecular box is formed from four ligands with cadmium ions at the vertices giving $(CdL)_4$ 48 membered metallocyclic rings. There are two different conformations of the ligand present which are bonded in a *cis* location with respect to each other. One ligand adopts a *trans–trans* conformation and the other a *gauche–gauche* conformation. The network resembles the square grids found in the structure of $[Cu(NO_3)_2(Py_2C_3H_6)_2]\cdot 0.25H_2O$ and $[Cu(ClO_4)_2(Py_2C_3H_6)_2]$ which contain similar conformations of the ligand in a 1 : 1 ratio.[11]

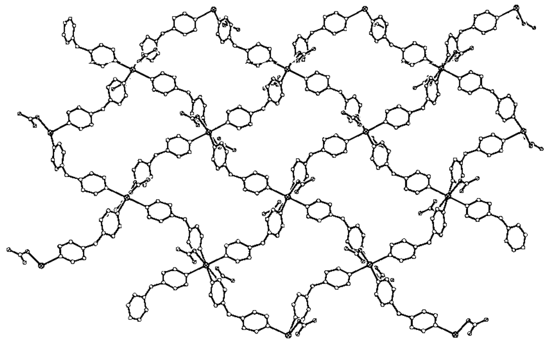

Fig. 2 Two-dimensional co-ordination network with (4,4) topology in **1**.

The corrugated 2-D nets are parallel interpenetrating (Fig. 5). Their base planes are parallel to (101). The hydrogen bonds mentioned above do not give rise to any additional network structure. Fig. 6 shows the mode of interpenetration, which is topologically different from that of three recently discussed examples of similar structures with two parallel interpenetrating nets based on the (4,4) topology, $[Cd(4\text{-pic})_2\{Ag(CN)_2\}_2](4\text{-pic})$ (4-pic = 4-methylpyridine), [Cu(tcm)(bipy)] [tcm^- = tricyanomethanide,] (bipy = 4,4′-bipyridine) and $[Re_4(CO)_{12}(OH)_4]\cdot 2bipy\cdot 2MeOH$.[12]

Crystal structure of $[Cd_2(SO_4)_2(Py_2C_3H_6)_3(H_2O)_{2.7}]\cdot 4.5H_2O$ 3

Neglecting the interactions with the sulfates, the structure consists of two equivalent sets of bidimensional layers, of novel topology, that are inclined and interpenetrating. Furthermore, this is an example of a structure with two types of nodes with different connectivity. Each 3-D net is based upon an infinite number of interconnected 2-D nets in which two of the three independent cadmium positions, Cd1 and Cd2, serve as nodes. Considering the geometry of one infinite 2-D net only, there is a total of *n* four-connected Cd1 nodes, 2*n* three-connected Cd2 nodes, 4*n* rods L (L = $Py_2C_3H_6$) and *n* rods with composition (CdL_2), where the latter includes the third cadmium position, Cd3. As a result, each 2-D net is an arrangement of two different metallocyclic ring systems one of which is 96-membered having a general formula $(CdL)_8$ (L = $Py_2C_3H_6$) and the other is 48-membered having a general formula $(CdL)_4$ (Fig. 8a). These 2-D nets are stacked parallel with a shift between adjacent sheets enabling linkage by bridging SO_4 anions. As a result, Cd1 and Cd2 are additionally co-ordinated by two and one bridging SO_4 anions, respectively. Thus, within the 3-D network structure, they become six- and four-connected nodes, respectively (Fig. 8b). The mode of interpenetration is shown in Fig. 9. Each of the $(CdL)_8$ rings in any sheet has parts of four other sheets passing through and each of the $(CdL)_4$ rings has parts of two

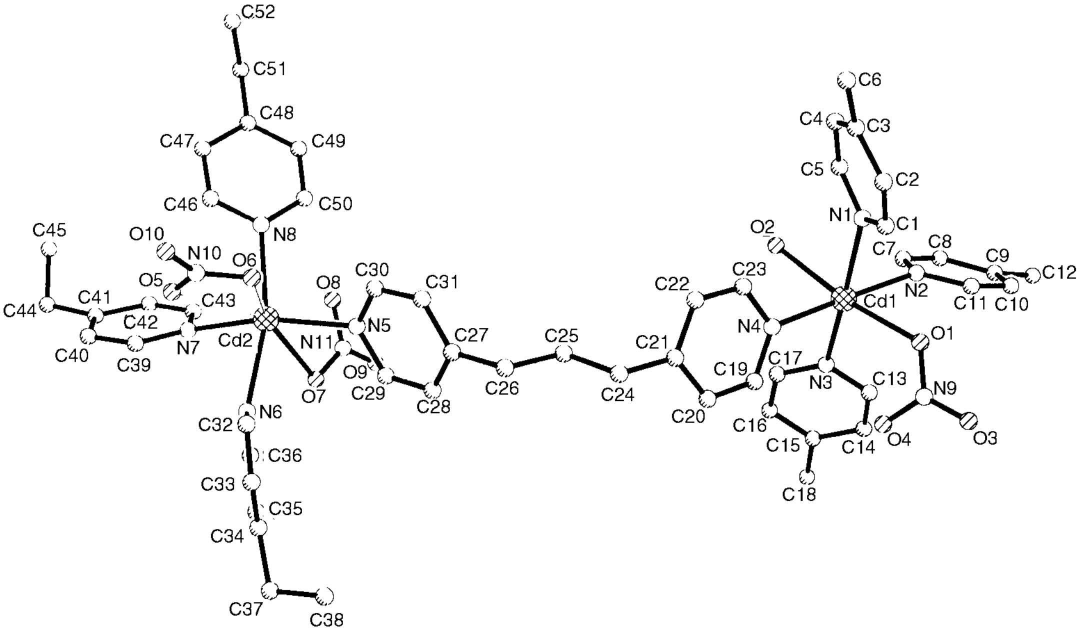

Fig. 3 Building block of structure **2** showing the atom numbering scheme.

