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## SYNTHESIS, STRUCTURE AND REDOX PROPERTIES OF A COPPER (I) COMPOUND INVOLVING MULTIRING NITROGEN-HETEROCYCLIC LIGAND

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### ABSTRACT

*Copper(I) complex [Cu(L)(PPh<sub>3</sub>)<sub>2</sub>] PF<sub>6</sub>(I) containing a new biologically relevant heterocyclic bis-bidentate ligand viz. 3,3'-dipyridine-2-yl-[1.1']bi[imidazo[1,5-a]pyridineyl] (L) has been prepared and characterized by single-crystal X-ray diffraction analysis. Compound in its solid state structure shows  $\pi$ - $\pi$ - $\pi$  sandwich noncovalent interactions as well as hydrogen bonding interactions that play dominant roles in shaping the extended structure of the molecule. Electrochemically, these compounds are quite interesting, undergoing ligand-based oxidations in two successive one-electron steps.*

**Keywords:** Copper(I) compound; N- heterocyclic ligand; X-ray diffraction analysis;  $\pi$ - $\pi$ - $\pi$  sandwich noncovalent interactions; hydrogen bonding.

### Introduction

Coordination compounds that combine redox active metals and non-innocent ligands, both capable of providing multiple electronic states, are the focus of a good number of recent publications because of their meaningful participations in catalytic and enzymatic reactions.<sup>1,2</sup> Such species are known to play pivotal role during substrate turnovers by a host of metalloenzymes viz. pyruvate formate lyase,<sup>3</sup> prostaglandin H synthase,<sup>4</sup> DNA photolyase,<sup>5</sup> cytochrome *c* peroxidase,<sup>6</sup> diol hydrazase,<sup>7</sup> biotin synthase,<sup>8</sup> lipoyl

synthase,<sup>9</sup> ribonucleotide reductase,<sup>10</sup> galactose oxidase,<sup>11</sup> lysine-2,3-aminomutase.<sup>12</sup> These enzymes containing redox-active metals and radical bearing residues *viz.* Tyr<sup>•</sup>, Cys<sup>•</sup>, Gly<sup>•</sup>, Trp<sup>•</sup> and TrpH<sup>•+</sup> are capable of storing and transferring redox equivalents to the biologically relevant target molecules as well as executing variety of complex reaction steps like proton transfer, single electron transfer, hydrogen atom abstraction, which are essential for the overall enzymatic actions.<sup>1,2</sup>

Non-covalent interactions involving  $\pi$ -systems have been extensively studied in recent years.<sup>13</sup> Such interactions play a crucial role in many frontline areas of contemporary science, from molecular biology to crystal engineering.<sup>14-15</sup> For example, face to face  $\pi$ -stacking interactions involving aryl rings of nucleobase pairs are important for the stability of DNA double helix.<sup>13,16</sup> Hydrogen bonds are also crucial and play distinctive roles in structural chemistry and biology.<sup>15b</sup>

We have recently synthesized<sup>17,18</sup> a  $\pi$ -electron-deficient *N*-heterocyclic compound, *viz.*, 3,3'-dipyridin-2-yl[1,1']bi[imidazo[1,5-a]pyridinyl] (L) containing a pair of biologically relevant<sup>19</sup> imidazo[1,5-a]pyridine moieties. Herein, we report the synthesis of a copper(I) complex (**1**) of a nitrogen-rich electron deficient heterocyclic ligand (L). The compound has been characterized by single-crystal X-ray diffraction analysis. In addition, the redox behavior of the complex has been investigated

## 2. Experimental Section

### 2.1. Materials

Bis-bidentate type ligand L was prepared as described elsewhere.<sup>17,18</sup> Precursor complex [Cu(PPh<sub>3</sub>)<sub>2</sub>NO<sub>3</sub>] was prepared following a literature method.<sup>20</sup> All other reagents are commercially available and used as received. Solvents were reagent grade, dried by standard methods<sup>21</sup> and distilled under nitrogen prior to their use.

