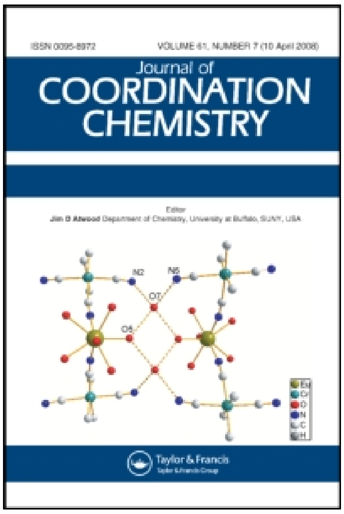

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Anion effect on construction of two Cd(II) coordination polymers with phenylformic acid-imidazole ditopic ligand: Hydrothermal synthesis, crystal structure and antimicrobial activity

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To cite this Article Gao, Jian , Wei, Kai-Ju , Ni, Jia and Zhang, Ju-Zhou(2009) 'Anion effect on construction of two Cd(II) coordination polymers with phenylformic acid-imidazole ditopic ligand: Hydrothermal synthesis, crystal structure and antimicrobial activity', Journal of Coordination Chemistry, 62: 2, 257 — 265

To link to this Article: DOI: 10.1080/00958970802206777

URL: http://dx.doi.org/10.1080/00958970802206777

Journal of Coordination Chemistry
Vol. 62, No. 2, 20 January 2009, 257–265

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Anion effect on construction of two Cd(II) coordination polymers with phenylformic acid-imidazole ditopic ligand: Hydrothermal synthesis, crystal structure and antimicrobial activity

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(*Received 14 November 2007; in final form 19 March 2008*)

Two new coordination polymers, $[Cd(L_{-H})_2]_\infty$ (**1**) and $[Cd(L_{-H})(NO_3)]_\infty$ (**2**) ($L = C_{10}H_8N_2O_2$), have been synthesized by hydrothermal reactions of 4-(imidazole-1-yl)-benzoic acid and CdX_2 ($X = ClO_4^-$ and NO_3^-). X-ray single crystal diffraction demonstrates that the counterion has an important effect on the assembly process. Crystals of **1** were orthorhombic, space group *Pnna*, with $a = 13.8052(6)$, $b = 16.5126(10)$ and $c = 8.2158(12)$. Complex **2** crystals were isolated as orthorhombic, space group *Pbca*, with $a = 7.9988(6)$, $b = 15.8290(11)$ and $c = 17.9580(13)$. Cd^{2+} is six-coordinate in a distorted octahedral geometry in both complexes. In **1**, L bridges the metal centers with the intramolecular $Cd \cdots Cd$ separation of 11.651 Å, resulting in an infinite rhombic grid; ClO_4^- is not in the grid. In **2**, adjacent Cd(II)'s were linked by L, and further by nitrate and carboxylate, producing an infinite zigzag chain. The toxicity of the two complexes is evaluated by testing antimicrobial activity against bacterial strands using the agar diffusion method.

Keywords: 4-(Imidazole-1-yl)-benzoic acid; Coordination polymer; Cd(II) complex; Crystal structure; Anion effect

1. Introduction

The chemistry of coordination polymers is of interest because of their structural diversities and potential applications as materials for molecular selection, ion exchange, absorption, separation and optical devices. A number of coordination polymers have been obtained by reactions between transition metal ions and designed organic ligands [1–6]. Assembly of coordination networks is not only controlled by metal ions and the

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802206777

principal ligands (building blocks), but also by counterions [7]. To obtain the desired polymers with predictable structure and properties, it is very important to choose appropriate multidentate ligands and anions. Herein, we report the syntheses, structures and toxicities of two coordination polymers derived from 4-(imidazole-1-yl)-benzoic acid, which has two coordination groups, 4-carboxylate and imidazole. 4-Carboxylate is a regular carboxylate linker with bridging capability [8]. Imidazole is usually unidentate, and its presence in many biological systems makes it significant to study the biological properties. The ligand possesses highly planar π-conjugated systems and has potential to form two (or three) dimensional coordination polymers with different configurations in the presence of different anions. Two Cd(II) coordination polymers derived from the title ligand were synthesized by hydrothermal methods, characterized by X-ray single crystal diffraction and evaluated for antimicrobial activity.

