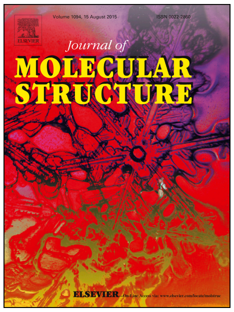

Synthesis and characterization of three new Cd(II) coordination polymers with bidentate flexible ligands: Formation of 3D and 1D structures

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PII: S0022-2860(18)30620-3

DOI: 10.1016/j.molstruc.2018.05.054

Reference: MOLSTR 25227

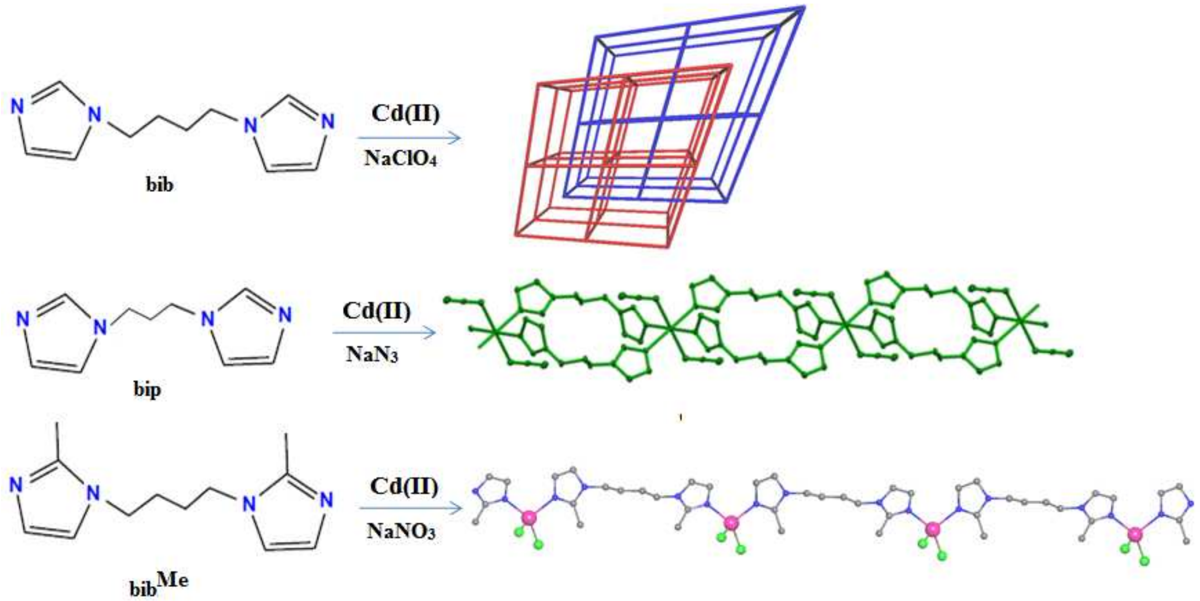
To appear in: *Journal of Molecular Structure*

Received Date: 22 January 2018

Revised Date: 19 April 2018

Accepted Date: 15 May 2018

Please cite this article as: M. Khalaj, A. Lalegani, J. Akbari, M. Ghazanfarpour-Darjani, K. Lyczko, J. Lipkowski, Synthesis and characterization of three new Cd(II) coordination polymers with bidentate flexible ligands: Formation of 3D and 1D structures, *Journal of Molecular Structure* (2018), doi: 10.1016/ j.molstruc.2018.05.054.


N
N
bib
Cd(II)
NaClO4
bip
Cd(II)
NaN3
bib^Me
Cd(II)
NaNO3

Synthesis and characterization of three new Cd(II) coordination polymers with bidentate flexible ligands: Formation of 3D and 1D structures

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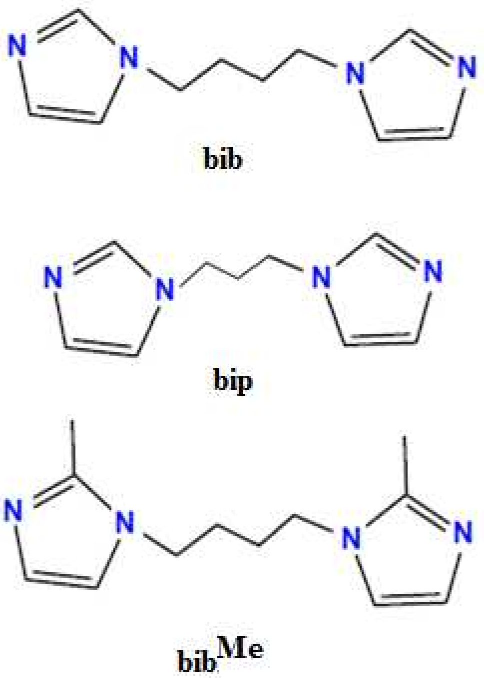
Abstract

Three new coordination polymers of $\{[Cd(bib)_3](ClO_4)_2\}_n$ (**1**), $[Cd(\mu_2\text{-bip})_2(N_3)_2]_n$ (**2**) and $[Cd(\mu\text{-bib}^{Me})Cl_2]_n$ (**3**) were prepared by using the neutral N-donor ligands 1,4-bis(imidazolyl)butane (**bib**), 1,3-bis(imidazolyl)propane (**bip**) and 1,4-bis(2-methylimidazolyl)butane (**bib^{Me}**) and CdX_2 ($X=ClO_4^-$, N_3^- and Cl^-). The results of the X-ray measurements demonstrate that in the crystal structure of **1** and **2** the cadmium(II) ion-adopts CdN_6 octahedral geometry while, in the structure of **3**, the metal ion forms CdN_2Cl_2 tetrahedral geometry. In compound **1**, six bib ligands are coordinated to one central cadmium(II) to form an open 3D 2-fold interpenetrating framework of the α-polonium (**pcu**) type topology, while in compound **2** and **3** the N_3^- or Cl^- groups are terminally bonded to the metal center and each linker compound (**bip** or **bib^{Me}**) acts as bridging ligand connecting two metal ions to form a one-dimensional zig-zag chain. The adjacent 1D chains of complex **2** and **3** are further extended into a non-covalent 2D network structure by C–H···N and C-H···Cl intermolecular hydrogen bonds, respectively. The complexes were characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction.

Keywords: Metal-organic frameworks; Cadmium(II) complexes; Coordination polymers; Crystal structure; Flexible nitrogen-donor ligands.

1. Introduction

During the past decade, the functional metal organic frameworks (MOF) and coordination polymers (CPs) with transition metal cores have stimulated great interests in the field of crystal engineering and material chemistry for not only their fascinating structures but also their potential applications in field such as sensing [1], luminescence [2,3], gas storage [4,5], separations [6], drug delivery [7], magnetism [8], catalysis [9] and bioapplications [10]. The final structures of coordination polymers are dependent upon the reaction medium, metal to ligand ratio, nature of ligand, metal center, counter ion and auxiliary ligand [11−16]. Therefore, the important factor for constructing CPs and MOFs mainly relies on selections of metal centers and bridging ligands. A relatively wide range of data is available in the literature concerning the preparation, characterization and application of copper, iron, mercury and zinc-containing MOFs [17-22]. The flexible N-donor ligand, 1,4-bis(imidazolyl)butane (**bib**) is a good candidate for the construction of coordination polymers [17,18,22], from which the most CPs show two- or three-dimensional structures. This ligand forms structures which have interpenetration and in this case, there is no free space in the solid state. To avoid interpenetration, the use of ligands **bip** and **bib**$^{\mathbf{Me}}$ is appropriate. The cadmium coordination polymers containing flexible organic ligands those derived from N, O and S-donor have been synthesized and structurally characterized [23-29]. Some Cd(II) coordination polymers were shown luminescent properties [23-25]. For example multicarboxylate ligand and bis imidazole was reacted with Cd(II) for constructing luminescent coordination polymers (LCPs) [30]. Also some Cd(II) networks were shown to enhance or quench the fluorescence emission of the organic ligand [31-32]. On the other hand, cadmium(II) compounds of thiones are important as simple structural model in metallothioneins [25-29]. For compounds of this metal, ligand-to-ligand charge transfer (LLCT) and ligand-to-metal charge transfer (LMCT) have been reported [33]. In turn, the d-d transitions are not expected for Cd(II) due to a d^{10} electronic configuration. In this paper we present the synthesis and structural characterization of three coordination polymers of Cd(II) ions with flexible imidazole based ligands (Scheme 1), in order to investigate the influence of the counter anion or coligand and ligand on the framework of the compounds.



