

Synthesis and Spectroscopic  
Properties of Group 11 Multinuclear Pyrazolate Structures With Bridging Ligand

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## Research Proposal

### Introduction

This research will be focused on the following two areas of study:

- Synthesis and characterization of coordination polymer of mixed ligands and mixed metals silver and copper pyrazolate complexes.
- Photophysical properties of the resulting metal complexes and coordination polymer above.

### Trinuclearazolate Complexes of Group 11 Metals:

The trinuclearazolate complex of *d*10 currency metals such as Cu (I), Ag (I), and Au (I) have generated an immense interest because of their unique and interesting photophysical and photochemical properties (Hayashi et al., 2002; Rawashdeh-Omary, 2012; Hu, Gahungu & Zhang, 2007). These complexes have been investigated for their intriguing and interesting structural architectures and properties (Crespo, 2009). The cyclic trinuclear

complexes of Au (I), Ag (I), and Cu (I) can interact with liquid, solid, or vapor of organic molecules. The interaction leads to noticeable photophysical transformation of the characteristics of the starting complex (Rawashdeh-Omary, 2012). These compounds show intermolecular metal-metal interaction (M...M) that leads to

supramolecular assemblies (Crespo, 2009). However, there are new opportunities required to be researched because of a hidden

path to ultra-long-lived, greatly well-organized phosphorescence of cyclic trinuclear (Xing et al., 2020). Most of these complexes exhibit intense and prolonged luminescence at different temperatures in the solid-state that span the entire visible region (Hu, Gahungu & Zhang, 2007)).

They clinch to common chemistry areas such as metallophilic bonding, host/guest chemistry, and

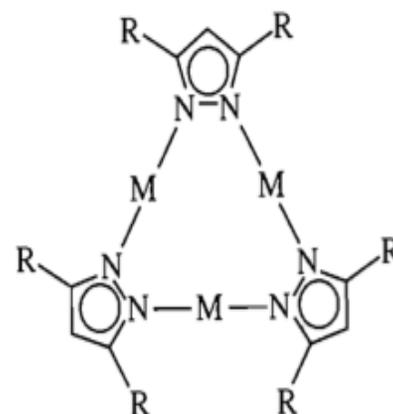


Figure (1) exhibits planar nine-membered M<sub>3</sub>N<sub>6</sub> rings.

M= Au, Ag, Cu. R= CH<sub>3</sub> (Omarv et al., 2003).

acid-base chemistry. Also, they apply in metalloaromaticity, exciplexes, M-M bonded, and supramolecular assemblies (Rawashdeh-Omary, 2012; Chimiche & Fackler, 2003; Omary, 2005). Nitrogen coordination from ligands such as pyrazolates, carbeniates, benzyimidazolates, amidinates, and related ligands to group 11 [Ag (I), Cu (I), and Au (I)] has resulted in fascinating chemistry (Rawashdeh-Omary, 2012; Yang & Raptis, 2003; Mohamed, Burini & Fackler, 2005). The pyrazolate and pyrazole monomers combination creates complexes that have been known for many decades (Crespo, 2009). Dimer molecules usually consist of two joining pyrazolate ligands. Notably, these dimeric molecules are found to have unusual reactions (urray, Raptis & Fackler 1988). There is a significant degree of flexibility in Pyrazoles that provides suitable coordination chemistry with the currency metal in many forms (Halcrow, 2009). Examples of rich coordination chemistry are anionic monodentate, Exo/endo bidentate, and neutral monodentate (Crespo, 2009; Yang & Raptis, 2003; Halcrow, 2009).

Fackler and co-workers were among the earliest people who started to study pyrazolate complexes of group 11 (Omary et al., 2005). The supramolecular structure of tri-nuclear pyrazolate complexes of group 11 is held together by intermolecular metallophilic interactions. It can be influenced by various factors such as substituents on the pyrazole rings, the metal, and the concentration (Yang & Raptis, 2003).

Group 11 trinuclear metal complexes, for example (Figure1), show two coordinated metal ions ( $M = Ag^+, Cu^+$ ) that behave like linear units, whereas the pyrazolate ligands appear like angular building blocks (Yang & Raptis, 2003). Trinuclearpyrazolate complexes of d10 coinage metals are known to exhibit  $\pi$  Lewis acid-base properties. The substituents (R) on ligands are the factors that impact the  $\pi$  acidity and basicity of the molecule, besides the type of metal. Electron-donating R

groups, such as methyl or other alkyl groups, can make the trimer metal complex behave as  $\pi$  Lewis bases. By contrast, if the R is an electron-withdrawing group such as Cl, F, or another halide, it can behave as a  $\pi$  Lewis acid (Omary et al., 2005).