2. Experimental

2.1. *Materials and methods*

All starting chemicals were of reagent-grade quality and obtained from commercial sources. All reagents and solvents were dried and purified by usual methods. ^{1}H NMR spectra were recorded on a Bruker 300 Ultrashield spectrometer operating at 300 MHz. The FT-IR spectra were recorded from 400–4000 cm^{-1} on a Bruker EQUINOX 55 VECTOR22 spectrophotometer as KBr pellets. Elemental analyses were carried out with an Elementar Vario EL-III analyzer. The melting points were measured with a IA9300 melting point apparatus. Differential scanning calorimetry (DSC) analyses were carried out on a NET ZSCH DSC 204 F1 Instrument at a heating rate of 10°C min^{-1} under nitrogen. The ES mass spectral measurements of 4-(imidazole-1-yl)-benzoic acid (L) were carried out on a LCQ System (Finngann MAT, USA) using methanol as the mobile phase.

2.2. *Preparation of the ligand and complexes*

2.2.1. Synthesis of 4-(imidazole-1-yl)-benzaldehyde. A mixture of 4-fluorobenzaldehyde (5.58 g, 45 mmol), imidazole (2.05 g, 30 mmol), anhydrous K_2CO_3 (4.14 g, 30 mmol) and 18-Crown-6 (0.159 g, 0.6 mmol) in anhydrous DMF (50 mL) was stirred for 48 h under dry nitrogen at 120°C. After the reaction mixture cooled to ambient temperature, the solvent was removed by vacuum distillation. Ice water was added to the residue, and the straw yellow solid product was obtained by filtering the mixture. Yield: 4.2 g, 81%. M.p. 139–140°C. IR (cm^{-1}, KBr): 3110(m), 1687(s), 1607(s), 1525(s), 1483(s), 1400(w), 1375(w), 1311(s), 1270(m), 1171(m), 1061(m), 834(s). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 9.2 (s, 1H), 8.03 (d, 2H), 8.00 (s, 1H), 7.59 (d, 2H), 7.43 (s, 1H), 7.26 (s, 1H).

2.2.2. Synthesis of 4-(imidazole-1-yl)-benzoic acid (L). 4-(Imidazole-1-yl)-benzaldehyde (3.12 g, 20 mmol) and 6 M NaOH (4 mL) were placed in a 200 mL flask, stirred at 0°C, then 30% H_2O_2 was added dropwise. After the mixture was stirred at 0°C for 12 h and at room temperature for 12 h, it was filtered. The filtrate was then adjusted to pH 5.0 with dilute hydrochloric acid to obtain solid product. The product was washed with water and dried to obtain a yellowish solid of 4-(imidazole-1-yl)-benzoic acid (L). Yield: 2.86 g, 76%. M.p. 310–312°C. IR (cm^{-1}, KBr): 3121(m), 2430(w), 1925(w), 1700(s), 1608(s), 1525(s), 1491(w), 1431(w), 13752(w), 1309(s), 1251(s), 1182(m), 1116(m), 1059(s), 962(m). ^1H NMR (300 MHz, $CDCl_3$, ppm) δ : 8.380 (s, 1H), 8.064−8.035 (d, 2H), 7.843−7.784 (t, 3H), 7.144 (s, 1H). MS *m*/*z* (%): 189.3 (M^+, 100).

2.3. *Synthesis of complexes*

2.3.1. $[Cd(L_{-H})_2]_\infty$ (1). Fresh $Cd(ClO_4)_2 6H_2O$ (0.46 g, 1.0 mmol) and 4-(imidazole-1-yl)-benzoic acid (0.188 g, 1.0 mmol) were mixed in water with stirring, then the mixture was sealed in a 30 mL stainless-steel reactor with a Teflon liner at 160°C for 72 h, resulting in formation of light yellow crystals of the title complex. Yield: 26%. M.p. 376°C (decomposition). The C, H and N contents were determined by elemental analysis: Anal. Calcd for $Cd(C_{10}H_7 N_2O_2)_2$ (%): C, 49.31; H, 2.88; N, 11.50. Found: C, 48.96; H, 2.89; N, 11.56.

