#### Inorganica Chimica Acta 387 (2012) 240-247

Contents lists available at SciVerse ScienceDirect

### Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# Synthesis, spectra, structure, redox properties and DFT computation of copper(I)–triphenylphosphine–pyridyl Schiff bases

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#### ARTICLE INFO

Article history: Received 6 August 2011 Received in revised form 12 January 2012 Accepted 13 January 2012 Available online 28 January 2012

Keywords: Copper(I)–pyridyl-Schiff base X-ray structure Electrochemistry DFT computation

#### ABSTRACT

The reaction of 2-(2'-pyridylmethyleneamino)pyridine (L<sup>1</sup>)/3-(2'-pyridylmethyleneamino)pyridine (L<sup>2</sup>)/ 4-(2'-pyridylmethyleneamino)pyridine (L<sup>3</sup>) with CuX (X = Cl, Br, I) and triphenylphosphine (PPh<sub>3</sub>) affords complexes of composition [Cu(L)(PPh<sub>3</sub>)X]. These are characterized by microanalytical data and spectroscopic studies (IR, UV–Vis, <sup>1</sup>H NMR). The single crystal X-ray structure determines the distorted tetrahedral geometry about Cu(I) in case of [Cu(L<sup>2</sup>)(PPh<sub>3</sub>)I]. Cyclic voltammogram shows Cu(II)/Cu(I) couple at 0.5–0.6 V, in addition [Cu(L)(PPh<sub>3</sub>)I] shows iodide oxidation peak at 0.3 V. Redox couple negative to SCE may be assigned to the reduction of chelated diimine function. Electronic structure, spectra, emission properties and redox activities are explained by DFT calculations of optimized geometry of [Cu(L<sup>2</sup>)(PPh<sub>3</sub>)X] and have been used to determine the composition and energy of the molecular levels. © 2012 Elsevier B.V. All rights reserved.

#### 1. Introduction

Metal complexes of Schiff bases are known since 1860 [1]. Significant development has been started on and from 1950 [2,3]. Ligands containing polyimine function are of potential interest in the development of coordination chemistry of lower valent metal redox states. Polypyridine, a class of diimine function (-N=C-C=N-), is useful in the development of transition and non-transition metal complexes [4–8]. The condensation of pyridinecarboxaldehyde with aromatic amine has synthesized diimine function [9–15]. The condensation of aminopyridine(s) and pyridine-2-carboxaldehyde produces useful Schiff base which can stabilize low valent metal ion like copper(I) [14–21].

Herein we describe the synthesis, spectral characterization of copper(I) halide complexes of 2-/3-/4-(2'-pyridylmethyleneamino)pyridine incorporating phosphine coordination. In one case the structural confirmation is achieved by single crystal X-ray structure analysis. The DFT and TD-DFT computations have been carried out to explain the spectroscopic and redox properties of the complexes.

#### 2. Experimental

#### 2.1. Materials

2-Aminopyridine, 3-aminopyridine, 4-aminopyridine and pyridine-2-carboxaldehyde were purchased from Sigma–Aldrich. CuX (X = Cl, Br, I) and triphenylphosphine were purchased from E. Merck, India. All other chemicals and solvents were of reagent grade and used as received.

Inorganica Chimica Acta

#### 2.2. Physical measurements

Microanalytical data (C, H, N) were collected from Perkin–Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV–Vis spectra, Perkin–Elmer; model Lambda 25, IR spectra (KBr disk, 4000–400 cm<sup>-1</sup>), Perkin–Elmer; model spectrum RX-1, <sup>1</sup>H NMR spectra, Bruker (AC) 300 MHz FTNMR spectrometer. Electrochemical measurements were performed using computer-controlled CH Instruments Electrochemical Workstations with Pt-disk electrodes. All measurements were carried out under nitrogen environment at 298 K at scan rate 50 mV S<sup>-1</sup> with reference to SCE in acetonitrile using  $[nBu_4N][CIO_4]$  as supporting electrolyte. The reported potentials are uncorrected for junction potential.

#### 2.3. Synthesis of ligands

The ligands were synthesized following a common procedure [22]. Detail of synthesis for L<sup>1</sup> is given below.



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2-Aminopyridine (1.213 g, 12.9 mmol) was dissolved in 30 ml methanol, pyridine-2-carboxyaldehyde (1.38 g, 12.9 mmol) was added to it and the mixture was refluxed for 6 h in the presence of molecular sieves, it was then filtered and filtrate was collected in a beaker and solvent was allowed to evaporate slowly. The crystalline product at the bottom of the beaker was collected, washed with methanol ( $2 \times 5$  ml) and dried over CaCl<sub>2</sub> in a desiccator. Yield was 64% and m.p. 196 ± 2 °C.

## 2.4. Synthesis of $[Cu(L^2)(PPh_3)(I)]$ (**3b**) and analytical data of the complexes

To a stirred solution of CuI (0.11 g, 0.58 mmol) in MeCN (10 ml), PPh<sub>3</sub> (0.162 g, 0.62 mmol) was added in small portion. To the resultant suspension,  $L^2$ , 3-(2'-pyridylmethyleneamino)pyridine (0.114 g, 0.62 mmol) in methanol (10 ml) was added in drops and refluxed for 3 h. The solution was filtered through G4 crucible and was allowed to evaporate slowly in air. Block shaped dark red microcrystal deposited on the wall of the beaker. These were collected by filtration and dried over CaCl<sub>2</sub> in desiccator. Yield: 0.297 g (77%).