Scheme 1. Structures of the flexible ligands; 1,4-bis(imidazolyl)butane **(bib)**, 1,3-bis(imidazolyl)propane **(bip)** and 1,4-bis(2-methylimidazolyl)butane (**bib^{Me}**).

2. Experimental

2.1. Materials and general methods

All experiments were carried out in air atmosphere. Starting materials were purchased from commercial sources and used without further purification. The ligands **bib** [34] and **bip** [35] were prepared according to the published methods. Infrared spectra (4000-400 cm^{-1}) were recorded using KBr pellets with a BOMEN MB102 FT-IR spectrometer. Elemental analyses for C, H and N were performed on a Thermo Finigan Flash EA 1120 CHN analyzer. X-ray powder diffraction patterns were recorded on a Philips X'Pert Pro diffractometer (Cu Ka radiation, λ = 1.54184 Å) in the 2θ range 5-50˚.

2.2. Preparation of 1,4-bis(2-methylimidazolyl)butane (bib^{Me})

This ligand was prepared according to the reported method [36] with some modification. Typically a mixture of 2-methylimidazole (4.1 g, 50 mmol) and KOH (2.8 g, 50 mmol) in THF (50 mL) was stirred at 66 °C for 1 h, and then the 1,4-dichlorobutane (3.2 g, 25 mmol) was added. The mixture was cooled to room temperature after being stirred at 60 °C for 24 h. In the next step THF was removed and the residue was extracted with ethyl acetate (100 × 3 mL). The extracted solution was put in a water bath (90 °C) for 3 h, and the colorless oil **bib^{Me}** was obtained in 70% yield. *Anal*. Calc. for $C_{12}H_{18}N_4$: C, 66.02; H, 8.31; N, 25.66;

found: C, 66.08; H, 8.34; N, 25.71%. Selected IR (KBr, cm^{-1}): 3162 (s), 2948 (s), 2681 (m), 2608 (m), 1672 (m), 1565 (m), 1500 (s), 1426 (s), 1362 (w), 1304 (m), 1280 (s), 1216 (s), 1146 (s), 1104 (s), 987 (s), 752 (s), 677 (s), 666 (s).

2.3. Preparation of $\{[Cd(bib)_3](ClO_4)_2\}_n$ (1)

A mixture of EtOH and water (1:1, 5 mL) was gently layered on the top of an aqueous solution (5 mL) of $CdCl_2$ (0.018g, 0.10 mmol) and $NaClO_4$ (0.025g, 0.20 mmol) in a test tube. A solution of **bib** (0.057g, 0.30 mmol) in EtOH (5 mL) was added carefully to the colorless solution as a third layer. Crystals suitable for X-ray crystallography were obtained after a few days. They were collected and washed with small amounts of water and dried in air (0.63 g, 69% based on Cd). *Anal.* Calc. for $C_{30}H_{42}CdCl_2N_{14}O_8$: C 39.59, H 4.65, N 21.55; found: C 39.63, H 4.68, N 21.59%. Selected IR (KBr, cm^{-1}): 3123 (m), 2949 (w), 2870 (m), 1630 (s), 1517 (s), 1460 (m), 1371 (s), 1283 (2), 1235 (s), 1094 (vs), 940 (s), 836 (s), 764 (m), 739 (w), 720 (s), 624 (s).

2.4. Preparation of $[Cd(\mu_2\text{-bip})_2(N_3)_2]_n$ (2)

A mixture of EtOH and water (1:1, 5 mL) was gently layered on the top of an aqueous solution (5 mL) of $CdCl_2$ (0.018 g, 0.10 mmol) in a test tube. A solution of **bip** (0.035 g, 0.2 mmol) and NaN_3 (0.013 g, 0.2 mmol) in EtOH/H_2O (2:1, 6 mL) was added carefully as a third layer. Transparent crystals were obtained after 4 days (0.44 g, 80% based on Cd). *Anal.* Calc. for $C_{18}H_{24}CdN_{14}$: C, 39.39; H, 4.41; N, 35.72; found: C, 39.43; H, 4.46; N, 35.43%. Selected IR (KBr, cm^{-1}): 3335 (w), 3114 (m), 2035 (vs), 1619 (w), 1516 (s), 1460 (w), 1440 (w), 1434 (w), 1395 (w), 1326 (m), 1233 (m), 1105 (s), 1085 (s), 930 (s), 828 (m), 750 (m), 660 (s).

2.5. Preparation of $[Cd(\mu\text{-bib}^{Me})Cl_2]_n$ (3)

This compound was obtained as an unexpected product in an attempt to synthesize $\{[Cd(bib^{Me})_3](NO_3)_2\}_n$. A mixture of EtOH and water (1:1, 5 mL) was gently layered on the top of an aqueous solution (5mL) of $CdCl_2$ (0.018g, 0.10 mmol) and $NaNO_3$ (0.012g, 0.20 mmol) in a test tube. A solution of **bib^{Me}** (0.065g, 0.30 mmol) in EtOH (5 mL) was added carefully to the colorless solution as a third layer. Colorless crystals suitable for X-ray crystallography were obtained after a few days. They were collected and washed with small amounts of water and dried in air. X-ray analysis reveals that the crystals, with the molecular formula of $[Cd(bib^{Me})Cl_2]$, were the product of this reaction (0.33 g, 82% based on Cd). Anal. Calc. for $C_{12}H_{18}CdCl_2N_4$: C 35.89, H 4.52, N 17.65; found: C 35.92, H 4.55, N 17.68%.

Selected IR (KBr, cm^{-1}): 3126 (m), 2920 (m), 1518 (s), 1454 (m), 1315 (m), 1307 (m), 1268 (m), 1035 (m), 807 (m), 683 (m), 562 (m).

Caution: Perchlorate and Azide compounds are potentially explosive and should be handled with care.

2.6. X-ray crystallography

X-ray diffraction data were measured at 100K with a Mo Kα radiation (λ = 0.7107 Å) using a Rigaku SuperNova E (dual source) or a Bruker APEX II CCD diffractometers. For all operations (data collection, cell refinement, data reduction and multi-scan absorption correction) with both diffractometers CrysAlis PRO or Bruker software was used, respectively. The structures were solved by direct methods and refined by a full-matrix least-squares technique on F^2 data using SHELXTL programs [37]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were inserted in calculated positions and refined isotropically as a riding model. Details concerning the data collections and refinements are given in Table 1.