2.3.2. $[Cd(L_{-H})(NO_3)]_\infty$ (2). This complex was prepared by the procedure described for **1** using $Cd(NO_3)_2 4H_2O$ instead of $Cd(ClO_4)_2 6H_2O$. Yellowish crystalline solid of **2** was obtained. Yield: 32%. M.p. 319°C (decomposition). The C, H and N contents were determined by elemental analysis: Anal. Calcd for $Cd(C_{10}H_7N_2O_2)(NO_3)$ (%): C, 33.19; H, 1.94; N, 11.62. Found: C, 33.26; H, 1.89; N, 11.69.

2.4. *Crystallographic studies*

X-ray diffraction data were collected on a Bruker APEX area-detector diffractometer at 293 K using ω rotation scans with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined with full-matrix least-squares using SHELXTL. Anisotropic thermal parameters were applied to all non hydrogen atoms. Hydrogen atoms in these structures are located from the differential electron density map and constrained to ideal positions in the refinement procedure. Crystallographic calculations were conducted using the SHELXL-97 programs [9] and molecular graphics were plotted using SHELXTL. Crystal data and experimental details for these crystals are given in table 1, and selected bond distances and angles are listed in tables 2 and 3.

2.5. *Toxicity determination*

The toxicities for the two complexes and L were evaluated by testing antimicrobial activity to bacterial strands using the agar diffusion method described in the literature [10]. Compounds dissolved in DMF were tested against standard strains of *Candida albicans* CMCC (F) 98 001, *Staphyloccus aureus* CMCC (B) 26 003, *Bacillus pumilus* CMCC (B) 63 202 and *Klebosiella pneumoniae* CMCC (B) 46 117. All tests were repeated three times and average data were taken as the final result.

Table 1. Crystallographic data for the two complexes.

	1	**2**
Formula	$C_{20}H_{14}CdN_4O_4$	$C_{10}H_7CdN_3O_5$
Formula weight	486.75	361.59
T (K)	293(2)	293(2)
λ(Mo-Kα) (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Crystal size (mm^3)	$0.35 \times 0.28 \times 0.26$	$0.28 \times 0.12 \times 0.12$
Space group	*Pnna*	*Pbca*
Unit cells and dimensions (Å, °)		
a	13.8052(6)	7.9988(6)
b	16.5126(10)	15.8290(11)
c	8.2158(12)	17.9580(13)
α	90	90
β	90	90
γ	90	90
V (Å^3)	1872.9(3)	2273.7(3)
D_{Calcd} (Mg m^{-3})	1.726	2.113
Z	4	8
F(000)	968	1408
μ (mm^{-1})	1.202	1.942
Reflections collected	11799	14329
Reflections unique	2316	2718
R_{int}	0.0301	0.0331
Data/restraints/parameters	2316/0/132	2718/0/172
R_1, wR_2 [$I > 2\sigma(I)$]	0.0342, 0.0853	0.0410, 0.1018
R_1, wR_2 (all data)	0.0501, 0.0929	0.0509, 0.1073
Goodness-of-fit on F^{2-}	1.037	1.085
CCDC	630120	612682

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

Cd(1)–N(2)#1	2.263(2)	Cd(1)–N(2)#2	2.263(2)
Cd(1)–O(2)	2.270(2)	Cd(1)–O(2)#3	2.270(2)
Cd(1)–O(1)	2.454(3)	Cd(1)–O(1)#3	2.454(3)
N(2)–Cd(1)#4	2.263(2)		
N(2)#1–Cd(1)–N(2)#2	90.33(12)	N(2)#1–Cd(1)–O(2)	125.70(10)
N(2)#2–Cd(1)–O(2)	93.18(10)	N(2)#1–Cd(1)–O(2)#3	93.18(10)
N(2)#2–Cd(1)–O(2)#3	125.70(10)	O(2)–Cd(1)–O(2)#3	126.12(16)
N(2)#1–Cd(1)–O(1)	85.43(9)	N(2)#2–Cd(1)–O(1)	133.56(9)
O(2)–Cd(1)–O(1)	54.71(10)	O(2)#3–Cd(1)–O(1)	100.72(9)
N(2)#1–Cd(1)–O(1)#3	133.56(9)	N(2)#2–Cd(1)–O(1)#3	85.43(9)
O(2)–Cd(1)–O(1)#3	100.72(9)	O(2)#3–Cd(1)–O(1)#3	54.71(10)
O(1)–Cd(1)–O(1)#3	128.78(14)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+3/2$, $-y+1$, $z-1$; #2: $-x+3/2$, $y+1/2$, $-z+1/2$; #3: x, $-y+3/2$, $-z-1/2$; #4: $-x+3/2$, $-y+1$, $z+1$.