Many pyrazolate-trinuclear metal complexes have been reported, and the resulting complex structures can be either  $\pi$ Lewis acids or bases, based on the influence of the atoms and the metal on the ligand (Rasika Dias, HPolach, &Wang, 2000).

Those complexes generate intense, clear, tunable fluorescence. Moreover, these metal complexes are believed to be probable light emitters used in MOLEDs (molecular light-emitting devices) due to their phosphorescence properties influenced by the existence of closed-shell transition metals and metal-metal

interaction (Dias, 2003) Also, the volatility of the complexes is increased by fluorination (Dias, 2003). The

photophysical properties of these complexes include bright multicolored fluorescent emissions.

These emissions are affected by heat, solution, and concentration (Figure 2)( Dias, 2003; Halcrow & Pyrazoles, 2009). Metal complexes with fluorinated ligands manifest different properties compared to their non-fluorinated analogs. For example, copper (I) derivatives of fluorinated ligands demonstrate significantly higher oxidation potentials than those of the non-fluorinated ligands (Rasika Dias, HPolach, &Wang, 2000; Dias et al., 1996). The metallophilic nature of the complexes affects their photophysical and photochemical properties. They also influence their biological activity (Dias et al., 1996; Satumtira et al., 2012). These were found in many reported trinuclearazolate metal complexes and were attributed partially to the properties of the adjoining

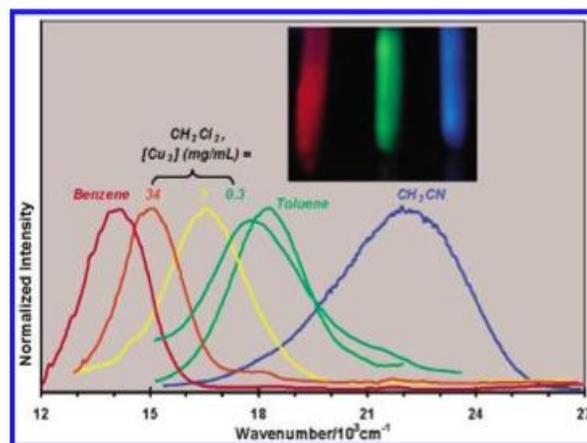


Figure (2) Emission spectra of Cu<sub>3</sub> frozen solutions (77 K) in different solvent and concentration immediately after removal from a liquid nitrogen bath<sup>(14)</sup>.

ligands and the ground, or excited state of the metals in the complexes, the nature of the ligand, the R substituent groups around the ligand, the metal center, concentration, reaction time, temperature, and solvent (Dias et al., 2003; Satumtira et al., 2012).

### Linearly Bridging Diimine Ligand

Bridging ligands with bimetallic complexes that contain transition metal ions belonging to the second and third-row respectively has unusual and exquisite electronic and electrochemical properties (Satumtira et al., 2012). Dinuclear Ru (II), Pd(II), Pt(II) complexes have been widely studied. However, there have been limited studies on Ir(III) systems that have demonstrated the “Ir(ppy)<sub>2</sub>” (ppy = 2-phenyl pyridine) motifs that comprise of two empty coordination sites. Also, there is a need to determine the oxidation level of the particular ligands complex, given that the central metal ion does not show significant back donation effects (Römelt et al., 2019). These sites could behave as building blocks for the construction of bimetallic. In general, the pyridine-based linkers have demonstrated the ability for the creation of dinuclear metal complexes, which has led some researchers to employ these types of ligands, as shown in (figure 3) to construct coordination polymer (Satumtira et al., 2012).

The choice of the pyridine-based ligands was informed by the following guidelines:

(1) “Difference of the spacer length between the pyridyl donor atoms would modulate the intermetallic distances,” and (2) “The bridging ligand conjugation would help to form metal–metal interaction” (Satumtira et al., 2012). The type of spacers connecting two groups of pyridyl in the joining ligand can determine the properties and structures

