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Synthesis, structure, photophysical and catalytic properties of Cu^{I}–Iodide complexes of di-imine ligands

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ABSTRACT

Two new multifunctional $Cu^{I}I$ based complexes $[CuI(L^{1})]$ **(1)** and $[Cu_2(\mu\text{-}I)_2(L^{2})]$ **(2)** with bidentate N–N donor ligands $\mathbf{L^1}$ and imino-pyridyl ligand $\mathbf{L^2}$ have been synthesized and characterized by elemental analysis, IR, UV–Vis, NMR and single crystal X-ray crystallography. The bidentate di-imine ligand ($\mathbf{L^1}$) forms monomeric Cu^{I} complex (**1**) whereas the bis-bidentate di-imine ligand ($\mathbf{L^2}$) favours the formation of dimeric Cu^{I} complex (**2**) in association with two bridging iodides. Structural analysis reveals that in complex **1** each monomeric units are connected by $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions to form 3D supramolecular structure whereas in complex **2** each molecules are connected by only $\pi\cdots\pi$ interactions to form 3D supramolecular structure. The photoluminescence properties of the complexes have been studied at room temperature. Theoretical analysis shows that HOMO is focused on the Cu and iodides while LUMO is focused on di-imine ligands and the luminescence behaviour arises due to metal to ligand charge transfer (MLCT) and halide to ligand charge transfer (XLCT). The complexes **1** and **2** are effective catalysts for the synthesis of 2-substituted benzoxazoles.

1. Introduction

Luminescent materials have attracted considerable attention for their numerous potential applications in solar energy conversion [1,2], luminescence-based sensors [3,4], organic light emitting diodes (OLEDs) [5–8] and biological labelling [9–11]. Monovalent group 11 metal ions, Au^{I}, Ag^{I}, and Cu^{I}, are well known for their interesting emissive properties [12]. Among these metal ions Cu^{I} is inexpensive and abundant and thus the synthesis and study of mono-/ploy-nuclear Cu^{I} complexes with di-imine ligands have become an important area of current research [13]. The judicious selection of N–N chelating ligands is the key point to control and tune the structure and luminescence properties [14–16]. The ancillary ligands such as halide and phosphine also have great effects on the emissive properties of the Cu^{I}-complexes [17–21]. Several excited states such as metal-centered transitions, intra-ligand transitions, and charge-transfer (CT) transitions between metal and ligands exist as emissive states, depending on the ligands and steric factors [22].

The largest class of luminescent Cu^{I} complexes has been investigated to date is that of $[Cu(N\text{–}N)_2]^{+}$, where N–N indicates a chelating ligand and the luminescence property of such complexes originates due to metal to ligand charge transfer (MLCT) [23–26]. In addition to the monomeric complexes, it has been noticed that the presence of halides favours the formation of polynuclear complexes with μ2-, μ3-, or μ4-bridging halide atoms, and their structures are also dependent on chelating ligand along with their synthetic procedure [27–31]. A number of complexes with a $\{Cu^{I}_2(\mu\text{-}I_2)\}$ unit have been prepared with various ligands and most of them possess a planar diamond core [32,33]. Studies on these complexes show that luminescence originates from $\{Cu^{I}_2(\mu\text{-}I_2)\}$ core to ligand charge transfer (MLCT) excited state, which is critical to the rigidity of the ligand.

In addition to this photophysical property, Cu(I) complexes are well-known for their catalytic properties. There are few examples in which Cu(I)-complexes act as efficient catalyst. G. Attilio Ardizzoia et al. have reported the catalytic cyclopropanation reactions of four Cu(I)-based complexes [34]. In another case, S. S. Chavan et al. have reported that the Cu(I)-complexes act as effective catalyst for the amination of aryl halides [35].