3. Results and discussion

3.1. Synthesis

Coordination polymers were prepared in ethanol-water solutions by the reactions 1-3 shown below.

$$CdCl_2 + 2NaClO_4 + 3bib \rightarrow Cd(bib)_3(ClO_4)_2 + 2NaCl \quad (1)$$

$$CdCl_2 + 2NaN_3 + 2bip \rightarrow Cd(\mu\text{-}bip)_2(N_3)_2 + 2NaCl \quad (2)$$

$$CdCl_2 + bib^{Me} \rightarrow Cd(bib^{Me})Cl_2 \quad (3)$$

They are stable and can be stored in a desiccator. Polymers are insoluble in common organic solvents such as DMF, MeCN and DMSO. The direct mixing of the reactants is not a general method for the preparation of these polymers because it leads to the formation of a precipitate of undefined compositions. In order to get suitable crystals of pure compound for the X-ray crystallography and further studies a three-layer diffusion method was used. In this method a buffer band (*ethanol-water*) is utilized to separate the two solutions, one of them is an aqueous solution of the cadmium(II) salt and the second is an ethanol solution of the imidazole based ligand. When these two solutions diffuse into the buffer band and meet with each other, the product slowly forms and crystallizes.

3.2. Description of Crystal Structures

3.2.1. Crystal Structure of 1

Single-crystal X-ray structural analysis reveals that this compound crystallizes in the trigonal space group *R-3* with Z=3 (Table 1). The crystal structure of **1** consists of 3D polymeric $[Cd(bib)_3]^{2+}$ macrocations and uncoordinated ClO_4^- anions. As shown in Fig. 1, the cadmium(II) ion lies on an inversion center and is coordinated by six nitrogen atoms from the imidazole rings of the six μ_2-bib ligands in an almost regular CdN_6 octahedral environment with the N-Cd-N bond angles close to 90˚ and the Cd-N distances being 2.356(11) and 2.355(11) Å (Table 2). The resemblance between the Cd-N bond lengths in **1** can be attributed to the fact that, the bib ligands represent one type of conformations, namely *anti-anti-anti* with shortest N···N and Cd···Cd distances of 10.25and 14.35 Å and dihedral angles of the two imidazole rings of 0˚. Six bib ligands are simultaneously coordinated to one central cadmium atom to form an open 3D 2-fold interpenetrating framework with α-polonium (pcu) topology [point symbol $(4^{12}.6^3)$] (Fig. 2). As is common for the 2-fold interpenetrating frameworks the values of the crystallographic parameters for both networks are the same. The topology of this coordination polymer was determined with the use of the ToposProprogram [38]. Examples of this topology have been reported in the literature for some coordination polymers [39-41]. In the structure of **1**, the ClO_4^- anions are located in the voids. Perchlorate anions are involved in the formation of the C-H···O hydrogen bonds between the oxygen atoms of the ClO_4^- anion and hydrogen atoms of the imidazole rings and $-(CH_2)_4-$ spacer of the μ_2-bib ligands (Fig. 3). Structural compression between **1** and $\{[Cd(btb)_3](PF_6)_2\}_n$ [**btb**=1,4-bis(1,2,4-triazol-1-yl)butane] shows that in the crystal structures of both compounds the conformation of the flexible ligands is *anti-anti-anti*, but **1** forms 3D 2-fold while, $\{[Cd(btb)_3](PF_6)_2\}_n$ 3D 3-fold interpenetrating framework [42]. Accordingly, flexible ligands are responsible for directing the interpenetrating of these polymers.

