

# Review of Synthesis and Characterization of Cu (I) Complexes

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## ABSTRACT

d-block metals show great promise in inorganic catalytic research. Particularly, copper, d<sup>9</sup> metal has contributed to catalytic properties of its complexes. A series of copper complexes was synthesized and structurally characterized. The copper (I) complexes of this series were investigated in regard to their reactivity towards dioxygen using stopped-flow techniques. For most complexes no “oxygen adduct” complexes as intermediates could be detected. In this article, some complexes of Cu (I) have been included and the ligands on which work had been done are mentioned below:

1,5-bis(benzimidazole-2-yl)-3-thiapentane  
Tridentate di-pyrazole -3,6-di-tert-butyl-carbazole (N, N, N-Pincer ligand)  
Methyl isocyanate  
N<sub>4</sub>Cu  
Tris(pyrazolyl) hydroborate ligand  
Scorpionate ligand  
Phenanthroline  
Tripodal amine ligands  
Triazole derivatives

**Keywords:** BBES (1,5-bis(benzimidazole-2-yl)-3-thiapentane), MeIN (Methyl isocyanate), CuSCN (copper thiocyanate), PPh<sub>3</sub>(triphenyl phosphine), PCy<sub>3</sub>(tricyclohexyl phosphine), TptBuPh (tris[3-(p-tert-butylphenyl)], Tp (tris pyrazolyl hydroborate), Me<sub>4</sub>p,3,3 (3,3-dimethylaminopropyl-(2-methylenpyridyl)-amine), Me<sub>2</sub>-pp<sub>3</sub> (3-dimethylaminopropyl-bis(2-methylenpyridyl)-amine)

## INTRODUCTION

Coordination of Cu (I) complexes has been subject of extensive investigation. Research involving the formations of Cu (I) complexes has been in substantial development since late 1960's. As part of an ongoing investigation into the biological activity of copper compounds we sought to summarize the work of preparation of its complexes done by the scientists. With the present work we have demonstrated the extent to which the stoichiometry of the complexes depends upon the size of the substituent groups. In recent chemical research, inorganic copper systems have been intensively studied to understand how the copper ion dictates rapid electron transfer with enzymes, particularly relating to the electron transport chain.

## STUDY OF Cu(I) COMPLEXES

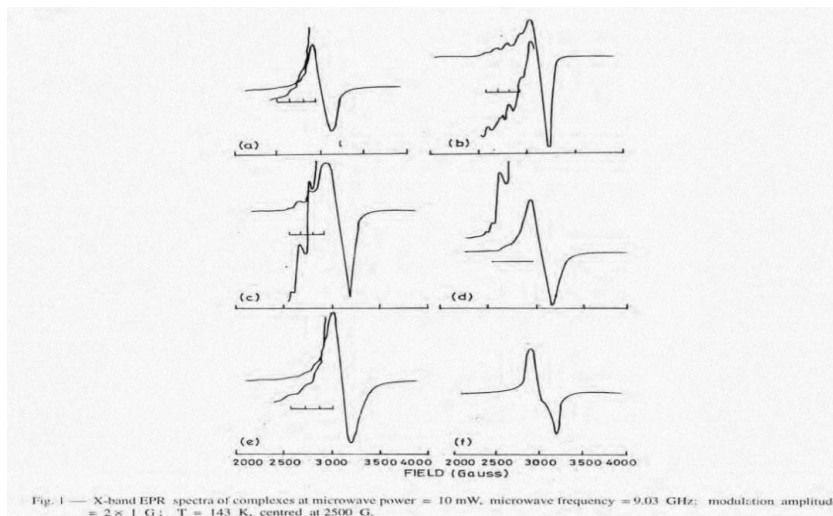
(1). **1,5-bis(benzimidazole-2-yl)-3-thiapentane:** The work on Cu(I) complexes with 1,5-bis(benzimidazole-2-yl)-3-thiapentane ligand was done by Lata Nohria et. al. as summarized below:

**SYNTHESIS:** Blue solution of Cu (NO<sub>3</sub>)<sub>2</sub> (2mmol) in 20ml methanol and 2mmol of hydroquinone. After that 2mmol BBES in NaOH, solution obtained was dark green and after washing stored in P<sub>2</sub>O<sub>5</sub> in vacuum.

**CHARACTERIZATION:** Complexes with this ligand provides N<sub>2</sub>S donor environment and characterized the complexes using spectral

and electrochemical techniques. EPR spectra at X-band show no signal indicate diamagnetic ground state Cu (I) complex. <sup>1</sup>H NMR broadening of peaks and shift in peak of

aliphatic / aromatic –NH protons. Well defined sharp multiplet due to aromatic protons were also broadened. –NH proton in free ligand shift from δ9.2 to 10 -10.6 ppm in Cu (I) complexes.

