

# Synthesis, Characterization and Catalytic Applications of Some Novel Copper(II) Chiral Schiff Base Complexes

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**Abstract:** A novel series of six chiral Schiff base complexes of Copper(II) were synthesized in good yields by involving six different Schiff bases as intermediate. The synthetic route leading to the title compounds is commenced from commercially available *ortho*-phthalaldehyde and *ortho*-aminobenzaldehyde. The chemical structures of the newly synthesized complexes were elucidated by their IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, mass and ESR spectral data and elemental analysis. Further, all the target complex compounds have been used to estimate their role as oxidizing catalyst in organic synthesis of different compounds.

**Keywords:** Schiff base, *ortho*-phthalaldehyde, chiral Schiff base,  $\text{Cu}^{+2}$  complexes, catalytic activity .

## Introduction:

The number of Schiff bases are known to be associated with broad spectrum of biological activities like antimicrobial [1], antipyretic [2], anticancer [3], antitumour [4], antitubercular [5] and sterease inhibitory [6] attribute to azomethine linkage. Some of the Schiff bases are reported to be used as chelating agents [7], analytical reagents [8] and catalyst [9] for epoxidation of olefins. Schiff base complexes have attracted increasing interest owing to their role in the understanding of molecular processes occurring in biochemistry, material science, encapsulation, activation, transport and separation phenomena. Coordination compounds with Schiff bases as ligands have vital role in biological systems and significant functions like photosynthesis and respiratory system in mammalian group [10, 11]. A lot of synthetic paths to synthesis Schiff bases and their metal complexes have been expanded by many scientists in this field. Design and synthesis of Schiff bases and their transition metal complexes is much attractive areas of current research owing to their catalytic applications in chemistry.

The Cu(II) ion is the well known metal ion in Coordination Chemistry and has  $d^9$  electronic configuration. It can easily forms complexes with variable coordination numbers such as four, five and six. Hexa coordinated complexes preferably shows distorted octahedral geometry, tetra coordinated complexes forms tetrahedral and square planar geometry and penta coordinated complexes exhibits square pyramidal or trigonalbipyramidal arrangements around the metal ion [12-18]. All Cu(II) complexes are crystalline powders, non-hygroscopic and light blue, light green and greenish blue in color.

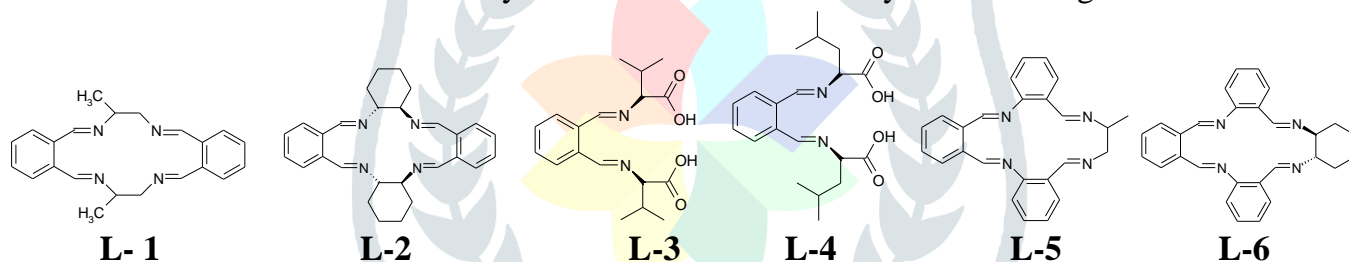
Schiff base complexes are significant participants in the homogeneous catalysis and this catalytic property depends on the nature of ligands, coordination sites and metal ions. Survey of the literature revealed that a huge number of Schiff base metal complexes show catalytic activities. Schiff base metal complexes are found to catalyze a large number of organic transformations such as polymerization reactions, epoxidation, ring opening of epoxides, reductions, oxidations, alkylation, Michel addition, Heck reaction, annulation, carbonylation, benzylation, cyclopropanation, Diels Alder reaction and aldol condensation etc [19-22].

## Present study:

Based on literature, noteworthy research has been done on Schiff bases and their complexes, but it is noted that the study of catalytic activity of chiral Schiff bases derived from *ortho*-phthalaldehyde, diamines and amino acids is inadequate.

