

# Effect of cooperative non-covalent interactions on the solid state heterochiral self-assembly: The concepts of isotactic and syndiotactic arrangements in coordination complex



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## ABSTRACT

Solid state diastereoselective self-assembly of five copper(II) heterochiral complexes containing racemic Schiff bases **L1H** and **L2H** (where **L1H** = 1-((1-(2-pyridyl)ethylimino)methyl)-2-naphthol; **L2H** = 2-((phenyl(2-pyridyl)methylimino)-methyl)phenol) in crystal engineering contexts are discussed. Complexes **1–5** are synthesized using ligand **L1H** (**1–3**), **L2H** (**4, 5**),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and co-ligands such as  $\text{N}_3^-$  or  $\text{N}(\text{CN})_2^-$  and are conclusively structurally characterized. Determination of molecular structures of **1–5** confirmed the presence of a di-copper core with an inversion center located directly between the two copper ions. In **1–5**, within one centrosymmetric dimer one of the ligands possess *R* configuration whereas other possess *S* configuration resulting a heterochiral dimerization of ligands around copper(II) center in chiral self-discriminating manner. The significant effects of different non-covalent interactions and co-ligands on self-assembly of heterochiral dimers into networks are studied. The presence of  $\pi \cdots \pi$  interaction between face to face benzene-naphthalene and naphthalene-naphthalene dimers are perceived. The isotactic and syndiotactic arrangements of the coordination complex through non-covalent interactions are also studied.

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## 1. Introduction

From the last two decades various synthetic strategies have been developed to design a wide variety of Schiff bases [1] and their metal complexes, as they find wide applications in coordination polymers [2], catalysis [3], biomimetic chemistry [4], metal organic framework (MOF) [5] and molecular magnetism [6]. Schiff bases having mix N, O donor sites are subject of interest because of their strong chelating nature. Among the transition metal ions, copper plays domino role in human tissue and is also associated with many important biological activities such as cytochrome c oxidase, superoxide dismutase and etc. [7]. It has been reported that, copper(II) complexes containing pyridine based Schiff bases show excellent reactivity towards photocleavage of DNA, antitumor and cytotoxic activities [8]. Among other pyridine based Schiff bases ligands, salicylaldehydes and  $\alpha$ -hydroxynaphthaldehydes derivatives were selectively employed for the synthesis of coordination complexes because they can promote chelation and provide extra stability to the metal centers.

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During the last few years; a significant amount of information related to the characterization of chiral Schiff bases and their complexes has been reported [9]. It is worthy to note that the self-assembly of coordination complexes containing chiral enantiopure ligands can be predictable but in case of racemic ligands it is difficult to predict [10]. Quite few information concerning the self-assembly of coordination complexes containing racemic Schiff bases are accessible. Significant results in this direction have been established by Stack and co-workers, Mascharak and co-workers and Kuroda and co-workers [11–13]. Factors affecting the diastereoselective self-assembly of coordination complexes containing chiral and racemic N-donor ligands have been reported in the literature [14]. Recently, the effect of ligand substitution on the coordination stereochemistry of phenoxo bridged copper(II) complexes containing achiral Schiff bases has been reported [15]. Furthermore the effects of ligand geometry, bridging ligands, co-ligands and non-covalent interactions on the solid state diastereoselective self-assembly of copper and zinc complexes containing racemic Schiff bases have been reported [16]. Thus, it is immense important to gather precise knowledge on how different factors affects the coordination stereochemistry and solid state structural self-assembly of racemic ligands which can find wide applications in synthesis of (homo- or hetero-) chiral coordination polymers, coordination networks and subsequently in synthesis of homo- or heterochiral MOF [17]. Therefore a system is presented here that

exhibits ligand self-discrimination based solely on chirality of the ligands and adds new examples to the very scarce reported chiral-discrimination process.

In continuation, herein two racemic Schiff bases (**L1H**, and **L2H**; Scheme 1) are synthesized and the solid state heterochiral self-assembly of five copper complexes in crystal engineering contexts are discussed.

### 1.1. Syntheses

2-Benzoylpyridine, 2-hydroxy-1-naphthaldehyde,  $\text{NaN}(\text{CN})_2$ , (Aldrich, USA);  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaN}_3$ , hydroxylamine hydrochloride, Zn dust (Merck India Ltd) and solvents were used as received without further purification. (*R,S*)-1-(2-pyridyl)ethylamine, (*R,S*)-phenyl(2-pyridyl)methanamine, and (*R,S*)-phenyl(2-pyridyl)methylimino)methyl)phenol (**L2H**) were prepared using our earlier reported procedure [16b,c].

