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RESEARCH ARTICLE

DNA BINDING AND ANTIMICROBIAL STUDIES ON BIVALENT TRANSITION METAL COMPLEXES WITH 2, 4-DIHYDROXYBENZALDEHYDE-2-PICOLYLAMINE

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ABSTRACT

Bivalent transition metal [Co(II), Ni(II), Cu(II) and Zn(II)] complexes with 2,4-dihydroxybenzaldehyde-2-picolylamine(BAPA) are synthesized and analyzed based on mass spectra, molar conductivity, FT-IR and UV-Vis spectral data. The complexes are found to be non-electrolytes. From FT-IR data it is evident that the BAPA acts as uni-negative tridentate ligand. Electronic spectral data confers octahedral structure for the complexes. The copper complex is also studied using ESR spectroscopy. The Spin Hamiltonian, orbital reduction and bonding parameters are determined for the complex. DNA binding properties of the complexes were uncovered by using UV-Visible spectrophotometry. Of all the compounds, the copper complex binds more strongly. The metal complexes are screened for their antibacterial activity against pathogenic bacterial strains viz. Gram-ve bacteria (*Escherichia coli*, *Klebsiella pneumonia*) and Gram +ve bacteria (*Bacillus cereus*, *Staphylococcus aureus*). The copper complex shows higher activity than other complexes under investigation.

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INTRODUCTION

Schiff bases are versatile and interesting class of organic ligands with diverse applications (Kumar, 2009) in the evergreen field of Coordination Chemistry. Schiff bases of aminoalkylpyridines derivatives are known possess significant biological activity, such as antimicrobial, anti-inflammatory and antiviral activity. Studies showed that the biological activity of free ligands sometimes become enhanced upon coordination with metal ions. Stable chelates are formed with Schiff bases containing multiple and assorted donor atoms. The presence of the heterocyclic ring in the ligand lends additional stability to the structure of Schiff base metal complexes. Transition metal complexes of pyridine containing ligands have been at the forefront, because of their unusual electronic properties, diverse chemical reactivity, and interesting structures which result in non-covalent interaction with DNA (Metclafe, 2003; Erkkila, 1999). The biologically accessible oxidative/reductive potential made Copper complexes a class of the most frequently studied metallo-nucleases. It has been demonstrated that Cu can accumulate in tumors due to the selective permeability of cancer cell membranes to Cu compounds.

Copper(II) complexes are the preferred over Pt(II) complexes for cancer inhibition. There is evidence that anticancer activity was due to the intercalation between the drug and base pairs of DNA, and interference with normal functioning of the enzyme topoisomerase II that was involved in the breaking and releasing of DNA strands. Hence, it appeared important to synthesize a molecule that bears an intercalating moiety. Small Schiff base ligands with N-heterocyclic aromatic ring in which the heteroatom can coordinate to the metal ion are expected to induce a good extent of planarity to the complexes because of the rigidity introduced in the ligand framework by the coordinating heterocycle. It seems, therefore, to be of considerable interest to conduct investigations of transition metal complexes of involving 2-picolylamine which contains a basic N-atom (pyridine) and possesses Pi-acceptor properties, which are assumed to be involved in p-p stacking effects with purine and pyrimidine bases. Since the aromatic moiety plays a decisive role in enhancing DNA binding through stacking interactions, it was considered important to study the DNA interaction of complexes of Schiff base derived from 2,4-dihydroxybenzaldehyde and 2-picolylamine with heterocyclic bases. 2-Picolylamine has been used as precursor to more complex multidentate ligands. 2-picolylamine is constituent ligand of Baratta's catalyst [RuCl₂(PPh₃)₂(ampy)] used in hydrogenation reactions. 2-picolylamine has been used in the synthesis of many biologically active compounds.

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For example, there are many reports where picolyamine derivatives were used to form metal complexes as models that mimic both the structure and reactivity of metal ion sites in complex biological systems, showing that picolyamine possess a broad spectrum of biological activities (Pingawer, 2013). Deoxyribonucleic acid (DNA) is the storage site of cellular information that is accessed continuously for storing and dispensing information required for existence. It acts as the main intracellular target for those who thrive to develop a new drug for innumerable diseases, especially cancer. Coordination compounds can bind and react with specific DNA sites. It provides a means to access and manipulate cellular information and functions. Metal-DNA interaction is an exciting area of research due to their potential use as drugs, tools for biochemical and biomedical applications in gene regulation. Considerable efforts are being made to investigate Metal - DNA interactions (Hussain Reddy, 2016; Mokshragni, 2017; Suseelamma, 2018) and to develop drugs. Thus, looking to the importance of DNA binding agents with complexes of essential metal ions for successful development of antimicrobial agents, herein we report synthesis, characterization, DNA binding properties and anti-bacterial activity of Cu(II), Ni(II), Co(II) and Zn(II) complexes of 2,4-dihydroxybenzaldehyde-2-picolyamine (BAPA).