All other complexes were prepared by identical procedure. Yield: 70-80%. Microanalytical data of the complexes are as follows: [Cu(L<sup>1</sup>)(PPh<sub>3</sub>)Cl] (1a) Anal. Calc. for C<sub>29</sub>H<sub>24</sub>CuClN<sub>3</sub>P: C, 63.97; H, 4.44; N, 7.72. Found: C, 63.91; H, 4.49; N, 7.68%. FT-IR (KBr disc, cm<sup>-1</sup>), v(PPh<sub>3</sub>), 611, 725; v(C=N), 1597 cm<sup>-1</sup>. UV-Vis spectral data in MeCN ( $\lambda_{max}(nm)$  ( $10^{-3} \in (dm^3 mol^{-1} cm^{-1}))$ ): 406 (0.430), 289 (9.42). [Cu(L<sup>2</sup>)(PPh<sub>3</sub>)Cl] (1b) Anal. Calc. for C<sub>33</sub>H<sub>29</sub>CuClN<sub>4</sub>P: C, 63.97; H, 4.44; N, 7.72. Found: C, 64.03; H, 4.42; N, 7.70%. FT-IR (KBr disc, cm<sup>-1</sup>), v(PPh<sub>3</sub>), 605, 707; v(C=N), 1616 cm<sup>-1</sup>. UV–Vis spectral data in MeCN ( $\lambda_{max}(nm)$  (10<sup>-3</sup>  $\in$ (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>))): 401 (0.802), 286 (9.24). [Cu(L<sup>3</sup>)(PPh<sub>3</sub>)Cl] (1c) Anal. Calc. for C<sub>29</sub>H<sub>24</sub>CuClN<sub>3</sub>P: C, 63.97; H, 4.44; N, 7.72. Found: C, 63.88; H, 4.39; N, 7.69%. FT-IR (KBr disc,  $cm^{-1}$ ),  $v(PPh_3)$ , 604, 701; v(C=N), 1590 cm<sup>-1</sup>. UV–Vis spectral data in MeCN ( $\lambda_{max}(nm)$ )  $(10^{-3} \in (dm^3 \text{ mol}^{-1} \text{ cm}^{-1})))$ ; 403 (1.027), 282 (9.93).  $[Cu(L^{1})(PPh_{3})Br$  (2a) Anal. Calc. for  $C_{29}H_{24}CuBrN_{3}P$ : C, 59.15; H, 4.11; N, 7.14. Found: C, 59.11; H, 4.07; N, 7.21%. FT-IR (KBr disc, cm<sup>-1</sup>), v(PPh<sub>3</sub>), 608, 702; v(C=N), 1592 cm<sup>-1</sup>. UV–Vis spectral data

Table 1

Summarized crystallographic data summarized crystallographic data for  $[Cu(L^2)(P-Ph_3)I]$  (3b).

Empirical formula	C <sub>29</sub> H <sub>24</sub> CuIN <sub>3</sub> P
Formula weight	635.92
T (K)	293(2)
Crystal system	monoclinic
Space group	C2/c
Crystal size (mm)	0.30  imes 0.30  imes 0.35
Unit cell dimensions	
a (Å)	33.739(4)
b (Å)	9.5890(10)
c (Å)	19.633(2)
β (°)	117.113(11)
V (Å) <sup>3</sup>	5653.8(11)
Ζ	8
$\mu$ (MoK $\alpha$ ) (mm <sup>-1</sup> )	1.942
$\theta$ range	2.94-25.0
hkl range	$-40 \leq h \leq 39$ ; $-11 \leq k \leq 11$ ; $-23 \leq l \leq 23$
$D_{\text{calc}}$ (mg m <sup>-3</sup> )	1.494
Refine parameters	316
Total reflections	25613
Unique reflections	4951
$R_1^a [I > 2\sigma(I)]$	0.0650
wR <sub>2</sub> <sup>b</sup>	0.1605
Goodness of fit (GOF)	1.223

<sup>a</sup>  $R = \Sigma ||F_0| - |F_c||/\Sigma |F_0|.$ 

<sup>b</sup>  $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}, w = 1/[\sigma^2(F_0^2) + (0.0490P)^2 + 63.9973P].$ 

