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Diastereoselection and induced chirality at-metal in distorted-tetrahedral *bis*[(*R* or *S*)-1-(*p*-R₁-C₆H₄)-*N*-(phenyl(pyridin-2-yl)methylene)ethanamino- κ^2 *N*,*N*]- Δ/Λ -copper(PF₆)₂

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Diastereoselection and induced chirality at-metal in distorted-tetrahedral *bis*[(*R* or *S*)-1-(*p*-R₁-C₆H₄)-*N*-(phenyl(pyridin-2-yl)methylene)ethanamino- $\kappa^2 N$,*N*]- Δ/Λ -copper(PF₆)₂

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ABSTRACT

The enantiopure Schiff bases (R or S)-1-(p-R₁-C₆H₄)-N-(phenyl(pyridin-2-yl)methylene)ethanamine ($R_1 = H$ and OCH₃) are synthesized from reaction between the 2-benzoyl-pyridine and chiralamine (R or S)-1-(p-R₁-C₆H₄)ethylamine, respectively. These Schiff bases react with the copper(II) acetate to give distorted-tetrahedral $bis[(R \text{ or } S)-1-(p-R_1-C_6H_4)-N-(phenyl(pyridin-2-yl)methylene)e$ thanamino- $\kappa^2 N_{,N}$]- Δ/Λ -Cu(PF₆)₂ in the presence of NH₄PF₆. A conformational change from cis- to trans-isomer occurs in solution and thereby, the copper(II) coordinates to the solely trans-form to provide the complexes. Cyclic voltammograms demonstrate two quasi-reversible one electron charge transfer processes for the Cu^{2+}/Cu^{+} and Cu^{+}/Cu^{0} couples in acetonitrile. ECD spectra reveal expected mirror-image relationships and indicate enantiopurity or enantiomeric excess of the R or S-ligands and their associated complexes in solution. Comparisons of experimental and simulated ECD spectra suggest induced chirality at-metal center, which diastereoselectively provides the Δ -Cu-R or Λ -Cu-S diastereomer as major product in solution. DFT/TDDFT optimized structures and excited state properties correspond well to the experimental results.

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1. Introduction

Tetrahedral or distorted-tetrahedral transition metal(II)-complexes with *chiral-N,O*-chelate Schiff base ligands are of continued interest in the context of syntheses, chiroptical properties, diastereoselection and induced chirality at-metal center [1–15]. The *chiral N,O*-chelate Schiff base ligands upon coordination to the metal(II) ion induce metal-centered chirality and provide the right (Δ)- and left (Λ)-handed diastereomers along C_2 -symmetry of the molecules [16–19]. The noncovalent interactions acting within the metal–ligand framework result in a free energy difference between the two diastereomers and hence, diastereoselectively prefer one over another (i.e. Δ vs. Λ) both in solution and at solid-state. The structure and/or chirality of the ligand, metal ion selection, solute–solvent interaction, temperature and time, counter anion, crystal solvent and crystallization protocol efficiently control the induced chirality and diastereoselection phenomenon [1–10].

In this connection, we have reported distorted-tetrahedral [M(*R* or *S*-*N* \circ *O*)₂] (M = Fe, Co, Ni, Cu, Zn; *N* \circ *O* = salicylaldiminato/OH-naphthaldiminato) with preferred formation of Δ -M-*R*-*N* \circ *O* or Λ -M-*S*-*N* \circ *O* and *vice versa* (i.e. Λ -M-*R*-*N* \circ *O* or Δ -M-*S*-*N* \circ *O*), as studied by solid-state X-ray structures of the enantiopure crystal [1–10]. However, in some cases, both diastereomers (Δ and Λ) co-exist in a single enantiopure crystal [1, 6, 12]. Indeed, both diastereomers appear simultaneously in solution and result in a dynamic diastereomeric equilibrium, as followed by variable-time and -temperature dependent ¹H NMR and ECD spectra, respectively [2, 3, 6–9]. Time-dependent ¹H NMR studies reveal a single diastereomer within 10 min of complex dissolution, which shifts to a diastereomeric mixture of about 33:67 (within 40 min) or 46:54 (within 36 h) for Δ/Λ -(*R* or *S*)-zinc(II)-aminoalcohol based Schiff base complexes in solution [9]. Similar studies demonstrate an equilibrium with diastereomeric mixture of about 77:23 within 10 min of complex dissolution, which remains unchanged even after 24 h for *bis*[{(*S*)-*N*-



 $Bis[(R \text{ or } S)-1-(p-R_1-C_6H_4)-N-(phenyl(pyridin-2-yl)methylene)ethanamino <math>\kappa^2 N, M]\Delta/\Lambda-Cu(PF_6)_2 \{R_1 = H (Cu-R \text{ or } S-L 1), OCH_3 (Cu-R \text{ or } S-L 2)\}$

Scheme 1. Synthetic route of the formation of *bis*[(*R* or *S*)-1-(*p*-R₁-C₆H₄)-*N*-(phenyl(pyridin-2-yl)me-thylene)ethanamino- $\kappa^2 N$,*N*] Δ/Λ -Cu(PF₆)₂.

(phenyl)ethyl-2-oxo-1-naphthaldiminato- $\kappa^2 N$,O}]- Δ/Λ -Zn [3]. Variable-temperature ¹H NMR studies on the latter complex also exhibit a shift of equilibrium from a diastereomeric ratio of about 87:13 at -50 °C to 73:27 at 35 °C. Similar results of equilibrium shifting were examined by variable-temperature ECD spectra in solution [2, 3]. However, our studies were limited to the metal(II)-complexes containing the *chiral N*,*O*-chelate Schiff bases including salicylaldimine/OH-naphthaldimine and their derivatives [1–10]. In view of further investigation on the phenomenon, we have planned to synthesize the *chiral N*,*N*-chelate Schiff bases react with the metal ions to provide *chiral*-metal catalysts for enantioselective hydrogenation/hydrosilylation and success-fully used for conformational analyses of diastereoisomers [20–26].

In the present endeavor, we report syntheses of the *chiral N*,*N*-chelate Schiff bases (*R* or *S*)-1-(*p*-R₁-C₆H₄)-*N*-(phenyl(pyridin-2-yl)methylene)ethanamine and their complexes *bis*[(*R* or *S*)-1-(*p*-R₁-C₆H₄)-*N*-(phenyl(pyridin-2-yl)methylene)ethanamino- $\kappa^2 N$,*N*] Δ / Λ -copper(II)(PF₆)₂ (Scheme 1). The Schiff bases and complexes are characterized by elemental, IR, UV–Vis, ECD, ¹H-NMR spectroscopy and cyclic voltammetry. A thorough computational procedure was employed by DFT/TDDFT to rationalize the experimental results and to examine the chiroptical properties in detail. Finally, combined studies of

experimental and computational results are considered to get insight into diastereoselection and metal entered chirality (Δ vs. Λ) induced by the *R*- or *S*-ligand in the complexes.

2. Experimental

2.1. Materials and methods

Vibrational spectra were recorded on a Nicolet iS10 (Thermo Scientific) spectrometer as KBr discs at ambient temperature. Electronic spectra were obtained with the Shimadzu UV 1800 spectrophotometer in methanol at 25 °C. ¹H NMR-spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz in CDCl₃ at 20 °C. ECD spectra were run with the JASCO spectropolarimeter (J810) in methanol at about 25 °C. EpsilonTM instruments (BASi) electrochemical analyzer was used for running cyclic voltammogram experiments containing tetra-N-butyl-ammonium-hexafluorophosphate (TBAP) as supporting electrolyte in acetonitrile at 25 °C. A three-electrode measurement system was used, which composed of a platinum disc working electrode, platinum wire auxiliary electrode and Ag/AgCl reference electrode, respectively. The solution containing the sample and TBAP was deoxygenated with purging nitrogen gas for 10 min prior to use. Working electrode was cleaned with supplied solution and dried prior to use in each scan to avoid any contamination caused by deposition of the metal. Reproducibility of CV patterns was checked at a scan rate of 0.10 Vs⁻¹ in acetonitrile. The molar conductance was measured using a Mettler Toledo Fivego (Model F3) conductivity meter in dimethylformamide (DMF) at 25 °C.

