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# Synthesis, Spectral Characterization and DNA Binding Properties of Copper(II) Complexes of Functionalized Hydrazones.

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**ABSTRACT**

Copper(II), complexes of a series of functionalized heterocyclic hydrazones viz. 2-acetylpyridineacetoylhydrazone(APAH),2-acetylpyridinebenzoyllhydrazone (APBH), 2-benzoyllpyridineacetoyl hydrazone (BPAH), 2-benzoylpyridinebenzoyllhydrazone (BPBH) have been synthesized and characterized on the basis of elemental analysis, molar conductivity measurements, magnetic susceptibility, electronic, infrared and electron spin resonance spectral data.. The molar conductance values indicate that complexes are non-electrolytic in nature. IR spectral data suggest that the ligands act as mono anionic trifunctional NNO-donor system. Electronic spectral data suggest octahedral geometry for complexes. Electrochemical properties of metal complexes are investigated by using cyclic voltammetry, The complexes undergo quasi-reversible one electron reduction. Absorption titration studies revealed that these complexes are avid binder to calf-thymus DNA.

**Keywords:** DNA, Coper (II), hydrazones, complex

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## INTRODUCTION

Metal complexes of hydrazones have wide applications in biological processes[1-2] . The complexes have been used as catalysts in chemical and petrochemical industries[3,4]. Hydrazones constitute an important class of biologically active drug molecules[5], which have attracted attention of bioinorganic chemist due to their wide range of pharmacological properties. Since the discovery of the DNA intercalation process by Lerman [6] in 1961 metal complexes have been investigated to discover potential anticancer drugs and diagnostic agents.

The biological activity of heterocyclic hydrazones as well as their metal complexes is of interest, especially due to their pharmacological properties [7-10].Metal complexes of aroylhydrazones exhibit antitumour [11] and antibacterial activity [12]. There is also much interest in the development of artificial nucleases. Artificial metallo-nucleases require ligands which effectively deliver metal ions to the vicinity of DNA. Investigations on metal-DNA interactions[13] have been an area of active research [14, 15]. Studies on chemical modification of nucleic acids with transition metal complexes are of great interest in the design of chemotherapeutic drugs, regulation of gene expression and design of tools for molecular biology[16]. Copper (II) has been shown to bind the DNA bases at the N(7) of purines and N(1) of pyrimidines [17].

In the light of the above and in continuation of our ongoing research work [18,19] a series of functionalized hydrazones have been synthesized and characterized. The design of such ligands is achieved by using corresponding precursors. A series of hydrazones have been synthesized by using aromatic carbonyl compounds and substituted hydrazides .

## EXPERIMENTAL

Analytical grade carbonyl compounds and hydrazides were purchased from Sigma-Aldrich Chemicals Pvt. Ltd. India. Metal chlorides and metal acetates were purchased from Merck chemicals. The solvents used in the synthesis of ligand and metal complexes were distilled before use. Calf-Thymus DNA (CT-DNA) was purchased from Genie 79 Bio labs, Bangalore, India. All other chemicals were of reagent grade quality and used without further purification.

### Preparation of ligands

Hot aqueous solution of hydrazide 0.5 mmol) was added to a boiling solution of methanolic solution of carbonyl compound (0.5 mmol) . The reaction mixture was heated under reflux for 1 hr. a pale yellow coloured crystalline products were formed in cooling the reaction mixture. The hydrazones collected by filtration, washed several times with hot water and dried in vacuo. The ligands were recrystallized from methanol. The colour, yield, melting point and analytical data of ligands are given in Table

2-Acetylpyridine acetoylhydrazone(APAH), Yield 85%, M.P. 162-164°C, elemental analysis C-61.32(61.00); H- 6.50 (6.25); N- 24.0( 23.71); IR spectra,: 3185, 1678, 1620 $cm^{-1}$ are assigned to v(NH), v(C=O) and v(C=N) stretching vibrations respectively. The $^{1}$H-NMR spectra in

$CDCl_3$ solvent.; δ (2.4) (singlet 3H), δ (2.5) (singlet 3H), δ(7.25) (singlet 1H), δ(7.75-7.85) (multiplet 4 H), are respectively assigned to $–CH_3$ (carbonyl), $–CH_3$ ( hydrazine), NH- and pyridine protons. LC-MS spectrum of HL shows molecular ion peaks at (*m/z*) 177. .

