

Chiral and achiral helical coordination polymers of zinc and cadmium from achiral 2,6-bis(imidazol-1-yl)pyridine: Solvent effect and spontaneous resolution

SARITA TRIPATHI, RENGANATHAN SRIRAMBALAJI, NAMITA SINGH and GANAPATHI ANANTHARAMAN*

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India
e-mail: garaman@iitk.ac.in

MS received 13 February 2014; revised 5 April 2014; accepted 7 April 2014

Abstract. Four 2D helical coordination polymers (CPs) (**1–4**) were synthesized using achiral 2,6-bis(imidazol-1-yl)pyridine (pyim₂) ligand with metal nitrates (metal = zinc and cadmium), which showed that variation in the solvent condition leads to difference in geometry around the central metal ion and results in chiral/achiral behaviour of these CPs. By using (pyim₂), [*trans*-Zn(pyim₂)₂(NO₃)₂]_n (**1**) was obtained by unary solvent (MeOH), while [*trans*-Cd(pyim₂)₂(NO₃)₂]_n (**2**) was formed under binary solvent mixtures (DMF/MeOH). On the other hand, in ternary solvent mixture (DMF/MeOH/H₂O) it resulted into an achiral {[*trans*-Zn(pyim₂)₂(H₂O)₂](NO₃)₂]_n (**3**) and homochiral {[*cis*-Cd(pyim₂)₂(H₂O)₂](NO₃)₂]_n (**4**) coordination polymer, respectively. The homochiral behaviour of the coordination polymer (**4**) was further studied by solid state CD spectra and also its optical behaviour was analyzed by polarimetry.

Keywords. Chirality; helical structures; spontaneous resolution; coordination polymers-cadmium; zinc

1. Introduction

Coordination polymers (CPs) have been an area of profound interest over the past two decades, not only for their rational design and intriguing topologies, but also for their potential application in various fields like storage, separation, magnetism, catalysis, and non-linear optics.^{1–5} Among the reported CPs, in recent years, a significant research interest has been devoted for chiral helical structural motifs.⁶ Chirality is one of the most important aspects of nature and is an intrinsic feature of various states of matters. Chirality and helicity are closely related terms and are strongly associated with the biological systems; in particular, chirality is often expressed as helical motifs in nature. Moreover, these helical architectures not only have fascinating structural features, but they have been playing several key functions in natural systems.⁷

Emulating nature's design in artificial systems like chiral helical CPs is an interesting area of research. Generally, there are four different strategies to prepare homochiral CPs.⁸ First, by the use of readily available chiral ligands, which serve as the building blocks and thus, transfer their chiral behavior to the resulting CP.⁹ Second, the use of chiral auxiliary ligands, which bind

to the metal ion and induce homochirality in the CP formed.¹⁰ Third, by using chiral templates, solvents or additives which may induce chirality in the resultant framework.¹¹ Finally, by simply using achiral ligands and metal precursors, in which spontaneous resolution occurs due to the chiral spatial arrangement of ligands coordination around the metal ion.^{12–15} The advantage provided by the last method lies in the fact that it does not use any chiral components, which are difficult to prepare and some of them are quite expensive.

In general, the synthesis of chiral helical CPs using semi-rigid/flexible achiral ligands is a challenging research field. Many of the structures reported in the literature are either racemic, with both *P*(Δ) and *M*(Λ) helices running along the crystallographic axis, or conglomerates, wherein both *P* and *M* crystals are present in the reaction mixture and the structure remains unpredictable.⁸

In contrast, the preparation of chiral coordination complexes is a very well established procedure and it dates back to Werner, who showed that the complex chirality depends on formation of *cis* coordination geometry around the metal ion with appropriate chelating/monodentate ligands. This can be understood based on the symmetry criteria that the absence of improper axis of rotation results in chirality.¹⁶ Keeping this in view, if one analyzes the coordination geometry of the

*For correspondence

metal centers in the reported structures of helical CPs, it can be seen that the racemic structures are present in cases where the metal coordination geometry is *trans*, whereas, homochiral CPs are found to have *cis* coordination geometry at the metal centers with at least one chelating or two heteroatomic mono-dentate ligands.^{12–15}

Considering these facts, we have chosen an angular semi-rigid achiral ligand, of 2,6-bis(imidazol-1-yl)pyridine (*pyim*₂)¹⁷ and carried out the reactions with zinc and cadmium nitrates under different solvent mixtures. In this paper, we report the synthesis of four CPs, [*trans*-M(*pyim*₂)₂(NO₃)₂]_n [M = Zn(**1**), Cd (**2**)], {[*trans*-Zn(*pyim*₂)₂(H₂O)₂](NO₃)₂}(**3**) and {[*cis*-Cd(*pyim*₂)₂(H₂O)₂](NO₃)₂}(**4**), (scheme 1). Among these CPs, **1–3** are achiral, whereas **4** crystallize in chiral space group *C*2. Also the solubility of **4** in DMSO helped in evaluation of its solution behaviour using NMR and polarimetry.

Previously, Lee and co-workers studied the conformational effects of *pyim*₂ in the preparation of zinc halide CPs under hydrothermal or solvothermal conditions.^{17a} Interestingly, the hydrothermal reactions resulted in the formation of conglomerates, with larger N···N···N angle (161°), whereas, zig-zag and single helical structures, with shorter N···N···N angle (142° and 122°), were formed respectively under the solvothermal reaction. In general, the hydrothermal or solvothermal reactions yield only the most stable products. However to understand structural transformations, milder experimental conditions are necessary.

2. Experimental

2.1 Materials and general procedures

Zn(NO₃)₂·6H₂O and Cd(NO₃)₂·4H₂O were obtained from SD fine Chemicals, India. All chemicals were used without further purification. Solvents were first dried and then used after distillation. Elemental analyses were performed with an EAI Exeter analytical, INC

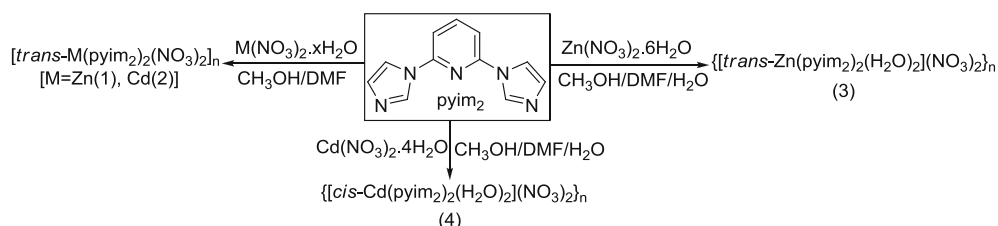
CE-440 Elemental analyzer. IR spectra were recorded by using KBr pellets in the region 400–4000 cm⁻¹ on Bruker model vertex 70. Thermogravimetric analyses were done in N₂ atmosphere with a heating rate of 10°C/min on Mettler Toledo Star System. NMR was recorded on JEOL ECX-500. The CD spectrum was recorded on Jasco J-815 spectropolarimeter. The polarimetry was recorded on Rudolph Research analytical Autopol II Automatic Polarimeter. Powder X-ray diffraction (PXRD) data were collected on a PANalytical X'Pert Pro X-ray diffractometer with radiation Cu Kα radiation (λ = 1.540598 Å) at room temperature with a scan step size of 0.02 in 2θ. DIAMOND (version 3.0) and Mercury (version 2.4) were used to view and draw the structures.