### 2.2. Synthesis

#### [Cu(L)(PPh<sub>3</sub>)<sub>2</sub>] PF<sub>6</sub>

To a stirred methanolic solution (40 mL) of L (39 mg, 0.1 mmol), solid [Cu(PPh<sub>3</sub>)<sub>2</sub>NO<sub>3</sub>] (65 mg, 0.1 mmol) was added in portions. The resulting mixture was stirred for 3 h when a yellow solution was obtained. To the solution was then added NH<sub>4</sub>PF<sub>6</sub> (15 mg, 0.1 mmol) and stirred for further 0.5 h. Finally, the solution was filtered and kept in the air

for ca. two days. Yellow crystalline compound deposited at this stage was collected by filtration and dried in vacuum over  $\text{CaCl}_2$ . Yield: 28%. Anal. Calcd for  $\text{C}_{60}\text{H}_4\text{N}_6\text{CuF}_6\text{P}_3$ : C, 64.20; H, 4.10; N, 7.49. Found: C, 63.97; H, 4.13; N, 7.42%. FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3463, 1587, 1498, 1481, 1434, 1313, 838, 786, 742, 696.

### 2.3. Physical measurements

Elemental (C, H, N, and S) analyses were performed on a Perkin-Elmer model 2400 Series II CHNS Analyzer. The IR spectra were recorded on a Shimadzu model 8400S FT-IR spectrometer with samples prepared as KBr pellets. Cyclic voltammetry in  $\text{CH}_3\text{CN}$  was recorded on a BAS model 100 B/W electrochemical workstation using a platinum or a glassy carbon working and platinum wire counter electrodes. Ag/AgCl was used for references and  $\text{Fc}/\text{Fc}^+$  couple as the internal standard.<sup>22</sup>

### 2.4. X-ray crystallography

Diffraction quality crystals of **1** (needle, yellow crystals,  $0.30 \times 0.10 \times 0.10 \text{ mm}^3$  obtained from methanol solution) were obtained from the designated solvents by slow evaporation at room temperature. Crystals were mounted on glass fibers and aligned on a Bruker SMART APEX II CCD diffractometer. Intensity data for compound **1** were measured employing a monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) source using phi and omega scan techniques at 223(2) K. In all cases, absorption corrections based on multiscan using the SADABS software<sup>23</sup> were applied. The structures were solved by direct methods<sup>24</sup> and least square refinement [anisotropic displacement parameters, hydrogen atoms in the riding model approximation and a weighing scheme of the form  $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$  for  $P = (F_0^2 + 2F_c^2)/3$ ] was on  $F^2$ .<sup>24</sup> Bruker SHELXTL<sup>25</sup> was used both for structure solutions and refinements. Crystallographic parameters and the final residuals are given in Table 1.

## 4.3. Results and Discussion

### 3.1. Syntheses

The protocol followed for the synthesis of **1** is summarized in scheme 1. The *cisoid* mode of the ligand to generate  $[\text{Cu}(\text{PPh}_3)_2(\text{L})]^+$ , we believe, is favored by the steric effect of the bulky coligands, stabilizing  $\pi$ - $\pi$ - $\pi$  interactions and tetrahedral environment around Cu(I). IR spectra of the complexes contain all the pertinent bands due to the coordinated bipyridine type ligands<sup>26</sup> appearing at ca. 1600, 1485, 1461, 1313, 1247, 770  $\text{cm}^{-1}$  region (compiled in

the experimental section) as prominent features. In the mononuclear copper(I) complex **1**, along with the signature bands<sup>27</sup> of the coordinated triphenylphosphine ligand at ca. 1434 and 696 cm<sup>-1</sup> also appears a strong band at 838 cm<sup>-1</sup> due to the PF<sub>6</sub><sup>-</sup> counter anion.<sup>28</sup>

