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Helicity-induced two-layered Cd(II) coordination polymers built with different kinked dicarboxylates and an organodiimidazole

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ABSTRACT

A new ligand bis-(4-imidazol-1-yl-phenyl)-diazene (azim), incorporating an azo moiety at the center and two imidazole groups at the terminals has been designed and synthesized. Under solvothermal conditions, this ligand reacts with $Cd(NO_3)_2{\cdot}6H_2O$ and different angular aromatic dicarboxylates to form layered coordination polymers: $[Cd(azim)(bcp)]_n$ (**1**) and $\{[Cd(azim)(oba)](H_2O)\}_n$ (**2**) [$bcpH_2$ = 1,3-bis-(4′-carboxy phenoxy)benzene; oba = 4,4′-oxybis(benzoate)]. Both **1** and **2** have been characterized by single-crystal X-ray diffraction technique, elemental analysis, PXRD and IR spectroscopy. The structure of each polymer looks like 2D grid where two layers are interpenetrated in a "cloth-like" topology. Both the structures contain single- and double-stranded helical coils where the pitches as well as the width are controlled by the carboxylate co-ligands. The hydrogen-bonding interactions between adjacent layers extend these structures to overall 3D supramolecular architectures.

1. Introduction

Coordination polymers from relatively simple sub-units have attracted considerable interest because of their potential applications such as materials for selective gas adsorption, catalysis, desirable optical properties [1–14] and so on. Apart from different coordination tendencies of metal ion, the modular construction of coordination polymers can be systematically tuned by elaborate selection of ligand bite angle, its length and relative orientation of the donor atoms, which ultimately alters their pore size and shape.

Aromatic polycarboxylates are by far the most extensively used ligands to generate MOFs having different supramolecular architectures. Aromatic group imparts rigidity to the ligand that is necessary to prevent collapse of the structure formed. Besides, coordination polymers built with carboxylates can be neutral that can eliminate problems associated with presence of the counter anions. A large variety of interpenetrating networks and entangled extended arrays are currently shaped within the areas of inorganic and coordination chemistry, especially due to the intensive search for new functional materials. The analysis of these species can be a difficult and time-consuming work because of their ever growing number and for their increasing structural complexity, as evidenced by the continuous finding of many types of entanglements of individual motifs, particularly in the field of crystal engineering of coordination polymers, or metal–organic frameworks (MOFs) [1–14]. 'Interpenetrating networks' [15–17] are nowadays the more numerous entangled arrays, that need for a classification of the topology of the individual nets [18–26].

Interpenetrated or entangled networks [18–26] represent an opportunity for achieving a 1D to 2D expansion through interweaving 1D chain. In this report, we show that helicity in entangled MOFs can be induced through proper selection of ligands. These helical chains interweave to form 2D coordination polymeric networks. Helical coordination polymers themselves have received great attention for potential applications in biomimetic chemistry as well as understanding of molecular self-assembly processes [27–29]. So far, much effort has been directed on the exploitation of rod-like ligands [30–33]. However, there has been comparatively little effort concentrated toward angular ligands with an angle other than 180° [34–37]. In principle, the extended structures based on helical chains can be produced through the twisted binding sites of bridging ligands, which can also connect neighboring helices via cross-linking. In this respect, our research has been focused towards designing of new ligands and investigating the rational control of their self-assembly with metal ions [38–42]. Herein, we describe the synthesis of two different entangled 2D layer structures from a long ligand incorporating imidazole at the terminals (Scheme 1) and one of two different bent aromatic dicarboxylates under solvothermal condition.

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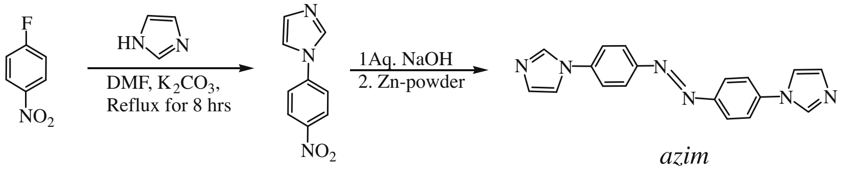


Scheme 1. Synthetic scheme for ligand azim.

2. Experimental

2.1. Chemicals and reagents

All the metal salts and H_2oba were procured from Aldrich and used as received. All other chemicals were acquired from S.D. Fine Chemicals, India. Solvents were purified prior to use. All solvothermal syntheses were performed in Teflon-lined stainless steel autoclaves under autogenous pressure.