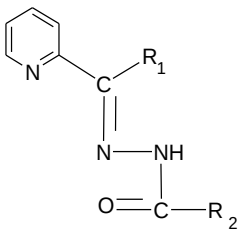
2-Acetylpyridine benzoyllhydrazone(APBH), Yield 85%, M.P. 145-147°C, elemental analysis C-68.75(70.27); H- 5.50 (5.47); N-17.12 (17.56); IR spectra, 3177, 1654, 1616 $cm^{-1}$ are assigned to ν(NH), ν(C=O) and ν(C=N) stretching vibrations respectively. The $^1$H-NMR spectra of HL was recorded in $CDCl_3$ solvent. Signals of HL at δ(2.5) (singlet 3H), δ(7.25) (singlet 1H), δ(7.75-7.85) (multiplet 9 H), δ(6.7) are respectively assigned to $–CH_3$, >NH- and aromatic (pyridine + phenyl ring) protons. LC-MS spectrum of HL shows molecular ion peaks at (*m/z*) 239.

2-Benzoyllpyridine acetoylhydrazone (BPAH), Yield 85%, M.P. 145-147°C, elemental analysis C-71.20(70.27); H- 5.70 (5.45); N-17.96 (17.56); IR spectra, 1668, 11615 $cm^{-1}$ are assigned to ν(C=O) and ν(C=N) stretching vibrations respectively. The $^1$H-NMR spectra in $CDCl_3$ solvent. δ(1.80) (singlet 3H), δ(7.40) (singlet 1H), δ(7.42- 8.80) (multiplet 9 H), δ(6.7) are respectively assigned to $–CH_3$, >NH- and aromatic (pyridine + phenyl ring) protons. LC-MS spectrum of HL shows molecular ion peaks at (*m/z*) 239.

2-Benzoylpyridine benzoyllhydrazone (BPBH) 2-benzoyllpyridine acetoylhydrazone (BPAH), Yield 85%, M.P. 135-137°C, elemental analysis C-75.9(75.72); H- 5.23 (5.01); N-14.02 (13.94); IR spectra, 1666 and 1614 $cm^{-1}$ are assigned to ν(C=O) and ν(C=N) stretching vibrations respectively. The $^1$H-NMR spectra in $CDCl_3$ solvent. δ(7.22) (singlet 1H), δ(7.30- 8.80) (multiplet 13 H), are respectively assigned to imine (>NH-) and aromatic (one pyridine + two phenyl ring) protons. LC-MS spectrum of HL shows molecular ion peaks at (*m/z*) 239.

**Synthesis of complexes**

The scheme for the synthesis of ligands and complexes is given in Figure 1. The complexes were prepared by mixing hot aqueous solution of $Cu(CH_3COO)_2$. $6H_2O$] and ligand in a molar ratio of 1:2. To the boiling solution of ligand ( 0.01 mol ) in methanol (100 ml) was added metal acetate salts (0.005 mol) dissolved in minimum quantity of water and the reaction mixture was heated under reflux for 3h. Crystalline complexes which separated out were collected by filtration, washed with hot water, small quantity of methanol and hexane and dried in *vacuo*. Analytical data of ligands and their copper complexes are given in Table 1.




| Entry | APAH | APBH | BPAH | BPBH |
|---|---|---|---|---|
| $R_1$ | $CH_3$ | $CH_3$ | $C_6H_5$ | $C_6H_5$ |
| $R_2$ | $CH_3$ | $C_6H_5$ | $CH_3$ | $C_6H_5$ |

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**Table 1: Analytical data of Cu(II) complexes**

| Complex | Colour (yield,%) | Mol. Wt. | Found (Calc.) (%) | | | | M. pt ($^oC$) | Molar conductivity ($\Omega$ $cm^2$ $mol^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | M | | |
| $[Cu(APBH)_2]$ | Dark green (62) | 541 (540.07) | 63.62 (62.26) | 4.57 (4.47) | 14.32 (15.56) | 10.89 (11.76) | 267-269* | 6.5 |
| $[Cu(APAH)_2]$ | Green (57) | 416 (415.92) | 52.06 (51.97) | 4.66 (4.84) | 19.71 (20.20) | 15.98 (15.27) | 258-259* | 1.74 |
| $[Cu(BPBH)_2]$ | Black (74) | 665 (664.21) | 69.02 (68.71) | 4.51 (4.24) | 12.98 (12.65) | 9.89 (9.56) | 262-264* | 1.16 |
| $[Cu(BPAH)_2]$ | Dark green (65) | 541 (540.06) | 63.54 (62.27) | 5.01 (4.47) | 16.12 (15.56) | 11.70 (11.76) | 249-251* | 2.81 |
| *Decomposes | | | | | | | | |

