

# Bio Active Bipyridyl Complexes: Synthesis, Structure and Antimicrobial Activities

S. Aruna kumari<sup>2</sup>, B. Kishore babu<sup>1\*</sup>, G. Neeraja<sup>1</sup>

<sup>1</sup>Department of Engineering Chemistry, A. U College of Engineering, Andhra University, Visakhapatnam

<sup>2</sup>Department of H & BS, Aditya Engineering College, Surampalem

\*Corresponding author: E-Mail: jacobkishore@gmail.com

## ABSTRACT

Copper (II) complexes with N-heterocyclic ligands, particularly derivatives of 2,2'-Bipyridyl and short bridging Pseudo halide ligand have been prepared and structurally characterized by IR,LC-MS,TG-DTA ,UV spectra. Copper in the complex is coordinated by two nitrogen atoms of Bipyridyl and two oxygen atoms of isocyanate ligands has a square planar geometry .Complex is screened for antibacterial activity.

**KEY WORDS:** 2, 2'-Bipyridyl, iso-cyanate, Antimicrobial activity.

## 1. INTRODUCTION

As transition metals exhibit different oxidation states can interact with a number of negatively charged molecules. Coordination of biologically important metals like copper to bioactive ligands improve bioactive profiles and acquire pharmacological properties. 2,2' Bipyridyl acts as powerful ligand because of the particular arrangement of the nitrogen atom as well as the rigidity and chemical stability. 2,2'-Bipyridyl have been structurally characterized with various ligands, complexes containing these ligands have been synthesized and their antibacterial ,antifungal and in vitro anticancer activity were studied . Metal complexes with heterocyclic compounds played an important role in regulating biological activities hence these compounds are used in medicinal chemistry.

## 2. MATERIAL AND METHODS

IR spectra are obtained with a Shimadzu IR Prestige 21 FT-IR spectrophotometer. Electronic spectra are recorded on LABINDIA UV3000+ UV /VIS spectrophotometer. LC-MS spectra are recorded on AGILANT QQQ (ESI-MS). Mass spectrometer. TG-DSC spectra are obtained using SDT Q600 V20.9 BUILD 20.

**Synthesis of [Cu (Bpy)(NCO)<sub>2</sub>]:** An methanolic (5ml) solution of Copper perchlorate hexahydrate (0.37g, 1.0 mmol) is added to an methanolic solution(5ml) of Bipyridyl (0.156g, 1.0 mmol) under stirring conditions at 60°C temperature, dark blue solution is formed and then aqueous solution(10 ml) of NaOCN (0.081 g, 1.0 mmol) is added which turned to sky blue precipitate. After constant stirring at 60°C temperature for 30 minutes, the solution is filtered off. Later blue precipitate is collected and dried when the solution is allowed for slow evaporation. The blue crystals are formed in one day. The crystals are washed with methanol. Yield is 0.23 gms (38 %). Anal. expt C<sub>14</sub>H<sub>12</sub>CuN<sub>4</sub>O<sub>2</sub>, Mol.Wt.331.82, C 50.68, H 3.65, N 16.88 (observed); C 50.48, H 3.60, N 16.83 (calculated). Important IR bands (KBR disc cm<sup>-1</sup>) 3082, 2199, 2169, 1601, 1444, 621 cm<sup>-1</sup>. Mass Peaks (m/z): 307, 219, 157.

**IR Spectrum of [Cu (Bpy) (NCO)<sub>2</sub>]:** The IR spectrum of the complex exhibited band at 3082 cm<sup>-1</sup> due to the C-H of pyridine rings of 2,2-Bipyridyl ligand. The peak at 1601 cm<sup>-1</sup> is the stretching vibration of C=N group of heterocyclic diamine ligand and confirms its coordination to metal ions<sup>13</sup>. The peak characteristic of coordinated 2,2-Bipyridyl are 1444 and 621 cm<sup>-1</sup>. In the IR spectrum of the complexes, the band due to ring vibrations of the uncoordinated 2,2-Bipyridyl observed at 1621 cm<sup>-1</sup> is shifted to 1601 cm<sup>-1</sup>. This shift by 20cm<sup>-1</sup> to lower frequency show that 2,2'-Bipyridyl is coordinated to the metal centers. The presence of peak at 2199 cm<sup>-1</sup> indicates the coordination of isocyanate ion. The end-on bridging mode via nitrogen atom of cyanate ion is supported by the shift to lower frequencies of ν<sub>as</sub> (NCO) band 2183 cm<sup>-1</sup> which is in accordance with that found for the complex found at 2199cm<sup>-1</sup>. Important peaks reported in table.1.

**Table.1. IR Spectrum of [Cu (Bpy) (NCO)<sub>2</sub>]**

	ν <sub>as</sub> C=N	ν <sub>as</sub> (NCO)
<b>Complex</b>	1601 cm <sup>-1</sup>	2183 cm <sup>-1</sup>

**LC-MS spectrum of [Cu(Bpy)(NCO)<sub>2</sub>]:** The peak at 157 (/z) correspond to Bipyridyl peak at 219 (m/z) complex bounded to Bipyridyl molecule [Cu (Bpy)] peak around 307 (m/z) correspond to complex bound to one Bipyridyl and two isocyanate molecules [Cu (Bpy)(NCO)<sub>2</sub>].

