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### Tetradentate amido azo Schiff base Cu(II), Ni(II) and Pd(II) complexes: Synthesis, characterization, spectral properties, and applications to catalysis in C-C coupling and oxidation reaction

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#### Abstract

New Schiff base ligands  $(H_2L^1 \& H_2L^2)$  were synthesized by the reaction of salicylaldehyde with (2-((2-aminophenyl)diazenyl)-N-alkylaniline), and were used for the preparation of complexes with Cu(II), Ni(II) and Pd(II) metal ions. The structural features of the synthesized compounds were examined by UV-Vis, IR and <sup>1</sup>H-NMR spectroscopy. The crystal structures of Schiff base  $(H_2L^1)$  and two metal complexes  $Cu(L^1)$  and  $Ni(L^2)$  were determined by single crystal X-ray diffraction. The studies revealed that the synthesized Schiff bases existed as tetradentate (N.N.N.O) ligands and bonded to the metal ions through the donor atoms of the amido nitrogen, azo nitrogen, azomethine nitrogen and phenolic oxygen atoms. The redox property of  $Cu(L^1)$  and  $Ni(L^1)$  and emission behavior of ligand  $H_2L^1$  and complexes  $Cu(L^1)$  and  $Ni(L^1)$  were examined. The complex  $Cu(L^1)$  shows excellent catalytic activity towards oxidation of benzyl alcohol to benzyldehyde (under solvent-free condition) using  $H_2O_2$  as the oxidant. Complex  $Pd(L^1)$  acts as highly efficient catalyst in the Suzuki–Miyaura cross–coupling reaction of various aryl halides with phenyl boronic acid to produce the corresponding biaryls with high yields under mild reaction conditions. Both the catalysts  $Cu(L^1)$  and  $Pd(L^1)$  were easily recovered by simple chromatographic separation and reused for next catalytic cycle.

*Keywords:* Copper(II), Nickel(II) and Palladium(II); Crystal structures; Redox; Emission; Oxidation and C-C coupling reactions

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#### 1. Introduction

Transition metal complexes with Schiff base ligands have explored continuously due to their interesting coordination chemistry and vast application in catalysis and bioinorganic chemistry [1-12]. Schiff bases play important roles in coordination chemistry due to their synthetic flexibility and the very good binding nature of azomethine nitrogen participating in chelation process and also they play an important role in inorganic chemistry due to their strong binding ability to form stable complexes with most of the transition metals [13-17]. These ligands may contain a variable of substituents having different electron-donating and / or withdrawing groups and therefore may have interesting chemical properties [18-22]. In the last few years the unsymmetrically substituted Schiff base metal complex systems have been reported with many new features. In particular unsymmetrically-substituted metal Schiff base complexes are more efficient catalysts than symmetrically-substituted complexes for olefin polymerization [1, 22]. Therefore the design and synthesis of a new Schiff base ligand is most important step in the development of metal complexes. Azo Schiff base ligands which contain both azo (-N=N-) and aldimine (-C=N-) function in their own structures. The molecules that have a large conjugated  $\pi$  bonds system are strongly form stable complexes with transition metals. Moreover, the coordination chemistry of transition metals with azo Schiff base ligands have been studied due to their interesting properties like C-H bond activation, oxygen insertion into the metal-carbon bond, oxidative addition, redox, catalytic and biological activity [23-29]. In our previous communication focus on the coordination chemistry of copper with amido azo aldimine ligand which was formed via reductive cleavage of aldimine function upon complexation and their spectroelectrochemical and catalytic activity [30]. From this background and in continuation of our ongoing interest directed towards the design, synthesis and development of new catalytically active materials [30-32], the present paper describes the coordination behaviour of a amido azo Schiff base derived from the condensation of

salicylaldehyde with (2-((2-aminophenyl)diazenyl)-N-alkylaniline) towards Cu(II), Ni(II), and Pd(II) transition metals.

Herein, we describe the synthesis and characterization of tetradentate azo-imine ligands  $H_2L^1 \& H_2L^2$ . Reactions of ligands  $H_2L$  with  $Cu(OAc)_2 \cdot H_2O$ ,  $Ni(OAc)_2 \cdot 4H_2O$  and  $[Na_2(PdCl_4)]$  separately in methanol afforded amido azo Schiff base complexes Cu(L), Ni(L) and Pd(L), have been described. All the ligands and complexes have been characterized by the elemental analysis, UV-Vis, IR and <sup>1</sup>H NMR spectra. The crystal structures of ligand  $H_2L^1$  and complexes  $Cu(L^1) \& Ni(L^2)$  were determined by X-ray diffraction analysis. The redox property and emission behavior of the ligand and complexes have been studied. The catalytic efficacy of the  $Cu(L^1)$  complex towards oxidation of benzyl alcohol using  $H_2O_2$  as the oxidant has been studied. The catalytic activity of the  $Pd(L^1)$  complex toward Suzuki–Miyaura cross–coupling reaction of several aryl halides with phenyl boronic acid under mild conditions have been examined.

#### 2. Experimental

#### 2.1. Materials

The solvents used in the reactions were of reagent grade (Merck, Kolkata, India) and were purified and dried by general procedure [33]. Methyl iodide, ethyl bromide, benzyl alcohol, salicylaldehyde were purchased from E. mark, India. Copper(II) acetate monohydrate, Nickel(II) acetate tetrahydrate, Iodobenzene, Bromobenzene, 1-iodo-2-nitrobenzene, 4-iodotoluene, 4-bromotoluene, 1-bromo-2-nitrobenzene, Phenyl boronic acid were purchased from Sigma-Aldrich. 2,2'-diaminoazobenzene and Sodium tetrachloropalladate were prepared following reported procedure [31,34].