2.1.1. Synthesis of bis-(4-imidazol-1-yl-phenyl)-diazene (azim)

This ligand was prepared by following a method (Scheme 1) as described below.

2.1.1.1. Synthesis of 1-(4-nitro-phenyl)-1H imidazole. A mixture of imidazole (2.1 g; 31.18 mmol) and anhydrous K_2CO_3 (42.52 mmol) in DMF (30 mL) was heated for 30 min with vigorous stirring. 4-fluoronitrobenzene (4 g, 28.34 mmol) was added to this over a period of 15 min and the reaction mixture was refluxed for 8 h. The reaction mixture was poured to ice-cold water and allowed to stand overnight. The resulting yellow precipitate was filtered off, washed with water and dried in air to get the pure compound in 85% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.21(s, 1H, H_{ar}), 7.32 (s, 1H, H_{ar}), 7.52(d, J = 9.28 Hz, 2H, H_{ar}), 7.94(s, 1H, H_{ar}), 8.31(d, J = 9.28 Hz, 2H, H_{ar}). *Anal.* Calc. for $C_{18}H_{22}N_4$: C, 73.44; H, 7.53; N, 19.03. Found: C, 73.59; H, 7.41; N, 19.12%.

2.1.1.2. Synthesis of bis-(4-imidazol-1-yl-phenyl)-diazene (azim). To a suspension of 1-(4-nitro-phenyl)-1H imidazole (5 g, 26.45 mmol) in 2-propanol, aqueous NaOH (12 g in 30 mL H_2O) and Zn powder (30 g) were added and the mixture was heated to reflux for 6 h. After cooling the reaction mixture to room temperature, the insoluble materials were separated by filtration and the filtrate was removed under reduced pressure to get orange oil and extracted with chloroform. The organic layer was washed several times with water and finally evaporated under reduced pressure to give a bright orange solid in 72% yield.

^1H NMR ($CDCl_3$, 400 MHz): δ 7.00 (s, 1H, H_{ar}), 7.31 (s, 1H, H_{ar}), 7.13(d, J = 8.56 Hz, 2H, H_{ar}), 7.56 (s, 1H, H_{ar}), 7.48 (d, J = 8.8 Hz, 2H, H_{ar}); IR (cm^{-1}, KBr disk): 3103(m), 1599(s), 1515(m), 1305(w); MS(ESI); m/z (rel. intensity): 315(100); calculated 314.65. *Anal.* Calc. for $C_{18}H_{14}N_6$: C, 42.83; H, 5.72; N, 1.85. Found: C, 43.93; H, 5.09; N, 1.22%.

2.1.2. Synthesis of 1,3- bis-(4′-carboxyphenoxy)benzene (bcpH_2)

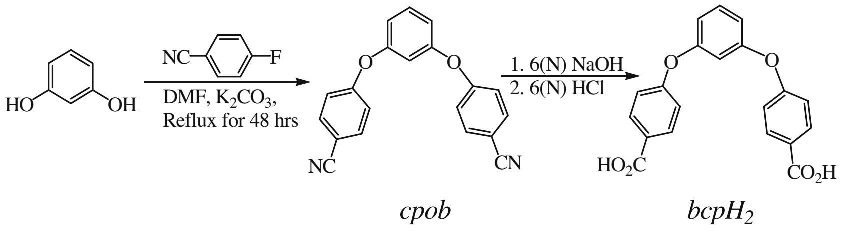
This ligand was prepared by following a method (Scheme 2) as described below.

2.1.2.1. Synthesis of 1,3-bis-(4′-cyanophenoxy)benzene (cpob). A mixture of resorcinol (1.1 g, 10 mmol) and anhydrous K_2CO_3 (7 g) in DMF (50 ml) was heated for 30 min under argon atmosphere. 4-fluorobenzonitrile (2.4 g, 20 mmol) was added drop wise to this and the reaction mixture was refluxed for 48 h. The resulting brown solution was poured in 250 ml ice-cold water and kept over-night. The light yellow crystalline compound was filtered, washed several times with water and finally air-dried. Melting point: 96 °C. FAB-MS, m/z (%): 335 (100) [*cpob*$^+$]. ^1H NMR (400 MHz, DMSO-d_6), TMS, 25 °C): δ (ppm) 6.76 (t, 1H, Ph-H), 6.89 (m, 2H, Ph-H), 7.04 (m, 4H, Ph-H), 7.41 (t, 1H, Ph-H), 7.61 (m, 4H, Ph-H). IR (KBr, cm^{-1}, selected peak): 2210 (ν(CN)). *Anal.* Calc. for $C_{20}H_{12}N_2O_2$: C, 76.91; H, 3.87; N, 8.97. Found: C, 76.83; H, 3.84, N, 8.89%.

