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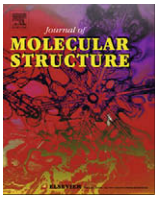

Metallosupramolecular zinc and cadmium complexes of Bis[4-(2-pyridyl)pyrimidinylthiomethyl]benzenes

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ABSTRACT

Reactions of L^1 and L^2 (L^1 = 1,4-bis[4-(2-pyridyl)pyrimidinylthiomethyl] benzene; L^2 = 1,3-bis[4-(2-pyridyl)pyrimidinylthiomethyl]benzene) with CdI_2, ZnI_2 and $Cd(NO_3)_2$ led to the formation of two discrete bimetallic complexes and one single-handed helix, respectively. Conformation changes of ligands after interactions with metal salts were found due to the positional isomerism of xylyl groups and the effect of anions.

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1. Introduction

A class of multi-armed organic ligands with a generalized formula (Scheme 1a) has been frequently used for constructing supramolecular architectures in recent years. Within these molecules, heterocyclic donors containing N atoms are attached to the central linking aryl core via the $-SCH_2$-spacer. Several reports on metallosupramolecular complexes assembled from these organic ligands reveal some common features [1–7]: (i) Attached arms within these molecules can be arranged in various conformations when interacting with different metal ions. (ii) Not only N atoms from heterocyclic donors but also S atoms of the thioether spacer are capable of binding metal ions with preference for the soft metal ions such as Cu(I) and Ag(I) ions. (iii) Discrete and polymeric structures with 1D, 2D and 3D dimensions have been obtained with these organic ligands. (iv) Apart from the metal ions, counterions also exert a significant impact on the final assembly outcome. In our previous study, we have reported an intriguing Cu_4S_4 cluster resulted from C–S cleavage of 2,6-bis((4-(pyridine-2-yl)pyrimidin-2-ylthio)-methyl)-4-chlorophenol (Scheme 1b) in the presence of copper (I) chloride [8]. In contrast, a discrete dinuclear cobalt complex has been generated from the assembly with cobalt nitrate in our following work [9].

As our continuing study, herein reported are metallosupramolecular zinc and cadmium complexes of bis[4-(2-pyridyl)pyrimidinylthiomethyl]benzenes (Scheme 1c, L^1 and L^2), two of which are discrete dinuclear complexes and one is a single-handed helix.

2. Experimental

All solvents were in analytic grade used as commercially available. Infrared spectra were performed on a Bruker Vector 22 spectrophotometer with KBr pellets in the 400–4000 cm^{-1}. ^1H NMR spectra were recorded on a Bruker DRX 500 MHz spectrometer. Electrospray ionization (ESI) mass spectra were performed employing a Finnigan MAT SSQ 710 mass spectrometer in a scan range 100–1200 amu.

2.1. Synthesis of L^1 and L^2

Both L^1 and L^2 were made by a similar way as following. To the solution of 4-(2-pyridinyl)pyrimidine-2-thiol (3.78 g, 20 mmol) and sodium hydroxide(0.80 g, 20 mmol) in dry ethanol (300 mL), 1,4-bis(bromomethyl)benzene or 1,3-bis(bromomethyl)benzene (2.64 g, 10 mmol) in CCl_4 (30 mL) was added. The mixture was stirred and refluxed for 8 h. After cooled, precipitates were filtered, washed by water and ethanol, and dried in vacuum. For L^1: yield 54.3%, m.p. 173–174 °C. Anal. Calcd for $C_{26}H_{20}N_6S_2$: C, 64.98; H, 4.19; N, 17.49%. Found: C, 64.61; H, 4.52; N, 17.39 %. IR (KBr, cm^{-1}): 1605 (w), 1557 (s), 1538 (s), 1471 (m), 1418 (s), 1346 (s), 1243 (m), 1194 (s), 1080 (w), 1042 (w), 829 (w), 797 (w),