### 3.2. Description of crystal structures

The molecular structure and atomic labeling scheme for **1** is shown in Figure 1. Selected bond distances and angles are summarized in Table 2. The complex crystallizes in a monoclinic space group *P2(1)/n* with eight molecular weight units per cell. The coordination environment around Cu(1) is distorted tetrahedral ( $\tau_4 = 0.82$ )<sup>29</sup> and is defined by two imidazole nitrogens N(1), N(4) in *cisoid* conformation and two phosphorous atoms P(1), P(2) from the triphenylphosphine co-ligands, leaving two pyridine nitrogen atoms free from coordination.

Of particular interest in this structure is the presence of two  $\pi$ - $\pi$ - $\pi$  sandwich interactions (Figure 2) involving one imidazole ring as central  $\pi$  system and one phenyl ring from a PPh<sub>3</sub> co-ligand and one azopy ring. The *cisoid* conformation of the ligand brings one of the phenyl rings of PPh<sub>3</sub> into close proximity to an imidazole ring to generate intramolecular  $\pi$ - $\pi$ -stacking. The imidazole ring further participates in intermolecular  $\pi$ - $\pi$  interactions with the azopy ring from an adjacent ligand strand. Here the centro-symmetric ligand is much short of planarity (twist angle about central im-im is ca. 31°), giving indications of the absence of intermolecular  $\pi$ - $\pi$ - $\pi$  interactions involving both sides of the ligand. The intramolecular  $\pi$ -stacking interactions are not quite of a classical type as judged by the dihedral angles (9.18 and 21.28°) between phenyl and im planes of both sides. One side deviates more from a classical nature than the other one. This is also reflected from the fact that some atoms of the phenyl ring of more deviated side come rather close to the centroid of the im, e.g. C(2E)-im<sub>centroid</sub> and H(2E)-im<sub>centroid</sub> distances are 3.132 Å and 2.970 Å, respectively. Intermolecular  $\pi$ -stackings are more classical in nature as evident from the dihedral angles (4.62 and 3.27°). As a consequence of two simultaneously existing intramolecular  $\pi$ - $\pi$ -stacking interactions involving two phenyl rings from two PPh<sub>3</sub> existing one above and one below the central im rings, the P(1)-Cu(1)-P(2) bond angle is significantly enlarged (131.10(5)°) than the values observed in other closely related compounds.<sup>30</sup> The distortion induced by  $\pi$ - $\pi$  stacking is also evident from Cu-P-C<sub>ph</sub> bond angles. The Cu(1)-P(1)-C(2B) and Cu(1)-P(2)-C(1E) angles of 110.15 and 108.06° are much reduced in comparison to the other Cu-P-C<sub>ph</sub> angles, ranging between 116-121°. Cu(I)-N bond distances (2.164(4) and 2.181(4) Å) are slightly longer than that observed in [Cu(Phen)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>NO<sub>3</sub>.<sup>30</sup>

Elongated Cu(I)-P distances (2.283(14) and 2.285(13) Å) are consistent with the corresponding values found in analogous compounds.<sup>31</sup>

### 3.3. Electrochemistry

The redox behavior of **1** has been examined by cyclic voltammetry (CV). Voltammogram of **1** (Figure 3) features a couple of oxidation processes involving electron transfers only on the ligand part of the compound. The product after second oxidation is quite unstable, survives only partially to show up in the reverse scan with diminished current height. However, at a much faster scan rate (ca. 2000 mVs<sup>-1</sup>) and at a very low temperature (-30 °C) (Figure 3, inset) this product does survive to become completely visible.

### 4. Concluding Remarks

The copper(I) compound (**1**) of the ligand L has been synthesized. The structures in the solid state involve multiple  $\pi$ -stacking interactions, extending up to several aromatic  $\pi$  systems. H-bonding interactions are also present in the solid state. These noncovalent interactions play dominant roles in shaping the extended structures of these compounds in the solid state. Electrochemically, this compound is also interesting, undergoing ligandbased oxidations in two successive single-electron steps.

