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Photoluminescent mixed ligand complexes of CuX (X = Cl, Br, I) with PPh_3 and a polydentate imino-pyridyl ligand – Syntheses, structural variations and catalytic property

Anupam Ghorai, Jahangir Mondal, Goutam K. Patra*

Department of Chemistry, Guru Ghasidas Vishwavidyalaya, Bilaspur, C.G., India

HIGHLIGHTS

- Synthesis of mixed ligand copper(I) complexes of polydentate imino-pyridyl ligand.
- Characterization by elemental analysis, IR, UV-visible and ¹H NMR spectral studies.
- X-ray diffraction of complexes **1** and **2** are homo-dinuclear species.
- Complex **3** is a *zig-zag* 1-D polymer.
- All the complexes worked as effective catalyst for synthesis of 2-substituted benzoxazoles.

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Three ternary copper(I) complexes $[Cu^1_2Cl_2(L^1)(PPh_3)_4]$ (1), $[Cu^1_2Br_2(L^1)(PPh_3)_4]$ (2) and $[Cu^1_2(\mu-I)_2(\mu-L^1)(PPh_3)_2]_n$ (3) have been prepared by reactions of CuX (X = Cl, Br and I) with PPh₃ and the polydentate imino-pyridyl ligand L¹. From single crystal structural analysis it has been found that complexes 1 and 2 are homo-dinuclear whereas complex 3 is a 1-D *zig-zag* polymer. All complexes function as effective catalysts for synthesis of 2-substituted benzoxazoles.



ABSTRACT

Three ternary copper(I) complexes $[Cu_2^1Cl_2(L^1)(PPh_3)_4]$ (1), $[Cu_2^1Br_2(L^1) (PPh_3)_4]$ (2) and $[Cu_2^1(\mu-I)_2 (\mu-L^1) (PPh_3)_2]_n$ (3) have been prepared by reactions of CuX (X = Cl, Br and I) with PPh₃ and the polydentate imino-pyridyl ligand L¹. These complexes have been characterized by elemental analysis, IR, UV–Vis, NMR and X-ray crystallography. From single crystal structural analysis it has been found that complexes 1 and 2 are homo-dinuclear having non-bridging halide ions whereas complex 3 is a 1-D *zig-zag* co-ordination polymer containing bridged iodide ions. Complexes 1, 2 and 3 are photoluminescent at room temperature in chloroform whereas ligand L¹ is non-emissive. The E_{i_2} values of the Cu^I–Cu^{II} couple of 1, 2 and 3 are 0.98 V, 0.92 V and 0.42 V respectively (vs Ag/AgCl in 1 M KCl, scan rate 100 mV s⁻¹). All three complexes function as effective catalysts for the synthesis of 2-substituted benzoxazoles.

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* Corresponding author. Tel.: +91 7587312992. E-mail address: patra29in@yahoo.co.in (G.K. Patra). MOLECULAR



Introduction

Studies of copper(I) complexes with mixed ligand systems containing triphenylphosphine and ligands having S and N donors, have been increasing because of the flexibility of these ligands and the different steric characteristics of the phosphine ligands, which can modify the compound geometry [1]. The length of the ligand moiety has also a great influence on the architectures of the metal complexes [2].

The attention in the coordination chemistry of copper(I) derivatives containing polydentate imino-pyridyl Schiff-base ligands is rapidly growing because of their rich photophysical properties [3], intriguing structures [4], and varied application in metallosupramolecular helicates [5]. Metal complexes bearing these ligands have biochemical, analytical, antimicrobial, antifungal, antitumor, therapeutic, herbicidal and industrial applications [6]. They are also useful as ionophores in ion-selective electrode studies [7].

Copper(I) complexes have been widely studied because of providing suitable models for the representation of several enzymatic sites as well as active intermediates in organic synthesis [8]. The copper(I) complexes show unusually diverse geometries and stoichiometries because of the relatively small energy difference between the various polymorphs depending on synthetic conditions such as ligand, anion and solvent [9]. As a part of our ongoing efforts [10], in preparing interesting materials of Cu(I) with various novel polydentate imio-pyridyl ligands we have synthesised three mixed ligand copper(I) complexes $[Cu_2^lCl_2(L^1)(PPh_3)_4]$ (1), $[Cu_2^IBr_2(L^1) (PPh_3)_4]$ (2) and $[Cu_2^I(\mu-I)_2 (\mu-L^1) (PPh_3)_2]_n$ (3) of triphenylphosphine and polydentate imino-pyridyl ligand L¹ (Scheme 1). We have examined the structural diversity, photo-physical, electrochemical properties and catalytic activity (for the synthesis of 2-substituted benzoxazole) of the ternary complexes 1, 2 and 3. The influence of halide ion in the nuclearity and bonding in the mixed ligand complexes described here is not common in the literature [11,12].