In the present investigation as part of our ongoing research, a novel series of six new chiral Schiff base ligands such as (5*E*,9*E*,15*E*,19*E*)-7,18-dimethyl-7,8,17,18-tetrahydrodibenzo-[*f,n*] [1,4,9,12]-tetraaza cyclo hexadecine (**L-1**), (4*aR*,5*E*,11*E*,12*aS*,16*aS*,17*E*,23*E*,24*aR*)-1,2,3,4,4*a*,12*a*,13,14,15,16,16*a*,24*a*-dodecahydro tetrabenzo-[*b,f,j,n*]-[1,4,9,12]-tetraazacyclohexadecine (**L-2**), (2*S*,2'*R*)-2,2'-((1*E*,1'*E*)-(1,2-phenylene-bis-(methanylylidene))-bis-(azanylylidene))-bis-(3-methylbutanoic acid) (**L-3**), (2*S*,2'*R*)-2,2'-((1*E*,1'*E*)-(1,2-phenylenebis(methanylylidene))-bis-(azanylylidene))-bis-(4-methylpentanoic acid) (**L-4**), (5*E*,11*E*,15*E*,21*E*) -13-Methyl-13,14-dihydrotribenzo[*f,j,n*][1,4,8,13]-tetraazacyclohexadecine (**L-5**) and (4*aS*,5*E*,11*E*,17*E*, 23*E*,24*aS*)-1,2,3,4,4*a*,24*a*-hexahydrododecabenzo-[*b,f,j,n*]-[1,4,8,13]-tetraazacyclohexadecine (**L-6**) with N/O or N and O as donor atoms were synthesized with less reaction times and high yields from the condensation of *ortho*-phthalaldehyde or *ortho*-aminobenzaldehyde with two diamines like 1,2-diaminopropane and cyclohexane-1,2-diamine and both amino acids such as *L*-proline and *L*-leucine.

Further, all the chiral Schiff base ligands reacted with various Copper(II) chloride to produce the corresponding chiral Schiff base-metal complexes. The chemical structures of the newly synthesized Schiff base ligands and complexes were elucidated by their IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass, electronic and ESR spectral studies and elemental analysis. Additionally, all the target complex compounds have been used to evaluate their catalytic efficiency in oxidation of Didanosine and Ascorbic acid, reduction of Prolidoxime iodide, hydrolysis of Ropinorole and formation of new C-C bond from aryl iodides with terminal alkynes via Sonogashira reaction.



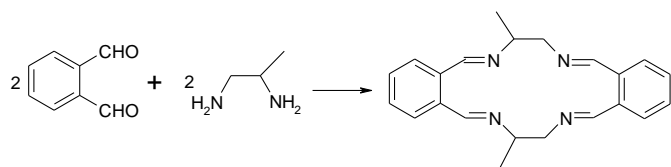
## Experimental section:

All reagents and solvents were used as purchased without further purification. Melting points of chiral Schiff ligands and Cu(II) complexes were determined on a Buchi-510 melting point apparatus and are uncorrected. Crude products were purified by column chromatography on silica gel of 60–120 mesh. UV-Visible spectra were recorded on Shimadzu UV-160A spectrophotometer. IR spectra were obtained on a Perkin-Elmer BX serried FTIR 5000 spectrometer using KBr pellet. NMR spectra were recorded on a Varian 300 MHz spectrometer for <sup>1</sup>H NMR and 100 MHz spectrometer <sup>13</sup>C NMR. The ESR spectra were recorded by using Bruker instrument. The chemical shifts were reported as ppm down field using TMS as an internal standard. Mass spectra were recorded on a VG-Micromass 7070H spectrometer operating at 70 eV. The elemental analysis has been carried out with Perkin-Elmer CHN analyzer at 24°C. Conductance measurements were done at 10<sup>-3</sup> M concentration in dichloromethane at 25 °C using Dig sun Digital conductivity meter model DL-909. Thermal studies (TGA and DTA) curves were recorded on Mettler instrument.