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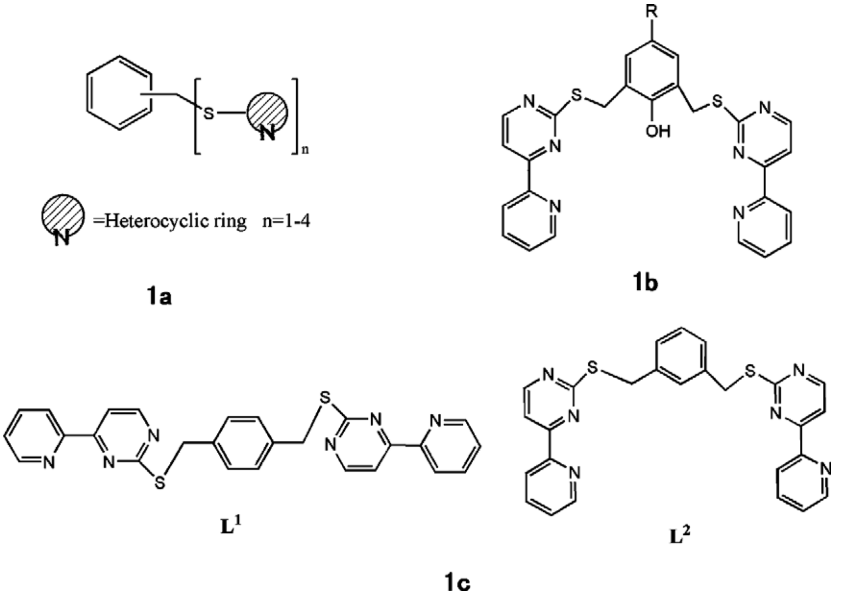

Scheme 1.

765(m). ESI-MS: 503.0 (100%) [L+Na]$^+$, 481.3 (25%) [L+H]$^+$. ^{1}H NMR (CDCl$_3$): δ 8.71 (d, 2H, pyridyl-H), 8.64 (d, 2H, pyrimidyl-H), 8.44 (d, 2H, pyrimidyl-H), 8.00 (d, 2H, pyridyl-H), 7.86 (t, 2H, pyridyl-H), 7.66 (s, 1H, aryl-H), 7.40 (m, 5H, pyridyl-H (2H) and aryl-H (3H)), 4.52 (s, 4H, methylene-H). For L^2: yield 74.6%, m.p. 110–111 °C. Anal. Calcd for $C_{26}H_{20}N_6S_2$: C, 64.98; H, 4.19; N, 17.49%. Found: C, 64.57; H, 4.37; N, 17.42%. IR (KBr, cm^{-1}): 1591 (w), 1562 (vs), 1531 (s), 1476 (w), 1421 (s), 1334 (s), 1289 (w), 1243 (w), 1215 (m), 1198 (m), 1023 (w), 832 (w). ESI-MS: 503.0 (100%) [L+Na]$^+$, 481.3 (10%) [L+H]$^+$. ^{1}H NMR (CDCl$_3$): δ 8.74 (d, 2H, pyridyl-H), 8.69 (d, 2H, pyrimidyl-H), 8.46 (d, 2H, pyrimidyl-H), 8.10 (d, 2H, pyridyl-H), 7.89 (t, 2H, pyridyl-H), 7.45 (s, 6H, pyridyl-H (2H) and aryl-H(4H)), 4.52 (s, 4H, methylene-H). Single crystals of L^1 and L^2 suitable for X-ray diffraction were grown from each methanol solution by slow evaporation in air at room temperature.

2.2. Preparation of zinc and cadmium complexes

2.2.1. Synthesis of [$Cd_2L^1I_4$] (**1**)

To a suspension of L^1 (24.0 mg, 0.050 mmol) in chloroform (5 mL) in a tube, a solution of CdI$_2$ (18.3 mg, 0.05 mmol) in methanol (5 mL) was very slowly dropped on the top of the ligand solution. Crystals formed after 10 days. (yield: 40%). Anal. Calcd for $C_{26}H_{20}I_4N_6S_2Cd_2$: C, 25.74; H, 1.66; N, 6.93%. Found: C, 32.20; H, 2.27; N, 10.78%. IR (KBr, cm^{-1}): 1597 (w), 1561 (s), 1547 (s), 1476 (w), 1416 (m), 1338 (vs), 1217 (m), 1198 (m), 1106 (w), 1016 (w), 821 (w).