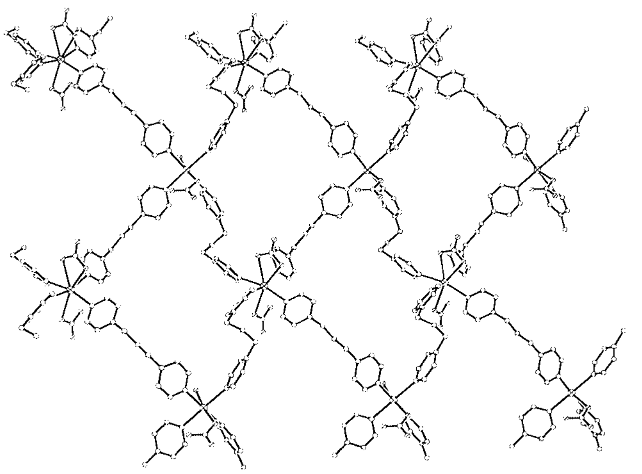

Fig. 4 Two-dimensional co-ordination network with (4,4) topology in **2**.

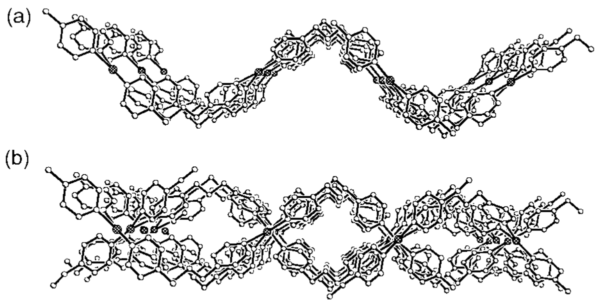

Fig. 5 (a) One single and (b) two interpenetrating (4,4) nets in **2**.

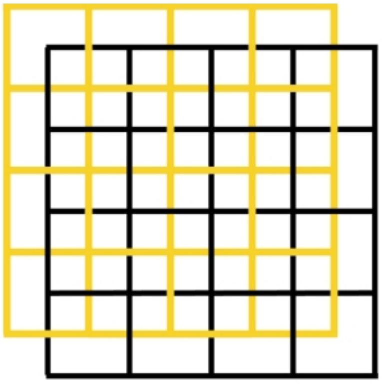

Fig. 6 Schematic representation of the mode of interpenetration in **2**.

other sheets passing through. The 3-D network is additionally stabilised through hydrogen bonds between the two H_2O attached to Cd3 and the uncoordinated oxygen atoms of the SO_4 anions.

The cadmium ion geometries are shown in Fig. 7. Cd1 has an octahedral geometry and is bonded to four pyridine nitrogens, one sulfate anion S1 and one water molecule. There are two alternative co-ordination modes of Cd2. The major component I (70% partial occupancy) shows hepta-co-ordination and is bonded by three pyridine nitrogens and one water molecule O11 whereas in the minor component II Cd2 is six co-ordinate and has no bond to a water molecule. This is associated with a rotation of the sulfate anion compared with I. Sulfate S1 co-ordinates in a bidentate manner and S2 co-ordinates in a monodentate manner. This disorder causes the sulfate anion S2 to rotate and gives two alternative positions for the four S–O bonds which are shown in Fig. 7. On changing from the major to the minor component, the bond angle O5–Cd2–N12b (79.7°) widens to 108.9°. This correlation was indicated by comparison of the geometries and by the fact that independent refinements

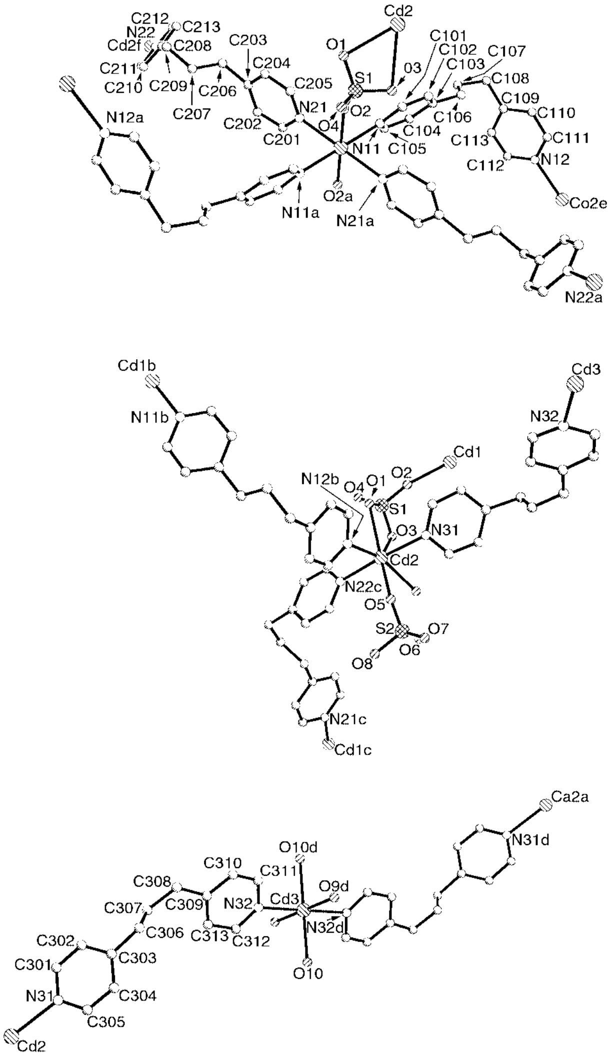

Fig. 7 Building blocks of structure **3** showing the atom numbering scheme.