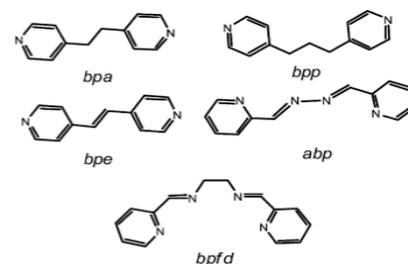


Figure (3) example for bis-pyridyl Linkers <sup>(16)</sup>

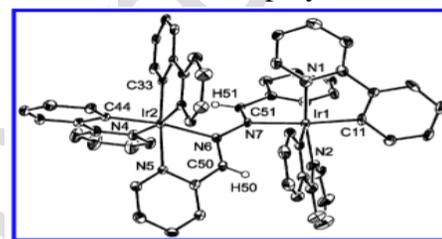


Figure (4) example for iridium dimer  $[\text{Ir}(\text{ppy})_2]_2(\mu\text{-abp})$  <sup>(16)</sup>

of the metallomacrocycles. For example, it was reported about the possibility of cleaning the life of the people of emissions and the possibility of adjusting the luminescent colors by using a variation of bridging ligand for the iridium dimer  $[\{\text{Ir}(\text{ppy})_2\}_2(\mu\text{-BL})_2](\text{OTf})_2$  (Satumtira et al., 2012). The properties such as the redox potentials of the metallomacrocycles iridium dimer  $[\{\text{Ir}(\text{ppy})_2\}_2(\mu\text{-BL})_2](\text{OTf})_2$  have changed altering the bridging ligand, and the conclusion can be made that the type of ligand determines the range at which the molecules undergo reduction. It has generally been seen that reduction at a higher negative electrode is linked to the ppy ligand, while reduction at a lower negative electrode is linked to bpa ligand (Satumtira et al., 2012).

### **Mixed Metal And Mixed Ligand For Group 11 Complexes:**

The majority of developments in cyclic trinuclear complexes of group 11 are homometallic cyclic trimers (Chimiche & Fackler, 2003; Omary et al., 2005; Dias et al., 2003). The three isomeric and photoluminescent complexes are  $[\text{Cu}_3(\text{L}_4)_3]_2[\text{CuI}]_2$  (Zhan et al., 2018). The complexes are labeled as (complexes **1, 2, and 3**) and formed from the similar bifunctional chemically organic ligand. However, heterometallic, or stacked cyclic trimers have been isolated and structurally identified upon the mixing of two homometallic cyclic trimers, each with a different ligand (Mohamed, Burini & Fackler, 2005; Omary et al., 2005), to obtain mixed metal/ligand complexes.

The bimetallic clusters of cyclic trinuclear silver-gold have presented structural, bonding, and electronic properties that can be used in different useful applications such as catalysis, medicine, electronic devices, and optics because of their selectivity (Satumtira et al., 2012; Lopez, 2002; I, C. B. L, 2000) (Fig 5a). Besides, mixing of ligands has also been studied. Tetranuclear gold (I) complexes are an example of the mixing of ligands that resulted from the reaction of the

bulky ligand dinuclearAu<sub>2</sub>(2, 6-Me<sub>2</sub>Ph-form)<sub>2</sub>(Au et al., 2007) (Fig 5b) with less bulky amidinates and pyrazolates.

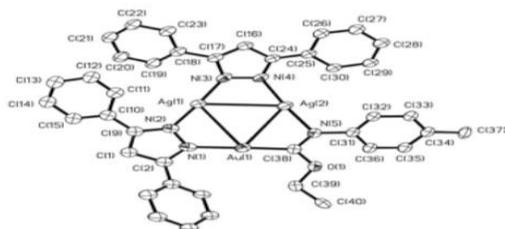


Figure 5a: The molecular structure of mixed metal gold/silver trimer [Au(carb)Ag<sub>2</sub>(μ-3,5 Ph<sub>2</sub>pz)<sub>2</sub>] (18)

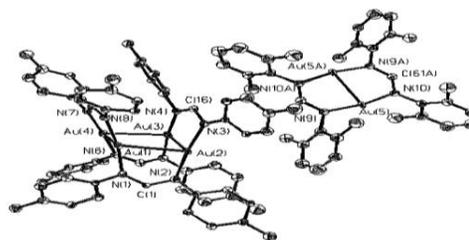


Figure 5b: A molecular structure of mixed ligands dinuclearAu<sub>2</sub>(2,6-Me<sub>2</sub>Ph-form)<sub>2</sub> (19)

## Potential Applications of Targeted Compounds

Our targeted compound most likely will form a metal-organic framework.

Metal-organic frameworks (MOFs), known as porous coordination polymers, have been intensively studied due to their applications in many areas such as solar cells, gas storage sensors, and semiconductors (Long & Yaghi, 2009; Reviews, 2012; Batten et al., 2013). The synthesis and characterization of various forms of MOFs have been reported recently (Abdou & Mohamed, 2009).