2.2.2. Synthesis of [$Zn_2L^2I_4$] (**2**)

2 was made in the same way as that of 1 except that ZnI$_2$ (16.0 mg, 0.05 mmol) and L^2 (20.9 mg, 0.05 mmol) were used. Crystals formed after six days. (yield: 42%). Anal. Calcd for $C_{26}H_{20}I_4N_6S_2Zn_2$: C, 27.91; H, 1.80; N, 7.51%. Found: C, 27.93; H, 1.82; N, 7.49%. IR (KBr, cm^{-1}): 1602 (w), 1561 (s), 1544 (s), 1478 (m), 1446 (w), 1414 (s), 1335 (s), 1210 (m), 1166 (w), 1085 (w), 828 (w), 791 (w), 760 (m).

2.2.3. Synthesis of [$CdL^2(NO_3)_2]_n$ (**3**)

L^2 was treated with Cd(NO$_3$)$_2$ in DMF in ration 1:1 at room temperature. The solution was introduced into crystallization tubes and diffused with ether. Colorless crystals were obtained. (yield: 47%). Anal. Calcd for $C_{26}H_{20}CdN_8O_6S_2$: C, 43.55; H, 2.814; N, 15.63%. Found: C, 43.59; H, 2.78; N, 15.58%. IR (KBr, cm^{-1}): 1652 (w), 1563 (m), 1546 (m), 1478 (w), 1415 (s), 1384 (vs), 1339 (m), 1296 (w), 1211 (w), 824 (w), 797 (w), 764 (w).

2.3. X-ray crystallography

Single crystal data for organic ligands, L^1 and L^2, together with complexes **1**–**3** were collected at 291(2) K on a Bruker SMART CCD-4K diffractometer employing graphite-monochromated MoKα radiation (λ = 0.71073 Å). The data were collected using SMART and reduced by the program SAINT [10]. All the structures were solved by direct methods and refined by the full-matrix least squares method on F^2_{obs} by using SHELXTL-PC software package [11]. Non-hydrogen atoms were placed in geometrically calculated positions. The crystallographic data and selected bonds length and angles are listed in Tables 1 and 2, respectively.

3. Results and discussion

3.1. Description of crystal structures of L^1 and its cadmium complex **1**

A perspective view of L^1 with the atom-numbering scheme is shown in Fig. 1. L^1 crystallizes in the monoclinic space group $P2_1/n$. It adopts a *trans* conformation with two arms on the opposite sides of the central phenyl ring. Both pyridyl and pyrimidinyl rings at the end of each arm are not coplanar with a deviation of 6.95°. It is worthwhile to note that N1 and N3 donor atoms in each arm are not situated in chelating positions but with a large torsion angle N3–C5–C4–N1of 173.45°. The mean plane across the pyrimidinyl ring is inclined to that of linking phenyl ring at the angle of 66.43°.

However, reaction of CdI$_2$ resulted in significant conformation changes in L^1. As depicted in Fig. 2a, each ligand connects two identical Cd ions in $\hat{N}N$ chelation modes to form a discrete dinuclear cadmium coordination complex **1**, which crystallizes in the monoclinic space group $P2_1/n$. The coordination geometry around each Cd atom is a distorted tetrahedron completed by