Experimental section

Materials and physical measurements

All chemicals used in this study were purchased from Aldrich chemical company, USA and Acros chemical company, USA and used without further purification unless otherwise mentioned. Tetrabutyl ammonium perchlorate (TBAP) used for electrochemical work is prepared as reported in the literature [13]. Methanol is purified using the established method [14]. The melting point was determined by an electro-thermal IA9000 series digital melting point apparatus and is uncorrected. Microanalyses were carried out using a Perkin–Elmer 2400II elemental analyzer. Infrared (IR) spectra and solution electronic spectra were recorded on Nicolet Magna-IR (Series II) and Shimadzu UV-160A spectrophotometers respectively. ¹H NMR, ¹³C and ³¹P NMR and Electrospray ionization mass (ESI-MS) measurements were made using a Bruker Advance 400 MHz NMR spectrometer and Finnigan LCQ Decaxp MAX mass



Scheme 1. Ligand system used in the study.

spectrometer respectively. X-ray powder patterns are collected on a Philips PW-1710 automated diffractometer. Fluorescence spectra were recorded on a Perkin Elmer LS55 Luminescence Spectrometer. Voltammetry has been carried out in Electrochemical Work Station of BAS, Epsilon model. The measurements have been carried out at 293 K in dichloromethane solutions containing 0.2 M TBAP as supporting 10^{-3} - 10^{-4} M electrolyte.

Synthesis of ligand L¹

1,8-Diaminooctane (0.145 g, 1 mmol) was dissolved in methanol (15 ml) and solution anhydrous to this 4-pyridinecarboxaldehyde (0.215 g, 2 mmol) was added. The reaction mixture was heated under reflux for 4 h. Then it was gradually cooled to room temperature. The solid that formed was recrystallized from methanol. Yield, 0.225 (70%); mp 120 °C. ¹H NMR (200 MHz, CDCl₃, TMS): § 8.67 (d, 4H), 8.25 (s, 2H), 7.58 (d, 4H), 3.62 (t, 4H), 1.69 (t, 4H), 1.36 (s, 8H). ¹³C NMR (200 MHz, CDCl₃, TMS): δ 159.18, 149.41, 148.59, 56.90, 31.83, 29.27, 26.63. FTIR/cm⁻¹ (KBr): 2932(w), 2902(w), 1979(w), 1642(vs), 1597(s), 1556(s), 1466(m), 1419(s), 1389(w), 1325(s), 1283(s), 1230(s), 1064(m), 1037(m), 954(w), 850(m), 822(s), 723(s), 641(vs), 523(s). ESI MS: 323.45 (LH⁺, 100%). Anal. Calc. for C₂₀H₂₆N₄: C, 74.50; H, 8.13; N, 17.38. Found C, 74.55; H, 8.09; N, 17.39%. UV-VIS: λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$)(CH₃OH): 251 (38,600); 280 (23,450).

Synthesis of $[Cu_2^I Cl_2(L^1) (PPh_3)_4]$ (**1**)

PPh₃ (0.066 g, 0.25 mmol) was added to a solution of copper(I) chloride (0.025 g, 0.25 mmol) in 15 ml CH₃CN, followed by stirring for 1 h. A colourless precipitate formed, to which the ligand L^1 (0.081 g, 0.25 mmol) and CHCl₃ (3 ml) were added. The mixture was stirred for 10 min. Yellow coloured compound appeared. It was filtered and dried in air. Single crystals were obtained by slow diffusion of hexane to the dilute solution of the compound in dichloromethane. Yield, 0.121 g (62%). FTIRcm⁻¹ (KBr): 3049(m), 2925(m), 2845(w), 2369(w), 1633(m), 1599(m), 1474(s), 1429(vs), 1316(w), 1089(s), 1022(m), 829(m), 750(vs), 693(vs), 512(vs), 409(w). Anal. found (calc. for [Cu¹₂Cl₂(L¹) (PPh₃)4]: C, 70.40 (70.48%); H, 5.52 (5.53%); N, 3.57 (3.58%), Cu, 8.09 (8.04%).