2.2. General procedure to synthesize the Schiff bases, (R or S)-1- $(p-R_1-C_6H_4)-N-(phenyl(pyridin-2-yl)methylene)ethanamine (R or S-L)$

The 2-benzoyl-pyridine (366 mg, 2.0 mmol) and 3–4 drops of concentrated H_2SO_4 were dissolved in 10 mL methanol, stirring the solution for about 10 min. An equimolar amount of *chiral*-amine (*R* or *S*)-1-(C₆H₅)ethylamine (242 mg, 2.0 mmol), dissolved in 5 mL methanol, was poured into this solution and continued to reflux for about 12 h. The color changed from brown–orange to orange–yellow. The solvent was evaporated in *vacuo* to obtain orange-yellow semi-liquid products of (*R* or *S*)-1-(C₆H₅)-*N*-(phenyl(-pyridin-2-yl)methylene)ethanamine (*R*-L1 or *S*-L1). The products were washed with *n*-hexane three times (2 mL in each) and dried in open air for several days. The same procedure was followed to synthesize the orange-yellow semi-liquid products of (*R* or *S*)-1-(*p*-OCH₃C₆H₄)-*N*-(phenyl(pyridin-2-yl)methylene)ethanamine (*R*-L2 or *S*-L2) using (*R* or *S*)-1-(*p*-OCH₃C₆H₄)ethylamine.

2.2.1. (R)-1-(C₆H₅)-N-(phenyl(pyridin-2-yl)methylene)ethanamine (R-L1)

Yield: 0.425 g (74%). ¹H NMR (400 MHz, CDCl₃) for *cis*-isomer, δ (ppm): 1.43* (d, $J_{HH} = 6.8$ Hz, 3H, CH₃), 4.78* (q, $J_{HH} = 6.8$ Hz, 1H, CH), 7.10 (m, 3H, Ar-H), 7.27 (d, $J_{HH} = 6.8$ Hz, 2H, Ar-H), 7.34 (m, 3H, Ar-H), 7.46 (m, 1H, Ar-H), 7.53 (m, 2H, Ar-H), 8.19 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H), 8.67 (d, $J_{HH} = 4.4$ Hz, 1H, Ar-H), 8.81 (d, $J_{HH} = 4.4$ Hz, 1H, Ar-H). For *trans*-isomer, δ (ppm): 1.65* (d, $J_{HH} = 6.8$ Hz, 3H, CH₃), 4.35* (q, $J_{HH} = 6.8$ Hz, 1H, CH),

7.37 (m, 3H, Ar-H), 7.47 (d, $J_{HH} = 6.8$ Hz, 2H, Ar-H), 7.50 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H), 7.52 (d, $J_{HH} = 8.0$ Hz, 2H, Ar-H), 7.62 (t, $J_{HH} = 7.2$ Hz, 1H, Ar-H), 7.93 (dt, $J_{HH} = 7.6$, 1.2 Hz, 1H, Ar-H), 8.07 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H), 8.09 (d, $J_{HH} = 7.6$ Hz, 2H, Ar-H), 8.76 (d, $J_{HH} = 4.4$ Hz, 1H, Ar-H) (**cis*- to *trans*-isomer ratio about 20:80, calculated from integration values for corresponding CH and CH₃ peaks, respectively).

2.2.2. (S)-1-(C_6H_5)-N-(phenyl(pyridin-2-yl)methylene)ethanamine (S-L1)

Yield 0.400 g (70%). ¹H NMR (400 MHz, CDCl₃) for *cis*-isomer, δ (ppm): 1.42* (d, $J_{HH} = 6.8$ Hz, 3H, CH₃), 4.71* (q, $J_{HH} = 6.8$ Hz, 1H, CH), 7.09 (m, 3H, Ar-H), 7.26 (m, 2H), 7.34 (m, 3H, Ar-H), 7.41 (m, 1H, Ar-H), 7.52 (m, 2H, Ar-H), 7.95 (m, 1H, Ar-H), 8.58 (m, 1H, Ar-H), 8.82 (m, 1H, Ar-H). For *trans*-isomer, δ (ppm): 1.59* (d, $J_{HH} = 6.8$ Hz, 3H, CH₃), 4.29* (q, $J_{HH} = 6.8$ Hz, 1H, CH), 7.35 (m, 3H, Ar-H),7.42 (d, $J_{HH} = 7.6$ Hz, 2H, Ar-H), 7.50 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H), 7.52 (d, $J_{HH} = 7.6$ Hz, 2H, Ar-H), 7.62 (t, $J_{HH} = 7.6$ Hz, 1H, Ar-H), 7.93 (t, $J_{HH} = 7.6$ Hz, 1H, Ar-H), 8.06 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H), 8.08 (d, $J_{HH} = 7.6$ Hz, 2H, Ar-H), 8.75 (d, $J_{HH} = 4.4$ Hz, 1H, Ar-H) (**cis*- to *trans*-isomer ratio about 17:83, calculated from integration values for corresponding CH and CH₃ peaks, respectively).

2.2.3. (R)-1-(p-OCH₃C₆H₄)-N-(phenyl(pyridin-2-yl)methylene)ethanamine(R-L2)

Yield: 0.450 g (71%). ¹H NMR (400 MHz, CDCl₃) for *cis*-isomer, δ (ppm): 1.51* (d, $J_{HH} = 6.8$ Hz, 3H, CH₃), 3.81 (s, 3H, OCH₃), 4.65* (q, $J_{HH} = 6.4$ Hz, 1H, CH), 6.88 (dd, $J_{HH} = 8.4$, 2.8, 2H, Ar-H17,19), 7.20 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H8), 7.30 (dd, $J_{HH} = 8.8$, 2.8 Hz, 2H, Ar-H2,16), 8.20 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H20), 7.62 (t, $J_{HH} = 7.6$ Hz, 1H, Ar-H4), 8.58 (d, $J_{HH} = 4.4$ Hz, 1H, Ar-H12), 7.52 (m, 1H, Ar-H9), 7.64 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H10), 7.64 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H11), 8.07 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H3), 8.80 (d, $J_{HH} = 4.4$ Hz, 1H, Ar-H5). For *trans*-isomer, δ (ppm): 1.53* (d, $J_{HH} = 6.8$ Hz, 3H, CH₃), 3.82 (s, 3H, OCH₃), 4.48* (q, $J_{HH} = 6.4$ Hz, 1H, CH), 6.88 (dd, $J_{HH} = 8.4$, 2.8, 2H, Ar-H17,19), 7.16 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H2), 7.20 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H8), 7.30 (dd, $J_{HH} = 8.8$, 2.8 Hz,1H, Ar-H20), 7.50 (m, 2H, Ar-H4,12), 7.77 (2dt, $J_{HH} = 7.6$, 1.6 Hz, 1H, Ar-H9), 7.93 (dt, $J_{HH} = 8.0$, 1.6 Hz, 1H, Ar-H10), 7.77 (2dt, $J_{HH} = 7.6$, 1.6 Hz, 1H, Ar-H9), 7.93 (dt, $J_{HH} = 8.0$, 1.6 Hz, 1H, Ar-H10), 7.77 (2dt, $J_{HH} = 7.6$, 1.6 Hz, 1H, Ar-H9), 7.93 (dt, $J_{HH} = 8.0$, 1.6 Hz, 1H, Ar-H10), 8.76 (d, $J_{HH} = 4.4$ Hz, 1H, Ar-H5) (**cis*- to *trans*-isomer ratio about 48:52, calculated from integration values for corresponding CH and CH₃ peaks, respectively) (see Scheme 2 for hydrogen atoms numbering).