2.1.2.2. Synthesis of 1,3- bis-(4′-carboxyphenoxy)benzene (bcpH$_2$). Aqueous ethanolic solution of ligand *cpob* (3.12 g; 0.01 mol) was allowed to reflux with 6 N NaOH solution (50 mL) until the smell of ammonia gas ceases. The reaction mixture was cooled to room temperature and acidified with HCl (6 N) while the temperature was maintained below 5 °C throughout. Colorless crystalline product in 60% yield was isolated by filtration, washed several times with water and dried in vacuum. Melting point: 210 °C. FAB-MS, m/z (%): 350 (100) [*bcpH*$_2^+$]. ^1H NMR (400 MHz, DMSO-d_6), TMS, 25 °C): δ (ppm) 6.62 (t, 1H, Ph-H), 6.77 (m, 2H, Ph-H), 7.19 (m, 4H, Ph-H), 7.22 (t, 1H, Ph-H), 7.96 (m, 4H, Ph-H). IR (KBr, cm^{-1}, selected peaks): 3480 (ν(OH)), 1683 (ν(CO)). *Anal.* Calc. for $C_{20}H_{14}O_6$: C, 68.57; H, 4.02. Found: C, 68.80; H, 3.98%.

2.1.3. Synthesis of [Cd(azim)(bcp)]$_n$ (**1**)

A mixture of *azim* (1 mmol), bcpH_2 (1 mmol) and $Cd(NO_3)_2 \cdot 6H_2O$ (2 mmol) was dissolved in 4 ml DMF. The mixture was placed in a Teflon-lined stainless steel autoclave. The vessel was sealed and heated to 110 °C for 72 h and then cooled to room temperature at the rate of 1 °C per minute. Orange rectangular crystals were collected in ~50% yield from the reaction mixture. *Anal.* Calc. for $C_{38}H_{26}CdN_6O_6$: C, 58.87; H, 3.38; N, 10.85. Found: C, 58.58; H, 3.25; N, 11.03%.



Scheme 2. Synthetic scheme for ligand bcpH_2.

Table 1
Crystal and structure refinement data for **1** and **2**.

Empirical formula	$C_{38}H_{26}CdN_6O_6$ (**1**)	$C_{32}H_{24}CdN_6O_6$ (**2**)
Formula weight	775.05	700.97
Temperature (K)	100(1)	100(1)
Radiation, wavelength (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Crystal system	monoclinic	triclinic
Space group	$P21/c$	$P\bar{1}$
a (Å)	6.876(5)	11.587(4)
b (Å)	26.827(5)	11.855(4)
c (Å)	17.715(5)	12.382(5)
α (°)	90.00	72.234(6)
β (°)	94.337(5)	69.414(5)
γ (°)	90.00	70.131(5)
U (Å^3)	3258(3)	1463.7(9)
Z	4	2
ρ_{calc} (Mg/m^3)	1.580	1.590
μ (mm^{-1})	0.730	0.803
F(0 0 0)	1568	708
Reflections collected	20272	7376
Independent reflections	5778	4803
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit (GOF)	1.066	1.122
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0645$ $wR_2 = 0.1120$	$R_1 = 0.0712$ $wR_2 = 0.1745$
R indices (all data)	$R_1 = 0.1085$ $wR_2 = 0.1928$	$R_1 = 0.1039$ $wR_2 = 0.2298$

Table 2
Selected bond distances (Å) and bond angles (°) in **1** and **2**.