Herein, we have designed two different di-imine ligands; one is bidentate ($\mathbf{L^1}$) and the other is bis-bidentate ($\mathbf{L^2}$) and synthesized their Cu(I) complexes, **1** and **2** exploiting Cu(I)-iodides. Both the complexes are characterized by elemental analysis, IR, UV–Vis and

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single crystal X-ray crystallography. The bidentate ligand ($\mathbf{L^1}$) forms the monomeric Cu^I complex (**1**) while the *bis*-bidentate ligand ($\mathbf{L^2}$) favours the formation of dimeric complex (**2**) with very short Cu–Cu bond (2.486 Å) (Scheme 1). In complex **1**, metal ions shows trigonal geometry while in complex **2** each metal ions show tetrahedral geometry. In **2**, the dimer formation is favoured by μ-2 bridging of iodides. Supramolecular $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions connect each monomeric units in **1** to form 3D supramolecular structure. And in **2**, each molecules are connected by supramolecular $\pi\cdots\pi$ interactions to form 3D supramolecular structure. The photoluminescence and catalytic properties of the complexes have been studied. However, as far we know, this is the first report of multifunctional properties of Cu(I)-complexes.

2. Experimental

2.1. Materials and measurements

All the reagents were procured commercially from Aldrich and used without further purification. Microanalyses were performed by Perkin–Elmer 2400II elemental analyzer. The melting point (mp) was determined by an electro-thermal IA9000 series digital melting point apparatus and is uncorrected. IR spectra (KBr disc) were recorded on a Nicolet Magna-IR spectrophotometer (Series II), UV–Vis spectra on a Shimadzu UV-160A spectrophotometer, ^{1}H and ^{13}C NMR spectra by a Brucker DPX200 spectrometer, EI mass spectra on a VG Autospec M–250 instrument. Photoluminescence spectra were recorded on a Perkin Elmer LS55 Luminescence Spectrometer.

2.2. Synthesis of ligands

2.2.1. Synthesis of ligand $\boldsymbol{L^1}$

3.45 g (15 mmol) of 1- pyrenecarboxaldehyde was dissolved in 100 ml of anhydrous methanol. To this light yellowish solution 0.625 ml (7.5 mmol) of freshly distilled 1,2-diaminopropane was added drop-wise with stirring. Then, the reaction mixture was allowed to reflux for 6 h, maintaining dry conditions. The solvent was evaporated under reduced pressure to obtain a yellow solid. It was thoroughly washed with methanol. Yield: 2.615 g (70%); mp: 202–205 °C. Anal. calc. for $C_{37}H_{26}N_2$: C, 89.19 (89.13); H, 5.20 (5.25); N, 5.66 (5.62)%. EI-MS: 499.6 (M^+, 85%). FTIR/cm^{-1} (KBr): 1637(s), 1583(s), 843(vs), 829(m), 759(m), 716(vs), 682(m), 610(m). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.81 (d, 1H), 9.51 (s, 1H), 9.42 (s, 1H), 8.71 (dd, 2H), 8.52 (dd, 2H), 8.36 (m, 2H), 8.22 (m, 4H), 8.13 (m, 4H), 7.90 (m, 4H), 7.60 (dd, 2H), 1.65 (s, 3H, methyl protons). UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH_3OH): 288 (27 500 260), 363 (10 250).