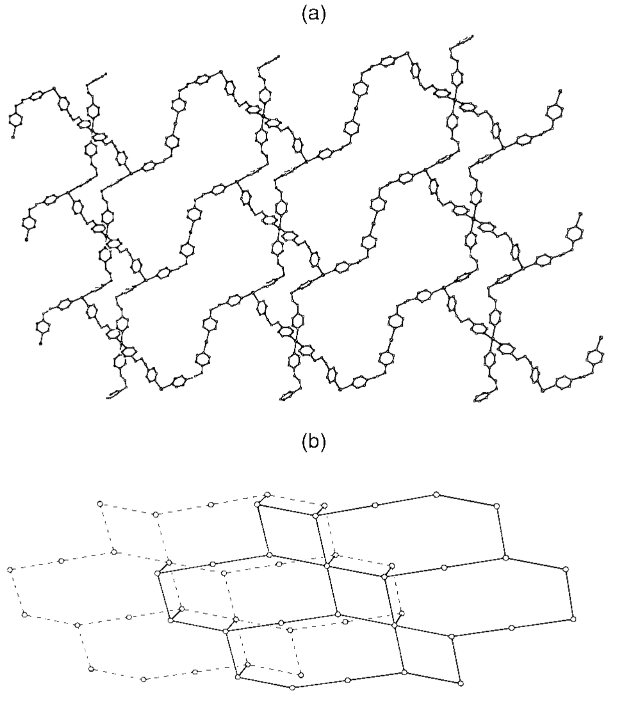

Fig. 8 (a) Two-dimensional network with (4,4) topology as part of the three-dimensional network in **3**. (b) Three-dimensional network. Adjacent 2-D nets are connected by bridging SO_4 anions.

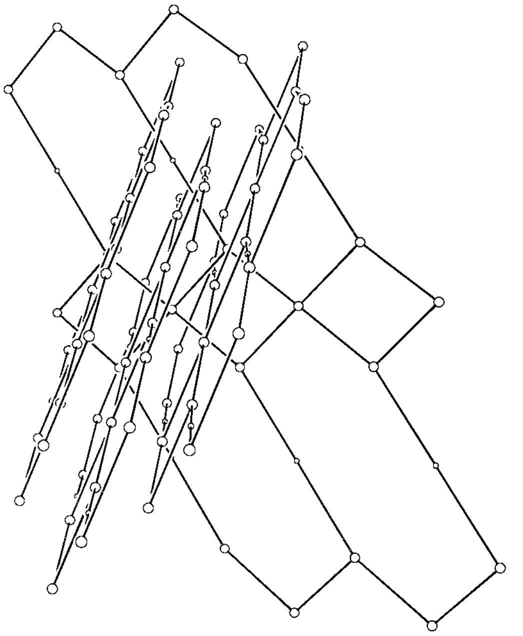

Fig. 9 Schematic representation of the 3-D inclined interpenetration of nets in **3**. The positions of Cd2 (small circles) are not nodes of the network. The SO_4 rods connecting adjacent sheets are omitted for clarity.

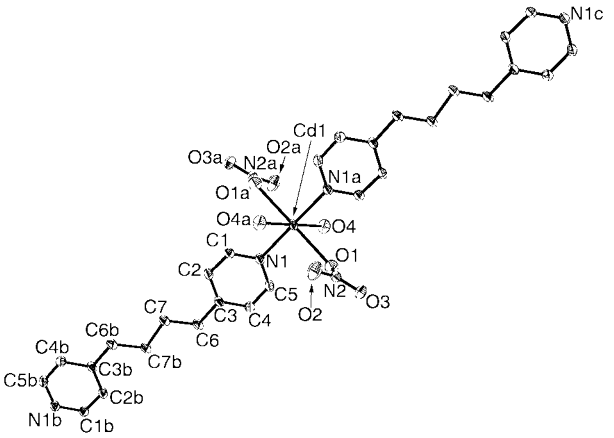

Fig. 10 Building block of structure **4** showing the atom numbering scheme and anisotropic displacement parameters.

of the site occupancies of the respective major components in each disordered fragment (O5, O6, O7, O8–71%) and (O11–69%) gave virtually the same result. Sulfate S1 bridges between Cd1 and Cd2. Cd3 is octahedral and is bonded to two pyridine nitrogens and four water molecules. The water molecules form hydrogen bonds to sulfate anions in adjacent layers. The ligands show some disorder which is discussed in the crystallographic characterisation section.

Crystal structure of $[Cd(NO_3)_2(Py_2C_4H_8)(H_2O)_2]$ 4

The molecular structure shown in Fig. 10 is an infinite 1-D chain. The cadmium ions are octahedral and are bonded to two pyridyl nitrogens in a linear manner, two nitrate anions and two water molecules. The ligand adopts an all *trans* configuration. The 1-D chains extending along [110] and [1–10] form two types of layers both lying perpendicular to the *c*-axis. Since chains within consecutive layers extend in two different directions, a criss-cross arrangement of adjacent chains shown in Fig. 11 is obtained. Furthermore, the structure contains a network of four independent monodentate hydrogen bonds with water as donor and the two unco-ordinated NO_3 oxygen atoms as acceptors. These bonds exist between both coplanar and criss-cross arranged chains as shown in Fig. 12. The hydrogen bonds form 2-D networks parallel to the (100) plane that complete the 3-D supramolecular assembly of the entire structure.

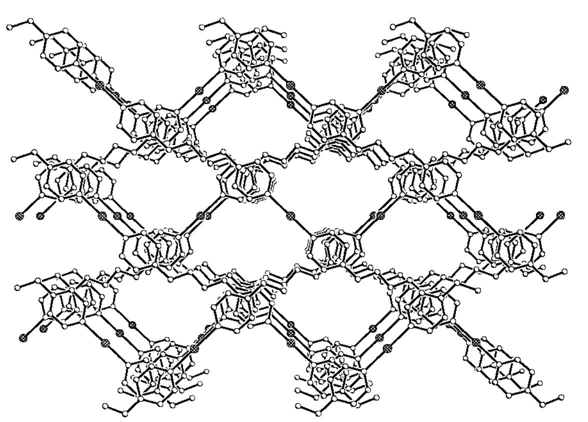

Fig. 11 Criss-cross arrangement of adjacent chains in **4**, view along [001]. The chains run along [110] and [1 − 1 0] (H_2O and NO_3 omitted for clarity).