2.2 Preparation of 2,6-bis(imidazol-1-yl)pyridine (*pyim*₂)

The ligand, *pyim*₂ was prepared according to the literature procedure.^{17b} ¹H-NMR (DMSO-*d*₆, 500 MHz, δ): 7.11 (*s*, 2H, H4-Im), 7.70 (*d*, *J* = 5 Hz, 2H, H3-Py), 8.08 (*s*, 2H, H5-Im), 8.13 (*t*, *J* = 10 Hz, 1H, H4-Py), 8.70 (*s*, 2H, H2-Im).

2.3 Synthesis of CPs 1-4

2.3a Synthesis of [*trans*-Zn(*pyim*₂)₂(NO₃)₂]_n(**1**): To a solution of Zn(NO₃)₂·6H₂O (0.074 g, 0.25 mmol) in methanol (40 mL), *pyim*₂ (0.106, 0.5 mmol) was added as solid and the solution was stirred for 30 min. The solution was allowed to evaporate at room temperature very slowly to afford colourless crystals after few weeks. Yield: 0.055 g, 36 % based on Zn(NO₃)₂·6H₂O. Anal. calcd. for C₂₂H₁₈N₁₂O₆Zn (611.85): C, 43.19; H, 2.96; N, 27.47. Found: C, 42.50; H, 2.73; N, 28.00. IR (KBr, cm⁻¹): 3182 (*s*), 3168 (*s*), 3136 (*vs*), 3119 (*vs*), 1606 (*vs*), 1585 (*vs*), 1502 (*vs*), 1462 (*vs*), 1420 (*vs*), 1309 (*vs*), 1254 (*vs*), 1238 (*s*), 1178 (*s*), 1139 (*vs*), 1120 (*vs*), 1073 (*s*), 1039 (*s*), 1007 (*s*), 837 (*s*), 805 (*s*), 777 (*s*), 763 (*s*), 675 (*s*), 658 (*m*), 532 (*w*).



Scheme 1. Synthesis of CPs 1-4

2.3b *Synthesis of [trans-Cd(pyim₂)₂(NO₃)₂]_n(2):* Pyim₂ (0.053, 0.25 mmol) in methanol (2 mL) was layered over a solution of Cd(NO₃)₂·4H₂O (0.039 g, 0.125 mmol) in DMF (1 mL). The solution was allowed to stand at room temperature to afford colourless crystals. The same product was obtained, if this reaction was carried out only in methanol. Yield: 62% based on Cd(NO₃)₂·4H₂O. Anal. Calcd. for C₂₂H₁₈N₁₂O₆Cd (658.88): C, 40.10; H, 2.75; N, 25.51. Found: C, 39.49; H, 2.27; N, 25.03. IR (KBr, cm⁻¹): 3159 (w), 2923 (w), 2853 (w), 1606 (s), 1585 (s), 1498 (vs), 1463 (vs), 1422 (s), 1310 (vs), 1250 (vs), 1236 (m), 1178 (m), 1139 (m), 1115 (m), 1070 (s), 1039 (s), 1007(s), 992(m), 964 (m), 929 (m), 882 (m), 833 (m), 807 (m), 777 (m), 764 (m), 753 (m), 674 (m), 655 (m), 621 (m), 533 (w), 469 (w).

2.3c *Synthesis of {[trans-Zn(pyim₂)₂(H₂O)₂](NO₃)₂]_n(3):* To a solution of Zn(NO₃)₂·6H₂O (0.074 g, 0.25 mmol) in DMF (4 mL), a solution of pyim₂ (0.106 g, 0.5 mmol) in methanol (8 mL) was layered. Further, distilled H₂O (25 mL) was layered over the top of this solution. The solution was allowed to stand at room temperature to afford colourless crystals in two days. Yield 0.11 g, 34% based on Zn(NO₃)₂·6H₂O. Anal. calcd. for C₂₂H₂₂N₁₂O₈Zn (647.89): C, 40.78; H, 3.42; N, 25.94. Found: C, 40.92; H, 3.33; N, 25.58. IR (KBr, cm⁻¹): 3387 (br), 3260 (br), 3128 (s), 1729 (w), 1672 (w), 1606 (vs), 1589 (m), 1493 (vs), 1462 (vs), 1388 (vs), 1348 (vs), 1289 (vs), 1253 (s), 1242 (vs), 1180 (m), 1137 (w), 1110 (m), 1081 (m), 1070 (s), 1006 (m), 993 (w), 963 (w), 930 (m), 868 (m), 826 (w), 802 (s), 759 (s), 677 (s), 659 (w), 620 (w), 537(br). ¹H-NMR (DMSO-*d*₆, 500 MHz, δ): 7.12 (*s*, 2H, H4-Im), 7.72 (*d*, *J* = 10 Hz, 2H, H3-Py), 8.10 (*s*, 2H, H5-Im), 8.14 (*t*, *J* = 25 Hz, 1H, H4-Py), 8.72 (*s*, 2H, H2-Im).