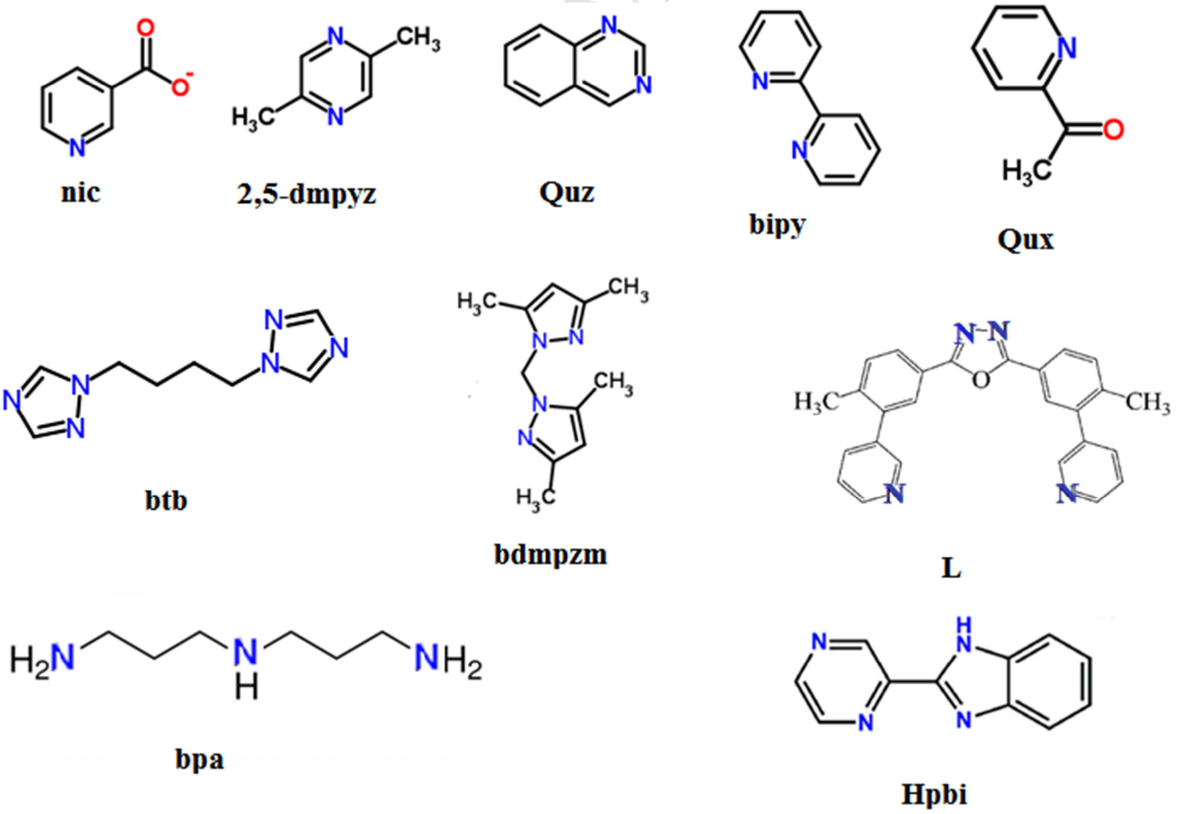
3.2.2. Crystal Structure of 2

Single crystal X-ray structural analysis reveals that this compound crystallizes in the triclinic space group P -1 with Z=1 (Table 1). In this structure there is one molecule in the unit cell (Table 1). This means that only half of the molecule is present in the asymmetric part of the unit cell. In this structure the cadmium atom is placed at the inversion center and is surrounded by six nitrogen atoms, which resemble the axially compressed octahedral coordination geometry. The equatorial plane is formed by four nitrogen atoms from the imidazole rings of the four symmetry related μ_2-**bip** ligands with the Cd-N distances being 2.356(1) and 2.329(1) Å. The axial positions are occupied by two azide nitrogen atoms with Cd-N bond lengths 2.365(2) Å. As a co-ligand, azide moiety is almost linear [N5-N6-N7 177.81(15)°] and bent at N5 atom [Cd1-N5-N6 122.61(10)°] (Table 2) what is common for the linear azide ligand which adopts an end-on terminal coordination mode (Fig. 4). In the structure **2**, two neighboring cadmium ions are interconnected by two bridging μ_2-**bip** ligands. As a result; a 20-membered macrocyclic dimeric unit is formed. The dimeric units are linked together and form infinite one-dimensional chains (Fig. 5). Crystal structure of **2** is built of layers formed by such chains. Each of the linker ligands adopts an *anti-gauche* conformation with the dihedral angle between the two imidazole rings of 72.3(1)° and links two Cd(II) ions through the imine nitrogen atoms. The shortest N···N and Cd···Cd distances are 7.64 and 10.69 Å, respectively. One H atom of the CH bond of the imidazole moiety of the bip ligand interacts with a N atom of azide to yield intermolecular C-H···N contacts with H···N distance of 2.52 Å. In the presence of these interactions, the neighboring chains are further extended into a 2D framework structure (Fig. 6). It is not surprising that small changes in the structure of flexible ligands as, for example a change of the position of the donor atoms or different spacer lengths can cause significant changes of the structures. Inserting the molecule of **nic** or **2,5-dmpyz** and **Quz** (see Scheme 2) to the structure of **2** instead of **bip** leads to the formation of 3D and 2D, respectively [9, 10]. In the others, where **bipy** or **acyp** are used instead of the **bip** ligand (see Scheme 2), the coordination polimers built of the 1D chains are also formed [43,44]. Moreover, the use of **bdmpzm** instead of **bip** leads to the formation of a monomer complex instead of a coordination polymer [45].

3.2.3. Crystal Structure of 3

This compound crystallizes in the orthorhombic space group $P\ 2_12_12_1$ with Z=4 (Table 1). As shown in Fig. 7, the cadmium(II) ion is coordinated by two chlorine anions with Cd-Cl distances of 2.438(1) and 2.446(1) Å and two N nitrogen atoms of two crystallographically equivalent μ-**bib**$^{\mathbf{Me}}$ ligands with Cd-N distance of 2.223(3) and 2.228(3) Å in a distorted tetrahedral CdN_2Cl_2 coordination geometry. The cadmium(II) ion has a slightly distorted tetrahedral geometry with large compression of the N6-Cd1-N7 angle [106.70(11)°] and enlargement of the Cl1-Cd1-N6 angle [112.56(8)°] (Table 2). In the crystal structure of **3**, the

~~μ~~-**bib**$^{\mathbf{Me}}$ compound acts as a bridging bidentate ligand, linking the Cd(II) centers into a one-dimensional zigzag chain structure running along the crystallographic b-axis (Fig. 8). Each of the linker ligands adopts an *anti- anti- anti* conformation with the dihedral angle between the two 2-methylimidazole rings of 35.51° and links two Cd(II) ions through the imine nitrogen atoms. The shortest N···N and Cd···Cd distances are10.12 and 13.58 Å, respectively. H atoms of the CH groups in the 2-methylimidazole moieties of the **bib**$^{\mathbf{Me}}$ ligand are involved in the intermolecular C-H···Cl contacts with the H··Cl distances of 2.77 (H9···Cl1) and 2.81 (H2···Cl2) Å. In the presence of these interactions, the neighboring chains are further extended into a 2D framework structure (Fig. 9). Inserting the molecule of **bpa** (see Scheme 2) to the structure of **3** instead of **bib**$^{\mathbf{Me}}$ leads to the formation of a dinuclear complex [46]. In the others, where **L** or **Hpbi** is used (see Scheme 2), the coordination polimers built of the 1D chains are formed, but the coordination geometry around cadmium is octahedral. On the other hand, **Hpbi** forms a 3D structure, through intermolecular X–H···Cl (X = N and C) hydrogen bonds and π–π stacking interactions [47,48]. Also the reaction of $CdCl_2$ and bib^{Me} ligand with variable ratios, in the absence of $NaNO_3$ led to obtain structure (3) (See Supplementary Information).



Scheme 2. Structures of the ligands: nicotinate anion (**nic**); 2,5- dimethylpyrazine (**2,5-dmpyz**); quinazoline (**Quz**); 2,2'-bipyridyl (**bipy**); 2-acetylpyridine (**acyp**); 1,4-bis(1,2,4-

triazol-1-yl)butane (**btb**); bis(3,5-dimethylpyrazol-1-yl)methane (**bdmpzm**); 3,5-bis(3-pyridyl-3-(3'-methylphenyl)-1,3,4-oxadiazole (**L**); bis(3-aminopropy1)amine (**bpa**) and 2-(pyrazin-2-yl)-1H-benzimidazole (**Hpbi**).

3.3. Spectroscopic characterization

The IR spectra of the complexes showed strong bands corresponding to the stretching vibration of the C=N bonds of the imidazole or 2-Methylimidazole rings of the bib, bip and bib^{Me} ligands at the range of 1516-1518 (s) cm^{-1}. The medium bands in the range of 3114-2870 cm^{-1} are mainly assigned to the C-H stretching vibrations of the CH_2 (for **1**-**3**) and CH_3 (**3**) groups of the bridging ligands. The infrared spectrum of **1** displays two sharp bands at 624 and 1094 cm^{-1} due to the vibrations of the ClO_4^- ion. In the case of **2** the intense absorption band at 2035 cm^{-1} is attributed to the azide ligand [49]. In order to confirm the phase purity of the synthesized polymers, X-ray powder diffraction (XRPD) experiments were carried out in which the experimental spectra were consistent with their simulated spectra (Fig. S1).

Conclusion

In conclusion, we have synthesized successfully three new cadmium(II) complexes with flexible imidazole-based ligands. These compounds display two different structures. Polymer **1** exhibits three-dimensional architecture while compounds **2** and **3** form one dimensional infinite polymeric chains. The structure of the last two complexes is extended into a 2D framework by means of hydrogen bonding interactions. Polymer **3** was obtained as an unexpected product in an attempt to synthesize the $\{[Cd(bib^{Me})_3](NO_3)_2\}_n$ compound. The results of this work indicate that the counter ions (such as ClO_4^-, N_3^- and Cl^-) and the structure of the flexible ligands have a significant influence on the formation and structure of these complexes.

Acknowledgement

We thank Young Researchers and Elite Club, Islamic Azad University Buinzahra Branch for financial support.

Appendix A. Supplementary data

CCDC 1562630, 1562476 and 1562477 contains the supplementary crystallographic data for **1**-**3**, respectively. Crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/datarequest/cif. 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

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Table 1. Crystal data and structure refinement for compounds 1-3.

	1	**2**	**3**
Chemical formula	$C_{30}H_{42}CdCl_2N_{12}O_8$	$C_{18}H_{24}CdN_{14}$	$C_{12}H_{18}CdCl_2N_4$
Formula weight	882.06	548.91	401.60
Diffractometer	APEX II CCD	SuperNova E	SuperNova E
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073
Crystal system	trigonal	triclinic	orthorhombic
Space group	R -3	P -1	$P\ 2_12_12_1$
a (Å)	13.543(4)	7.8163(3)	9.30590(10)
b (Å)	13.543(4)	9.0013(4)	9.8889(2)
c (Å)	18.048(5)	9.4913(3)	16.5699(3)
α (°)	90	76.215(3)	90
β (°)	90	75.570(3)	90
γ (°)	120	64.676(4)	90
V (Å^3)	2866.6(13)	577.91(4)	1524.85(4)
Z	3	1	4
$D_{calcd.}$ (g·cm^{-3})	1.533	1.577	1.749
μ (mm^{-1})	0.775	0.982	1.774
F(000)	1356	278	800
Crystal size (mm)	0.26 x 0.19 x 0.16	0.30 x 0.15 x 0.12	0.18 x 0.10 x 0.08
Reflections collected	10149	26093	49032
R_{int}	0.0668	0.0396	0.0445
Data/restraints/parameters	668/ 0/ 85	3219/ 0/ 151	4054/ 0/ 174
Final R [$I>2\sigma$(I)] R_1, wR_2	0.0935, 0.1868	0.0186, 0.0475	0.0276, 0.0712
GOF	1.112	1.063	1.206
Largest diff. peak/hole (e·Å^{-3})	1.065/ -2.007	1.022/ -0.528	1.609/ -0.628

Table 2. Selected bond distances (Å) and angles (°) for compounds 1-3.