### 5. References

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## Table

**Table 1.** Summary of the Crystallographic Data for Complex **1**

| Parameter   | <b>1</b>   |
|---|--|
| Composition   | C <sub>30</sub> H <sub>23</sub> Cu <sub>0.5</sub> F <sub>3</sub> N <sub>3</sub> P <sub>1.5</sub> |
| Formula wt.   | 560.74   |
| Crystal system  | Monoclinic   |
| Space group   | P2(1)/n  |
| <i>a</i> , Å  | 12.9044(6)   |
| <i>b</i> , Å  | 18.2795(7)   |
| <i>c</i> , Å  | 21.7660(9)   |
| $\alpha$ , deg  | 90.00  |
| $\beta$ , deg   | 93.2050(10)  |
| $\gamma$ , deg  | 90.00  |
| <i>V</i> , Å <sup>3</sup>   | 5125.8(4)  |
| <i>D</i> <sub>calc</sub> , Mgm <sup>-3</sup>  | 1.453  |
| Temp, K   | 223(2)   |
| $\lambda$ , Å   | 0.71073  |
| <i>Z</i>  | 8  |
| <i>F</i> (000)/ $\mu$ mm <sup>-1</sup>  | 2304/0.590   |
| 2 $\theta$ <sub>max</sub> [°]   | 50.00  |
| Reflections Collected/Unique  | 30254/9030   |
| <i>R</i> <sub>int</sub> / GOF on <i>F</i> <sup>2</sup>  | 0.0726/1.036   |
| No of parameters  | 680  |
| <i>R</i> 1( <i>F</i> <sub>0</sub> ), <i>wR</i> 2( <i>F</i> <sub>0</sub> ) ( <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )) | 0.0694, 0.1706   |
| Largest diff. peak  | 0.857  |

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **1**

| Bond Distances (Å) |            |
|--------------------|------------|
| Cu(1)—N(1)         | 2.181(4)   |
| Cu(1)—N(4)         | 2.164(4)   |
| Cu(1)—P(1)         | 2.2832(14) |
| Cu(1)—P(2)         | 2.2855(13) |
| Bond Angles (deg)  |            |
| N(4)—Cu(1)—N(1)    | 80.81(14)  |
| N(4)—Cu(1)—P(1)    | 113.78(10) |
| N(1)—Cu(1)—P(1)    | 102.20(11) |
| N(4)—Cu(1)—P(2)    | 103.87(11) |
| N(1)—Cu(1)—P(2)    | 113.95(10) |
| P(1)—Cu(1)—P(2)    | 131.10(5)  |

### Figure Legends

**Scheme 1:** Protocol followed for the synthesis of Compound **1**

**Figure 1:** Molecular structure and atomic labelling scheme for **1**. Hydrogen atoms have been omitted for clarity.

**Figure 2:** Crystalpacking of **1** showing  $\pi$ - $\pi$ - $\pi$  sandwich interactions.

**Figure 3:** Cyclic voltammogram of **1** in DMF at 298 K and at a platinum electrode at varying scan rates (50, 100, 200, 500, 1000 and 2000 mVs<sup>-1</sup>). The inset shows the increased reversibility of the second oxidation process at low temperature (-30 °C).