3. Results and discussion

3.1. *Thermal analysis of ligand*

Thermal analyses of 4-(imidazole-1-yl)-benzaldehyde and 4-(imidazole-1-yl)-benzoic acid in the temperature range 80–200°C and 150–500°C, respectively, on 1 mg samples show two different endothermic processes. The aldehyde is at 138.0 ~ 147.8°C with a peak at 145.1°C, and its endothermic enthalpy is 205.9 J g^{-1}, while L is at

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

Cd(1)–O(1)	2.211(3)	Cd(1)–O(4)	2.472(4)
Cd(1)–N(2)#1	2.219(3)	Cd(1)–O(4)#3	2.547(4)
Cd(1)–O(3)	2.349(4)	Cd(1)–O(2)	2.625(3)
Cd(1)–O(2)#2	2.387(3)		
O(1)–Cd(1)–N(2)#1	134.34(12)	N(2)#1–Cd(1)–O(4)#3	83.00(11)
O(1)–Cd(1)–O(3)	86.52(13)	O(3)–Cd(1)–O(4)#3	78.19(12)
N(2)#1–Cd(1)–O(3)	135.39(12)	O(2)#2–Cd(1)–O(4)#3	173.54(9)
O(1)–Cd(1)–O(2)#2	92.09(12)	O(4)–Cd(1)–O(4)#3	106.53(13)
N(2)#1–Cd(1)–O(2)#2	90.67(11)	O(1)–Cd(1)–O(2)	53.17(10)
O(3)–Cd(1)–O(2)#2	107.44(11)	N(2)#1–Cd(1)–O(2)	82.77(10)
O(1)–Cd(1)–O(4)	128.29(11)	O(3)–Cd(1)–O(2)	126.23(11)
N(2)#1–Cd(1)–O(4)	96.41(11)	O(2)#2–Cd(1)–O(2)	107.88(12)
O(3)–Cd(1)–O(4)	52.48(11)	O(4)–Cd(1)–O(2)	176.61(10)
O(2)#2–Cd(1)–O(4)	75.39(12)	O(4)#3–Cd(1)–O(2)	70.12(12)
O(1)–Cd(1)–O(4)#3	91.41(12)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+3/2$, $-y+1$, $z+1/2$; #2: $x+1/2$, y, $-z+1/2$; #3: $x-1/2$, y, $-z+1/2$; #4: $-x+3/2$, $-y+1$, $z-1/2$.