Compound 1			
Cd1-N1	2.356(11)	Cd1-N1	2.355(11)
N1-Cd1-N1	90.0(4)	N1-Cd1-N1	180.0(6)
Compound 2			
Cd1-N1	2.356(1)	Cd1-N5	2.365(1)
Cd1-N3	2.329(1)	N5-Cd1-N5	180.00(4)
N1-Cd1-N5	88.08(4)	N5-Cd1-N3	88.93(4)
N1-Cd1-N1	180.00(4)	N5-Cd1-N3	91.07(4)
N1-Cd1-N5	91.92(4)	N3-Cd1-N3	180.00(4)
N1-Cd1-N3	93.95(4)	N5-N6-N7	177.81(15)
N1-Cd1-N5	86.05(4)	Cd1-N5-N6	122.61(10)
Compound 3			
Cd1-Cl1	2.438(1)	Cd1-N6	2.228(3)
Cd1-Cl2	2.446(1)	Cd1-N7	2.223(3)
Cl1-Cd1-Cl2	111.51(3)	Cl1-Cd1-N6	112.56(8)
Cl2-Cd1-N6	108.52(8)	Cl1-Cd1-N7	107.14(8)
Cl2-Cd1-N7	110.29(8)	N6-Cd1-N7	106.70(11)

Figure Captions:

Fig. 1. View of the coordination environment of Cadmium(II) in **1**.

Fig. 2. (a) View of the 3D α-polonium for single network of **1**. Hydrogen atoms and ClO_4^- are omitted for clarity. **(b)** View of the 2-fold interpenetrating network of **1**.**(c)** Schematic drawing of the 2-fold interpenetrated 3D structure of **1.**

Fig. 3. Non-classic C–H···O hydrogen bonds in the structure of **1**.

Fig. 4. View of the coordination environment of Cadmium(II) in **2**.

Fig. 5. Layered structures of **2** formed by 1D chain. Hydrogen atoms omitted for clarity.

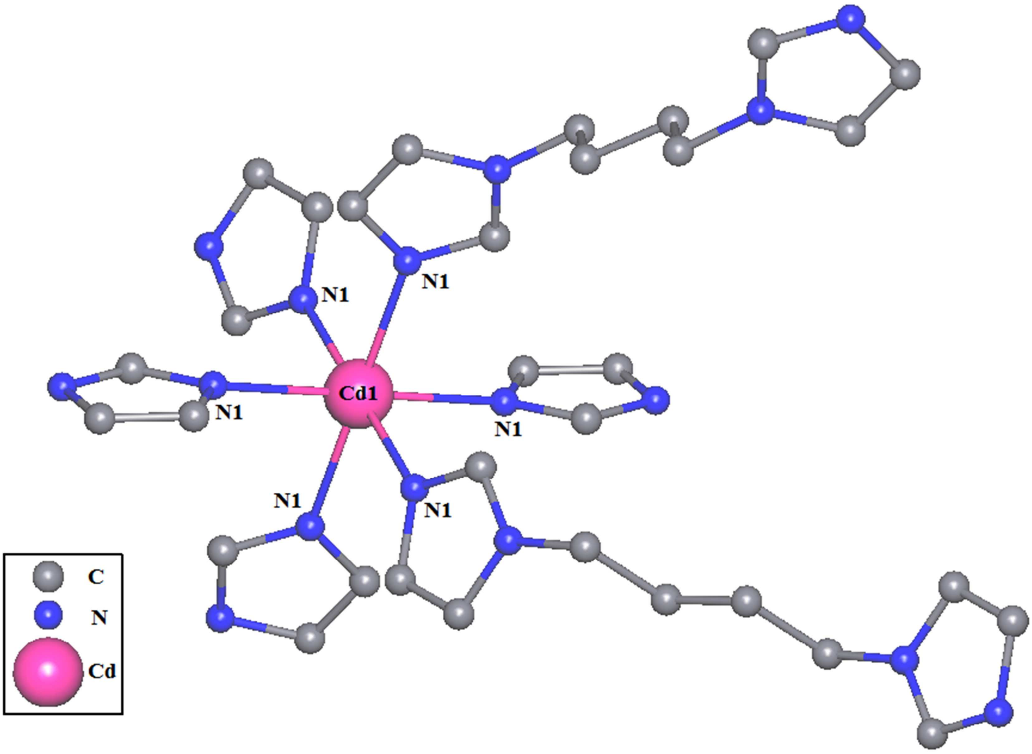
Fig. 6. View of the 2D of **2** formed by non-classic C–H···N hydrogen bonds.

Fig. 7. View of the coordination environment of Cadmium(II) in **3**.

Fig. 8. Layered structures of **3** formed by 1D chain. Hydrogen atoms omitted for clarity.

Fig. 9. View of the 2D of **3** formed by non-classic C–H···Cl hydrogen bonds.

