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Networks with hexagonal circuits in co-ordination polymers of metal ions (Zn^{II}, Cd^{II}) with 1,1′-(1,4-butanediyl)bis(imidazole)

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Three new compounds, $[ZnL_{1.5}(H_2O)(SO_4)]\cdot6H_2O$ **1**, $[ZnL_{1.5}(H_2O)_2][NO_3]_2\cdot2H_2O$ **2** and $[CdL_{1.5}(H_2O)_2(SO_4)]\cdot4H_2O$ **3** were obtained from self-assembly of the corresponding metal salts with 1,1′-(1,4-butanediyl)bis(imidazole) (L). In both **1** and **2** zinc ion is five-co-ordinated, showing a less-common trigonal bipyramidal co-ordination polyhedron, while cadmium ion of **3** is six-co-ordinated with a common octahedral arrangement. The sulfate ions of **1** and **3** are co-ordinated, however the nitrate ions of **2** are not. Each of the three compounds is composed of a (6, 3) network with the hexagonal smallest circuit containing six metal ions and six L; each L is co-ordinated to two metal ions, acting as a bridging ligand. In **1** the 2-D sheet of (6, 3) networks is interpenetrated in an inclined mode by symmetry related, identical sheets to give an interlocked 3-D structure, while the (6, 3) networks of both **2** and **3** stack in a parallel fashion to construct frameworks having channels.

Introduction

The role of co-ordination bond and hydrogen bond in crystal engineering is currently of great interest due to their use in constructing two- and three-dimensional polymers[1] with special properties, such as electrical conductivity,[2] magnetism,[3] host–guest chemistry[4] and catalysis.[5] So far most of these materials are formed with rigid ligands, such as 4,4′-bipyridine[6] and pyrazine.[7] Most of these structures have relatively large voids and potential interest for guest–host interaction and molecular recognition. Studies on flexible ligands are relatively rare,[8] and we are interested in co-ordination polymers containing flexible ligands. Based on its structure, 1,1′-(1,4-butanediyl)bis(imidazole) (L) can be used as a flexible divergent ligand to construct co-ordination polymer materials. Such co-ordination polymers with various manganese salts have been studied recently.[9] Here we report the preparation and crystal structures of three co-ordination polymers of L with zinc or cadmium salts, namely $[ZnL_{1.5}(H_2O)(SO_4)]\cdot6H_2O$ **1**, $[ZnL_{1.5}(H_2O)_2][NO_3]_2\cdot2H_2O$ **2** and $[CdL_{1.5}(H_2O)_2(SO_4)]\cdot4H_2O$ **3**.

Experimental

All reagents were commercially available and used as received. The C, H and N microanalysis were carried out with a Carlo Erba 1106 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer.

Synthesis

1,1′-(1,4-Butanediyl)bis(imidazole) (L). A mixture of imidazole (3.4 g, 50 mmol) and NaOH (2.0 g, 50 mmol) in DMSO (10 mL) was stirred at 60 °C for 1 h then 1,4-dichlorobutane (3.2 g, 25 mmol) was added. The mixture was cooled to room temperature after stirring at 60 °C for 2 h, then poured into 200 mL of water and a white solid formed immediately which weighed 4.1 g after drying in air. Calc. for $C_5H_7N_2$: C, 63.16; H, 7.37; N, 29.47. Found: C, 63.11; H, 7.42; N, 29.31%.

$[ZnL_{1.5}(H_2O)(SO_4)]\cdot6H_2O$ 1. A mixture of $ZnSO_4\cdot7H_2O$ (0.14 g, 0.5 mmol) and L (0.19 g, 1.0 mmol) in water (25 mL) was refluxed for 30 min, then filtered. Colorless crystals (0.23 g) were obtained from the filtrate after standing for several days at room temperature. The compound is not soluble in water or common organic solvents. Calc. for $C_{15}H_{35}N_6O_{11}SZn$: C, 31.45; H, 6.16; N, 14.67. Found: C, 31.71; H, 5.92; N, 14.82%. IR (cm^{-1}): 3415vs, 3116m, 2946w, 1637m, 1618m, 1536m, 1523m, 1448w, 1243w, 1150s, 1108s, 1040m, 954m, 839w, 758m, 659m, 624m and 473m.