2.2.4. Simulated ¹H NMR for the R-L2 (with GIAO method at B3LYP/6-311G (2d,p)) For cis-isomer, δ (ppm): 1.04, 1.12, 1.70 (3H, CH₃), 3.88, 3.90, 4.03 (3H, OCH₃), 5.20 (1H, CH), 7.06, 7.27 (2H, Ar-H17,19), 7.30 (1H, Ar-H8), 7.60 (1H, Ar-H16), 7.62 (1H, Ar-H2), 7.64 (1H, Ar-H9), 7.80 (1H, Ar-H4), 7.87 (1H, Ar-H10), 7.91 (1H, Ar-H11), 8.24 (1H, Ar-H3), 8.36 (1H, Ar-H20), 8.97 (1H, Ar-H12), 9.38 (1H, Ar-H5). For *trans*-isomer, δ (ppm): 1.25, 1.28, 1.82 (3H, CH₃), 3.89, 3.91, 4.05 (3H, OCH₃), 4.92 (1H, CH), 7.09, 7.24 (2H, Ar-H19,17), 7.20 (1H, Ar-H2), 7.49 (1H, Ar-H8), 7.58 (1H, Ar-H20), 7.66 (1H, Ar-H4), 7.71 (1H, Ar-H12), 7.88 (1H, Ar-H9), 7.91 (1H, Ar-H11), 7.95 (1H, Ar-H10), 7.97 (1H, Ar-H3), 8.20 (1H, Ar-H16), 9.31 (1H, Ar-H5) (see Scheme 2 for hydrogen atoms numbering).



Scheme 2. Hydrogen atoms numbering.

2.2.5. (*S*)-1-(*p*-OCH₃C₆H₄)-N-(*phenyl(pyridin-2-yl)methylene)ethanamine* (*S-L2*) Yield: 0.435 g (69%). ¹H NMR (400 MHz, CDCl₃) for *cis*-isomer, δ (ppm): 1.51* (d, $J_{HH} = 6.8$ Hz, 3H, CH₃), 3.81 (s, 3H, OCH₃), 4.65* (q, $J_{HH} = 6.4$ Hz, 1H, CH), 6.88 (dd, $J_{HH} = 8.4$, 2.8 Hz, 2H, Ar-H17,19), 7.30 (dd, $J_{HH} = 8.8$, 2.8 Hz, 1H, Ar-H2), 7.20 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H8), 7.30 (dd, $J_{HH} = 8.8$, 2.8 Hz, 1H, Ar-H16), 8.20 (d, $J_{HH} = 8.0$ Hz, 1H, Ar-H20), 8.58 (d, $J_{HH} = 4.4$ Hz, 1H, Ar-H12), 7.61 (t, $J_{HH} = 7.6$ Hz, 1H, Ar-H4), 7.52 (m, 1H, Ar-H9), 7.65 (d, $J_{HH} = 6.8$ Hz, 1H, Ar-H10), 7.65 (d, $J_{HH} = 6.8$ Hz, 1H, Ar-H11), 8.07 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H3), 8.81 (d, $J_{HH} = 4.4$ Hz, 1H, Ar-H5). For *trans*-isomer, δ (ppm): 1.53* (d, $J_{HH} = 6.8$ Hz, 3H, CH₃), 3.82 (s, 3H, OCH₃), 4.48* (q, $J_{HH} = 6.4$ Hz, 1H, CH), 6.88 (dd, $J_{HH} = 8.4$, 2.8 Hz, 2H, Ar-H17,19), 7.16 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H2), 7.20 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H8), 8.10 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H16), 7.30 (dd, $J_{HH} = 8.8$, 2.8 Hz, 1H, Ar-H20), 7.49 (m, 2H, Ar-H4,12), 7.77 (2dt, $J_{HH} = 7.6$, 1.6 Hz, 2H, Ar-H9,11), 7.92 (dt, $J_{HH} = 7.6$, 1.6 Hz, 1H, Ar-H10), 8.10 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H3), 8.75 (d, $J_{HH} = 4.4$ Hz, 1H, Ar-H5) (**cis*- to *trans*-isomer ratio about 56:44, calculated from integration values for corresponding CH and CH₃ peaks, respectively; see Scheme 2 for hydrogen atoms numbering).

2.3. General procedure to synthesize the copper(II)-Schiff bases complexes

Two equivalents of Schiff base (R or S)-1-(C_6H_5)-N-(phenyl(pyridin-2-yl)methylene)ethanamine (R or S-L1) (286 mg, 1.00 mmol) were dissolved in 10 mL methanol; this solution was poured into one equivalent of copper(II)-acetate (127 mg, 0.50 mmol) dissolved in 5 mL methanol. The reaction mixture was stirred for about 12 h at 40 °C and the color turned from light yellowish-green to deep green. For anion exchange, two equivalents of NH₄PF₆ were added into this solution and continued stirring for 30 min. The volume of solvent was reduced to about 50% and the solution was left standing for precipitation at room temperature, filtered off and the green filtrate was collected and dried in vacuo at 40°C. The dried green product was washed with n-pentane 3 times (2 mL in each) and dried again in vacuo at 40 °C. The green product was dissolved in 5 mL dichloromethane, filtered off and the filtrate dried in vacuo at 40 °C followed by nitrogen flash to obtain deep green microcrystals of $bis[(R \text{ or } S)-1-(C_6H_5)-N-$ (phenyl(pyridin-2-yl)methylene) ethanamino- $\kappa^2 N_1 N_2 Cu(II)(PF_6)_2$, $[Cu(R \text{ or } S-L1)_2](PF_6)_2$. The same procedure was followed to synthesize bis[(R or S)-1-(p-OCH₃C₆H₄)-N-(phenyl(pyridin-2-yl)methylene)ethanamino- $\kappa^2 N_r N_r Cu(II)(PF_6)_2$, [Cu(R or S-L2)₂](PF₆)₂ using the R or S-L2 (316 mg, 1.00 mmol) except stirring the reaction mixture for about 6 h at room temperature. No precipitate was formed upon left standing the concentrated (volume reduced to ca. 50%) solution to room temperature.

2.3.1. $Bis[(R)-1-(C_6H_5)-N-(phenyl(pyridin-2-yl)methylene)ethanamino-\kappa^2N,N]copper(II)$ (PF_6)₂, [$Cu(R-L1)_2$](PF_6)₂, (Cu-R-L1)

Yield 300 mg (65%). IR (ATR, cm⁻¹): 3418br v(H₂O), 3063, 3034, 2981, 2938w v(C-H), 1622, 1593, 1570vs v(C = N), 1525sh v(C = C), 839vs v(PF₆). C₄₀H₃₆CuN₄(P₂F₁₂) (926.23): Calcd. C 51.87, H 3.92, N6.05; found C 50.76, H 4.22, N 5.85%. Λ_m (DMF) = 215 S cm² mol⁻¹ (0.5 mmol).

2.3.2. $Bis[(S)-1-(C_6H_5)-N-(phenyl(pyridin-2-yl)methylene)ethanamino-\kappa^2N,N]copper(II)$ $(PF_6)_2$, $[Cu(S-L1)_2](PF_6)_2$, (Cu-S-L1)

Yield 280 mg (60%). IR (ATR, cm⁻¹): 3420br v(H₂O), 3063, 3032, 2980, 2934w v(C-H), 1622, 1593, 1570vs v(C = N), 1525sh v(C = C), 841vs v(PF₆).