Fig. S1. View of the X-ray powder diffraction (XRPD) experimental spectra and simulated spectra **1-3**.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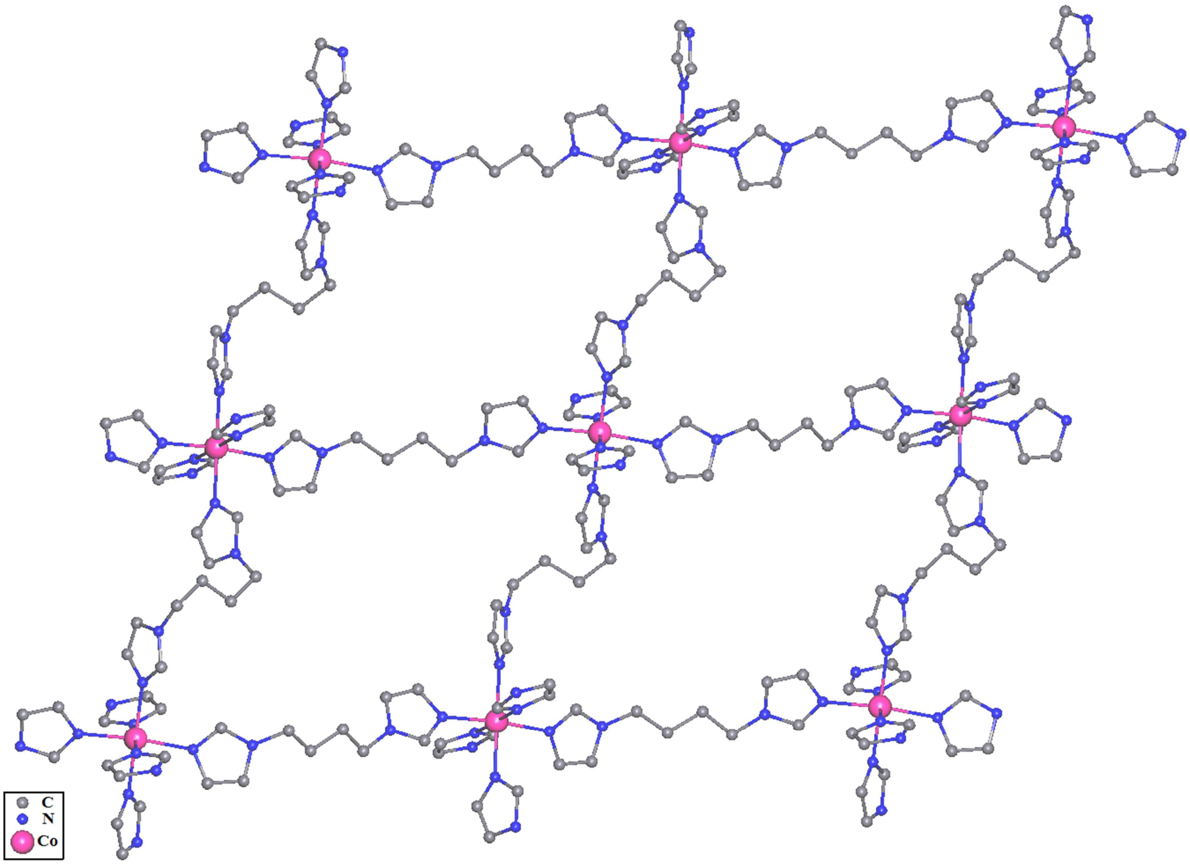
N1
N1
Cd1
N1
N1
N1
C
N
Cd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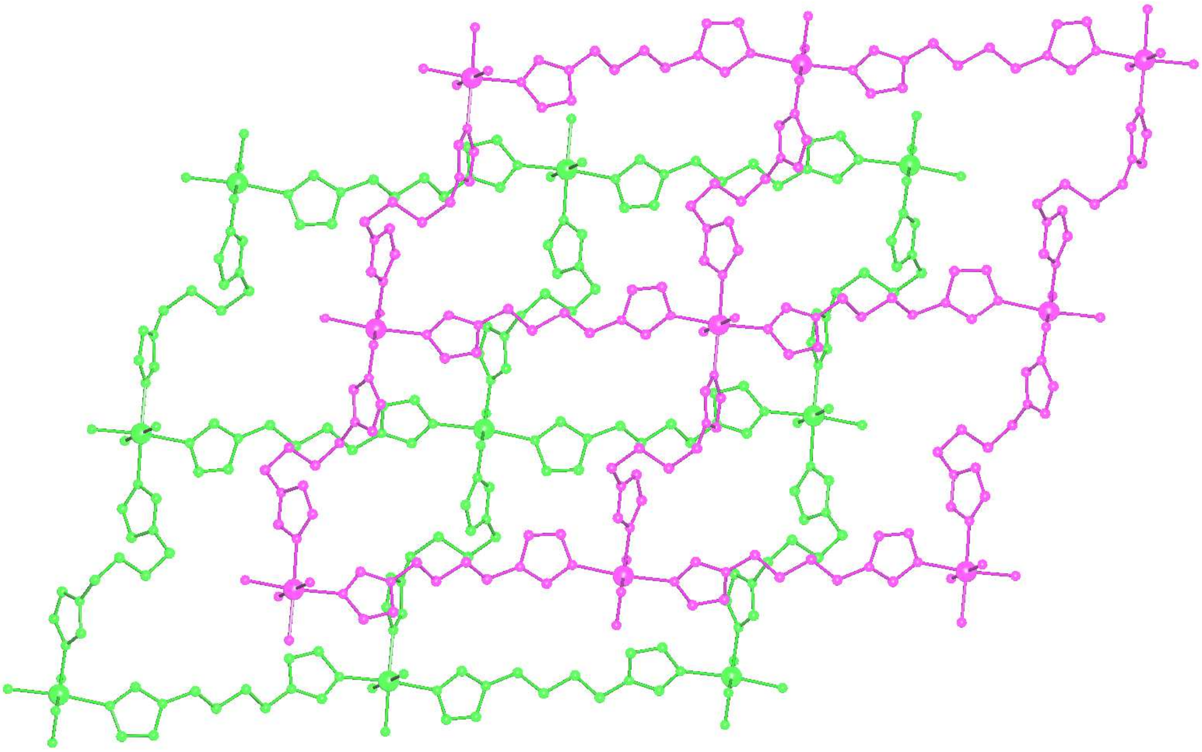