EXPERIMENTAL

MATERIALS AND METHODS

The reactants employed in the synthesis of 2,4-dihydroxybenzaldehyde-2-picolyamine (BAPA) were procured from Aldrich company and were used without further purification. Metal salts used were of reagent grade (Merck). Solvents were distilled before use. Calf thymus DNA was purchased from Genie Bio labs, Bangalore, India. All other chemicals were of AR grade and used without purification.

Synthesis of ligand(BAPA): Equimolar (5 mmol) quantities of 2,4-dihydroxybenzaldehyde and 2-picolyamine were taken in a 100-ml round bottom flask loaded with 20ml of methanol. The contents were heated under reflux for 2 hrs. A brown coloured product was formed on cooling the flask to room temperature. The product was collected by filtration, washed with a few drops of ethanol and dried in vacuum. Yield of the product, 82%; M.P. 140°C. Preparation of BAPA ligand is shown in Figure 1.

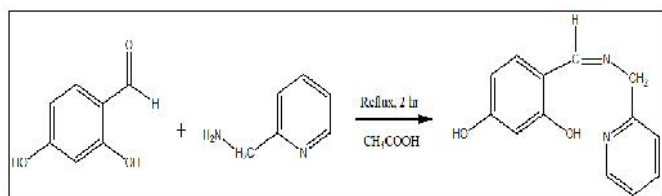


Figure 1. Preparation of 2,4-dihydroxybenzaldehyde-2-picolyamine(BAPA) ligand

IR spectra: Peaks at 3305, 1591 cm⁻¹ are assigned to (OH), and (C=N) stretching vibrations respectively.

¹H-NMR spectra: (in DMSO solvent). 13.50 (s, 2H, OH), 9.90 (s, 1H, CHO), 8.6-7.40 (m, 4H, py), 7.53-6.25 (m, 3 H, phenyl); GC-MS spectrum of BAPA is shown in Figure 1.

Peaks at m/z values of 108 and 91 and 79 are respectively assigned to dihydroxy phenyl cation radical and 2-methylpyridine cation and pyridine cation radical indicating the synthesis of BAPA ligand. (Molecular formula the ligand is C₁₃H₁₂O₂N₂).

Synthesis of complexes: The complexes were prepared by mixing hot methanolic solution (20 ml) of BAPA (0.46g, 20 mmol) with suitable metal salt (CoCl₂.6H₂O, NiCl₂.6H₂O CuCl₂.2H₂O, ZnCl₂. 10 mmol) dissolved in methanol (20ml) in 1:2 ratio in a clean 100- ml round bottom flask containing 0.5 g of NaOH. The contents were heated under reflux on water bath for 1 hr . On slow evaporation, coloured complexes which separated out were collected by filtration, washed with methanol followed by hexane and dried in vacuum. Physicochemical and analytical data of complexes are given in Table 1. The details of Physical measurements, DNA binding experiments and antibacterial activity are described in our recently published articles (Srinivasulu, 2018 ; Kasimbi, 2020; Nagamani, 2020)

RESULTS AND DISCUSSION

The complexes are prepared by reacting BAPA with suitable metal chloride. The compounds are non-hygroscopic, and soluble in ethanol and freely soluble DMF and DMSO solvents. Colour, yield, ESI-MS and molar conductivity data of complexes are given table 1. Typical ESI-Mass spectrum of Cu (BAPA)₂ is shown in Figure 2. A peak is observed at 517.8 due to the formation molecular ion peak in conformity with molecular formula, [Cu(C₁₃H₁₁N₂O)₂]. Molar conductivity data suggest that the complexes are non-electrolytes. Electronic spectra: Typical electronic spectrum of Cu(BAPA)₂ complex is shown in Figure 3. Electronic spectral data and assignment of bands are given in table 2. Co(BAPA)₂ complex does not show peak in the visible region due to the masking of intense C-T band. In the visible spectra of Ni(BAPA)₂ and Cu(BAPA)₂ complexes weak bands are respectively observed at 22,883 and 15,797 cm⁻¹ which are assigned to ³A_{2g} - ³T_{2g} and ²E_g - ²T_{2g} electronic transitions respectively in favour octahedral structures(Lever, 1968) for the complexes.