241

in MeCN ( $\lambda_{max}(nm)$  ( $10^{-3} \in (dm^3 \text{ mol}^{-1} \text{ cm}^{-1})$ )): 405 (0.845), 284 (10.59).  $[Cu(L^2)(PPh_3)Br]$  (**2b**) Anal. Calc. for  $C_{29}H_{24}CuBrN_3P$ : 59.15; H, 4.11; N, 7.14. Found: 59.03; H, 4.04; N, 7.19%. FT-IR (KBr disc, cm<sup>-1</sup>), v(PPh<sub>3</sub>), 597, 708; v(C=N), 1612 cm<sup>-1</sup>. UV-Vis spectral data in MeCN ( $\lambda_{max}(nm)$  ( $10^{-3} \in (dm^3 mol^{-1}cm^{-1}))$ ): 401 (0.568), 288 (11.71). [Cu(L<sup>3</sup>)(PPh<sub>3</sub>)Br] (2c) Anal. Calc. for C<sub>29</sub>H<sub>24</sub>CuBrN<sub>3</sub>P: 59.15; H, 4.11; N, 7.14. Found: 59.19; H, 4.17; N, 7.08%. FT-IR (KBr disc, cm<sup>-1</sup>), v(PPh<sub>3</sub>), 607, 719; v(C=N), 1599 cm^{-1}. UV–Vis spectral data in MeCN ( $\lambda_{max}(nm)$  ( $10^{-3} \in$ (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>))): 404 (0.946), 285 (9.86). [Cu(L<sup>1</sup>)(PPh<sub>3</sub>)I] (**3a**) Anal. Calc. for C<sub>29</sub>H<sub>24</sub>CuIN<sub>3</sub>P: C, 54.77; H, 3.80; N, 6.61. Found: C, 54.71; H, 3.88; N, 6.53%. FT-IR (KBr disc, cm<sup>-1</sup>), v(PPh<sub>3</sub>), 610, 719; v(C=N), 1597 cm<sup>-1</sup>. UV–Vis spectral data in MeCN ( $\lambda_{max}(nm)$ )  $(10^{-3} \in (dm^3 \text{ mol}^{-1} \text{ cm}^{-1}))$ : 410 (0.464), 288 (10.10). [Cu(L<sup>2</sup>)(P-Ph<sub>3</sub>)I] (**3b**) Anal. Calc. for C<sub>29</sub>H<sub>24</sub>CuIN<sub>3</sub>P: C, 54.77; H, 3.80; N, 6.61. Found: C, 54.84; H, 3.87; N, 6.68%. FT-IR (KBr disc, cm<sup>-1</sup>),  $v(PPh_3)$ , 622, 706; v(C=N), 1620 cm<sup>-1</sup>, UV-Vis spectral data in MeCN  $(\lambda_{max}(nm) (10^{-3} \in (dm^3 \text{ mol}^{-1} \text{ cm}^{-1})))$ : 409 (1.72), 285 (19.79). [Cu(L<sup>3</sup>)(PPh<sub>3</sub>)I] (**3c**) Anal. Calc. for C<sub>29</sub>H<sub>24</sub>CuIN<sub>3</sub>P: C, 54.77; H, 3.80; N, 6.61. Found: C, 54.73; H, 3.72; N, 6.59%. FT-IR (KBr disc, cm<sup>-1</sup>), v(PPh<sub>3</sub>), 609, 703; v(C=N), 1598 cm<sup>-1</sup>. UV-Vis spectral data in MeCN ( $\lambda_{max}(nm)$  ( $10^{-3} \in (dm^3 \text{ mol}^{-1} \text{ cm}^{-1})$ )): 401 (1.02), 287 (12.32).

#### 2.5. X-ray crystal structure analyses

Single crystals suitable for X-ray diffraction study of [Cu(L<sup>2</sup>)(P- $Ph_3$ ]I] (**3b**) (0.30 × 0.30 × 0.35 mm) were obtained on slow evaporation of acetonitrile–methanol (1:2 v/v) solution of the complex. Diffraction data were collected with the CrysAlis CCD, Oxford Diffraction Ltd. area-detector diffractometer using fine focused sealed tube graphite-monochromatized MoKα radiation (0.71073 Å). Cell refinement and data reduction were carried out with CrysAlis RED, Oxford Diffraction Ltd. Unit cell parameters were determined from least-squares method. A summary of the crystallographic data and structure refinement parameters are given in Table 1. Data were corrected for Lorentz and polarization effects. The structure was solved by direct method using SHELXS-97 [23] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Full matrix least squares refinements on  $F_0^2$  were carried out using SHELXL-97 [24] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon or nitrogen atoms with anisotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement of their parent atom in all cases. All calculations were carried out using SHELXS 97 [23], PLATON 99 [25], ORTEP-3 [26] programs.

#### 2.6. Computational methods

All computations were performed using the GAUSSIAN03 (G03) program [27]. Full geometry optimizations of the complexes 1b, 2b and 3b were carried out using the DFT method at the B3LYP level of theory [28,29]. The 6-31G(d) basis set was used for C, H and N, while LanL2TZ(f) basis set with effective core potential was employed for the Cu atom [30] and the MIDI! basis functions for P, Cl, Br and I atoms [31]. The LanL2TZ(f) and MIDI! basis set for the respective elements were downloaded from EMSL basis set library. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima of potential energy surface and there are only positive eigen values. The lowest 30 singlet-singlet vertical electronic excitations based on B3LYP optimized geometries were computed using the timedependent density functional theory (TD-DFT) formalism [32-34] in methanol using conductor-like polarizable continuum model (CPCM) [35–37] using the same B3LYP level and basis sets.



Scheme 1. Ligands (L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup>) used this work.

GaussSum [38] was used to calculate the fractional contributions of various groups to each molecular orbital.