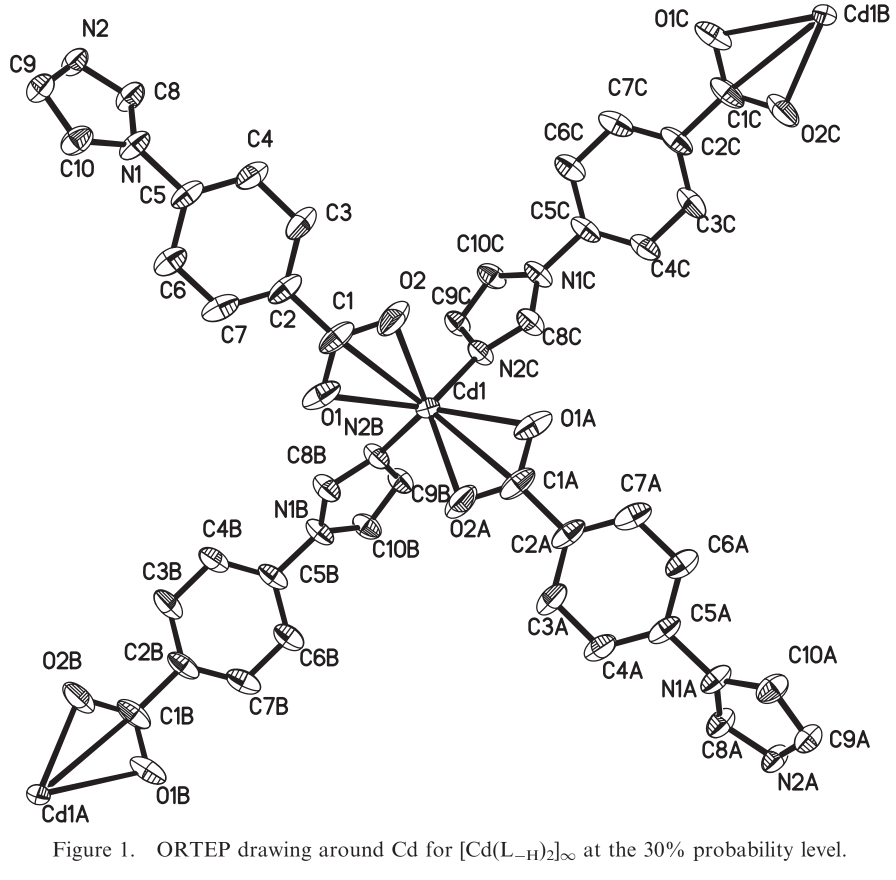

Figure 1. ORTEP drawing around Cd for $[Cd(L_{-H})_2]_\infty$ at the 30% probability level.

303.6 ~ 313.5°C with a peak at 311.2°C, and its endothermic enthalpy is 685.4 J g^{-1}. These results are consistent with the melting points.

3.2. *Description of the structure of [Cd($C_{10}H_7N_2O_2$)$_2$]$_\infty$ (1)*

The crystal structure of **1**, shown in figure 1, is a neutral polymeric molecule with the repeat unit containing one cadmium(II) and two 4-(imidazole-1-yl)-benzoic acid ions. The Cd(II) located on the crystallographic inversion center is coordinated by two N atoms from two ligands and four O atoms from two carboxylates. The coordination geometry around the cadmium center in the molecule can be described as a distorted octahedron. The *cis*-angles vary from 54.71(10)° to 133.56(9)°. The Cd–O bond distances range from 2.270(2) to 2.454(3) Å and Cd–N bond distance is 2.263(2) Å, in the normal ranges [10, 11]. The ligand L is multidentate chelating, bridging metal centers with intramolecular Cd···Cd separation of 11.651 Å, resulting in an infinite rhombic grid (shown in figure 2). In one L, the dihedral angles of the two aromatic rings (benzene and imidazole) and benzene ring to carboxyl plane are 51.5° and 7.7°, respectively, indicating serious distortion occurred during formation of the complex.