Table 1
Crystal and structure refinemental data for ligand and complexes **1–3**

Complex	L^1	**1**	L^2	**2**	**3**
Formula	$C_{26}H_{20}N_6S_2$	$C_{26}H_{20}Cd_2I_4N_6S_2$	$C_{26}H_{20}N_6S_2$	$C_{26}H_{20}I_4N_6S_2Zn_2$	$C_{26}H_{20}CdN_8O_6S_2$
Formula weight	480.62	1213.00	480.62	1119.00	717.05
Crystal size (mm)	0.10 × 0.20 × 0.60	0.04 × 0.20 × 0.10	0.40 × 0.60 × 0.80	0.10 × 0.20 × 0.40	0.10 × 0.20 × 0.40
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P21/n$	$P21/c$	$P-1$	$P-1$	$P21/c$
a (Å)	4.1704(13)	7.6879(15)	9.241(2)	11.6667(14)	15.837(3)
b (Å)	16.407(5)	17.822(3)	11.281(3)	12.6015(15)	9.808(2)
c (Å)	16.275(5)	12.652(3)	11.546(3)	12.8564(16)	18.661(4)
α (°)	90	90	79.827(4)	114.148(2)	90
β (°)	90.000	103.519(4)	87.086(4)	98.539(2)	107.746(4)
γ (°)	90	90	72.829(4)	90.164(2)	90
V (Å^3)	1113.6(6)	1685.5(6)	1131.9(5)	1701.4(4)	2760.7(10)
Z	2	2	2	2	4
T (K)	291(2)	291(2)	291(2)	291(2)	291
D_{calcd} (mg/m^3)	1.433	2.390	1.407	2.184	1.725
μ (mm^{-1})	0.268	5.075	0.264	5.188	1.001
$F(000)$	500	1116	498	1044	1440
Ref. collected/unique	5441/1943 (R_{int} = 0.097)	8300/2961 (R_{int} = 0.063)	5654/3925 (R_{int} = 0.035)	8466/5868 (R_{int} = 0.049)	13,957/5142 (R_{int} = 0.089)
Parameters	154	181	307	361	388
R_1[a]	0.0543,	0.0550,	0.0586	0.0446	0.0517
wR_2[b]	0.1088,	0.0922,	0.1603	0.1224	0.0885
GOF	0.78	0.92	0.96	0.95	0.75
Min/max $\Delta\rho$ (e Å^{-3})	−0.21/0.20	−0.56/0.83	−0.47/0.37	−1.57/1.17	−0.34/0.61

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$.
[b] $wR_2 = \left[\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\right]^{1/2}$.

Table 2
Selected bonds length (Å) and angles (°)

Complex 1			
Cd1–I1	2.6535(15)	Cd1–I2	2.6469(14)
Cd1–N1	2.318(7)	Cd1–N3	2.298(8)
I1–Cd1–I2	123.94(4)	I1–Cd1–N1	108.4(2)
I1–Cd1–N3	111.6(2)	N1–Cd1–N3	71.0(3)
I2–Cd1 –N1	119.7(2)	I2–Cd1–N3	109.9(2)
Complex 2			
I1–Zn1	2.5139(14)	I2–Zn1	2.5265(12)
Zn1–N1	2.103(7)	Zn1–N3	2.074(8)
I3–Zn2	2.5262(13)	I4–Zn2	2.5234(15)
Zn2–N4	2.072(8)	Zn2–N6	2.023(8)
I1–Zn1–I2	123.04(5)	I1–Zn1–N1	119.2(2)
I1–Zn1–N3	107.4(2)	I2–Zn1–N1	103.2(2)
I2–Zn1–N3	117.5(2)	N1–Zn1–N3	78.2(3)
I3–Zn2–I4	120.54(5)	I3–Zn2–N4	115.7(2)
I3–Zn2–N6	107.6(2)	I4–Zn2–N4	111.3(2)
I4–Zn2–N6	114.4(2)	N4–Zn2–N6	80.5(3)
Complex 3			
Cd1–O1	2.369(6)	Cd1–O2	2.755(7)
Cd1–O4	2.335(7)	Cd1–N1	2.423(6)
Cd1–N3	2.320(5)	Cd1–N4	2.525(5)
Cd1–N6	2.299(5)	O1–Cd1–O4	108.9(2)
O1–Cd1–N1	111.1(2)	O1–Cd1–N3	81.95(19)
O1–Cd1–N4	158.35(18)	O1–Cd1–N6	91.33(19)
O2–Cd1–O4	155.6(2)	O2–Cd1–N4	125.12(17)
N1–Cd1–N4	80.02(18)	N1–Cd1–N6	115.74(19)
N3–Cd1–N4	119.70(19)	N3–Cd1–N6	173.2(2)
O4–Cd1–N4	75.2(2)	O4–Cd1–N6	96.37(19)
O4–Cd1–N3	84.77(19)	O4–Cd1–N1	127.0(2)

two N atoms from one arm and two I atoms. The average Cd–N and Cd–I bond lengths are 2.308 Å and 2.650 Å, respectively. Notably, the pyridyl ring in each arm is obliged to rotate to chelation sites along C4–C5 bond axis due to the metal coordination, whilst the dihedral angle between the two heterocyclic rings of each arm is decreased to 3.36° compared with that in a free ligand. In addition, the mean plane of pyrimidinyl ring is nearly perpendicular to that of central phenyl ring in sharp contrast with the situation in the free ligand. As shown in Fig. 2b, complex **1** is further joined together via C–H···I hydrogen bonds ($d_{C–I}$ = 3.818(11), ∠C–H···I = 153.1°; symmetry code: 1 − x, 1 − y, −z), giving a chain-like structure.