$[ZnL_{1.5}(H_2O)_2][NO_3]_2\cdot2H_2O$ 2. A mixture of $Zn(NO_3)_2\cdot6H_2O$ (0.15 g, 0.5 mmol) and L (0.19 g, 1.0 mmol) in water (20 ml) was refluxed for 20 min, then filtered whilst hot. When cooling some oil appeared at the bottom of the filtrate. The oil became a crystalline solid after standing at room temperature for several days. The solid was collected, washed with water and ethanol successively, and dried in air (0.21 g). Compound **2** does not dissolve in common organic solvents or water. Calc. for $C_{15}H_{29}N_8O_{10}Zn$: C, 32.95; H, 5.35; N, 20.49. Found: C, 33.21; H, 5.12; N, 20.62%. IR (cm^{-1}): 3417m, 3118m, 2946w, 1625w, 1536m, 1524m, 1446w, 1384vs, 1240m, 1097s, 1040w, 954m, 836m, 754m, 658m and 624w.

$[CdL_{1.5}(H_2O)_2(SO_4)]\cdot4H_2O$ 3. Compound **3** was prepared analogously to **1**. Calc. for $C_{15}H_{33}CdN_6O_{10}$: C, 29.93; H, 5.53; N, 13.97. Found: C, 30.11; H, 5.35; N, 14.34%. IR (cm^{-1}): 3416vs, 3124m, 2946w, 1637m, 1618m, 1521m, 1449w, 1234m, 1146s, 1106s, 1087s, 954w, 838w, 760w, 661m and 624m.

It can also be synthesized by a diffusion method. A solution of L (0.19 g, 1.0 mmol) in ethanol (8 ml) was slowly diffused into an aqueous solution of $CdSO_4$ (0.10 g, 0.5 mmol) in water (10 ml). Colorless plate-shaped single crystals of compound **3** slowly formed around the solution interface. The crystals were collected, washed with water and ethanol successively, and dried in air (0.25 g). The compound is not soluble in water or common organic solvents.

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X-Ray crystallography

Crystals obtained directly from the reaction mixture were suitable for single-crystal X-ray diffraction study. Diffraction intensities for complexes **1**, **2** and **3** were collected on a Siemens P4 diffractometer using the ω–2θ scan technique. Lorentz polarization and absorption corrections were applied.[10] The structures were solved with the direct method of SHELXS 86[11] and refined with full-matrix least-squares techniques using the SHELXL 93 program.[12] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms were generated geometrically, while the aqua hydrogen atoms were not located. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections incorporated.[13] The crystallographic data for the complexes are listed in Table 1, selected interatomic distances and angles given in Table 2. Drawings were produced with SHELXTL PLUS.[14]

CCDC reference number 186/2003.

See http://www.rsc.org/suppdata/dt/b0/b002433n/ for crystallographic files in .cif format.

Results and discussion

Crystal structures

Part of the structure of complex **1** is shown in Fig. 1(a). Each zinc ion is co-ordinated to three nitrogen atoms from three L molecules in equatorial positions, one water molecule and one oxygen atom of sulfate ion in apical positions, showing a less-common trigonal bipyramidal co-ordination polyhedron. The Zn–N distances of 2.007(4), 2.012(4) and 1.993(4) Å are similar to those of other zinc complexes.[6b,8d,16] The Zn–O (water) distance of 2.270(3) Å is also similar to that of other zinc complexes.[6b,16a] The Zn–O (sulfate ion) distance of 2.157(4) Å is shorter than Zn–O (water) distance. The presence of a co-ordinated sulfate ion is somewhat unexpected because water is a better ligand than sulfate ion for zinc(II) ion. Each L molecule has a 2_1 screw axis through the midpoint of two central methylene carbon atoms.

