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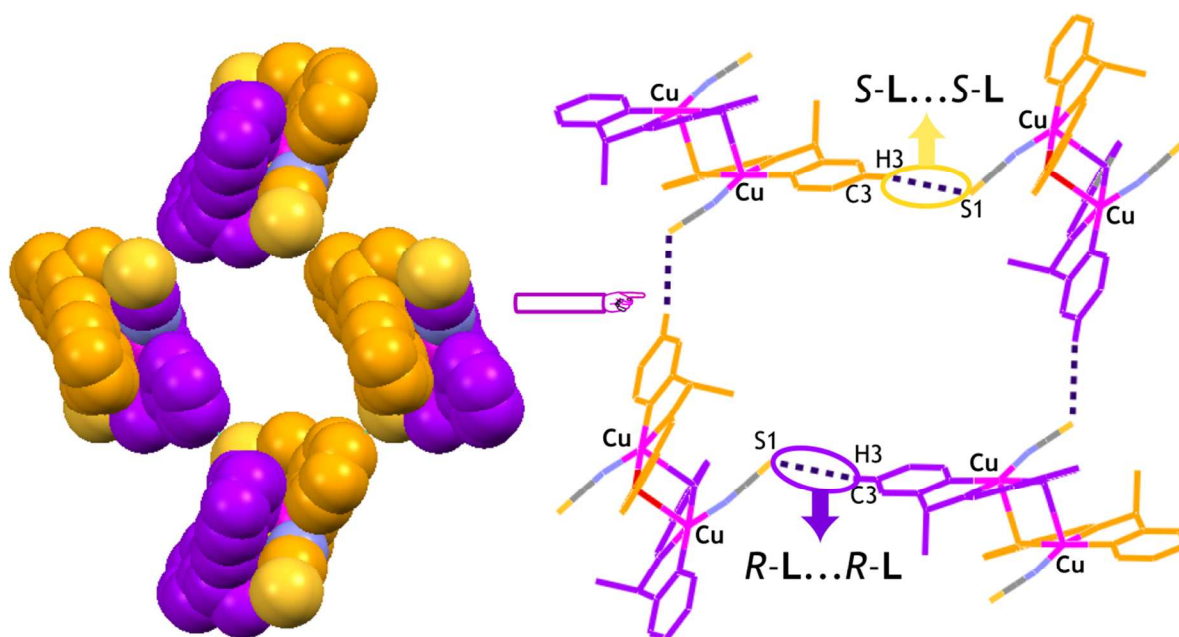
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The effect of  $\pi\cdots\pi$  interaction between benzene-pyridine rings on diastereoselective self-assembly of Cu(II) compounds in chiral self-discrimination process are studied.

## ARTICLE

# Effect of non-covalent interaction on the diastereoselective self-assembly of Cu(II) complexes containing a racemic Schiff base in a chiral self-discriminating process

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Diastereoselective self-assembly of five Cu(II) heterochiral complexes containing a racemic Schiff base ligand **LH** (where **LH** = (*R,S*) 2-(1-(pyridin-2-yl)ethylimino)methyl)phenol) in a chiral self-discriminating process are reported. Complexes **1-5** are synthesized using ligand **LH**, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, co-ligands such as N<sub>3</sub><sup>-</sup>, NCS<sup>-</sup>, NCO<sup>-</sup> and are conclusively structurally characterized. Determination of molecular structures of **1-5** confirmed the presence of a di-copper core with an inversion centre located directly between the two copper ions. In **1-5**, each ligand in the di-copper core discriminates the chirality of its own and results a heterochiral dimerization in chiral self-discriminating manner. The crystal packing pattern of compounds **1-5** are analyzed in terms of non-covalent C-H...O, C-H...N, C-H...π, and parallel displaced π...π interactions. In the crystal structure of compound **1-4**, parallel displaced π...π interaction between pyridine and benzene rings in two adjacent heterochiral dimers is perceived, which act cooperatively with other different non-covalent interactions. In **2**, the coordinated water molecule acts as bifurcated H-bond donor to phenoxo-O and perchlorate-O in a diastereoselective and enantioselective manner respectively. The results described here address new examples of rarely occurs chiral self-discriminating process.

## Introduction

Chiral ligands have been used extensively in asymmetric synthesis and catalysis, as well as supramolecular chemistry due to their ability to create an asymmetric environment around the metal centre.<sup>1</sup> In this direction, the ability to predict and control the coordination geometry of a chiral tri-dentate Schiff base ligand when bound to a metal centre is certainly an important aspect, because the geometry can dictate the shape of the molecule and the asymmetric environment around the metal centre.<sup>2,3</sup> Meanwhile although non-covalent interactions are weaker than the coordinate bonds, they are common and play critical roles in forming the supramolecular structures due to their significant contribution to the self-assembly process.<sup>4</sup> They are also imperative in biological systems<sup>5</sup> and generally govern the physicochemical properties of molecular systems in the solid state, thus their exploration and understanding in the supramolecular systems is essential for crystal engineers who design structures, in particular those of materials based on coordination compounds with racemic ligands. Among the non-covalent interactions, H-bonding is the most widely used synthons over other and can able to generate flexible materials which are more elastic in nature.<sup>6</sup> Among the other types of non-covalent interactions, π...π stacking between the aromatic

rings are used in construction of flexible materials.<sup>7</sup> Although various intelligence of crystal engineering approach on the formation and control of coordination complexes are reported, none of them discuss about their diastereoselective nature i.e. what their selectivity is when a particular system contains racemic ligand.<sup>8</sup> For example if a coordination complex contains chiral enantiopure ligand the possible non-covalent interactions interlinks only the enantiopure moieties. But the outcomes are more complicated if the coordination complex contains racemic ligands i. e. whether the possible non-covalent interaction interlinks two coordination complex containing ligands of same chirality (homochiral) or of different chirality (heterochiral).<sup>3</sup> Thus, it is immense important to gather precise knowledge on how different factors affect the structural self-assembly of racemic ligands to form (homo- or hetero-) chiral coordination polymers, coordination networks and subsequently in synthesis of homo- or heterochiral Metal Organic Frameworks (MOFs).<sup>9</sup> Noteworthy results describing the effect of hydrogen bonding and π...π interactions on the diastereoselectivity of coordination complexes were reported by Constable *et al.*,<sup>10</sup> Scott *et al.*,<sup>11</sup> and others<sup>12</sup>. Of late coordination stereo-chemistries of chiral and achiral tridentate ligands around the metal centre has been reported by Ghosh and his co-workers.<sup>13</sup> The key aim of the

present article is to explore the diastereoselective nature of non-covalent interactions in coordination complexes containing racemic ligands.

In the earlier report, the effect of bridging ligands or co-ligands on the diastereoselectivity of racemic tridentates imines and amines around the bimetallic core (Ni, Cu and Zn) have been studied.<sup>14</sup> Also the effect of steric congestion on the diastereoselective self-assembly of Zn(II) complexes in chiral self-discrimination process has also been reported.<sup>14a</sup> In addition recently the effect of non-covalent interaction on the heterochiral self-assembly of Cu(II) complexes has been substantially studied.<sup>14b</sup> In this direction, herein we report the synthesis and structural characterization of five Cu(II) complexes derived from a chiral tridentate Schiff base ligand (**LH**), and pseudohalogens. The main intention is to explore the effect of non-covalent interactions on the diastereoselective self-assembly of coordination complexes. Different coligands such as azide, thiocyanate and cyanate ions were selected with intention of investigating their effect on stereochemical transfer from monomer and dimer to coordination polymers. Also rarely occur  $\pi\cdots\pi$  stacking interactions between pyridine $\cdots$ benzene dimers are perceived. The above findings adds new examples to the Yan's concept of *chiral induction and transfer* in coordination complexes<sup>15</sup> and also to the rarely occur chiral-discrimination process.

## Materials and methods

All the solvents and reagents were purchased from commercial sources and used as received. 2-acetyl pyridine, NaCNO (Aldrich, USA);  $\text{NaN}_3$ , NaSCN, 2-hydroxybenzaldehyde,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , hydroxylamine hydrochloride and Zn dust (Merck India Ltd) and solvents were used as received without further purification. (*R, S*) phenyl(2-pyridyl)methaneamine and (*R, S*) 2-(1-(pyridin-2-yl)ethylimino)methylphenol) were prepared using our earlier reported procedures.<sup>14e</sup> The elemental analyses were performed on a Perkin-Elmer PE 2400 II CHN analyzer. The IR spectra were recorded on a Perkin-Elmer-Spectrum One FT-IR spectrometer with KBr disks in the range 4000-400  $\text{cm}^{-1}$ . The UV-vis spectra were recorded on a Perkin-Elmer-Lambda 750 UV-vis spectrometer at room temperature.

## Crystallographic data collection and refinement

X-ray crystallographic data for compound **1-5** were collected using Bruker SMART APEX-CCD diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The intensity data were corrected for Lorentz and polarization effects and multi-scan absorption corrections was applied using SAINT program.<sup>16, 17</sup> All the structures were solved by direct methods using SHELXS-97.<sup>18</sup> Non-hydrogen atoms located from the difference Fourier maps were refined anisotropically by full-matrix least-squares on  $F^2$ , using SHELXL-97.<sup>18</sup> All hydrogen atoms were included in the calculated positions (except for the water molecules of crystallization for which hydrogen atoms could neither be added at calculated positions and nor be located from FMAP) and refined isotropically using a riding model.

## Syntheses

### Synthesis of $[\text{Cu}(\text{L})(\text{NO}_3)]_2$ (**1**)

To the methanolic (40 mL) solution of ligand **LH** (0.226 g, 1 mmol),  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.241 g, 1 mmol) dissolved in methanol was added and was allowed to stir for 4 h and the resulting green solution was allowed to evaporate slowly at room temperature. After few days, the green solution deposited dark green crystals suitable for X-ray crystallographic analysis and were collected by filtration and dried in desiccators. A suitable crystal was selected for X-ray crystallographic analysis. Yield: 56% (based on copper salt). Anal. Calc. for  $\text{C}_{28}\text{H}_{23}\text{Cu}_2\text{N}_6\text{O}_8$ : C, 48.14; H, 3.32; N, 12.03%. Found: C, 47.81; H, 2.88; N, 11.87%. IR (KBr,  $\text{cm}^{-1}$ ): 3069(w), 2980(s), 1627(s), 1602(s), 1572(w), 1541(w), 1443(s), 1384(s), 1337(s), 1294(s), 1282(w), 1255(w), 1200(w), 1147(w), 1131(s), 1103(s), 1058(w), 991(s), 769(s), 752(s), 740(s), 656(w), 602(w), 519(s), 505(w). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ),  $\text{CH}_3\text{OH}$  solution]: 637(326); 375(12700); 269(41120); 242(50070); 219(57780).  $\mu_{\text{eff}}/\text{Cu} = 1.84$  B. M. EPR ( $\text{CH}_3\text{OH}$  solution, 298 K):  $g_{\text{av}} = 2.091$ ,  $A = 73$  G.