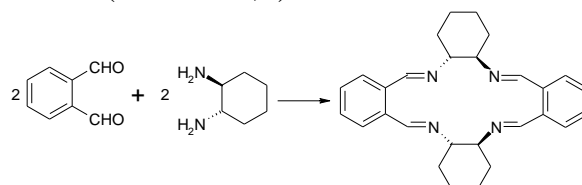
## Synthesis of chiral Schiff base ligands (L-1, L-2)

A solution of *ortho*-phthalaldehyde (0.012 mol, 1.70 g) in absolute ethanol (20 mL) was added drop wise to a stirred solution of 1,2-diamino propane/(1*R*, 2*R*)-diamino cyclohexane (0.012 mol) in warm ethanol (10 mL) and the resulting solution was refluxed for 16-24 h. After

completion of the reaction (scanned by the TLC), the solution was concentrated on rotary evaporator and the ligand was precipitated by petroleum ether (Scheme 1,2).



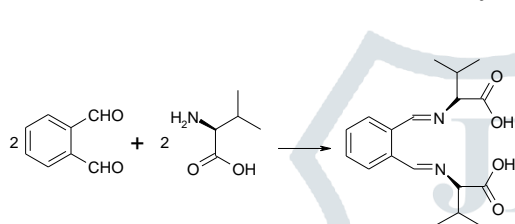
Scheme 1



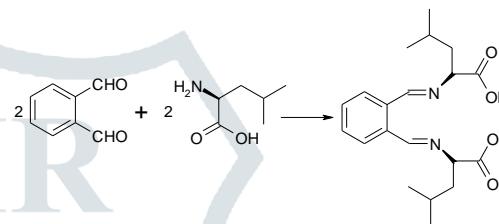
Scheme 2

### Synthesis of chiral Schiff base ligands (L-3, L-4)

To the solution of *L*-valine/*L*-leucine (0.011 mol, 1.39 g) in aqueous NaOH (0.47 g in 5 mL water) was added a solution of *ortho*-phthalaldehyde (0.0059 mol, 0.8 g) in ethanol (5 mL). The resulted solution was stirred constantly under reflux for 3-4 h. After realization of the reaction (monitored by the TLC), the volume of the solution was reduced to half, on cooling a green coloured solid product formed was filtered washed with ethanol followed by ether, dried and stored in vacuum desiccator over anhydrous calcium chloride (Scheme 3,4).



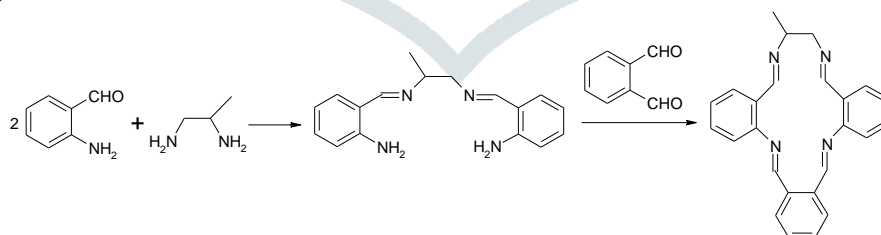
Scheme 3



Scheme 4

### Synthesis of chiral Schiff base ligand (L-5)

A solution of *ortho*-amino benzaldehyde (0.013 mol, 2.0 g) in absolute ethanol (15 mL) was added drop wise to a stirred solution of 1,2-diamino propane (0.006 mol, 0.5 g) in ethanol (15 mL). The resulted mixture was refluxed for 2-3 h with uniform stirring. After accomplishment of the reaction (examined by the TLC), resulting solution was cooled to room temperature and concentrated. The crude product formed was filtered, washed with diethyl ether, purified by recrystallization, dried in *vacuum*. The resulted compound (0.003 mol, 1.04 g) was dissolved in ethanol (15 mL) was added to a stirred solution of *ortho*-phthalaldehyde (0.003 mol, 0.5 g) dissolved in ethanol (15 mL). Thus obtained solution was refluxed on water bath with steady stirring for 3-4 h. After achievement of the reaction (tested by the TLC), the solution was concentrated on rotary evaporator and the crude product of ligand was precipitated by petroleum ether (Scheme 5).