Table The elemental analyses were performed at RSIC, CDRI Lucknow. Magnetic measurements of complexes were carried out at 298 K in Faraday's magnetic susceptibility balance (Sherwood Scientific, Cambridge, UK). High purity pentahydrated copper sulphate was used as a standard. The conductivity measurements at 298±2 in dry and purified DMF were carried out on CM model 162 conductivity cell (ELICO). The electronic spectra of metal complexes were recorded in DMF with UV lamda 50 (Perkin Elmer) spectrophotometer. The infrared spectra were recorded in the range 4000-400 $cm^{-1}$ with Perkin Elmer spectrum 100 spectrometer in KBr discs. ESR spectra were recorded in Varian E-112 X-band spectrophotometer at room temperature and liquid nitrogen temperature (LNT) in both solution (DMF) and solid state. The cyclic voltammetry was performed with a CH Instruments660C electrochemical analyzer and a conventional three electrode configuration with glassy carbon working electrode, silver/silver chloride reference electrode and platinum counter electrode. Nitrogen was used as a purge gas and all solutions were 0.1M concentration in tetrabutylammonium hexafluorophosphate ($TBAPF_6$) supporting electrolyte.

**DNA binding experiments**

Interaction of complexes with calf thymus DNA was studied by electronic absorption spectroscopy. A solution of CT-DNA in 5mM Tris–HCl/50mM NaCl (pH 7.0) gave a ratio of UV absorbance at 260 and 280 nm ($A_{260}/A_{270}$) of 1.8–1.9, indicating that the DNA is sufficiently free from proteins[20] . A concentrated stock solution of DNA was prepared in 5 mM Tris-HCl/50 mM NaCl in water at pH 7.0 and the concentration of CT–DNA was determined per nucleotide by taking the absorption coefficient (6,600 $dm^3$ $mol^{-1}$ $cm^{-1}$) at

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260 nm[21]. Stock solutions are stored at 4°C and were used after no more than 4 days. Doubly distilled water was used to prepare buffer solutions. Solutions were prepared by mixing the complex and CT–DNA in DMF medium. After equilibrium reached (ca. 5 min) the spectra were recorded against an analogous blank solution containing the same concentration of DNA.

UV-spectral data were fitted into Eq. 1 to obtain the intrinsic binding constant ($K_b$)

$$[DNA] / (\varepsilon_a-\varepsilon_f) = [DNA] / (\varepsilon_b-\varepsilon_f) + 1/ K_b(\varepsilon_b-\varepsilon_f) \quad \text{----------(1)}$$

Where [DNA] is the concentration of DNA in base pairs, $\varepsilon_a$, $\varepsilon_b$ and $\varepsilon_f$ are apparent extinction coefficient ($A_{obs}/[M]$), the extinction coefficient for the metal (M) complex in the fully bound form and the extinction coefficient for free metal (M) respectively. A plot of [DNA] / ($\varepsilon_a$-$\varepsilon_f$) versus [DNA] gave a slope of 1/($\varepsilon_b$-$\varepsilon_f$), and vertical intercept equal to 1/ $K_b(\varepsilon_b–\varepsilon_f)$; $K_b$ was calculated from these values.

## RESULTS AND DISCUSSION

All the complexes are stable at room temperature, non-hygroscopic, sparingly soluble in water, partially soluble in methanol, ethanol and readily soluble in acetonitrile ($CH_3CN$), DMF and DMSO. The analytical data (Table 1) are consistent with the proposed molecular formulae of complexes. The molar conductivity data suggest that the complexes are non-electrolytes. The magnetic moment values of the complexes correspond to their respective spin-only values.

Electronic spectral data of metal complexes are summarized in Table 2. In all metal complexes, a strong band in the range 26246 - 29672 $cm^{-1}$ may be associated with M-L charge transfer transition. The high energy band of moderately intense band in the range 32258-37735 are assigned to intra-ligand transition band in the spectra of all metal complexes. The copper complexes showed one weak peak which is assigned to d-d transition [22 ]in favour of octahedral structure.

**Table 2 Electronic spectral data ($cm^{-1}$) of metal complexes in solution state***

| Complex | Intraligand transition | Charge transfer transition | d-d transition |
|---|---|---|---|
| $[Cu(APBH)_2]$ | 37593 | 26385 | 15037 |
| $[Cu(APAH)_2]$ | 36630 | 27100 | 13140 |
| $[Cu(BPBH)_2]$ | 37593 | 24570 | 14556 |
| $[Cu(BPAH)_2]$ | 37735 | 26178 | 14705 |

*Spectral of complexes were recorded in DMF solvent.
Molar absorptivity (L.mol.$cm^{-1}$) values are in parenthesis.