Synthesis of $[Cu_2^I Br_2(L^1)(PPh_3)_4]$ (2)

PPh₃ (0.066 g, 0.25 mmol) was added to a solution of copper(I) bromide (0.036 g, 0.25 mmol) in 15 ml CH₃CN, followed by stirring for 1 h. A colourless precipitate formed, to which the ligand L¹ (0.081 g, 0.25 mmol) and CHCl₃ (10 ml) were added. The mixture was stirred for 30 min. Yellow coloured compound appeared. It was filtered and dried in air. Single crystals were obtained by slow diffusion of hexane to the dilute solution of the compound in chloroform. Yield, 0.118 g (57%). FTIR (KBr pellet, cm⁻¹): 3049(m), 2928(m), 2845(w), 2369(w), 1633(m), 1609(m), 1476(s), 1429(vs), 1316(w), 1089(s), 1022(m), 829(m), 756(vs), 693(vs), 512(vs), 409(w). Anal. found (calc. for [Cu¹₂Br₂(L¹)(PPh₃)₄]: C, 66.63 (66.64%); H, 5.23 (5.22%); N, 3.38 (3.39%), Cu, 7.66 (7.67%). UV–Vis: (CH₂Cl₂) [λ_{max} , nm]: 402, 390.

Synthesis of $[Cu_{2}^{I}(\mu-I)_{2}(\mu-L^{1})(PPh_{3})_{2}](3)$

To a solution of triphenylphosphine (0.262 g, 1 mmol) in CH₃CN (50 ml), solid cuprous iodide (0.19 g, 1 mmol) was added. The reaction mixture was stirred for 1 h to obtain a white turbid solution. Then the ligand L^1 (0.322 g, 1 mmol) in 20 ml CHCl₃ was added drop-wise with constant stirring at room temperature to give a clear yellowish solution. Then the reaction mixture was stirred

additionally for 1 h. Bright yellow needle shaped crystals, suitable for X-ray analysis were obtained by slow evaporation of the solution after 2 days. Yield 0.420 g (68%). ¹H NMR (200 MHz, CDCl₃, TMS): δ 8.72 (d, 4H), 8.22 (s, 2H), 7.55–7.48 (m, 8H), 7.37–7.28 (m, 15H), 3.64 (t, 4H), 1.72 (t, 4H), 1.34 (s, 8H). ³¹P NMR (200 MHz, CDCl₃, TMS): δ –8.06. FTIRcm⁻¹ (KBr): 3078(w), 2924(w), 2833(w), 2333(w), 2179(vw), 1988(w),1637(w), 1590(w), 1487(m), 1448(m), 1077(m), 820(m), 743(s), 691(vs), 513(s), 486(s), 397(w). UV–Vis (CH₂Cl₂) [λ _{max}, nm]: 402, 396. *Anal.* Calc. For C₅₆H₅₆Cu₂I₂N₄P₂: C, 54.78; H, 4.60; N, 4.56; Found C, 54.84; H, 4.53; N, 4.62%.

X-ray crystallography

X-ray single crystal data were collected using Mo K α ($\lambda = 0.7107$ Å) radiation on a BRUKER APEX II diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution/refinement were carried out using the software package of SMART APEX [15]. The structures were solved by direct methods (*SHELXS-97*) and standard Fourier techniques, and refined on *F2* using full matrix least squares procedures (*SHELXL-97*) using the *SHELX-97* package [16] incorporated in *WinGX* [17]. In most of the cases, non-hydrogen atoms were treated anisotropically. Hydrogen atoms were fixed geometrically at their calculated positions following riding atom model. The crystallographic details of **1–3** are listed in Table 2.

Results and discussion

Synthetic aspects

The Schiff-base ligand L^1 was prepared in good yield by the condensation of 1,8-diamino octane with 4-pyridine carboxaldehyde in dry methanol. Reactions of CuX (X = Cl, Br, I) with PPh₃ and the ligand L^1 in a molar ratio 1:1:1 in room temperature yielded

Table 1

X-ray cystallographic data for 1-3.