3.2. L^2 and its zinc (**2**) and cadmium complexes (**3**)

Fig. 3 shows a perspective view of L^2 with the atom-numbering scheme. It crystallizes in the triclinic space group $P\bar{1}$. Like L^1, two N donor atoms belonging to two different heterocyclic rings in each arm are not arranged in a chelation mode, with the torsion angle N–C–C–N of 169.98° and 178.50°, respectively. Two pyrimidinyl rings of each arm are inclined to the central phenyl ring at the angles of 67.67° and 75.28°, respectively. Despite that the thioether spacers are arrayed in a *trans* conformation, each arm is pointed toward the same direction.

Attempt to assemble with CdI_2 fails to obtain single crystals suitable for X-ray crystallography. Replacement of ZnI_2 affords a discrete dinuclear zinc complex **2** analogous to complex **1**. Similar to the situation in L^1, coordination of zinc atom promotes the pyridyl ring to rotate to chelation positions. More importantly, metal chelation significantly alters the whole conformation of organic ligand L^2. On one hand, space arrangement of two arms distinctly varies from in *trans* to in *cis* conformation. On the other hand, the dihedral angle of two pyrimidinyl rings with respect to the central phenyl ring changed to 72.34° and 82.39°, respectively (see Fig. 4).

Treatment of $Cd(NO_3)_2$ with L^2 generates a polymeric complex **3** rather than the discrete one. The compound crystallizes in the space group $P2_1/n$, consisting of one Cd atom, one ligand and two nitrate. The coordination environment around the Cd atom is a distorted octahedron, equatorially coordinated by three N atoms from two arms and one O atom from one nitrate and apically occupied by one N atom and one O atom. It is noted that two nitrate anions are different in coordination modes. One is unidentate with Cd–O bond length of 2.335 Å and the other is semi-bidentate with one exceptional longer Cd–O distance of 2.755 Å apart from normal Cd–O bond length of 2.369 Å. Each ligand bridges two Cd atoms via N–N chelation to produce a single-handed helix with a period of 18.661 Å. Furthermore, as shown in Fig. 5b, helices are joined together via C–H···O hydrogen bonds ($d_{C–O}$ = 3.305(9), ∠C–

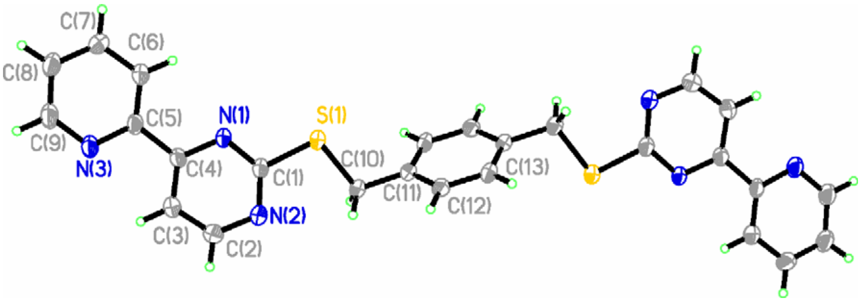

Fig. 1. Perspective view of L^1 with the atom-numbering scheme (30% probability ellipsoids).