2.3.3. Bis[(R)-1-(p-OCH₃C₆H₄)-N-(phenyl(pyridin-2-yl)methylene)ethanamino- κ^2 N,N] copper(II)(PF₆)₂, [Cu(R-L2)₂](PF₆)₂, (Cu-R-L2)

Yield 300 mg (61%). IR (ATR, cm⁻¹): 3427br v(H₂O), 3061, 2982, 2936w v(C-H), 1611, 1589, 1576vs v(C = N), 1514s v(C = C), 843vs v(PF₆). C₄₂H₄₀CuN₄O₂(P₂F₁₂) (986.28): Calcd. C 51.15, H 4.09, N 5.68; found C 50.27, H 4.32, N 5.35%. Λ_m (DMF) = 230 S cm² mol⁻¹ (0.5 mmol).

2.3.4. Bis[(S)-1-(p-OCH₃C₆H₄)-N-(p-(p-v)(p-

Yield 312 g (63%). IR (ATR, cm⁻¹): 3431br v(H₂O), 3061, 2980, 2938w v(C-H), 1610, 1591, 1572vs v(C = N), 1514s v(C = C), 843vs v(PF₆). Λ_m (DMF) = 220 S cm² mol⁻¹ (0.5 mmol).

2.4. Decomplexation of Cu-R-L2 with NaCN and isolation of free R-L2

Cu-*R*-L2 of 30 mg was dissolved in 5 mL methanol and an excess amount of NaCN was added into this solution. The solution was stirred for 30 min and the color changed from deep brown to orange–yellow, then filtered off and the filtrate was dried in *vacuo* at 40 °C for several hours. The dried product was dissolved into 5 mL dichloromethane, filtered off and the filtrate dried in *vacuo*. The product was dissolved again into 5 mL *n*-pentane, filtered off and dried in *vacuo* at 40 °C to obtain orange–yellow semi-liquid products of *R*-L2.

2.4.1. ¹H NMR (400 MHz, CDCl₃)

For *cis*-isomer, δ (ppm): 1.51* (d, $J_{HH} = 7.2$ Hz, 3H, CH₃), 3.81 (s, 3H, OCH₃), 4.64* (q, $J_{HH} = 6.4$ Hz, 1H, CH), 6.88 (dd, $J_{HH} = 8.4$, 2.8, 2H, Ar-H), 7.19 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H), 7.31 (dd, $J_{HH} = 8.8$, 2.8 Hz, 2H, Ar-H), 7.52 (d, $J_{HH} = 8.0$ Hz, 2H, Ar-H), 7.61 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H), 7.92 (dt, $J_{HH} = 7.6$, 1.6 Hz, 1H, Ar-H), 8.06 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H), 8.09 (d, $J_{HH} = 7.2$ Hz, 2H, Ar-H), 8.75 (d, $J_{HH} = 4.4$ Hz, 1H, Ar-H). For *trans*-isomer, δ (ppm): 1.53* (d, $J_{HH} = 7.2$ Hz, 3H, CH₃), 3.82 (s, 3H, OCH₃), 4.48* (q, $J_{HH} = 6.4$ Hz, 1H, CH), 6.87 (dd, $J_{HH} = 8.4$, 2.8 Hz, 2H, Ar-H), 7.16 (d, $J_{HH} = 8.0$ Hz, 1H, Ar-H), 7.19 (d, $J_{HH} = 7.6$ Hz, 1H, Ar-H), 7.28 (m, 1H, Ar-H), 7.49 (t, $J_{HH} = 10.4$ H, 2H, Ar-H), 7.63 (t, $J_{HH} = 6.4$ Hz,



Figure 1. Optimized structures for the diastereomeric pair Δ -Cu-S-L2 and Λ -Cu-S-L2, calculated at B3LYP/6-31G(d), respectively.

2H, Ar-H), 7.76 (2dt, J_{HH} = 8.0, 1.6 Hz, 1H, Ar-H), 8.19 (d, J_{HH} = 8.0 Hz, 1H, Ar-H), 8.56 (d, $J_{\rm HH} = 4.4$ Hz, 1H, Ar-H), 8.79 (d, $J_{\rm HH} = 4.4$ Hz, 1H, Ar-H) (**cis*- to *trans*-isomer ratio about 55:45, calculated from integration values for corresponding CH and CH₃ peaks, respectively).

2.5. Computational method

Computational procedure was performed on the Schiff bases and complexes with Gaussian 09 [27]. The gas phase equilibrium geometries for the Schiff bases (R- or S-L1 and R- or S-L2) with both the cis- and trans-forms were optimized with DFT using the functional B3LYP and the basis set LANL2DZ, respectively (Supporting Information Figure S1). The optimized structures were used as input file to obtain the simulated ¹H NMR spectra for the *cis*- and *trans*-isomers for *R*-L2 using the GIAO method at B3LYP/6-311G (2d,p) with polarization continuum model (PCM) in chloroform as solvent, respectively. Assignments of protons peaks for experimental ¹H NMR spectra were estimated based on these simulated spectra and the data are listed in the Experimental section. The four-coordinate metal(II)-complexes with asymmetric chiral N,N-chelate type Schiff base ligands in tetrahedral or distorted-tetrahedral geometry exhibit induced chirality at-metal, and hence provide two possible diastereomers of Δ -Cu and Λ -Cu along C₂-symmetry of the molecule [1–10, 15–18]. Thus, we optimized the diastereomeric pairs of Δ -Cu-R-L1/ Λ -Cu-R-L1, Δ -Cu-S-L1/ Λ -Cu-S-L1, Δ -Cu-R-L2/ Λ -Cu-*R*-L2 and Δ -Cu-*S*-L2/ Λ -Cu-*S*-L2 at B3LYP/6-31G(d), respectively (Figure 1 and Supporting Information Figure S2). For optimization, we used both the cis- and transforms of the ligands to coordinate to the copper(II), and hence, to form the complexes as depicted in the reaction Scheme 1. However, only the complexes designed with the trans-form were succeeded to optimize with reasonable minimum energy (Figure 1 and Supporting Information Figure S2). The simulated electronic spectra (UV-Vis and ECD) for the diastereomeric pairs Δ -Cu-*R*-L2/ Λ -Cu-*R*-L2 and Δ -Cu-*S*-L2/ Λ -Cu-*S*-L2 were



Figure 2. Experimental UV–Vis spectra for *R*-L2 (0.06 mM) and Cu-*R*-L2 (0.8 mM) in methanol at 25 °C. Simulated spectra for Δ -Cu-*R*-L2 at B3LYP/6-31G(d) using PCM in methanol (Gaussian band shape with exponential half-width, σ = 0.33 eV).

obtained by TDDFT at B3LYP/6-31G(d) (Figures 2 and 3 and Supporting Information Figure S4). The PCM using methanol as solvent was incorporated and the 72 excited states (roots) were considered for calculations (Supporting Information Table S1). The simulated UV–Vis and ECD spectra for Λ -Cu-*R*-L2 were also obtained at different combinations of the functionals and the basis sets such as B3LYP/6-31G(d), M06/6-31G(d) and M06/DEF2SVP, respectively. The results show almost identical spectra with little shifted bands maxima (Supporting Information Figures S5 and S6), strongly supporting the reliability and validity of the methods used. The best fit to the experimental spectra was at B3LYP/6-31G(d) (Figures 2 and 3). Assignments of excited state properties and molecular orbitals (MOs) calculations were carried out at the same level of theory. The electronic spectra (UV–Vis and ECD) were generated using the program SpecDis [28] by applying Gaussian band shape with exponential half-width $\sigma = 0.33$ eV.