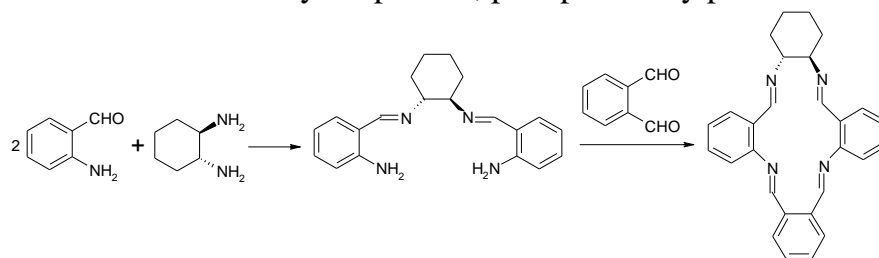


Scheme 5

### Synthesis of chiral Schiff base ligand (L-6)

A solution of *ortho*-amino benzaldehyde (0.0437 mol, 1.32 g) in absolute ethanol (15 mL) was added drop wise to a stirred solution of (1*R*, 2*R*)-1,2-diamino cyclohexane (0.0087 mol, 0.5 g) dissolved in ethanol (15 mL). The resulted solution was refluxed in water bath with constant stirring for 2-3 h. After fulfilment of the reaction (detected by the TLC), the solution was cooled to room temperature and concentrated. The resulted solid formed was filtered, washed with ether, purified by recrystallization and dried in *vacuum* to get the intermediate ligand (0.0037 mol, 1.194 g) which was dissolved in ethanol (15 mL) and added to a stirred solution of *ortho*-

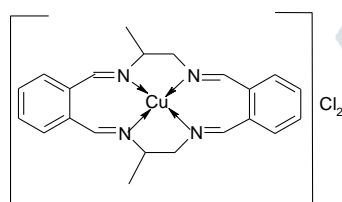
phthalaldehyde (0.0037 mol, 0.5 g) in ethanol (15 mL). Now the this solution was refluxed on water bath with steady stirring for 3-4 h. After successful of the reaction (examined by the TLC), the solution was concentrated on rotary evaporator, precipitated by petroleum ether (Scheme 6).



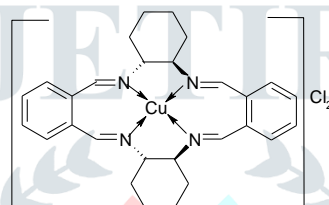
**Scheme 6**

### Synthesis of chiral Schiff base Cu(II) complexes

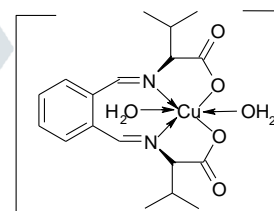
A solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.003 mol, 0.51g) in methanol (20 mL) was added to a solution of corresponding ligand (0.003 mol) in methanol (20 mL). The resulted solution was constantly stirred for 3-6h and concentrated up to 5-6 mL to initiate crystallization a few mL of diethyl ether was added. After completion of the reaction (monitored by the TLC), the precipitate formed was filtered and washed with diethyl ether. The product obtained was purified by recrystallization with a mixture of dichloromethane and diethyl ether, subsequently dried in *vacuum*.



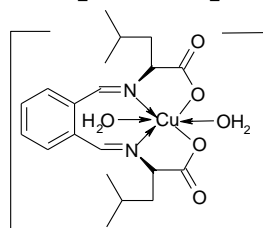
**Complex compound 1**



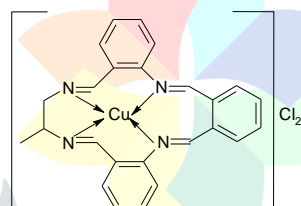
**Complex compound 2**



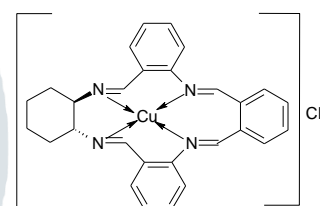
**Complex compound 3**



**Complex compound 4**



**Complex compound 5**



**Complex compound 6**

### ESR Analysis

The ESR spectra of Cu(II) complexes in solid state at room temperature have been recorded and the bonding parameters are determined by using approximations of Kneubuhl [23]. The spectra of all the Cu(II) complexes contain two clear peaks at room temperature. The peak high field side is more intense than the peak at low field side. The  $g_{||}$ ,  $g_{\perp}$ ,  $g_{ave}$ , and  $G$  is calculated for the two peaks as described in literature [24].