1					
Cd1–N6	2.229(6)	Cd1–N1	2.237(6)	Cd1–O5	2.254(5)
Cd1–O1	2.339(6)	Cd1–O2	2.398(5)	Cd1–O6	2.407(6)
N6–Cd1–N1	101.8(2)	N6–Cd1–O5	101.22(19)	N1–Cd1–O5	116.5(2)
N6–Cd1–O1	103.1(2)	N1–Cd1–O1	132.3(2)	O5–Cd1–O1	97.6(2)
N6–Cd1–O2	91.2(2)	N1–Cd1–O2	85.0(2)	O5–Cd1–O2	151.7(2)
O1–Cd1–O2	54.55(19)	N6–Cd1–O6	156.53(18)	N1–Cd1–O6	85.4(2)
O5–Cd1–O6	56.18(17)	O1–Cd1–O6	87.5(3)	O2–Cd1–O6	111.8(2)
2					
Cd1–O2	2.235(5)	Cd1–O4	2.239(6)	Cd1–N4	2.244(6)
Cd1–N1	2.251(7)	Cd1–O5	2.512(7)	Cd1–O3	2.541(6)
O2–Cd1–O4	140.3(2)	O2–Cd1–N4	114.8(2)	O4–Cd1–N4	91.8(2)
O2–Cd1–N1	89.0(2)	O4–Cd1–N1	113.8(2)	N4–Cd1–N1	103.8(2)
O2–Cd1–O5	98.8(2)	O4–Cd1–O5	54.8(2)	N4–Cd1–O5	145.3(2)
N1–Cd1–O5	84.4(3)	O2–Cd1–O3	54.37(18)	O4–Cd1–O3	99.3(2)
N4–Cd1–O3	90.2(2)	N1–Cd1–O3	143.2(2)	O5–Cd1–O3	103.3(3)

2.1.4. Synthesis of {[Cd(azim)(oba)](H_2O)}$_n$ (**2**)

A mixture of *azim* (1 mmol), $obaH_2$ (1 mmol) and $Cd(NO_3)_2 \cdot 6H_2O$ (2 mmol) was dissolved in DMF (4 mL) and the resulting slurry was stirred at room temperature for 3 h. After the orange precipitate had been filtered off, the solution was heated to 110 °C in a Teflon-lined stainless steel autoclave for 60 h and then cooled to room temperature at the rate of 1 °C per minute. Block-shaped orange crystals were collected in ~60% yield from the reaction mixture. *Anal.* Calc. for $C_{32}H_{24}N_6O_6Cd$: C, 54.83; H, 3.45; N, 11.99. Found: C, 54.88; H, 3.42; N, 11.97%.

2.2. Physical measurements

Spectroscopic data were collected as follows: IR (KBr disk, 400–4000 cm^{-1}) Perkin–Elmer Model 1320; X-ray powder pattern (Cu Kα radiation at a scan rate of 3°/min, 293 K) with either Siefert ISODEBYEFLEX-2002 or Phillips PW 100 diffractometers; thermogravimetric analysis (heating rate of 5 °C/min) Perkin–Elmer Pyris 6. Microanalyses for the compounds were obtained from the Central Drug Research Institute, Lucknow, India. FAB-MS (positive ion) data were recorded on a JEOL SX 102 /DA-6000 mass spectrometer using argon as the FAB gas at 6 kV and 10 mA with an accelerating voltage of 10 kV at 298 K. ^{1}H NMR spectra recorded on a JEOL JNM-LA400 FT (400 MHz) instrument in DMSO-d^6 with Me_4Si as internal standard. Melting points were recorded with an electrical melting point apparatus by PERFIT, India.

2.3. X-ray crystallography

Single-crystal X-ray data on **1** and **2** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT [43] software. An empirical absorption correction was applied to the collected reflections with SADABS [44] using XPREP [45]. The structure was solved by the direct method using SHELXTL [46] and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97 [47] program package. The non-hydrogen atoms were refined anisotropically unless otherwise mentioned. The hydrogens were treated as riding atoms using SHELXL default parameters. Each of the C atoms of (C18–C23) of one benzene ring in the 'azim' ligand of complex **2** is disordered over two positions with occupancy of 0.5. Similarly N5, N6, O5 are also disordered over two positions. Atom Ow1 is disordered over three positions. All of these disordered atoms were refined isotropically. Details of the data collections, solutions and refinements for **1** and **2** are