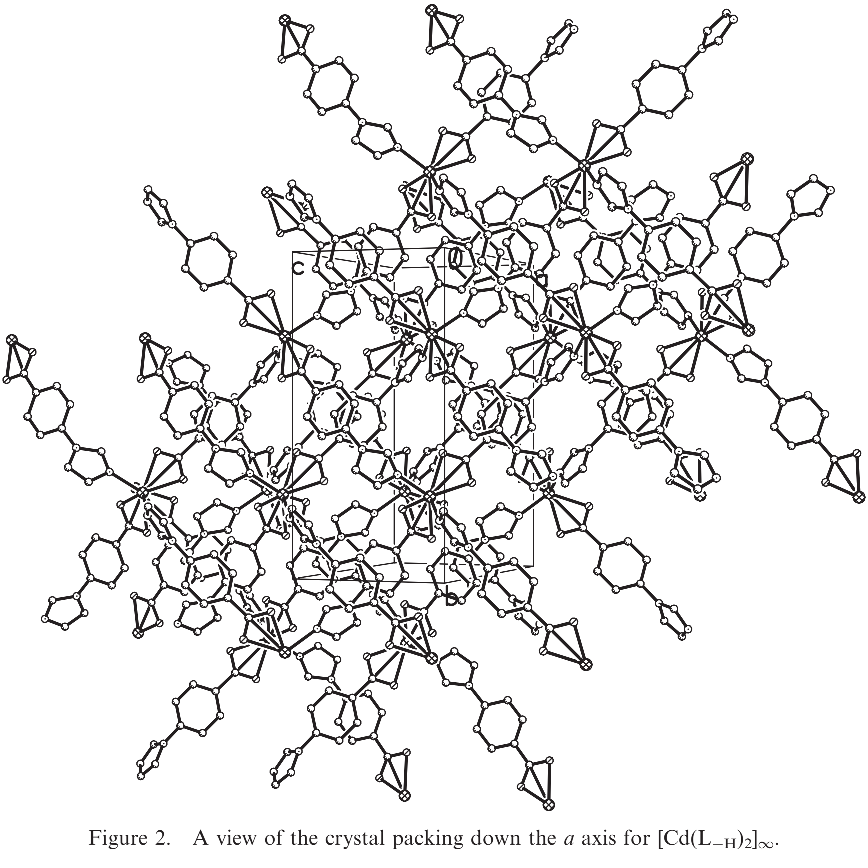

Figure 2. A view of the crystal packing down the *a* axis for [Cd(L_{-H})$_2$]$_\infty$.

3.3. *Description of the structure of [Cd(L_{-H})(NO_3)]$_\infty$ (2)*

Figure 3 shows an ORTEP around Cd for [Cd(L_{-H})(NO_3)]$_\infty$ with atomic numbering scheme, and figure 4 shows a perspective view of the crystal packing in the unit cell. The repeat unit of **2** contains one Cd(II), one 4-(imidazole-1-yl)-benzoate, and one nitrate. Each cadmium(II) adopts a distorted octahedral geometry, coordinated with five oxygens and one nitrogen from two different carboxylates, one nitrate anion, and imidazole. Dihedral angles of the two aromatic rings, and benzene ring to carboxylate plane are 171.0° and 159.8°, respectively, indicating less distortion than with **1**. The ligand bridges metal centers with intramolecular Cd···Cd separation of 12.290 Å. Another bridge is between metal centers and oxygens from nitrate and carboxylate, the Cd···Cd separation being 4.001 Å. Thus, an infinite zigzag chain extending along the crystallographic *c* axis is formed. These networks form a 3-D structure (figure 4) stabilized by weak π–π interactions of nearby aromtic rings and C–H···O hydrogen bonds (the distance of C···O ranging from 3.098 to 3.390 Å).

3.4. *Antimicrobial activity*

Toxicity of L, **1** and **2** were investigated by preliminary screening for antimicrobial activity. The diameters of inhibition zone (mm) of L and the complexes are listed in table 4. All three compounds were active against all four test organisms with different antimicrobial activities. The complexes were more active than L, attributed to its higher lipophilic character. The highest antimicrobial activity among the group of these

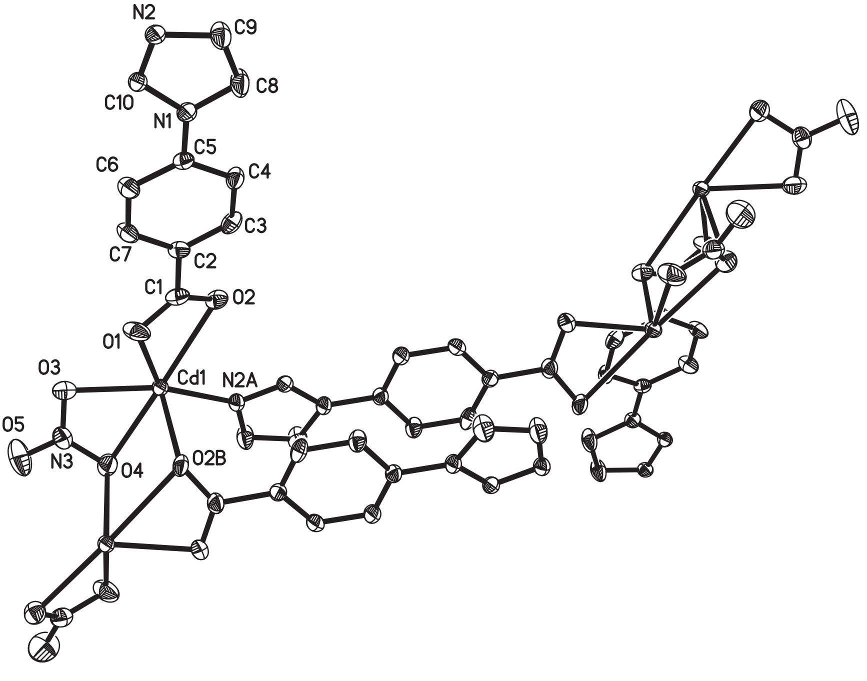

Figure 3. ORTEP drawing around Cd for [Cd(L_{-H})(NO_3)]$_\infty$ at the 30% probability level.

