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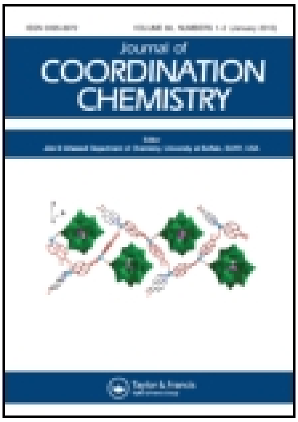

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Mohammed Enamullah[a] & Mohammad Khairul Islam[a]

[a] Department of Chemistry, Jahangirnagar University, Dhaka, Bangladesh

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Syntheses, spectroscopy, optical properties, and diastereoselectivity of copper(II)-complexes with chiral aminoalcohol based Schiff bases

MOHAMMED ENAMULLAH* and MOHAMMAD KHAIRUL ISLAM

Department of Chemistry, Jahangirnagar University, Dhaka, Bangladesh

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Chiral aminoalcohol based Schiff bases (*R* or *S*)-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenol and (*R*/*S*)-2-{(E)-(2-hydroxy-2-phenylethylimino)methyl}phenol coordinate to copper(II)acetate to give enantiopure Λ/Δ- or Δ/Λ-*bis*[(*R* or *S*)-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenoxide-κ^2*N*,*O*]copper(II), {Λ/Δ-Cu(*R*-L1)$_2$ (**1**) or Δ/Λ-Cu(*S*-L1)$_2$ (**2**)}, and racemic Δ/Λ- and Λ/Δ-*bis*[(*R*/*S*)-2-{(E)-(2-hydroxy-2-phenylethylimino)methyl}phenoxide-κ^2*N*,*O*]copper(II), {Δ/Λ- and Λ/Δ-Cu(*R*/*S*-L2)$_2$ (**3**)}, respectively. The complexes are characterized by elemental analyzes, IR, UV–Vis, polarimetry, circular dichroism (CD), differential scanning calorimeter (DSC), and mass spectroscopy. Polarimetry shows the rotation to the left at −113.6° (**1**) and to the right at +106.4° (**2**). CD spectra show the expected mirror-image relationship with opposite sign of ellipticity maxima ($\Delta\varepsilon_{\max}$ = +0.43 for **1** and −0.42 M^{-1} dm^3 cm^{-1} for **2** at 638 nm) due to the d-d transitions of the metal ion. CD spectral analyzes further reveal a diastereoselectivity or diastereomeric excess towards Λ-Cu(*R*-L1)$_2$ or Δ-Cu(*S*-L1)$_2$ configuration for **1** or **2** in solution. Similarly, the enantiomeric pair of Δ-Cu(*R*-L2)$_2$ and Λ-Cu(*S*-L2)$_2$ configurations (CD inactive) for **3** will be preferred in solution. Electronic spectra in different solvents reveal a negative solvatochromism by shifting absorption maxima of the MLCT band to higher energies in solvents of increasing polarity as well as acceptor number. DSC analyzes show an endothermic peak at 525.5 (**1**) or 528.7 K (**2**), corresponding to a thermally induced structural phase transformation from distorted square-planar to regular tetrahedral.

Keywords: Chiral aminoalcohol Schiff bases; Cu(II)-chiral Schiff base complexes; CD spectroscopy; Enantiopurity; Diastereoselectivity

1. Introduction

Syntheses, spectroscopy, optical properties, and molecular structures of transition metal complexes with chiral aminoalcohol based Schiff bases are of continued interest [1–4]. Enantiopure Cu(II)-Schiff base complexes have been used extensively as efficient asymmetric catalysts for nitroaldol and cyclopropanation reactions [5]. Cu(II)-chiral aminoalcohol Schiff base complexes further show particular interest due to their metallo-supramolecular architectures in the crystal lattices. Mononuclear distorted square-planar [Cu{(*S*)-N-2-(*p*-nitro-salicylaldiminato)-2-phenylethanol}Cl] exhibits right-handed supramolecular homochiral helices via O–H···Cl–Cu hydrogen bonds among adjacent molecules [1a]. Similarly, the dinuclear [Cu{(*S*)-N-2-(*p*-bromo-salicylaldiminato)-2-phenylethanolato}Cl]$_2$ and [Cu{(*S*)-N-2-(salicylaldiminato)-3-phenyl-1-propanolato}Cl]$_2$

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*Corresponding author. Email: enamullah@juniv.edu show strong hydrogen bonding of copper bound chloride that directs the self-assembly of the molecules via C–H···Cl–Cu interactions, leading to intriguing hydrogen-bonded metallo-supramolecular architectures in the crystal lattices [1b].

We have recently given attention to chiral N^O-chelate type Schiff bases such as chiral aminoalcohol based Schiff bases (*R*)-2-(X-benzaldimine)-2-phenylethanol (*R*-HL) [6a], (*R* or *S*)-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenol (*R*- or *S*-HL1) [6b], and (*R*/*S*)-2-{(E)-(2-hydroxy-2-phenylethylimino)methyl}phenol (*R*/*S*-HL2) [6b]. The Schiff base ligands coordinate to Rh(η^4-cod) to give enantiopure [Rh(η^4-cod)(*R*-HL)](acetate) [6a], [Rh(η^4-cod)(*R*- or *S*-L1)] [6b] and racemic [Rh(η^4-cod)(*R*/*S*-L2)] [6b], respectively. Coordination of two asymmetric N^O chelate units in tetrahedral or pseudo-tetrahedral metal-complexes affords C_2-symmetric Λ- and Δ-configurations at the metal center [7–11]. Thus, the use of enantiopure *R*- or *S*-N^O chelate leads to the formation of two diastereomers Λ/Δ-M(*R*-N^O)$_2$ or Δ/Λ-M(*S*-N^O)$_2$. Due to intramolecular non-covalent interactions within the chiral metal chelate complexes there is a free-energy difference between the diastereomers, leading to preferential formation of one diastereomer Λ-M(*R*-N^O)$_2$ or Δ-M (*S*-N^O)$_2$. Accordingly, use of racemic *R*/*S*-N^O ligand provides all four diastereomers, Λ/Δ-M(*R*-N^O)$_2$ and Δ/Λ-M(*S*-N^O)$_2$ with preferential formation of a enantiomeric pair Λ-M(*R*-N^O)$_2$ and Δ-M(*S*-N^O)$_2$.