3. Results and discussion

3.1. Synthesis and characterization of the Schiff bases and complexes

Reaction of 2-benzoyl-pyridine with (*R* or *S*)-1-(*p*-R₁-C₆H₄)ethylamine under reflux affords the enantiopure Schiff bases (*R* or *S*)-1-(*p*-R₁-C₆H₄)-*N*-(phenyl(pyridin-2-yl)methylene)ethanamine {R₁ = H (*R*- or*S*-L1), OCH₃ (*R*- or*S*-L2)}, respectively. These Schiff bases readily react with copper(II) acetate in the presence of NH₄(PF₆) to provide *bis*[(*R* or *S*)-1-(*p*-R₁-C₆H₄)-*N*-(phenyl(pyridin-2-yl)methylene)ethanamino- $\kappa^2 N$,*N*]copper(II)(PF₆)₂, [Cu(*R*- or *S*-L)₂](PF₆)₂ {R₁ = H (Cu-*R*-L1 or Cu-*S*-L1), OCH₃ (Cu-*R*-L2 or Cu-*S*-L2)}, respectively (Scheme 1). Vibrational spectra of the complexes (Supporting Information Figure S3) show the main characteristic band at 1610–1570 cm⁻¹ for the v(C = N) and the band at 839–843 cm⁻¹ for the counter



Figure 3. Experimental ECD spectra for Cu-*R*-L2 and Cu-S-L2 (6.70 and 10.12 mM at 800–420 nm; 1.82 and 2.23 mM at 420–280 nm) in methanol at 25 °C (experimental $\Delta \epsilon x 6$ at 800–420 nm and $\Delta \epsilon x 3$ at 420–280 nm). Simulated ECD spectra for Δ -Cu-*R*-L2/ Λ -Cu-*R*-L2 and Δ -Cu-S-L2/ Λ -Cu-S-L2 at B3LYP/6-31G(d) with PCM in methanol.

anion v(PF₆). The values of molar conductance ($\Lambda_m = 215-230 \text{ S cm}^2 \text{ mol}^{-1}$) indicate 1:2 electrolytic nature of the complexes in DMF [29].

3.2. Experimental and simulated ¹H NMR spectra

¹H NMR spectra of the Schiff bases in CDCl₃ (Figure 4) are essentially identical for each enantiomeric pair and the spectral data are listed in the Experimental section. The



Figure 4. ¹H NMR spectrum for (*R*)-1-(*p*-OCH₃C₆H₄)-*N*-(phenyl(pyridin-2-yl)methylene)ethanamine (*R*-L2) in CDCl₃ at 20 °C (c/t stands for the *cis-/trans*-isomer).

spectra show two sets of peaks for each proton, associated to the cis- and trans-isomers of the Schiff base in solution [22]. The ratios of *cis*- to *trans*-isomer are estimated based on the integration values of corresponding methyl (CH_3) and/or methane (CH) protons peaks. The cis- to trans-isomer ratios are about 20:80 (R-L1), 17:83 (S-L1), 48:52 (R-L2) and 56:44 (S-L2), and the different ratios represent a dynamic isomerization equilibrium of the Schiff base in solution. The methyl protons show two doublets at $\delta = 1.42 - 1.51$ and 1.53-1.65 ppm ($J_{HH} = 6.8$ Hz) for the *cis*- and *trans*-isomers, respectively. The methine proton attached to the *chiral*-carbon atom shows two quartets at a significant distance at $\delta = 4.29-4.48$ and 4.65-4.78 ppm ($J_{HH} = 6.8$ Hz) for the *trans*and *cis*-isomers, respectively. Assignment of the quartet in the *cis*-isomer at relatively downfield (by ca. 0.30 ppm) is based on the fact that the methine proton moves toward the imino-/pyridyl-nitrogen atoms and experiences significant inductive effect than in the trans-isomer. The methoxy protons show two sharp singlets at about $\delta =$ 3.81 and 3.82 ppm for the *cis*- and *trans*-isomers, respectively. The proton adjacent to the pyridyl nitrogen atom (Ar-H5) reveals two doublets at the most downfield at about $\delta = 8.75$ and 8.80 ppm for the trans- and cis-isomers, respectively. However, the remaining aromatic protons show several peaks in pairs at the range of $\delta = 6.88-8.81$ ppm (Figure 4). The simulated ¹H NMR spectra for both the *cis*- and trans-isomers of R-L2 are obtained using the GIAO method at B3LYP/6-311G (2d,p) with PCM in chloroform as solvent. The spectral data are listed in the Experimental section. Assignments of the proton peaks including the cis- and trans-isomers are made based on these simulated spectra. The simulated spectra also show the methine proton peaks in the cis- and trans-isomers of R-L2 at a distance by about 0.30 ppm $(\delta = 5.20 \text{ and } 4.92 \text{ ppm})$, in accord with the experimental results discussed above.

3.3. Optimized structures

The optimized structures (gas phase) for the Schiff bases (*R*- or S-L1 and *R*- or S-L2) with both *cis*- and *trans*-forms reveal that the *cis*-isomers are relatively more stable

Table 1. Selected bond l 6-31G(d).	engths (Å) and an <u>c</u>	gles $(^{\circ})$ in the dia	istereomeric pairs	Δ-Cu-R-L2/Λ-Cu-R-I	L2 and Δ -Cu-S-L2/ Λ -Cu-S-I	.2, calculated at B3LYP/
		DFT-str	uctures		X-ray	tructures
Bond lengths (Å)/angles ($^\circ$)	Δ-Cu-S-L2	A-Cu-S-L2	Δ-Cu-R-L2	A-Cu-R-L2	[CpCo(S-NN ¹)]](I/PF ₆) ^a	[Ru(mes)(S-NN ²)Cl](BF ₄) ^b
Cu-N1/Cu-N1/	2.001/2.017	1.987/1.987	1.987/1.987	2.016/2.001	Co-N1 = 1.91(1)	Ru-N1 = 2.066(5)
Cu-N2/Cu-N2/	1.986/1.975	1.994/1.994	1.994/1.994	1.975/1.986	Co-N2 = 1.99(1)	Ru-N2 = 2.086(5)
C6-N2/C6'-N2'	1.301/1.297	1.299/1.299	1.299/1.299	1.297/1.302	C6-N2 = 1.29(2)	1.277(I)
N1-Cu-N2	83.2	82.9	82.9	82.5	N1-Co-N2 = 81.6(5)	N1-Ru-N2 = 76.3(2)
C6-N2-C13/C6'-N2'-C13'	121.1/121.7	121.5/121.5	121.5/121.5	121.7/121.1	C6-N2-C7 = 120.0(1)	C6-N2-C8 = 122.5(5)
θ (°) ^c	63.20	61.72	61.71	63.19	I	I
${}^{a}NN^{1} = (S)-N-(2-phenylethyl)-2-$	oyridyl-acetylimine [24].	ŝ				

 $^{\rm D}NN^4$ = (5)-N-(2-(1-phenylethyl-amine)acetyl-pyridine) [23]. $^{\rm C\theta}$ (°) = Dihedral angle between the two coordinating planes N1–Cu–N2 and N1′–Cu–N2′.