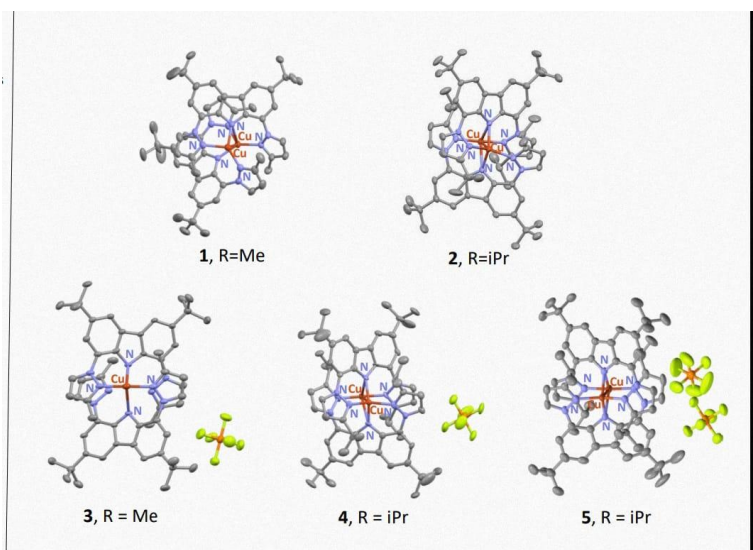


**RESULTS:** Flaky white crystals were obtained in this complex.

**(2) Tridentate di-pyrazole -3,6-di-tert-butyl-carbazole (N, N, N-Pincer ligand):** The work on Cu(I) complexes with N, N, N-Pincer ligand was done by Isabel Garcia et. al. (*This research is supported by Loyola University Chicago and the Mulcahy Research Fellowship Program.*) as summarized below:

**SYNTHESIS:** Lithium-di-isopropyl amide is used to deprotonate the ligand and reacted it with copper (I) chloride to obtain the complexes.

**CHARACTERIZATION:** Molecular structure revealed metal centre exist at plane of ligand making it more accessible for redox reaction.



(Molecular Structure)

**RESULTS:** Using these complexes electron transfer self-exchange reactions studies can be performed to provide insight to differences in electron transfer rate between methyl and isopropyl complexes. The studied Cu complexes show potential to enhance rapid electron transfer similar to cytochrome-C-oxidase which complete electron Cu sites.

**(3). Methyl isocyanate:** The work on Cu(I) complexes with Methyl isocyanate ligand was done by MOHAMED A. S. GOHER et. al. as summarized below:

**SYNTHESIS:** Complex with this ligand prepared by simply mixing ligand and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in appropriate stoichiometric ratio in aqueous or ethanolic medium followed by addition of ascorbic acid as reducing agent and then desired anion.

**CHARACTERIZATION:** X-ray powder diffraction show 1:1 bromide and 1:2 halide complexes were isomorphous electronic spectra shown absorption band at 275- 280 nm ( $\Pi$  to  $\Pi^*$ ) visible region. For Cu (I) – MeIN complex accepted for 1:2 perchlorate show metal to ligand charge transfer.

**IR SPECTRA:** At  $668\text{ cm}^{-1}$  - new bond for Cu (I) complex attributes  $995\text{ cm}^{-1}$  vibration. At  $485\text{-}507\text{ cm}^{-1}$  weak to medium intensity band attributed  $485\text{ cm}^{-1}$  ring vibration mode for Cu (I) - MeIN complex. C-C, C-N structure, C-H in plane show blue shift MeIN  $220\text{-}234\text{ cm}^{-1}$  and around  $200\text{ cm}^{-1}$  Cu (I) bond and structure vibration.

Microanalysis of C, H, N were carried out on the Perkin-Elmer 240 elemental analyzer. Halogens were determined gravimetrically as AgX. Copper was determined either by titration against disodium EDTA or gravimetrically as  $\text{CuSCN}$  after degradation and oxidation of the complexes with boiling mixtures of concentrated and 30%  $\text{H}_2\text{O}_2$ .

**RESULTS:** Faint yellow Cu(I) perchlorates 1:2 compounds show 2 bands  $201$  and  $264\text{ cm}^{-1}$

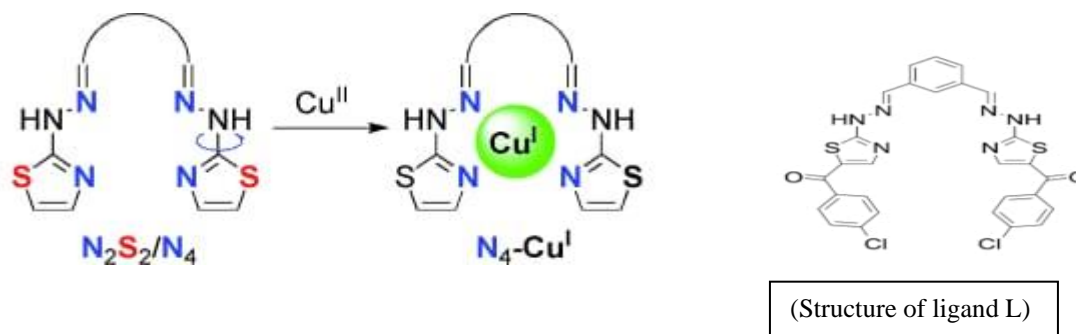
$^1$  confirmed perchlorate acts as bidentate ligand in complex. Magnetic measurements were made by the Faraday method at room temperature. X-Ray powder patterns were taken on a Mikrometa 2 (Chirana, Prague) instrument,  $\phi = 53.3\text{ mm}$ , with  $\text{LCuK}\alpha$  radiation. Conductivity measurements were carried out at  $25\text{ }^\circ\text{C}$  on F solutions in chloroform, nitrobenzene, and acetone under dry nitrogen with a Radiometer conductivity bridge model CDM 2e. Electronic spectra were recorded on a Unicam spectrophotometer SP 800.