Diastereoselection of enantiopure (*R* or *S*)-HL1 or racemic (*R*/*S*)-HL2 with zinc(II)acetate leads to four-coordinate, non-planar Λ/Δ or Δ/Λ-Zn(*R*- or *S*-L1)$_2$ or Λ/Δ- and Δ/Λ-Zn(*R*/*S*-L2)$_2$ with preferential formation of one diastereomer {i.e. Λ-Zn(*R*-L1)$_2$ or Δ-Zn(*S*-L1)$_2$} or an enantiomeric pair {Δ-Zn(*R*-L2)$_2$ and Λ-Zn(*S*-L2)$_2$}, respectively, in the solid state [10]. Chloroform solution from solid products provides the major diastereomer of Λ-Zn(*R*-L1)$_2$ or Δ-Zn(*S*-L1)$_2$ (*ca.* 67%) and minor diastereomer of Δ-Zn(*R*-L1)$_2$ or Λ-Zn(*S*-L1)$_2$ (*ca.* 33%), respectively, as evidenced by ^{1}H NMR. The racemic compound gives the major diastereomers of enantiomeric pair Δ-Zn(*R*-L2)$_2$, Λ-Zn(*S*-L2)$_2$ (*ca.* 67%) and minor diastereomers of Λ-Zn(*R*-L2)$_2$, Δ-Zn(*S*-L2)$_2$ (*ca.* 33%) in solution. In fact, the racemic compound crystallizes in the non-centrosymmetric polar space group *Iba*2 with the formation of an enantiomeric pair Δ-Zn (*R*-L2)$_2$ and Λ-Zn(*S*-L2)$_2$ as a racemic mixture as evidenced by X-ray diffraction studies [10]. In our recent investigations, the *R*- or *S*-ligand chirality diastereoselectively induces a Λ-Cu(*R*-L)$_2$ or Δ-Cu(*S*-L)$_2$ {L = (*R*- or *S*)-N-1-(4-X-phenyl)ethyl-naphthaldiminate} configuration as deduced by combined circular dichroism (CD), DFT, and X-ray structural studies [11].

The present article, in continuation, describes the syntheses, spectroscopy, optical properties, diastereoselectivity and solvatochromism of the analogous Cu(*R* or *S*-L1)$_2$ and Cu(*R*/*S*-L2)$_2$ complexes, respectively. In contrast to earlier communications [1a,b], where one molecule of *S*-HL1 is involved in coordination, the present study shows that the two molecules of *R*- or *S*-HL1 coordinate to copper(II).

2. Experimental

2.1. *Materials and methods*

IR-spectra were recorded on a Nicolet iS10 spectrometer as KBr disks at ambient temperature. UV–Vis spectra were obtained with a Shimadzu UV 3150 spectrophotometer in DMF, CH_2Cl_2, $CHCl_3$, THF, DMSO, C_6H_6, C_6H_{12}, CH_3OH, C_2H_5OH, $(CH_3)_2CO$ (AC), CH_3CN, and dioxane at 25 °C. Elemental analyzes were done on a Vario EL instrument from Elementaranalysensysteme. Thermal analyzes were performed on a SHIMADZU DSC-60 differential scanning calorimeter (DSC), where the heating rate was 10 K min^{-1} from 303 to 553 K. Polarimetric measurements were carried with a UniPol L instrument in $CHCl_3$ at 25 °C. CD spectra were obtained with a JASCO J600 spectropolarimeter in CH_2Cl_2 at 25 °C. EI-/APCI-mass spectra were taken on a Thermo-Finnigan TSQ 700. Mass spectra show metal isotope pattern arising from the distribution of ^{63}Cu 69.17 (100%) and ^{65}Cu 30.83 (44.6%) and peaks were given for the more abundant isotope. The enantiopure Schiff bases (*R* or *S*)-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenol (*R*- or *S*-HL1) and racemic (*R*/*S*)-2-{(E)-(2-hydroxy-2-phenylethylimino)methyl}phenol (*R*/*S*-HL2) were synthesized according to our previous communication [6b].

2.2. *General procedure to synthesize the complexes*

Enantiopure Schiff bases (*R* or *S*)-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenol (*R* or *S*-HL1) (310 mg, 1.29 mM) dissolved in 5 mL methanol were added into 5 mL hot methanol solution of $Cu(CH_3CO_2)_2{\bullet}H_2O$ (128 mg, 0.64 mM) and stirred for 6–8 h at room temperature. Color changes from orange to yellow to green. Volume of this solution is reduced to 50% in *vacuo* and left standing for crystallization via slow evaporation of solvent at room temperature, but no crystals suitable for X-ray analyzes were formed even after 6–7 d. The solution was dried in air, giving deep green products of Λ/Δ- or Δ/Λ-*bis*[(*R* or *S*)-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenoxide-κ^2*N*,*O*]copper(II), {Λ/Δ-Cu(*R*-L1)$_2$ (**1**) or Δ/Λ-Cu(*S*-L1)$_2$ (**2**)}. The same procedure was followed for the synthesis of racemic Δ/Λ- and Λ/Δ-*bis*[(*R*/*S*)-2-{(E)-(2-hydroxy-2-phenylethylimino)methyl}phenoxide-κ^2*N*,*O*]copper(II), {Δ/Λ- and Λ/Δ-Cu(*R*/*S*-L2)$_2$ (**3**)} using the racemic (*R*/*S*-HL2). Here, a light brown precipitate was formed while stirring the solution for 6–8 h. Filtering off the precipitate and washing three times with methanol (3 mL) gave light brown **3** after drying in air for 3–4 d.