2.3d *Synthesis of {[cis-Cd(pyim₂)₂(H₂O)₂](NO₃)₂]_n(4):* Similar procedure as that of **3** except that Cd(NO₃)₂·4H₂O (0.078 g, 0.25 mmol) was used in place of Zn(NO₃)₂·6H₂O. The solution was allowed to stand at room temperature to afford white crystals within a day. Yield, 0.24 g, 71 % based on Cd(NO₃)₂·4H₂O. Anal. calcd. for C₂₂H₂₂N₁₂O₈Cd (694.92): C, 38.03; H, 3.19; N, 24.19. Found: C, 38.46; H, 3.02; N, 23.85. IR (KBr, cm⁻¹): 3392 (br), 3263 (br), 3157 (w), 3124 (m), 1673 (w), 1605 (vs), 1589 (m), 1489 (vs), 1462 (vs), 1389 (s), 1345 (vs), 1289 (s), 1253 (s), 1242 (vs), 1180 (m), 1137 (w), 1111 (m), 1068 (s), 1005 (w), 963 (w), 927 (w), 867 (w), 827 (m), 802 (w), 757 (w), 677 (m), 656 (w), 619 (w), 535 (br). ¹H-NMR (DMSO-*d*₆, 500 MHz, δ): 7.13 (*s*, 2H, H4-Im), 7.73 (*d*,

J = 10 Hz, 2H, H3-Py), 8.11 (*s*, 2H, H5-Im), 8.14 (*t*, *J* = 20 Hz, 1H, H4-Py), 8.72 (*s*, 2H, H2-Im).

2.4 X-ray crystallography

The single crystal X-ray data were collected on Bruker Smart Apex diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). All the structures were solved using SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97. All hydrogen atoms were included in idealized positions using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters.^{20–22}

3. Results and Discussion

3.1 Synthesis

The room temperature syntheses of all the CPs were carried out by taking the metal nitrates of zinc and cadmium with pyim₂ in the stoichiometric ratio 1:2. By using a unary solvent (MeOH) and binary solvent systems (MeOH/DMF), the CPs **1** and **2** were obtained respectively. These polymers were insoluble in common organic solvents. The formulations were confirmed by the elemental analyses and it is in very good agreement with the single crystal X-ray crystallographic studies.

It has been established that the use of solvents in the reaction medium play a critical role in the formation of CPs.¹⁷ In particular, water assisted structural changes have been studied recently by Zhang and co-workers.¹⁸ Also, earlier, Aoyoma and others had shown that the solvent assisted formation of stereoisomeric products resulted in the formation of chiral CPs, in some cases.¹⁵ In order to ascertain the possibility of the formation of stereoisomeric product, the reactions of metal nitrates of zinc and cadmium with pyim₂ were carried out in 1:2 molar ratios using the ternary solvent system (MeOH/DMF/H₂O). Indeed the products obtained (**3** and **4**) were different, from **1** and **2** irrespective of the similar composition of the starting materials. Both the compounds (**3** and **4**) were insoluble in common organic solvents except in DMSO, in which they show moderate solubility. The ¹H NMR spectra of **3** and **4** recorded in DMSO-*d*₆ did not have any appreciable change from the ligand spectrum. The IR spectra indicated a broad absorption peak around 3400 cm⁻¹ suggesting the presence of water molecules in **3** and **4**. The final structure were confirmed unambiguously by the single crystal X-ray structural analysis.

3.2 Crystal structures

The single crystal X-ray structure analysis reveals that both the polymeric structures **1** and **2** crystallize in monoclinic space group $P2_1/n$ and they are *isostructural* (table 1). The important bond distances and angles are given in legend of figure 1. The zinc and cadmium ions are in octahedral *trans* coordination geometry of MN_4O_2 environment with ligation from four nitrogen atoms of different imidazole units of *pyim*₂ in the plane and two oxygen atoms of two different nitrate ions bound to the metal from its axial position (figure 1a). The other imidazole ring of *pyim*₂ connects the metal ions by the planes of the octahedron to form the 2D rhombic grid structures (figure 1b). Within the 2D network of **1** and **2**, all the 1D chains run into two nearly perpendicular directions and no interpenetration between the chains were observed.

The average Zn-N and the Cd-N bond distances are 2.135(3) Å and 2.327(3) Å respectively (figure 1). The Zn-O and the Cd-O bond distances are 2.201(3) Å and 2.344(4) Å respectively and are consistent with those of reported values $[M(2,5\text{-bis}(4'\text{-(imidazol-1-yl)benzyl)}\text{-}3,4\text{-diazaz-}2,4\text{-hexadiene})_2(\text{NO}_3)_2]_n$ [M = Zn, Cd].¹⁹ However, in these structures one of the imidazole ring deviated from the plane of the pyridine ring with a dihedral angle of 37.527(13)° and 33.376(13)°

(figure S4). Consequently, the individual chains are arranged into a helical mode, with different chirality, left-handed *M* (Δ) and right-handed *P* (Δ), to form a racemic structure (figure 1c). The 2D network of **1** and **2** was further connected by C-H...O interactions arising from the C-H of the pyridine ring and oxygen of nitrate ion from the adjacent layer and packed to complete the 3D structure (figure 1d-e).

Single crystal X-ray diffraction study reveals that the complex $\{[trans\text{-Zn}(\text{pyim}_2)_2(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2\}_n$ (**3**) crystallize in monoclinic space group $P2_1/c$ (table 1). Similar to **1**, the structure of **3** is a 2D helical rhombic grid structure with some marked differences. It consists of a ZnN_4O_2 octahedral unit, where zinc is coordinated by four different nitrogen atoms of imidazole ring of *pyim*₂ ligand, which are *trans* to each other in the plane. Whereas, unlike in **1**, the axial positions of the metal centres are occupied by water molecules, instead of nitrate ions, and they are also *trans* to each other (figure 2a). The adjacent layers of zinc octahedral units are oriented perpendicular to each other and they are connected through the planes by nitrogen atoms of imidazole rings of *pyim*₂ to form the 2D structure (figure 2b). Like **1**, here every non-interpenetrating 1D chain has opposite helicity and thus results in the formation of a racemic structure (figure 2c). Zn-N bond distances in **3** are shorter as compared to **1** and they are

Table 1. Crystallographic data and structural refinement summary of **1–4**.