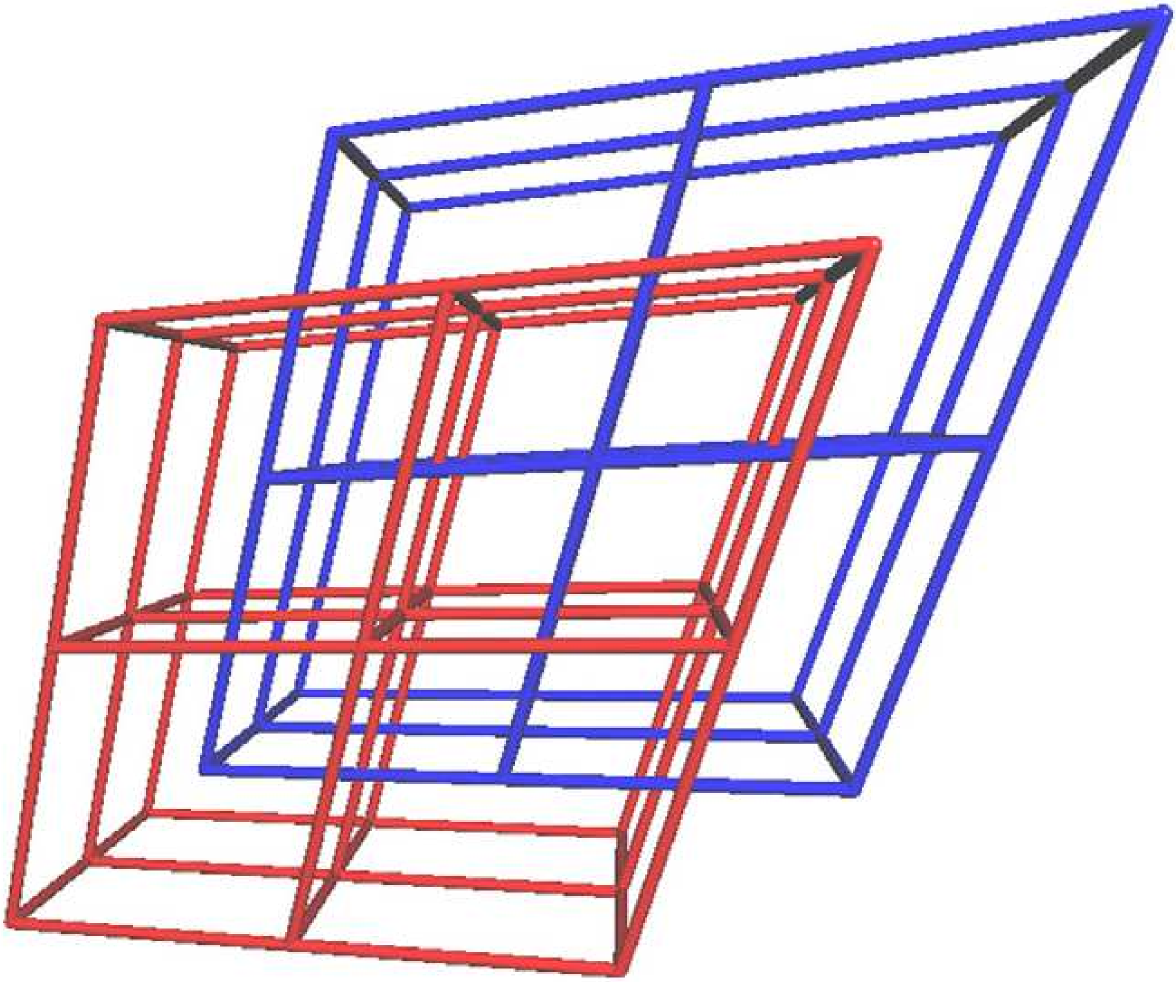

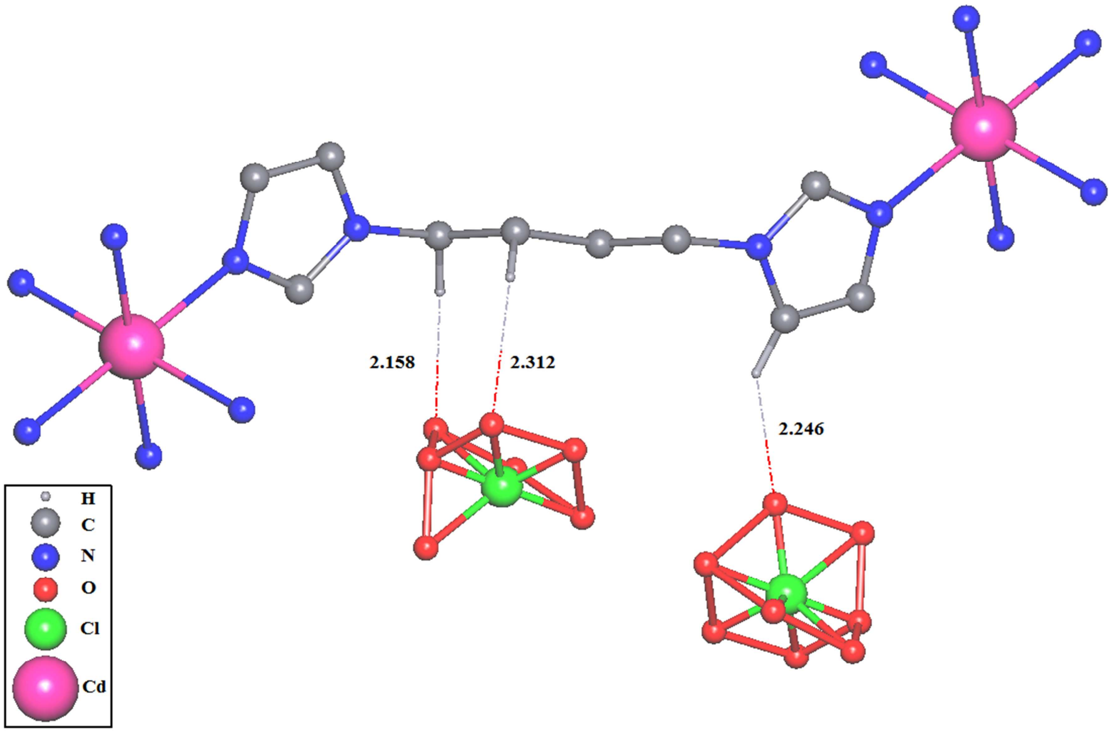
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2.246
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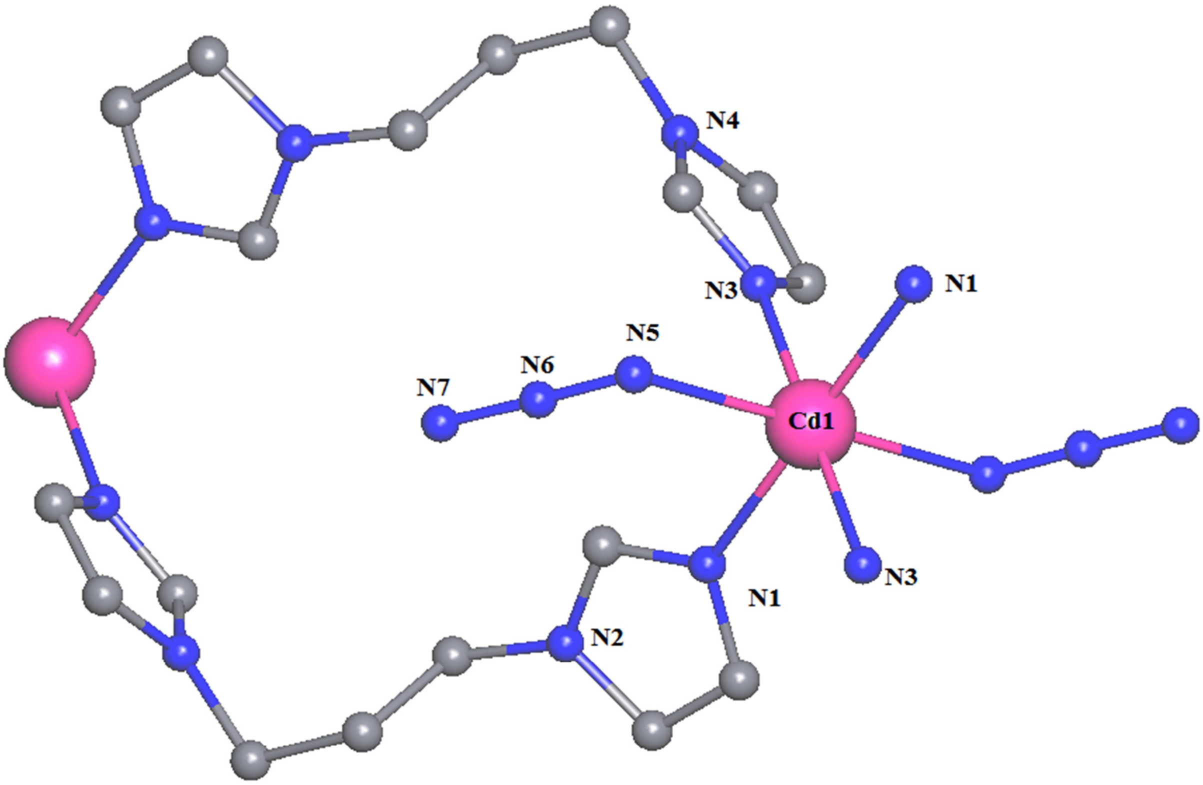
C
N
O
Cl
Cd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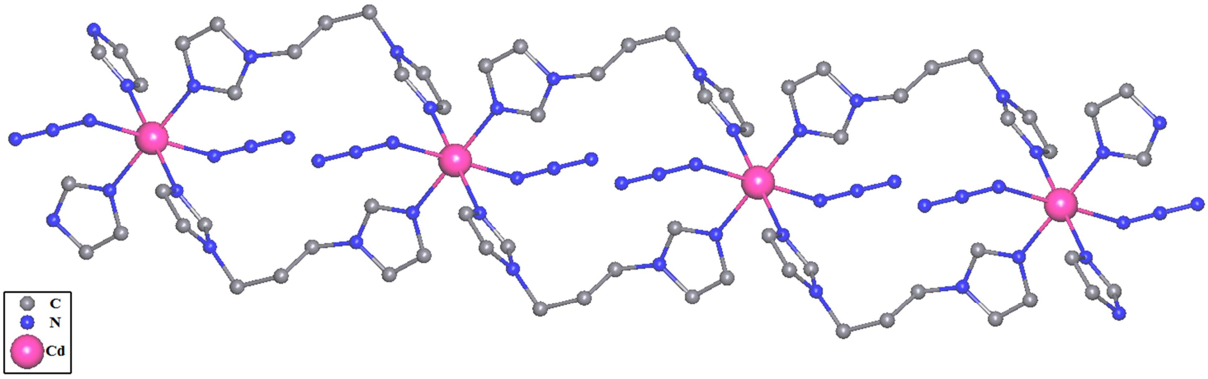
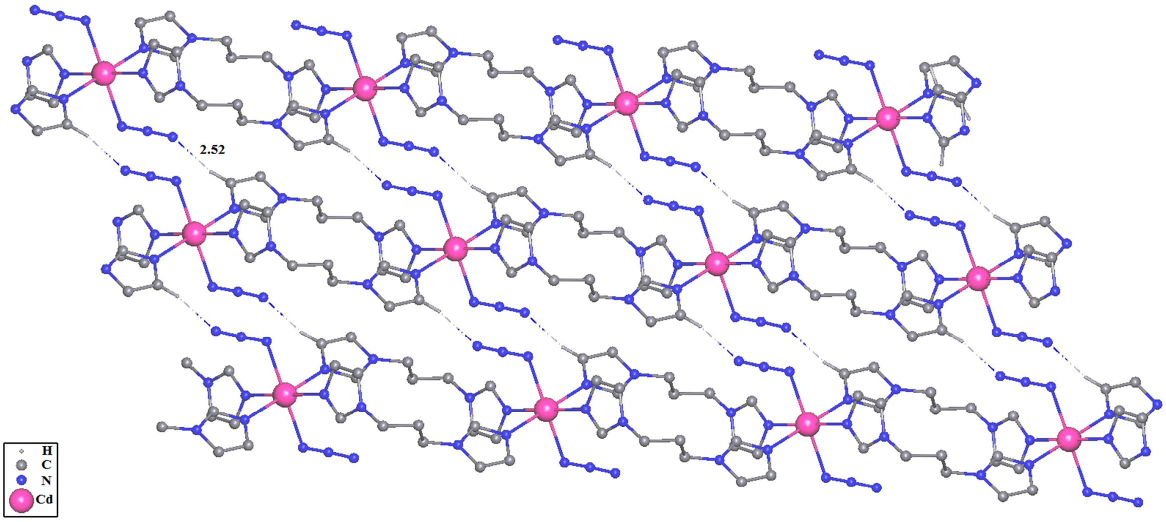
N3
N1
N5
N6
N7
Cd1
N3
N1
N2