### Synthesis of $[\text{Cu}(\text{L})(\text{ClO}_4)(\text{H}_2\text{O})]$ (**2**)

Compound **2** was synthesized by following the procedure described for **1** by using  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.370 g, 1 mmol) instead of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . Yield: 62% (based on copper salt). Anal. Calc. for  $\text{C}_{14}\text{H}_{15}\text{ClCuN}_2\text{O}_6$ : C, 41.39; H, 3.72; N, 6.90%. Found: C, 40.92; H, 3.13; N, 6.54%. IR (KBr,  $\text{cm}^{-1}$ ): 3062(w), 2926(w), 1629(s), 1600(s), 1573(w), 1540(s), 1468(s), 1445(s), 1404(s), 1377(w), 1351(s), 1304(s), 1197(w), 1147(w), 1130(w), 1103(s), 1092(b), 1030(s), 903(s), 858(w), 764(s), 754(s), 741(s), 601(w), 563(w), 518(s), 460(w). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ),  $\text{CH}_3\text{OH}$  solution]: 631(175); 376(5980); 269(22120); 242(26900); 219(31510).  $\mu_{\text{eff}}/\text{Cu} = 1.86$  B. M. EPR ( $\text{CH}_3\text{OH}$  solution, 298 K):  $g_{\text{av}} = 2.110$ ,  $A = 73$  G.

### Synthesis of $[\text{Cu}(\text{L})(\text{N}_3)]_2$ (**3**)

To ligand **LH** (0.226 g, 1.0 mmol) dissolved in methanol (10 mL), solid  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.241 g, 1.0 mmol) was added and stirred for 10 min. To this light green solution, methanol solution of (5 mL)  $\text{NaN}_3$  (0.065 g, 1.0 mmol) was added and further stirred for another 3 h. The resulting dark green solution was filtered to remove the white precipitates which might be due to the formation of NaCl on anion metathesis and stored at room temperature for crystallization. Green colored single crystals of **3** suitable for X-ray diffraction study were obtained from the slow evaporation of the solution after one week time. Yield: 54% (based on copper salt). Anal. Calc. for  $\text{C}_{28}\text{H}_{26}\text{Cu}_2\text{N}_{10}\text{O}_2$ : C, 50.83; H, 3.96; N, 21.17%. Found: C, 50.34; H, 3.64; N, 20.67%. IR (KBr,  $\text{cm}^{-1}$ ): 3061(w), 2969(w), 2884(w), 2035(s), 1646(s), 1597(s), 1571(m), 1546(s), 1470(m), 1443(m), 1396(m), 1358(s), 1315(w), 1281(s), 1251(w), 1195(m), 1153(w), 1130(m), 1103(w), 1052(w), 921(m), 898(s), 855(w), 816(w), 767(s), 738(m), 653(w), 586(m), 548(m), 509(m), 445(m). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ),  $\text{CH}_3\text{OH}$  solution]: 630(217); 375(7810); 270(28890); 242(37750); 218(42240).  $\mu_{\text{eff}}/\text{Cu} = 1.92$  B. M. EPR ( $\text{CH}_3\text{OH}$  solution, 298 K):  $g_{\text{av}} = 2.128$ ,  $A = 74$  G.

### Synthesis of [Cu(L)(NCS)]<sub>2</sub> (4)

Compound **4** was synthesized by following the procedure described for **3** by using NaSCN (0.081 g, 1 mmol) instead of NaN<sub>3</sub>. Yield: 58% (based on copper salt). Anal. Calc. for C<sub>30</sub>H<sub>26</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub>: C, 51.94; H, 3.78; N, 12.11; S, 9.24%. Found: C, 51.14; H, 3.67; N, 11.62; S, 8.89%. IR (KBr, cm<sup>-1</sup>): 3055(w), 2958(w), 20888(s), 1629(s), 1600(s), 1567(s), 1507(w), 1445(s), 1489(w), 1345(s), 1304(s), 1295(s), 1249(w), 1158(w), 1108(s), 1037(s), 980(s), 910(s), 874(s), 794(s), 621(s), 524(s), 487(w). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>), CH<sub>3</sub>OH solution]: 625(123); 493(140); 463(187); 373(3625); 299(2800); 270(13690); 242(17580); 219(23790).  $\mu_{\text{eff}}/\text{Cu} = 1.84$  B. M. EPR (CH<sub>3</sub>OH solution, 298 K):  $g_{\text{av}} = 2.092$ ,  $A = 76$  G.

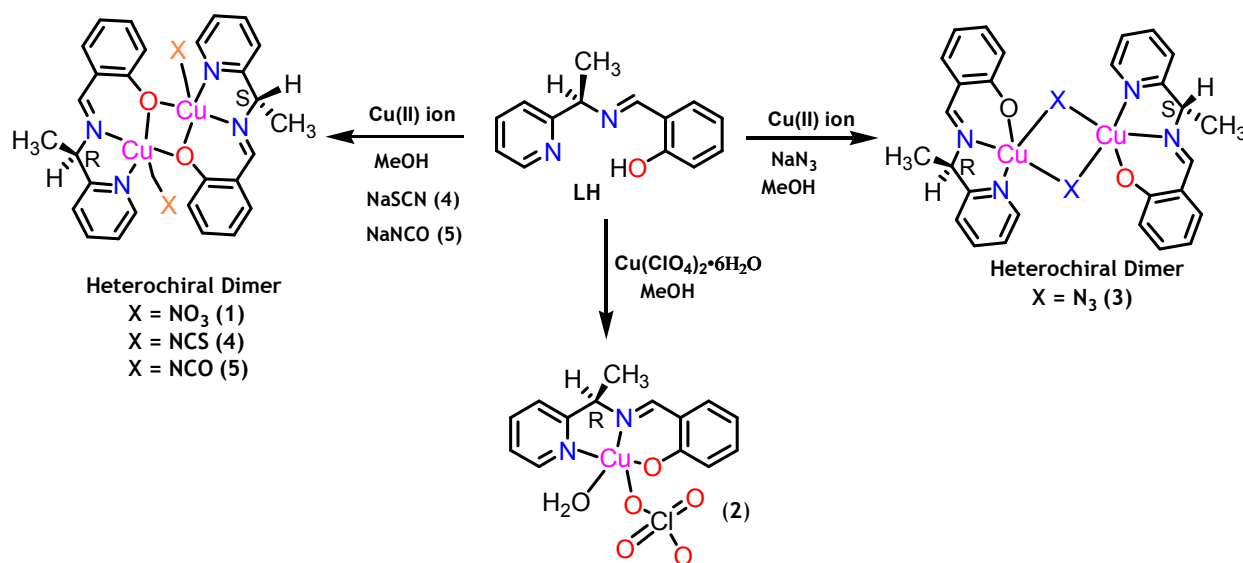
### Synthesis of [Cu(L)(NCO)]<sub>2</sub> (5)

Compound **5** was synthesized by following the procedure described for **3** by using NaCNO (0.065 g, 1 mmol) instead of NaN<sub>3</sub>. Yield: 58% (based on copper salt). Anal. Calc. for C<sub>30</sub>H<sub>26</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>4</sub>: C, 54.46; H, 3.96; N, 12.70%. Found: C, 54.14; H, 3.67; N, 12.12%. IR (KBr, cm<sup>-1</sup>): 3055(w), 2958(w), 2189(s), 1629(s), 1600(s), 1567(s), 1507(w), 1445(s), 1489(w), 1345(s), 1304(s), 1295(s), 1249(w), 1158(w), 1108(s), 1037(s), 980(s), 910(s), 874(s), 794(s), 621(s), 524(s), 487(w). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>), CH<sub>3</sub>OH solution]: 625(123); 493(140); 463(187); 373(3625); 299(2800); 270(13690); 242(17580); 219(23790).  $\mu_{\text{eff}}/\text{Cu} = 1.84$  B. M. EPR (CH<sub>3</sub>OH solution, 298 K):  $g_{\text{av}} = 2.092$ ,  $A = 76$  G.

## Results and discussions

### Synthesis of the complexes

The mono-condensed Schiff base (**LH**) is prepared following the simple condensation strategy using our earlier synthesized chiral amine (*R,S*)-1-(2-pyridyl)ethylamine with commercial available 2-hydroxy benzaldehyde in 1:1 ratio and isolates as **Scheme 1**. Synthetic scheme for complexes **1-5**.



yellow oil. The complexes **1-5** are synthesized simply by allowing ligand **LH** to react with respective Cu(II) salts followed by anion metathesis with azide (**3**), thiocyanate (**4**) and cyanate (**5**) ions in 1:1:1 ratio respectively (Scheme 1). The mono-negative tridentate Schiff bases and the anions/co-ligands such as nitrate, perchlorate, azide, thiocyanate and cyanate ions satisfies the charge of the coordination complexes. All the complexes except complex **2** and **3**, are phenoxo bridged and consequences di-copper (Cu<sub>2</sub>O<sub>2</sub>) core whereas complex **3** results  $\mu$ -1,1-azide bridged di-copper core and complex **2** results H-bonded di-copper core. In **1-5**, the axial bond is quite large due to Jahn-Teller (J-T) distortion. Such distorted square pyramidal complexes having long axial bonds finds application in MOF and acts as attractive building blocks proposing weak axial binding and coordination versatility.<sup>19</sup> The key aim of the present article is to explore the stereo selective nature of non-covalent interactions in heterochiral dimeric coordination complexes containing racemic ligand. Also the uncoordinated nitrogen atom of azide ions, sulfur atom of thiocyanate ion and oxygen atom of cyanate ions are often involved in intermolecular or intramolecular non-covalent interactions to regulate and stabilize the supramolecular structures.

The IR spectra of **1-5**, show a strong peak in the range 1610-1640 cm<sup>-1</sup> assignable to azomethine group. In addition the characteristic peaks for nitrate ion in **1** at 1384 cm<sup>-1</sup>, perchlorate ion in **2** at 1092 cm<sup>-1</sup>, azide ion in **3** at 2035 cm<sup>-1</sup>, thiocyanate ion in **4** at 2088 cm<sup>-1</sup> and cyanate ion in **5** at 2189 cm<sup>-1</sup> are noteworthy. In methanol the electronic spectra of compounds **1-4** display a *d-d* transition at around 630 nm. The allowed transitions in **1-5** were observed at around 380 and 287 nm. The room-temperature magnetic moment values of polycrystalline samples are consistent with the presence of one unpaired electron in **1-5**. In methanol medium, the EPR spectra of **1-5** at 298 K are isotropic in nature with the hyperfine splitting.