#### 1.1.1. (*R, S*) 2-((1-(2-pyridyl)ethylimino)methyl)naphthol (**L1H**)

A mixture of 1-(2-pyridyl)ethylamine (1.22 g, 10.0 mmol) and 2-hydroxy-1-naphthaldehyde (1.72 g, 10.0 mmol) in methanol (60 mL) was stirred for 2 h. The solutions were evaporated to dryness and dried under vacuum which results reddish oil. Yield: 2.62 g (95%). ESI-MS: *m/z* Calc. for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}^+$  277.33. Found: ( $\text{M}^+\text{H}$ ) 277.40. IR (KBr,  $\text{cm}^{-1}$ ): 3467(b), 3062(w), 2973(w), 2925(w), 1627(s), 1595(m), 1543(w), 1520(m), 1492(m), 1434(w), 1403(m), 1361(s), 1314(m), 1246(m), 1212(m), 1187(m), 1142(w), 1120(w), 1066(w), 993(s), 837(m), 779(m), 749(s), 718(w), 550(w), 474(m), 439(w). 400 MHz  $^1\text{H}$  NMR ( $\delta$  (J, Hz),  $\text{CDCl}_3$ ): 8.98 (1H, s), 8.59 (1H, d, 6.4), 7.90 (1H, d, 8.4), 7.72 (1H, t, 4.6), 7.63 (1H, d, 8.0), 7.46 (1H, d, 6.4), 7.43 (2H, t, 6.2), 7.28 (1H, d, 7.6), 7.25 (2H, m), 6.96 (1H, d, 8.0), 4.89 (1H, q), 1.79 (3H, d, 6.8). 100 MHz  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 175.0, 161.0, 157.6, 149.4, 137.6, 137.4, 133.7, 129.3, 128.1, 126.5, 124.2, 123.08, 123.01, 120.6, 118.2, 107.2, 64.5, 22.9.

#### 1.1.2. Synthesis of $[\text{Cu}(\text{L1})\text{Cl}]_2$ (**1**)

To **L1H** (0.288 g, 1.0 mmol) dissolved in methanol (10 mL), solid  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.300 g, 1.0 mmol) was added and stirred for 2 h. The resulting light green solution was allowed to evaporate at room temperature. Light green color single crystals of **1** suitable for X-ray diffraction study were obtained from the slow evaporation for about one week time. Yield: 0.68 g (82%). *Anal. Calc.* for  $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_2$ : C, 57.76; H, 4.04; N, 7.48. Found: C, 57.74; H, 4.01; N, 7.45%. Selected IR (KBr,  $\text{cm}^{-1}$ ): 3438(b, OH), 1621(s, C=N). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ),  $\text{CH}_3\text{OH}$  solution]: 638(304); 356(4456); 292(8028). EPR (solid state, 298 K):  $g = 2.102$ ,  $A = 70$  G,  $\mu_{\text{eff}}/\text{Cu}$  (298 K), 1.84 B.M.

#### 1.1.3. Synthesis of $[\text{Cu}(\text{L1})(\text{N}_3)]_2$ (**2**)

To **L1H** (0.226 g, 1.0 mmol) dissolved in methanol (10 mL), solid  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.300 g, 1.0 mmol) was added and stirred for 10 min. To this light green solution, methanol solution of (5 mL)  $\text{NaN}_3$  (0.65 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 **2** suitable for X-ray diffraction study were obtained from the slow evaporation of the solution after one week time. Yield: 0.56 g (73%). *Anal. Calc.* for  $\text{C}_{36}\text{H}_{30}\text{Cu}_2\text{N}_{10}\text{O}_2$ : C, 56.76; H, 3.97; N, 18.39. Found: C, 56.73; H, 3.95; N, 18.35%. Selected IR (KBr,  $\text{cm}^{-1}$ ): 3436(b, -OH), 2032(s, azide), 1625(s, C=N). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ),  $\text{CH}_3\text{OH}$  solution]: 636(324); 358(5436); 292(9874). EPR (solid state, 298 K):  $g = 2.113$ ,  $A = 71$  G,  $\mu_{\text{eff}}/\text{Cu}$  (298 K), 1.82 B.M.