#### 2.2. Physical measurements

Microanalysis (C, H, N) was performed using a Perkin-Elmer 2400 C, H, N, S / O series II elemental analyzer. Infrared spectra were recorded on a Perkin Elmer BX-1 FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-

1800 PC spectrophotometer. <sup>1</sup>H NMR spectra were obtained on Bruker 400 NMR spectrometers in CDCl<sub>3</sub> using TMS as the internal standard. Emission spectra were recorded with a Perkin Elmer LS-55 Luminescence Spectrometer. Electrochemical measurements were made under dinitrogen atmosphere using a CH instruments model 600D potentiostat. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

#### 2.3. Syntheses

#### 2.3.1. Syntheses of ligands

Compound **3** (2-((2-aminophenyl)diazenyl)-N-alkylaniline) (Scheme 1) was prepared by following reported procedure using alkyl halides (methyl iodide and ethyl bromide) with 2,2'-diaminoazobenzene in (1:1) molar ratio [32].

Yield: **3a**, 75%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.89 (CH<sub>3</sub>, s, 3H), 5.43 (NH<sub>2</sub>, s, 2H), 6.64-6.73 (ArH, m, 4H), 7.06 (ArH, t, 1H), 7.19 (ArH, t, 1H), 7.56 (ArH, d, 1H), 7.61 (ArH, d, 1H), 7.88 (NH, s, 1H).

Yield: **3b**, 70%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.28 (CH<sub>3</sub>, s, 3H) 3.23 (CH<sub>2</sub>, d, 2H), 5.41 (NH<sub>2</sub>, s, 2H), 6.64-6.74 (ArH, m, 4H), 7.08 (ArH, t, 1H), 7.17 (ArH, t, 1H), 7.56 (ArH, d, 1H), 7.62 (ArH, d, 1H), 7.99 (NH, s, 1H).

Ligands,  $H_2L^1$  and  $H_2L^2$ , were prepared following similar procedures. A representative procedure for  $H_2L^1$  is given below.

To a solution of **3a** (0.3 g, 1.33 mmol), in 25 mL diethyl ether was added salicylaldehyde (0.165 g, 1.33 mmol). The resulting mixture was then heated to reflux for 4 h. After slow evaporation of the solvents, a red crystal of pure  $H_2L^1$  was obtained. The solid product was then washed with diethyl ether.

Yield:  $H_2L^1$ , 95%. Anal. Calc. for  $C_{20}H_{18}N_4O$ : C, 72.71; H, 5.49; N, 16.96. Found: C, 72.53; H, 5.58; N, 16.47%. UV/VIS ( $\lambda_{max} / nm$  ( $\epsilon / dm^2 mol^{-1}$ ), dichloromethane): 475 (25330), 315 (46920), 260 (51720), 210 (75950). IR (KBr, cm<sup>-1</sup>): 3060 v(N-H/O-H), 1607 v(C=N), 1378 v(N=N), 1279 v(O-C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.81 (CH<sub>3</sub>, t, 3H), 6.70-6.80 (ArH, m, 2H), 6.95 (ArH, t, 1H), 7.06 (ArH, d, 1H), 7.20-7.29 (ArH, m, 2H), 7.33-7.45 (ArH, m, 4H), 7.87-7.90 (ArH, m, 2H), 8.63 (CH, s, 1H), 9.27 (NH, s, 1H), 13.46 (OH, s, 1H).

Yield:  $H_2L^2$ , 93%. Anal. Calc. for  $C_{21}H_{20}N_4O$ : C, 73.23; H, 5.85; N, 16.27. Found: C, 73.45; H, 5.55; N, 16.51%. UV/VIS ( $\lambda_{max}$  / nm ( $\epsilon$  / dm<sup>2</sup> mol<sup>-1</sup>), dichloromethane): 480 (25450), 315 (22050), 265 (32600), 230 (45490). IR (KBr, cm<sup>-1</sup>): 3064 v(N-H/O-H), 1608 v(C=N), 1379 v(N=N), 1279 v(O-C). <sup>1</sup>H NMR (400 MHz, CDCl3): 0.98 (CH<sub>3</sub>, t, 3H), 3.11-3.16 (CH<sub>2</sub>, m, 2H), 6.68 (ArH, t, 2H), 6.87 (ArH, t, 1H), 6.96 (ArH, d, 1H), 7.15-7.20 (ArH, m, 2H), 7.25-7.38 (ArH, m, 2H), 7.72 (ArH, d, 1H), 7.80 (ArH, d, 1H), 8.55 (CH, s, 1H), 9.04 (NH, s, 1H), 13.29 (OH, s, 1H).

### 2.3.2. Syntheses of complexes $Cu(L^1)$ and $Cu(L^2)$

Complexes,  $Cu(L^1)$  and  $Cu(L^2)$ , were prepared following similar procedures. A representative procedure for  $Cu(L^1)$  is given below.

A solution of  $H_2L^1$  (0.1 g, 0.3 mmol) in 10 mL methanol was added to a solution of  $Cu(OAc)_2 \cdot H_2O$  (0.06 g, 0.3 mmol) in 10 mL methanol. The mixture was stirred for 2 h. The pink violet solid precipitate was separated by filtration and the solid mass was dissolved in dichloromethane. After the evaporation of the solvent, a pink-violet solid of pure  $Cu(L^1)$  was obtained.

Yield: **Cu**(**L**<sup>1</sup>), 70%. Anal. Calc. for C<sub>20</sub>H<sub>16</sub>CuN<sub>4</sub>O: C, 61.29; H, 4.12; N, 14.30. Found: C, 61.03; H, 4.42; N, 13.97%. UV/VIS ( $\lambda_{max}$ /nm ( $\epsilon$ / dm<sup>2</sup> mol<sup>-1</sup>), dichloromethane): 550 (11520), 430 (13700), 385 (15700), 310 (20030), 245 (39800). IR (KBr, cm<sup>-1</sup>): 1614 v(C=N), 1425 v(N=N), 1330 v(O-C).