C
N
Cd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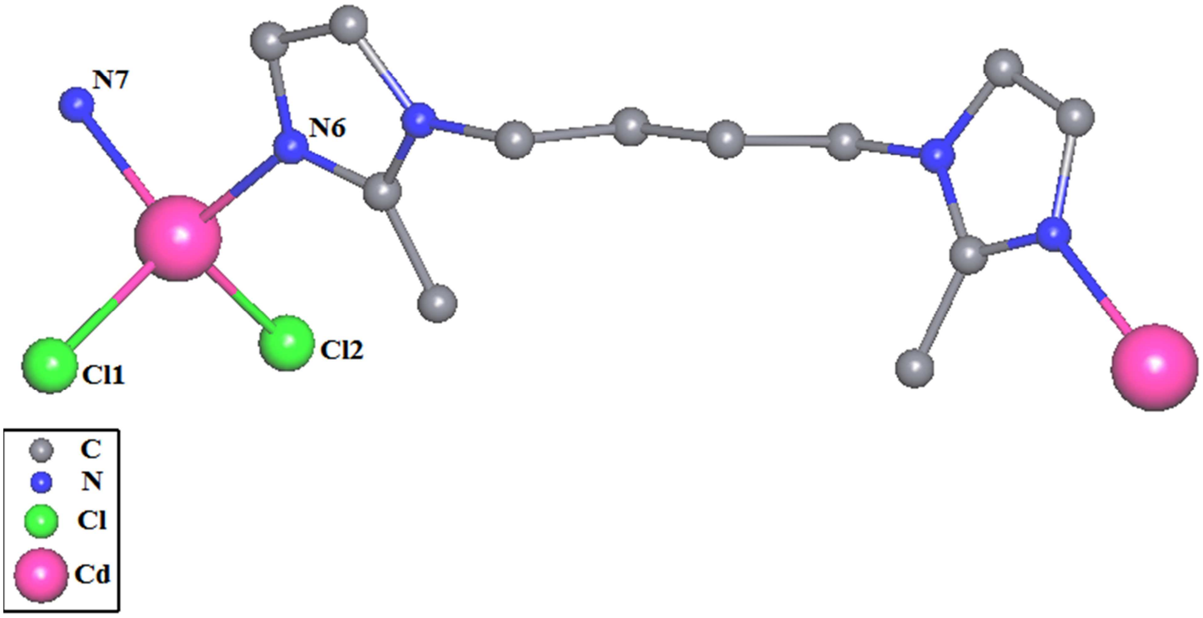
H
C
N
Cd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N6
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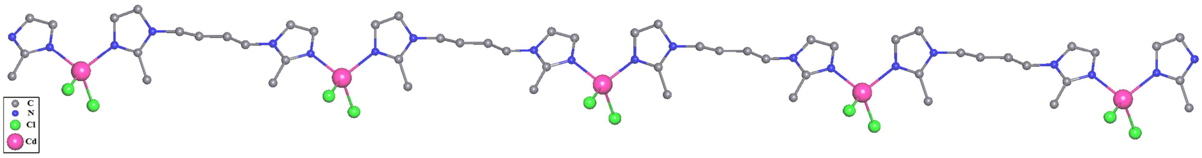
Cl2
C
N
Cl
Cd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N
Cl
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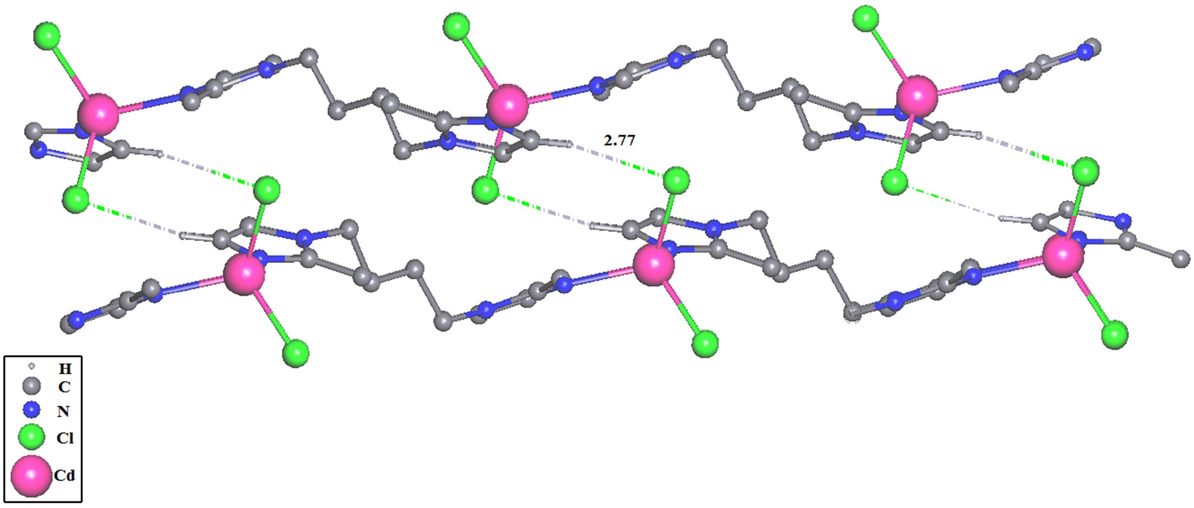
2.77
H
C
N
Cl
Cd

- **Highlights**

- Structure of the organic ligands plays a dominant role in the structure coordination polymers.
- Also counter ions such as ClO_4^-, N_3^- and Cl^- impact on the structure.
- The polymers have been characterized by X-ray diffraction, elemental and infrared spectroscopy.