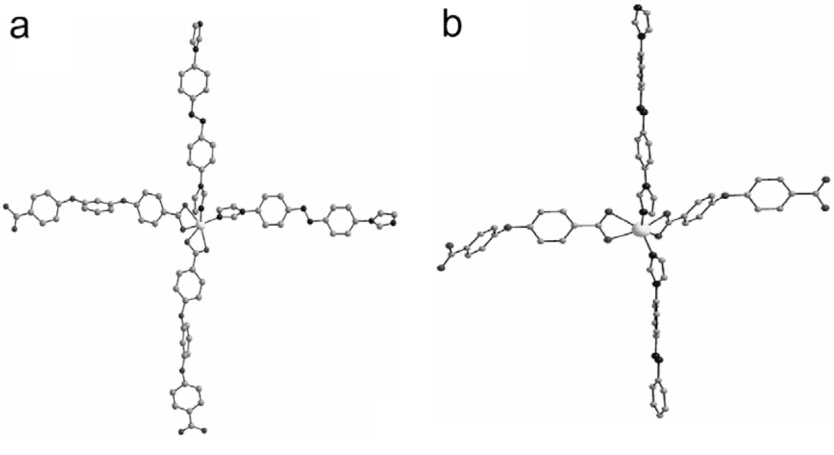


Fig. 1. Coordination environment around Cd(II) centers in (a) **1** and (b) **2**. All the H-atoms have been omitted for clarity.

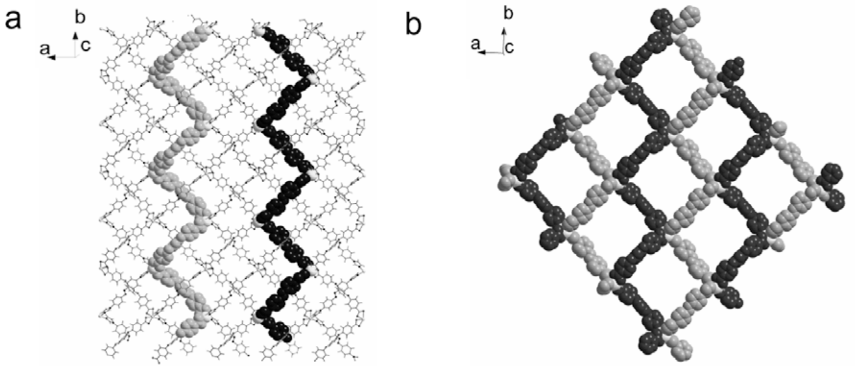


Fig. 2. (a) Perspective view of (a) the right-handed helical chains and (b) unprecedented 2D grid structure in **1**. Two different layers are shown in two different shades of grayscale.

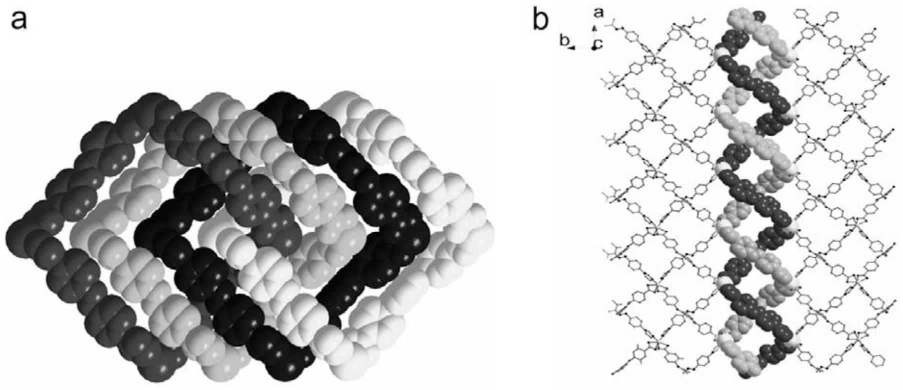


Fig. 3. (a) Unprecedented 4fold network and (b) double helical chains built with [Cd(bcp)(azim)] units along the crystallographic *a* axis in **1**.

given in Table 1 while their selective bond distances and bond angles are summarized in Table 2.

3. Results and discussion

Single-crystal X-ray diffraction study reveals that asymmetric unit of **1** consists of one Cd(II) ion, one azim ligand and one bcp^{2-} ligand. Each metal is bonded to two imidazole nitrogen atoms from two different azim ligands and four oxygen atoms from two different *cis*-oriented bcp^{2-} ligands (Fig. 1a). This binding mode forms a distorted octahedral coordination geometry around each metal ion with average Cd(II)···N(imidazole) distance of 2.23 Å and average Cd(II)···O (carboxylate) distance of 2.344 Å which are slightly longer compared to reported [48] octahedral Cd(II) complexes.