Compound	1	2	3
Formula	C ₉₂ H ₈₆ Cl ₂ Cu ₂ N ₄ P ₄	C ₉₂ H ₈₆ Br ₂ Cu ₂ N ₄ P ₄	$C_{56}H_{58}Cu_2I_2N_4P_2O$
Formula weight	1569.51	1658.43	1237
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1 (No. 2)	P-1 (No. 2)	P-1 (No. 2)
a (Å)	11.2646(4)	11.3929(4)	9.416(10)
b (Å)	13.6155(6)	13.4511(5)	13.109(13)
c (Å)	13.6231(5)	13.6332(5)	14.79(2)
α (°)	83.69(0)	83.48(0)	107.65(3)
β (°)	84.52(0)	73.4	100.19(3)
γ (°)	72.77(0)	86.04(0)	106.91(2)
V (Å ³)	1979.17(25)	1987.73(18)	4014(3)
Ζ	1	1	1
D(calc) (g/cm ³)	1.31675	1.38536	1.434
μ(Mo Kα) (/mm)	1.670	1.670	1.392
F(000)	818	854	1742
Temperature (K)	293	293	293
Radiation (Å) Mo Kα	0.71073	0.71073	0.71073
Theta min-max (°)	2.27, 27.50	2.29, 27.50	1.3, 24.9
Total data	15,521	15,831	26,224
Unique data	8764	8811	12,827
R(int)	0.0363	0.0335	0.111
Observed data [I > 2.0 sigma(I)]	7033	7150	5490
Nref	8764	8811	9131
Npar	469	469	469
R	0.0481	0.0447	0.0671
wR ²	0.1232	0.1125	0.2004
S	1.036	1.045	0.97

Table 2

Selected bond distance (Å) and bond angles (°) for the complexes 1-3.

Compound 1			
Bond distance in Å			
Cu1–N1	2.094(2)	Cu1—P2	2.2516(8)
Cu1—P1	2.2496(8)	Cu1–Cl1	2.3248(7)
Bond angles (°)			
N1-Cu1-P1	110.59(7)	N1-Cu1-Cl1	101.63(7)
N1-Cu1-P2	104.11(7)	P1—Cu1—Cl1	101.35(3)
P1—Cu1—P2	124.38(3)	P2-Cu1-Cl1	112.70(3)
Compound 2			
Bond distance in Å			
Br1–Cu1	2.4534(5)	Cu1—P1	2.2573(8)
Cu1–N1	2.095(2)	Cu1—P2	2.2603(9)
Bond angles (°)			
N1-Cu1-P1	103.97(7)	N1-Cu1-Br1	102.20(7)
N1-Cu1-P2	110.95(7)	P1-Cu1-Br1	113.49(3)
P1—Cu1—P2	123.84(3)	P2-Cu1-Br1	100.59(3)
N1-Cu1-P1	103.97(7)	N1-Cu1-Br1	102.20(7)
N1-Cu1-P2	110.95(7)	P1—Cu1—Br1	113.49(3)
P1—Cu1—P2	123.84(3)	P2-Cu1-Br1	100.59(3)
Compound 3			
Bond distance in Å			
N1-Cu1	2.05(2)	Cu1—I1	2.641(3)
P4—Cu1	2.223(6)	Cu1—I1*	2.679(3)
Bond angles (°)			
N1-Cu1-P4	116.8(5)	Cu1—I1—Cu1	67.69(7)
N1-Cu1-I1	103.6(4)	C13-N1-C17	117(2)
P4-Cu1-I1	112.0(4)	C13-N1-C1	119(1)
P4-Cu1-I1	108.8(1)	C17-N1-Cu1	123(1)
I1—Cu1—I1	112.31(8)		

the homo-dinuclear complexes **1** and **2** and a copper(1) polymer **3**. The synthetic procedures for **1**, **2** and **3** are given in Scheme 2. All the complexes are air-stable in solid state for at least 10 weeks. The stability of the dissolved complexes depends on the nature of the solvent. In dicholoromethane and chloroform the dissolved complexes are more stable than dissolved in acetonitrile and dimethyl formamide.