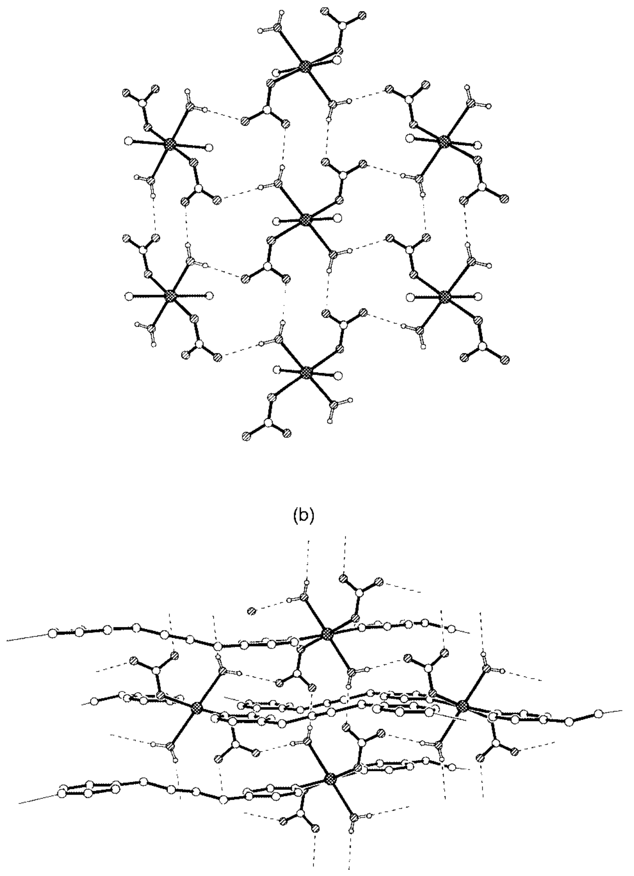

Fig. 12 (a) Two-dimensional hydrogen network in **4**, view along [100] (C and H atoms omitted for clarity), O4–H1O···O3c [2.13(3), 2.994(3) Å; 171(3)°]; O4–H2O···O2d [2.11(4), 2.904(3) Å; 164(3)°]; symmetry operations: a: *x*, −*y* + 1/2, *z* + 1/2; *x*, *y*, *z* + 1. (b) Connection of the infinite chains *via* hydrogen bonds.

Crystal structure of $[Cd_2(NO_3)_4(Py_2C_5H_{10})_3(H_2O)]$ 5

The building blocks of compound **5** are shown in Fig. 13. The structure is an infinite sequence of layers each consisting of three parallel interpenetrating 2-D nets based on the (6,3) topology. All 2-D nets are equivalent. They are composed of a rectangular grid of 84-membered $(CdL)_6$ ($L = Py_2C_5H_{10}$) metallocyclic rings (Fig. 14) and contain four crystallographically independent Cd positions. Each cadmium ion is bonded to

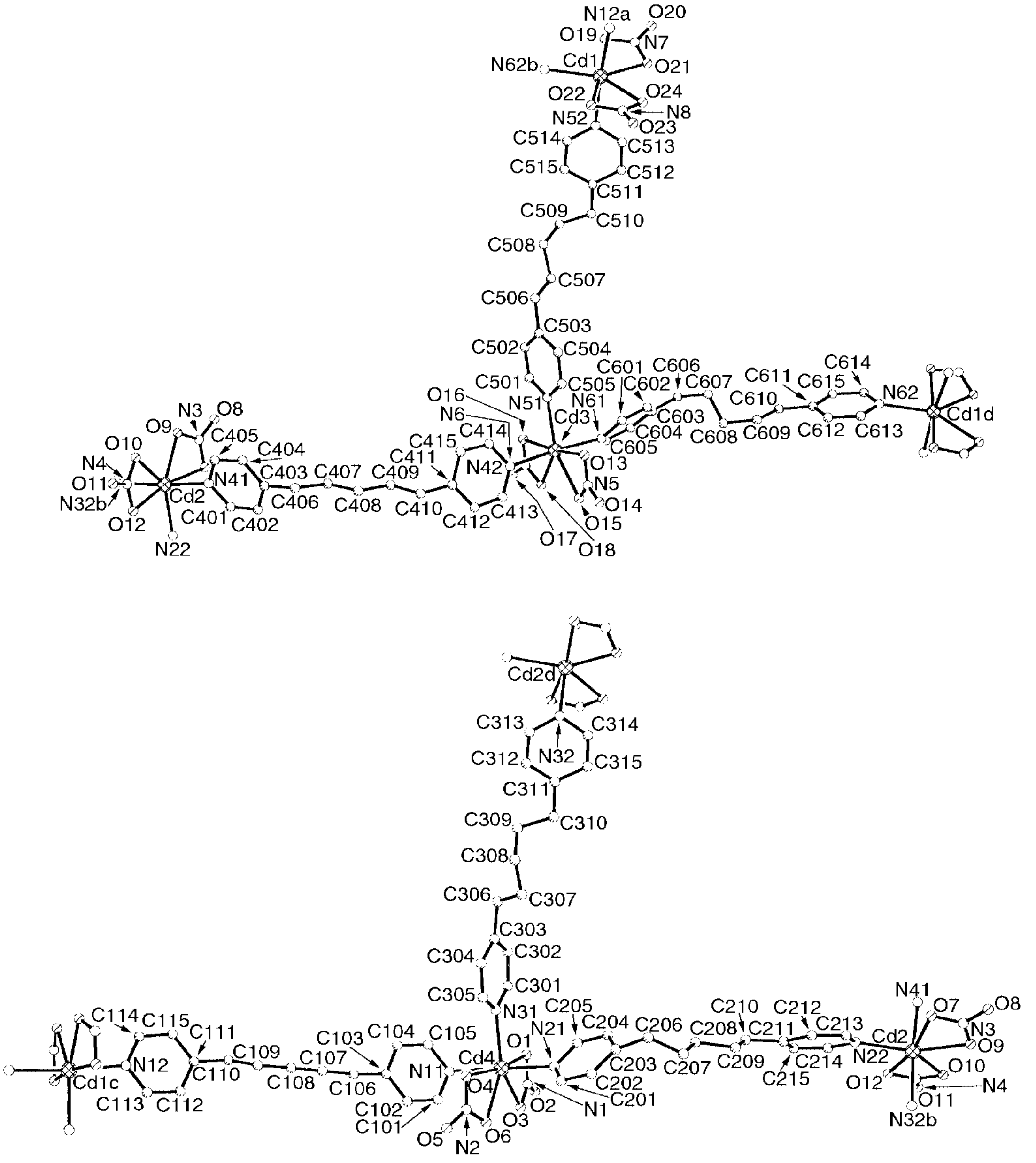

Fig. 13 Building blocks of structure **5** showing the atom numbering scheme.