ESR spectra of copper complex: ESR spectra of Cu (BAPA)₂ complex (Solid and Liquid) in DMF at room temperature (RT) and at liquid nitrogen temperature (LNT) are shown in Figure 4 . ESR spectral data of in solid and liquid state in DMF are given in table 3. The g values were computed from the spectrum using tetracyanoethylene (TCNE) free radical as the g marker

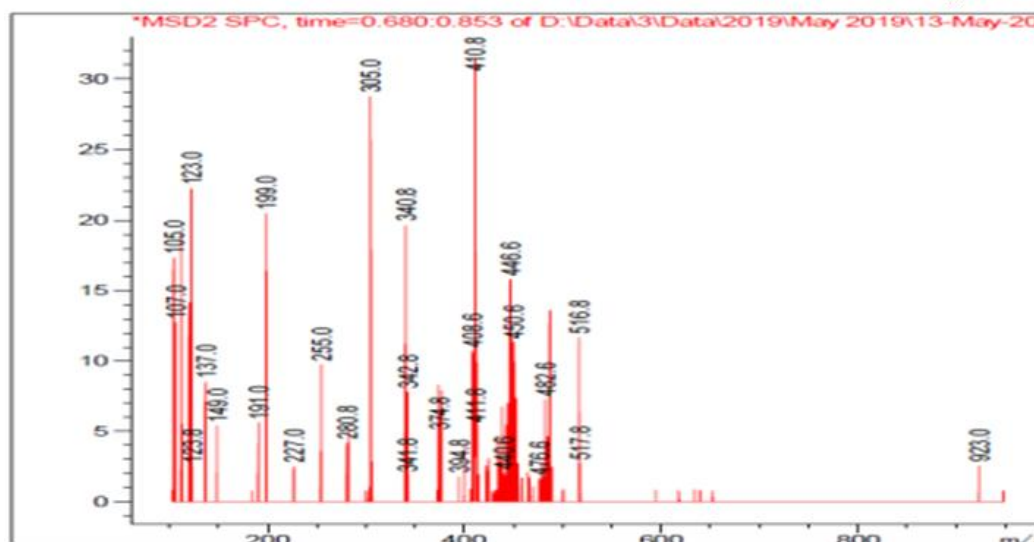
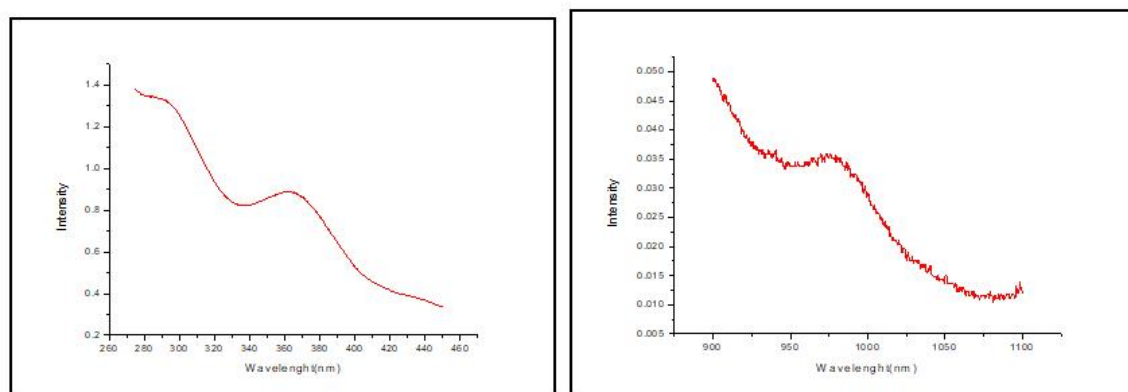
Solid state ESR spectra: The g and g' values for Cu(BAPA)₂ complex are respectively found to be 2.15 and 2.03 in solid state at room temperature and liquid nitrogen temperature. According to Kivelson and Neiman the g is less than 2.3 indicates covalent character and if it is greater than 2.3 suggests ionic character of the metal -ligand bonding. The g' value for the present complex suggests covalent character in M-L bond. The trend, g > g' > 2.0023 suggest that the unpaired electron predominantly in the d_{x²-y²} orbital characteristic of octahedral geometry for copper (II) complex . The axial symmetry parameter G is defined as,

$$G = (g - 2.003) / (g' - 2.003)$$

Table 1. Physicochemical and Analytical data of Co(II) Ni(II) Cu(II) and Zn(II) complexes