2.2.1. Λ/Δ-*bis*[(*R*)-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenoxide-κ^2*N*,*O*] copper(II), {Λ/Δ-Cu(*R*-L1)$_2$} (1). Yield 200 mg (69%). –$[\alpha]^{25} = -113.6°$ (c = 0.31 g/100 mL) at 589 nm in $CHCl_3$. IR (KBr, cm^{-1}): ~3270sh (νO–H), 3060, 3027, 2924w (νC–H), 1629 *versus* (νC=N), and 1535s (νC=C). CD ($1.30 \times 10^{-3}\,\text{M}\,\text{dm}^{-3}$, CH_2Cl_2): λ_{max} ($\Delta\varepsilon_{\text{max}}/\text{dm}^3\,\text{M}^{-1}\,\text{cm}^{-1}$) = 642 nm (+0.40). –$C_{30}H_{28}N_2O_4Cu$ (544.09): Calcd C 66.23, H 5.19, N 5.15; found C 65.83, H 5.00, N 4.92.

2.2.2. Δ/Λ-*bis*[(*S*)-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenoxide-κ^2*N*,*O*] copper(II), {Δ/Λ-Cu(*S*-L1)$_2$} (2). Yield 210 mg (72%). –$[\alpha]^{25}$: +106.4° (c = 0.38 g/100 mL) at 589 nm in $CHCl_3$. IR (KBr, cm^{-1}): ~3270sh (νO–H), 3059, 3026, 2922w (νC–H), 1629 *versus* (νC=N), and 1534s (νC=C). CD ($3.62 \times 10^{-3}\,\text{M}\,\text{dm}^{-3}$, CH_2Cl_2): λ_{max} ($\Delta\varepsilon_{\text{max}}/\text{dm}^3\,\text{M}^{-1}\,\text{cm}^{-1}$) = 642 nm (−0.43). –$C_{30}H_{28}N_2O_4Cu$ (544.09): Calcd C 66.23, H 5.19, N 5.15; found C 65.72, H 4.96, N 4.80.

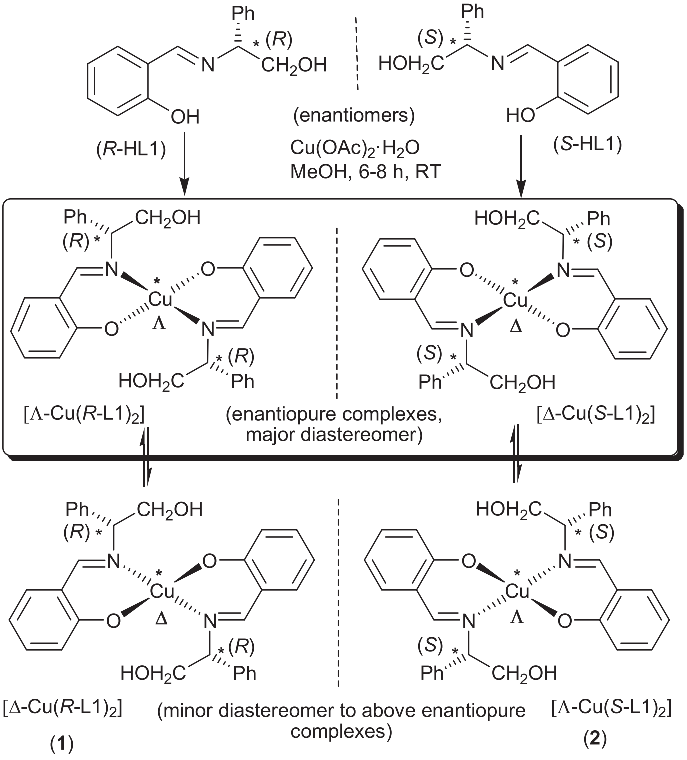
2.2.3. Δ/Λ- and Λ/Δ-*bis*[(*R*/*S*)-2-{(E)-(2-hydroxy-2-phenylethylimino)methyl}phenoxideκ^2*N*,*O*]copper(II), {Δ/Λ- and Λ/Δ-Cu(*R*/*S*-L2)$_2$} (3). Yield 195 mg (67%). IR (KBr, cm^{-1}): 3288sb (νO–H), 3060, 3029, 2922w (νC–H), 1624 *versus* (νC=N), and 1540s (νC=C). –$C_{30}H_{28}N_2O_4Cu$ (544.09): Calcd C 66.23, H 5.19, N 5.15; found C 66.01, H 5.30, N 5.06.