| | 1 | 2 | 3 | 4 |
|--|---|---|---|---|
| Empirical Formula | C ₂₂ H ₁₈ N ₁₂ O ₆ Zn | C ₂₂ H ₁₈ N ₁₂ O ₆ Cd | C ₂₂ H ₂₂ N ₁₂ O ₈ Zn | C ₂₂ H ₂₂ N ₁₂ O ₈ Cd |
| Fw | 611.85 | 658.88 | 647.89 | 694.92 |
| Crystal dimensions (mm ³) | 0.150 × 0.12 × 0.08 | 0.12 × 0.09 × 0.07 | 0.20 × 0.10 × 0.12 | 0.21 × 0.19 × 0.10 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P 2_1/n$ | $P 2_1/n$ | $P 2_1/c$ | $C 2$ |
| <i>a</i> , Å | 9.3561(9) | 9.3490(18) | 8.607(2) | 9.3655(9) |
| <i>b</i> , Å | 10.9855(11) | 11.162(2) | 16.275(4) | 16.551(2) |
| <i>c</i> , Å | 11.4548(12) | 11.688(2) | 9.231(2) | 8.6129(8) |
| β , (°) | 95.176(2) | 95.094(3) | 92.960(4) | 93.664(2) |
| <i>V</i> , Å ³ | 1172.5(2) | 1214.9(4) | 1291.3(6) | 1332.4(2) |
| <i>Z</i> | 2 | 2 | 2 | 2 |
| ρ_{calcd} , mg/m ³ | 1.733 | 1.801 | 1.666 | 1.732 |
| μ , mm ⁻¹ | 1.118 | 0.967 | 1.026 | 0.892 |
| <i>F</i> (000) | 624 | 660 | 666 | 700 |
| <i>T</i> (K) | 100(2) | 100(2) | 100(2) | 100(2) |
| $\theta_{\text{min/max}}$ range (°) | 2.57–28.33 | 2.53–28.35 | 2.57–28.33 | 2.37–25.00 |
| Range of <i>h,k,l</i> | –11/12, –14/11, –15/11 | –12/5, –13/14, –15/14 | –8/11, –21/18, –12/9 | –11/10, –18/19, –7/10 |
| Reflections collected/unique | 7513/2892 | 7698/2983 | 8211 | 3445/2189 |
| Data/restraints /parameter | 2892/0/187 | 2983/0/187 | 3159/3/201 | 2189/182/ 200 |
| GOF on <i>F</i> ² | 1.156 | 1.216 | 1.145 | 1.073 |
| <i>R</i> _{int} | 0.0370 | 0.0308 | 0.0327 | 0.0270 |
| <i>R</i> 1; <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)] | 0.0494; 0.0958 | 0.0396; 0.0762 | 0.0534; 0.1291 | 0.0598; 0.1451 |
| <i>R</i> 1; <i>wR</i> 2 (all data) | 0.0704; 0.1325 | 0.0610; 0.1210 | 0.0789; 0.1901 | 0.0639; 0.1570 |

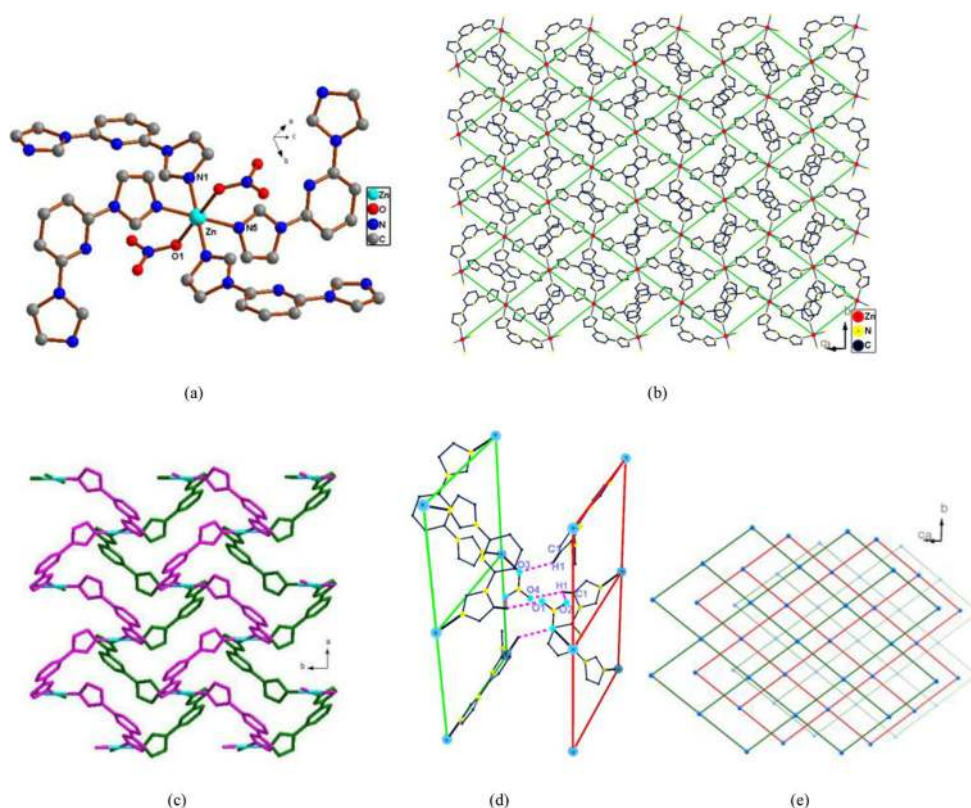


Figure 1. (a) The coordination environment around Zn(II) ions in **1** (hydrogen atoms omitted for clarity). (b) Stick view of the 2-D helical coordination polymer of **1** along a-axis. (c) View of two-dimensional layer comprising left-handed (pink) and right-handed (green) helical chains in **1**. (d) C-H...O interaction between the grids in **1** (bond distances (Å) and angles (°)): O1...H5 = 2.638(3), O3...H9 = 2.600(2), O2...H9 = 2.666(2), C5-H5...O1 = 130.02(15), C9-H9...O3 = 161.98(15), C9-H9...O2 = 108.75(15). (e) Stacking of 2-D grid structures in **1** along a-axis. Symmetry codes: (i) $-x + 3/2, y - 1/2, -z - 1/2$; (ii) $x + 1/2, -y + 1/2, z + 1/2$; (iii) $-x + 2, -y, -z$; (iv) $-x + 3/2, y + 1/2, -z - 1/2$. Important bond distances (Å) and angles (°) for **1**: Zn-N1, 2.201(3); Zn-N5, 2.123(3); Zn-O1, 2.201; N1-Zn-N1, 180; N5-Zn-N5, 180; O1-Zn-O1, 180; N1-Zn-N5, 87.07(11); N5-Zn-O1, 85.22(11); N1-Zn-O1, 87.70(11). Symmetry codes in **2**: (i) x, y, z ; (ii) $-x + 1/2, y + 1/2, -z + 1/2$; (iii) $-x, -y, -z$; (iv) $x - 1/2, -y - 1/2, z - 1/2$. Important bond distances (Å) and angles (°) for **2**: Cd-N1, 2.3103(3); Cd-N5, 2.344(3); Cd-O4, 2.344(4); N1-Cd-N1, 180; N5-Cd-N5, 180; O4-Cd-O 4, 180; N1-Cd-N5, 93.87(14); N1-Cd-O1, 85.67(14); N5-Cd-O1, 83.98(16).

closer to the other reported values in the literature of zinc imidazole system.¹⁸ Interestingly, two of the oxygen atoms of nitrate ions show moderate to weak hydrogen bonding interactions with the axially coordinated water molecules of octahedral zinc leading to the formation of a 2D helical pattern along crystallographic *c* axis (table S1). Further, the third oxygen atom of the nitrate ions shows shorter C-H interactions of two imidazole rings and a pyridine to form 3D network of this 2D helical coordination polymer (figure 2d).