**Electronic spectrum of complex [Cu(Bpy)(NCO)<sub>2</sub>]:** The electronic absorption spectrum of the Cu(II) complexes were recorded at room temperature using DMF as the solvent. The UV-VIS spectrum of Cu(II) complex displays a broad band at 280nm. They correspond to the d-d transitions for Cu(II) ion in a square planar geometry. Important absorption band mentioned in table.2.

**Table.2. Electronic Spectrum of [Cu (Bpy) (NCO)<sub>2</sub>]**

	Absorbance	assignment
<b>Complex</b>	280	d-d

**Thermo gravimetric analysis of [Cu(Bpy)(NCO)<sub>2</sub>]:** Thermal decomposition of the complex compound [Cu(Bpy)(NCO)<sub>2</sub>] takes place in two stages. In the first step occurs in the interval 50-220°C corresponding to partial decomposition of Bipyridyl ligand from the complex (remaining wt% obs/calcd; 13.6/15.8). After this temperature, a loss in weight has been observed in general up to 240°C corresponding to decomposition Bipyridyl ligand from the complex (remaining wt% obs/calcd 28.1/28.7). This is further confirmed by the exothermic band observed in the DSC curve in the temperature region at 250-300°C. Above this temperature a weight loss has been occurred up to 300°C this correspond to loss of isocyanate (remaining Wt% obs/calcd 5.9/5.9). The final decomposition step appeared above 290°C corresponding to the complete thermal decomposition of the complexes and the loss of their organic portion resulting in the formation of Copper Oxide as final product. TG-DTA spectrums shows fig.4 and 5.

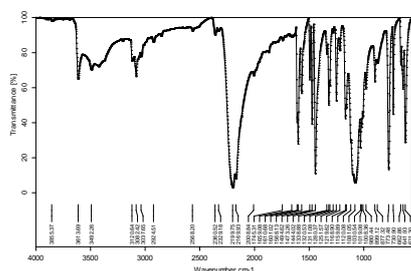
**Proposed Structure of [Cu (Bpy) (NCO)<sub>2</sub>]:** In the title mononuclear complex [Cu (Bpy) (NCO)<sub>2</sub>] Cu<sup>+2</sup> in the complex has a square planar geometry comprised of two nitrogen atoms of Bipyridyl and two oxygen atoms of two isocyanate ligands. Structure shows in Fig.6.

**Antimicrobial Screening of complex [Cu (Bpy) (NCO)<sub>2</sub>]:** The complex is screened in vitro for Antibacterial activity against *E. coli*, *S. aureus* and Antifungal activity against *R. oligosporos* by disc diffusion method.

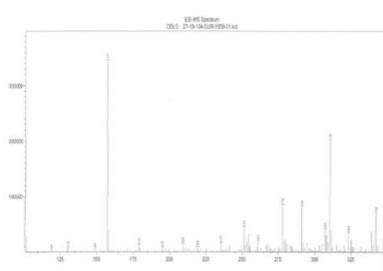
The *in vitro* Antimicrobial properties of the complex is tested against these gram - positive and gram - negative bacteria- *S. aureus*, *E. coli*, *P. aeruginosa* and fungi like *R. oligosporos*. Complex showed Anti-bacterial activity of inhibition zone equal to 10 and 7.5 mm, respectively for *S. aureus* & *E. coli* while no inhibition zone is found for *R. oligosporos*. The Antimicrobial activity of all the complexes are listed in table.3 and inhibition zones mentioned in fig.7, 8.

**Table.3. Inhibition zones for complex [Cu (Bpy) (NCO)<sub>2</sub>]**

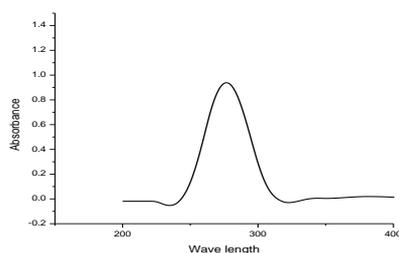
Micro organism	MIC values
<b>Bacteria</b>	<b>Inhibition zone (mm)</b>
<i>E.coli</i>	7.5
<i>S.aureus</i>	10
<b>Fungi</b>	<b>Inhibition zone (mm)</b>
<i>R.oligosporos</i>	Nil



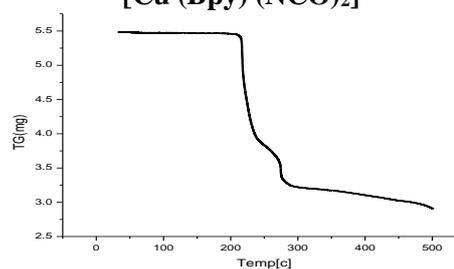
**Figure.1. Ir spectrum of complex [Cu (Bpy) (NCO)<sub>2</sub>]**