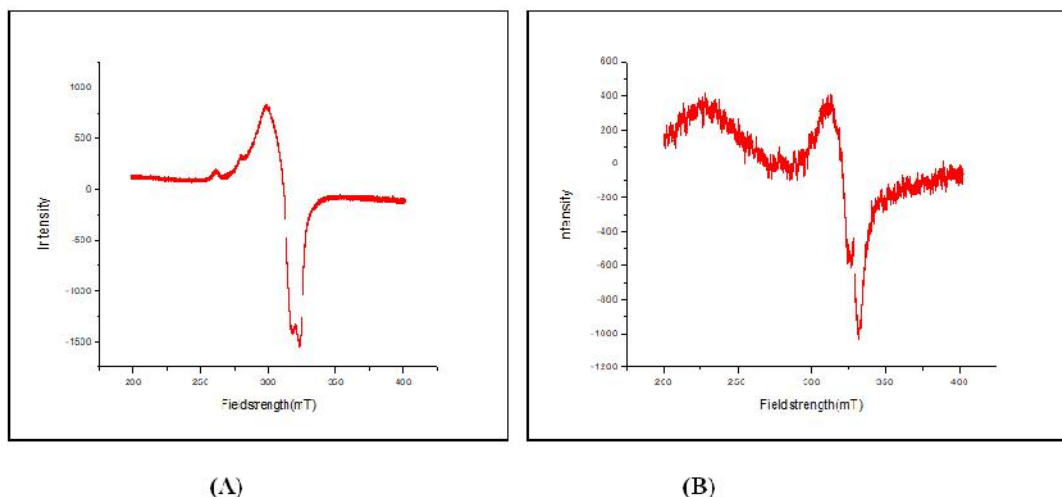
| S.No | Complex | ESI-MS (F.W)* | Melting Point (°C) | Colour (Yield %) | Molar Conductivity |
|------|-----------------------|-----------------|--------------------|---------------------|--------------------|
| 1 | Co(BAPA) ₂ | 517 (514.93) | 274-275 | Brown (88.94) | 19.44 |
| 2 | Ni(BAPA) ₂ | 516.8 (516.6) | 283-284 | Brown (88.65) | 32.13 |
| 3 | Cu(BAPA) ₂ | 520.06 (519.54) | 256-257 | Brown (88.24) | 36.70 |
| 4 | Zn(BAPA) ₂ | 517.8 (521.38) | 239-240 | Light Brown (87.00) | - |

*Calculated values are given in parenthesis

**Figure 2. ESI-Mass spectrum of Cu (BAPA)₂ complex****(a) UV-spectrum****(b) Visible spectrum****Figure 3. Electronic spectra of Cu(BAPA)₂ complex in a) in UV and (b) in visible regions**

| S.No | Complex | Wavelength max (nm) | Frequency (cm ⁻¹) | Assignment |
|------|-----------------------|---------------------|-------------------------------|----------------|
| 1 | Co(BAPA) ₂ | 271 | 36,900 | - * transition |
| | | 352 | 28,409 | CT transition |
| | | 269 | 37,174 | - * transition |
| | | 348 | 28,735 | CT transition |
| 2 | Ni(BAPA) ₂ | 437 | 22,883 | d-d transition |
| | | 289 | 34,602 | - * transition |
| 3 | Cu(BAPA) ₂ | 363 | 27,548 | CT transition |
| | | 633 | 15,797 | d-d transition |

| Complex | ESR Spectral parameters | | | | | | | | | |
|-----------------------|-------------------------|-------------|------------------|--------------|------------------------------------|----------------------|-----------------|------|-----------------|-------|
| | g | g | g _{avg} | G | A × 10 ⁻⁵ | A × 10 ⁻⁵ | K | K | g _{av} | 2 |
| Cu(BAPA) ₂ | 2.32 (2.15) | 2.02 (2.03) | 2.12 (2.07) | 13.23 (4.64) | 0.01614 | 0.00592 | 0.99 | 1.21 | 645 | 0.271 |

Figure 4. ESR spectra of Cu (BAPA)₂ complex: A) in Liquid state at LNT and B) in liquid state at RTTable 4. IR Spectral data (cm⁻¹) of BAPA and its metal complexes

| BAPA | Co(BAPA) ₂ | Ni(BAPA) ₂ | Cu(BAPA) ₂ | Zn(BAPA) ₂ | Assignment |
|------|-----------------------|-------------------------|-------------------------|-------------------------|-------------|
| 3305 | - | - | - | - | OH |
| 1591 | 1539 | 1537 | 1538 | 1560 | C=N |
| 1530 | - | - | - | - | |
| 1441 | 1437 | 1444 | 1435 | 1401 | phenyl ring |
| 1223 | 1202 | 1219 | 1215 | 1222 | phenyl ring |
| 1151 | - | - | - | - | |
| - | 1105 | 1095 | 1132 | 1128 | C=O |
| 965 | 980 | - | - | - | |
| 751 | 749 | 760 | 752 | 761 | Py |
| 629 | 627 | 639 | 623 | 618 | Py |
| - | 585 | 591 | 554 | 596 | M-O |
| - | 481 | 465 | 448 | 459 | M-N |