NMR and IR spectral studies

The ¹H NMR spectra of the ligand **L**¹ in CDCl₃ gives a singlet at δ 8.25 ppm which we assign as (HC=N) proton. The aryl protons resonate at δ ; 8.67–7.58 ppm and the methylene protons resonate at 3.62, 1.69 and 1.36 ppm respectively. In complex **2**, these protons resonate at δ ; 8.22, 8.72–7.48, 3.64, 1.72 and 1.34 ppm respectively; and in the ³¹P NMR, the P atoms appear at δ ; 8.71, 8.22, 7.55–7.48, 7.35–7.26, 3.64, 1.72 and 1.34 ppm; and in the ³¹P NMR, the P atoms resonate at δ ; 8.71, 8.22, 7.55–7.48, 7.35–7.26, 3.64, 1.72 and 1.34 ppm; and in the ³¹P NMR, the P atom appears at δ ; -8.05 ppm. The appearance of single signal in the ³¹P NMR spectrum in **2** and **3** indicate the stability of the structures in the solution state.

The complexation processes of the ligands have been monitored by IR spectroscopy. The IR spectrum of the ligand L^1 shows characteristic bands at 1642 and 1597 cm⁻¹ which we assign to the pyridine ring and imine C=N stretching frequencies. For complexes **1**, **2** and **3** these bands appear at 1599 and 1474 cm⁻¹; 1609 and 1476 cm⁻¹; and 1637 and 1590 cm⁻¹ respectively.

Crystal structure of 1

It crystallized in the triclinic *P*-1(2) space group. The two Cu(I) ions are bridged by one imino-pyridyl Schiff base ligand, L^1 forming a homo-dinuclear inversion symmetric copper(I) complex. Each Cu^I cation is tetracoordinated by one pyridyl nitrogen atom of the ligand L^1 , two phosphorous atoms of the PPh₃ ligand and one chloride ion in distorted tetrahedral geometry (Fig. 1). The Cu–Cl distance is 2.325(7) Å. The other bond distances are Cu–N = 2.094(2) Å,



Scheme 2. Synthetic route of the complexes 1, 2 and 3.



Fig. 1. The molecular structure of 1, showing 50% probability displacement ellipsoids.

Cu—P1 = 2.250(8) Å, Cu—P2 = 2.252(8) Å respectively. The main bond angles are N—Cu—P1 = 110.59(7)°, N—Cu—P2 = 104.11(7)°, P1—Cu—P2 = 124.38(3)° and N—Cu—Cl1 = 101.63(7)° respectively. The Cl—Cu—P1 and Cl—Cu—P2 bond angles are 101.35(3)° and 111.70(3)°. In this molecule there is no intermolecular hydrogen bonding. The molecular structure of **1** is shown in Fig. 1. The supramolecular association of compound **1** through C—H···Cl interaction and the supramolecular arrangement with $\pi \cdots \pi$ stacking in **1** are given in Figs. 2 and 3 respectively.

Crystal structure of 2

It crystallized in the triclinic *P*-1(2) space group. The three phospho rus-bound (atom P1) benzene rings make dihedral angles



Fig. 2. Supramolecular association of compound 1 through C–H. Cl interaction.



Fig. 3. The supramolecular arrangement in **1** with $\pi \cdots \pi$ stacking.

of 67.2(3)°, 81.5(2)° and 71.9(3)° with each other. The coordination number in all Cu atoms is four with a distorted tetrahedral geometry. Cu is coordinated by one nitrogen atom Cu1—N = 2.095(2) Å; one bromine atom [Cu1—Br = 2.453(5) Å] and two phosphorus atoms [Cu1—P1 = 2.257(8) and Cu1—P2 = 2.260(9) Å]. The main bond angles are N1—Cu—P1 = 103.97(7)°, N1—Cu—P2 = 110.95 (7)°, P1—Cu—P2 = 123.8(3)° and N1—Cu—Br1 = 102.20(7)° respectively. The Br—Cu—P1 and Br—Cu—P2 bond angles are 113.49(3)° and 100.59 (3)° comparable to the bond angles observed in **1**. The molecular structure of **2** is shown in Fig. 4. The supramolecular arrangement in 2 with $\pi \cdots \pi$ stacking is given in Fig. 5.