Part of the structure of complex **2** is shown in Fig. 2(a). The zinc ion shows a similar co-ordination geometry to that of **1** except that the sulfate ion is replaced by another water molecule. The Zn–N distances of 2.002(3), 2.015(3) and 2.007(3) Å are quite similar to those of **1** as are the Zn–O distances of 2.146(3) and 2.321(3) Å. Although nitrate ion is a better ligand than sulfate ion, the nitrate ions of complex **2** do not co-ordinate to zinc ions as in the complex of zinc with 4,4′-bipyridine.[16b] Each L molecule has an inversion center at the midpoint of the two central methylene carbon atoms.

Part of the structure of complex **3** is shown in Fig. 3(a). The local geometry of cadmium ion is an octahedral arrangement with three nitrogen atoms from three molecules of L in *cis* positions and three oxygen atoms from two water molecules and one sulfate ion is *cis* positions. The Cd–N distances of 2.280(5), 2.264(5) and 2.280(5) Å are similar to reported Cd–N (aromatic) distances.[5,6e,17] The Cd–O (water) distances of 2.407(5) and 2.403(5) Å are also similar to reported distances.[6e] The presence of a co-ordinated sulfate ion is also somewhat unexpected as in complex **1**. The Cd–O (sulfate ion) distance of 2.323(5) Å is shorter than the Cd–O (water) distances. As in complex **2**, each L molecule has an inversion center at the midpoint of the two central methylene carbon atoms.

In each of the complexes **1**, **2** and **3** each L co-ordinates to two metal ions through its two aromatic nitrogen atoms acting as a bridging bidentate ligand. Metal ions are bridged by L molecules to form infinite (6, 3) networks which contain extra large edge-sharing hexagons (66-membered rings) with a metal ion at each corner and a molecule of L at each edge connecting two metal ions (Figs. 1b, 2b and 3b). The lengths of the opposite edges are equal, and the edge lengths are 12.0, 12.2 and 13.6 Å for **1**, 12.1, 12.5 and 13.8 Å for **2** and 12.5, 12.9 and 14.1 Å for **3**. The metal ions of the (6, 3) network are arranged in chair form, and do not lie in the same plane but have a layer of thickness 5.3 Å for **1**, 5.3 Å