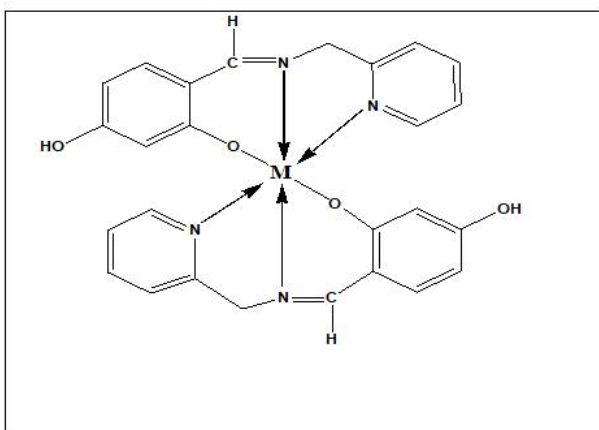


Figure 5. Proposed structure for the complexes [M = Co(II), Ni(II), Cu(II) and Zn(II)]

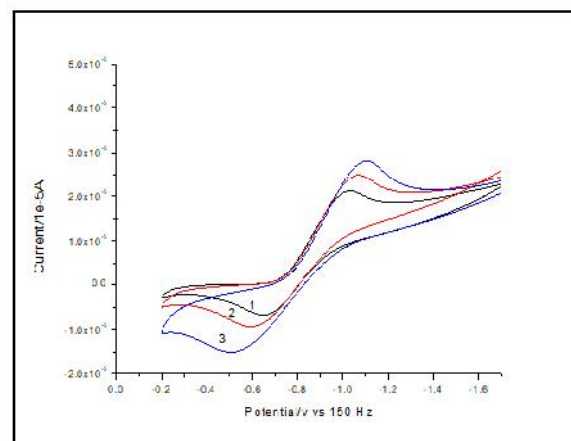
Figure 6. Cyclic voltammogram of Ni (BAPA)₂ Complex

Table 5. CV data of Co (II), Ni (II), Cu (II) and Zn(II) complexes.

| S.No | Complex | Redox couple | E _{pc} | E _{pa} | E _p (mV) | E _{1/2} | -i _c /i _a | LogK _c ^a | -G ^b |
|------|-----------------------|--------------|-----------------|-----------------|---------------------|------------------|---------------------------------|--------------------------------|-----------------|
| 1 | Co(BAPA) ₂ | II/I | -0.99 | -0.60 | 390 | -0.795 | 0.237 | 0.086 | 494 |
| 2 | Ni(BAPA) ₂ | II/I | -1.04 | -0.66 | 380 | -0.850 | 0.373 | 0.088 | 507 |
| 3 | Cu(BAPA) ₂ | II/I | -0.075 | 0.145 | 220 | 0.110 | 0.489 | 0.108 | 582 |
| 4 | Zn(BAPA) ₂ | II/I | -1.03 | -0.59 | 440 | -0.810 | 0.220 | 0.076 | 438 |