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**Table 3: Important IR Spectral bands* ($cm^{-1}$) and their assignment**

| $[Cu(APBH)_2]$ | $[Cu(APAH)_2]$ | $[Cu(BPBH)_2]$ | $[Cu(BPAH)_2]$ | Assignment |
|---|---|---|---|---|
| ---(3185) | ---(3177) | --- | --- | $\nu_{N-H}$ |
| 1630(1678) | ---(1654) | 1628(1668) | 1634(1666) | $\nu_{C=O}$ |
| 1601(1620) | 1609(1616) | 1603(1615) | 1604(1614) | $\nu_{C=N}$ |
| 570 | 573 | 504 | 509 | $\nu_{M-O}$ |
| 493 | 478 | 462 | 492 | $\nu_{M-N}$ |

*Ligands' bands are given in parenthesis

IR spectra of hydrazone ligands are compared with those of copper complexes to determine donor atoms of ligand. Important IR spectral bands and their assignment are given in Table 4. The IR spectra of the ligands have several prominent bands due to $\nu_{N-H}$, $\nu_{C=O}$ and $\nu_{C=N}$ stretching modes. The first two bands disappeared in spectra of complexes (due to enolization followed by complexation) and a new $\nu_{C-O}$ band in the range1043-1051 $cm^{-1}$ is appeared. The $\nu_{C=N}$ is shifted to lower frequency in the spectra of all complexes suggesting the involvement of azomethine nitrogen in chelation. IR data suggest that the ligands acts as mono basic tridentate ligands in all copper complexes The non- ligand bands in 597-565 and 493-481 $cm^{-1}$ regions are tentatively assigned to $\nu_{(M-O)}$, and $\nu_{(M-N)}$ vibrations respectively.

**Table 4: The Hamiltonian and orbital reduction parameters of copper (II) complexes**

| Complex | In solid state | | | | In solution state | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $g_{II}$ | $g_{\perp}$ | $g_{av}$ | G | $g_{II}$ | $g_{\perp}$ | $g_{av}$ | G | λ | $K_{II}$ | $K_{\perp}$ | $All_{x10^5}$ | $A_{\perp x10^5}$ |
| $[Cu(APBH)_2]$ | 2.305 | 2.073 | 2.150 | 4.24 | 2.313 | 2.067 | 2.149 | 4.80 | 538 | 1.022 | 0.932 | ----- | ----- |
| $[Cu(APAH)_2]$ | 2.109 | 2.027 | 2.054 | 4.27 | 2.382 | 2.066 | 2.171 | 5.95 | 543 | 1.053 | 0.862 | 1395.42 | ----- |
| $[Cu(BPBH)_2]$ | 2.264 | 2.062 | 2.13 | 4.33 | 2.212 | 2.053 | 2.106 | 4.14 | 384 | 0.995 | 0.978 | 1209.36 | ----- |
| $[Cu(BPAH)_2]$ | 2.120 | 2.027 | 2.058 | 4.71 | 2.254 | 2.056 | 2.122 | 4.67 | 441 | 1.015 | 0.939 | 1410.86 | ----- |

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Based on physicochemical and spectral data a general structures of complexes is proposed (Figure 2 )

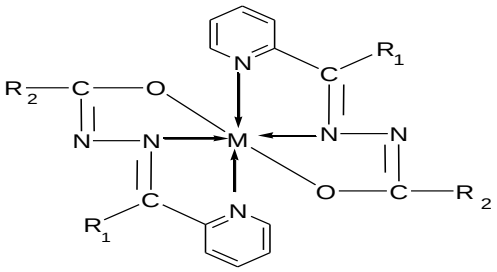

Figure-2: Proposed general structure for copper complexes

| Entry | APAH | APBH | BPAH | BPBH |
|---|---|---|---|---|
| $R_1$ | $CH_3$ | $CH_3$ | $C_6H_5$ | $C_6H_5$ |
| $R_2$ | $CH_3$ | $C_6H_5$ | $CH_3$ | $C_6H_5$ |

ESR spectral data of complexes in solid state and in DMF are given in Table 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 g values were computed from the spectrum using tetracyanoethylene (TCNE) free radical as the g marker. The typical ESR spectrum of $Cu(APBH)_2$ complex is given in Fig. 4. Kivelson and Neiman[23] have reported that the $g_{\parallel}$ is less than 2.3 for covalent character and greater than 2.3 for ionic character of the metal –ligand bonding. As seen from Table 5 the $g_{\parallel}$ values for copper complexes less than 2.3 suggesting a significant covalent character in the metal-ligand bonding. The trend $g_{\parallel} > g_{\perp} > 2.0023$ suggest that the unpaired electron predominantly in the $d_x2_{--y}2$ orbital [24] characteristic of octahedral geometry in copper(II) complexes. The $g_{av}$ value for these complexes is greater than 2 indicating the presence of covalent character [25]. The axial symmetry parameter (G ) values of copper(II) complexes suggest no interactions between the metal centers in either solid or in solvent medium. The orbital reduction parameters ($K_{\parallel}$ and $K_{\perp}$)are calculated. The observed relation $K_{\parallel} > K_{\perp}$ for $CuL_2$ complex indicates the absence of significant in plane π- bonding.