Unlike in the case of **3**, the single crystal X-ray diffraction study shows that the complex $\{[cis-Cd(pyim_2)_2(H_2O)_2] \cdot (NO_3)_2\}_n$ (**4**) crystallize in chiral monoclinic space group *C2* (table 1). The structure of **4** consists of octahedral cadmium unit CdN_4O_2 , where cadmium atom is surrounded by oxygen atoms (O1)

from two H_2O molecules, and four nitrogen atoms (N1 and N5) from different $pyim_2$ forming a *cis* coordination geometry (figure 3a). The imidazole nitrogen atoms of $pyim_2$ connect adjacent layers of the cadmium centre through an equatorial-axial fashion to form the 2D CPs (figure 3b). Among the two imidazoles, one of the imidazole rings is out of plane (24.367°) with respect to the pyridine rings, which originates the helical structures between the adjacent layers of the **4**. Unlike **1–3**, these helices are of the same type, right-handed helix (*P*) along *b* axis (figure 3c). The layers consisting of double helices are further stabilized through $\pi-\pi$ interaction between pyridine rings which are stacked face to face on one another. The centroid to centroid distance is 3.168 Å and the angle between the planes is 0.91° . This $\pi-\pi$ interaction leads to a 3D

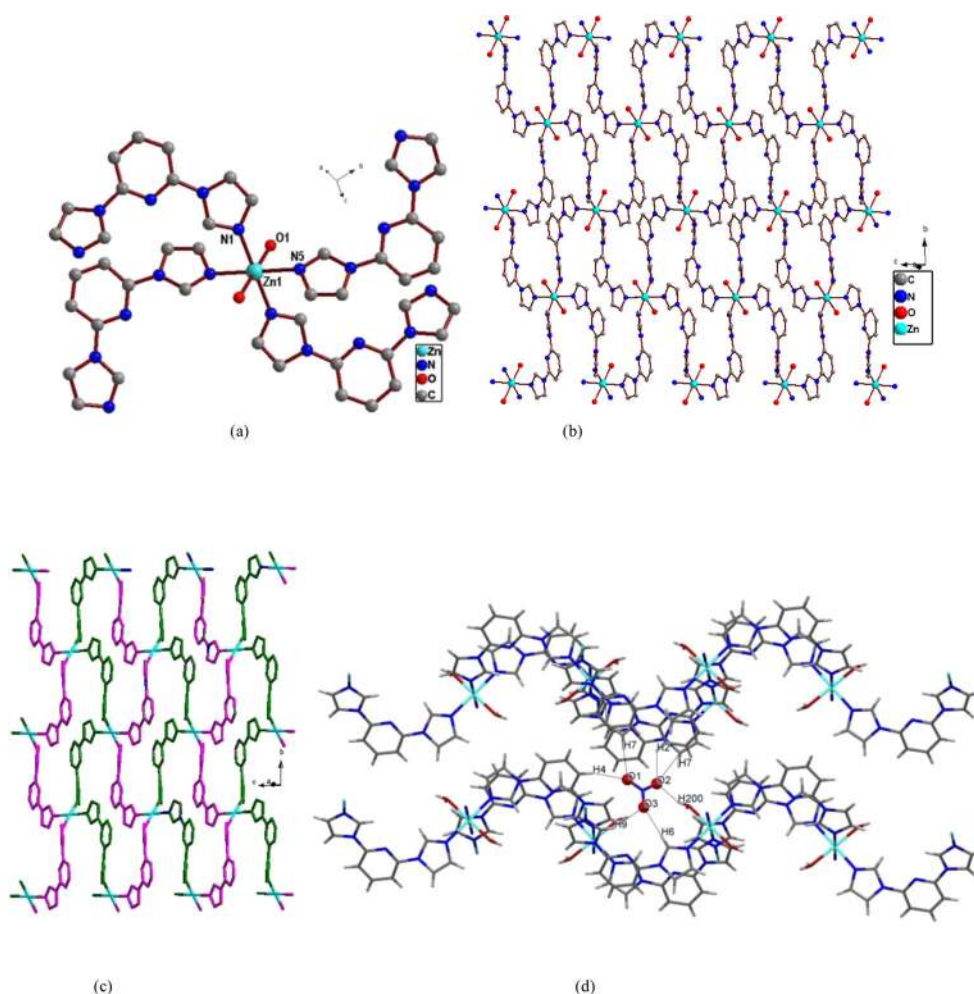


Figure 2. (a) Coordination environment of Zn (II) ions in **3** (hydrogen atoms are omitted for clarity). (b) Ball and stick view of metal-ligand 2-D coordination polymer. (c) View of two-dimensional layer comprising left-handed (pink) and right-handed (green) helical chains in **3**. (d) 3-D supramolecular structure showing H-bonding by nitrate ions (along *c*-axis). Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $x, -y + 1/2, z - 1/2$; (iii) $x, -y + 1/2, z + 1/2$. Important bond distances (Å) and angles (°): Zn-N1, 2.139(3); Zn-N5, 2.152(3); Zn-O1, 2.140(3); N1-Zn-N1, 180.0; N5-Zn-N5, 179.99(1); O1-Zn-O1, 180.0; N1-Zn-N5, 85.62(13); N5-Zn-O1, 91.04(12); N1-Zn-O1, 89.72(12).

supramolecular arrangement of this 2D coordination polymer (figure 3d-e).

The stereoisomeric changes in the coordination geometry from CPs **1–3** coupled with the C-N bond rotation greatly influences the structural changes observed in this 2D coordination polymer, **4**. Thus, the chirality (Δ) is observed due to the combined effect of *cis*-orientation of the pym_2 and water molecules around the cadmium centre as well as the non-planarity between imidazole and pyridine rings due to the twist in C-N bond between pyridine and imidazoles of the ligand.

The homochirality of **4** in bulk was confirmed by taking crystals of different reaction batches for single crystal X-ray diffraction measurements. In all these cases, the structural solution led to the single-handed helicity with the same chirality of **4**, having the least

Flack parameter value [0.001(1)]. Further, the bulk samples of two to three different batches were taken for the solid state CD spectrum and solution state polarimetry studies as well as PXRD (figure S2).