$${}^a \log K_c = 0.434ZF/RT \quad E_p; {}^b G^\circ = -2.303RT \log K_c$$

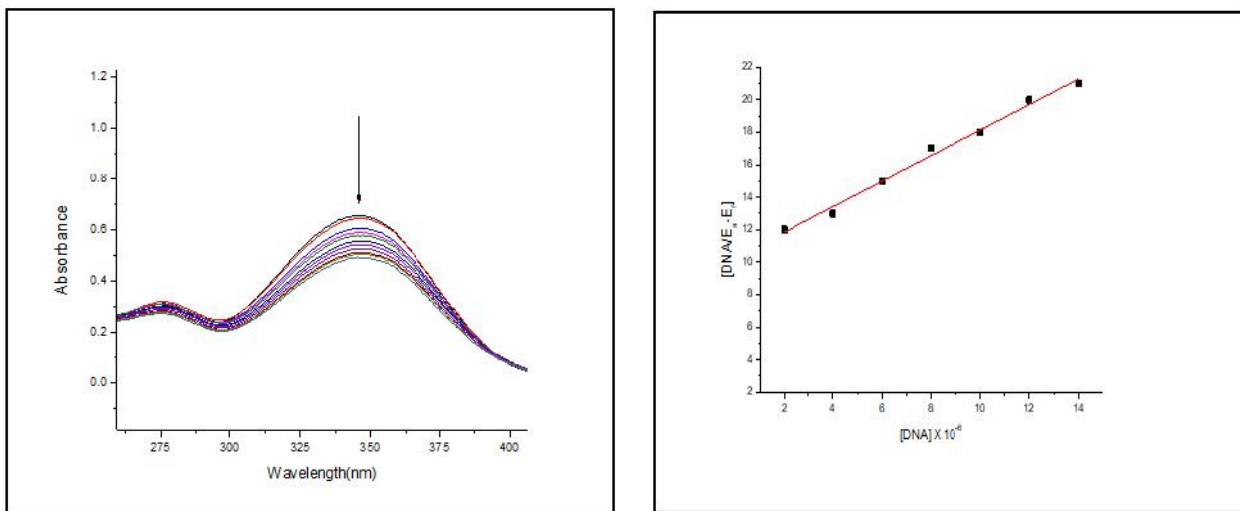


Figure 7. (A) Absorption spectra of Cu(BAPA)₂ complex in the absence(top curve) and in the presence of increasing concentration of DNA (B) A plot [DNA]/(a - a₀) vs [DNA] x 10⁻⁶.

| S.No | Complex | max (nm) | | H% | K _b [M ⁻¹] |
|------|-----------------------|----------|-------|-------|-----------------------------------|
| | | Free | Bound | | |
| 1 | Co(BAPA) ₂ | 352 | 353 | 18.60 | 2.8 X10 ⁵ |
| 2 | Ni(BAPA) ₂ | 348 | 349 | 23.71 | 3.3 X10 ⁵ |
| 3 | Cu(BAPA) ₂ | 363 | 365 | 35.81 | 3.7 X10 ⁵ |
| 4 | Zn(BAPA) ₂ | 345 | 346 | 19.23 | 2.4 X10 ⁵ |

Table 7. Antibacterial activity of different Metal Complexes against pathogenic bacterial strains

| S.No | Sample | Treatment (Concentration) | <i>E. coli</i> (Mean±SE) | <i>K.pneumoniae</i> (Mean±SE) | <i>S. aureus</i> (Mean±SE) | <i>B.cereus</i> (Mean±SE) |
|------|-----------------------|---------------------------|--------------------------|-------------------------------|----------------------------|---------------------------|
| 1 | S-Ciprofloxacin | (5µg/µL) | 10.50±0.02 | 09.80±0.09 | 10.03±0.03 | 12.16±0.05 |
| 2 | Co(BAPA) ₂ | 100µg/µL | 1.98±0.04 | 1.17±0.07 | 1.87±0.08 | 2.14±0.05 |
| | | 200µg/µL | 2.13±0.05 | 2.47±0.05 | 2.80±0.02 | 2.45±0.08 |
| | | 300µg/µL | 2.18±0.01 | 2.93±0.08 | 2.97±0.06 | 2.87±0.12 |
| 3 | Ni(BAPA) ₂ | 100µg/µL | 2.25±0.12 | 2.27±0.02 | 2.04±0.04 | 2.57±0.01 |
| | | 200µg/µL | 3.34±0.17 | 2.50±0.04 | 2.98±0.01 | 3.33±0.02 |
| | | 300µg/µL | 3.18±0.15 | 3.17±0.05 | 3.70±0.02 | 3.40±0.05 |
| 4 | Cu(BAPA) ₂ | 100µg/µL | 2.40±0.11 | 2.40±0.01 | 3.10±0.05 | 3.12±0.10 |
| | | 200µg/µL | 3.67±0.09 | 3.67±0.04 | 3.34±0.08 | 3.25±0.02 |
| | | 300µg/µL | 4.98±0.06 | 4.33±0.07 | 3.50±0.02 | 4.40±0.05 |
| 5 | Zn(BAPA) ₂ | 100µg/µL | 1.15±0.12 | 1.07±0.07 | 1.20±0.04 | 1.20±0.01 |
| | | 200µg/µL | 1.35±0.07 | 1.13±0.01 | 1.45±0.08 | 1.71±0.02 |
| | | 300µg/µL | 1.55±0.04 | 1.25±0.08 | 1.73±0.03 | 1.83±0.05 |

Values are the mean ± SE of inhibition zone in mm.