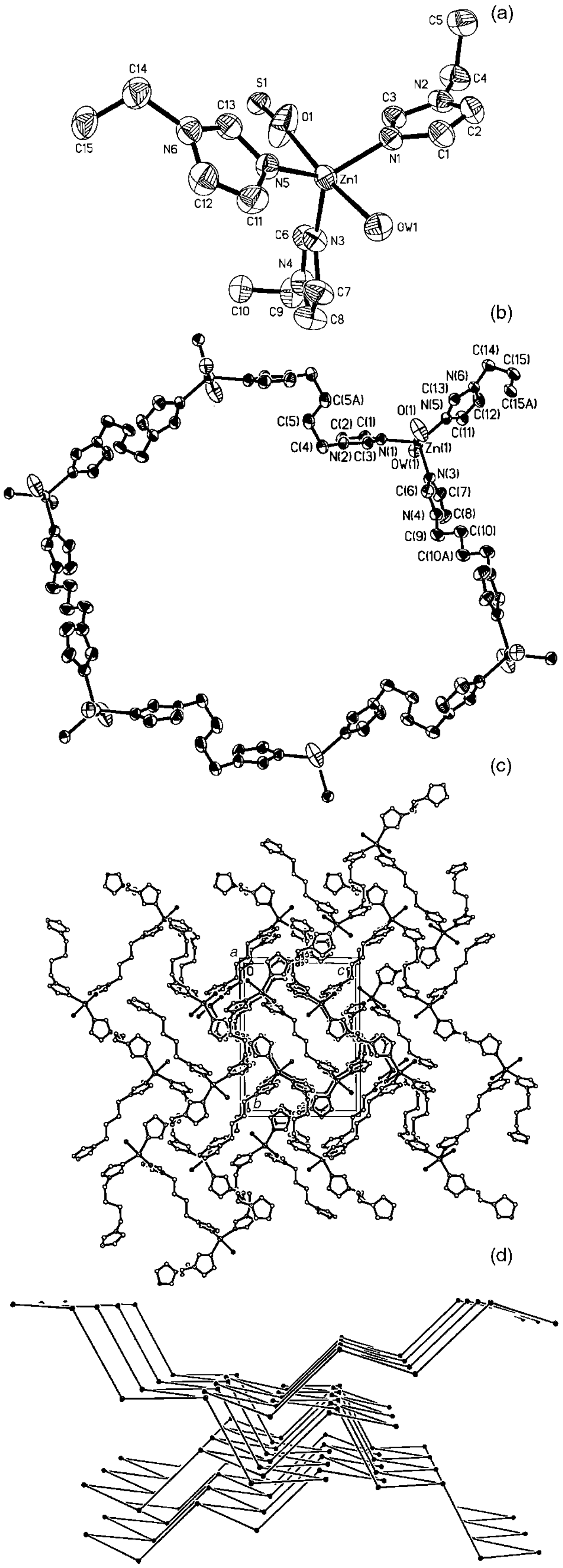

Fig. 1 (a) An ORTEP[15] drawing of the local co-ordination of Zn in complex **1**. (b) The extra large ring of the (6, 3) network in **1**. (c) Extended structure of **1**. (d) Schematic representation of the interpentration of (6, 3) networks in **1**. The nodes represent zinc ions and the lines L molecules.