**Table 1.** Crystallographic and refinement parameters for compounds **1-5**.

	1	2	3	4	5
Chem. formula	C <sub>28</sub> H <sub>23</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>8</sub>	C <sub>14</sub> H <sub>15</sub> ClCuN <sub>2</sub> O <sub>6</sub>	C <sub>28</sub> H <sub>26</sub> Cu <sub>2</sub> N <sub>10</sub> O <sub>2</sub>	C <sub>30</sub> H <sub>26</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	C <sub>30</sub> H <sub>26</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>4</sub>
CCDC	974876	974877	974878	974879	974880
Formula weight	702.39	406.28	661.69	693.81	661.656
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	8.2841(4)	23.672(2)	20.0960(16)	7.5390(4)	7.9869(4)
<i>b</i> (Å)	8.9822(4)	8.6741(7)	7.3459(5)	18.0643(9)	16.1585(7)
<i>c</i> (Å)	9.6248(4)	27.466(3)	23.542(2)	11.6901(6)	10.9541(5)
$\alpha$ (°)	86.725(3)	-	-	-	-
$\beta$ (°)	82.846(2)	139.368(5)	127.245(6)	109.230(3)	99.580(2)
$\gamma$ (°)	81.578(2)	-	-	-	-
<i>V</i> (Å <sup>3</sup> )	702.39(5)	3672.5(6)	2766.6(4)	1503.21(13)	1393.98(11)
<i>Z</i>	1	8	4	2	4
$\mu$ (mm <sup>-1</sup> )	1.577	1.364	1.582	1.592	1.574
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.659	1.470	1.589	1.533	1.576
No. of rflns collected	3221	4195	2570	6949	4980
No. of unique rflns	2818	3993	2113	5638	3751
$\theta_{\text{min}}$ , $\theta_{\text{max}}$ (°)	2.13, 27.45	1.74, 27.45	2.12, 25.51	2.16, 35.64	2.27, 32.36
$R_1^a$ , $wR_2^b$ ( $I \geq 2\sigma(I)$ )	0.0131, 0.1082	0.0525, 0.1845	0.0566, 0.1383	0.0425, 0.0755	0.0305, 0.0833
Goodness of fit (GOF on $F^2$ )	1.057	1.006	1.009	1.004	1.045
largest peak/hole (e Å <sup>-3</sup> )	0.150/-0.287	0.589/-0.464	0.103/-0.284	0.357/-321	0.306/-0.478

$$\text{GOF} = [\sum(w(F_o^2 - F_c^2)^2) / (M - N)]^{1/2} \quad (M = \text{number of reflections, } N = \text{number of parameters refined}). \quad {}^a R_1 = \sum||F_o| - |F_c|| / \sum|F_o|. \quad {}^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

### Structural description of compounds **1-5**

The molecular structures of compounds **1-5** were determined using single crystal X-ray diffraction techniques. The crystal data and refinement parameters are listed in Table 1. Selected bond parameters are listed in Table S1. The conventions followed in discussions are: **L** = 1-((1-(2-pyridyl)ethylimino)methyl)phtholate ion; O<sub>p</sub> = phenolate-O; N<sub>γ</sub> = pyridyl-N; N<sub>1</sub> = imine-N; O<sub>L</sub> = perchlorate-O; N<sub>Z</sub> = azide-N and O<sub>C</sub> = cyanate-O.

#### Structure of [Cu<sub>2</sub>(L)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (**1**)

Compound **1** crystallized in space group *P*-1. The asymmetric unit of **1** contains mononuclear Cu(II) centre bridged by *S* isomer of ligand **L** (*S*-L) in *meridional* fashion. In **1**, the coordination geometry around Cu(II) centre is gratified by one N<sub>p</sub>N<sub>1</sub>O<sub>p</sub>-donor set of the ligand *S*-L and one nitrate ion on the square plane and O<sub>p</sub> atom of *R*-L in the axial site. Such O<sub>p</sub> bridging mode of ligand **L** leads to a di-copper core having Cu<sub>2</sub>O<sub>2</sub> unit. Thus the coordination geometry around the copper

centre can be best described by the distorted square pyramidal geometry as inferred from the  $\tau$  value of 0.04.<sup>20</sup> It is worthy to mention that within one dimer one of the ligand **L** possess *R* configuration whereas other possess *S* configuration resulting a heterochiral dimerization (*RS*) of ligand **L** around di-copper core in chiral self-discriminating manner. Thus complex **1** crystalizes in centrosymmetric space group with the inversion centre located directly between the two copper ions in Cu<sub>2</sub>O<sub>2</sub> unit. ORTEP diagram with the atom labeling scheme of the centrosymmetric dimer is displayed in Fig. 1. The presence of long axial Cu-O1A bond (2.480(1) Å) is due to J-T distortion and sited nearly perpendicular to the square plane (O1A - Cu1 - O2 = 92.56(4)° and O1A - Cu1 - N2 = 94.48(5)°) formed by ligand **L** and nitrate ion around the copper centre. The distance between two plane containing N1N2Cu1O1 atoms in the dimer is 2.456 Å. In **1**, ligand **L** is bound to the Cu(II) atom by both a five-membered and a six-membered chelate ring. The asymmetric carbon atom deviates from the otherwise nearly planar five-membered chelate ring, which is evident from the dihedral angle of 10.96° between the two planes C5C6N2 and

C5N1Cu1N2. The six-membered chelate ring is slightly puckered and has an envelope form with the Cu1 being displaced out-of-plane, as is inferred from the dihedral angle of  $19.25^\circ$  between the planes formed by N2Cu1O1 and O1C14C9C8N2. The cisoid angles are lying in the range of  $82.66(5) - 95.07(5)^\circ$  and the trans angles are in the range of  $172.58(5) - 175.18(5)^\circ$ . The bond order around the Cu(II) centre follows the trend  $\text{Cu-N}_p > \text{Cu-N}_l > \text{Cu-O}_p$ .

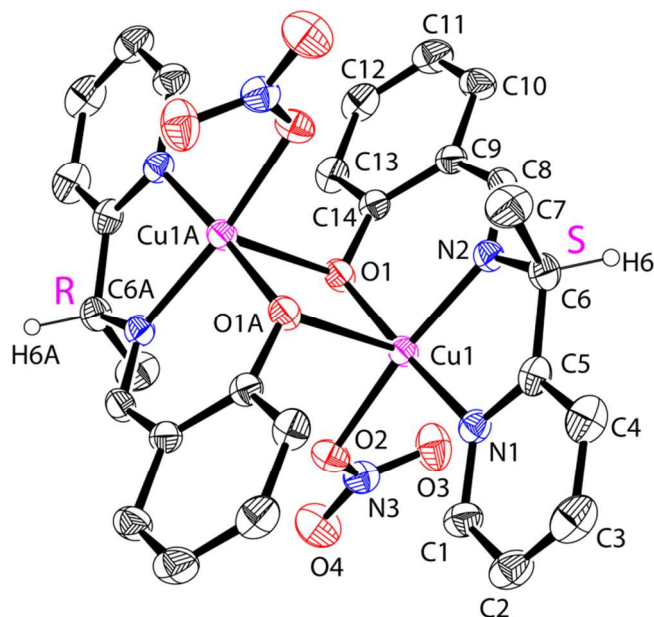


Fig. 1 ORTEP diagram (30%) and atom labeling scheme of **1** (H-atoms except H6 are omitted for clarity).

The stemmed  $\text{Cu}_2\text{O}_2$  unit has slightly butterfly in shape having the bond parameters,  $\text{Cu1} \cdots \text{Cu1A} = 3.172(1) \text{ \AA}$ ,  $\text{Cu1} - \text{O1} =$

$1.901(1) \text{ \AA}$ ,  $\text{Cu1} - \text{O1A} = 2.480(1) \text{ \AA}$ ,  $\text{Cu1} - \text{O1} - \text{Cu1A} = 91.80(4)^\circ$  and  $\text{O1} - \text{Cu1} - \text{O1A} = 88.20(4)^\circ$ . Janiak et al.<sup>7a</sup> has substantially described the effect of electron withdrawing or electron donating substituents on the face-to-face  $\pi \cdots \pi$  stacking interactions between aromatic rings i. e. electron withdrawing substituents or heteroatoms lead to the strongest  $\pi \cdots \pi$  interaction whereas electron donating substituents disfavoured a  $\pi \cdots \pi$  interaction. The order of stability in the interaction of two  $\pi$  systems is  $\pi$ -deficient- $\pi$ -deficient  $>$   $\pi$ -deficient- $\pi$ -rich  $>$   $\pi$ -rich- $\pi$ -rich. Janiak et al. also specified that a nitrogen heteroatom within the ring is also an electron-withdrawing perturbation i. e. pyridine, bipyridines and other aromatic nitrogen heterocyclic are known as electron poor ring systems. On metalation to the nitrogen heteroatom will further enhance the electron-withdrawing effect through its positive charge. Hence, aromatic nitrogen heterocycles should in principle is well suited for  $\pi \cdots \pi$  interactions because of their low  $\pi$ -electron density. The introduction of heterocyclic N increases the tendency to stack. Since the multidentate ligands with pyridine groups or nitrogen heterocycles act as most important building blocks in the design of metal-ligand networks. Therefore the present article emphasises more on the effect of  $\pi \cdots \pi$  stacking interaction on the diastereoselective self-assembly. In **1**, a notably parallel displaced  $\pi \cdots \pi$  interaction ( $\text{C11} \cdots \text{C5} = 3.327(1) \text{ \AA}$ ) between rarely occurred benzene-pyridine moiety between two nearby heterochiral dimers to 1D self-assembly (Fig. 2a). Also a notable C-H $\cdots$ O interaction ( $\text{C10-H10} \cdots \text{O3} = 3.503(1) \text{ \AA}$ ) between uncoordinated O atom (O3) of nitrate ion and ligand moiety assemble the heterochiral dimers in 1D fashion (Fig. 2a).