**(4).  $\text{N}_4\text{Cu}$  ligand:** The work on Cu(I) complexes with  $\text{N}_4\text{Cu}$  ligand was done by Dr. Ewen Bodio et. al. as summarized below:

**SYNTHESIS:** These complexes were formed from copper (II) salts. The copper complex CuL was synthesized by the reaction of one equivalent of ligand with one equivalent of copper (II) diacetate in dimethyl formamide (DMF). For one hour at room temperature or 5 minutes at  $110\text{ }^\circ\text{C}$  under microwave irradiations.

**Synthesis of bifunctional ligand:** The group provides a binding site and the variation of R2, R3, and R4 enables the chelation properties of the ligand (changing electronic and steric effects) to be modified. Ewen Bodio, Mohammed Boujtita, Eric Renault broadened the scope of our strategy by using 2,6-diacetylpyridine instead of isophthalaldehyde and by functionalizing the central aromatic ring. They chose to introduce the functional group on the arene bearing the two arms of the complex, to have the smallest influence on the chelation. Thus, they had developed a versatile and efficient method of designing new chelating agents, which enables a linker to be easily constructed on the aromatic ring. The overall yields were good to excellent, even for compounds that required a multistep synthesis.

|   |    |                                  |    |    |
|---|----|----------------------------------|----|----|
|   | R1 | R2                               | R3 | R4 |
| L | H  | pClC <sub>6</sub> H <sub>4</sub> | H  | H  |



**CHARACTERIZATION:** Although various crystallogenes experiments (gel permeation, “H-tube” crystallization, and slow solvent evaporation) were performed, a monocrystal suitable for X-ray analysis could not be obtained. Unfortunately, NMR and EPR studies of CuL were unsuccessful (relaxation was very fast and thus the NMR signals were very broad and no significant EPR signal was observed). Several analytical techniques were therefore combined to determine the structure of the complex CuL.

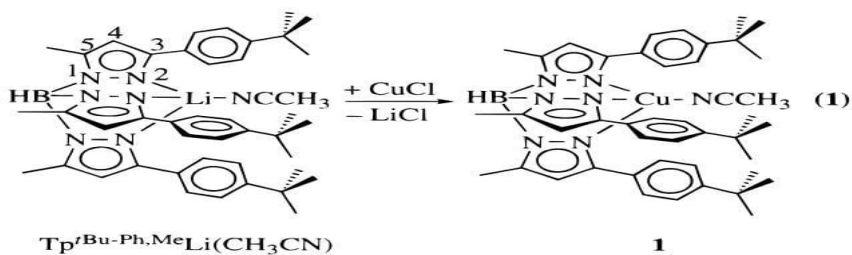
**Radioanalysis:** Copper-64 dichloride in 0.1m hydrochloric acid was obtained from ARRONAX cyclotron (Saint-Herblain, France). Radionuclide purity was determined by gamma spectroscopy using a DSPEC-JR-2.0 type 98-24B HPGE detector (AMETEK) and chemical purity was controlled by inductively coupled plasma–optical emission spectroscopy with an iCAP 6500 DUO instrument (Thermo Fisher Scientific). TLC analyses were performed using silica gel on TLC-PET foils (Fluka Analytical).

**RESULTS:** Priliminary study was performed with ligand L which was chosen because Cl atoms on this chelating agents would be used as a probe for energy dispersive X-ray spectroscopy analysis.

EDX analysis linked to scanning electron microscopy(SEM) performed on ligand L and CuL. The results show the presence of two equivalents of chlorine and one Cu. That means complex had ligand/Cu stoichiometry 1:1. The stoichiometry was confirmed by mass spectroscopy, spectra(MALDI,2,5-dihydroxybenzoic acid). For CuL possesses isotropic pattern corresponding to(CuL+H<sup>+</sup>) at m/z = 667.

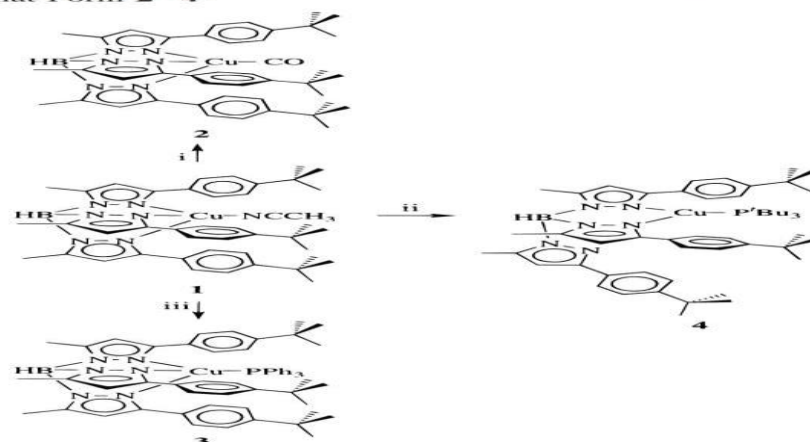
**(5). Tris(pyrazolyl) hydroborate ligand:** The work on Cu(I) complexes with Tris(pyrazolyl) hydroborate ligand was done by Rebecca R. Conry et. al. as summarized below:

**SYNTHESIS:** The stoichiometric reaction of TptBu-Ph,MeLi(CH<sub>3</sub>CN) and CuCl in a mixture of CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN produces TptBu-Ph,MeCu-(CH<sub>3</sub>CN) (1) in excellent yield (eq 1 shown as)



The aceto-nitrile ligand in complex 1 can be readily replaced by other ligands, such as CO, PPh, and PtBu<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> to form 2 through 4 (Scheme 1), as discussed below.