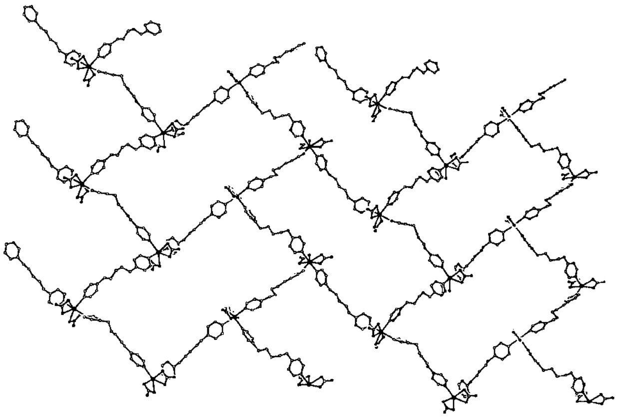

Fig. 14 Two-dimensional network with (6,3) topology in **5**.

three pyridine nitrogens forming a T-shape and to two nitrate anions which co-ordinate in a bidentate manner. The geometry of the cadmium ions is similar to the distorted pentagonal bipyramid that occurs in [$Cd_2(NO_3)_4(Py_2C_2H_4)_3$].[8] For each cadmium ion one of the nitrate anions is significantly asymmetric. For Cd1, Cd2 and Cd3 the short asymmetric Cd–O bond lengths are in the range 2.36–2.38 Å and the long Cd–O bond lengths are in the range 2.50–2.52 Å. For Cd4 both nitrate anions are bonded with less asymmetry. The Cd–O bond lengths of the symmetric nitrate anions are in the range 2.43–2.49 Å. There are two water molecules in the asymmetric unit which are hydrogen bonded to nitrate anions. There are six different ligands in the network of which four are disordered. Diagrams of the disordered ligands are given as ESI.† Disorder occurs in the alkyl chains and in six of the twelve pyridyl rings. The disorder was refined to two different positions for each ligand except for ligand 3 which adopted three different positions. Interestingly the two ligands that are not disordered have aliphatic dihedral angles that are all *trans* and close to 180°. This is the lowest energy conformation of the ligand. Disorder occurs in the ligands when they adopt *gauche* dihedral angles and where conformations of similar energy may occur. Fig. 15 shows the interpenetration mode for three (6,3) nets which results in identical relative interpenetration topologies for each of the three 2-D nets. Structures are known which exhibit 2-D nets with the same topology but they have a different mode of interpenetration.[13,14] The three interpenetrating nets are related by a translation in y, *i.e.* by the symmetry operations (x, y, z), (x, $y + 1$, z) and (x, $y + 2$, z). The layers composed of three

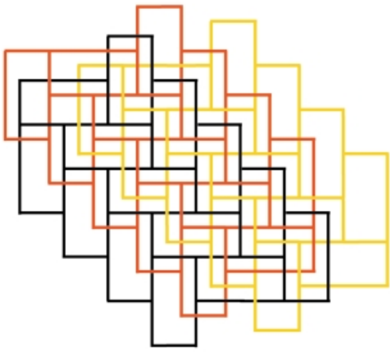

Fig. 15 Schematic representation of the three parallel interpenetrating (6,3) nets in **5**.

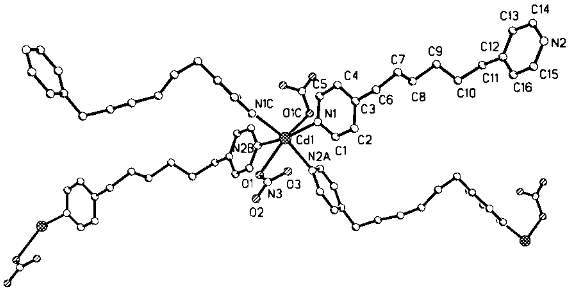

Fig. 16 Building block of structure **6** showing the atom numbering scheme.

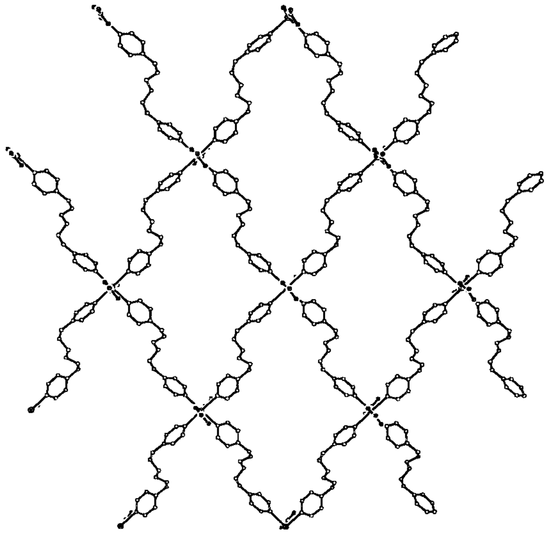

Fig. 17 Two-dimensional network with (4,4) topology in **6**.

interpenetrating 2-D nets form stacks that lie parallel to the *a*-axis. Adjacent layers are related by inversion.