Yield: **Cu**(**L**<sup>2</sup>), 65%. Anal. Calc. for C<sub>21</sub>H<sub>18</sub>CuN<sub>4</sub>O: C, 62.13; H, 4.47; N, 13.80. Found: C, 62.05; H, 4.64; N, 13.63%. UV/VIS ( $\lambda_{max}$ /nm ( $\epsilon$ / dm<sup>2</sup> mol<sup>-1</sup>), dichloromethane): 550 (11830), 430 (13800), 385 (15300), 310 (18730), 250 (33050). IR (KBr, cm<sup>-1</sup>): 1614 v(C=N), 1417 v(N=N), 1326 v(O-C).

### 2.3.3. Syntheses of complexes $Ni(L^1)$ and $Ni(L^2)$

Complexes,  $Ni(L^1)$  and  $Ni(L^2)$ , were prepared following similar procedures. A representative procedure for  $Ni(L^1)$  is given below.

A solution of  $H_2L^1$  (0.1 g, 0.3 mmol) in 10 mL methanol was added to a solution of  $Ni(OAc)_2 \cdot 4H_2O$  (0.075 g, 0.3 mmol) in 10 mL methanol. The mixture was stirred for 1 h. The colour of the solution immediately changed to deep green. The resulting solution was then filtered and allowed to stand at room temperature. After slow evaporation of the solvent at room temperature, dark green coloured crystals suitable for X-ray analysis were obtained.

Yield: **Ni**(**L**<sup>1</sup>), 75%. Anal. Calc. for C<sub>20</sub>H<sub>16</sub>N<sub>4</sub>NiO: C, 62.06; H, 4.17; N, 14.47. Found: C, 61.76; H, 4.42; N, 14.64%. UV/VIS ( $\lambda_{max}$  / nm ( $\epsilon$  / dm<sup>2</sup> mol<sup>-1</sup>), dichloromethane): 680 (6750), 410 (68630), 335 (38900), 265 (166200). IR (KBr, cm<sup>-1</sup>): 1610 v(C=N), 1438 v(N=N), 1324 v(O-C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.15 (CH<sub>3</sub>, t, 3H), 6.60 (ArH, t, 1H), 6.66 (ArH, t, 1H), 6.96 (ArH, d, 1H), 7.08 (ArH, d, 2H), 7.17 (ArH, t, 3H), 7.29-7.35 (ArH, m, 2H), 7.53 (ArH, d, 1H), 7.63 (ArH, d, 1H), 8.05 (ArH, d, 1H), 8.45 (CH, s, 1H).

Yield: Ni(L<sup>2</sup>), 72%. Anal. Calc. for C<sub>21</sub>H<sub>18</sub>N<sub>4</sub>NiO: C, 62.89; H, 4.52; N, 13.97. Found: C, 63.14; H, 4.65; N, 13.76%. UV/VIS ( $\lambda_{max}$ /nm ( $\epsilon$ / dm<sup>2</sup> mol<sup>-1</sup>), dichloromethane): 680 (6940), 410 (21520), 335 (13880), 270 (42500). IR (KBr, cm<sup>-1</sup>): 1611 v(C=N), 1440 v(N=N), 1321 v(O-C). <sup>1</sup>H NMR (400 MHz, CDCl3): 1.33 (CH<sub>3</sub>, t, 3H), 3.68 (CH<sub>2</sub>, s, 2H), 6.59-6.61 (ArH, m, 1H), 6.68 (ArH, t, 1H), 6.95 (ArH, d, 1H), 7.15-7.23 (ArH, m, 4H), 7.32 (ArH, t, 1H), 7.40 (ArH, d, 1H), 7.58 (ArH, d, 1H), 7.70 (ArH, d, 1H), 8.13 (ArH, d, 1H), 8.54 (CH, s, 1H).

2.3.4. Syntheses of complexes  $Pd(L^1)$  and  $Pd(L^2)$ 

Complexes,  $Pd(L^1)$  and  $Pd(L^2)$ , were prepared following similar procedures. A representative procedure for  $Pd(L^1)$  is given below.

A solution of  $H_2L^1$  (0.05 g, 0.15 mmol) in 10 mL methanol was added to a solution of  $Na_2PdCl_4$  (0.045 g, 0.15 mmol) in 5 mL methanol. The mixture was stirred for 4 h. The colour of the solution slowly changed to blue. The resulting solution was then filtered and allowed to stand at room temperature. After slow evaporation of the solvent at room temperature, blue coloured crystalline products were obtained.

Yield: **Pd**(**L**<sup>1</sup>), 80%. Anal. Calc. for C<sub>20</sub>H<sub>16</sub>N<sub>4</sub>OPd: C, 55.25; H, 3.71; N, 12.89. Found: C, 55.12; H, 3.79; N, 13.02%. UV/VIS ( $\lambda_{max}$  / nm ( $\epsilon$  / dm<sup>2</sup> mol<sup>-1</sup>), dichloromethane): 575 (8620), 365 (7110), 235 (33890). IR (KBr, cm<sup>-1</sup>): 1615 v(C=N), 1418 v(N=N), 1335 v(O-C). <sup>1</sup>H NMR (400 MHz, CDC13): 3.17 (CH<sub>3</sub>, s, 3H), 6.50-6.53 (ArH, m, 2H), 6.99 (ArH, d, 1H), 7.15-7.21 (ArH and CH, m, 4H), 7.24-7.30 (ArH, m, 3H), 7.39 (ArH, d, 1H), 7.54 (ArH, d, 1H), 8.11 (ArH, d, 1H).