**Scheme 1. Ligand Substitution Reactions of Complex 1 That Form 2–4<sup>a</sup>**

<sup>a</sup> Reaction conditions: (i) + CO; (ii) + P'Bu<sub>3</sub>; (iii) + PPh<sub>3</sub>.

**CHARACTERIZATION:** Complex 1 is a white solid that is soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and Et<sub>2</sub>O and is insoluble in CH<sub>3</sub>CN and saturated hydrocarbon solvents. Complex 1 is stable to the air for at least a month as a solid but is sensitive to air oxidation in nonacetonitrile containing solvents, for instance turning green within an hour in a chloroform solution open to the air. In addition, 1 is subject to acetonitrile loss under vacuum at ambient temperatures, forming more than one product, as indicated by <sup>1</sup>H NMR spectroscopy. No attempts were made to isolate and purify these products. Complex 1 and the other three copper complexes reported here have been fully characterized, by IR and NMR spectroscopies, FAB/MS, elemental analysis and X-ray crystallography. Copper(I) ligation is indicated by the shifting of

significant <sup>1</sup>H NMR and IR peaks for 1 versus TptBu-Ph<sub>2</sub>MeLi-(CH<sub>3</sub>CN), such as  $\nu(\text{B-H})$  to 2498 cm<sup>-1</sup>. The nitrile stretches for 1 was observed at 2268 cm<sup>-1</sup>, which is just outside the range given for most typical metal-acetonitrile complexes (2270-2300cm<sup>-1</sup>). However, it compares favorably with other CuI-NCCH<sub>3</sub> complexes, which most frequently exhibit  $\nu(\text{CN})$  in the 2260-2280 cm<sup>-1</sup> range. There is a second weak peak in the IR spectrum of 1 at 2236 cm<sup>-1</sup> that could be the combination band seen for acetonitrile complexes; however, it is well outside of the typical range (2290-2320 cm<sup>-1</sup>), making such an assignment tentative. Colorless single crystals were grown by diffusion of CH<sub>3</sub>-CN into a CH<sub>2</sub>Cl<sub>2</sub> solution of 1. As these crystals desolvated at room temperature over several hours, the X-ray data were collected at low temperature (Table 1).

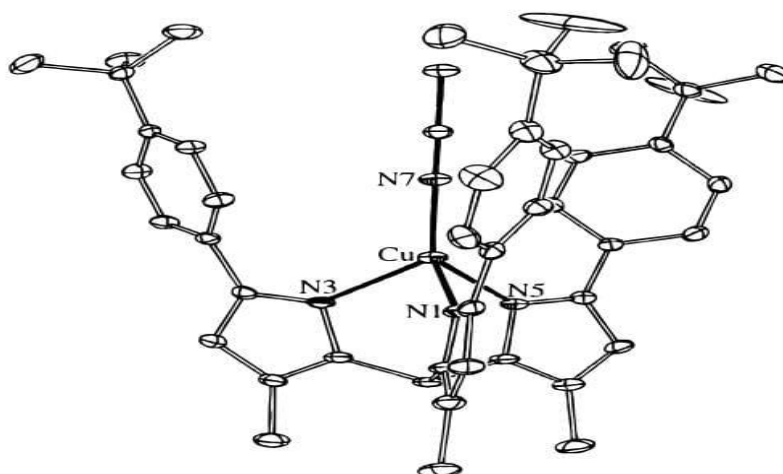
**Table 1.** Crystallographic Data for 1–4