3. Results and discussion

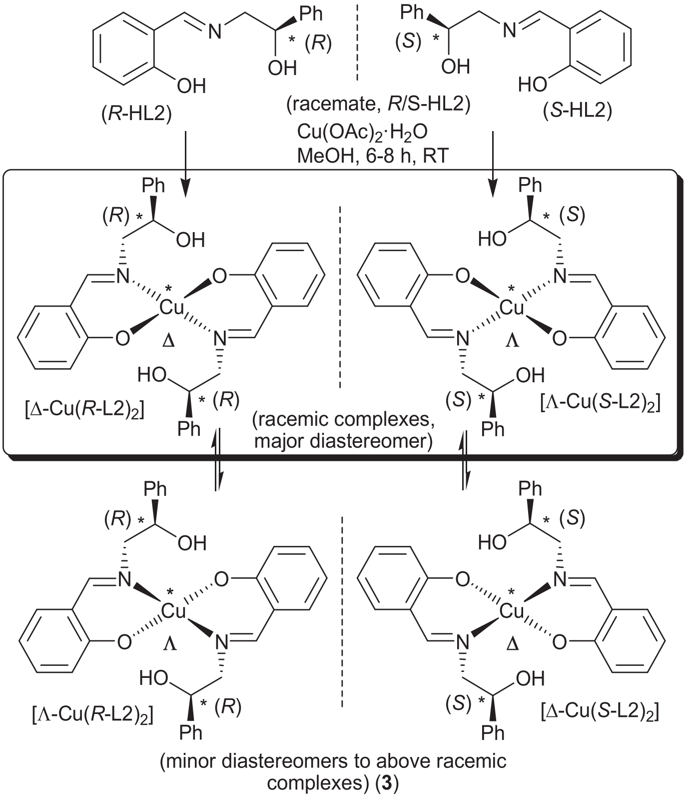
Enantiopure Λ/Δ- or Δ/Λ-*bis*[(*R* or *S*)-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenoxide-κ^2*N*,*O*]copper(II), {Λ/Δ-Cu(*R*-L1)$_2$ (**1**) or Δ/Λ-Cu(*S*-L1)$_2$ (**2**)} or racemic Δ/Λ- and Λ/Δ-*bis*[(*R*/*S*)-2-{(E)-(2-hydroxy-2-phenylethylimino)methyl}phenoxide-κ^2*N*,*O*]copper(II), {Δ/Λ- and Λ/Δ-Cu(*R*/*S*-L2)$_2$} (**3**) are synthesized from reactions of (*R* or *S*)-HL1 or (*R*/*S*)-HL2 with copper(II)acetate (schemes 1 and 2).

3.1. *Mass spectra*

EI-mass spectra (figure 1 and table 1) show parent ion peaks at *m*/*z* 544 ([M+H]$^+$) for **1** and 535 ([M−4H$_2$]$^+$) for **3** including the peaks for the Schiff base ions at *m*/*z* 241 ([HL1 or HL2]$^+$). APCI-mass spectra are mainly dominated by the ion peaks of di-/tri-/tetramers of copper(II)-mono-ligand species [Cu(L1 or L2)]$^+$ (i.e. [{Cu(L1 or L2)}$_2$]$^+$/[{Cu(L1 or L2)}$_3$]$^+$/[{Cu(L1 or L2)}$_4$]$^+$) including the peaks for the protonated Schiff base ions at *m*/*z* 242 (figure 1 and table 1). However, several ions peaks are also found in both the EI-/APCI-mass spectra.



Scheme 1. Synthesis of enantiomeric Λ/Δ-Cu(*R*-L1)$_2$ (**1**) or Δ/Λ-Cu(*S*-L1)$_2$ (**2**). The Cahn-Ingold-Prelog (CIP) priority is N > CH$_2$OH > Ph [12].



Scheme 2. Synthesis of racemic Δ/Λ- and Λ/Δ-Cu(*R*/*S*-L2)$_2$ (**3**). The CIP priority is OH > CH$_2$N > Ph [12].

3.2. *Vibrational spectra*

Vibrational spectra show very strong νC=N bands at 1628–1623 and 1603–1598 cm^{-1} for azomethine of coordinated Schiff bases in the complexes [6–13]. Medium bands/shoulders are found at 3288–3270 cm^{-1} due to νO–H (alcoholic), which appears as a strong broad band at 3340–3200 cm^{-1} in the free Schiff bases [6b]. The spectra further show several bands at 3060–2922 and 1540–1534 cm^{-1} due to νC–H and νC=C, respectively.

3.3. *Polarimetry*

Polarimetric measurements show the rotations to the left at −113.6° (c = 0.31 g/100 mL) for **1** and to the right at +106.4° (c = 0.38 g/100 mL) for **2** in chloroform at 589 nm and 25 °C.

3.4. *Electronic spectra*

Dilute solutions of **1–3** (0.1–0.3 mM dm^{-3}) are very light green resulting in identical electronic spectra (figure 2, table 2), though **1** and **2** are deep green, and **3** is light brown in the solid state. The spectra feature a very strong band below 300 nm and a medium band/shoulder at 300–335 nm with absorption maxima (λ_{max}) at 310–320 nm (ε = 4000–6000 dm^3 M^{-1} cm^{-1}) due to the intra-ligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively, for the azomethine [1, 6–16]. These bands are found below 280 nm and at 280–350 nm