Yield: **Pd**(**L**<sup>2</sup>), 75%. Anal. Calc. for C<sub>21</sub>H<sub>18</sub>N<sub>4</sub>OPd: C, 56.20; H, 4.04; N, 12.48. Found: C, 56.13; H, 4.15; N, 12.76%. UV/VIS ( $\lambda_{max}/nm$  ( $\epsilon/dm^2 mol^{-1}$ ), dichloromethane): 580 (8740), 365 (7620), 235 (35780). IR (KBr, cm<sup>-1</sup>): 1617 v(C=N), 1403 v(N=N), 1346 v(O-C). <sup>1</sup>H NMR (400 MHz, CDC13): 1.65 (CH<sub>3</sub>, s, 3H), 3.27 (CH<sub>2</sub>, b, 1H), 3.82 (CH<sub>2</sub>, b, 1H), 6.18 (ArH, d, 1H), 6.26 (ArH, s, 1H), 6.40 (ArH, t, 1H), 6.74 (ArH, s, 1H), 6.96 (ArH, t, 1H), 7.12-7.32 (ArH & CH, m, 6H), 7.39 (ArH, d, 1H), 7.70 (ArH, d, 1H).

#### 2.3.5. General procedures for the Suzuki-Miyaura reaction

Aryl halides (1.0 mmol) and phenyl boronic acid (1.2 mmol), were dissolved in THF (10 mL) in a 25 mL round bottomed flask and stirred for 10 min.  $K_2CO_3$  (2.0 mmol) and catalyst (1.0 mol %) were added to the reaction flask. The reaction mixture was stirred at 80  $^{\circ}$ C for 5h. After completion, the reaction mixture was cooled to room temperature and the mixture was filtered and then extracted with dichloromethane. The organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, passed through silica column (60-120 mesh), the complex remain trapped. Upon removal

of the solvent, solid of pure products were obtained. The yields of the products obtained (based on the aryl halides) from all the reactions were determined after isolation, and characterized by <sup>1</sup>H NMR spectra and melting points with the literature data.

#### 2.3.6. Procedure for catalytic oxidation of benzyl alcohol

Benzyl alcohol (5 mmol), catalyst  $Cu(L^1)$  (0.05 mmol), and 50 %  $H_2O_2$  5 mL were taken in a 25 mL round bottomed flask. The mixture was vigorously stirred at 80<sup>o</sup>C for 3 h. After completion, reaction mixture was cooled to room temperature then mixture was poured into water and the product was extracted with dichloromethane. The organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, passed through silica column (60-120 mesh), the complex remain trapped. Upon removal of the solvent, pure products were obtained and characterized by <sup>1</sup>H NMR spectra.

#### 2.6. Crystallography

Single crystals of ligand  $H_2L^1$ , Ni( $L^2$ ) were grown by slow evaporation of ether and methanolic mother solutions at 25  ${}^{0}$ C and Cu( $L^1$ ) was grown by slow evaporation of dichloromethane-methanol mixed solvent at room temperature. Data were collected by  $\omega$ - scan technique on a Bruker Smart CCD diffractometer with Mo-K<sub>a</sub> radiation monochromated by graphite crystal. Structure solution was done by direct method with SHELXS–97 program [35-36]. Full matrix least square refinements on F<sup>2</sup> were performed using SHELXL–97 program [35-36]. All non-hydrogen atoms were refined anisotropically using reflections I > 2 $\sigma$  (I). The C-bound hydrogen atoms were included in calculated positions and refined as riding atoms and O, N-bound hydrogen atoms were assigned and refined. Data collection parameters and relevant crystal data are collected in Table 1.

Please insert Table 1 here

#### 3. Results and discussion

#### 3.1. Synthesis

The ligand  $H_2L$  used in this work, synthesized by two step reaction (i) mono alkylation of 2,2'-diaminoazobenzen with alkyl halides (ii) the condensation of mono alkyl product **3** with salicylaldehyde in diethyl ether. The ligand was isolated as red-brown solid crystals on cooling. The preformed ligand  $H_2L$  upon reaction with copper(II), nickel(II) and palladium(II) metal salts separately in methanol afforded pink-violet, green and blue (respectively) amido azo aldimine complexes of compositions (Cu(L), Ni(L) and Pd(L)) where the ligand (H<sub>2</sub>L) offers (N,N,N,O) coordination mode (Scheme 1). In all the complexes ligand H<sub>2</sub>L binds in tetradentate (N,N,N,O) bianionic fashion through deprotonated amino nitrogen, azo nitrogen, imine nitrogen and deprotonated phenolato oxygen atom forming two six membered and one five membered ring.

Please insert Scheme 1 here

### 3.2. UV-Vis and Fluorescence spectra

UV-visible spectra of ligands  $H_2L^1 \& H_2L^2$  and their complexes Cu(L), Ni(L) and Pd(L) were recorded at room temperature, using dichloromethane as a solvent. Representative for  $H_2L^2$  and its corresponding complexes Cu(L<sup>2</sup>), Ni(L<sup>2</sup>) and Pd(L<sup>2</sup>) have been shown in Fig. 1. Spectral data are collected in experimental section. The absorption spectrum of the free ligands  $H_2L$  consists of four relatively intense absorption peaks centered at ~230, ~260, 315 and ~480 nm, the first three high energy can be assigned to the  $\pi$ - $\pi$ \* transitions of the phenyl rings and last one characteristic of the overlapping n- $\pi$ \* transitions of azo (-N=N-) and aldimine (-N=CH-) function [37-39]. Upon coordination of the ligands  $H_2L$ , the  $\pi$ - $\pi$ \* transitions of the phenyl rings in the complexes Cu(L), Ni(L) and Pd(L) were shifted to different wavelengths which indicating the coordination of Cu(II), Ni(II) and Pd(II) atoms with the (L)<sup>2-</sup> units. A characteristic broad absorption peak is observed at 550 nm [Cu(L)], 680 nm [Ni(L)] and 580 nm [Pd(L)] this new absorption peak can be assigned to mixed metal ligand charge transfer transition [38-40].