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Figure 5. Experimental ECD spectra for (a) *R*-L2 and *S*-L2 in chloroform and (b) Cu-*R*-L2 and Cu-*S*-L2 (6.70 and 10.12 mM at 800–450 nm; 1.82 and 2.23 mM at 450–280 nm) in methanol at 25° C (cell path-length: 1.0 mm).

than *trans*-isomers by 3.15-4.11 kcal/mol (Supporting Information Figure S1). This might be due to inductive effect between the methine hydrogen and imino-/pyridyl nitrogen atoms that stabilizes the *cis*-form rather than the *trans*-form, as evidenced by relatively downfield shift of the methine proton peak (in *cis*-form) both in experimental and simulated ¹H NMR spectra (discussed above). The optimized structures (gas phase) for the diastereomeric pairs Δ -Cu-*R*-L1/ Λ -Cu-*R*-L1, Δ -Cu-*S*-L1/ Λ -Cu-*R*-L2/ Λ -Cu-*R*-L2 L2 and Δ -Cu-*S*-L2/ Λ -Cu-*S*-L2 (Figure 1 and Supporting Information Figure S2) show



Figure 6. The frontier molecular orbitals HOMO, HOMO-10 and LUMO for Δ -Cu-*R*-L2, calculated at B3LYP/6-31G(d), for β -spin consideration.

that the Λ -Cu (for *R* or S-L1) and Δ -Cu (for *R* or S-L2) configured complexes are slightly more stable by 0.95-1.06 and 0.38-0.87 kcal/mol, respectively. Optimizations further reveal that complexation is only possible via coordination of the *trans*-isomer to the copper(II), as shown in Scheme 1. However, some selected bond lengths and angles in the optimized structures are listed in Table 1, comparable to the X-ray results reported for the related Co/Ru(II)-*chiral-N,N* Schiff bases complexes [23, 24]. The values of the imine bond length (i.e. N2-C6/N2'-C6' = 1.27–1.30 Å) indicate the carbon–nitrogen double bond character, while bonds angles for C6-N2-C13/C6'-N2'-C13' (120-122°) represent the sp²-hybridization of the imino-nitrogen atom [23, 24, 30]. The values of dihedral angles (θ = 61–63°) between the two coordinating planes N1–Cu–N2 and N1'–Cu–N2' (Table 1) comply well with the distorted-tetrahedral geometry for the complexes.

3.4. Experimental and simulated electronic spectra (UV-Vis and ECD)

UV–Vis spectra for the Schiff base (*R*-L2) and complex (Cu-*R*-L2) in methanol show a very strong common band below about 400 nm ($\lambda_{max} = 342$ nm), due to the intra-ligand $\pi \rightarrow \pi^*/n \rightarrow \pi^*$ transitions (LL; Figure 2). The spectrum for the complex shows a moderate band at 450–550 nm ($\lambda_{max} = 501$ nm), attributed to the metal-ligand charge-transfer (MLCT) transitions. The spectrum further shows two broad bands at visible region at 550–1100 nm ($\lambda_{max} = 687$ and 950 nm) for the *d*-*d* (MM) transitions for the copper(II)-core electrons [1, 8, 10, 14, 31, 32]. The electronic circular dichroism (ECD) spectra for the free Schiff bases *S*-L2 and *R*-L2 (Figure 5(a)) and the complexes Cu-*S*-L2 and Cu-*R*-L2 (Figure 5(b)) show several bands with opposite Cotton effects, associated

λ/nm ^a	Oscillator strength (f)	MOs contributions (%) ^b	Assignments ^{c,d}
992 (950)	0.0031	H-10→L, H-8→L	LM
855 (687)	0.0087	H-1→L, H→L	MM, LM
472 (501)	0.0144	H-4 \rightarrow L, H-1 \rightarrow L + 1	MM, ML/LM, LL
447	0.0628	$H-1 \rightarrow L+2, H \rightarrow L+2$	MM, ML, LL
343 (342)	0.0689	H-7 \rightarrow L+2, H-6 \rightarrow L+1	ML/LM, LL
294	0.1247	H-14 \rightarrow L, H-8 \rightarrow L + 1	ML, LL

Table 2. Some selected and simplified assignments on simulated spectrum for Δ -Cu-*R*-L2, calculated at B3LYP/6-31G(d) with PCM in methanol.

^aExperimental values are in parentheses;

 ${}^{b}H = HOMO$ and L = LUMO;

^cMM = metal-centered (d-d), ML/LM = metal-ligand/ligand-metal, LL = ligand-centered transitions;

 $^{d}\beta$ -spin MOs are considered.

to different electronic transitions found in the UV–Vis spectra. Observed mirror-image relationships indicate the enantiopurity or enantiomeric excess of the *S*- and *R*-ligands and their associated complexes Cu-*S*-L2 and Cu-*R*-L2 in solution, respectively. The comparisons of ECD spectra between the free Schiff bases (Figure 5(a)) and the complexes (Figure 5(b)) reveal several bands at 320-800 nm in the complexes, and hence, confirm formation of the complexes. ECD spectra for Cu-*R*-L2/Cu-*S*-L2 are characterized by the following series of bands (sign and strength): about 600 nm (+/–, weak), 490 nm (-/+, weak), 335 nm (+/–, strong) and 300 nm (-/+, very strong), respectively.

The experimental and simulated UV-Vis spectra are almost similar with little shifted bands maxima (Figure 2 and Supporting Information Figure S5). The simulated UV-Vis spectra for the diastereomeric pair Δ -Cu-*R*-L2/ Λ -Cu-*R*-L2 or Δ -Cu-S-L2/ Λ -Cu-S-L2 are essentially identical (Supporting Information Figure S4). The simulated ECD spectra for the diastereomeric pair Δ -Cu-R-L2/ Λ -Cu-R-L2 or Δ -Cu-S-L2/ Λ -Cu-S-L2 show expected mirror-image relationships with opposite Cotton effects (Figure 3). Selected and simplified assignments on simulated UV-Vis spectra are made based on orbital and population analyses for Δ -Cu-*R*-L2 at the same level of theory (Table 2) [1, 8, 10, 14]. The band at 992 nm with oscillator strength 0.0031 (f) is assigned for the ligand π -moiety (i.e. HOMO-8 and HOMO-10) to the metal- d_{z}^{2} (LUMO) transitions. Another band at 855 nm (f = 0.0087) results from combination of the metal- d_z^2 and ligand π -moiety (i.e. HOMO and HOMO-10) to the metal- d_z^2 (LUMO) transitions. There are also intense bands on the simulated spectra which are close to the experimental bands (Figure 2, Table 2). The frontier molecular orbitals HOMO, HOMO-10 and LUMO are shown in Figure 6. The HOMO orbital is mainly localized on the pyridyl- π and metal-d_{xy} electron moieties, while LUMO is localized on the metal- d_z^2 electrons. The energy gap between the HOMO and LUMO is very narrow (i.e. $\Delta Eq = 0.96$ kcal/mol) and thus involves a significant contribution to the excitation protocol.

3.5. ECD spectra and absolute configuration at-metal (Λ vs. Δ)

It has well been documented that the overall nature of the *chiral*-metal complexes is reflected on their ECD spectra in solution. Spectral analyses of the *d*-*d* transitions bands in the visible region predict the absolute configuration at-metal center (i.e. Λ vs. Δ) in the complexes. Comparisons of experimental and simulated ECD spectra determine the absolute configuration resulting from diastereoselection and induced



Scheme 3. Reaction pathway for decomplexation of Cu-R-L2 with NaCN in MeOH.

chirality at-metal by the coordinated ligands (*S* or *R*-L2) [1–8]. Hence, the experimental spectrum for Cu-*R*-L2 or Cu-*S*-L2 shows best fit to the simulated spectrum for the diastereomer Δ -Cu-*R*-L2 or Λ -Cu-*S*-L2 (Figure 3). These results conclude that Cu-*R*-L2 or Cu-*S*-L2 corresponds to the diastereomeric excess of Δ -Cu-*R*-L2 or Λ -Cu-*S*-L2 (i.e. major product) in solution. It has been reported that a dynamic diastereomeric equilibrium between the two diastereomers prevails in solution [2, 3, 6–9]. Further, the spectrum for Cu-*R*-L2 or Cu-*S*-L2 or Λ -Cu-*R*-L2 (Figure 3). These results are parallel to the preferred formation of Δ -M-*R* or Λ -M-*S* (i.e. major products) in the *bis*[(*R* or *S*)-N-(1-(*p*-OCH₃C₆H₄)ethyl)salicylaldiminato- κ^2 N,O]- Δ/Λ -M(II) (M = Cu [8] and Fe [11]), as evidenced by experimental and simulated ECD/VCD spectra in solution.