#### 3. Results and discussion

#### 3.1. Synthesis and formulation

The ligands used in this work are 2-(2'-pyridylmethyleneamino)pyridine (L<sup>1</sup>), 3-(2'-pyridylmethyleneamino)pyridine (L<sup>2</sup>) and 4-(2'-pyridylmethyleneamino)pyridine (L<sup>3</sup>). They are synthesized by the condensation of pyridine-2-carboxaldehyde and aminopyridine in dry methanol (Scheme 1) in presence of molecular sieves as dehydrating agent. The ligands (L) act as *N*,N' bidentate chelating agent. The reaction between CuX and PPh<sub>3</sub> forms the tetramer [Ph<sub>3</sub>PCuX]<sub>4</sub> [39] which reacts with L in MeOH–MeCN (2:1, v/v) mixture to afford the coordination complexes of composition [Cu(L)(PPh<sub>3</sub>)X] (X = Cl (1); Br (2), I (3); L<sup>1</sup> = (a), L<sup>2</sup> = (b), L<sup>3</sup> = (c)) (Scheme 2). The compounds are non-conducting and their composition has been supported by microanalytical data. The structure has been established for **3b** by single-crystal X-ray diffraction study.

#### 3.2. Molecular structure of $[Cu(L^2)(PPh_3)I]$ (**3b**)

The molecular structure of  $[Cu(L^2)(PPh_3)I]$  is shown in Fig. 1. The bond parameters are listed in Table 2. Each discrete molecular



Fig. 1. ORTEP plot of [Cu(L<sup>2</sup>)(PPh<sub>3</sub>)I] (3b) (35% ellipsoidal probability).

unit consists of CuN<sub>2</sub>PI fragment. The atomic arrangements Cu, N(1), C(5), C(6), N(2), constitute the chelate plane (deviation <0.02 Å). Cu(I) is positioned at distorted tetrahedron centre. The pendant pyridyl ring makes a dihedral angle  $10.9(5)^{\circ}$  with chelated diimine function. The acute bite angle  $78.4(3)^{\circ}$  is extended by L<sup>2</sup> on coordination to Cu(I). The Cu–N(1)(pyridyl) (2.161(7) Å) is longer than Cu(I)–N(2) (2.084 (7) Å) distance which reflects stronger interaction of Cu(I) with N(2) compared to N(1).

The presence of I...H,  $\pi$ ... $\pi$  and C—H... $\pi$  interactions has generated a supramolecular sheet (Fig. 2). The I....H(3)—C(3) bond parameters are 3.073 Å and I....H(3)—C(3), 146.48° (symmetry: x, -1 + y, z). The heterochelate  $\pi$ ... $\pi$  interaction observed between Cg(3) (C(7)–C(8)–C(9)–C(10)–C(11)–N(3); symmetry: -x, -y, -z) and Cg(2) (C(1)–C(2)–C(3)–C(4)–C(5)–N(1); symmetry: -x, -y, -z) of 3-pyridyl ring (3.814 Å) constitutes a  $\pi$ -sheet. The C—H... $\pi$  is observed between the phenyl rings of PPh<sub>3</sub> and pyridyl ring of neighboring molecular unit enhances the strength of supramolecular union.

The molecular geometry of  $[Cu(L^2)(PPh_3)X]$  (X = Cl (**1b**), Br (**2b**) and I (**3b**)) in the gas phase singlet state have been optimized and the selected bond parameters are given in Table 2. The experimental data obtained by single crystal X-ray diffraction study is closer to the calculated metric parameters for **3b**; the bond lengths are increased by 0.01–0.07 Å and the bond angles are changing within



Scheme 2. The complexes,  $[Cu(L)(PPh_3)X]$  (where,  $L = L^1$  (1),  $L^2$  (2) and  $L^3$  (3) and X = Cl (a), Br (b) and I (c)).



**Fig. 2.** Supramolecular sheet formation through I - H (•••••),  $\pi - \pi$  (•••••) and  $C - H - \pi$  (•••••) interactions of **3b**. <sup>#</sup>The distances are as follows: C(23) - H(23) - Cg(1), 2.912 Å (Cg(1): C(1), N(1),C(5),C(6), N(2); symmetry: -x, -y, -z; C(9) - H(9) - Cg(5), 2825 Å (Cg(5): C(18) to C(23) of PPh<sub>3</sub>, symmetry: -x, y, -1/2 - z; C(20) - H(20) - Cg(6), 3.160 Å (Cg(6): C(24) to C(29) of PPh<sub>3</sub>; symmetry: 1/2 - x, -1/2 - y, z; C(20) - H(26) - Cg(4), 3.382 Å (Cg(4): C(12) to C(17) of PPh<sub>3</sub>; symmetry: x, y, z).

 $1-3^{\circ}$  limiting value. Thus close resemblance of experimental structure and theoretical data may calculate accurate frontier molecular functions to account the electronic and redox properties. This conjecture has been extended to two other complexes **1b** and **2b** whose experimental structure have not been determined. However, the spectroscopic characterization of the complexes supports the proposed structure.

#### 3.3. Spectral studies

The ligands (L) show sharp stretch at 1600–1630 cm<sup>-1</sup> due to the presence of v(C=N). In the complexes v(C=N) is shifted to lower frequency at 1590–1620 cm<sup>-1</sup> that suggests the coordination of the function to Cu(I). The  $v(PPh_3)$  appears at 600–612, 700– 725 cm<sup>-1</sup>. The solution electronic spectra of the complexes show an intense UV band ( $\in \sim 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) at 282–289 nm that is referred to the ligand centered charge transitions. A weak band is observed at 400–410 nm ( $\in \sim 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) which is characteristic to MLCT transition of tetrahedral [Cu(diimine)<sub>2</sub>]<sup>+</sup> [11] (Fig. 3). DFT and TD-DFT calculation using optimized geometry of representative complexes has assigned the transition (400– 410 nm) as admixture of MLCT (d $\pi$ (Cu)  $\rightarrow \pi$ \*(diimine)) and XLCT (I( $\pi$ )  $\rightarrow \pi$ \*(diimine)) and the UV band (282–289 nm) is ligand centered,  $\pi \rightarrow \pi$ \*, transitions. The effect of solvent polarity on the visible band is significant. The  $\lambda_{max}$ , when recorded in a series of



**Fig. 3.** Solution (in MeOH) (-) and theoretically (- - -) calculated spectra (oscillator strength vs. wavelength (nm)) of  $[Cu(L^2)(PPh_3)I]$  (**3b**).