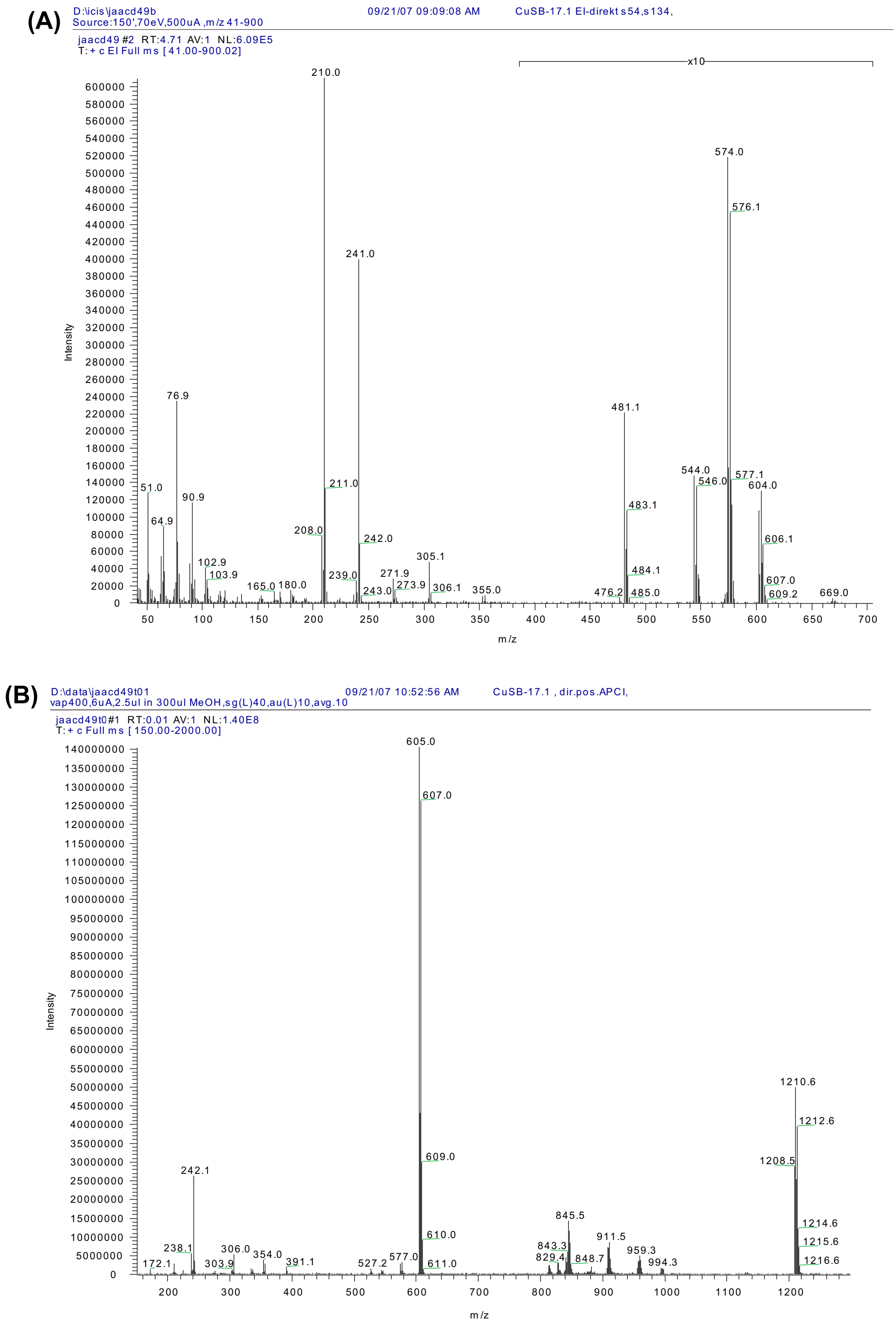


Figure 1. EI- and APCI-mass spectra of **1** (**A** and **B**) and **3** (**C**).

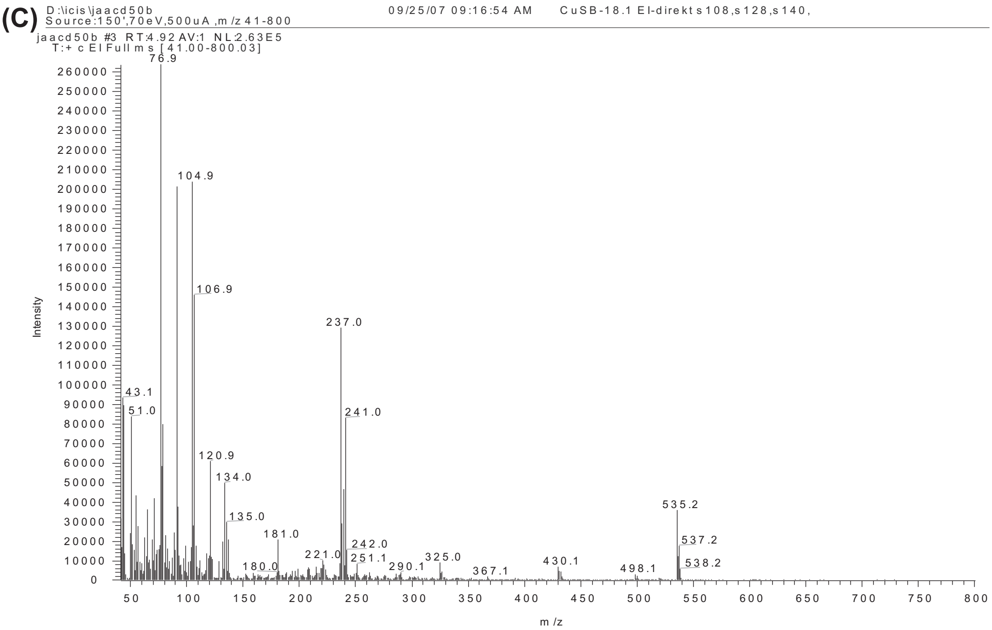


Figure 1. (*Continued*).

Table 1. Electron impact (EI) and atmospheric pressure chemical ionization (APCI) mass spectral data.