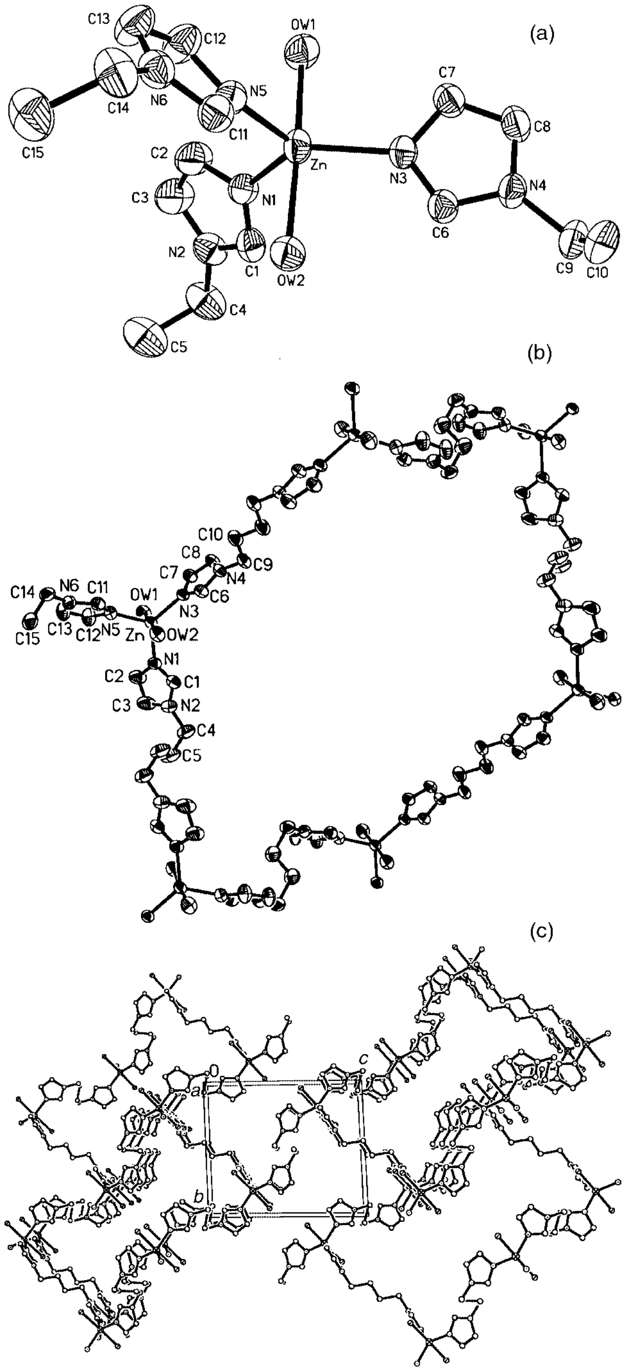

Fig. 2 (a) An ORTEP drawing of the local co-ordination of Zn in complex **2**. (b) The extra large ring of the (6, 3) network in **2**. (c) Extended structure of **2**.

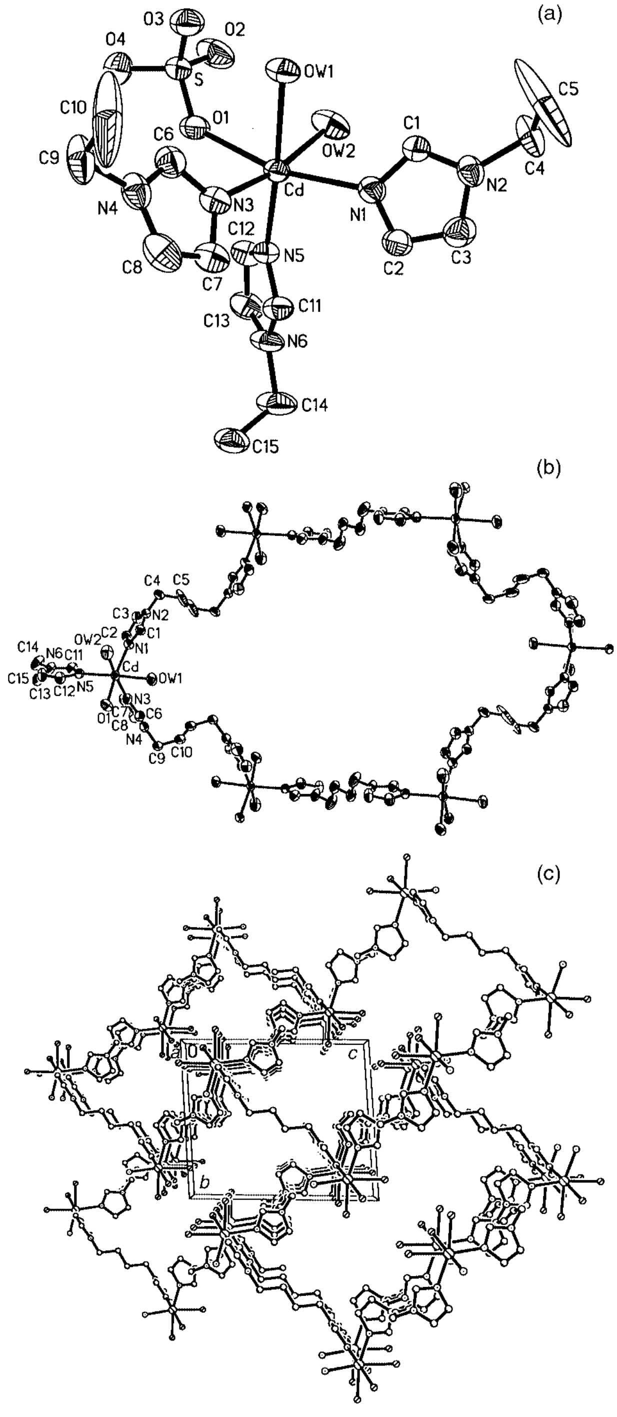

Fig. 3 (a) An ORTEP drawing of the local co-ordination of Cd in complex **3**. (b) The extra large ring of the (6, 3) network in **3**. (c) Extended structure of **3**.

for **2**, and 6.0 Å for **3**. This results in stacking of the L molecules within the sheets.