| parameter                              | 1-CH <sub>3</sub> CN                                | 2   | 3-CH <sub>2</sub> Cl <sub>2</sub>                                   | 4-0.5hexane   |
|--|---|---|---|---|
| empirical formula                      | C <sub>23</sub> H <sub>27</sub> N <sub>11</sub> BCu | C <sub>41</sub> H <sub>52</sub> N <sub>8</sub> BCuO | C <sub>61</sub> H <sub>60</sub> N <sub>6</sub> BCl <sub>2</sub> CuP | C <sub>57</sub> H <sub>60</sub> N <sub>6</sub> BCuP |
| fw                                     | 920.52  | 743.26  | 1062.44   | 960.64  |
| temperature (K)                        | 173   | 296   | 173   | 298   |
| $\lambda$                              | 0.710 73 Å (Mo K $\alpha$ )                         | 0.710 73 Å (Mo K $\alpha$ )                         | 0.710 73 Å (Mo K $\alpha$ )   | 0.710 73 Å (Mo K $\alpha$ )                         |
| space group                            | P1 (No. 2)  | C2/c (No. 15)                                       | P1 (No. 2)  | P1 (No. 2)  |
| a (Å)                                  | 13.4201(10)   | 25.592(4)   | 12.5080(13)   | 13.337(2)   |
| b (Å)                                  | 15.132(2)   | 12.434(2)   | 15.159(3)   | 13.435(2)   |
| c (Å)                                  | 15.2125(13)   | 28.044(3)   | 17.151(2)   | 17.386(2)   |
| $\alpha$ (deg)                         | 60.743(6)   | 90  | 64.271(10)  | 88.371(7)   |
| $\beta$ (deg)                          | 73.211(4)   | 104.073(9)  | 79.073(7)   | 71.863(8)   |
| $\gamma$ (deg)                         | 74.839(5)   | 90  | 86.572(8)   | 80.223(9)   |
| V (Å <sup>3</sup> )                    | 2553.3(4)   | 8656(2)   | 2875.6(7)   | 2916.5(6)   |
| Z                                      | 2   | 8   | 2   | 2   |
| calculated $\rho$ (g/cm <sup>3</sup> ) | 1.197   | 1.141   | 1.227   | 1.094   |
| cryst dimens (mm)                      | 0.48 × 0.42 × 0.31                                  | 0.62 × 0.40 × 0.21                                  | 0.96 × 0.51 × 0.18  | 0.60 × 0.35 × 0.08                                  |
| $\mu$ (mm <sup>-1</sup> )              | 0.473   | 0.542   | 0.544   | 0.440   |
| R1 <sup>a</sup>                        | 0.0681  | 0.0747  | 0.0513  | 0.0696  |
| wR2 <sup>b</sup>                       | 0.1891  | 0.2208  | 0.1328  | 0.1862  |

<sup>a</sup> R1 =  $\sum ||F_o| - |F_c|| / \sum |F_o|$  (observed data,  $I > 2\sigma(I)$ ). <sup>b</sup> wR2 =  $[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$  (all data).

**RESULT:** The solid-state structure of **1** (Figure 1) shows that the copper ion is four-coordinate, bound to the three pyrazole nitrogen atoms as well as the nitrogen from the acetonitrile ligand. A few other TpCuI (CH<sub>3</sub>CN) complexes are known although apparently only two have been recently crystallographically characterized. Geometry about the copper center in **1** is distorted tetrahedral, with angles ranging from 90.9 to 124.8°. As is typical for Tp four-coordinate structures, there are clearly two sets of angles, ones averaging near 90° for the angles between the pyrazole groups and larger angles, closer to 125°, between the Tp ligand and the fourth ligand. The three copper-pyrazole nitrogen distances are equal within error and are slightly

longer (averaging 2.088 Å) than the Cu-N acetonitrile distance (1.891(5) Å). The Cu-N acetonitrile distance falls within the 1.86-2.16 Å range seen for some other four-coordinate copper(I)-acetonitrile complexes. The nitrile C-N distance in **1**, 1.140(7) Å, falls within the typical range found for transition metal acetonitrile complexes, 1.11-1.15 Å. The acetonitrile ligand is essentially linear ( $\angle$ NC-C, 179.4(7) Å), which is typical for copper-acetonitrile complexes. The copper-nitrile angle for **1** is within the usual range for transition metal complexes ( $\angle$ M-NC of 175±5°) and is clearly near that of other Cu-NCCH<sub>3</sub> complexes (157-180°).



**Figure 1.** Thermal ellipsoid depiction of  $\text{Tp}^{\text{tBu-Ph,Me}}\text{Cu}(\text{CH}_3\text{CN})$  (**1**) at the 20% probability level; hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Cu–N1, 2.089(5); Cu–N3, 2.083(5); Cu–N5, 2.092(5); Cu–N7, 1.891(5); C≡N7, 1.140(7); N1–Cu–N7, 124.8(2); N3–Cu–N7, 123.8(2); N5–Cu–N7, 124.7(2); N1–Cu–N3, 91.2(2); N1–Cu–N5, 90.9(2); N3–Cu–N5, 91.4(2); Cu–N7≡C, 178.4(5); N7≡C–C, 179.4(7).

**(6). Scorpionate complex:** The work on Cu(I) complexes with Scorpionate ligand was done by Miriam Jackson et. al. as summarized below:

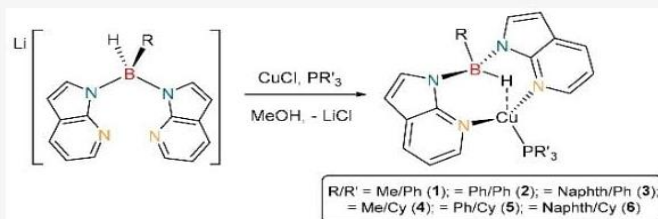
**SYNTHESIS:** The synthesis of copper (I) phosphine complexes containing scorpionate ligands was well known. They were readily synthesized via standard literature protocols. Despite this, there is only one example of a copper complex containing a 7-azaindolyl-

borate-based ligand known. Therefore a set of copper complexes with the general formula  $[\text{Cu}(\text{RBai})(\text{PR}'_3)]$  (where R = Me, Ph or Naphthalene and R' = Ph or Cy) were prepared. These were synthesized via a direct reaction of stoichiometric quantities of copper(I) chloride and the corresponding ligand precursor Li[RBai] in the presence of one equivalent of either triphenylphosphine or tricyclohexylphosphine (Scheme 1). The

reactions were performed in methanol solvent from which the products precipitated out as white/off-white solids. These solids were washed further with acetonitrile and

subsequently dried to provide the products, namely, complexes 1–6, in yields ranging between 72% and 92%.