Crystal structure of 3

Compound **3** crystallized in triclinic *P*^T space group. Analysis of single crystal crystallography of **3**, has revealed that the complex is a neutral compound that consists of $(PPh_3)_2Cu_2(\mu-I)_2$ units (Fig. 6) bridged by the ligand **L**¹ to construct an infinite *zig-zag* chain architecture (Fig. 6). 1D coordination polymer of Cu¹ in **3** comprises of triphenylphosphine (TPP), Schiff base **L**¹ and bridged iodide ion. The symmetry related Cu¹ centers have tetrahedral coordination geometries where each center is coordinated to nitrogen of one

ligand, L^1 , phosphorous of triphenylphosphine and two bridging iodides forming CuNPI₂ chromophore. Cu—N bond length is 2.054(6). The degree of distortion from the ideal tetrahedral geometry of Cu¹ centers are reflected in the bond angles, 102.0(4)– 116.8(4)°.

Photophysical studies

Organic–inorganic hybrid Cu(I) coordination complexes have been investigated for fluorescence properties because of their potential applications as luminescence materials, light-emitting diodes (LEDs) and sensors [18,19]. Because of the higher thermal stability of organic–inorganic coordination polymers and the capacity to influence the emission wavelength of organic materials, syntheses of organic–inorganic coordination polymers by the rational design of conjugated organic spacers and metal centers can be an efficient method for obtaining new types of electroluminescence materials, especially for d¹⁰ systems [20,21]. The photoluminescence properties of the ligand L^1 and complexes 1–3 in chloroform at room temperature were studied. It has been found that ligand L^1 is non-emissive whereas complexes 1, 2 and 3 show structured emission bands on exciting at 300–330 nm. These



Fig. 4. The molecular structure of 2 showing 50% probability displacement ellipsoids for non-H atoms.



Fig. 5. The supramolecular arrangement in **2** with $\pi \cdots \pi$ stacking.

emission spectroscopic data are given in Table 3. The emission spectra of complexes 2 and 3 are given in Fig. 7. The emission properties of the three complexes are almost similar in nature. It may be assigned to copper(I) to ligand, L^1 charge transfer (MLCT).

Electrochemistry

The electrochemical properties of copper(I) complexes **1**, **2** and **3** have been studied by cyclic voltammetry in dichloromethane using a glassy carbon electrode under dry nitrogen atmosphere. It has been found that all the complexes show quasi-reversible voltammograms. For complexes **1** and **2**, single Cu^I–Cu^{II} couple, occur at $E_{V_2} = 0.98$ V and $E_{V_2} = 0.92$ V respectively (vs Ag/AgCl in 1 M KCl, scan rate 100 mV s⁻¹) Fig. 7. The ΔE_p values are 200 mV and 210 mV respectively for the complexes **1** and **2**. Complex **3** also shows quasi-reversible voltammogram of a single Cu^I–Cu^{II} couple

occurring at $E_{\frac{1}{2}}$ = 0.42 V, vs Ag/AgCl in 1 M KCl, scan rate 100 mV s⁻¹. The ΔE_p value for **3** is 220 mV (at scan rate 100 mV s⁻¹) (see Fig. 8).

Catalytic activity

1,3-Benzoxazoles are very important because of their biological activities like anti-rheumatic effects [22], H37Rv inhibition [23], elastase inhibition [24], 5HT3 receptor agonistic activity [25], and cytotoxicity toward P338cell [26]. These can also be used as precursors for chemosensors [27]. There are some previously reported catalysts for the synthesis of 2-substitued 1,3-benzoxazoles [28–31]. But use of Schiff-base complex as catalyst for the synthesis of 1,3-benzoxazoles was unprecedented to the best of our knowledge. Herein, we are reporting the catalytic activity of the



Fig. 6. The molecular structure of 3 showing 50% probability displacement ellipsoids (inset: 1-D zig zag polymeric view of 3).

Table 3

Luminescence properties of L^1 and the complexes 1--3 in the CHCl_3 solution, λ_{ex} = 300 nm.

Compd.	Emission maxima (λ_{em})	Compd.	Emission maxima (λ_{em})
L ¹	No emission	1	408, 430, 460
2	410, 432, 460	3	410, 435, 463

 λ_{ex} = excitation wave length.