#### Please insert Fig. 1 here

The fluorescence properties of ligand  $H_2L^1$  and complexes  $Cu(L^1)$  and  $Ni(L^1)$  were examined in dilute chloroform solution at room temperature (Fig. 2). The ligand  $H_2L^1$  show low intensity emissions bands at 450 nm upon excitation at 315 nm whereas  $Ni(L^1)$  do not show noticeable fluorescence upon excitation at 335 & 410 nm but complex  $Cu(L^1)$  show very high intensity emissions bands at 465 nm upon excitation at 385 nm. High fluorescent intensity of  $Cu(L^1)$  due to the strong chelate formation leading to reduction of photoinduced electron transfer process (PET) [41-42]. In the copper complex both five and six-membered chelate ring increases rigidity in comparison to  $H_2L^1$ , which in turn, reduces the loss of energy by vibrational decay and enhances the fluorescence intensity [42-44].

Please insert Fig. 2 here

#### 3.3. IR and $^{1}$ H-NMR

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The azomethine vibration at 1608 cm<sup>-1</sup> in the free ligands (H<sub>2</sub>L<sup>1</sup> & H<sub>2</sub>L<sup>2</sup>) undergoes positive shift and appears in the range 1610-1617 cm<sup>-1</sup> in the complexes (Cu(II), Ni(II) and Pd(II)) indicating coordination to the metal ions [23-26,30]. The characteristic band due to v(Ar–OH / or N-H) at 3367 cm<sup>-1</sup> and 3064 in free ligands disappears due to deprotonation in all the complexes [30]. Furthermore, the phenolic v(C–O) vibrations at 1279 cm<sup>-1</sup> in the free ligands shows shift in higher energy upon complexation with metal ions (Cu(II), Ni(II) and Pd(II)), and appears at ~1328 cm<sup>-1</sup> (Cu(II)), ~1323 cm<sup>-1</sup> (Ni(II)) and ~1340 cm<sup>-1</sup> (Pd(II)), which is further established by the presence of v(Ar-O-M) vibration at ~1375 cm<sup>-1</sup>, ~1378 cm<sup>-1</sup> and ~1384 cm<sup>-1</sup> respectively, signifying its coordination to metal ions via the phenoxy hydroxyl group [37,45]. Similarly the v<sub>N=N</sub> band (~1378 cm<sup>-1</sup>) of the ligands shifted to higher energy (1425 (Cu), 1438 (Ni) and 1418 (Pd) in the

complexes, consistent with coordination of the azo nitrogen [23-27, 30]. Spectral data are collected in experimental section.

The –OH resonances at 13.46 ppm  $(H_2L^1)$  & 13.29 ppm  $(H_2L^2)$  and –NH resonances at 9.27 ppm  $(H_2L^1)$  & 9.04 ppm  $(H_2L^2)$  in the ligands disappears in the complexes (Ni & Pd), suggesting the formation of Ni–O and Pd–O bond due to deprotonation [23,24]. A sharp singlet at 8.63 ppm  $(H_2L^1)$  & 8.55 ppm  $(H_2L^2)$  due to azomethine proton in free ligands is shifted upfield in Ni(II) complexes and appears at 8.45 ppm & 8.54 ppm, confirms that azomethine nitrogen is linked to the nickel ion whereas in palladium complexes the azomethine protons are more shielded and appears in the range 7.11-7.21 ppm. The phenyl ring protons observed at 6.68–7.90 ppm in both the ligands undergoes small shifts and appears in the range 6.22-8.05 in all the complexes. Furthermore, resonances due to –CH<sub>3</sub> of H<sub>2</sub>L<sup>1</sup> (2.81 ppm) and –C<sub>2</sub>H<sub>5</sub> protons of H<sub>2</sub>L<sup>2</sup> at 0.98 & 3.11-3.16 ppm, in the ligands show large shift upon coordination to Ni(II) & Pd(II) ion, suggesting ligand is coordinated to metal ions. Spectral data are collected in experimental section.

#### 3.4. X-ray crystallography

Crystals suitable for X-ray diffraction analysis of  $H_2L^1$  were obtained by slow evaporation of diethyl ether solution at room temperature, which crystallizes in the space group Pbca. The crystallographic and measurement data are shown in Table 1. The crystal structure of ligand  $H_2L$  is shown in Fig. 3. Selected bond lengths and bond angles are given in Table 2. The non-planar structure of ligand  $H_2L$  stabilized by two intra molecular hydrogen bonding between phenolic proton and imine nitrogen [O(1)-H....N(3)] and amine proton and azo nitrogen N(4)-H....N(1)]. The O(1)-C(20), N(3)-C(14), N(1)-C(8), N(2)-N(3) and N(2)-C(13) bond lengths 1.346(2), 1.281(9), 1.416(9), 1.246(19) and 1.426(2) Å are in agreement with the reported values [30-32].

Please insert Fig. 3 and Table 2 here
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The crystal structure of  $Cu(L^1)$  is shown in Fig. 4 along with the atom labels. Hydrogen atoms are omitted for the clarity. Selected bond lengths and bond angles are listed in Table 3.

Please insert Fig. 4 and Table 3 here

Cu(L<sup>1</sup>) crystallizes in the P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space group and also has a square planar geometry. All the nonhydrogen atoms of Cu(L<sup>1</sup>) make a good plane (mean deviation 0.222Å). The dianionic ligand (L<sup>1</sup>)<sup>2-</sup> is coordinated through (N,N,N,O) with Cu(II) ion, forming two six membered chelate ring and one five membered ring. The copper(II) centre is coordinated to imine nitrogen N1, azo nitrogen N2, amido nitrogen N4 and phenolate oxygen O1 atoms to constitute the equatorial plane. The deviations of the four coordinating atoms from their mean plane are within  $\pm$  2.645 Å. The shorter bond lengths of O1-C1 (~0.05 Å), N3-C14 (~0.04 Å), C6-C7 (~0.03 Å) and one longer bond N1-C8 (~0.02 Å) in the Cu(L<sup>1</sup>) complex relative to the ligand H<sub>2</sub>L<sup>1</sup> shows the effect of metal ion coordination. The Cu1-O1, Cu1-N2, Cu1-N4 and Cu1-N1 bond distances are 1.902(6), 1.924(6), 1.927(6) and 1.982(6) Å respectively are in typical range as found in related Cu(II) complexes [30, 46-48]. The O1-Cu1-N1, N2-Cu1-N4, N2-Cu1-N1 and O1-Cu1-N4 angles are 91.2(3), 91.1(3), 84.3(3) and 93.6(3)° respectively are very close to 90° and O1-Cu1- N2 (174.2(3), N4-Cu1- N1 (173.9(3)<sup>0</sup> angles are close to 180° are similar to other reported Cu(II) complexes [30, 46-48].