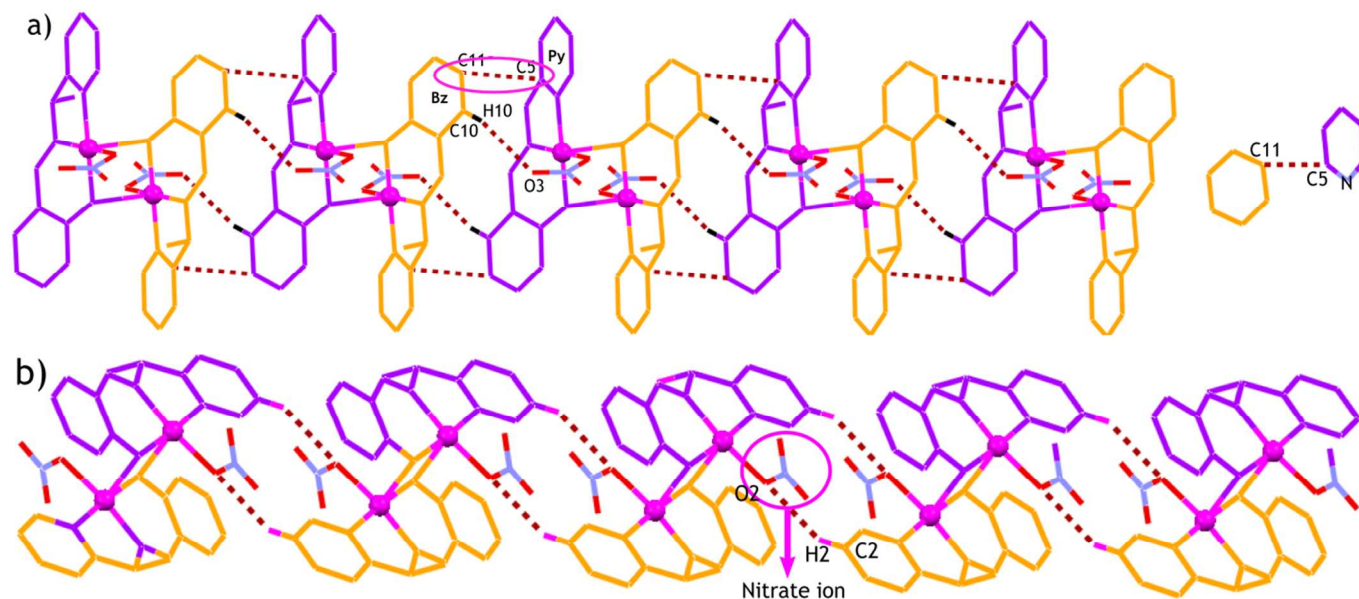


Fig. 2 Illustration of 1D self-assembly of heterochiral dimers found in **1** through (a) parallel displaced benzene-pyridine  $\pi \cdots \pi$  stacking ( $\text{C5} \cdots \text{C11}$ ; highlighted in pink) and C-H $\cdots$ O interaction ( $\text{C10-H10} \cdots \text{O3}$ ); (b) through C-H $\cdots$ O interaction ( $\text{C2-H2} \cdots \text{O2}$ ) which accumulates the asymmetric carbon atoms (C6) in an isotactic manner (orange color and brinjal color corresponds to S and R isomer of ligand L respectively).

Similarly a notable C-H...O interaction (C2-H2...O2 = 3.529(1) Å) between coordinated O atom (O2) of nitrate ion and ligand moiety assemble the heterochiral dimers in 1D fashion where isotactic arrangements of asymmetric carbon atoms occurs (Fig. 2b).

It is significant to note that the aforementioned non-covalent C-H...O interactions are between ligand of different chirality in two heterochiral dimers ( $R\cdots S$ ) i. e.  $R$  isomer of ligand **L** (in bringal colors) is linked to the  $S$  isomer (in orange colors) of ligand **L** in two nearby heterochiral dimers. In other words each ligand in the heterochiral dimers discriminates of its own chirality in nearby heterochiral dimers thru non-covalent C-H...O interaction. In packing the cooperativity between the above non-covalent interactions results a 3D sheet structure.

### Structure of [Cu(L)(H<sub>2</sub>O)(ClO<sub>4</sub>)] (2)

Compound **2** crystallized in space group  $C2/c$ . The asymmetric unit of **2** contains mononuclear Cu(II) centre bridged by  $R$  isomer of ligand **L** ( $R$ -L) in *meridional* fashion. In **2**, the coordination geometry around the five coordinated Cu(II) centre is satisfied by one N<sub>p</sub>N<sub>1</sub>O<sub>p</sub>-donor set of the ligand **L**, one equatorial coordinated H<sub>2</sub>O molecule and one axial coordinated perchlorate ion. Thus the coordination geometry around Cu(II) centre can be best described as distorted square pyramidal geometry as inferred from the  $\tau$  value of 0.01. ORTEP diagram with the atom labeling scheme of **2** is displayed in Fig. 3.

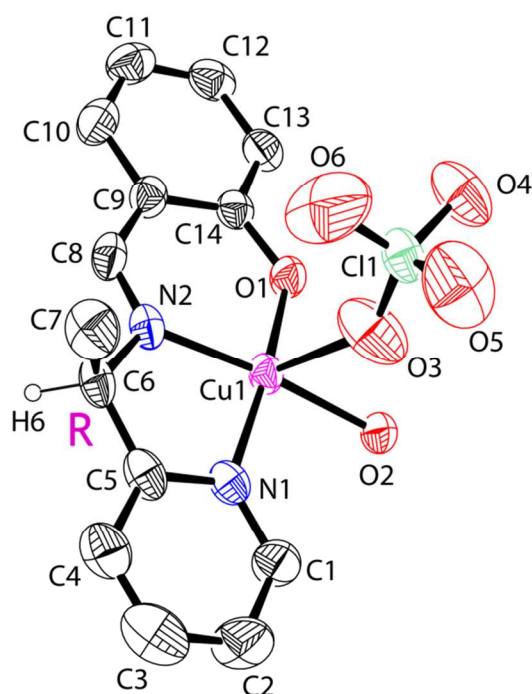


Fig. 3. ORTEP diagram (30%) and atom labeling scheme of **2** (H-atoms except H6 are omitted for clarity).

However the equatorial coordinated H<sub>2</sub>O (O2) molecule is strongly H-bonded with the phenoxo-O (O1) (O2 - O1 = 2.680(4) Å; O2 - H1-O1 = 151.7(2)°; -x,-y+1,-z+2) and

perchlorate ion (O4) ((O2 - O4 = 2.81(1) Å; O2 - H1-O1 = 173.9(3)°; -x,-y+1,-z+2) simultaneously to self-assemble the dimer formation. The aforementioned H-bonded interactions can be stated as diastereoselective H-bonding interactions as it links between two enantiomer of opposite chirality ( $R\cdots S$ ) (Fig. 4). The presence of long axial Cu-O3 bond (2.463(8) Å) is due to J-T distortion and is sited nearly perpendicular to the square plane (N2 - Cu1 - O3 = 103.5(2)° and O2 - Cu1 - O3 = 81.3(2)°) formed by ligand **L** and H<sub>2</sub>O molecule around the copper centre.

During the dimer formation chiral self-discrimination process plays domino role in favor of heterochiral dimerization ( $RS$ ) of ligand **L** around the di-copper core. Thus compound **2** crystallizes in centrosymmetric space group with the inversion centre located directly between the two copper ions in Cu<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> unit.

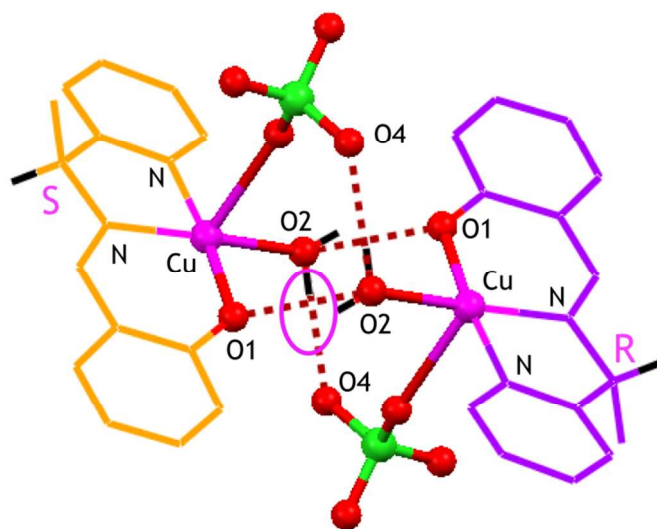


Fig. 4 Illustration of heterochiral dimerization through diastereoselective H-bonding interactions found in compound **2**. Color code same as Fig. 2.

In **2** ligand **L** is bound to the Cu(II) atom by a five-membered and a six-membered chelate ring. The asymmetric carbon atom deviates from the otherwise nearly planar five-membered chelate ring, which is evident from the dihedral angle of 10.95° between the two planes C5C6N2 and C5N1Cu1N2. In **2**, the axial coordinated perchlorate ion forces the ligand to be nearly planar which minimizes the out-of-displacement of Cu1 from the nearly planar six membered rings in comparison to compound **1**. The cisoid angles are lying in the range of 81.3(2) - 103.5(2)° and the trans angles are in the range of 173.2(2) - 173.8(1)°. The bond order around the copper centre follows the trend Cu-N<sub>p</sub> > Cu-N<sub>1</sub> > Cu-O<sub>p</sub>.

A notably C-H...O (C8-H8...O4 = 3.477(6) Å) interaction between uncoordinated O atom of the perchlorate ion (O4) and ligand moiety in nearby heterochiral dimers assembles to a 1D structure (Fig. 5). Thus the noted C-H...O interactions are enantioselective ( $R\cdots R$  or  $S\cdots S$ ) in nature.



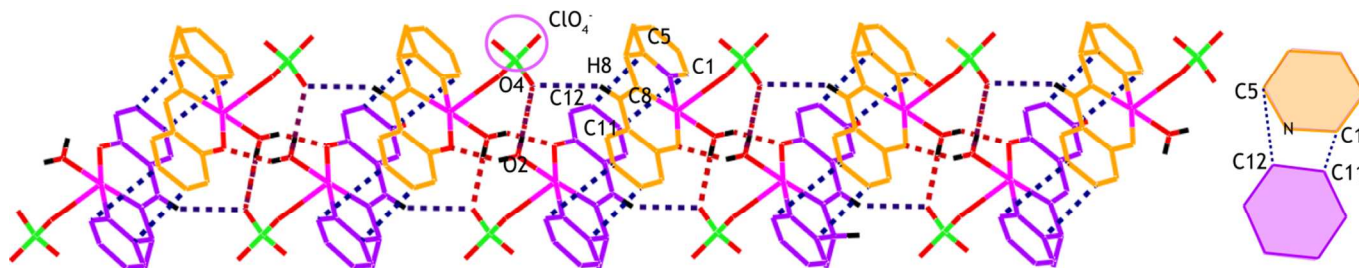


Fig. 5 Illustration of 1D chain found in **2** through C-H...O and parallel displaced  $\pi\cdots\pi$  interactions. Color codes same as Fig. 2.