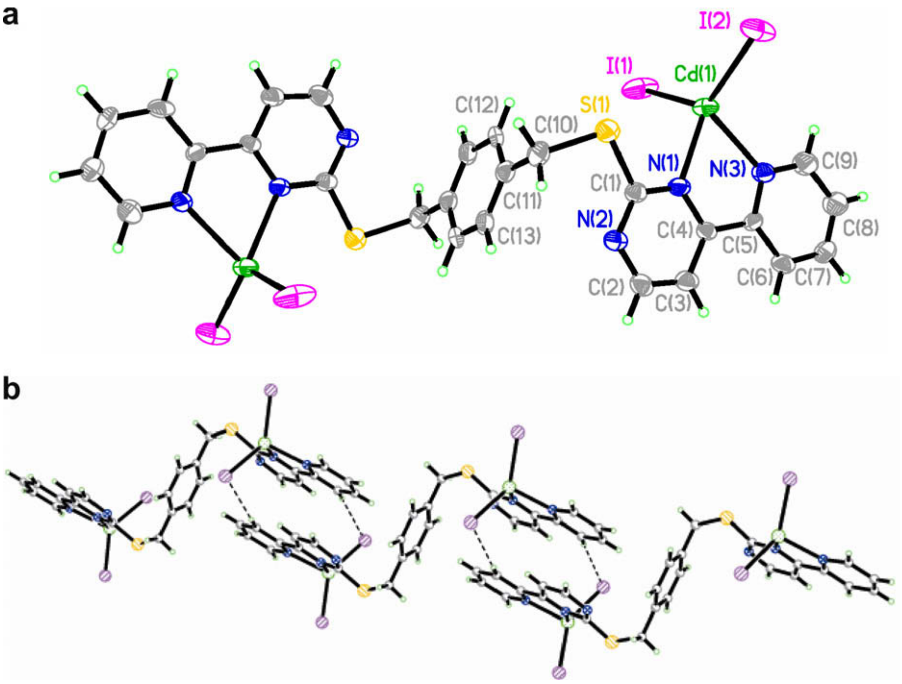

Fig. 2. (a) Perspective view of cadmium complex **1** with the atom-numbering scheme (30% probability ellipsoids). (b) View of the packing structure of complex **1** along *a* axis.

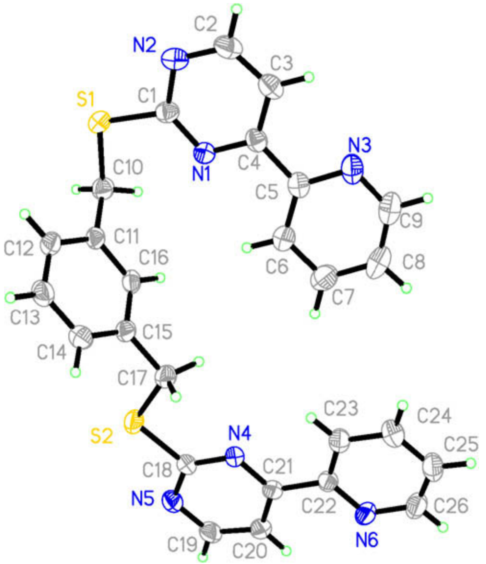

Fig. 3. Perspective view of L^2 with the atom-numbering scheme (30% probability ellipsoids).

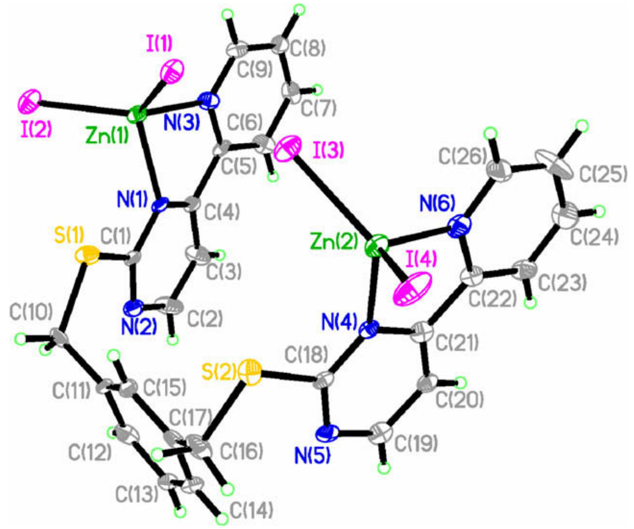

Fig. 4. Perspective view of complex 2 with the atom-numbering scheme (30% probability ellipsoids).