#### 1.1.4. Synthesis of $[\text{Cu}(\text{L1})(\text{N}(\text{CN})_2)]_2$ (**3**)

To **L1H** (0.226 g, 1.0 mmol) dissolved in methanol (10 mL), solid  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.300 g, 1.0 mmol) was added and stirred for 10 min. To this light green solution, methanol solution of (5 mL)  $\text{NaN}(\text{CN})_2$  (0.81 g, 1.0 mmol) was added and further stirred for another 3 h. The resulting 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 on standing for about one week time. Yield: 0.58 g (70%). *Anal. Calc.* for  $\text{C}_{40}\text{H}_{30}\text{Cu}_2\text{N}_{10}\text{O}_2$ : C, 59.32; H, 3.73; N, 17.30. Found: C, 59.31; H, 3.71; N, 17.28%. Selected IR (KBr,  $\text{cm}^{-1}$ ): 3443(b, -OH), 2295(s), 2238(s), 2182(s) (dicyanamide), 1626 (s, C=N). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ),  $\text{CH}_3\text{OH}$  solution]: 635(357); 345(3436); 298(7688). EPR (solid state, 298 K):  $g = 2.110$ ,  $A = 71$  G,  $\mu_{\text{eff}}/\text{Cu}$  (298 K), 1.91 B.M.

#### 1.1.5. Synthesis of $[\text{Cu}(\text{L2})(\text{ClO}_4)(\text{H}_2\text{O})]$ (**4**)

Same procedure was followed for the synthesis of complex **4** by using ligand **L2H** in place of **L1H** and using  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in place of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in the same molar ratio as described for complex **1**. Green colored single crystals of **4** suitable for X-ray diffraction study were obtained from the slow evaporation of the solution. Yield: 0.68 g (73%). *Anal. Calc.* for  $\text{C}_{19}\text{H}_{17}\text{ClCuN}_2\text{O}_6$ : C, 48.73; H, 3.66; N, 13.57. Found: C, 48.71; H, 3.63; N, 13.54%. Selected IR (KBr,  $\text{cm}^{-1}$ ): 3449(b, -OH), 1618(s, C=N), 1090(b, perchlorate). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ),  $\text{CH}_3\text{OH}$  solution]: 634(237); 402(468); 378(6742). EPR (solid state, 298 K):  $g = 2.102$ ,  $A = 70$  G,  $\mu_{\text{eff}}/\text{Cu}$  (298 K), 1.88 B.M.

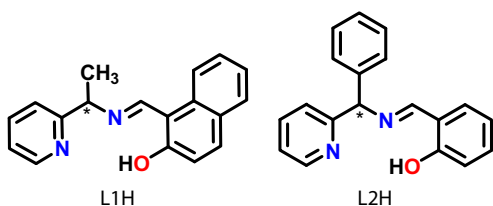
#### 1.1.6. Synthesis of $[\text{Cu}(\text{L2})(\text{N}_3)]_2$ (**5**)

Same procedure was followed for the synthesis of complex **5** by using ligand **L2H** in place of **L1H** in the same molar ratio as described for complex **2**. Green colored single crystals of **5** suitable for X-ray diffraction study were obtained from the slow evaporation of the solution. Yield: 0.40 g (75%). *Anal. Calc.* for  $\text{C}_{38}\text{H}_{30}\text{Cu}_2\text{N}_{10}\text{O}_2$ : C, 58.08; H, 3.85; N, 17.82. Found: C, 58.04; H, 3.82; N, 17.79%. Selected IR (KBr,  $\text{cm}^{-1}$ ): 3449(b, -OH), 2035(s, azide), 1621(s, C=N). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ),  $\text{CH}_3\text{OH}$  solution]: 636(365); 395(546); 383(5672). EPR (solid state, 298 K):  $g = 2.114$ ,  $A = 71$  G,  $\mu_{\text{eff}}/\text{Cu}$  (298 K), 1.91 B.M.

## 2. Materials and methods

A Perkin-Elmer Spectrum One spectrometer (4000–450  $\text{cm}^{-1}$ ), Perkin-Elmer Series II CHNS/O Analyzer 2400, Perkin-Elmer Lambda 25 spectrometer, and Brüker 400 MHz spectrophotometer were used for obtaining relevant data.

X-ray crystallographic data were collected using Brüker SMART APEX-CCD diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections was applied using SAINT program [18,19]. All the structures were solved by direct



Scheme 1. Racemic Schiff bases (**L1H**, **L2H**) used for study.

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