The crystal structure of  $Ni(L^2)$  is shown in Fig. 5 along with the atom labels. Hydrogen atoms are omitted for the clarity. Selected bond lengths and bond angles are listed in Table 4.

Please insert Fig. 5 and Table 4 here

 $Ni(L^2)$  crystallizes in the P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space group, similarly to the complex Cu(L<sup>1</sup>), and also has a square planar geometry (mean deviation 0.126Å). The dianionic ligand  $(L^2)^{2^-}$  is coordinated through imine nitrogen N1, azo nitrogen N2, amido nitrogen N4 and phenolate oxygen O1 atoms to constitute the equatorial plane with Ni(II) ion and forming two six membered chelate ring and one five membered ring like Cu(L<sup>1</sup>). The deviations of the four coordinating atoms from their mean

plane are within  $\pm 2.62$  Å. The shorter bond lengths of O1-C1 (~0.04 Å), N4-C15 (~0.02 Å), N3-C14 (~0.06 Å) and C6-C7 (~0.04 Å) in the Ni(L<sup>2</sup>) complex relative to the ligand H<sub>2</sub>L<sup>1</sup> (though the H<sub>2</sub>L<sup>1</sup> is little differ from coordinated ligand in Ni(L<sup>2</sup>)) shows the effect of metal ion coordination. The N2-N3 azo and N1-C7 imine distances in Ni(L<sup>2</sup>) are longer ((~0.02 Å) than that of ligand H<sub>2</sub>L<sup>1</sup>. The Ni1-O1, Ni1-N2, Ni1-N4 and Ni1-N1 bond distances are 1.853(3), 1.832(3), 1.893(3) and 1.887(3) Å and O1-Ni1-N1, N2-Ni1-N4, N2-Ni1-N1 and O1-Ni1-N4 angles are 92.33(14), 92.55(14), 85.33(14), 89.83(13) respectively are in typical range as found in related Ni(II) complexes [48-50].

#### 3.5. Electrochemistry

The electrochemical behavior of two complexes Ni(L<sup>1</sup>) and Cu(L<sup>1</sup>) were examined in dichloromethane acetonitrile mixed solvent (0.1 M TBAP) by cyclic voltammetry with a scan rate of 0.1 V s<sup>-1</sup> (Fig. 6) vs. SCE. The cyclic voltammogram of Ni(L<sup>1</sup>) displayed one electron reversible oxidative and reductive responses at 1.1 V and -1.04 V whereas Cu(L<sup>1</sup>) displayed only one electron quasi reversible oxidative response at 1.03 V (Fig.S21). The reduction and oxidation have been assigned to the couple of equations (1) & (2). The report of our previous work of copper(II) complex with similar ligand system which support the oxidative responses of Cu(L<sup>1</sup>) and Ni(L<sup>1</sup>) both are ligand centric [30]. The reductive response of Ni(L<sup>1</sup>) due to the metal centred Ni(II)/Ni(I) reduction [37].

Please insert Fig. 6 here

#### 3.4. The Suzuki–Miyaura coupling reactions

The catalytic activity of  $Pd(L^1)$  was studied in C–C bond formation by means of Suzuki– Miyaura cross–coupling of aryl halides with phenyl boronic acid (Eq. 3) and results were shown in Table 5. In the present study we report the coupling reactions of several aromatic halides having different substituents in the aromatic ring under atmospheric pressure with changing amount of

catalyst and reaction temperature. Before detailed study on the catalytic reactions, initially we first optimized the reaction conditions by choosing iodobenzene with phenyl boronic acid as the model substrate. The important two factors for the reaction, catalyst amount and temperature, were compared for the purpose of attaining the optimal conditions. The conclusion of the optimization of

Please insert Eq. 3 and Table 5 here

the conditions is shown in Table S1 (SI). The reaction was carried out when various amounts of the catalyst  $Pd(L^1)$  1 mol % - 4 mol % based on the Pd element were present at 80 °C. It was observed that nearly the same yields were obtained with catalyst amounts varying from 1-4 mol %. The influence of temperature was studied from 25°C-80°C, to obtain the optimum temperature for the reaction. Hence, the boiling temperature (80°C) was selected as the optimum temperature. After the completion of the catalytic reaction the palladium complex was intact and isolated from the reaction mixture easily by column chromatography. The isolated catalyst  $Pd(L^1)$  was reused and its reusability was examined up to three times for a reaction without sufficient loss of its catalytic activity keeping other condition intact.