3.6. Decomplexation of Cu-R-L2 with NaCN and cis-trans interconversion

We employed an indirect method to prove the existence of the Schiff base in the paramagnetic Cu(II)-complexes and hence, conducted a decomplexation reaction of Cu-*R*-L2 with NaCN in methanol and isolated the free Schiff base (Scheme 3, details in Experimental section). The reaction results in the formation of the diamagnetic $[Cu^{I}(CN)_{4}]^{3-}$ and *R*-L2 via reduction of the Cu(II) to Cu(I) accompanies a color change from deep-green to light-orange (Scheme 3) [1, 5, 31, 32]. ¹H NMR spectrum of *R*-L2 (Figure 7) (isolated via decomplexation, see subsection 2.4) shows two sets of peaks for each proton, indicating the presence of both *cis*- and *trans*-isomers in solution. The methyl protons show two doublets at $\delta = 1.51$ and 1.53 ppm ($J_{HH} = 7.2$ Hz), while the methine proton shows two quartets at $\delta = 4.48$ and 4.64 ppm ($J_{HH} = 6.8$ Hz). The methoxy protons show two sharp singlets at $\delta = 3.81$ and 3.82 ppm. The ratio of the *cis*- to *trans*-isomer is about 55:45. These results are similar to the ¹H NMR spectrum of *R*-L2 (as described in subsection 3.2), strongly suggesting the presence of the Schiff base in the copper(II)-complexes.

We further run ¹H NMR spectrum (Figure 8) of *in situ* reaction mixture of Cu-*R*-L2 and NaCN in dmso-d₆ (in NMR tube), which also shows two sets of peaks for each proton and indicates both the *cis*- and *trans*-isomers of the Schiff base in solution. Here, the methyl protons show two doublets at $\delta = 1.36$ and 1.38 ppm ($J_{HH} = 6.8 \text{ Hz}$) and the methoxy protons show two singlets at $\delta = 3.70$ and 3.72 ppm. The methine proton shows two quartets at $\delta = 4.51$ and 4.65 ppm ($J_{HH} = 6.8 \text{ Hz}$) with *cis*-to *trans*-isomer ratio of about 8:92. In comparison to almost equal amounts of *cis*- to *trans*-isomer (i.e. ca. 48:52 or 55:45) in the free *R*-L2 in solution (discussed above), the present ratio indicates the *trans*-isomer as the major product (ca. 92%) in the reaction mixture. The results indicate coordination of copper(II) to the solely *trans*-form of the Schiff base



Figure 7. ¹H NMR spectrum for *R*-L2 (isolated via decomplexation of Cu-*R*-L2 with NaCN) in CDCl₃ at 20 °C (c/t stands for *cis-/trans-*isomer).



Figure 8. ¹H NMR spectrum of the *in situ* reaction mixture of Cu-*R*-L2 and NaCN in DMSO-d₆ at 20 °C (c/t stands for *cis-/trans*-isomer).

(resulting from *cis*- to *trans*-interconversion during complexation reaction) and hence, provide the complexes as depicted in Scheme 1. The results further suggest that the *trans*-isomer undergoes interconversion to the *cis*-isomer (ca. 8%) immediately upon its discharge via decomplexation in solution (Scheme 3). Finally, with complete conversion, the isolated free *R*-L2 shows almost equal amounts of *cis*- to *trans*-isomer (ca. 55:45) in solution, as discussed above.

3.7. Cyclic voltammetry

Cyclic voltammograms for Cu-*R*-L2 were run at the range of -1.30 to 1.00 V (vs. Ag/AgCl) at varying scan rates in acetonitrile at 25 °C, respectively (Figure 9). The forward scans exhibit two weak cathodic peaks at about -0.62 (*E*c1) and about -0.93 V (*E*c2) at a scan rate of 0.10 Vs⁻¹, which become more populated at faster scan rates. These peaks are referred to two electron charge transfer processes for the [Cu-*R*-L2]²⁺/[Cu-*R*-L2]⁺ and [Cu-*R*-L2]⁺/[Cu-*R*-L2]⁰ couples (L2 = Schiff base ligand), respectively. The reverse scans show two corresponding strong anodic peaks at about -0.19 (*E*a2) and about +0.45 V (*E*a1) for [Cu-*R*-L2]⁰/[Cu-*R*-L2]⁺ and [Cu-*R*-L2]²⁺ couples,



Figure 9. Cyclic voltammograms for Cu-*R*-L2 (0.5 mM); TBAP (0.1 M) at varying scan rates (v/Vs^{-1}) in acetonitrile at 25 °C.

respectively. The relatively weak cathodic peaks on the forward scans reflect instability of the reduced species. For comparison, CV for the Schiff base (R-L2) was run under the same experimental conditions (Supporting Information Figure S7), which shows two pairs of redox peaks at about +0.80 to +1.20 V ($E_{C_{TRAP}}/E_{a_{TRAP}}$) for the electrolytes (TBAP) [5, 14] and two pairs of redox peaks at about +1.30 to +2.00 V ($Ec1_{12}/Ea_{12}$ and $Ec2_{1,2}/Ea_{1,2}$) for the Schiff base. The results suggest that the observed peaks at lower potential (i.e. at +0.50 to -1.30 V) are exclusively due to the $[Cu-R-L2]^{2+} \rightleftharpoons [Cu-R-L2]^{+}$ and $[Cu-R-L2]^+ \rightleftharpoons [Cu-R-L2]^0$ couples in solution (Figure 9), since the Schiff base shows no peaks at this range (Supporting Information Figure S7). Thus, the CV results unequivocally demonstrate two quasi-reversible one electron charge transfer processes for the Cu²⁺/Cu⁺ and Cu⁺/Cu⁰ couples in acetonitrile, respectively [14, 31, 33, 34]. In addition, analyses of voltammograms at varying scan rates show that both the cathodic and anodic peaks become more populated and shift to lower and higher potentials, respectively, with faster scan rates. Indeed, plot for the anodic to cathodic peak current ratios versus square root of the scan rates (i.e. la2/lc2 vs. $v^{1/2}$ [Vs⁻¹]) exhibits a linear increase, and plot for the potential differences between the two anodic peaks versus square root of the scan rates (i.e. $\Delta Ea = Ea_2 - Ea_1$ [V] vs. $v^{1/2}$ [Vs⁻¹]) remains unchanged with faster scan rates (Supporting Information Figure S8), suggesting a diffusion-controlled electrochemical process in solution [1, 14, 31, 33, 34].