Crystal structure of $[Cd(NO_3)_2(Py_2C_6H_{12})_2]$ 6

The building blocks of compound **6** are shown in Fig. 16. The structure is an arrangement of inclined 2D-nets based on the (4,4) topology. The infinite grids are composed of 60-membered metallocyclic rings, $(CdL)_4$ ($L = Py_2C_6H_{12}$). The 2-D network is shown in Fig. 17. All cadmium atoms are equivalent and serve as four-coordinated nodes. The cadmium ions have an octahedral geometry and are bonded to four pyridine nitrogens and two monodentate nitrate anions The Cd–O bond length of 2.46 Å is longer than the Cd–O bond length of the monodentate nitrate anions seen in complexes **1**, **2** and **4** (Cd–O 2.35–2.37 Å)[15] but similar to the Cd–O bond lengths found in nitrate anions co-ordinating in a symmetric bidentate manner (2.43–2.49 Å). The mode of inclination is schematically represented in Fig. 18 and is also shown in the ESI†. Every ring of any sheet has parts of three other sheets passing through it.

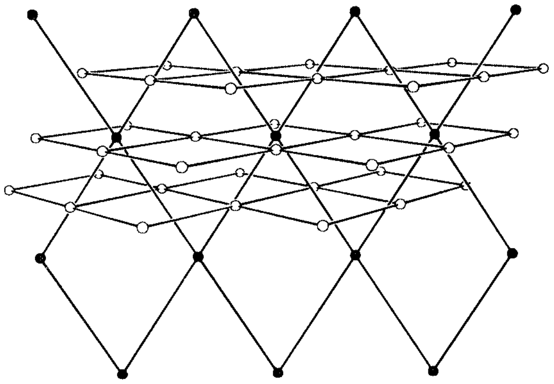

Fig. 18 Schematic representation of the 2-D inclined interpenetration in **6**.

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

Cd1–O1	2.362(1)	Cd1–N1	2.330(1)
Cd1–N2b	2.369(1)		
N1–Cd1–N2a	85.25(5)	N1a–Cd1–N2a	94.75(5)
N1–Cd1–O1	90.30(5)	O1a–Cd1–N2b	76.86(5)

Symmetry operations: a $-x, -y + 1; -z + 1$; b $x - 1, -y + 3/2, z - \frac{1}{2}$.

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

Cd1–O1	2.358(3)	Cd1–O2	2.331(3)
Cd2–O7	2.571(5)	Cd1–N1	2.354(3)
Cd1–N2	2.368(3)	Cd1–N3	2.347(4)
Cd1–N4	2.349(3)	Cd2–N5	2.350(3)
Cd2–N6	2.366(3)	Cd2–N7	2.362(3)
Cd2–N8	2.333(3)		
N3–Cd1–N1	171.4(1)	N4–Cd1–N2	177.0(1)
N3–Cd1–N4	98.6(1)	N8– Cd2–N5	103.4(1)
N1–Cd1–N2	91.8(1)	N4–Cd1–N1	87.3(1)
N8–Cd2–N7	85.5(1)	N5–Cd2–N7	165.2(1)
N8–Cd2–N6	164.4(1)	N2–Cd1–N3	82.7(1)
N7–Cd2–N6	88.1(1)	N6–Cd2–N5	85.9(1)

In summary flexible dipyridyl ligands are useful for the construction of novel interpenetrating co-ordination networks with cadmium ions. With nitrate as the counter-ion the cadmium ions adopt either a distorted octahedral or a distorted trigonal bipyramidal geometry. The formation of 3-D networks is less favoured. However on changing the counter anion from nitrate to divalent sulfate a 3-D network results because the sulfate anions can form bridges between the 2-D layers. For all structures the Cd–N bond lengths fall in the range 2.25–2.34 Å which are similar to previously reported Cd–N bond lengths.[7,8] Owing to the flexibility of their torsion angles, the alkyl chains ($n = 5$ or 6) show a tendency towards disorder.

Structure determinations

Selected bond lengths and angles for structures **1**–**6** are shown in Tables 1–6 and crystallographic data for structures **1**–**6** are shown in Table 7. Data were collected on a Nonius Kappa CCD area-detector diffractometer at the window of a rotating anode FR591 generator (Mo-Kα radiation, $\lambda = 0.71073$ Å) and controlled by the Collect software package.[16] Collected images were processed using Denzo.[17] Data were corrected for absorption by using the empirical method employed in Sortav.[18] The structures were solved using direct methods (SHELXS97).[19] All structures were refined by full-matrix least-squares refinements on F^2 (SHELXL97).[20]

Structure 2. Two nitrate molecules are disordered over an inversion centre. 18 distance restraints were used in order to refine their respective positions.

Structure 3. Parts of two of the alkyl chains (C206, C207 and C307–313) were found to be disordered. For their refinement and that of one disordered sulfate molecule, distance restraints were applied.

Structure 5. Four out of six crystallographically independent alkyl chains were found to be disordered. In result, 1246 restraints for chemically equivalent distances were applied for the refinement of their alternative positions.

Structure 6. 67 distance restraints were applied to refine the disordered alkyl chains (C7–10), and the atoms involved in the disorder were kept isotropic. An investigation of the diffraction pattern below room temperature showed the reflections splitting reversibly from 200 K onwards.

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

Cd1–O2	2.341(4)	Cd1–N11	2.286(7)
Cd1–N21	2.395(6)	Cd2–O1	2.515(5)
Cd2–O3	2.673(7)	Cd2–O5	2.292(5)
Cd2–O5a	2.271(8)	Cd2–N31	2.325(7)
Cd2–N12b	2.333(8)	Cd2–O11	2.539(12)
Cd2–N22c	2.337(7)	Cd3–O9	2.301(7)
Cd3–N32	2.317(11)	Cd3–O10	2.282(7)
N11a–Cd1–N21	84.2(2)	O5–Cd2–O3	143.2(2)
N21–Cd1–N11	95.8(2)	O5–Cd2–N12b	79.7(2)
N21a–Cd1–N11a	95.8(2)	O5–Cd2–O1	160.6(2)
N31–Cd2–N22c	174.4(3)	O5a–Cd2–O3	112.7(3)
N31–Cd2–N12b	94.1(3)	O5a–Cd2–N12b	108.9(3)
O5a–Cd2–O1	166.8(3)		

Symmetry operations: a $-x, -y, -z$; b $x - 1, y, z$; c $x, y - 1, z$.