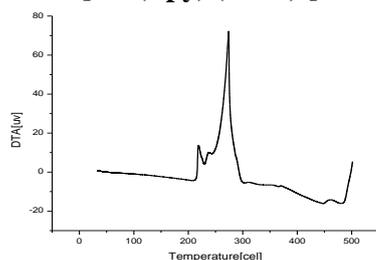
**Figure.2. LC-MS Spectrum of Complex [Cu (Bpy) (NCO)<sub>2</sub>]**



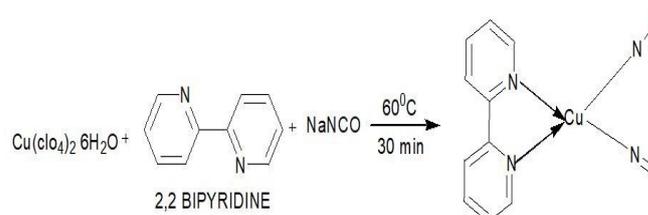
**Figure.3. Electronic Spectrum of Complex [Cu (Bpy) (NCO)<sub>2</sub>]**



**Figure.4. TG Spectrum of complex [Cu (Bpy) (NCO)<sub>2</sub>]**



**Figure.5. DTA Spectrum of Complex [Cu (Bpy) (NCO)<sub>2</sub>]**



**Figure.6. Synthetic route and proposed structure of complex**



**Figure.7. Inhibition zones for complex against *S.aureus* and *E.coli***



**Figure.8. Inhibition zones for complex against *R. oligosporos***

### 3. RESULTS AND DISCUSSIONS

Transition metal complex of copper complex involving bipyridyl and pseudohalide as secondary ligand is synthesized by self-assembled method which were analysed by means of IR, LC-MS, UV and Thermo gravimetric analysis.

The IR spectrum show that the bipyridyl acts as bidentate ligand with coordination involving nitrogen of heterocyclic diamine, oxygen of isocyanate ligand. The electronic spectrum confirms square planar for complex. The metal complex is screened for antimicrobial activities and evaluated against three different bacteria (*E. coli*, *S.aureus* and *P.aeruginosa*) and fungi (*R.oligosporos*) results show that complex exhibit good antibacterial activity in comparison with standard drug streptomycin and inactive against fungi.

### 4. CONCLUSION

In this article our work on the synthesis of copper, 2,2'-Bipyridyl, isocyanate complex and their antimicrobial studies. The results for complex revealed that they are good in microbial activity.

### REFERENCES

- Amani V, Safari N, Khavasi HR, Mirzaei P, Iron (III) mixed-ligand complexes, Synthesis, characterization and crystal structure determination of iron(III) hetero-ligand complexes containing 1,10 phenanthroline, 2,2'-bipyridyl, chloride and dimethyl sulfoxide, [Fe(phen) Cl<sub>3</sub>(DMSO)] and [Fe(bipy) Cl<sub>3</sub>(DMSO)], Polyhedron, 26 (17), 2007, 4908–4914.
- Bond A.M, Martin R.L, Electrochemistry and redox behaviour of transition metal dithiocarbamates, Coord. Chem. Rev., 1984, 54, 23.
- Felder D, Nierengarten J.N, Barigelletti F, Ventura B, Armaroli N, Highly luminescent Cu(I)-phenanthroline complexes in rigid matrix and temperature dependence of the photophysical properties., J. Am. Chem. Soc., 123, 2001, 6291-6299.
- Howell B.A, Sastry B.B.S, Comparison of the activation energies for the thermal decomposition of copper and nickel compounds obtained by various thermogravimetric methods, Thermochim. Acta., 340-341, 1999, 311-314.
- Howell B.A, Sastry B.B.S, Mixed ligand complexes of nickel (II), copper (II) and zinc (II) with nicotinanilide and thiocyanate. Thermochim. Acta., 1999, 311-341.
- Maurya R.C, Hourasia J.C, Sharma P, Synthesis, characterization and 3D molecular modeling of some ternary complexes of Cu(II), Ni(II), Co(II), Zn(II), Sm(III), Th(IV) and UO<sub>2</sub>(VI) with Schiff base derived from the sulfa drug sulfabenzamide and 1,10-phenanthroline, Indian Journal of Chemistry, 46, 2007, 1594.
- Patel R.N, Singh N, Gundla V.L.N, Synthesis, characterization and superoxide dismutase activity of some octahedral nickel(II) complexes, Polyhedron, 26, 2007, 749-948.
- Prashanthi Y, Kiranmai K, Ira., Sathish, Kumar K, Vijay Kumar C, Shivaraj, Spectroscopic Characterization and Biological Activity of Mixed Ligand Complexes of Ni(II) with 1, 10-Phenanthroline and Heterocyclic Schiff Bases, Bioinorganic Chemistry and Applications, 2012,
- Yam V.W.W and K.K.W Lo, Luminescent polynuclear d10 metal complexes, Chem. Soc. Rev., 28, 1999, 323.
- Zheng K, Jaing M, Li Y, Wua Z, Yan C, Computational strategies for predicting free radical scavengers protection against oxidative stress, Where are we and what might follow, Jour. Mol. Struct., 2014, 1058-1097.