Complex[a]	1		3
EI–MS			
Ion peaks	*m*/*z* (%)	Ion peaks	*m*/*z* (%)
$[\{Cu(L1)\}_2–H_2]^+$	604 (2)		
$[\{Cu(L1)\}_2–CH_3OH]^+$	574 (9)		
$[M+H]^+$	544 (3)	$[M–4H_2]^+$	535 (15)
$[M–2CH_2OH+H_2]^+$	481 (4)		
$[HL1]^+$	241 (65)	$[HL2]^+$	241 (35)
$[HL1–CH_3OH+H]^+$	210 (100)	$[HL2–2H_2]^+$	237 (50)
		$[C_6H_5CHO–H]^+$	105 (80)
$[C_6H_5]^+$	77 (38)	$[C_6H_5]^+$	77 (100)
APCI-MS			
$[\{Cu(L1)\}_4–H_2–H]^+$	1211 (35)		
$[\{Cu(L1)\}_3]^+$	911 (6)	$[\{Cu(L2)\}_3–H_2]^+$	909 (3)
$[\{Cu(L1)\}_2–H]^+$	605 (100)	$[\{Cu(L2)\}_2–H]^+$	605 (90)
$[HL1+H]^+$	242 (20)	$[HL2+H]^+$	242 (70)
		$[HL2–CH_3OH–H_2]^+$	207 (100)

[a] The isotopic distribution patterns for $^{63/65}Cu$ containing ions are visible.

(λ_{max} = 319–321 nm, ε = 7000–10,500 dm^3 M^{-1} cm^{-1}), respectively, in the free Schiff bases. The spectra further show a strong broad band at 335–490 nm with λ_{max} = 360–380 nm (ε = 5000–14,000 dm^3 M^{-1} cm^{-1}) due to metal-to-ligand charge transfer (MLCT) transitions. This band is relatively more intense than the corresponding $\pi \rightarrow \pi^*$ band. In addition, a weak broad band is observed in the visible region with λ_{max} = 612–694 nm (ε = 130–220 dm^3 M^{-1} cm^{-1}) due to d-d transitions of the metal ion (figure 2, inset)

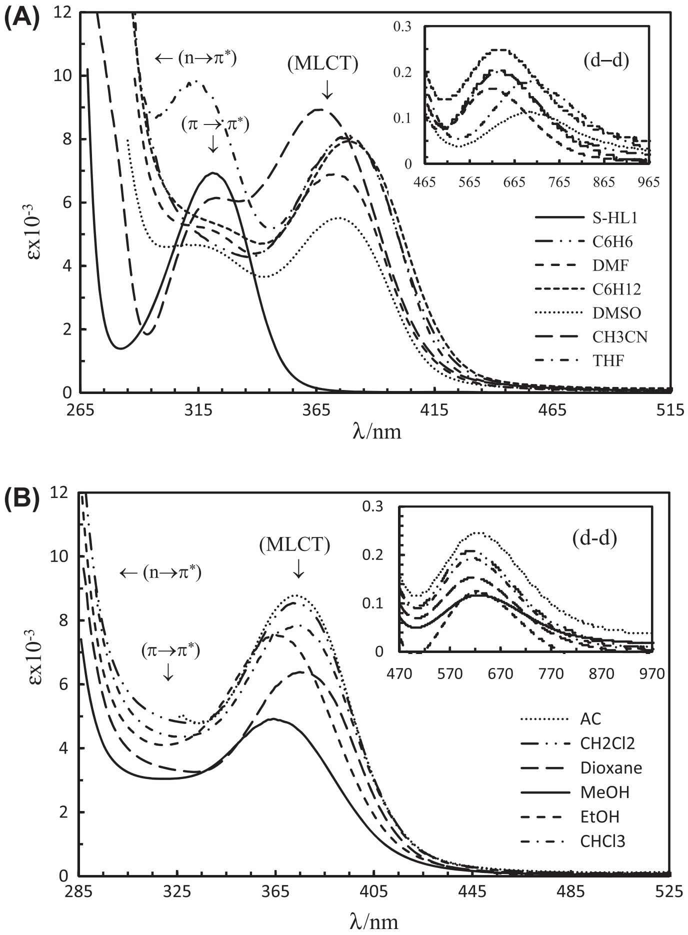


Figure 2. Electronic spectra of **2** in different solvents, and *S*-HL1 in cyclohexane at 25 °C.

[1, 8, 11]. The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are revealed separately in DMF, THF, DMSO, C_6H_6, C_6H_{12}, and CH_3CN (figure 2(A)) while $\pi \rightarrow \pi^*$ band shifts to higher energy and overlaps with the nearby very strong $n \rightarrow \pi^*$ band in CH_2Cl_2, $CHCl_3$, MeOH, EtOH, and dioxane (figure 2(B)). The analogous distorted tetrahedral Zn(II)-complexes with the same ligands [10] show identical electronic spectra in solution except the d-d band. Similar electronic spectra are also revealed from related distorted square-planar Λ/Δ- or Δ/Λ-Cu(*R*- or *S*-L)$_2$ {L = (*R*- or *S*)-N-1-(4-X-phenyl)ethyl-naphthaldiminate} [11]. The MLCT/d-d bands and their corresponding extinction coefficients values (ε_{max}) are almost the same as the present complexes. Thus based on the similarity of electronic spectra as well as CD spectra (discussed below), the present complexes are considered to possess distorted square-planar geometry.

3.5. *Solvatochromism*

To study solvatochromism, time-dependent electronic spectra were taken to check the stability of the coordination environment around the metal ion in solution. Thus, spectra of

Table 2. Electronic spectral data of **1–3** in different solvents at 25 °C.