Scheme 1



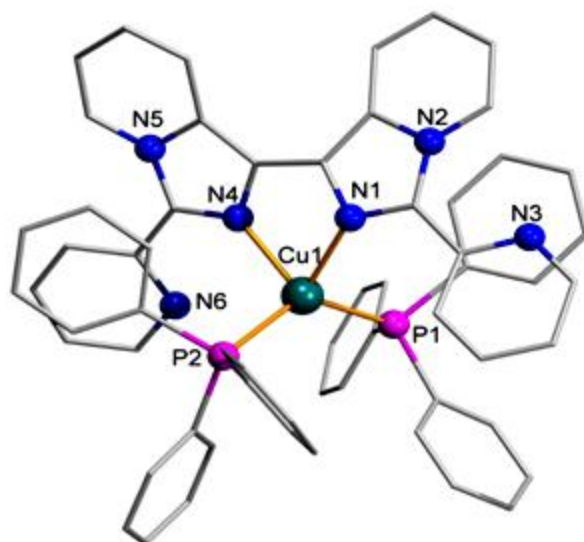


Figure 1

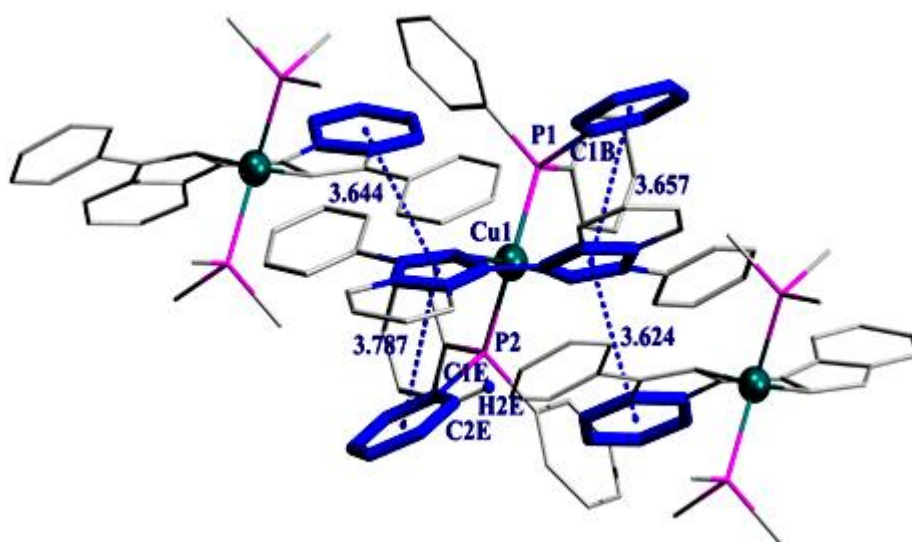


Figure 2

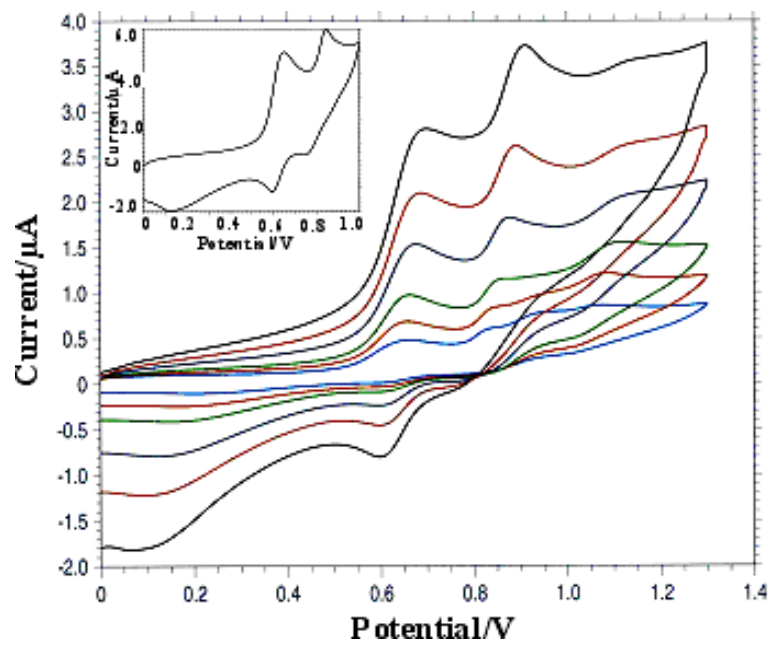


Figure 3