The ability of compounds to act as a MOF is influenced by the type of metal and bridging ligand. Metal-organic frameworks (MOFs) are formed by using the coordination bonds between the linker (bridging ligands) and the organic building units, which might be metal ion or cluster (Yaghi, Li &

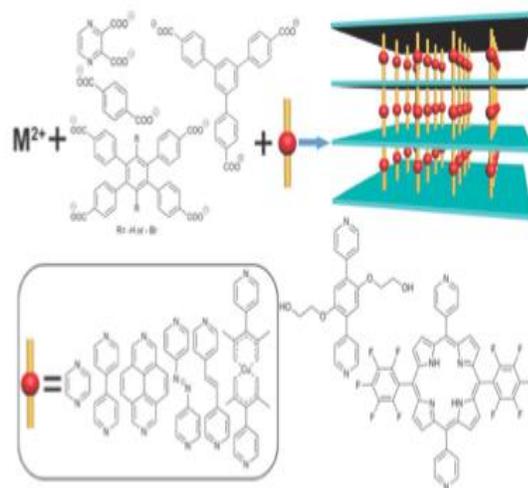


Figure (6) "Synthetic scheme for MOFs with polycarboxylate and dipyrindyl linkers" (Lu et al., 2014)

Li, 1995). Although the coordination polymers were described before in 1990, the construction and the methodical design of coordination polymers by using the trinuclear ions with organic building ligands appeared only in the first half of the 1990s (Yaghi, Li & Li, 1995). Since that time, more than 20000 MOF have been studied and reported. Bridging ligands have been used successfully to coordinate metal ions with clusters, to form metal-organic frameworks (MOFs) such as pillared-layer MOFs, which are one of the mixed-linker structures (Fig. 6). The perpetual porosity of MOFs that is regularly formed in MOFs constructed from metal groups is their most crucial hallmark. These linkers are frequently pre-shaped, while the groups or clusters are usually built in situ. The structure of the resulting (MOFs) depends on the geometry and communication of the bridging ligands. Knowing and determining the ratio, length, and functional group of the linker helps in adjusting the MOFs' intrinsic surface properties, such as the size and shape that is required for a specific application (Lu et al., 2014).

The inorganic units (metal ions or clusters) are widely specified as secondary building units (SBUs). The group, or the metal ion constitutes an inorganic unit. However, the organic units are created by the carboxylates or organic anion units. These units include heterocyclic compounds, sulfonate, and phosphonate. Scientists have studied MOFs because of their unique porosities structure and diversity (Thompson, Thompson, 1989). More recently, scientists have used MOFs for specific applications by selecting specific SBUs and linkers with selected sizes, shapes, and functionality, and tailoring them together as matrixes. In reality, there are many factors such as the temperature, concentration, and solvent that make the predictability of MOF design sometimes hard to realize, especially when the size of the MOF is increased in more complex cases. On the other hand, there are many factors, which may affect the morphology and crystallinity of MOFs,

such as solvent, temperature, and concentration. The organic building units are of many types based on the linkers (bridging ligands) they may connect with, which are

1. Mixed building unit
2. Desymmetrized building unit
3. Metallo- building unit or linkers
4. N-Heterocyclic building unit
5. Monocyclic carboxylate building unit
6. Tritopic carboxylate building unit
7. Tetratopic carboxylate building unit
8. Hexatopic carboxylate building unit
9. Octatopic carboxylate building unit

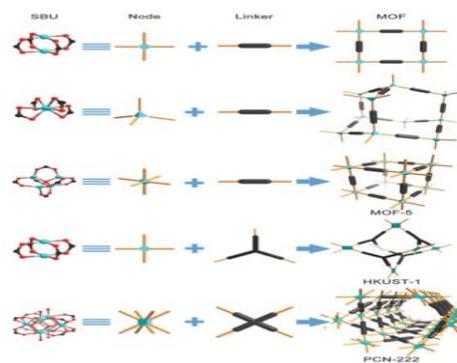


Figure (7) “The construction of some coordination polymers/MOFs from SBUs and rigid linkers”<sup>(lu et al., 2014)</sup>

Scientists have studied different types of carboxylate linkers intensively after they discovered the MOFs; it is because of their approachability and their easily understood structures when synthesized with various SBUs (Lu et al., 2014).

Similarly, a complex of mixed-ligand copper (II) regulates angiogenesis and osteogenesis in medicine. Quercetin-Cu(II)-neocuproine [Cu + Q(Neo)], complexes of mixed ligands, and copper (II) compounds have been characterized and synthesized (Vimalraj et al., 2018). C-rings are involved in chelation of the metal among the three complexes of copper. Notably, the copper complexes are identified to possess angiogenic and osteogenic properties.

### Research Goals:

This research involves the synthesis and characterization of various complexes of copper (I) and silver (I)pyrazolate with different types of bridging diimine ligands that can be potentially used in various applications such as MOFs.