**Scheme 1.** Synthesis of  $[\text{Cu}\{\kappa^3\text{-N,N,H-RBai}\}(\text{PR}_3)]$  complexes 1–6.



**CHARACTERIZATION:** They were characterized by multinuclear NMR spectroscopy, IR spectroscopy and mass spectrometry. Selected characterization data for complexes 1–6 are presented in following table 1, along with data for the corresponding lithium ligand salt precursors for comparison. First, the  $^3\text{P}\{^1\text{H}\}$  NMR spectra for complexes 1–6 in  $\text{C}_6\text{D}_6$  revealed one single resonance with a moderate downfield shift

with respect to their respective ligand precursors, namely,  $\text{PPh}_3$  (–5.26 ppm) and  $\text{PCy}_3$  (9.86 ppm). The phosphorus signals in the spectra for complexes 1, 2 and 3 were located at 1.41 ppm, 1.17 ppm and 1.64 ppm, respectively, whilst the corresponding signals in 4, 5 and 6 were found at 17.74 ppm, 18.08 ppm and 18.63 ppm, respectively. These values are in agreement with similar related scorpionate copper(I) phosphine complexes.

**Table 1.** Selected NMR (ppm; Hz) and IR ( $\text{cm}^{-1}$ ) spectroscopic data for  $[\text{R}^i\text{Bai}]$  ligand salt precursors and their corresponding copper complexes. The solvent used for the NMR studies was  $\text{C}_6\text{D}_6$ .

| Ligand/Complex                                    | $^3\text{P}\{^1\text{H}\}$ NMR | $^{11}\text{B}\{^1\text{H}\}$ NMR | h.h.w in $^{11}\text{B}/^{11}\text{B}\{^1\text{H}\}$ | $^1\text{H}\{^{11}\text{B}\}$ NMR B-H | IR (B-H) Powder Film |
|---|--------------------------------|-----------------------------------|--|---------------------------------------|----------------------|
| $\text{Li}[\text{MeBai}]$                         | -                              | -8.14                             | -  | 4.66                                  | 2396, 2272           |
| $\text{Li}[\text{PhBai}]$                         | -                              | -6.80                             | -  | 5.47                                  | 2394, 2264           |
| $\text{Li}[\text{NaphthBai}]$                     | -                              | -6.87                             | -  | 6.05                                  | 2429, 2272           |
| $[\text{Cu}(\text{MeBai})(\text{PPh}_3)]$ (1)     | 1.41                           | -7.27                             | 186/129  | 5.63                                  | 2143, 2089           |
| $[\text{Cu}(\text{PhBai})(\text{PPh}_3)]$ (2)     | 1.17                           | -6.24                             | 184/121  | 6.58                                  | 2120, 2062           |
| $[\text{Cu}(\text{NaphthBai})(\text{PPh}_3)]$ (3) | 1.64                           | -6.23                             | 180/133  | 6.97                                  | 2125, 2082           |
| $[\text{Cu}(\text{MeBai})(\text{PCy}_3)]$ (4)     | 17.74                          | -7.65                             | 181/123  | 5.49                                  | 2141, 2087           |
| $[\text{Cu}(\text{PhBai})(\text{PCy}_3)]$ (5)     | 18.08                          | -6.37                             | 175/129  | 6.36                                  | 2169, 2076           |
| $[\text{Cu}(\text{NaphthBai})(\text{PCy}_3)]$ (6) | 18.63                          | -6.96                             | 213/123  | 6.72                                  | 2189, 2090           |

**RESULTS:** The synthesis and characterization of a series of copper(I) complexes containing the novel [<sup>R</sup>Bai]<sup>-</sup> scorpionate ligands were reported herein. These new complexes were structurally characterized via X-ray crystallography. In all cases, a  $\kappa^3$ -*N,N,H* coordination mode, where both 7-azaindolyl “arms” were coordinated, along with the BH unit, was observed. The crystal structures confirmed significant B–H–Cu interactions. This was supported by solid-state infrared spectroscopy, where the structures were maintained, to some degree, in solution, as evidenced by multinuclear spectroscopy data. Furthermore, the structural characterization highlights a high degree of flexibility in terms of the size of the N–M–N angles and the approach of the B–H unit within the <sup>R</sup>Bai ligands upon coordination. These new copper(I) complexes add to the family of complexes containing flexible 7-azaindole-based scorpionate ligands, which, despite being first reported in 2005, are still underdeveloped. This investigation consolidated the fact that the  $\kappa^3$ -*N,N,H* coordination mode is the preferred mode of binding. The crystal structures demonstrated flexibility in the N–M–N chelating angles. This had an impact on the positioning of the B–H–M interaction. The potential of the azaindolyl-based “flexible scorpionates” in terms of reactivity and applications has yet to be fully realized. The reactivity of the BH unit with the metal center is likely to be instrumental in defining this reactivity. These aspects are currently under investigation.