Entity[a]	Solvent	Assignments		
		$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$: λ_{max} (ε)[1]	MLCT: λ_{max} (ε)[1]	d-d: λ_{max} (ε)[1]
(*S*-HL1) (2.79×10^{-4})	C_6H_{12}	<278, 321 (6934)	–	–
(**1**) (0.79×10^{-4})	C_6H_{12}	<305, 300–340 sh	379 (8818)	635 (280)
(**1**) (1.42×10^{-4})	DMF	<305, 305–340 sh	373 (9760)	613 (226)
(**2**) (1.21×10^{-4})	C_6H_{12}	<300, 316 (5504)	378 (7934)	632 (248)
(**2**) (3.00×10^{-4})	C_6H_6	<310, 310–330 sh	376 (8040)	632 (203)
(**2**) (2.76×10^{-4})	DMF	<300, 300–335 sh	373 (6895)	615 (181)
(**2**) (1.03×10^{-4})	CH_3CN	<320, 323 (6141)	366 (8926)	626 (203)
(**2**) (3.45×10^{-4})	DMSO	<300, 309 (4675)	375 (5508)	696 (113)
(**2**) (2.22×10^{-4})	THF	<300, 316 (9738)	377 (8122)	697 (181)
(**2**) (3.79×10^{-4})	MeOH	<310	364 (4918)	628 (116)
(**2**) (2.24×10^{-4})	EtOH	<310	365 (7548)	626 (125)
(**2**) (3.10×10^{-4})	$CHCl_3$	<320	373 (7865)	614 (194)
(**2**) (1.75×10^{-4})	CH_2Cl_2	<320	371 (8510)	612 (208)
(**2**) (2.87×10^{-4})	Dioxane	<320	376 (6381)	616 (153)
(**2**) (1.55×10^{-4})	$(CH3)_2CO$	–	374 (8775)	625 (245)
(**3**) (1.10×10^{-4})	DMF	<290, 302 (11,000)	364 (14,267)	613 (226)

[a]Concentration in M dm^{-3}; [1]Λ in nm and ε in dm^3 M^{-1} cm^{-1}.

1 in cyclohexane and **3** in DMF show that the complexes are quite stable even after 20 h of solution. While, spectra of **2** show a little dissociation (<5%) after 20 h of solution preparation in DMSO, spectra of **2** show moderate dissociation to 1.7, 3.5, 10, 33, 65, and 85% within 45 min, 90 min, 4 h, 9 h, 20 h, and 30 h, respectively, in THF (figure 3). Here, the $\pi \rightarrow \pi^*$ band becomes intense with disappearance of MLCT band with time. Solvent likely coordinates to metal ion as evidenced by the presence of a weak d-d band (figure 3, inset). In addition, spectrum taken within 30 h is almost identical to that of the free Schiff base (*S*-HL1) except the d-d band.

Spectra of **2** were taken within 2–5 min of solution preparation, to study the solvatochromism, in 12 solvents (figure 2, table 1). Both the absorption maxima (λ_{max}) and intensities (ε_{max}) of different transitions are changed with the polarity (μ/Debye) or acceptor number

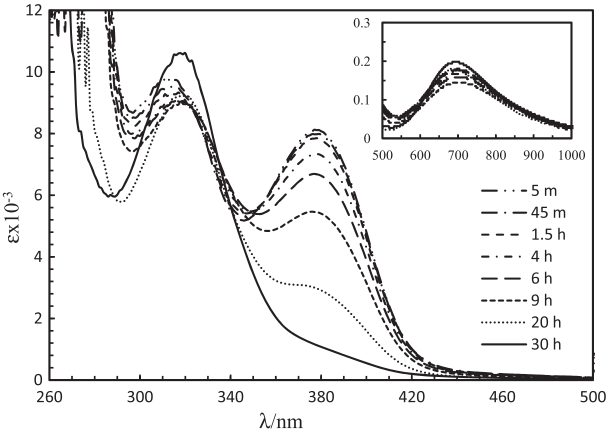


Figure 3. Time dependent electronic spectra of **2** in THF at 25 °C.

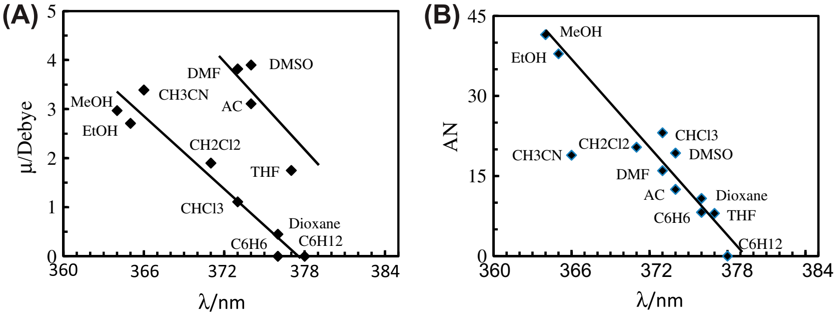


Figure 4. Change of MLCT maxima (λ_{max}) in solvents of increasing polarity (μ/Debye) or AN of **2** at 25 °C.

(AN) of the solvents. It was attempted to make correlation between solvent's polarity (μ/Debye) [8, 17] or AN [18] and observed MLCT maxima (λ_{max}) (figure 4). A negative solvatochromism is revealed by shifting λ_{max} to higher energies (blue shift) in the solvents of increasing polarity (figure 4(A)) with some exception in DMF, DMSO, THF, and acetone. A parallel trend of negative solvatochromism is also found in these solvents. Indeed, a good correlation of negative solvatochromism is found in solvent of increasing AN (figure 4(B)). Similar solvatochromic behaviors are reported for the related distorted tetrahedral Cu/Ni/Zn(II)-chiral Schiff base complexes [8].