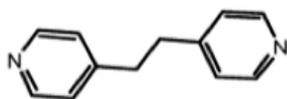
To reach this goal, we will:

- A. Synthesize copper (I) and silver (I) trinuclear-fluorinated pyrazolate complexes.
- B. React the trinuclear-pyrazolate complexes of silver (I) and copper (I) with variable bridging diimine ligands under different conditions using different molar ratios.
- C. Synthesize mixed metal and/or mixed ligand of copper (I) and silver (I) trinuclear complexes.
- D. Characterize the electrochemical and photophysical properties of each product and investigate its potential use in different applications.

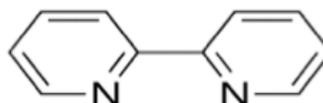
**Research Plan:**

**Synthesis and Structural Characterization of d10 coinage metal complexes with different organic building ligands**

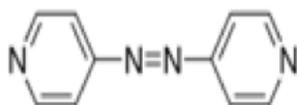
- All synthesis will be carried out in an inert atmosphere using purified nitrogen gas standard Schlenk techniques.
- We will synthesize the fluorinated trinuclear-pyrazolate complexes from the copper (I) and silver (I) to use them as our starting materials based on published methods.
- Fluorinated tri-nuclear pyrazolate complexes of silver {[3,5-(CF<sub>3</sub>)<sub>2</sub>Pz]Ag}<sub>3</sub> and copper {[3,5-(CF<sub>3</sub>)<sub>2</sub>Pz]Cu}<sub>3</sub> will be reacted with various linearly-bridging diimine ligands listed below:
  - Pyrazine.
  - 4,4'-Azopyridine (Azo)
  - 1,2-bis(4-pyridyl)ethane(bpa)
  - 2,2'-Dipyridyl
  - 1.10 phenanthroline



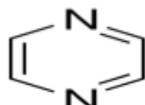
1,2-Bis(4-pyridyl)ethane



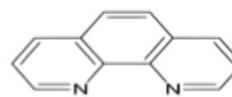
2,2'-Dipyridyl



4'4'-Azopyridine

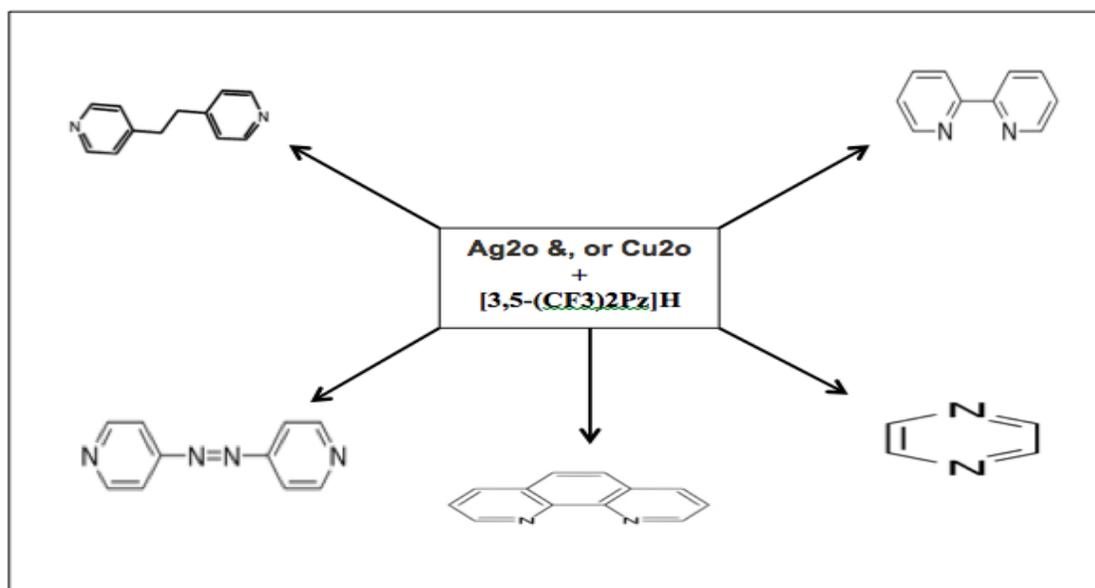


Pyrazine



1.10 phenanthroline

1. Different reactions will be carried out using different molar ratios of the metal to the bridging ligand.
2. Our goal is to synthesize and characterize mixed metals and/or mixed ligands coordination polymer.
3. The product will be described and analyzed using the following various techniques:
  - MP melting point.
  - NMR spectroscopy
  - FT-IR spectroscopy
  - Thermogravimetric analysis (TGA)
  - X-ray crystallography analysis
  - Luminescence spectroscopy
  - UV-Vis spectroscopy Raman



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