4. Conclusion

The enantiopure Schiff bases (*R* or *S*)-1-(*p*-R₁-C₆H₄)-N-(phenyl(pyridin-2-yl)methylene)ethanamine react with copper(II) acetate to give distorted-tetrahedral *bis*[(*R* or *S*)-1-(*p*-R₁C₆H₄)-N-(phenyl(pyridin-2-yl)methylene)ethanamino- κ^2 N,N] Δ/Λ -Cu(PF₆)₂ in the presence of NH₄PF₆. ¹H NMR spectra (experimental and simulated) of the Schiff bases reveal two sets of peaks for each proton, resulting from *cis*- and *trans*-isomers in solution. A conformational change from *cis*- to *trans*-isomer occurs in solution and the copper(II) coordinates to the solely *trans*-form to provide the complexes. CV results demonstrate two quasi-reversible one electron charge transfer processes for the Cu²⁺/Cu⁺ and Cu⁺/Cu⁰ couples in acetonitrile. ECD spectra show several bands with opposite Cotton effects (mirror-image), indicating enantiopurity or enantiomeric excess of the *R* or *S*-ligands and their associated complexes in solution. Analyses of experimental and simulated ECD spectra suggest induced chirality at-metal, which diastereoselectively prefers formation of the Δ -Cu-*R* or Λ -Cu-*S* diastereomeric solution. These results are of particular interest to synthesize the *chiral*-at-metal complexes and to use them as potential catalysts in a stereoselective way.

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Disclosure statement

No potential conflict of interest was reported by the authors.

References

- [1] M. Enamullah, A.K.M. Royhan Uddin, G. Pescitelli, R. Berardozzi, G. Makhloufi, V. Vasylyeva, A.-C. Chamayou, C. Janiak. *Dalton Trans.*, **43**, 3313 (2014).
- [2] G. Pescitelli, S. Lüdeke, A.-C. Chamayou, M. Marolt, V. Justus, M. Górecki, L. Arrico, L. Di Bari, M.A. Islam, I. Gruber, M. Enamullah, C. Janiak. *Inorg. Chem.*, 57, 13397 (2018).
- [3] M. Enamullah, G. Makhloufi, R. Ahmed, B. Alif Joy, M.A. Islam, D. Padula, H. Hunter, G. Pescitelli, C. Janiak. *Inorg. Chem.*, **55**, 6449 (2016).
- [4] M. Enamullah, M.A. Quddus, M.R. Hasan, G. Pescitelli, R. Berardozzi, G. Makhloufi, V. Vasylyeva, C. Janiak. *Dalton Trans.*, **45**, 667 (2016).
- [5] M. Enamullah, M.A. Quddus, M.R. Hasan, G. Pescitelli, R. Berardozzi, G.J. Reiß, C. Janiak. Eur. J. Inorg. Chem., 2015, 2758 (2015).
- [6] M. Enamullah, V. Vasylyeva, M.A. Quddus, M.K. Islam, S.-P. Höfert, C. Janiak. CrystEngComm, 20, 4724 (2018).
- [7] A.-C. Chamayou, S. Lüdeke, V. Brecht, T.B. Freedman, L.A. Nafie, C. Janiak. *Inorg. Chem.*, 50, 11363 (2011).
- [8] A.-C. Chamayou, G. Makhloufi, L.A. Nafie, C. Janiak, S. Lüdeke. *Inorg. Chem.*, 54, 2193 (2015).
- [9] M. Enamullah, V. Vasylyeva, C. Janiak. Inorg. Chim. Acta, 408, 109 (2013).
- [10] M. Enamullah, M.K. Islam. J. Coord. Chem., 66, 4107 (2013).
- [11] M. Enamullah, K.S. Banu, M.A. Hossain, Ü. Kökçam-Demir. *J. Mol. Struct.*, **1199**, 126947 (2020).
- [12] M. Enamullah, M.A. Islam, B.A. Joy, B. Dittrich, G.J. Reiss, C. Janiak. *Inorg. Chim. Acta*, **482**, 935 (2018).
- [13] M. Enamullah, M.K. Islam, S.-P. Höfert, C. Janiak. Inorg. Chim. Acta, 501, 119245 (2020).

- [14] M. Enamullah, M.A. Quddus, M.M. Rahman, T.E. Burrow. J. Mol. Struct., 1130, 765 (2017).
- [15] N. Kordestani, H.A. Rudbaria, G. Bruno, S. Rosario, J.D. Braun, D.E. Herbert, O. Blacque, I. Correia, M. Al-M. Zaman, M.M. Bindu, C. Janiak, M. Enamullah. *Dalton Trans.*, **49**, 8247 (2020).
- [16] (a) A. von Zelewsky. Stereochemistry of Coordination Compounds, p. 69, Wiley, Chichester (1996);(b) H. Amouri, M. Gruselle. Chirality in Transition Metal Chemistry: Molecules, Supramolecular Assemblies and Materials, p. 40 Wiley, Chichester (2008).
- [17] (a) C. Evans, D. Luneau. J. Chem. Soc., Dalton Trans., 83 (2002); (b) K.A. Jensen. Inorg. Chem., 9, 1 (1970);(c) T. Akitsu, Y. Einaga. Acta Crystallogr. C, 60, m640 (2004).
- [18] (a) H. Sakiyama, H. Okawa, N. Matsumoto, S. Kida. *Bull. Chem. Soc. Jpn.*, **64**, 2644 (1991);
 (b) H. Sakiyama, H. Okawa, N. Matsumoto, S. Kida. *J. Chem. Soc., Dalton Trans.*, 2935 (1990).
- [19] (a) H. Ōkawa, M. Nakamura, S. Kida. Inorg. Chim. Acta, 120, 185 (1986); (b) T. Akitsu, Y. Einaga. Polyhedron, 24, 2933 (2005);(c) T. Akitsu, Y. Einaga. Polyhedron, 24, 1869 (2005).
- [20] I. Bernal, W. Ries, H. Brunner, D.K. Rastogi. J. Organomet. Chem., 290, 353 (1985).
- [21] G. Zassinovich, R. Bettella, G. Mestroni, N. Bresciani-Pahor, S. Geremia, L. Randaccio. J. Organomet. Chem., 370, 187 (1989).
- [22] H. Brunner, B. Reiter, G. Riepl. Chem. Ber., 117, 1330 (1984).
- [23] D.L. Davies, J. Fawcett, R. Krafczyk, D.R. Russell. J. Organomet. Chem., 545–546, 581 (1997).
- [24] I. Bernal, G.M. Reisner, H. Brunner, G. Riepl. Inorg. Chim. Acta, 103, 179 (1985).
- [25] H. Brunner, D.K. Rastogi. Inorg. Chem., 19, 891 (1980).
- [26] D. Gutiérrez, S. Bernès, G. Hernández, O. Portillo, G.E. Moreno, M. Sharma, P. Sharma, R. Gutiérrez. J. Coord. Chem., 68, 3805 (2015).
- [27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski. D.J. Fox. *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford, CT (2009).
- [28] T. Bruhn, A. Schaumlöffel, Y. Hemberger, G. Bringmann. Chirality, 25, 243 (2013).
- [29] (a) H.E.L. Hamdani, M.E.L. Amane. J. Mol. Struct., **1184**, 262 (2019);(b) J.M. Seco, M.J.G. Garmendia, M. Quiros. J. Coord. Chem., **55**, 345 (2002).
- [30] M. Enamullah, A.K.M. Royhan Uddin, G. Hogarth. J. Coord. Chem., 65, 4263 (2012).
- [31] M. Enamullah, M. Al-M. Zaman, M.M. Bindu, M.K. Islam, M.A. Islam. J. Mol. Struct., 1201, 127207 (2020).
- [32] M. Enamullah, A.K.M. Royhan Uddin. J. Bangladesh Chem. Soc., 22, 44 (2009).
- [33] M. Enamullah, M.A. Islam, A.-C. Kautz, C. Janiak. J. Coord. Chem., 71, 2557 (2018).
- [34] M. Enamullah, M.A. Islam, B.A. Joy, G.J. Reiss. Inorg. Chim. Acta, 453, 202 (2016).