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

Cd1–O1	2.411(2)	Cd1–O4	2.370(2)
Cd1–N1	2.254(2)		
N1–Cd1–O4a	88.96(6)	N1–Cd1–O1	70.74(6)
O4a–Cd1–O1a	89.14(6)		

Symmetry operations: a $-x + 1, -y + 1, -z + 1$.

CCDC reference number 186/2106.

See http://www.rsc.org/suppdata/dt/b0/b002251i/ for crystallographic files in .cif format.

Experimental

Cadmium salts were purchased from BDH, 4-methylpyridine and 1,3-bis(4-pyridyl)propane from Aldrich, while all other reagents were purchased from Lancaster Synthesis. 4-Methylpyridine was distilled from calcium hydride and stored over molecular sieves before use. 1,4-Bis(4-pyridyl)butane was prepared by reductive dimerisation of 4-vinylpyridine at a mercury cathode in wet DMF.[21,22] 1,1-Bis(4-pyridyl)methane, 1,5-bis(4-pyridyl)pentane and 1,6-bis(4-pyridyl) hexane were obtained by the treatment of 4-methylpyridine with potassium amide and a carbon electrophile in liquid ammonia.[23] 1,1-Bis(4-pyridyl)-methane and 1,6-Bis(4-pyridyl)hexane were purified by vacuum distillation while 1,5-bis(4-pyridyl) pentane was recrystallised from ethanol–water. All infrared spectra were recorded on KBr

Table 5 Selected bond lengths (Å) for structure **5**

Cd1–O21	2.356(6)	Cd1–O19	2.507(6)
Cd1–O24	2.432(5)	Cd1–O22	2.444(5)
Cd2–O9	2.372(6)	Cd2–O10	2.435(5)
Cd2–O7	2.518(6)	Cd2–O12	2.468(5)
Cd3–O15	2.442(4)	Cd3–O18	2.382(4)
Cd3–O16	2.485(5)	Cd3–O13	2.487(4)
Cd4–O4	2.455(5)	Cd4–O6	2.407(5)
Cd4–O3	2.428(5)	Cd4–O1	2.458(4)
Cd1–N12c	2.287(4)	Cd1–N12a	2.287(4)
Cd1–N62b	2.310(5)	Cd1–N52	2.316(4)

Symmetry operations: a $x, y + 3, z - 1$; b $x, y, z - 1$; c $x, y - 3, z + 1$.

Table 6 Selected bond lengths (Å) and angles (°) for structure **6**

Cd1–N2a	2.363(5)	Cd1–N1	2.364(5)
Cd1–O1	2.455(6)		
N2a–Cd1–N2b	88.5(2)	N2a–Cd1–N1	93.3(2)
N2b–Cd1–N1	165.9(2)	N1c–Cd1–N1	88.3(2)
N2a–Cd1–O1	84.5(2)	N1–Cd1–O1c	82.0(2)
N2b–Cd1–O1	80.2(2)	N1–Cd1–O1	113.9(2)
O1–Cd1–O1c	158.6(3)		

Symmetry operations: a $-x + 3/2, -y + 1, z + 1/2$; b $x - 1/2, y - 1/2, z + 1/2$; c $-x + 1, -y + 1/2, z$.

Table 7 Summary of crystal data for structures **1**–**6**

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{22}H_{20}CdN_6O_6$	$C_{52}H_{58}Cd_2N_{12}O_{13}$	$C_{39}H_{56.40}Cd_2N_6O_{15.20}S_2$	$C_{14}H_{20}CdN_4O_8$	$C_{45}H_{56}Cd_2N_{10}O_{13}$	$C_{32}H_{40}CdN_6O_6$
M	576.84	1283.90	1141.42	484.74	1169.80	717.10
T/K	150	150	150	293	150	293
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Tetragonal
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$I4_1/a$
Z	2	2	4	2	4	8
a/Å	7.3876(2)	11.012(1)	13.8375(7)	9.2143(2)	16.4766(4)	19.347(1)
b/Å	16.7331(4)	15.042(1)	15.7403(8)	13.2282(2)	16.6590(3)	
c/Å	9.6100(2)	18.065(1)	22.0228(8)	7.3919(2)	20.4339(4)	17.7404(7)
α/°		79.95(1)			90.298(1)	
β/°	109.7609(5)	80.23(1)	98.841(1)	97.106(1)	108.124(1)	
γ/°		72.85(1)			106.547(1)	
V/Å^3	1118.01(5)	2793.1(4)	4739.7(4)	894.07(3)	5082.6(2)	6640.3(6)
μ/mm^{-1}	1.030	0.834	1.057	1.273	0.907	0.709
Colour, aspect	Colourless block	Colourless plate	Colourless plate	Colourless plate	Colourless plate	Colourless pyramid
Crystal size/mm	0.20 × 0.20 × 0.20	0.50 × 0.35 × 0.20	0.20 × 0.20 × 0.10	0.10 × 0.10 × 0.04	0.08 × 0.08 × 0.08	0.15 × 0.15 × 0.15
Reflections collected	9599	19128	41088	19772	52439	22616
Independent reflections (R_{int})	2250 (0.038)	9836 (0.110)	7372 (0.105)	1753 (0.077)	15615 (0.077)	3004 (0.107)
$R1/wR2$ [$F^2 > 2\sigma(F^2)$]	0.020 (0.052)	0.043 (0.108)	0.066 (0.118)	0.026 (0.071)	0.054 (0.126)	0.054 (0.120)
$R1/wR2$ (all data)	0.023 (0.052)	0.062 (0.118)	0.128 (0.131)	0.031 (0.073)	0.100 (0.141)	0.171 (0.140)

discs using a ATI Mattson Genesis series FTIR spectrometer. The CHN and Cd microanalyses were performed by Butterworth Laboratories Ltd. **WARNING:** Cadmium salts are carcinogenic and toxic.[24,25]