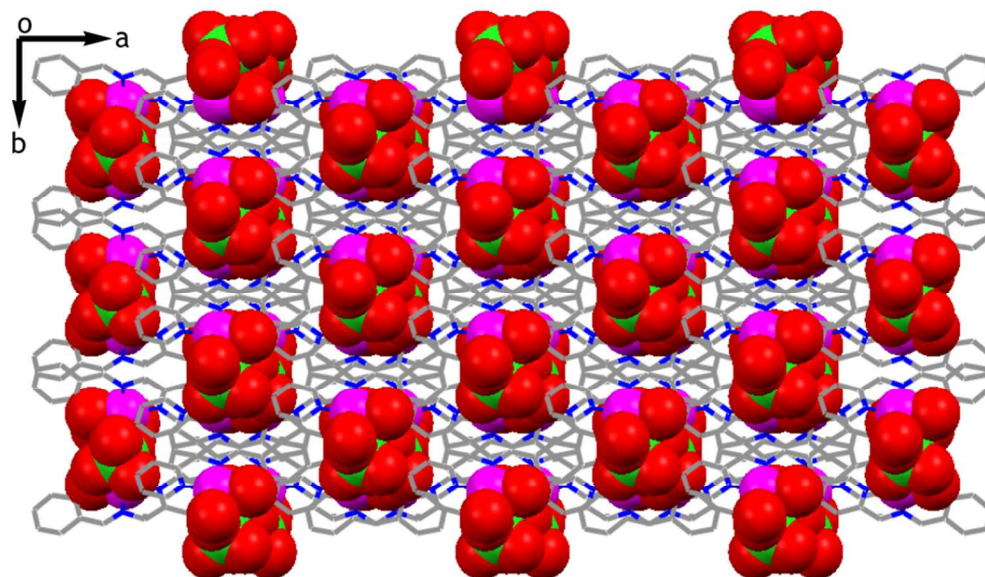


Fig. 6 Illustration of 3D self-assembly found in **2** showing hydrophilic channels inside the lattice. Color codes same as Fig. 2.

In other words each ligand in the heterochiral dimers recognizes of its own chirality in nearby heterochiral dimers thru the non-covalent C-H...O interaction. Hence it can be stated that in **2**, phenoxo-O bridges results heterochiral dimerization whereas C-H...O interaction results homochiral dimerization in a particular 1D chain. Similar to **1**, in **2** parallel displaced  $\pi\cdots\pi$  interaction ( $C1\cdots C11 = 3.386(9)$  Å,  $C5\cdots C12 = 3.395(8)$  Å) between benzene-pyridine dimers further support the above noted 1D chain. Such parallel displaced  $\pi\cdots\pi$  interaction exists between two enantiomers of opposite chirality and retains a centre of symmetry in between them. In packing, the hydrophilic region composed of coordinated water and perchlorate ions are accumulated similar to channels as shown in Fig. 6. It is worthy note that structurally similar copper complex containing Ph-substituted ligand L resulted 3D self-assembly where 1D hydrophilic regions are sandwiched between two hydrophobic layers.<sup>14b</sup> Thus the noted structural dissimilarity arises from the ligand substitution and conveys the important effect of ligand substitution on the structural arrangements.

### Structure of $[Cu_2(L)_2(N_3)_2]$ (**3**)

Compound **3** crystallized in space group  $C 2/c$ . The asymmetric unit of **3** contains mononuclear Cu(II) centre bridged by *R* isomer of ligand L (*R*-L) in *meridional* fashion and one azide ion on the square plane. The N3 atom of azide ion further bridges to the other Cu(II) centre through  $\mu$ -1,1- bridge leading to a di-copper core. Similar to compound **1** and **2**, in **3** one dimer contains both *R* and *S* configuration of ligand L and consequences a heterochiral dimerization (*RS*) around di-copper core in chiral self-discriminating manner i. e. the inversion centre located directly between the two copper ions in  $Cu_2(N_3)_2$  unit. It has been reported that such  $\mu$ -1,1-azide bridge engenders antiferromagnetic interactions (since  $Cu1-N3-Cu1A = 96.4(1)^\circ > 90^\circ$ ) between the two copper centres. Thus the coordination geometry around Cu(II) centre can be best described as distorted square pyramidal geometry ( $\tau = 0.06$ ). ORTEP diagram with the atom labeling scheme of the centrosymmetric dimer is displayed in Fig. 7. In **3** the asymmetric carbon atom deviates from the otherwise nearly planar five-membered chelate ring, which is evident from the dihedral angle of  $9.35^\circ$  between the two planes  $C5C6N2$  and  $C5N1Cu1N2$ . The cisoid angles are lying in the range of  $82.1(1) - 106.0(1)^\circ$  and the trans angles are in the range of

169.4(1) - 173.3(1)°. The bond order around the copper centre follows the trend  $\text{Cu-N}_p > \text{Cu-N}_i > \text{Cu-O}_p$ .

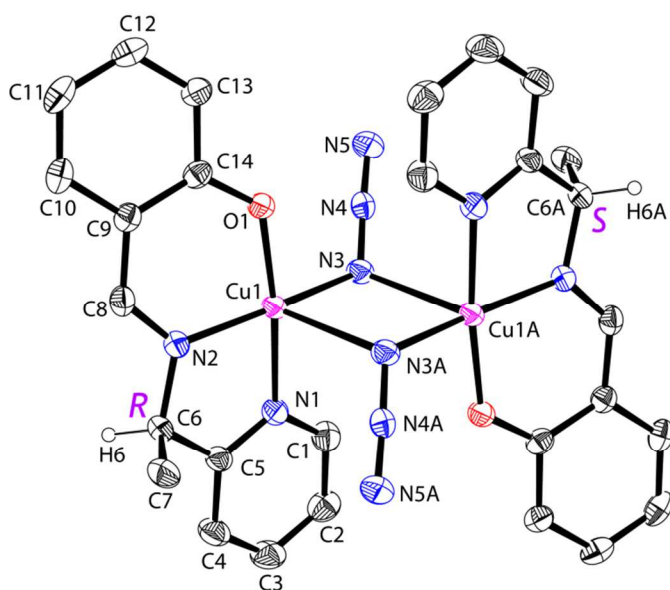


Fig. 7 ORTEP diagram (30%) and atom labeling scheme of **3** (H-atoms except H6 are omitted for clarity).

The stemmed  $\text{Cu}_2(\text{N}_7)_2$  unit has slightly butterfly in shape having the bond parameters,  $\text{Cu1} \cdots \text{Cu1A} = 3.44(1) \text{ \AA}$ ,  $\text{Cu1} -$

$\text{N3} = 1.992(3) \text{ \AA}$ ,  $\text{Cu1} - \text{N3A} = 2.591(3) \text{ \AA}$ ,  $\text{Cu1} - \text{N3} - \text{Cu1A} = 96.4(1)^\circ$  and  $\text{N3} - \text{Cu1} - \text{N3A} = 83.6(1)^\circ$ .

Similar to compound **1** and **2**, in **3** a notably parallel displaced  $\pi \cdots \pi$  interaction between benzene-pyridine dimer ( $\text{C2} - \text{C9} = 3.393(6) \text{ \AA}$ ) assembles the  $\mu$ -1,1- $\text{N}_7$  bridge heterochiral dimers to 1D polymer as illustrated in Fig. 8a. In other words each ligand in the heterochiral dimers discriminates of its own chirality in nearby heterochiral dimers through the non-covalent parallel displaced  $\pi \cdots \pi$  interaction. So it can be stated that in a 1D chain, one heterochiral dimerization occurs through  $\text{O}_p$  bridges and another through parallel displaced  $\pi \cdots \pi$  interaction.

Detail analysis of the 1D chains reveals that the above noted  $\pi \cdots \pi$  interaction links two opposite enantiomers of **L** in nearby heterochiral dimers and hence consequence another heterochiral dimerization. Also a notable  $\text{C-H} \cdots \text{N}$  interaction between ( $\text{C7} - \text{H7B} \cdots \text{N5} = 3.516(8) \text{ \AA}$ ) uncoordinated N atom of azide ion ( $\text{N5}$ ) and the methyl ( $\text{C7}$ ) group appended to the asymmetric carbon atom assemble the heterochiral dimers to 1D polymeric structure where isotactic arrangements of asymmetric carbon atoms occur as shown in Fig. 8b. Similarly another  $\text{C-H} \cdots \text{N}$  interaction ( $\text{C11-H11} \cdots \text{N4} = 3.509(4) \text{ \AA}$ ) and  $\text{C-H} \cdots \pi$  interaction ( $\text{C6-H6} \cdots \text{C11} = 3.705(5) \text{ \AA}$ ) self-assembles the heterochiral dimers to 2D sheet structures. The noted 2D sheet structures further link through the aforementioned  $\text{C-H} \cdots \text{N}$  interaction to form 3D flower structures down the  $c$  axis.