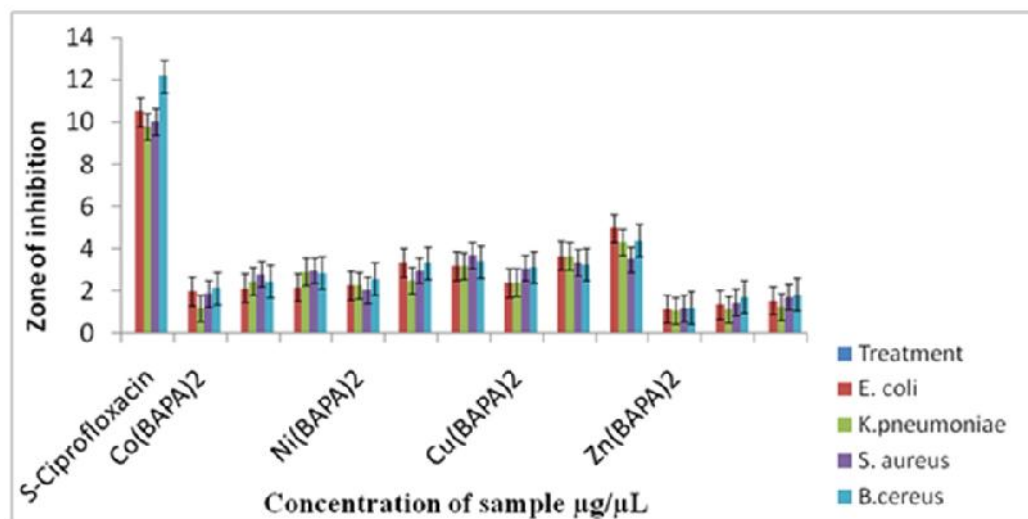


Figure 8. Graphical representation of antibacterial activity of metal complexes against pathogenic bacterial strains

The calculated G value for the complex is found to be 3.0 which indicates the absence of exchange coupling and misalignment of molecular axes.

Liquid state ESR spectra: The typical ESR spectrum of $\text{Cu}(\text{BAPA})_2$ complex in DMF at Liquid nitrogen temperature (LNT) and Room temperature is shown in Figure.5 ESR spectra of complexes in DMF at liquid nitrogen temperature (LNT) exhibit well resolved peaks at low field and at high field corresponding to g_{\parallel} and g_{\perp} respectively. The spin Hamiltonian, orbital reduction and bonding parameters of complexes are incorporated in table 3. The A_{\parallel} and A_{\perp} are the separation between two adjacent g_{\parallel} and two adjacent g_{\perp} peaks respectively (in cm^{-1}). Hathaway pointed that for pure sigma bonding $K_{\parallel} = K_{\perp} = 0.77$ and for in-plane pi bonding $K_{\parallel} < K_{\perp}$, while for out-plane pi bonding $K_{\parallel} > K_{\perp}$. For the complex K_{\parallel} and K_{\perp} are 0.99 and 1.21 respectively. These values suggest the presence of in-plane pi bonding in the complex. The g value (0.271) of the complex suggests the covalent nature of metal ligand bond.

IR spectra: IR spectrum of BAPA ligand is compared with those of metal complexes to determine donor atoms of ligand. Important IR spectral bands and their assignment are given in table 4. The IR spectrum of the ligand shows prominent bands at 3305cm^{-1} due to O-H stretching mode. The low value is due to strong hydrogen bonding between hydrogen atom of aromatic O-H and pyridine nitrogen atom. This band is disappeared in spectra of complexes due to deprotonation of aromatic O-H group and subsequent covalent bond formation between phenolic oxygen and metal ion. New band in the $1105\text{-}1132\text{cm}^{-1}$ range is appeared in the spectra of complexes due to C-O vibration. A strong peak is observed in the spectrum of BAPA ligand. It is assigned to $>\text{C}=\text{N}$ - (azomethine) stretching vibration. This band is shifted to lower frequency in the spectra of complexes indicating the involvement of azomethine ($\text{C}=\text{N}$) nitrogen in coordination. The pyridine ring deformation modes are observed in $629\text{--}751\text{cm}^{-1}$ region respectively. These bands are shifted to higher wave number in the spectra of complexes indicating coordination of heterocyclic nitrogen in coordination. The new bands in $554\text{--}596$ and $448\text{--}481\text{cm}^{-1}$ regions appeared in the spectra of complexes are assigned to M-O and M-N vibrations respectively. IR data suggest that the ligand acts as mono basic tridentate ligands in all the complexes. Based on physicochemical and spectral data a general structure Figure 5 for the complexes is proposed.