$[Cd(NO_3)_2(Py_2CH_2)_2]$ 1

Cadmium nitrate (409 mg, 1.33 mmol) in water (4 ml) was mixed with 1,1-bis(4-pyridyl)methane (560 mg, 6.08 mmol) dissolved in ethanol (4 ml). The vial was subjected to vigorous shaking and a cloudy mixture resulted. On standing for 7 days colourless crystals formed (296 mg, 39%). These crystals were collected by filtration and washed with water and then ethanol before being dried in air. Found: C, 45.8; H, 3.2; N, 14.5. $[Cd(NO_3)_2(C_{11}H_{10}N_2)_2]$ requires C, 45.8; H, 3.5; N, 14.6%; IR (KBr) ν/cm^{-1} 2926m, 2852m, 1617s, 1560w, 1500w, 1436s, 1423s, 1384s, 1354w, 1345w, 1296s, 1225m, 1208w, 1068m, 1031m, 1016m, 883w, 840w, 824w, 808w, 792w, 661w, 625s, 565m, 494w and 476w.

$[Cd_2(NO_3)_4(Py_2C_3H_6)_4(H_2O)]$ 2

A solution of 1,3-bis(4-pyridyl)propane (1.6 g, 7.98 mmol) in ethanol (10 ml) was layered on top of a solution of cadmium nitrate (1.5 g, 4.86 mmol) in water (10 ml). These solutions were mixed rapidly by shaking. The tube was allowed to stand undisturbed overnight. The next day colourless crystals (1.12 g, 44%) were collected by filtration. After washing with water and ethanol, the crystals were dried in a dessicator. The crystals used for X-ray crystallography were not allowed to dry fully. The sample for microanalysis was dried thoroughly before analysis. Found: C, 49.6; H, 4.5; N, 13.1; Cd, 17.4. $[Cd_2(NO_3)_4(C_{13}H_{14}N_2)_4]$ requires C, 49.3; H, 4.5; N, 13.3; Cd, 17.8%; IR (KBr) ν/cm^{-1} 3423br, 3055m, 3041m, 2928s, 2931s, 2863m, 1613s, 1559m, 1505m, 1430s, 1384s, 1306s, 1225m, 1150w, 1122w, 1107w, 1070m, 1038m, 976w, 883w, 851m, 820 (sh), 807m, 760m, 738w, 733w and 610.

$[Cd_2(SO_4)_2(Py_2C_3H_6)_3(H_2O)_{2.7}]\cdot 4.5H_2O$ 3

A solution of 1,3-bis(4-pyridyl)propane (1.75 g, 8.84 mmol) in ethanol (15 ml) was layered onto a solution of cadmium sulfate hydrate (1.27 g, 1.65 mmol) in water (10 ml). On standing overnight colourless crystals formed (1.80 g, 65%). Found: C, 44.2; H, 4.9; N, 7.5; S, 5.6. $[Cd_2(SO_4)_2(C_{13}H_{14}N_2)_3(H_2O)_{7.2}]$ requires C, 44.9; H, 5.4; N, 8.0; S, 6.1%. IR (KBr) ν/cm^{-1} 3450br s, 2930m, 2864w, 1637 (sh), 1616s, 1561w, 1505w, 1458w, 1429m, 1383w, 1232w, 1123m, 1017w, 968w, 850w, 819w, 801w, 758w and 620w.

$[Cd(NO_3)_2(Py_2C_4H_8)(H_2O)_2]$ 4

A mixture of 1,4-bis(4-pyridyl)butane (1.37 g, 6.45 mmol) dissolved in ethanol (30 ml) was added to cadmium nitrate (1.02 g, 3.30 mmol) in water (10 ml). After standing for 24 h colourless crystals were obtained (0.453 g, 21%). The material was not phase pure so satisfactory microanalytical data was not obtained. IR (KBr) ν/cm^{-1} 1637m, 1614s, 1560w, 1542w, 1508w, 1448s, 1430s, 1384s, 1299m, 1223m, 1072w, 1031m, 1019m, 993w, 882w, 851w, 818m, 807m, 734w and 614m.

$[Cd_2(NO_3)_4(Py_2C_5H_{10})_3H_2O]$ 5

A solution of 1,5-bis(4-pyridyl)pentane (1.7 g, 7.52 mmol) in ethanol (10 ml) was added to a solution of cadmium nitrate (1.5 g, 4.86 mmol) in water (5 ml) and ethanol (5 ml). After filtration, washing with ethanol and water then drying colourless crystals (2.20 g, 79%) were obtained. Found: C, 46.8; H, 4.8; N, 11.6 $[Cd_2(NO_3)_4(Py_2C_5H_{10})_3]$ requires C, 46.9; H, 4.7; N, 12.2%). IR (KBr) ν/cm^{-1} 2934s, 2859m, 1643 (sh), 1615s, 1560w, 1507w, 1457m, 1429m, 1384s, 1294m, 1225w, 1121w, 1107w, 1091w, 1071w, 1019w, 844w, 818w, 733w, 669w, 591w and 514w.

$[Cd(NO_3)_2(Py_2C_6H_{12})_2]$ 6

A solution of 1,6-bis(4-pyridyl)hexane (1.25 g, 5.20 mmol) in ethanol (10 ml) was added to a solution of cadmium nitrate (783 mg, 2.54 mmol) in water (5 ml) and ethanol (5 ml). After filtration, washing with water and ethanol and drying, colourless crystals (1.49 g, 81%) were obtained. Found: C, 53.7; H, 5.6; N, 11.6 $[Cd(NO_3)_2(C_{16}H_{20}N_2)_2]$ requires C, 53.6; H, 5.6; N, 11.7%. IR (KBr) ν/cm^{-1} 3043w, 2931s, 2856s, 1614s, 1557w, 1501w, 1428s, 1384s, 1365 (sh), 1299s, 1226m, 1212 (sh), 1070w, 1038w, 1014m, 873w, 823w, 788w, 723w, 586m, 544w, 511w and 480w.

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