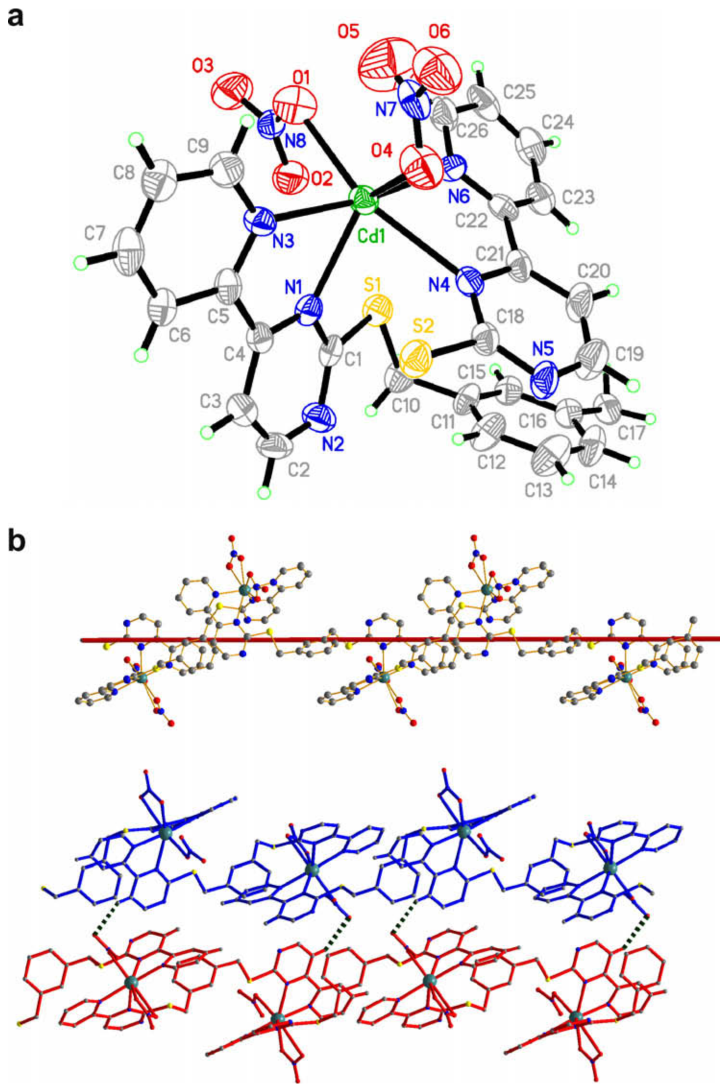

Fig. 5. (a) Perspective view of asymmetric unit of complex 3 with the atom-numbering scheme (30% probability ellipsoids). (b) View of helix in complex 3 (top), perspective view of the helices held by hydrogen bonds (bottom).

H···O = 146.0°; symmetry code: $2-x$, $1/2+y$, $3/2-z$) between the adjacent helical chains with opposite chirality.

In addition, L^2 in **3** adopts a *trans* conformation to open its two heterocyclic arms to connect metal ions, which are on the opposite side of the central phenyl ring. The pyrimidinyl and pyridyl rings are not parallel each other with a dihedral angle of 14.92° and 12.31°, respectively. The dihedral angle of two pyrimidinyl rings with respect to the central phenyl ring changed to 76.93° and 67.61°, respectively.

4. Conclusions

In this study, three novel complexes with different architectures, $[Cd_2L^1I_4]$ (**1**), $[Zn_2L^2I_4]$ (**2**), $[CdL^2(NO_3)_2]_n$ (**3**) were constructed from L^1 and L^2, respectively. In contrast to that in a free ligand, the pyridyl ring in each arm in the complexes is forced to rotate to connect metal ions. L^1 kept the same configuration in **1** with that of the free ligand, while in the structures of **2** and **3**, L^2 takes different configurations, i.e. two arms are distinctly in a *cis* conformation in **2** and adopt a *trans* conformation in **3**. The present study demonstrates that the nature of positional isomerism and geometric needs of metal atoms as well as the effect of anions play an important role in the crystal packing of MOFs.

5. Supplementary

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center with CCDC deposition numbers 673988–673992 for organic ligands L^1, L^2 and for metal complexes **1**–**3**, respectively. Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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