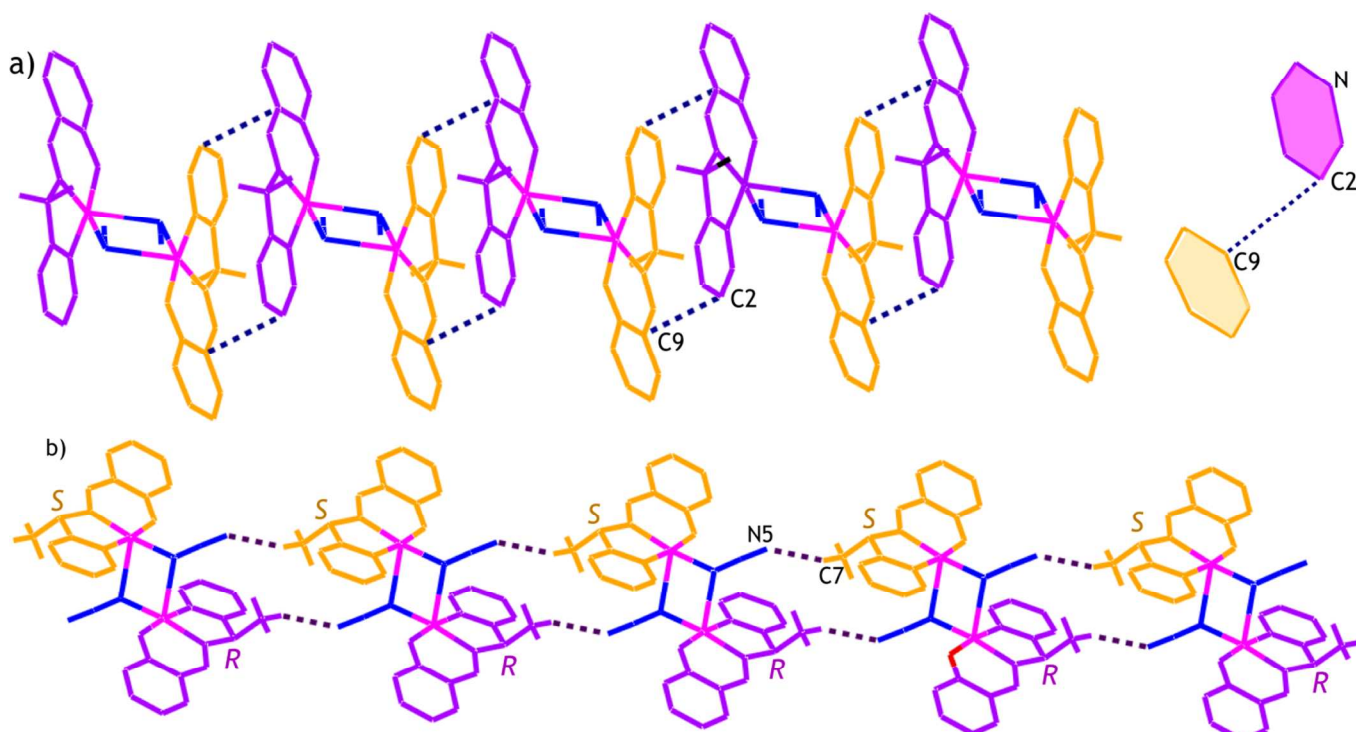


Fig. 8 Illustration of 1D self-assembly of  $\mu$ -1,1-azide bridged  $\text{Cu(II)}$  heterochiral dimers found in **3** through (a) diastereoselective parallel displaced  $\pi \cdots \pi$  interactions between benzene-pyridine dimers and (b) diastereoselective  $\text{C-H} \cdots \text{N}$  interactions between uncoordinated N atom of azide ion ( $\text{N5}$ ) and methyl group ( $\text{C7}$ ) appended to asymmetric carbon atoms. Color codes same as Fig. 2.

### Structure of $[\text{Cu}_2(\text{L})_2(\text{NCS})_2]$ (**4**)

Compound **4** crystallized in space group  $P 2_1/c$ . The asymmetric unit of **4** contains mononuclear Cu(II) centre bridged by *R* isomer of ligand **L** (*R*-L) in *meridional* fashion and one terminal coordinated thiocyanate ion on the square plane. The O1 atom of **L** further bridges to the other Cu(II) centre through  $O_P$  bridge leading to a di-copper core having  $\text{Cu}_2\text{O}_2$  unit. It is worthy to mention that compound **1** upon anion metathesis with azide ion results  $\mu$ -1,1- azide bridged di-copper core whereas upon metathesis with thiocyanate ion results  $O_P$  bridged di-copper core. Similar to compound **1**, in **4** the resulted dimer encompasses both *R* and *S* configuration of **L** and hence results a heterochiral dimerization (*RS*) of ligand **L** around di-copper core in chiral self-discriminating manner and retains an inversion centre directly between the two copper ions in  $\text{Cu}_2\text{O}_2$  unit. Thus the coordination geometry around Cu(II) centre can be best described as distorted square pyramidal geometry ( $\tau = 0.11$ ). ORTEP diagram with the atom labeling scheme of the centrosymmetric dimer is displayed in Fig. 9. The presence of axial Cu1 - O1A bond (2.413(1) Å) is due to J-T distortion and sited perpendicular to the square plane ( $\text{O1A} - \text{Cu1} - \text{O2} = 87.57(5)^\circ$  and  $\text{O1A} - \text{Cu1} - \text{N2} = 93.75(7)^\circ$ ) formed by ligand **L** and thiocyanate ion around the copper centre.

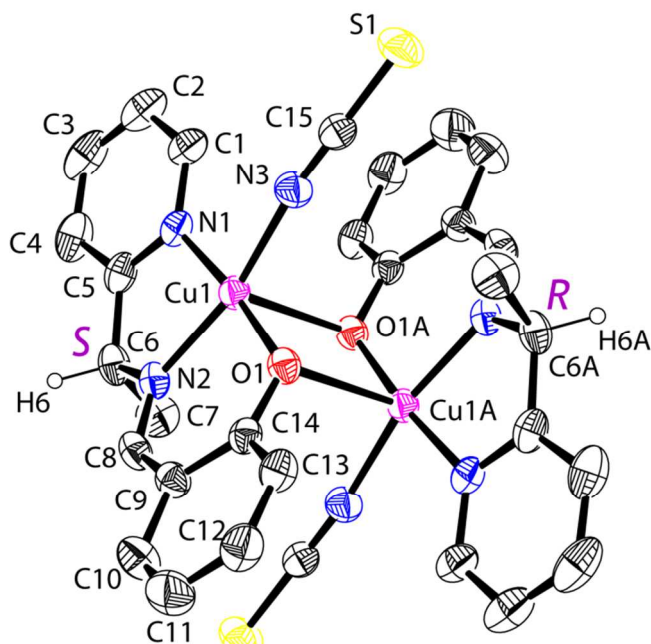


Fig. 9 ORTEP diagram (30%) and atom labeling scheme of **4** (H-atoms except H6 are omitted for clarity).

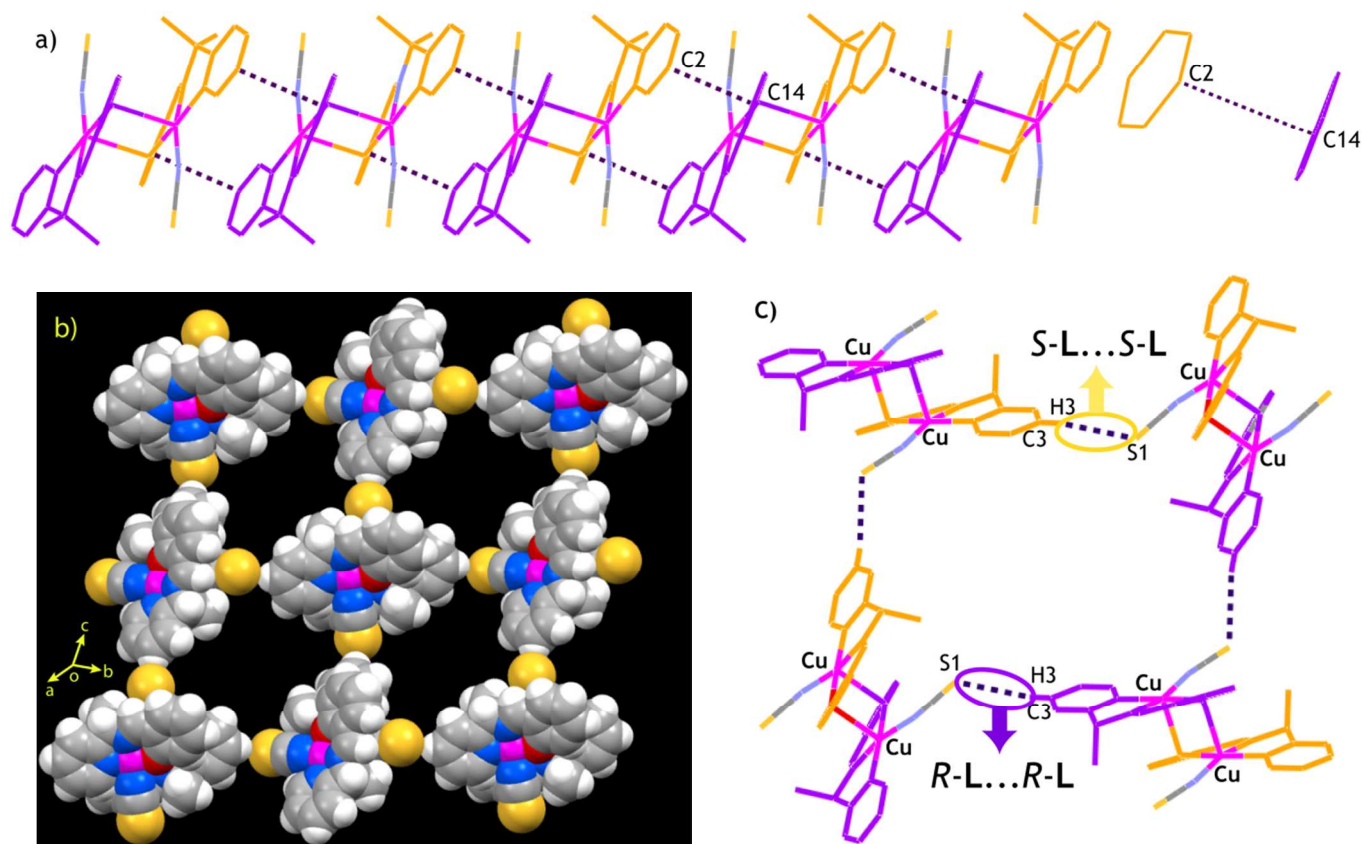


Fig. 10 Illustrations of (a) 1D self-assembly of heterochiral dimers through parallel displaced  $\pi\cdots\pi$  interactions between benzene-pyridine dimers; (b) 2D supramolecular MOF originating from the weak  $\text{C-H}\cdots\text{S}$  interaction; (c) enantioselective weak  $\text{C-H}\cdots\text{S}$  interaction which accumulates the heterochiral dimers into a non-covalent MOF. Color codes same as Fig. 2.

The distance between two plane containing N1N2Cu1O1 atoms in the dimer is 2.387 Å. Similar to compound **1-3**, in **4** the asymmetric carbon atom deviates from the otherwise nearly planar five-membered chelate ring, this is evident from the dihedral angle of 17.51° between the two planes C5C6N2 and C5N1Cu1N2. In **4** the deviations of asymmetric carbon atom from the planar five membered ring is more in comparison to others which might be due to anion metathesis with different anions. The six-membered chelate ring is slightly puckered and has an envelope form with the Cu1 being displaced out-of-plane, as is inferred from the dihedral angle of 15.14° between the planes formed by N2Cu1O1 and O1C14C9C8N2. The cisoid angles are lying in the range of 82.01(7) - 98.52(6)° and the trans angles are in the range of 167.30(8) - 174.19(7)°. The bond order around the copper centre follows the trend  $\text{Cu-N}_p > \text{Cu-N}_l > \text{Cu-O}_p$ . The resulted  $\text{Cu}_2\text{O}_2$  unit has slightly butterfly in shape having the bond parameters,  $\text{Cu1} \cdots \text{Cu1A} = 3.150(4)$  Å,  $\text{Cu1} - \text{O1} = 1.926(2)$  Å,  $\text{Cu1} - \text{O1A} = 2.413(1)$  Å,  $\text{Cu1} - \text{O1} - \text{Cu1A} = 92.43(5)^\circ$  and  $\text{O1} - \text{Cu1} - \text{O1A} = 87.57(5)^\circ$ .