Cyclic voltammetry: Electrochemical behaviour of the complexes was investigated by cyclic voltammetry in DMF using 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The cyclic voltammogram of $\text{Ni}(\text{II})$ complex is shown in Figure 6 and the electrochemical data of metal complexes are summarized in table 5. The cathodic peak current function values were found to be independent of the scan rate. Repeated scans at various scan rates suggest that the presence of stable redox species in solution. It has been observed that cathodic (I_{pc}) and anodic (I_{pa}) peak currents were not equal. Metal complexes presumably undergo one electron reduction to their respective $\text{M}(\text{I})$ complexes. The non-equivalent current intensities of cathodic and anodic peaks indicate quasi-reversible behaviour. The difference, E_p in all the complexes be better than the Nerstian requirement $59/n\text{ mV}$ (n = number of electrons involved in oxidation reduction),

which demonstrate quasi-reversible character of electron transfer. The complexes show large separation between anodic and cathodic peaks indicating quasi-reversible character.

DNA binding studies: The interaction of metal complexes with calf-thymus DNA was monitored by UV-visible spectroscopy. Absorption spectra Figure. 8 were recorded in $250\text{-}500\text{ nm}$ range in presence and in absence of DNA. Metal complexes exhibit an intense absorption band in high energy region, which is attributed to metal-ligand charge transfer (MLCT) transitions. The change in absorbance values with increasing amounts of CT-DNA was used to evaluate the intrinsic binding constant K_b , for the complexes. Based on the variation in absorption, the intrinsic binding constant or association constant (K_b) of the metal complex may be calculated according to the Benesi-Hildebrand equation (Wolfe, 1987). $[\text{DNA}]/(a - f) = [\text{DNA}]/(b - f) + 1/K_b (b - f)$ Where, a , f and b correspond to $A_{\text{observed}}/[\text{complex}]$, the extinction coefficient for the free metal complex, and the extinction coefficient for the metal complex fully bound to DNA, respectively, K_b represents the binding constant. The binding constants of these complexes are given in the table 6. In the presence of increasing amounts of CT-DNA, the UV-visible absorption spectra of metal complexes show a small bathochromic shift (Red shift) ($\lambda_{\text{max}} = 0.5\text{-}1.0\text{ nm}$). The calculated binding constants are found in the range $2.4\text{--}3.7 \times 10^5\text{ M}^{-1}$. The observed binding constants for the present complexes are in accordance with groove binding with DNA as reported in the literature (Ramakrishna, 2011). It is pertinent to note that the binding constant for $\text{Cu}(\text{BAPA})_2$ complex is quite high. The increasing order of binding constant is: $\text{Zn}(\text{BAPA})_2 < \text{Co}(\text{BAPA})_2 < \text{Ni}(\text{BAPA})_2 < \text{Cu}(\text{BAPA})_2$. The above order suggest that the $\text{Cu}(\text{BAPA})_2$ complex binds DNA more strongly.

Antibacterial activity studies: The metal complexes were screened for their antibacterial activity by using agar well diffusion method against pathogenic bacterial strains viz. *Escherichia coli*, *Klebsiella pneumonia*, *Bacillus cereus* and *Staphylococcus aureus*. Inhibition zones were estimated in the presence of varying amounts ($100, 200$ and $300\text{ }\mu\text{g/mL}$) of complexes with reference to the positive control viz. *ciprofloxacin*. The diameters of inhibition of zone were measured with Vernier callipers in mm and its values are given in table 7. Antibacterial activity of present complexes is compared with the standard compound (Figure 8) as shown in bar graph. The zone of inhibition by $\text{Cu}(\text{BAPA})_2$ complex is highly significant.

Conclusion

Spectral data suggest that the ligand, 2,4-dihydroxybenzaldehyde-2-picolylamine (BAPA) acts as monoanionic tridentate ligand and complexes have octahedral structure. The complexes have covalent character as suggested by ESR spectral data copper (II) complex. The cyclic voltammetric studies suggest that all the complexes undergo quasi-reversible one electron reduction. The non-equivalent current intensity of cathodic and anodic peak indicates quasi-reversible behaviour of these complexes. The K_b values and variation in absorption spectra of metal complexes suggest groove binding of complexes to DNA. The copper complex binds DNA more strongly than other complexes. The copper

complex also shows more antibacterial activity than other complexes.

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Conflict of interest: The authors declare that there is no conflict of interests regarding the publication of this article.

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