3.3 CD spectra

The solid state CD spectrum of coordination polymer **4** was recorded between 190–500 nm at 20°C. The CD spectrum showed very small negative Cotton effects between 190–350 nm range indicating the existence of homochirality of the coordination polymer, **4** (figure S3).

3.4 Polarimetry

However, the solution state polarimetric measurements recorded in DMSO solvent showed rotation of the plane

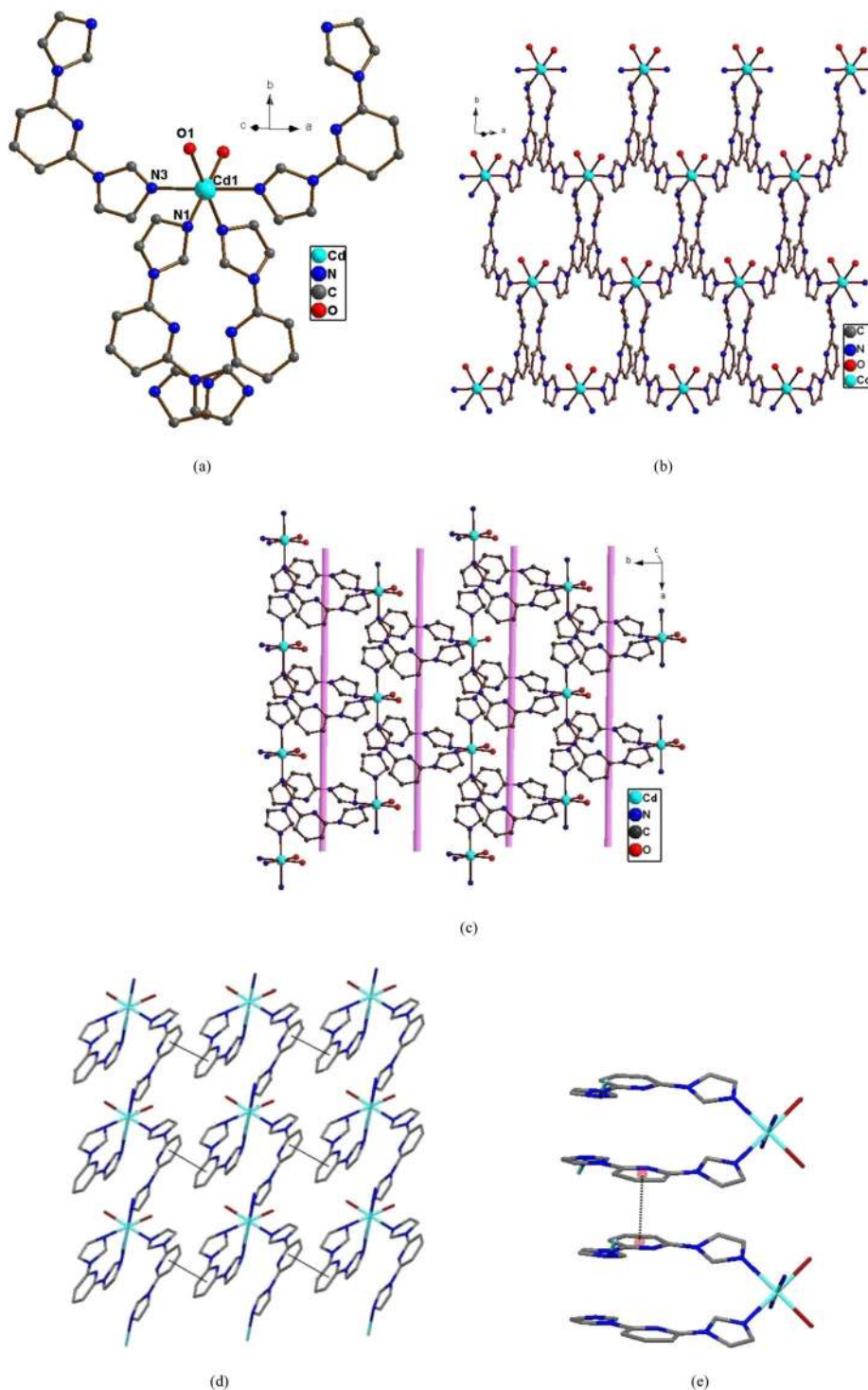


Figure 3. (a) Coordination environment of Cd(II) ions in **4** (hydrogen atoms are omitted for clarity). (b) Ball and stick view of metal-ligand 2-D coordination polymer. (c) Two right-handed helices running across each other. (d) and (e) $\pi - \pi$ interaction between adjacent layers to form a 3-D supramolecular structure (along a-axis). Symmetry codes: (i) $-x + 1, y, -z + 2$; (ii) $x - 1/2, y - 1/2, z$; (iii) $x + 1/2, y + 1/2, z$. Important bond distances (\AA) and angles ($^\circ$) Cd-N1, 2.297(11); Cd-N3, 2.329(6); Cd-O1, 2.297(10); N1-Cd-N1, 91.7(5); N3-Cd-N3, 178.5(8); O1-Cd-O1, 92.7(5); N1-Cd-N3, 86.9(4); O1-Cd-N3, 92.3(5); O1-Cd-N1, 179.0(6).

of polarized light to right, and the specific rotation, $[\alpha]_{\lambda}^T$ was found to be +1.65 confirming the homochirality of the product. However, it is to be mentioned that after an hour, the loss of chirality of **4** was observed in the same solution.

3.5 Thermogravimetric analysis

The thermal stability of **1–4**, was studied using the thermogravimetric analysis (TGA) (figure S4). The TGA profiles indicated that **1** is thermally stable up to 240°C without any loss of weight. Around 240–400°C the framework showed 46.0% weight loss corresponding to the loss of one ligand and one nitrate molecule (calculated, 44.63 wt%). The second weight loss of 39.3% around 400–680°C corresponded to the loss of another ligand and another nitrate molecule (calculated, 44.63 wt%) (residue 14.1%). The TGA profile indicated that **2** is thermally stable up to 311°C without any loss of weight. Around 311–372°C the framework showed 39.1% weight loss corresponding to the loss of one ligand and one nitrate molecule (calculated, 41.44 wt%). The CP shows a gradual weight loss around 380°C corresponding to the loss of another ligand and another nitrate molecule (residue 13.1%). The TGA profile of **3** indicated that it was thermally stable up to 150°C and showed first weight loss of around 6% due to two water molecules at 150–190°C (calculated, 5.55 wt%). The second weight loss of 47.6% was observed at around 250–390°C due to the loss of two nitrate ions and one ligand (calculated, 51.72 wt %). The third weight loss of 30% was observed at 530–700°C for another ligand (calculated, 32.58 wt %) (residue 22.0%). The TGA profile of **4** indicated that it was thermally stable upto 140°C without any weight loss. At around 140–190°C it showed weight loss of 6.0 % due to loss of two water molecules (calculated, 5.18 wt %). Then the next weight loss of 43.0 % was observed around 250–400°C corresponding to two nitrate ions and one ligand (calculated, 48.22 wt %). The third weight loss of 28.0% was at around 550–740°C due to another ligand molecule (calculated, 30.37 wt%) (residue 26.1%).