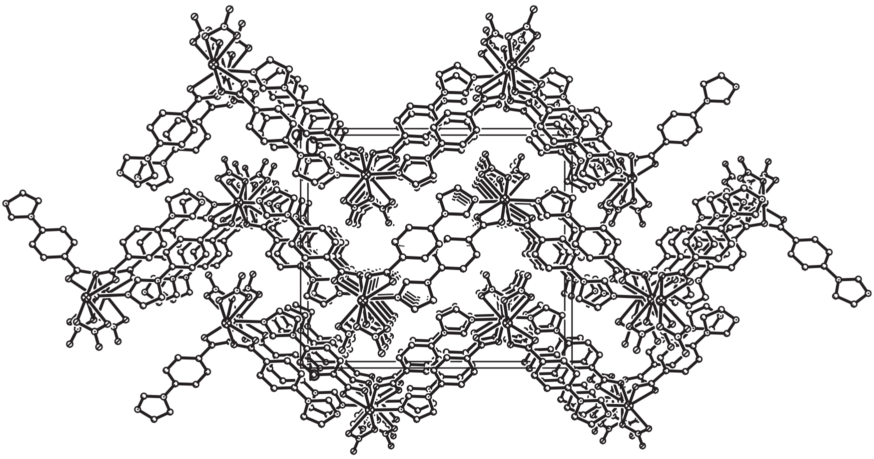

Figure 4. A view of the crystal packing down the *a* axis for $[Cd(L_{-H})(NO_3)]_{\infty}$.

Table 4. The diameter of inhibition zone (mm) of L, **1** and **2**.

		Diameter of inhibition zone (mm)			
Compound	Concentration ($mmol\,L^{-1}$)	*Candida albicans*	*Staphyloccus aureus*	*Bacillus pumilus*	*Klebosiella pneumoniae*
L	5.0	12.4	15.9	11.6	11.8
	2.5	11.1	13.8	10.5	11.2
	1.2	9.2	12.1	9.7	9.9
	0.6	6.16	9.0	7.9	7.2
1	5.0	21.6	31.5	26.6	23.8
	2.5	19.3	26.2	21.3	20.3
	1.2	15.9	19.6	15.1	12.5
	0.6	12.2	11.0	13.1	9.2
2	5.0	21.4	28.6	23.3	23.9
	2.5	18.5	20.5	18.5	19.1
	1.2	13.8	16.9	13.2	15.2
	0.6	8.2	12.3	9.8	8.6

organisms was observed against *Staphyloccus aureus*. In the range 0.6–5.0 $mmol\,L^{-1}$, the compounds were more active against the test strains with increase of concentration. Complex **1** was more active than **2**, perhaps related to the different coordination geometry and different stability [12].

4. Conclusions

Two supramolecular networks based on a multidentate bridging ligand 4-(imidazole-1-yl)-benzoic acid and metal salts with different anions, CdX_2 ($X = ClO_4^-, NO_3^-$), have been obtained from hydrothermal reactions. The structures depend on anions; in **1**, ClO_4^- does not exist in the grid structure due to its weak coordination ability and large ion volume, but in **2**, an infinite zigzag chain linked by NO_3^- is formed due to the coordination ability of nitrate. Complex **1** showed more activity than **2** in preliminary screening for antimicrobial activity.

Supplementary materials

CCDC-630120 and 612682 for the title compounds contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgements

The project was supported by Six Projects Sponsoring Talent Summits of Jiangshu Province (07-A-029), Open-end Funds of Jiangsu Key Laboratory of Marine Biotechnology, Huaihai Institute of Technology (No. 2006HS007) and Lianyungang Technical College (No. YKJ200712).

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