**Fig. 4.** Solvatochromic effect on visible band of  $[Cu(L^2)(PPh_3)I]$  (**3b**) in different solvents. Inset figure is the plot of  $E_{MLCT}$  vs.  $f(D, \eta^2)$  values.  $\lambda_{max}$ (solvent, dielectric constant): (1) 404 (dimethylsulfoxide (DMSO), 47.2); (2) 407 (*N*,*N*-dimethylform-amide (DMF), 38); (3) 409 (acetonitrile (MeCN), 36.6), (4) 447 (methanol (MeOH), 32.6); (5) 452 (ethanol (EtOH), 24.3); (6) 456 (acetone, 20.7), (7) 466 (ethylene-glycolmonomethyl ether (EGME), 17); (8) 467 (dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), 9.1), (9) 645 (tetrahydrofuran (THF), 7.6), (10) 708 nm (chloroform (CHCl<sub>3</sub>), 4.9).

non-hydroxylic and hydroxylic solvents, shifts from the lower energy (higher  $\lambda$ ) to the higher energy (shorter  $\lambda$ ) with increase

Table 2

Selected bond distances (Å) and angles (°) for [Cu(L<sup>2</sup>)(PPh<sub>3</sub>)X] (for X = I (**3b**), both X-ray structure and DFT calculated data) (X = Cl (**1b**) and Br (**2b**) only DFT calculated data).

Bonds (Å)	X-ray structure (X = I), <b>3b</b>	DFT optimized (X = I), <b>3b</b>	DFT optimized (X = Br), <b>2b</b>	DFT optimized (X = Cl), <b>1b</b>
Cu(1)-N(1)	2.161(7)	2.174	2.191	2.195
Cu(1) - N(2)	2.084(7)	2.151	2.150	2.140
Cu(1) - X(1)	2.6016(11)	2.577	2.452	2.312
Cu(1) - P(1)	2.2011(19)	2.276	2.249	2.250
Angles (°)				
N(1)-Cu(1)-N(2)	78.4(3)	77.19	77.01	77.02
N(1)-Cu(1)-X(1)	107.16(18)	105.6	105.3	107.5
N(1)-Cu(1)-P(1)	114.58(19)	117.6	117.0	116.7
N(2)-Cu(1)-X(1)	111.76(18)	108.5	108.5	108.2
N(2)-Cu(1)-P(1)	124.27(19)	124.1	125.9	127.4
X(1)-Cu(1)-P(1)	114.34(6)	116.4	115.7	113.6



Fig. 5. Contour plots of  $[Cu(L^2)(PPh_3)X]$  in gas and methanol phase.

in polarity of the solvents. This implies that the polar solvents stabilize the ground state of the molecules relative to the excited state [40]. Fig. 4 shows solvatochromic effect in the visible region while the transition remains unshifted at UV region with the change of the solvent polarity. The superior solvation of the dipolar ground state (HOMO) and inferior solvation of the less dipolar excited state by the polar solvent may cause the shift of  $\lambda_{max}$ . This observation is also supported by the plot of  $E_{MLCT}$  (calculated from spectral data of different solvents) versus  $f(D, \eta^2)$  (function of dipole moment (D) and refractive index  $(\eta)$  of solvent (Fig. 4, inset) obtained from literature [40,41]). The energy shifting between Frank-Condon ground and excited states is related to the dielectric constant (D) and the refractive index  $(\eta)$  of the solvent. This is related to the difference in dipole moment of the solute in the ground and excited energy states. If the excited state dipole is greater than the ground state then the solvent effect is described as positive solvatochromism and the reverse is negative solvatochromism. Fig. 5 shows some of the molecular orbitals and their energy and composition. The HOMO-LUMO energy difference increases on moving from gas phase ( $\Delta E$  (gas phase), 2.29 eV) to methanol phase ( $\Delta E$  (methanol phase), 3.12 eV).



**Fig. 6.** Emission spectra of (a)  $[Cu(L^1)(PPh_3)Cl]$  (**1a**), (b)  $[Cu(L^1)(PPh_3)Br]$  (**2a**), (c)  $[Cu(L^1)(PPh_3)I]$  (**3a**), and (d)  $L^1$  in MeCN.

Table 3
<sup>1</sup> H NMR spectral data of L and $[Cu(L)(PPh_3)(X)]$ (X = Cl (1), Br (2), I (3)) complexes in CDCl <sub>3</sub> at 300 K.