#### 3.7. Oxidation of benzyl alcohol

As the complex  $Cu(L^1)$  was soluble in benzyl alcohol so our interest to examine this compound as homogeneous catalyst for organic transformations in organic media. The homogeneous oxidation reaction was carried out under atmospheric pressure and in absence of any additive other than the substrate, benzyl alcohol,  $H_2O_2$  (50%) and catalyst  $Cu(L^1)$  (Eq.4) and results were shown in Table 6. The oxidation of alcohols was carried out in the presence of catalytic amounts (1 mol %) of  $Cu(L^1)$  and using as oxidant  $H_2O_2$  (5 eqv.) in an aqueous / organic biphasic system or solvent-free condition. Before detailed study on the catalytic oxidation of substituted benzyl alcohols, initially we chose benzyl alcohol as the model substrate for optimization of the reaction. The oxidation of benzyl alcohol by  $H_2O_2$  at room temperature was very low yield ~20%

for 10 h. The conversion of benzaldehyde significantly increased when temperature above 70  $^{0}$ C. The influence of temperature was studied to obtain the optimal condition for the oxidation reactions (Table S2 in SI). The best yield of benzaldehyde was obtained during the oxidation of benzyl alcohol, with (5 eqv.) 50% H<sub>2</sub>O<sub>2</sub> for 3 h at 80  $^{0}$ C. The products were isolated after separation and characterized by IR spectra. The conversions were calculated on the basis of isolated yields.

Please insert Eq.4 here

#### 4. Conclusion

In conclusion new Cu(II), Ni(II) and Pd(II) complexes Cu(L), Ni(L) and Pd(L) have been synthesized using newly developed Schiff based ligand H<sub>2</sub>L and characterized by different physicochemical and spectroscopic techniques. The solid-state structures of H<sub>2</sub>L<sup>1</sup>, Cu(L<sup>1</sup>) and Ni(L<sup>2</sup>) were determined by single crystal X-ray crystallography, which revealed square planar geometry. The newly synthesized ligand (H<sub>2</sub>L), bound with metal ions in a bi-negatively tetradentate manner, with N, N, N, O donor atoms of the amido nitrogen, azo nitrogen, azomethine nitrogen and phenolic oxygen atoms. The redox property of complexes Cu(L<sup>1</sup>) and Ni(L<sup>1</sup>) and emission behavior of both the ligand and complexes were examined. Newly synthesized Pd(L<sup>1</sup>) complex was investigated as highly active and efficient catalyst in the Suzuki–Miyaura cross– coupling reaction of various aryl halides with phenyl boronic acid to produce the corresponding biaryls with high yields under mild reaction conditions. Also we examined the catalytic activity of Cu(L<sup>1</sup>) for the oxidation of benzyl alcohol using H<sub>2</sub>O<sub>2</sub> as an oxidant under mild conditions.

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#### Appendix A. Supplementary data

Figures S1–S12 shows the UV-Vis, IR spectra of the ligand and complexes and Figure S13-S18 <sup>1</sup>H NMR spectrum of the ligands, nickel and palladium complexes and Figure S19 CV of Cu(L<sup>1</sup>). CCDC 1874624, 1874625 and 1874626 contains the supplementary crystallographic data for compounds  $H_2L^1$ , Ni(L<sup>2</sup>) & Cu(L<sup>1</sup>). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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### Scheme 1



## Table 1

Crystallographic data for1, 2a and 2b

Parameter	$H_2L^1$	Cu(L <sup>1</sup> )	Ni(L <sup>2</sup> )
Chemical formula	$C_{20}H_{18}N_4O$	$C_{20}H_{16}CuN_4O$	C <sub>21</sub> H <sub>18</sub> N <sub>4</sub> NiO
Formula weight	330.38	391.91	401.10
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
space group	Pbca	P212121	P212121
a/Å	11.5377(12)	4.9090(3)	5.4146(2)
b/Å	14.3666(12)	10.6808(7)	15.5889(7)
c/Å	20.920(3)	31.746(2)	20.5140(8)
$\alpha = \beta = \gamma/\text{deg}$	90	90	90
$\lambda/\dot{\mathrm{A}}$	0.71073	0.71073	0.71073
$V/Å^3$	3467.7(6)	1664.50(19	1731.54(12)
F(000)	1392	800	832
Crystal Size [mm]	0.3 x 0.2 x 0.15	0.30 x 0.04 x 0.02	0.25 x 0.08 x 0.08
Ζ	8	4	4
T/K	296(2)	296(2)	296(2)
D/mg/m <sup>-3</sup>	1.266	1.560	1.539
$\mu/\mathrm{mm}^{-1}$	0.081	1.329	1.140
Theta Min-Max [deg]	1.947-28.306	2.012-28.456	1.641-28.341
Reflections measured	31992	15895	16875
Unique reflections (Rint)	4307	4144	4303
No. of reflections used $[I > 2\sigma(I)]$	2389	2424	3426
R1,wR2(all data)	0.1024, 0.1425	0.1268, 0.1477	0.0570, 0.0994
R1, wR2[ $I > 2\sigma(I)$ ]	0.0503, 0.1169	0.0532, 0.1021	0.0370, 0.0804
GOF	1.011	1.038	0.979

### Table 2

Selected Bond Distances (Å) and Angles (deg) for Compound  $H_2L^1$ .

	Ľ	Distances	
N(1)-N(2)	1.2706(17)	N(3)-C(5)	1.4152(19)
N(1)-C(6)	1.4214(19)	N(4)-C(12)	1.347(2)
N(2)-C(7)	1.3990(19)	N(4)-C(13)	1.447(2)
N(3)-C(14)	1.2809(19)	O(1)-C(20)	1.346(2)
C(7)-C(12)	1.423(2)	C(14)-C(15)	1.452(2)
C(5)-C(6)	1.399(2)	C(15)-C(20)	1.388(2)
	·	Angles	0
N(2)-N(1)-C(6)	114.24(12)	C(6)-C(5)-N(3)	118.65(13)
N(1)-N(2)-C(7)	116.62(13)	C(5)-C(6)-N(1)	116.52(13)
C(14)-N(3)-C(5)	120.13(14)	N(2)-C(7)-C(12)	126.51(14)
C(12)-N(4)-C(13)	124.52(15)	N(4)-C(12)-C(7)	121.80(14)
N(3)-C(14)-C(15)	121.88(16)	O(1)-C(20)-C(15)	121.74(17)

### Table 3

Selected Bond Distances (Å) and Angles (deg) for Compound  $Cu(L^1)$ .