**(7). Phenanthroline complex:** The work on Cu(I) complexes with phenanthroline ligand was done by Alexander J. Pallenberg et. al. as summarized below:

**SYNTHESIS:** A vacuum degassed solution of neo-cuproine hydrate (4.53 g, 20.0 mmol) in absolute ethanol (150 mL) was added to cuprous chloride (990mg, 10.0 mmol) via

cannula under an atmosphere of nitrogen. The resulting bright solution was stirred at room temperature for 2 h. This mixture was filtered, to remove a small amount of insoluble matter, and evaporated to give 5.64g (100%) of bright red solid. Recrystallization from aqueous methanol gave very fine needles. The remaining complexes were prepared by similar means, except that they were performed using dichloromethane as solvent. Alexander J.Pallenburg, Kristina S. Koeing obtained identical results if the cuprous chloride was simply added to the degassed solutions in solid form.

**CHARACTERIZATION:** Following is the data obtained for copper phenanthroline complexes. MP 238-238.5°C; IR (film) 3058, 2915, 1632, 1504, 1359, 860, 732, 548 cm<sup>-1</sup>; UV Vis  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>) 232 nm ( $\epsilon = 91\ 800\ \text{M}^{-1}\ \text{cm}^{-1}$ ), 275 nm ( $\epsilon = 70\ 800$ ), 456 nm ( $\epsilon = 6410$ ): <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) 8.75 (2H, br s), 8.22 (2H, s), 7.96 (2H, br s), 2.40 (6H, s): <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) 157.6, 142.2, 137.3, 127.1, 125.8, 125.6, 25.0: MS m/z (relative intensity) 481 (M(<sup>65</sup>Cu) – Cl)<sup>+</sup> (50), 479 (M(<sup>63</sup>C) – Cl<sup>-1</sup>) (100), 273 (50), 271 (100), 209 (5); MS m/z (relative intensity, negative ion FAB) 37 (40), 35 (100). Anal. Calcd for C<sub>28</sub>H<sub>24</sub>ClCuN<sub>4</sub>: C, 65.24; H, 4.69; N, 10.87; Cl, 6.88; Cu, 12.33. Found: C, 65.01; H, 4.73; N, 10.75; Cl, 6.84; Cu, 12.70.

**RESULTS:** The present work had demonstrated that substituted 1,10 phenanthrolines tend to adopt structures, regardless of net stoichiometry, which contained the pseudotetrahedral [(2,9-dialkyl 1,10-phenanthroline)]. Furthermore, it was relatively straightforward to tell whether a given complex possesses such a structure by a simple <sup>1</sup>H NMR experiment, due to the distinctive aromatic ring-current phenomena exhibited by these complexes. These experiments served to highlight the anomalous behavior of (2,9-dimethyl- 1,10-phenanthroline) CuCl, which appears to had a different structure in crystalline form than it



was in solution in organic solvents. Hindered phenanthrolines are forced to adopt a geometry in which only one such ligand is coordinated to copper, giving the copper atom a pseudotrigonal geometry. It was hoped that this increase in the depth of understanding of these compounds will aid the efforts to correlate structure with activity, because of the investigation of biological effects of these copper compounds.

**(8). Tripodal amine ligand:** The work on Cu(I) complexes with tripodal amine ligand was done by Frank Mehlich et. al. as summarized below:

**SYNTHESIS:** Under inert conditions copper(I) complexes were prepared and crystallised by ether diffusion at  $-40\text{ }^{\circ}\text{C}$  in the glovebox.

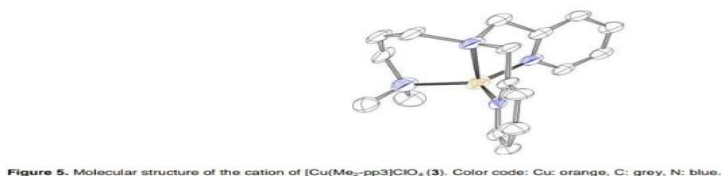
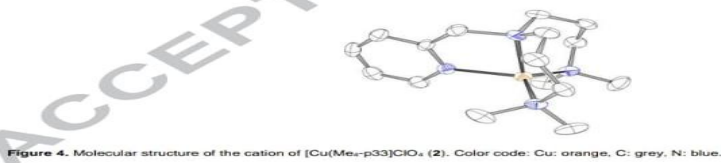
$[\text{Cu}(\text{CH}_3\text{CN})_4]\text{SbF}_6$  (134 mg, 0.29 mmol) in a small amount of propionitrile was added dropwise to a stirred solution of  $\text{Me}_6\text{-2,3,3}$  (50 mg, 0.3 mmol) in propionitrile.

$[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$  (98 mg, 0.3 mmol) in a small amount of acetone was added dropwise to a stirred solution of  $\text{Me}_4\text{-p33}$  (100 mg, 0.4 mmol) in acetone.

$[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$  (98 mg, 0.3mmol) in a small amount of acetone was added dropwise to a stirred solution of  $\text{Me}_2\text{-pp3}$  (100 mg, 0.4 mmol) in acetone.