Compd.	$\Delta (\text{ppm}) (J (\text{Hz}))$										
	2-H	3-H	4-H	5-H	6-H <sup>d</sup>	7-H <sup>s</sup>	3'-H <sup>d</sup>	$4'-H^m$	$5'-H^m$	6′-H <sup>d</sup>	PPh <sub>3</sub>
L <sup>1</sup> (Ref. [18])	-	8.75 <sup>d</sup> (7.0)	7.81 <sup>m</sup>	7.81 <sup>m</sup>	8.20 (6.5)	9.19	7.36 (7.0)	7.77	7.46	8.52 (7.0)	
L <sup>2</sup>	8.59 <sup>s</sup>	-	8.71 <sup>d</sup> (6.0)	8.48 <sup>m</sup>	8.52 (6.0)	9.29	7.38 (7.0)	7.55	7.42	8.20 (7.0)	
L <sup>3</sup>	8.26 <sup>d</sup> (7.0)	8.81 <sup>d</sup> (7.0)	-	8.81 <sup>d</sup> (7.0)	8.26 (7.0)	9.98	7.36 (7.0)	7.60	7.46	8.05 (7.0)	
$[Cu(L^1)(PPh_3)Cl]$ (1a)	-	8.84 <sup>d</sup> (7.0)	7.91 <sup>m</sup>	7.91 <sup>m</sup>	8.31 (6.0)	10.01	7.42 (7.0)	7.93	7.45	8.77 (7.0)	7.28-7.39
$[Cu(L^2)(PPh_3)Cl]$ (1b)	8.52 <sup>s</sup>		8.76 <sup>d</sup> (7.0)	7.53 <sup>m</sup>	7.89 (7.0)	10.10	7.45 (7.0)	7.83	7.41	8.80 (7.0)	7.29-7.43
$[Cu(L^3)(PPh_3)Cl]$ (1c)	7.89 <sup>d</sup>	8.41 <sup>d</sup> (7.0)	_ ```	8.41 <sup>d</sup> (7.0)	7.89 (7.0)	10.04	7.46 (6.5)	7.93	7.43	8.76 (7.0)	7.25-7.41
[Cu(L1)(PPh3)Br] ( <b>2a</b> )	-	$8.80^{d}$ (6.5)	7.91 <sup>m</sup>	7.91 <sup>m</sup>	8.29 (7.0)	9.99	7.41 (6.5)	7.90	7.47	8.74 (7.0)	7.26-7.41
$[Cu(L^2)(PPh_3)Br]$ (2b)	8.49 <sup>s</sup>	-	8.74 <sup>d</sup> (7.0)	7.50 <sup>m</sup>	7.86 (7.0)	10.08	7.45 (7.0)	7.89	7.40	8.77 (7.0)	7.27-7.42
$[Cu(L^3)(PPh_3)Br]$ (2c)	7.93 <sup>d</sup>	8.38 <sup>d</sup> (7.0)	-	8.38 <sup>d</sup> (7.0)	7.93 (6.0)	10.01	7.40 (7.0)	7.91	7.37	8.73 (6.5)	7.24-7.40
$[Cu(L^1)(PPh_3)I]$ ( <b>3a</b> )	-	8.84 <sup>d</sup> (7.0)	7.89 <sup>m</sup>	7.89 <sup>m</sup>	8.28 (7.0)	9.98	7.40 (7.0)	7.87	7.40	8.71 (7.0)	7.22-7.39
$[Cu(L^2)(PPh_3)I]$ ( <b>3b</b> )	8.50 <sup>s</sup>		8.72 <sup>d</sup> (7.0)	7.48 <sup>m</sup>	7.84 (7.0)	10.08	7.42 (6.5)	7.88	7.40	8.73 (7.0)	7.27-7.42
$[Cu(L^3)(PPh_3)I]$ (3c)	7.91 <sup>d</sup>	8.35 <sup>d</sup> (7.0)	-	8.35 <sup>d</sup> (7.0)	7.91 (6.0)	10.00	7.42 (6.5)	7.87	7.39	8.10 (6.5)	7.25-7.41

d = doublet, m = multiplet, s = singlet.



Photoluminescence study of the ligands (L) and the complexes are carried out at room temperature in CH<sub>3</sub>CN (Fig. 6). The compounds upon excitation at 280–290 nm exhibit fluorescence at 350–370 nm. Free ligands are excited at  $\pi\pi^*$  state at 291, 290, 292 nm for L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup>, respectively and emission are observed

Table 4	
Cyclic voltammetric dat	a of [Cu(L)(PPh <sub>3</sub> )X]. <sup>a</sup>

at 358, 367 and 362 nm at 298 K. The complexes [Cu(L)(PPh<sub>3</sub>)X] (1–3) show emission at ~355 nm when excited at  $\pi\pi^*$  state (complex (λ<sub>ex</sub> and λ<sub>em</sub>): **1a** (289, 359 nm); **1b** (286, 357); **1c** (282, 354); 2a (284, 360); 2b (288, 364); 2c (285, 362) 3a (288, 356); 3b (283, 353); 3c (287, 355 nm). The complexes do not show significant emission when they are excited at MLCT band maxima (>400 nm). Thus, the emission may belong to intraligand charge transfer (ILCT), ligand-to-ligand charge transfer (LLCT) transitions or mixture of them. The mechanism of fluorescence enhancement for the complexes is believed to work through photo-induced electron transfer (PET) and rigidity to chelated L in the complexes may suppress vibrational relaxation. In PET, the complex fails to fluoresce or very weakly fluoresce because the excited state is quenched by electron transfer, unless the relative energies of the fluorophore are perturbed. Heteroatom containing fluorophores develop partial charges due to internal charge transfer (ICT) and interaction with charged groups can affect its energy. It has been reported that the metal ions can enhance or quench the fluorescence emission of pyridine containing compounds [42]. In the complexes, the PET process is effectively reduced due to the presence of metal ion and  $\pi$ -acidic PPh<sub>3</sub> which also helps to populate the excited states [43]. Intersystem crossing due to spin-orbit coupling introduced by the metal centre may also influence the emission intensity. This enhances fluorescence intensity upon coordination to the metal ion.