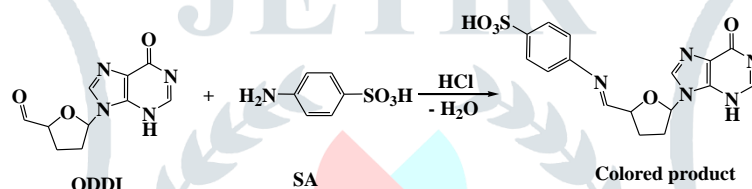
The  $g_{||}$  and  $g_{\perp}$  values calculated are useful in distinguishing the coordination environment around the Cu(II) ion. The  $g_{||}$  values are from 2.108-2.219 while  $g_{\perp}$  values are from 2.031-2.062. In conformity with this the  $g$  values of the complexes are fairly consistent. The average  $g$  values of these complexes are very close indicating that all of them have similar type of distortion [25]. According to Kivelson and Neiman [26] the  $g_{||}$  is a fairly susceptible function for representing covalency of metal ligand bonds in the complexes. The  $g_{||} > 2.3$  normally represents ionic atmosphere round the metal ion while  $g_{||} < 2.3$  represents covalent surroundings. It can be observed from the table that the  $g_{||}$  values for all the six complexes are less than 2.3 indicating the extent of covalency metal-ligand bond. As studied by Procter et al,  $G$  value shows whether the metal ion is in crystallographically equivalent environment or not. They noticed that thiocyanate, perchlorate and tetrafluoroborate complexes having  $G$  values less than 4 have their Cu(II) ion in crystallographically equivalent environment on the other hand, the  $[\text{Cu}(\text{en})_2](\text{NO}_3)_2$  with  $G$  value greater than 4 has the Cu(II) ion in the non-equivalent crystallographic surroundings. The  $G$  value of all six complexes determined from the given expression has been found to be greater than 4.

Based on the above two studies it is concluded that, in these complexes, crystallographic equivalent environment exists.

### Catalytic activity:

A plausible mechanism is proposed for macrocyclic Cu(II) complex catalyzed oxidation of ODDI. Cu(II) oxidizes two moles of ODDI containing alcoholic group to two molecules of ODDI having aldehydic groups by the loss of four hydrogens in the presence of hydrogen peroxide. In this process, Cu(II) gains two electrons and converts to Cu(0) with the release of two chlorine atoms. Two moles each of hydrochloric acid and water generates as by products. Finally, macrocyclic Cu(0) complex reacts with two hydrochloric acid molecules in situ to regenerate the original macrocyclic Cu(II) complex. The pink colored product forms by the condensation of aldehyde group of ODDI with amino group of sulfanilic acid in acid medium with the elimination of water molecule. The percent yields of coloured products with all the ten macrocyclic Cu(II) catalysts were determined spectrophotometrically and the results are presented in Table-1.

Highly efficient macrocyclic Cu(II) catalyst were synthesized and used for the oxidation of didanosine via alcoholic group. The catalytic method allows the rapid synthesis of carbonyl derivatives. This is an environmentally friendly method, simple to set-up, requires short reaction time, produces high product yields and does not require co-oxidant. The reusability of the catalyst is the most significant aspect of this method.



**Table-1: Percent yields of coloured product formed by using Cu(II) complexes as catalysts.**

Entry.	Catalyst	Yield (%)
4.1.	[Cu(L-1)]Cl <sub>2</sub>	97.02
4.2.	[Cu(L-2)]Cl <sub>2</sub>	95.25
4.5.	[Cu(L-3)]Cl <sub>2</sub>	90.02
4.6.	[Cu(L-4)]Cl <sub>2</sub>	92.87
5.1.	[Pd(L-1)]Cl <sub>2</sub>	88.41
5.2.	[Pd(L-2)]Cl <sub>2</sub>	87.47
5.5.	[Pd(L-3)]Cl <sub>2</sub>	94.36
5.6.	[Pd(L-4)]Cl <sub>2</sub>	93.98