**CHARACTERIZATION:** Copper(I) complexes with  $\text{Me}_6\text{-233}$ ,  $\text{Me}_4\text{-p33}$  and  $\text{Me}_2\text{-pp3}$  could be prepared and crystals suitable for crystallographic characterization were obtained. So far, no crystals of a copper(I) complex were obtained with  $\text{Me}_6\text{-233}$ . However, the molecular structure was not expected to be much different from  $[\text{Cu}(\text{233})]\text{SbF}_6$  (1). There was nothing unusual about the molecular structures of these three coppers(I) complexes, and they were well in line with related complexes reported. The molecular structures of the cations of  $[\text{Cu}(\text{233})]\text{SbF}_6$  (1),  $[\text{Cu}(\text{Me}_4\text{-p33})]\text{ClO}_4$  (2) and  $[\text{Cu}(\text{Me}_2\text{-pp3})]\text{ClO}_4$  (3). These complexes were not characterized further due to their sensitivity towards dioxygen and some problems with disproportionation.

**RESULTS:** The structure of three complexes prepared were shown below. (Reference: <https://doi.org/10.1016/j.ica.2018.11.032>)



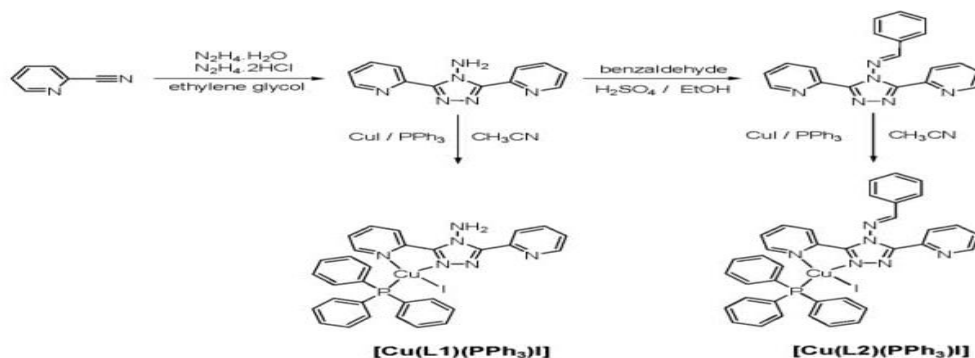
**(9). Triazole derivatives:** This work was supported by the National Science Council of Taiwan (ROC) and Tamkang University.

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**SYNTHESIS:** Two cuprous complexes Cu(L1)(PPh<sub>3</sub>)I (1) and Cu(L2)(PPh<sub>3</sub>)I (2) were obtained by reaction of Cu(PPh<sub>3</sub>)<sub>3</sub>I

(PPh<sub>3</sub> = triphenylphosphine) with two different  $\alpha$ -diimine ligands L 1 (3,5-di(2'-pyridyl)-4-amino-1,2,4-triazole) and L 2 (N-benzylidene-3,5-di(2'-pyridyl)-4-amino-1,2,4-triazole, respectively.



**CHARACTERIZATION:** These two complexes had been characterized by UV-Vis, luminescence, <sup>1</sup>H NMR spectroscopy and cyclic voltammetric studies. The structures were confirmed by the single crystal X-ray diffraction study. The compound Cu(L1)(PPh<sub>3</sub>)I (1) crystallizes in the triclinic space group P-1 with a = 8.3188(14), b = 9.2243(15), c = 21.177(4),  $\alpha$  = 78.156(3),  $\beta$  = 86.45(3),  $\gamma$  = 65.966(3), Z = 2 and the compound Cu(L2)(PPh<sub>3</sub>)I (2) crystallizes in the triclinic space group P-1 with a = 8.9671(7), b = 13.9737(11), c = 14.6850(12),  $\alpha$  = 82.2580(10),  $\beta$  = 75.7020(10),  $\gamma$  = 72.2790(10), Z = 2. Both complexes shown an MLCT band at 340 ~ 545 nm region and complex 2 exhibited luminescence at room temperature in a dichloromethane solution. The cyclic voltammogram of Cu(L1)(PPh<sub>3</sub>)I

shown the redox couples at + 0.36 and - 0.545 V.

**RESULTS:** The synthesized diimine ligands benzylidene-3,5-Di(2'-pyridyl)-4-amino-1,2,4-triazole (L1) and N-benzylidene-3,5-Di(2'-pyridyl)-4-amino-1,2,4-triazole (L2) which were used to prepare complexes 1 and 2 with Cu(PPh<sub>3</sub>)<sub>3</sub>I. The two copper complexes were structurally characterized by X-ray and <sup>1</sup>H-NMR methods. The absorption spectra of complexes 1 and 2 shown an MLCT bond in the region of 345–545 nm. We had also measured the emission properties of complex 2 which was shown to have a  $\lambda_{\text{max}}$  636 nm. Cyclic voltammogram of complex 1 shown the redox couples of the copper center at E = -0.545 V and E = + 0.685 V, the former corresponds to the reduction of Cu(I)/Cu(0), and the latter corresponds to the reversible oxidation of Cu(I)/Cu(II).



FIGURE 1 Crystal structure of Cu(L1)(PPh<sub>3</sub>)I and Cu(L2)(PPh<sub>3</sub>)I.

### Declaration by Authors

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**Conflict of Interest:** The authors declare no conflict of interest.

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