1.902(6)      1.924(6)      1.927(6)      1.982(6)      1.271(10)      1.432(9)      1.279(9)      1.391(11)	N(2)-C(13)        N(3)-C(14)        N(4)-C(19)        O(1)-C(1)        C(1)-C(6)        C(6)-C(7)        C(14)-C(19)	1.427(9)      1.358(9)      1.339(10)      1.295(9)      1.445(11)      1.422(12)      1.437(10)
1.924(6)      1.927(6)      1.982(6)      1.271(10)      1.432(9)      1.279(9)      1.391(11)	N(3)-C(14)        N(4)-C(19)        O(1)-C(1)        C(1)-C(6)        C(6)-C(7)        C(14)-C(19)        Angles	1.358(9)      1.339(10)      1.295(9)      1.445(11)      1.422(12)      1.437(10)
1.927(6)      1.982(6)      1.271(10)      1.432(9)      1.279(9)      1.391(11)	N(4)-C(19)        O(1)-C(1)        C(1)-C(6)        C(6)-C(7)        C(14)-C(19)        Angles	1.339(10)      1.295(9)      1.445(11)      1.422(12)      1.437(10)
1.982(6)      1.271(10)      1.432(9)      1.279(9)      1.391(11)      174.2(3)	O(1)-C(1) C(1)-C(6) C(6)-C(7) C(14)-C(19) Angles	1.295(9)      1.445(11)      1.422(12)      1.437(10)
1.271(10)      1.432(9)      1.279(9)      1.391(11)      174.2(3)	C(1)-C(6) C(6)-C(7) C(14)-C(19) Angles	1.445(11)      1.422(12)      1.437(10)
1.432(9)      1.279(9)      1.391(11)      174.2(3)	C(6)-C(7) C(14)-C(19) Angles	1.422(12)    1.437(10)
1.279(9) 1.391(11) 174.2(3)	C(14)-C(19) Angles	1.437(10)
1.391(11)	Angles	
174.2(3)	Angles	
174.2(3)		
	O(1)-Cu(1)-N(1)	91.2(3)
93.6(3)	N(2)-Cu(1)-N(1)	84.3(3)
91.1(3)	N(4)-Cu(1)-N(1)	173.9(3)

### Table 4

		stances	
Ni(1)-N(2)	1.832(3)	N(3)-C(14)	1.338(5)
Ni(1)-O(1)	1.853(3)	N(4)-C(15)	1.329(5)
Ni(1)-N(1)	1.887(3)	N(2)-C(9)	1.425(5)
Ni(1)-N(4)	1.893(3)	C(1)-C(6)	1.408(6)
O(1)-C(1)	1.302(5)	C(8)-C(9)	1.394(6)
N(1)-C(7)	1.301(5)	C(6)-C(7)	1.412(5)
N(1)-C(8)	1.413(5)	C(14)-C(15)	1.444(5)
N(2)-N(3)	1.295(4)		
	A	ngles	
N(2)-Ni(1)-O(1)	177.14(16)	O(1)-Ni(1)-N(4)	89.83(13
N(2)-Ni(1)-N(1)	85.33(14)	N(1)-Ni(1)-N(4)	177.48(2
O(1)-Ni(1)-N(1)	92.33(14)	N(2)-Ni(1)-N(4)	92.55(14

Selected Bond Distances (Å) and Angles (deg) for Compound  $Ni(L^2)$ .

### Table 5

Suzuki–Miyaura cross-coupling reaction of various aryl halides with phenyl boronic acid catalyzed by  $Pd(L^1)$ 



Solvent = THF, Base =  $K_2CO_3$ , Time = 5h, Catalyst = 4 mol%, Substrate = 1:1.2 mmol (Aryl halide : Phenyl boronic acid)

### Table 6

Oxidation of benzyl alcohol derivatives catalyzed by  $Cu(L^1)$ 



Solvent =  $CH_3CN$  or solvent free, Catalyst = 1 mol%, Substrate = 5 mmol



Fig. 1 UV-Vis spectra of  $H_2(L^2)$  (—),  $Cu(L^2)$  (—),  $Ni(L^2)$  (—) and  $Pd(L^2)$  (—) in dichloromethane



Fig. 2 Emission spectra of  $H_2(L^1)$  (—),  $Cu(L^1)$  (—) and  $Ni(L^1)$  (—) in chloroform.

RCC



Fig. 3 Molecular structure of  $H_2(L^1)$  (40% probability ellipsoids) with atom numbering scheme. Hydrogen atoms are omitted for clarity except N4, O1 and C14.

C



**Fig. 4** Molecular structure of  $Cu(L^1)$  (40% probability ellipsoids) with atom numbering scheme. Hydrogen atoms are omitted for clarity.



**Fig. 5** Molecular structure of  $Ni(L^2)$  (40% probability ellipsoids) with atom numbering scheme. Hydrogen atoms are omitted for clarity.

RCC



Fig. 6 CV of  $Ni(L^1)$  in dichloromethane acetonitrile mixed solvent.

### **Graphical Abstract**

Tetradentate amido azo Schiff base Cu(II), Ni(II) and Pd(II) complexes: Synthesis, characterization, spectral properties, and applications to catalysis in C-C coupling and oxidation reaction

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A CCI



### **Graphical Abstract Synopsis**

Tetradentate amido azo Schiff base Cu(II), Ni(II) and Pd(II) complexes: Synthesis, characterization, spectral properties, and applications to catalysis in C-C coupling and oxidation reaction

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Synthesis of newly designed tetradentate ligands and its nickel(II), copper(II) and palladium(II) complexes. The fluorescence and redox property of both the ligand and complex were examined. The newly synthesized air and moisture stable copper(II) and palladium(II) complexes act as potential catalyst towards oxidation of benzyl alcohol to benzyldehyde and C-C coupling reaction respectively, under mild conditions.