### Physical and Spectral data of chiral Schiff base ligands and Cu(II) complexes

**(5E,9E,15E,19E)-7,18-dimethyl-7,8,17,18-tetrahydrodibenzo[f,n][1,4,9,12]-tetraaza cyclohexadecine (1):** Color: Brown solid. Yield: 80%. Mp: 110-112 °C. IR (KBr):  $\nu/\text{cm}^{-1}$  3039 (C-H, Ar), 1648 (C=N), 1471 (C=C, Ar). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.25 (s, 2H, N=CH), 8.10 (s, 2H, N=CH), 7.90-7.62 (m, 8H, Ar-H), 4.12-3.96 (m, 4H, CH<sub>2</sub>), 3.11 (m, 2H, CH), 1.32 (d, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  163.1 (4C, N=CH), 141.7-132.5 (12C, Ar), 62.3 (2C, N-CH<sub>2</sub>), 60.1 (2C, N-CH), 18.5 (2C, CH<sub>3</sub>). MS: *m/z* 367 (M<sup>+</sup>+Na). Anal. Calcd. for C<sub>22</sub>H<sub>24</sub>N<sub>4</sub>: C-75.36, H-6.98, N-16.08. Found: C-76.71, H-7.02, N-16.27.

**(4aR,5E,11E,12aS,16aS,17E,23E,24aR)-1,2,3,4,4a,12a,13,14,15,16,16a,24a-dodecahydrotetrabenzo-[b,f,j,n]-[1,4,9,12]-tetraazacyclohexadecine (2):** Color: Yellow solid. Yield: 82%. Mp: 124-126 °C. IR (KBr):  $\nu/\text{cm}^{-1}$  3052 (C-H, Ar), 1643 (C=N), 1485 (C=C, Ar). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.24 (s, 2H, N=CH), 7.92-7.58 (m, 8H, Ar-H), 5.24 (m, 4H, CH), 2.21-1.95 (m, 8H, CH<sub>2</sub>), 1.52-1.15 (m, 8H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  163.7 (4C, N=CH), 140.2-130.2 (12C, Ar), 73.8 (4C, N-CH), 28.6 (4C, CH-CH<sub>2</sub>-CH<sub>2</sub>), 23.9 (4C, CH<sub>2</sub>-CH<sub>2</sub>-

CH<sub>2</sub>). MS:  $m/z$  447 (M<sup>+</sup>+1). Anal. Calcd. for C<sub>28</sub>H<sub>32</sub>N<sub>4</sub>: C-78.69, H-7.54, N-12.89. Found: C-79.21, H-7.60, N-13.20.

**(2S,2'R)-2,2'-((1E,1'E)-(1,2-phenylene-bis-(methanylylidene))-bis-(azanylylidene))-bis-(3-methylbutan oic acid) (3):** Color: Green solid. Yield: 85%. Mp: 138-140 °C. IR (KBr):  $\nu/cm^{-1}$  3035 (C-H, Ar), 2925 (O-H), 1721 (C=O), 1631 (C=N). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  10.92 (s, 2H, COOH), 8.68 (s, 2H, N=CH), 7.78-7.46 (m, 4H, Ar-H), 3.84 (d, 2H, CH-CO), 2.32 (m, 2H, CH-CH-CO), 1.03 (d, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  175.3 (2C, CO-OH), 161.4 (2C, N=CH), 142.5-128.3 (6C, Ar), 73.5 (2C, N-CH-CO), 30.2 (2C, CH-CH<sub>3</sub>), 19.1 (4C, CH<sub>3</sub>). MS:  $m/z$  333 (M<sup>+</sup>+1). Anal. Calcd. for C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>: C-64.58, H-7.12, N-8.36, O-19.94. Found: C-65.04, H-7.28, N-8.43 O-20.21.