Similar to compound **1-3**, in **4** notably parallel displaced  $\pi \cdots \pi$  interactions ( $\text{C14} \cdots \text{C2} = 3.249(4)$  Å) between benzene-pyridine dimers gathers the heterochiral dimers in 1D fashion as illustrated in Fig. 10a. The resulted  $\pi \cdots \pi$  interactions are in between the ligand of opposite chirality in two nearby heterochiral dimers ( $R \cdots S$ ) and consequences another heterochiral dimerization thru the non-covalent  $\pi \cdots \pi$  interaction. Also a notably weak  $\text{C-H} \cdots \text{S}$  interaction ( $\text{C3-H3} \cdots \text{S1} = 3.791(3)$  Å) between uncoordinated S atom of thiocyanate ion and the ligand moiety consequences 2D supramolecular MOF<sup>21</sup> as illustrated in Fig. 10b. The above noted  $\text{C-H} \cdots \text{S}$  interaction interlinks two enantiomer of ligand **L** between two nearby heterochiral dimers as shown in Fig. 10c and hence can be termed as enantioselective  $\text{C-H} \cdots \text{S}$  interaction. In other words ligand in the heterochiral dimers recognizes of its own chirality in the nearby heterochiral dimers thru the noted non-covalent  $\text{C-H} \cdots \text{S}$  interaction. The aforementioned 2D non-covalent MOF further associates with aforementioned parallel displaced  $\pi \cdots \pi$  interactions between benzene-pyridine dimers and consequences a 3D structure.

### Structure of $[\text{Cu}_2(\text{L})_2(\text{NCO})_2]$ (**5**)

Compound **5** crystallized in space group  $P 2_1/n$ . The asymmetric unit of **5** contains mononuclear Cu(II) centre bridged by *S* isomer of ligand **L** (*S-L*) in *meridional* fashion and one terminal coordinated cyanate ion on the square plane. Thus compound **1**, **4** and **5** are pseudo-isomorphous in nature. Similar to compound **1** and **4**, in **5** the O1 atom of **L** further bridges to the other Cu(II) centre through phenoxo-O bridge leading to a di-copper core having  $\text{Cu}_2\text{O}_2$  unit. Hence the coordination geometry around the di-copper core can be best described as distorted square pyramidal geometry ( $\tau = 0.04$ ). It is worthy to mention that compound **1** upon anion metathesis with azide ion results  $\mu$ -1,1- azide bridged di-copper core whereas upon metathesis with thiocyanate ion (**4**) and cyanate ion (**5**) results phenoxo bridged di-copper core. ORTEP

diagram with the atom labeling scheme of the centrosymmetric dimer is displayed in Fig. 11.

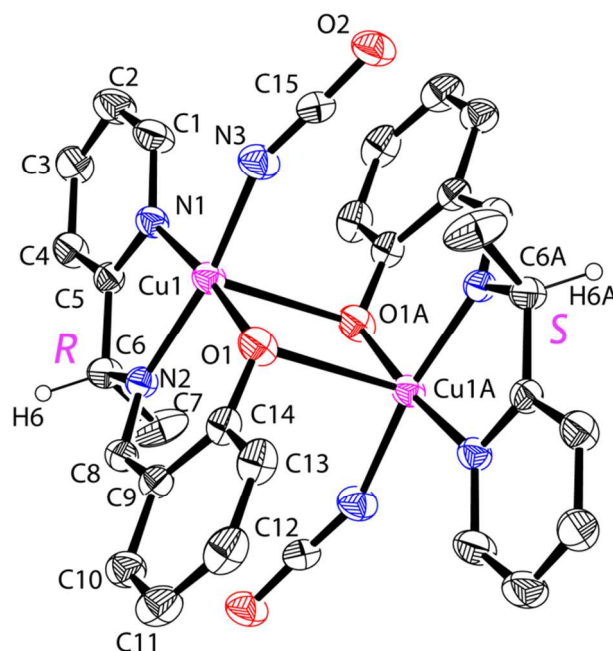
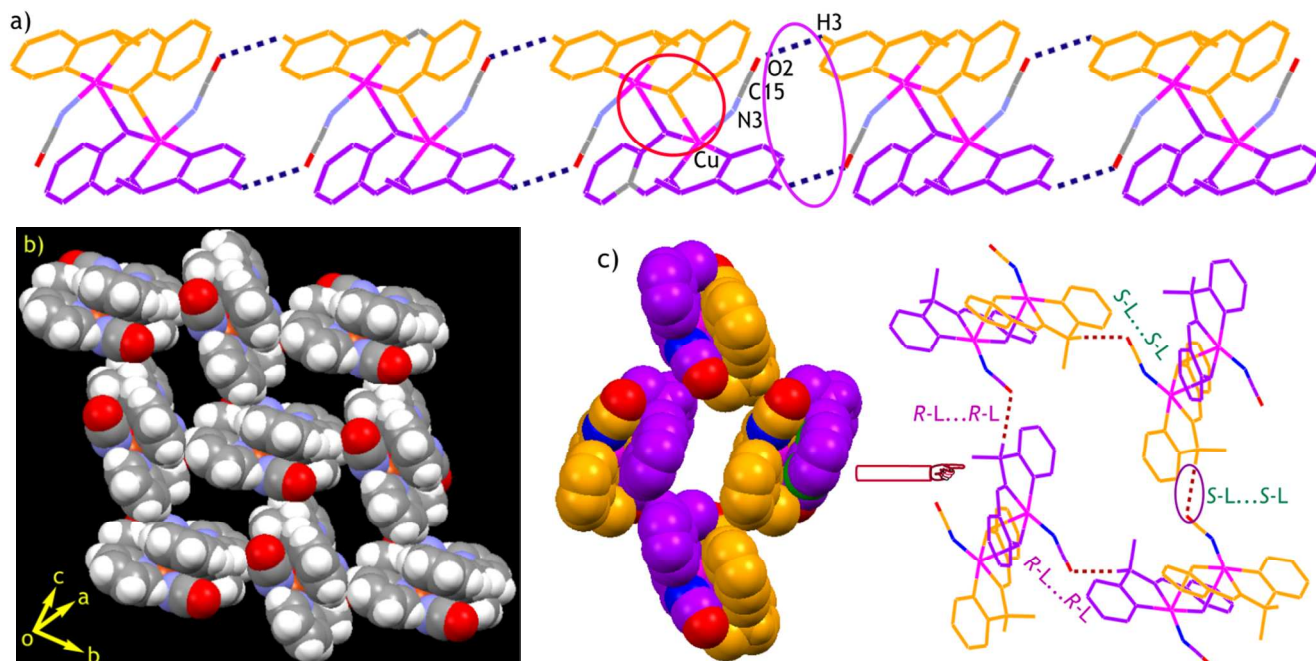


Fig. 11 ORTEP diagram (30%) and atom labeling scheme of **5** (H-atoms except H6 are omitted for clarity).

The presence of long axial  $\text{Cu1} - \text{O1A}$  bond (2.693(1) Å) is due to J-T distortion and sited perpendicular to the square plane ( $\text{O1A} - \text{Cu1} - \text{N2} = 92.87(4)^\circ$  and  $\text{O1A} - \text{Cu1} - \text{N3} = 94.91(5)^\circ$ ) formed by ligand **L** and cyanate ion around the copper centre. The distance between two plane containing N1N2Cu1O1 atoms in the dimer is 2.693 Å. In comparison to compound **4**, in **5** the deviation of the asymmetric carbon atom from the nearly planar five-membered chelate ring is less, which is evident from the dihedral angle of 10.81° between the two planes C5C6N2 and C5N1Cu1N2 and is due to anion metathesis with different anion. The cisoid angles are lying in the range of 82.32(5) - 94.91(5)° and the trans angles are in the range of 170.96(6) - 173.73(5)°. The bond order around the copper centre follows the trend  $\text{Cu-N}_p > \text{Cu-N}_l > \text{Cu-O}_p$ . The resulted  $\text{Cu}_2\text{O}_2$  unit has slightly butterfly in shape having the bond parameters,  $\text{Cu1} \cdots \text{Cu1A} = 3.343(3)$  Å,  $\text{Cu1} - \text{O1} = 1.927(1)$  Å,  $\text{Cu1} - \text{O1A} = 2.693(1)$  Å,  $\text{Cu1} - \text{O1} - \text{Cu1A} = 91.17(4)^\circ$  and  $\text{O1} - \text{Cu1} - \text{O1A} = 88.83(4)^\circ$ .

Detail structural analysis of **5** reveals several important features through different non-covalent interactions. It has been noticed that although compound **5** contains same ligand and same metal ion as compound **1-4**, “parallel displaced  $\pi \cdots \pi$  interactions” those are earlier found in **1-4**, are absent in compound **5**. Thus the absence of parallel displaced  $\pi \cdots \pi$  interactions in **5** substantiates the profound effect of anion metathesis on the existence of non-covalent interactions. However a notably  $\text{C-H} \cdots \text{O}$  interaction ( $\text{C3-H3} \cdots \text{O2} = 3.316(2)$  Å) between uncoordinated O atom (O2) of cyanate ion and the ligand moiety consequences 1D structure as illustrated in Fig. 12a.



**Fig. 12** Illustrations of (a) 1D self-assembly of phenoxo bridged heterochiral dimers through C-H...O interaction; (b) 2D non-covalent MOF originating from C-H...O interaction between asymmetric carbon atoms and cyanate-O (O3) atoms; (c) notably C-H...O interaction accumulating the heterochiral dimers to 2D supramolecular MOF structures and homochiral dimerization through C-H...O interactions. Color codes same as Fig. 2.