The sheet of complex **1** is interpenetrated in an inclined mode[18] by symmetry related, identical sheets to give an interlocked 3-D structure (Fig. 1c). The manner of interpenetration is such that each smallest hexagonal circuit of each sheet has parts of two other sheets passing through it (Fig. 1(d)). To the best of our knowledge, complex **1** is the second compound having such interpenetrating topology. A similar mode has so far only been reported in the structure of a silver complex.[19] Some interpenetrating structures containing (6, 3) networks have been reported.[20]

In the complexes **2** and **3** no interpenetration occurs as in the co-ordination polymers of Cu^I with a rigid aromatic ligand benzothiadiazole.[21] The (6, 3) networks of **2** and **3** stack in a parallel fashion to result in large channels in the materials (Figs. 2(c) and 3(c)). In **2** the network is positively charged, and the channels are filled with nitrate ions and lattice water molecules. In **3** the network is neutral, and the channels are filled with water molecules.

The structures of MnL_3X_2 ($X = BF_4^-$ or ClO_4^-) and MnL_2Cl_2 have been reported.[9] The 1 : 3 (M : L) complexes are composed of two equivalent, mutually interpenetrating three-dimensional networks, while the structure of the 1 : 2 complex is composed of two-dimensional sheets. The smallest circuit in the networks of these manganese complexes is a tetragon (44-membered ring) containing four manganese ions and four molecules of L. The frameworks with (6, 3) and (4, 4) networks are two common two-dimensional polymeric structures for co-ordination polymers. Co-ordination polymers containing flexible bidentate ligands as connectors with (4, 4)[9b,22] and (6, 3)

Table 1 Crystallographic and experimental data for complexes **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{15}H_{35}N_6O_{11}SZn$	$C_{15}H_{29}N_8O_{10}Zn$	$C_{15}H_{33}CdN_6O_{10}$
M	572.92	546.83	601.93
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	12.285(3)	8.335(2)	8.561(2)
b/Å	16.375(3)	11.173(2)	11.054(2)
c/Å	12.407(3)	13.049(3)	13.012(3)
α/°		87.36(3)	85.99(3)
β/°	91.45(3)	83.12(3)	83.91(3)
γ/°		83.49(3)	85.62(3)
V/Å^3	2495.1(9)	1198.0(4)	1218.5(4)
Z	4	2	2
T/°C	20(2)	20(2)	20(2)
λ/Å	0.71073	0.71073	0.71073
μ/mm^{-1}	1.132	1.091	1.042
$R1$ ($I > 2\sigma(I)$)	0.0513	0.0428	0.0511
$wR2$ (all data)	0.1373	0.1141	0.1503