3.6. *CD spectra and diastereoselectivity*

Electronic CD spectra in the visible region (400–800 nm) of enantiomeric pair Λ/Δ-Cu (R-L1)$_2$ (**1**) and Δ/Λ-Cu(S-L1)$_2$ (**2**) show the expected mirror-image relationship in dichloromethane (figure 5). The spectra show a weak broad band at 480–800 nm with opposite sign of ellipticity maxima ($\Delta\varepsilon_{max}$ = +0.43 for **1** and −0.42 dm^3 M^{-1} cm^{-1} for **2**) at 638 nm, relating to the d-d transitions of the metal ion [8, 11]. However, the spectra further show bands with opposite sign of ellipticity (−/+ for **1** and +/− for **2**) below 480 nm due to the MLCT transitions. These bands are obviously absent in the racemic **3**.

Diastereoselectivity of chiral *N*,*O*-chelation of two molecules of *R*- or *S*-HL1 or *R*/*S*-HL2 to four-coordinated, non-planar Λ/Δ- or Δ/Λ-Cu(*R* or *S*-L1)$_2$ (**1** or **2**) or Δ/Λ- and Λ/Δ-Cu (R/S-L2)$_2$ (**3**) leads to preferential formation of one diastereomer Λ-Cu(R-L1)$_2$ or Δ-Cu

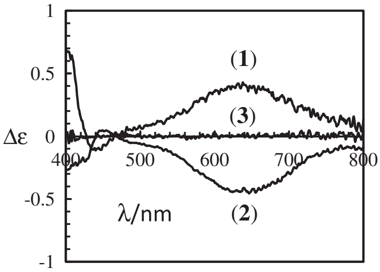


Figure 5. CD spectra of **1** (1.30 × 10^{-3} M dm^{-3}), **2** (3.62 × 10^{-3} M dm^{-3}), and **3** (1.95 × 10^{-3} M dm^{-3}) in dichloromethane at 25 °C.

(S-L1)$_2$ or an enantiomeric pair Δ-Cu(R-L2)$_2$ and Λ-Cu(S-L2)$_2$, respectively, in the solid state [8–11]. However, both diastereomers Λ-Cu(R-L1)$_2$ or Δ-Cu(S-L1)$_2$ (major diastereomer) and Δ-Cu(R-L1)$_2$ or Λ-Cu(S-L1)$_2$ (minor diastereomer) will exist for **1** or **2** in solution. The observed CD pattern (figure 5) corresponds to diastereoselectivity or diastereomeric excess towards Λ-Cu(R-L1)$_2$ (+, −/+) or Δ-Cu(S-L1)$_2$ (−, +/−) configuration in solution. Similarly, a mixture of diastereomers of enantiomeric pairs Δ-Cu(R-L2)$_2$ and Λ-Cu(S-L2)$_2$ (major diastereomers) and Λ-Cu(R-L2)$_2$ and Δ-Cu(S-L2)$_2$ (minor diastereomers) will exist for racemic **3** in solution, which are optically inactive and result in no CD bands (figure 5). This assignment of diastereoselectivity is made based on the analogous distorted square-planar Cu(R- or S-L)$_2$ {L = (R- or S)-N-1-(4-X-phenyl)ethyl-naphthaldiminate} [11] having Λ-Cu (R-L)$_2$ or Δ-Cu(S-L)$_2$ configuration (as major diastereomer) and Δ-Cu(R-L)$_2$ or Λ-Cu(S-L)$_2$ configuration (as minor diastereomer) as deduced by combined CD, TDDFT, and X-ray structural studies. Similar results of diastereoselectivity with diastereomeric excess towards Λ-Zn(R-L1)$_2$ or Δ-Zn(S-L1)$_2$ configuration and towards enantiomeric pair of Δ-Zn(R-L2)$_2$ and Λ-Zn(S-L2)$_2$ configurations were also reported for the analogous distorted tetrahedral Zn(R or S-L1)$_2$ and Zn(R/S-L2)$_2$, respectively, in solution and solid state [10].

3.7. *Thermally induced structural phase transition*

Thermally induced structural phase transition has been reported for the analogous Cu(II)-/Ni(II)-chiral *N*,*O*-chelate complexes [8, 19], accompanying a change from distorted square planar/tetrahedral to regular tetrahedral on heating. The DSC curves of heating show an endothermic peak at 525.5 (**1**) or 528.7 K (**2**). This structural phase transition, in analogy with the related complexes, corresponds to a transformation from distorted square-planar to regular tetrahedral, which is irreversible.

4. Conclusion

The present article reports the results of syntheses, spectroscopy, and optical properties of enantiopure Cu(R or S-L1)$_2$ or racemic Cu(R/S-L2)$_2$. Polarimetry shows the enantiopurity of the complexes in solution. CD spectra show the expected mirror-image relationship for the enantiomeric pair, and no absorption band for the racemic compound. CD spectral analyzes further reveal a diastereoselectivity towards Λ-Cu(R-L1)$_2$ or Δ-Cu(S-L1)$_2$ configuration and towards enantiomeric pair Δ-Cu(R-L2)$_2$ and Λ-Cu(S-L2)$_2$ in solution. Electronic spectra show a negative solvatochromism in solvents of increasing polarity as well as AN. DSC curves of heating correspond to a thermally induced structural phase transformation from distorted square-planar to regular tetrahedral.

The results demonstrate, in contrast to earlier communications, that two molecules of chiral *N,O*-chelate ligands (R- or S-HL1) coordinate to copper(II) and induce Λ/Δ-chirality at the metal that might be efficiently controlled by ligand chirality. Indeed, the results are in agreement with those of analogous Zn/Cu(II)-complexes containing the same/related chiral Schiff base ligands.

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