**(2S,2'R)-2,2'-((1E,1'E)-(1,2-phenylenebis(methanylylidene))-bis-(azanylylidene))-bis-(4-methylpentan oic acid) (4):** Color: Yellow solid. Yield: 78%. Mp: 142-144 °C. IR (KBr):  $\nu/cm^{-1}$  3062 (C-H, Ar), 2943 (O-H), 1710 (C=O), 1636 (C=N). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  11.12 (s, 2H, COOH), 8.72 (s, 2H, N=CH), 7.85-7.41 (m, 4H, Ar-H), 4.18 (t, 2H, CH-CO), 1.98 (t, 4H, CH<sub>2</sub>), 1.68 (m, 2H, CH), 1.06 (d, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  176.1 (2C, CO-OH), 162.2 (2C, N=CH), 140.2-131.4 (6C, Ar), 72.8 (2C, N-CH-CO), 31.3 (2C, CH-CH<sub>3</sub>), 22.4 (2C, CH-CH<sub>2</sub>-CH), 20.2 (4C, CH<sub>3</sub>). MS:  $m/z$  361 (M<sup>+</sup>+1). Anal. Calcd. for C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>: C-65.69, H-7.69, N-7.65, O-18.97. Found: C-66.64, H-7.83, N-7.77, O-19.09.

**(5E,11E,15E,21E)-13-Methyl-13,14-dihydrotribenzo[*f,j,n*][1,4,8,13]-tetraazacyclohexadecine (5):** Color: Brown solid. Yield: 75%. Mp: 133-135 °C. IR (KBr):  $\nu/cm^{-1}$  3054 (C-H, Ar), 1652 (C=N), 1483 (C=C, Ar). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.36 (s, 2H, N=CH), 8.16 (s, 1H, N=CH), 8.11 (s, 1H, N=CH), 7.95-7.12 (m, 12H, Ar-H), 4.25-3.90 (d, 2H, J = 6.0 Hz, CH<sub>2</sub>), 3.55 (m, 1H, CH), 1.42(d, 3H, J = 5.3 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  164.1 (4C, N=CH-), 142.5-121.8 (18C, Ar), 60.2 (1C, CH<sub>2</sub>-N), 58.7 (1C, N-CH), 20.8 (1C, CH<sub>3</sub>). MS:  $m/z$  401 (M<sup>+</sup>+Na). Anal. Calcd. for C<sub>25</sub>H<sub>22</sub>N<sub>4</sub>: C-78.67, H-5.74, N-14.35. Found: C-79.34, H-5.86, N-14.08.

**(4a*S*,5E,11E,17E,23E,24a*S*)-1,2,3,4,4a,24a-hexahydrotetrabenzo-[*b,f,j,n*]-[1,4,8,13]-tetraazacyclohexadecine (6):** Color: Snuff solid. Yield: 75%. Mp: 141-144 °C. IR (KBr):  $\nu/cm^{-1}$  3058 (C-H, Ar), 1652 (C=N), 1495 (C=C, Ar). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.41 (s, 2H, N=CH), 8.20 (s, 2H, N=CH), 7.83-7.10 (m, 12H, Ar-H), 5.28 (m, 2H, CH), 2.18-1.95 (m, 4H, CH<sub>2</sub>), 1.69-1.52 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  163.3 (4C, N=CH), 141.5-120.6 (18C, Ar), 74.2 (2C, CH-N), 28.6 (2C, CH-CH<sub>2</sub>-CH<sub>2</sub>), 25.1 (2C, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>). MS:  $m/z$  419 (M<sup>+</sup>+1). Anal. Calcd. for C<sub>28</sub>H<sub>26</sub>N<sub>4</sub>: C-79.80, H-6.15, N-13.39. Found: C-80.35, H-6.26, N-13.39.

**Complex compound 1: [Cu(L-1)]Cl<sub>2</sub>:** Reaction time: 70 mins. Color: Light green solid, Yield: 60%. Mp: 240-241 (decompose) °C. IR (KBr):  $\nu/cm^{-1}$  1616 (C=N), 526 (Cu-N). MS:  $m/z$  478 (M<sup>+</sup>). ESR:  $g_{11} - 2.205$ ,  $g_{\perp} - 2.062$ ,  $|g|_{avg} - 2.093$ ,  $G - 4.501$ . Anal. Calcd. for C<sub>22</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>Cu: C-55.06, H-5.01, N-11.60, Cu-13.14. Found: C-55.17, H-5.05, N-11.70, Cu-13.27.