4. Conclusion

Four new CPs (**1–4**) were synthesized using achiral angular ditopic ligand (pyim₂) and structurally characterized, in which lone pair on pyridine nitrogen were not involved in coordination with metal centres. The latter can be used as a source of Lewis base assisted organic reaction or transformation. These CPs showed different metal coordination environment and structures with change of solvent conditions. The result was the

formation of a homochiral coordination polymer **4** by spontaneous resolution. The homochirality in bulk of the product **4** was further supported by recording the optical activity using polarimetry and in solid state CD spectra. In fact, to the best of our knowledge, this is the first time that the solution state polarimetric measurements were carried out for the CPs. Further, studies on the preparation of chiral CPs using different metal salts using pyim₂ and other co-ligands under soft route and their use as chiral platform for the separation and catalysis are under progress.

Supplementary Information

CCDC-972289-972292 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths and angles, additional figures, TGA and powder X-ray diffraction patterns. For supplementary Information, see www.ias.ac.in/chemsci.

Acknowledgements

The authors thank Council of Scientific and Industrial Research (CSIR), Department of Science and technology (DST), Government of India for financial support and Indian Institute of Technology (IIT), Kanpur for infrastructural facilities. Also we thank “Thematic Unit of Excellence on Soft Nanofabrication with Application in Energy, Environment and Bioplatfrom at IIT Kanpur” for PXRD facility. ST (CSIR), RS (IITK), and NS (University of Grant Commission, UGC) thank the respective agencies mentioned in the brackets for research fellowships. We are thankful to Dr. Mrinalini G. Walawalkar and M. Nethaji for crystallographic support on complex **4**.

References

- (a) Furukawa H, Cordova K E, O’Keeffe M and Yaghi O M 2013 *Science* **341**; (b) Sumida K, Rogow D L, Mason J A, McDonald T M, Bloch E D, Herm Z R, Bae T H, and Long J R 2012 *Chem. Rev.* **112** 724; (c) Wu H, Gong Q, Olson D H and Li J 2012 *Chem. Rev.* **112** 836; (d) Getman R B, Bae Y S, Wilmer C E and Snurr R Q 2012 *Chem. Rev.* **112** 703; (e) Suh M P, Park H J, Prasad T K and Lim D W 2012 *Chem. Rev.* **112** 782; (f) Li J R, Ma Y, McCarthy M C, Sculleya J, Yub J, Jeong H K, Balbuena P B and Zhou H C 2011 *Coord. Chem. Rev.* **255** 1791; (g) Han S S, Mendoza-Cortés J L and Goddard III W A 2009 *Chem. Soc. Rev.* **38** 1460; (h) Czaja A U, Trukhan N and Müller U 2009 *Chem. Soc. Rev.* **38** 1284; (i) Murray L J, Dincă M and Long