Each bcp^{2-} ligand in **1** adopts a bent structure with average C–O–C bond angle of 118.95° at the substituted ring and each carboxylate donates both its O atoms to a single Cd(II) ion. The resultant neutral [Cd(bcp)]$_n$ units extend as an infinite right-handed –C–O–Cd– helical chain along the crystallographic *b* axis with minimum Cd(II)···Cd(II) separation of 19.11 Å. In the same direction, *trans*-azim ligands join Cd(II) ions to form cationic {[Cd(azim)]$^{2+}$}$_n$ units as an infinite –C–N–Cd– right-handed helical chain where minimum separation between metal ions is 19.31 Å (Fig. 2a). Top view of [Cd(bcp)]$_n$ helix is oval-shaped while that of {[Cd(azim)]$^{2+}$}$_n$ helix is rectangular due to different steric requirements of the two ligands [49].

Both [Cd(bcp)]$_n$ and {[Cd(azim)]$^{2+}$}$_n$ helical chains are interconnected to each other through a common Cd(II) center and generates an unprecedented 2D grid structure (Fig. 2b). Each grid is composed of four Cd(II) ions as corners and two azim and two bcp^{2-} ligands as edges. As a result, large almost square-shaped cavity (19.11 × 19.31 Å^2) is produced. An interesting feature in **1** is the independent interpenetration of two exactly similar square grids within each other like a “one over/one under” clothlike topology

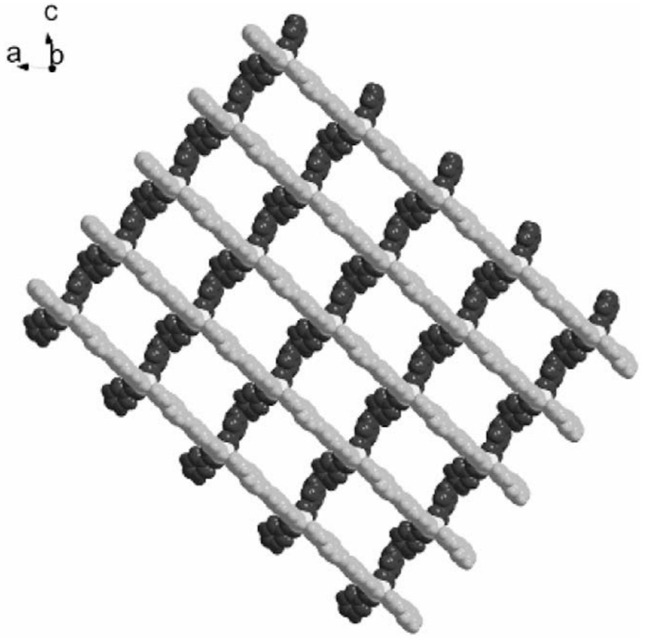


Fig. 4. Space filling view of 2D grid structure in **2**.

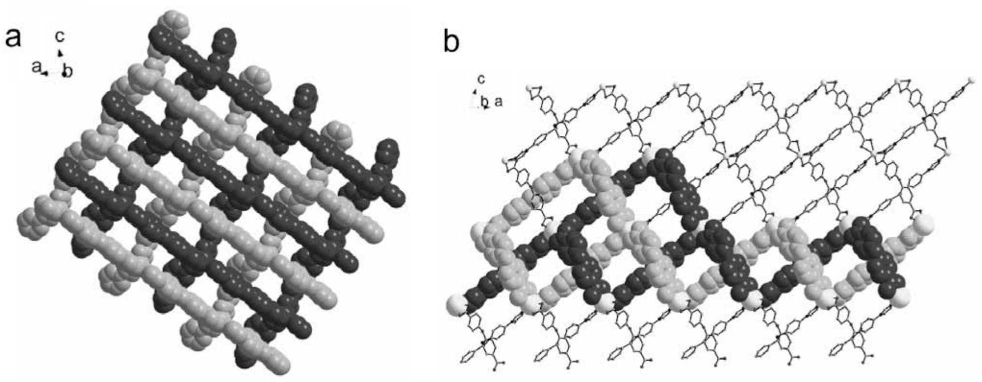


Fig. 5. (a) A perspective view of the interpenetrated structure and (b) the double-stranded helical structure along crystallographic *a* axis in **2**. For clarity, all the H-atoms have been omitted.