It is worthy mention to note that in the above 1D structure the noted C-H...O interaction interlinks between *R* and *S* isomer of ligand **L** in between two nearby heterochiral dimers. Also a notable C-H...O interaction (C6-H6...O2 = 3.416(2) Å) between the asymmetric carbon atoms and the uncoordinated O atom (O2) of the cyanate ions assembles the heterochiral dimers to a 2D supramolecular MOF similar to compound **4** as shown in Fig. 12b. A close look towards a particular framework reveals that the above noted C-H...O interactions are enantioselective in nature i. e. it links two ligand **L** of same chirality (*R*...*R* or *S*...*S*) in nearby heterochiral dimers as illustrated in Fig. 12c. Such enantioselective nature of the above C-H...O interactions results a homochiral dimerization of two nearby heterochiral dimers in a 1D chain. In lattice the cooperation between above noted C-H...O interactions assembles the heterochiral dimers to a 3D structure.

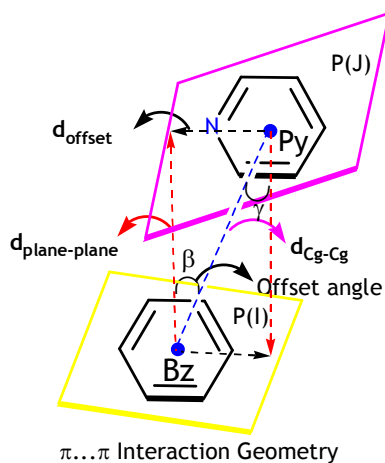
### Effect of cooperative non-covalent interactions on the solid state structural self-assembly: An overall discussion

Herein solid state diastereoselective self-assembly of heterochiral dimers on crystal engineering context are discussed. It is noteworthy to mention that during synthesis of compounds **1-5**, a racemic mixture of **LH** has been used and hence the isolated five Cu(II) compounds are racemic in nature and monochelated tridentate ligand **L** binds to the metal centre in tridentate *meridional* fashion. Overall in compounds **1-5**, copper centre exhibits distorted square pyramidal geometry.

The long axial bond is due to the J-T distortion. It is immense important to note that all the isolated compounds have a centre of symmetry within the di-copper core and hence are heterochiral in nature. In other words during dimerization of ligand **L** around the di-copper core, each ligand discriminates the chirality of its own and results a heterochiral dimerization. Thus in the present circumstances isolated heterochiral self-assembly of racemic Schiff bases around the di-copper core is the preferred and stable one over the homochiral self-assembly. The aforementioned results address new examples of rarely occurs chiral self-discriminating process. Although the difference in structural arrangements can be explained mostly in terms of cooperative non-covalent interactions, the role of the different terminal anions should not be neglected. From the structural point of view, it is noticed that in **1-5**, the methyl group attached to the asymmetric carbon atom (C6) and the anions are *trans* to each other i. e. the two anions are oriented away from the Cu<sub>2</sub>O<sub>2</sub> unit and the two methyl group attached to the asymmetric carbon atoms are orientated towards the Cu<sub>2</sub>O<sub>2</sub> unit. Thus such arrangement of anions and the methyl group minimize the steric congestion<sup>13a</sup> between two monomers and accumulate a centre of symmetry in between them to form heterochiral dimer in self-discriminating manner. Also the role of anions and non-covalent interactions on the solid state diastereoselective self-assembly are elaborately discussed. Recently, Aakeröy et al.,<sup>22</sup> Brammer et al.<sup>23</sup> and others<sup>24, 25</sup> reported the effect of non-covalent interactions on the self-assembly of Cu(II) dimers. In this context, crystal packing pattern of compounds **1-5** are further analyzed in terms of non-

covalent C-H $\cdots$ O, C-H $\cdots$ N, C-H $\cdots$  $\pi$ , and parallel displaced  $\pi\cdots\pi$  interactions. It was found that in **1-5** heterochiral dimers are interweaved through above noted cooperative non-covalent interactions into dimensional supramolecular networks. In other words each ligand in particular heterochiral dimers discriminates the chirality of its own and its opposite in nearby heterochiral dimers through the above noted non-covalent interactions. In the crystal structure of compound **1-4**, parallel displaced  $\pi\cdots\pi$  interaction between pyridine and benzene rings in two adjacent heterochiral dimers is perceived, which act cooperatively with other different non-covalent interactions. It is unprecedented to note that although compound **1-5** contains same ligand **L** and same Cu(II) ion, only compound **1-4** have such parallel displaced  $\pi\cdots\pi$  interactions. The pragmatic parallel displaced  $\pi\cdots\pi$  interaction between pyridine and benzene rings in two nearby heterochiral dimers can be classified as energetically favorable parallel-displaced  $\pi\cdots\pi$  interaction with C - C distances of range 3.249(4) - 3.395(8) Å<sup>7, 26</sup> (Scheme 2). The above parallel-displaced  $\pi\cdots\pi$  interaction chooses a more favorable head-to-tail arrangements of benzene and pyridine

rings in two nearby heterochiral dimers (Fig. 17). A graphical representation of geometrical parameters for  $\pi\cdots\pi$  interaction observed for compound **1-4** are presented in Scheme 2 and the relevant data are illustrated in Table 2. In **2** the coordinated water (O<sub>w</sub>) molecules involved in bifurcated H-bonding interactions with perchlorate ion and O<sub>p</sub> atoms simultaneously to result heterochiral dimer. The noted H-bonded heterochiral dimer extends through different C-H $\cdots$ O and  $\pi\cdots\pi$  interactions to 3D structures where the hydrophilic regions are accumulated like channels surrounded by the hydrophobic regions. Thus the above results substantially demonstrate that non-covalent interactions have profound effect on the self-assembly of coordination complexes containing racemic Schiff base ligands and explore their enantioselective and diastereoselective nature. It can be anticipated that the present discussion will boost the preliminary knowledge for the possible self-assembly of racemic Schiff bases on complexation with suitable metal ions and also explore the role of anions and non-covalent interactions on the coordination networks or supramolecular coordination framework in future.



**Scheme 2.** Graphical representation of the geometric parameters for the description of  $\pi\cdots\pi$  interactions in pyridine-benzene dimer.

**Table 2.** Distances (*d*/Å) and angles (°) for the description of the  $\pi\cdots\pi$  interactions in **1-4**.

Compound	C-C	$d_{\text{Cg-Cg}}^a$	$\alpha^b$	$d_{\text{plane-plane}}^c$	$\beta, \gamma^d$	$d_{\text{offset}}^e$
1	C5-C11=3.327(2) <sup>#1</sup>	4.403	21.54	2.752, 3.758	51.31, 31.40	3.437, 2.294
	C1-C11=3.386(9) <sup>#2</sup>					
2	C5-C12=3.395(8) <sup>#3</sup>	3.953	11.54	3.555, 3.147	26.30, 37.23	1.728, 2.392
	C2-C9=3.393(6) <sup>#4</sup>					
3	C2-C9=3.393(6) <sup>#4</sup>	4.464	16.52	2.971, 3.759	48.26, 32.63	3.331, 2.407
	C2-C14=3.249(4) <sup>#5</sup>					
4	C2-C14=3.249(4) <sup>#5</sup>	4.825	22.89	3.727, 2.283	39.42, 61.74	3.064, 4.250

For definition of parameters see Scheme 2. <sup>a</sup> Cg - Cg distance; <sup>b</sup> Dihedral angle between the ring planes. <sup>c</sup> Perpendicular distance of Cg(I) on ring J and perpendicular distance of Cg(J) on ring I. <sup>d</sup> Offset angles: angle between Cg(I) - Cg(J) vector and normal to plane I, angle between Cg(I)-Cg(J) vector and normal to plane J ( $\beta = \gamma$  when  $\alpha = 0$ ). <sup>e</sup> Horizontal displacement between Cg(I) and Cg(J), two values if the two rings are not exactly parallel ( $\alpha = 0$ ). Symmetry code: #1: -x+2, -y+2, -z+1, 3/2; #2: -x, -y+2, -z+2; #3: -x, -y+2, -z+2; #4: -x, -y+1, -z; #5: -x+2, -y, -z.

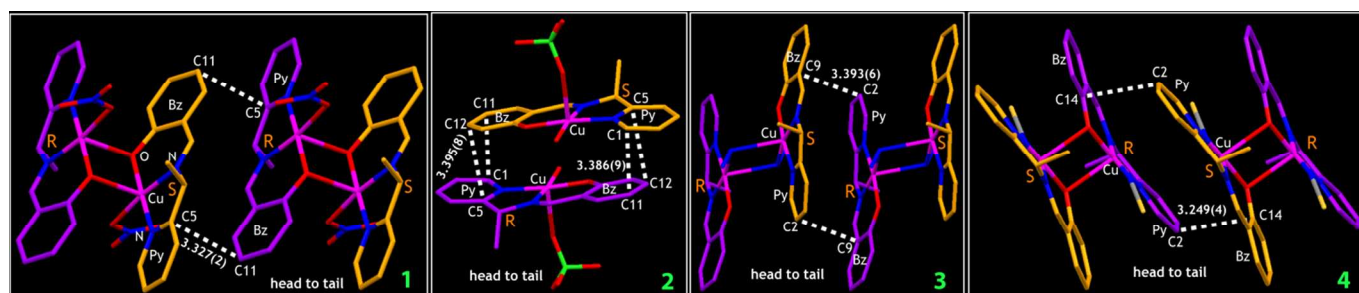


Fig. 17 Perspectives view of head to tail parallel displaced  $\pi\cdots\pi$  interaction between benzene (Bz) and pyridine (Py) rings of two nearby molecules found in compounds 1-4. Color codes same as Fig. 2.

## Conclusion

To reconnoiter the significant effect of non-covalent interactions and anions on the solid state diastereoselective self-assembly of heterochiral coordination complex containing racemic Schiff base, five Cu(II) heterochiral complexes are synthesized and structurally characterized. Determination of molecular structures of 1-5 confirmed the presence centrosymmetric dimer where ligand retains both *R* and *S* configurations resulting heterochiral dimerization around di-copper core in chiral self-discriminating manner. It was found that in 1-5 heterochiral dimers are interweaved through cooperative non-covalent interactions into dimensional supramolecular networks. In other words each ligand in particular heterochiral dimers discriminates the chirality of its own and its opposite in nearby heterochiral dimers through the above noted non-covalent interactions. In the crystal structure of compound 1-4, parallel displaced  $\pi\cdots\pi$  interaction between pyridine and benzene rings in two adjacent heterochiral dimers is perceived, which act cooperatively with other different non-covalent interactions. Although the original reason behind such heterochiral dimerization of ligand around the di-copper core and the stereo selective nature of the non-covalent interactions are not revealed, it may be the anions that drive such divergence. The aforementioned results demonstrate anions and non-covalent interactions plays domino role on controlling the supramolecular solid state structural rearrangements of the compounds. Further studies on diastereoselective self-assembly of coordination complex containing newly designed racemic Schiff bases are in progress.

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## Notes and references

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