The <sup>1</sup>H NMR spectral data are given in Table 3. The NMR characterization of  $L^1$  is known in literature [20] while  $L^2$  and  $L^3$  are new and the protons have been assigned with reference to spinspin interaction and on comparing with  $L^1$ . There are two pyridyl groups about CH=N function. Important observation is the downfield shifting of 3'-H-6'-H protons of [Cu(L)(PPh<sub>3</sub>)X] from those of

Complex	Metal redox couple <i>E</i> , $V(\Delta E_p, mV)$		Ligand redox couple <i>E</i> , $V (\Delta E_p, mV)$
	I/I <sup>-b</sup>	Cu <sup>II</sup> /Cu <sup>I</sup>	
$[Cu(L^1)(PPh_3)Cl]$ (1a)		0.51 (140)	-0.68 (140)
$[Cu(L^2)(PPh_3)Cl]$ (1b)		0.53 (150)	-0.70 (150)
$[Cu(L^3)(PPh_3)Cl]$ (1c)		0.58 (160)	-0.78 (150)
$[Cu(L^1)(PPh_3)Br]$ ( <b>2a</b> )		0.46 (160)	-0.69 (160)
$[Cu(L^2)(PPh_3)Br]$ ( <b>2b</b> )		0.50 (150)	-0.67 (150)
$[Cu(L^3)(PPh_3)Br]$ ( <b>2c</b> )		0.53 (150)	-0.74 (160)
$[Cu(L^1)(PPh_3)I]$ ( <b>3a</b> )	0.32	0.52 (160)	-0.75 (160)
$[Cu(L^2)(PPh_3)I]$ (3b)	0.35	0.58 (160)	-0.74 (150)
$[Cu(L^3)(PPh_3)I]$ ( <b>3c</b> )	0.38	0.54 (150)	-0.79 (140)

<sup>a</sup> Solvent: MeCN, Pt-disk working electrode, supporting electrolyte, [*n*Bu<sub>4</sub>](ClO<sub>4</sub>) (0.01 M); reference, SCE; solute concentration,  $10^{-3}$  M; scan rate, 0.05 V s<sup>-1</sup>;  $\Delta E_p = |E_{-pa} - E_{pc}|$ , mV;  $E_{pa} =$  anodic peak potential,  $E_{pc} =$  cathodic peak potential, V;  $E_{1/2} = 0.5(E_{pa} + E_{pc})$ .

Calculated electronic transitions and their assignment to $[Cu(L^2)(PPh_3)I]$ (3b) by TD DFT data in methanol using optimized geometry.					
Excitation energy (eV)	Wavelength (nm)	Osc. strength (f)	Key transitions		
2.2905	541.3	0.0215	(83%) HOMO $\rightarrow$ LUMO		

Excitation energy (CV)	wavelength (IIII)	Osc. strength (1)	Key transitions	Character
2.2905	541.3	0.0215	(83%) HOMO $\rightarrow$ LUMO	$Cu(d\pi)/I(p\pi) \rightarrow L(\pi^*)$
2.9696	417.5	0.0351	(87%) HOMO $-3 \rightarrow$ LUMO	$Cu(d\pi)/I(p\pi) \rightarrow L(\pi^*)$
3.6179	342.7	0.0215	(51%) HOMO $-5 \rightarrow$ LUMO	$Cu(d\pi)/L(\pi) \rightarrow L(\pi^*)$
			(22%) HOMO $-7 \rightarrow$ LUMO	$Cu(d\pi)/PPh_3(\pi) \rightarrow L(\pi^*)$
4.0799	303.9	0.2175	(73%) HOMO $-10 \rightarrow$ LUMO	$L(\pi) \rightarrow L(\pi^*)$
4.2243	293.5	0.1782	(81%) HOMO $-11 \rightarrow$ LUMO	$L(\pi) \rightarrow L(\pi^*)$

free ligand (L) data. Protons of pendant pyridyl ring 2-H to 6-H are influenced by the position of pyridyl-N at 2-/3- or 4-Py-N.