(Fig. 3a) [50–52], which can be designated as 4-fold "sql" stacking [20] as ABAB along [0 0 1] direction. This interpenetration leads to double helical chains built with [Cd(bcp)(azim)] units along the crystallographic *a* axis (Fig. 3b). A deep insight into the structure of **1** reveals that the double helix is stabilized by C–H$\cdots\pi$ stacking interactions involving aromatic H atoms of bcp^{2-} ligand with nearby benzene ring of azim ligand [49]. These 2D interwoven networks are stacked in a parallel manner along the crystallographic *c* axis into a 3D network such that metal ions are not on top of each other.

Crystals of **2** are also obtained in high yield following solvothermal reaction of azim ligand with $Cd(NO_3)_2{\cdot}6H_2O$ and V-shaped $obaH_2$ ligand. The asymmetric unit consists of one ligand each, a Cd(II) ion and one water molecule. Here, the Cd(II) ion is distorted octahedral with equatorial coordination from four O atoms from two different oba^{2-} ligands and axial coordination from two different *trans* oriented azim ligands (Fig. 1b). Unlike in case of **1**, here each similar ligand is bonded in a *trans*-fashion in **2** and this difference in bonding leads to different overall 2D structure (described later).

Similar to **1**, both the average Cd(II)–O (2.381 Å) and Cd(II)–N distances (2.247 Å) in this complex are slightly longer compared [50–52] to published octahedral Cd(II) complexes. The oba^{2-} ligand maintains its V-shape with the C–O–C bond angle showing 115.8°. Here, each Cd(II) ion serves as 4-connected node and linked by oba^{2-} and azim ligands to form rectangular grid corrugated sheets (Fig. 4) of dimension (14.35×19.61 Å^2). The average diagonal distance of each rectangle is 24.30 Å.

It is noteworthy that the metal ions in **2** are not coplanar but are present in stair-like conformation. These stair-like layers are interpenetrated to each other, resulting in the formation of a doubly interpenetrated 2D layered network (Fig. 5a). This type of interpenetration leads to the formation of double-stranded helical structure along the crystallographic *a* axis (Fig. 5b). The 2D interpenetrated layers are stacked as ABAB fashion along [0 1 0] direction attaining a 2-fold "sql" net structure [20].

The interlayer aggregation is supplemented by relatively strong C–H$\cdots\pi$ interaction (ranging from 4.326–4.798 Å) between aromatic H atoms of azim benzene rings and benzene rings of oba^{2-} of the adjacent layer. These layers are also interdigitated via $\pi\cdots\pi$ interactions (3.618 Å) viewed down [1 0 1] direction where the imidazole and benzene rings are parallels to each other. Neighboring layers are related by crystallographic inversion centers with average interlayer M–M contact distance 12.14 Å.

In spite of interpenetration in **2** there is still some void space where one lattice water molecule is accommodated. The FTIR spectrum of as synthesized **2** shows a broad band centered on 3500 cm^{-1} due to the O–H stretching frequency of the water molecule. Thermal analysis of **2** shows [49] that the lattice water molecule is lost between 80 and 100 °C along with a steady weight loss of ~10% up to 350 °C. Complete decomposition is achieved soon after. In comparison, **1** loses weight steadily beginning at ~80 °C and about 25% weight loss occurs up to 330 °C before complete decomposition.

4. Conclusion

In conclusion, we have successfully prepared two 2D coordination polymers of different morphology using a long dimidazole ligand and different angular dicarboxylates with a molecular angle less than 180°. This work demonstrates that extended structural motifs can be constructed through neutral or cationic 1D helical chains and assembly of mixed bridging organic ligands with metal ions can afford a broader way to construct helical architecture than using single bridging ligand. This is the first report of mixed-ligand polymer comprising helical chains from previously unknown azim and $bcpH_2$ ligands. We believe that judicious variance of the conformational flexibility and donor disposition of long rigid or angular ligands is likely to exploit in the context of rational design of coordination polymers.

Acknowledgements

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Appendix A. Supplementary data

CCDC 686278 and 686279 contains the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.09.005.

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