2.2.2. Synthesis of ligand $\boldsymbol{L^2}$

2.36 g (15 mmol) of 2-quinolinecarboxaldehyde was dissolved in 100 ml of anhydrous methanol. To this yellowish solution 0.5 ml (7.5 mmol) of freshly distilled ethylene diamine was added drop-wise with stirring. Then, the reaction mixture was allowed to reflux for 6 h, maintaining dry conditions. The solvent was evaporated under reduced pressure to obtain a yellow semi-solid, which on re-crystallization from diethyl ether gave yellow crystalline solid. Yield: 1.75 g (69%); mp: 128–130 °C. Anal. found (calc. for $C_{22}H_{18}N_4$): C, 77.65 (78.07); H, 5.37 (5.36); N, 16.65 (16.56)%. EI-MS: 338.1 (M^+, 84%); 181.1 ($M^+ - C_{10}H_6NO$, 25%); 169.1 ($M^+/2$, 98%). FTIR/cm^{-1} (KBr): 3451(vb), 3050 (m), 2890 (m), 1642(vs) (C=N), 1592(vs), 1557(s), 1500(vs), 1461(s), 1432(s), 1382(m), 1321(w), 1280(s), 1206(m), 1142 (m), 1108(s), 1030(s), 1015(w), 971(s), 941(m), 893(s), 868(s), 840(vs), 748(vs), 619(m), 492(m). ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 8.63 (s, 2H), 8.17 (s, 4H), 8.11 (d, $J = 4$ Hz, 2H), 7.83-7.69 (m, 4H), 7.57 (t, $J = 4$ Hz, 2H), 4.18 (s, methylene, 4H). ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ 163.91, 154.52 (quaternary), 147.65 (quaternary), 136.50, 129.70, 129.50, 128.71 (quaternary), 127.63, 127.34, 118.40, 61.43. UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH_3OH): 290 (10 260), 242 (42 710).

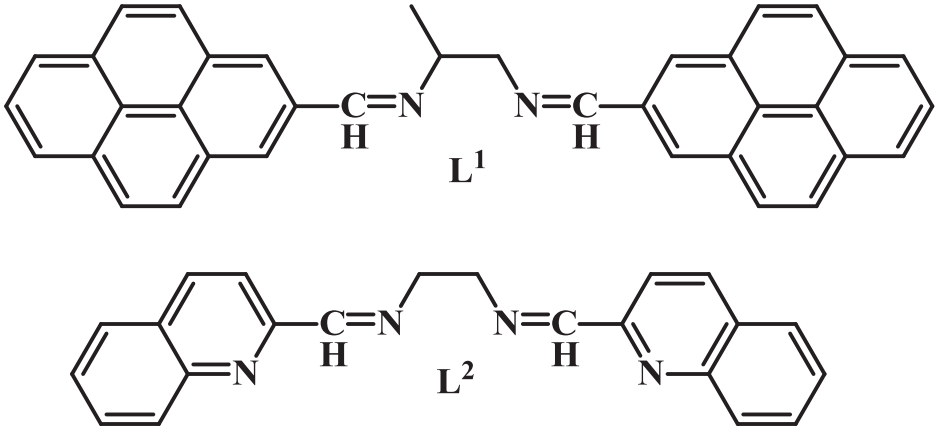
2.3. Preparation of complexes

2.3.1. Synthesis of [CuI(L^1)] **(1)**

CuI (0.19 g, 1 mmol) dissolved in acetonitrile (30 ml) is added dropwise into a 20 ml chloroform solution of the ligand L^1 (0.498 g, 1 mmol) within 1 h. Then the brownish reaction mixture is stirred for another 1 h at room temperature. Reddish brown complex has appeared. It is filtered out and washed with 5 ml acetonitrile and dried *in vacuo*; yield, 4.485 g (65%). Deep red single crystals suitable for X-ray analysis are obtained by careful layering of CuI (1.9 mg, 0.01 mmol) dissolved in acetonitrile (4 ml) onto a 4 ml chloroform solution of the ligand L^1 (5 mg, 0.01 mmol). Anal. Calcd. for $C_{37}H_{26}N_2CuI$: C 64.49, H 3.80, N 4.06; found: C 64.43, H 3.87, N 4.10. FTIR cm^{-1} (KBr): 3047(m), 2922(m), 1613(s), 1593(s), 1252(m), 1234(s), 1108(m), 994(m), 844(vs), 824(m), 767(s), 715(vs), 475(m). UV–Vis (MeCN) [λ_{max}, nm]: 283, 366.

2.3.2. Synthesis of [$Cu_2(\mu$-$I)_2(L^2)$] **(2)**

CuI (0.19 g, 1 mmol) dissolved in acetonitrile (30 ml) is added dropwise into a 20 ml chloroform solution of the ligand L^2 (0.338 g, 1 mmol) within 1 h. Then the reddish reaction mixture is stirred for



Scheme 1. Chemical structure of the ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ used in this study.