#### 3.4. Electrochemistry

Redox properties of the complexes are examined by cyclic voltammetric experiment and the electrochemical behavior of the molecules are alike. Fig. 7 shows the cyclic voltammogram of  $[Cu(L^2)(PPh_3)I]$  (**3b**) in MeCN at a Pt-disk milli electrode in the potential range +1.5 to -1.5 V versus SCE reference electrode (Table 4) at 50 mV S<sup>-1</sup> scan rate. [Cu((L)(PPh<sub>3</sub>)Cl] (**1**) and [Cu((L)(PPh<sub>3</sub>)Br] (2) show a quasireversible oxidative response at 0.5–0.6 V  $(\Delta E_p = 140-160 \text{ mV})$ . This is corresponding to Cu(II)/Cu(I) couple [44,45].  $[Cu((L)(PPh_3)I]$  (3) shows an anodic peak  $(E_{pa})$  at 0.3 V which may be assigned to  $\frac{1}{2} I_2/I^-$  couple [45] and Cu(II)/Cu(I) is observed at 0.52–0.58 V and the guasireversibility is supported by large peak-to-peak potential separation ( $\Delta E_{\rm p}$  = 140–160 mV). The complexes, [Cu(L(PPh<sub>3</sub>)X], show Cu(II)/Cu(I) couple at more positive value than oxidative response of  $[Cu(diimine)_2]^+$  [11] which may be due to the influence of coordination of strongly  $\pi$ -acidic PPh<sub>3</sub>. On scanning to -ve direction 0.0 to -1.5 V we observe an irreversible response,  $E_{pc}$  at -0.65 to -0.80 V that may be assigned to reduction of imine group  $[(-C=N-)/(-C=N-)^{-}]$  of the chelated ligands. Free ligand does not show any oxidation but irreversible reductive responses appear at <-1.0 V.

## 3.5. DFT calculation: Structure, electronic structure and redox properties

The electronic structure of  $[Cu(L^2)(PPh_3)X]$  (X = Cl (1b), Br (2b), I (3b)) has been calculated by DFT computation technique from optimized structure. The structural agreement has been observed from the comparison of bond distances and angles between calculated and X-ray determined structure of **3b** (Table 2). The orbital energies along with contributions from the ligands and metal both in gas and methanol phase are given in Supplementary table (Table S1) and surface plots of some selected MOs are given in Fig. 5 and detail are available from Supplementary material (Fig. S1). The HOMO-LUMO energy gap in gas phase is  $[Cu(L^2)(PPh_3)Cl]$  (1b), 2.52 eV; [Cu(L<sup>2</sup>)(PPh<sub>3</sub>)Br] (**2b**), 2.46 eV and [Cu(L<sup>2</sup>)(PPh<sub>3</sub>)I] (**3b**), 2.29 eV and is lower than methanol phase (1b, 3.09 eV; 2b, 3.08 eV; 3b, 3.12 eV)). This implies the blue shifting of charge transfer transition in polar medium and better stabilization of for **3b**,  $\Delta E_{\text{HOMO}} = 0.67 \text{ eV}$ ,  $(E_{\text{HOMO}}(\text{gas}) = -4.80 \text{ eV}$ ; HOMO  $E_{\text{HOMO}}(\text{methanol}) = -5.47 \text{ eV})$  than LUMO in methanol,  $\Delta E_{\text{LU-}}$  $_{MO}$  = 0.16 eV,  $E_{LUMO}$ (gas) = -2.51 eV;  $E_{LUMO}$ (methanol) = -2.35 eV) (see Supplementary materials). Gas phase composition of HOMO and HOMO–1 of **3b** carry high contribution of I (I, 76% (HOMO); 84% (HOMO-1)) and 15% (HOMO) and 12% (HOMO-1) Cu contribution. The TD-DFT calculation in methanol phase has shown that the low energy band (>400 nm) corresponds to HOMO/HOMO- $-1 \rightarrow$  LUMO which is the admixture of XLCT and MLCT (X = halide) transitions (Table 5). The oscillator strength (f) defines the probability of effective transition. The oscillator strength and wavelength plot (Fig. 3) shows high intense band at 303.9 (f, 0.2175) and

293.5 nm (*f*, 0.1782) those are assigned to the intra-ligand  $\pi \to \pi^*$  transitions of electrons localized on the azomethine group of the Schiff base, L( $\pi$ )  $\to$  L( $\pi^*$ ). Three weak bands calculated at 541.3 (*f*, 0.0215), 417.5 (*f*, 0.0351) and 342.7 nm (0.0215) are assigned to Cu/l( $\pi$ )  $\to$  L( $\pi^*$ ) transitions and because of weak intensity these transitions may not appreciably visible. The emission spectra (Fig. 6) are also originated from  $\pi\pi^*$  transition.

Chanastan

There are two oxidative responses in  $[Cu(L^2)(PPh_3)I]$  those may be assigned to  $Cu(I) \rightarrow Cu(II)$  and  $I^- \rightarrow 1/2 I_2$ . This is confirmed from the composition of HOMO and HOMO-1. The LUMO is basically made of ligand orbitals (>90%) and the reduction is explained as electron accommodation into the LUMO.

#### 4. Conclusion

Pyridyl Schiff bases of diimine family are used to synthesize copper(I)–halide complexes. The structure has been confirmed by spectroscopic data and by single crystal X-ray structure determination in one representative case. Both ligands and their complexes are emissive upon excitation at  $\pi\pi^*$  state. The cyclic voltammetric experiment shows Cu(II)/Cu(I) redox couple and reduction of diimine function. The electronic structure calculation has proved the redox activity and spectral transitions of the compounds.

#### Acknowledgments

Financial supports from the Council of Scientific and Industrial Research and University Grants Commission (under CAS programme), New Delhi are thankfully acknowledged. One of us, GS, thanks the University Grants Commission, New Delhi for sanctioning a project under minor scheme.

#### **Appendix A. Supplementary material**

Supplementary material CCDC 778766 contains the supplementary crystallographic data for the structure of [Cu(L2)(PPh3)I] (**3b**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2012.01.030.

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