**Complex compound 2: [Cu(L-2)]Cl<sub>2</sub>:** Reaction time: 65 mins. Color: Blue green solid, Yield: 70%. Mp: 235-236 (decompose) °C. IR (KBr):  $\nu/cm^{-1}$  1625 (C=N), 530 (Cu-N). MS:  $m/z$  559 (M<sup>+</sup>). ESR:  $g_{11} - 2.219$ ,  $g_{\perp} - 2.058$ ,  $|g|_{avg} - 2.049$ ,  $G - 5.102$ . Anal. Calcd. for C<sub>28</sub>H<sub>32</sub>Cl<sub>2</sub>N<sub>4</sub>Cu: C-60.13, H-5.70, N-10.00, Cu-11.21. Found: C-60.16, H-5.77, N-10.02, Cu-11.37.

**Complex compound 3: [Cu(L-3)(H<sub>2</sub>O)<sub>2</sub>]:** Reaction time: 75 mins. Color: Dark green solid, Yield: 86%. Mp: 298-301 (decompose) °C. IR (KBr):  $\nu/cm^{-1}$  1609 (C=N), 1598, 1378 (C=O), 759 (Cu-H<sub>2</sub>O), 527 (Cu-N), 432 (Cu-O). MS:  $m/z$  430 (M<sup>+</sup>). ESR:  $g_{11} - 2.172$ ,  $g_{\perp} - 2.042$ ,  $|g|_{avg} -$

2.081, G – 4.612. Anal. Calcd. for  $C_{18}H_{26}N_2O_6Cu$ : C-50.21, H-6.05, N-6.45, Cu-14.64. Found: C-50.28, H-6.10, N-6.52, Cu-14.78.

**Complex compound 4: [Cu(L-4)(H<sub>2</sub>O)<sub>2</sub>]:** Reaction time: 95 mins. Color: Pale green solid, Yield: 85%. Mp: 245-246 (decompose) °C. IR (KBr):  $\nu/cm^{-1}$  1616 (C=N), 1590, 1369 (C=O), 740 (Cu-H<sub>2</sub>O), 520 (Cu-N), 428 (Cu-O). MS:  $m/z$  458 (M<sup>+</sup>). ESR:  $g_{11} - 2.186$ ,  $g_{\perp} - 2.031$ ,  $|g|_{avg} - 2.062$ , G – 5.254. Anal. Calcd. for  $C_{20}H_{30}N_2O_6Cu$ : C-52.40, H-6.54, N-6.08, Cu-13.35. Found: C-52.45, H-6.60, N-6.12, Cu-13.87.

**Complex compound 5: [Cu(L-5)]Cl<sub>2</sub>:** Reaction time: 85 mins. Color: Light green solid, Yield: 85%. Mp: 232-236 (decompose) °C. IR (KBr):  $\nu/cm^{-1}$  1624 (C=N), 526 (Cu-N). MS:  $m/z$  513 (M<sup>+</sup>). ESR:  $g_{11} - 2.108$ ,  $g_{\perp} - 2.049$ ,  $|g|_{avg} - 2.114$ , G – 4.710. Anal. Calcd. for  $C_{25}H_{22}Cl_2N_4Cu$ : C-58.41, H-4.27, N-10.21, Cu-12.12. Found: C-58.45, H-4.32, N-10.92, Cu-12.39.

**Complex compound 6: [Cu(L-6)]Cl<sub>2</sub>:** Reaction time: 75 mins. Color: Yellowish green solid, Yield: 72%. Mp: 238-239 (decompose) °C. IR (KBr):  $\nu/cm^{-1}$  1621 (C=N), 539 (Cu-N). MS:  $m/z$  553 (M<sup>+</sup>). ESR:  $g_{11} - 2.214$ ,  $g_{\perp} - 2.055$ ,  $|g|_{avg} - 2.115$ , G – 4.892. Anal. Calcd. for  $C_{28}H_{26}Cl_2N_4Cu$ : C-60.61, H-4.65, N-10.03, Cu-11.38. Found: C-60.82, H-4.74, N-10.13, Cu-11.49.

\* Chiral Schiff base ligand

## Conclusion

Based on the spectral data and elemental analysis, condensation of *ortho*-phthalaldehyde with different diamines leads to the formation of six novel chiral Schiff base ligands had been confirmed. Among them, four ligands perform N<sub>4</sub> as donor system and rest of ligands act N<sub>2</sub>O<sub>2</sub> as donor groups in six Cu(II) complex compounds.

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