Table 2 Selected bond distances (Å) and angles (°) for complexes **1**–**3**

$[ZnL_{1.5}(H_2O)(SO_4)]\cdot 6H_2O$ **1**			
Zn(1)–N(1)	2.007(4)	Zn(1)–N(3)	2.012(4)
Zn(1)–N(5)	1.993(4)	Zn(1)–O(1)	2.157(4)
Zn(1)–Ow(1)	2.270(3)		
N(5)–Zn(1)–N(1)	133.6(2)	N(5)–Zn(1)–N(3)	114.5(2)
N(1)–Zn(1)–N(3)	111.9(2)	N(5)–Zn(1)–O(1)	88.8(2)
N(1)–Zn(1)–O(1)	88.1(2)	N(3)–Zn(1)–O(1)	95.7(2)
N(5)–Zn(1)–Ow(1)	90.1(1)	N(1)–Zn(1)–Ow(1)	87.6(1)
N(3)–Zn(1)–Ow(1)	91.2(1)	O(1)–Zn(1)–Ow(1)	172.8(2)
$[ZnL_{1.5}(H_2O)_2][NO_3]_2\cdot 2H_2O$ **2**			
Zn–N(1)	2.002(3)	Zn–N(3)	2.015(3)
Zn–N(5)	2.007(3)	Zn–Ow(1)	2.146(3)
Zn–Ow(2)	2.321(3)		
N(5)–Zn–N(1)	109.9(1)	N(5)–Zn–N(3)	123.8(1)
N(1)–Zn–N(3)	126.2(1)	N(5)–Zn–Ow(1)	88.9(1)
N(1)–Zn–Ow(1)	91.6(1)	N(3)–Zn–Ow(1)	93.3(1)
N(5)–Zn–Ow(2)	88.9(1)	N(1)–Zn–Ow(2)	88.1(1)
N(3)–Zn–Ow(2)	88.8(1)	Ow(1)–Zn–Ow(2)	177.5(1)
$[CdL_{1.5}(H_2O)_2(SO_4)]\cdot 4H_2O$ **3**			
Cd–N(1)	2.280(5)	Cd–N(3)	2.264(5)
Cd–N(5)	2.280(5)	Cd–O(1)	2.323(5)
Cd–Ow(1)	2.407(5)	Cd–Ow(2)	2.403(5)
N(3)–Cd–N(5)	98.4(2)	N(3)–Cd–N(1)	98.9(2)
N(5)–Cd–N(1)	100.2(2)	N(3)–Cd–O(1)	89.8(2)
N(5)–Cd–O(1)	90.4(2)	N(1)–Cd–O(1)	165.2(2)
N(3)–Cd–Ow(2)	169.9(2)	N(5)–Cd–Ow(2)	90.2(2)
N(1)–Cd–Ow(2)	84.8(2)	O(1)–Cd–Ow(2)	84.8(2)
N(3)–Cd–Ow(1)	85.8(2)	N(5)–Cd–Ow(1)	172.1(2)
N(1)–Cd–Ow(1)	85.7(2)	O(1)–Cd–Ow(1)	82.9(2)
Ow(2)–Cd–Ow(1)	85.1(2)		

network[20c,f] have been reported, and the structures are related to the molar ratio of the metal ion and ligand. The complexes reported in this paper have a ratio of M : L of 1 : 1.5, and this composition is consistent with the (6, 3) network structure with a hexagon (66-memered ring).

The structures of complexes **1** and **2** imply a role of counter ions in construction of the framework. Indeed, in the related zinc(II) complexes with 4,4′-bipyridine various frameworks can be formed by changing the counter ions.[16b] In our case, although nitrate ion is a better ligand for zinc(II) ions than sulfate ion, it is not co-ordinated and sulfate ion is co-ordinated. The reason is not clear. The two unco-ordinated nitrate ions may be the main reason for the non-interpenetrating structure of **2**. Moreover, the structures of **1** and **3** imply a role of the size of the metal ion in construction of the framework since zinc and cadmium belong to the same periodic group, and show similar co-ordination behavior. In this case the co-ordination number of cadmium ion of 6 is higher than that of zinc ion of 5. This results in a larger co-ordination polyhedron in **3**, and a smaller one of zinc ion in **1**. This may give an explanation to the non-interpenetrating structure of **3**.

Syntheses

1 : 2 and 1 : 3 types of manganese complexes of L have been prepared, and the stoichiometries of the complexes depend on the anion.[9] Each of **1**, **2** and **3** can be synthesized in aqueous solution, and they are not soluble in water and common organic solvents. Although we have tried metal salts with L in different molar ratios of 1 : 1, 1 : 2 and 1 : 3, only the 1 : 1.5 complexes were obtained under all conditions.

Conclusion

Three co-ordination polymers containing 1,1′-(1,4-butanediyl)bis(imidazole) have been prepared and their structures determined. Each complex is composed of (6, 3) networks, in which metal ions are bridged by L molecules. Complex **1** is interpenetrated in an inclined mode by symmetry related, identical sheets to give an interlocked 3-D structure. Each smallest hexagonal circuit of each sheet has parts of two other sheets passing through it, and this is the second compound having such a topological structure. In both complexes **2** and **3** the infinite (6, 3) networks stack in a parallel fashion to result in large channels with a positively-charged framework in **2** and a neutral framework in **3**.

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