- J R 2009 *Chem. Soc. Rev.* **38** 1294; (j) Kitagawa S, and Matsuda R. 2007 *Coord. Chem. Rev.* **251** 2490; (k) Kitagawa S and Uemura K 2005 *Chem. Soc. Rev.* **34** 109
2. Li J R, Sculley J and Zhou H C 2012 *Chem. Rev.* **112** 869
3. (a) Landee C P and Turnbull M M 2013 *Eur. J. Inorg. Chem.* 2266; (b) Zhang W and Xiong R G 2012 *Chem. Rev.* **112** 1163; (c) Rogez G, Viart N and Drillon M 2010 *Angew. Chem. Int. Ed.* **49** 1921; (d) Kurmoo M 2009 *Chem. Soc. Rev.* **38** 1353; (e) Train C, Gheorghie R, Krstic V, Chamoreau L M, Ovanesyan N S, Rikken G L J A, Gruselle M and Verdagner M 2008 *Nat. Mater.* **7** 729; (f) Bogani L, Cavigli L, Bernot K, Sessoli R, Gurioli M and Gatteschi D 2006 *J. Mater. Chem.* **16** 2587; (g) Coronado E, Galán-Mascarós J R, Gómez-García C J and Martínez-Agudo J M 2001 *Inorg. Chem.* **40** 113
4. (a) Yoon M, Srirambalaji R and Kim K 2012 *Chem. Rev.* **112** 1196; (b) Corma A, García H and Llabrés i Xamena F X 2010 *Chem. Rev.* **110** 4606; (c) Yu L, Wang Z, Wu J, Tu S and Ding K 2010 *Angew. Chem. Int. Ed.* **49** 3627; (d) Liu Y, Xuan W and Cui Y 2010 *Adv. Mater.* **22** 4112; (e) Ma L, Abney C and Lin W 2009 *Chem. Soc. Rev.* **38** 1248; (f) Lee J Y, Farha O K, Roberts J, Scheidt K A, Nguyen S T and Hupp J T 2009 *Chem. Soc. Rev.* **38** 1450; (g) Jammi S, Rout L, Saha P, Akkilagunta V K, Sanyasi S and Punniyamurthy T 2008 *Inorg. Chem.* **47** 5093; (h) Ding K, Wang Z and Shi L 2007 *Pure Appl. Chem.* **79** 1531; (i) Ding K, Wang Z, Wang X, Liang Y and Wang, X. *Chem. Eur. J.* 2006, **12** 5188
5. (a) Cui Y, Yue Y, Qian G and Chen B 2012 *Chem. Rev.* **112** 1126; (b) Wang C, Zhang T and Lin W 2012 *Chem. Rev.* **112** 1084; (c) Allendorf M D, Bauer C A, Bhakta R K and Houka R J T 2009 *Chem. Soc. Rev.* **38** 1330; (d) Liu Y, Li G, Li X and Cui Y 2007 *Angew. Chem. Int. Ed.* **46** 6301; (e) Janiak C 2003 *Dalton Trans.* 2781; (f) Evans O R and Lin W 2002 *Acc. Chem. Res.* **35** 511
6. (a) Zheng X D and Lu T B 2010 *CrystEngComm.* **12** 324; (b) Han L and Hong M 2005 *Inorg. Chem. Commun.* **8** 406; (c) Albrecht M 2001 *Chem. Rev.* **101** 3457; (d) Piguet C, Bernardinelli G and Hopfgartner G 1997 *Chem. Rev.* **97** 2005
7. Lehn J M 1995 In *Supramolecular Chemistry* (Germany: VCH, Weinheim)
8. (a) Crassous J 2009 *Chem. Soc. Rev.* **38** 830; (b) Morris R E and Bu X 2010 *Nature Chem.* **2** 353; (c) Lin W 2005 *J. Solid State Chem.* **178** 2486
9. (a) He W W, Yang J, Yang Y, Liu Y Y and Ma J F 2012 *Dalton Trans.* **41** 9737; (b) Dong D P, Sun Z G, Tong F, Zhu Y Y, Chen K, Jiao C Q, Wang C L, Li C and Wang W N 2011 *CrystEngComm* **13** 3317; (c) Ryoo J J, Shin J W, Dho H S and Min K S 2010 *Inorg. Chem.* **49** 7232; (d) Wang Y, Fu H, Shen F, Sheng X, Peng A, Gu Z, Ma H, Ma J S and Yao J 2007 *Inorg. Chem.* **46** 3548; (e) Wu C D, Ngo H L and Lin W 2004 *Chem. Commun.* 1588; (f) Cui Y, Ngo H L and Lin W 2003 *Chem. Commun.* 1388; (g) Cui Y, Ngo H L, White P S and Lin W 2002 *Chem. Commun.* 1666; (h) Bernhard S, Takada K, Díaz D J, Abuña H D and Mürner H 2001 *J. Am. Chem. Soc.* **123** 10265
10. Amghouz, Z, Rocés L, García-Granda S and García J R 2010 *Inorg. Chem.* **49** 7917
11. Kang Y, Chen S, Wang F, Zhang J and Bu X 2011 *Chem. Commun.* **47** 4950
12. (a) Cai S L, Zheng S R, Wen Z Z, Fan J and Zhang W G 2012 *Cryst. Growth Des.* **12** 2355; (b) Zuo Y, Fang M, Xiong G, Shi P F, Zhao B, Cui J Z and Cheng P 2012 *Cryst. Growth Des.* **12** 3917; (c) Chang C C, Huang Y C, Huang S M, Wu J Y, Liu Y H and Lu K L 2012 *Cryst. Growth Des.* **12** 3825; (d) Yi F Y, Zhang J, Zhang H X, Sun Z M 2012 *Chem. Commun.* **48** 10419; (e) Zhang H X, Wang F, Tan Y X, Kang Y and Zhang J 2012 *J. Mater. Chem.* **22** 16288; (f) Tan X, Zhan J, Zhang J, Jiang L, Pan M and Su C Y 2012 *CrystEngComm* **14** 63; (g) Zheng S R, Cai S L, Tan J B, Fan J and Zhang W G 2012 *CrystEngComm* **14** 6241; (h) Bisht K K and Suresh E 2012 *Inorg. Chem.* **51** 9577
13. (a) Croitor L, Coropceanu E B, Siminel A V, Kravtsov V C and Fonari M 2011 *Cryst. Growth Des.* **11** 3536; (b) Chen S C, Zhang J, Yu R M, Wu X Y, Xie Y M, Wang F and Lu C Z 2010 *Chem. Commun.* **46** 1449; (c) Liu W T, Ou Y C, Lin Z J and Tong M L 2010 *Cryst. Eng. Comm.* **12** 3487; (d) Han Z B, Ji J W, An H Y, Zhang W, Han G X, Zhang G X and Yang L G 2009 *Dalton Trans.* 9807; (e) Lennartson A and Håkansson M 2009 *Angew. Chem. Int. Ed.* **48** 5869; (f) Zhang J, Chen S, Wu T, Feng P and Bu X 2008 *J. Am. Chem. Soc.* **130** 12882; (g) Lu W G, Gu J Z, Jiang L, Tan M Y and Lu T B 2008 *Cryst. Growth Des.* **8** 192; (h) Feller R K and Cheetham A K 2008 *Dalton Trans.* 2034; (i) Hou S Z, Cao D K, Li Y Z and Zheng L M 2008 *Inorg. Chem.* **47** 10211; (j) Zou R Q, Zhong R Q, Du M, Pandey D S and Xu Q 2008 *Cryst. Growth. Des.* **8** 452
14. (a) Zhang Q, Bu X, Lin Z, Biasini M, Beyermann W P and Feng P 2007 *Inorg. Chem.* **46** 1419; (b) Li F, Li T, Li X, Li X, Wang Y and Cao R 2006 *Cryst. Growth Des.* **6** 1458; (c) Gu X and Xue D 2006 *Inorg. Chem.* **45** 9257; (d) Tian G, Zhu G, Yang X Fang Q, Xue M, Sun J, Wei Y and Qiu S 2005 *Chem. Commun.* 1396; (e) Balamurugan V and Mukherjee R 2005 *Cryst. Eng. Comm.* **7** 337; (f) Wang Y T, Tong M L, Fan H H, Wang H Z and Chen X M 2005 *Dalton Trans.* 424; (g) Gao E Q, Yue Y F, Bai S Q, He Z and Yan C H 2004 *J. Am. Chem. Soc.* **126** 1419
15. Ezuhara T, Endo K and Aoyama Y 1999 *J. Am. Chem. Soc.* **121** 3279
16. Miessler G L and Tarr D A 2009 In *Inorganic Chemistry*. 3rd Ed., Dorling Kindersley Ind. Pvt. Ltd
17. (a) Chen C Y, Cheng P Y, Wu H H and Lee H M 2007 *Inorg. Chem.* **46** 5691; (b) Caballero A, Díez-Barra E, Jalón F A, Merino S and Tejada J 2001 *J. Organomet. Chem.* **617** 395
18. Zhang S, Lan J, Mao Z, Xie R. and You J 2008 *Cryst. Growth Des.* **8** 3134
19. (a) Chun-Long Chen C L, Goforth A M, Smith M D, Cheng-Yong Su C Y and Zur Loye H C 2005 *Inorg. Chem.* **44** 8762; (b) Masciocchi N, Pettinari C, Alberti E, Pettinari R, Nicola C D, Albisetti A F and Sironi A 2007 *Inorg. Chem.* **46** 10501
20. Sheldrick G M 1997 *SHELXL-97: Program for Crystal Structure Refinement*: University of Göttingen, Göttingen, Germany
21. Sheldrick G M 1998 *SHELXTL Reference Manual*: Version 5.1, Bruker AXS, Madison, WI
22. G M Sheldrick 2000 SADABS 2.0