Fig. 7. Emission spectra of **1** (green), **2** (blue line) and **3** (black line) and in CHCl₃ at room temperature on excitation at 300 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ternary complexes of copper(I) halides **1**, **2** and **3** for the first time in the synthesis of 2-substituted 1,3-benzoxazoles (**1a**, **1b** and **1c**).

Complexes 1–3 have been found promising for the condensation of benzaldehyde/its bromo and chloro derivatives with o-aminophenol. The effect of 1, 2 and 3 as catalysts for the synthesis of 2-phenyl-1,3 benzoxazoles was investigated and it was found that the reactions worked well in affording the corresponding benzoxazoles in moderate to good yields. The catalytic responses of the three catalysts were investigated in solution. In this protocol we report the catalytic efficiency of these complexes under mild and environmental friendly conditions and thus all the reactions were carried out at room temperature using methanol (a non-toxic



Fig. 8. Cyclic voltammogram for **1** in CH₂Cl₂/0.1 M Bu₄NClO₄ at the scan rate of 100 mV s⁻¹. Inset, cyclic voltammogram for **3** in CH₂Cl₂/0.1 M Bu₄NClO₄ at the scan rate of 100 mV s⁻¹.

solvent). It was observed that no further increase in the yield of the product occurred even when the reaction time was increased (4 h).

The efficiency of these catalysts **1–3**, having various structural diversities (due to different anions) is different. Copper(I) complex **3** (with bridged I[–] anion) shows greater activity than the other two complexes **1** and **2**, (with Cl[–], Br[–] as anions) and the percentage of yield for complex **3** reached up to 55–76% (Table 4). It was also found that the catalytic activity of these complexes decreases in the order of I[–] > Cl[–] \approx Br– as their counter anions. These results could be attributed to the self-repeating unit of ligand in polymeric complex **1**, having infinite number of azo-methine groups, which might be the key factor for the complexes to exhibit the catalytic property.

The reaction in general is simple enough as the solid products were purified by recrystallization from ethanol. Tedious purification by column chromatography was thus avoided in this protocol. The pure isolated products were then characterized by their melting points which were consistent with those described in the literature (the corresponding references were given in Table 4). Further these compounds were characterized by UV–Vis and NMR spectroscopy.

Table 4		
Synthesis	of 2-aryl	1,3-benzoxazole

Entry	Ar—CHO	Time (min)	Product	Complex	Yield (%)	Melting point °C		Ref.
						Observed	Reported	
1.		30	1a	1	48	110-113	112-114	[32]
				2	52			
				3	55			
2.		27	1b	1	62	129-131	130-131	[33]
				2	63			
				3	68			
3.		22	1c	1	69	113-116	114-116	[32]
				2	69			
				3	76			

Conclusions

Herein we have reported three new ternary copper(I) complexes $[Cu_{2}^{l}Cl_{2}(L^{1})(PPh_{3})_{4}]$ (1), $[Cu_{2}^{l}Br_{2}(L^{1})(PPh_{3})_{4}]$ (2) and $[Cu_{2}^{l}(\mu-I)_{2}(\mu-L^{1})]$ $(PPh_3)_2]_n$ (**3**) bearing a novel polydentate imino-pyridyl ligand L¹ and triphenylphosphine. From single crystal X-ray analysis it has been found that complexes **1** and **2** are homo-dinuclear species whereas **3** is 1-D *zig-zag* polymer, containing bridged iodide and ligand, L^1 . We have shown that mere changing of the anion in CuX (X = Cl, Br and I) at the same reaction condition, changes the nuclearity and coordination of mixed ligand complexes drastically. These complexes 1, 2 and 3 have been successfully employed as catalysts for the synthesis of 2-substituted 1,3-benzoxazoles. Both the phenomena - the change in nuclearity in the ternary complexes by simple change of the anion, and the application of the mixed ligand complexes as catalysts for the synthesis of 1,3-benzoxazoles are not common in the literature.

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Appendix A. Supplementary material

UV-Vis and NMR characterizations of 1,3-benzoxazoles have been given as the supplementary data. CCDC reference numbers of the complexes 1-3 are 1027697, 1027696 and 860659 respectively. These data can be obtained free of charge via http://www. ccdc.cam.ac.uk/conts/retrieving.html. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2015.05.010.

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