**Table 5 : Electronic absorption data upon addition of CT-DNA to the complexes**

| Complex | $\lambda_{max}$ (nm) | | Δλ | H(%) | $K_b$ ($M^{-1}$) |
|---|---|---|---|---|---|
| | Free | Bond λ | | | |
| $[Cu(APBH)_2]$ | 357 | 359 | 2 | + 35.34 | $1.44x10^6$ |
| $[Cu(APAH)_2]$ | 236 | 235 | 1 | + 3.07 | $4.58x10^5$ |
| $[Cu(BPBH)_2]$ | 376 | 378 | 2 | + 23.38 | $5.8x10^4$ |
| $[Cu(BPAH)_2]$ | 348 | 352 | 4 | +14.48 | $6.43x10^5$ |

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**Cyclic voltammetric studies**

Redox behavior of the complexes has been investigated by cyclic voltammetry in DMF using 0.1M tetrabutylammonium hexaflouro phosphate (TBAHEP) as supporting electrolyte..

Repeated scans at various scan rates suggest that the presence of stable redox species in solution. $E_{1/2}$ values of copper complexes APAH, APBH, BPAH and BPBH , are respectively observed at 0.410 - 0.483 vs. Ag/AgCl [26-28]. It may be inferred that all the Cu(II) complexes undergo reduction to their respective Cu(I) complexes. The non-equivalent current in cathodic and anodic peaks for complexes indicates quasi-reversible behavior[29]. The difference $\Delta E_p = E_{pc} - E_{pa}$ in all the complexes exceeds the Nerstian requirement 59/n mV (n= number of electrons involved in oxidation reduction) which suggests quasi-reversible character associated with a considerable reorganization of the coordination sphere during electron transfer [30]. The complexes have large separation (89-512 mv) between anodic and cathodic peaks indicating quasi-reversible character.

**Electronic absorption titrations**

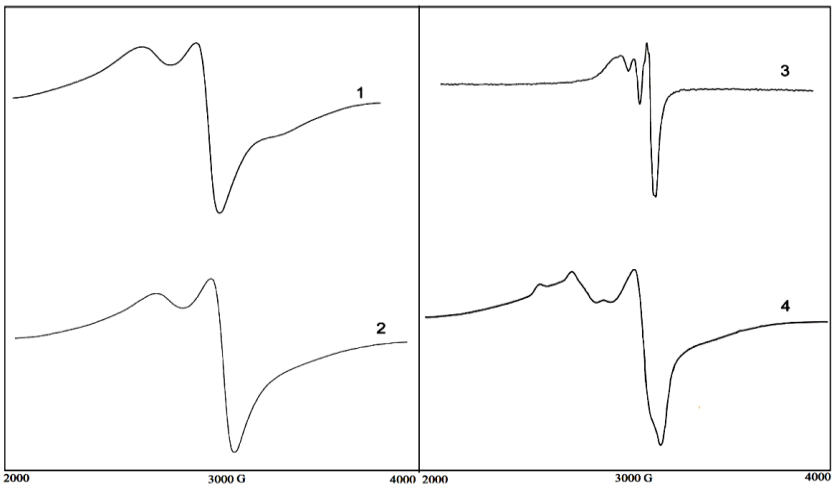


**Figure 3: X-band powder ESR spectra of [Cu (APBH)$_2$] at (1) 300K and (2) at LNT. ESR spectra of [Cu (APBH)$_2$] in DMF at (3) 300K and (4) at LNT.**

The binding interaction of complexes with CT-DNA was monitored by comparing their absorption spectra with and without CT-DNA. All the complexes exhibit an intense absorption band in 265- 310 nm region attributed to $\pi \rightarrow \pi^*$ transition. Absorption spectra of complex in the absence and presence of CT-DNA are shown Figure 5. With increasing DNA concentrations, the absorption bands of the complexes are affected, resulting in hyperchromism or hypochromism with bathochromic/ hypochromic shift.. The binding of intercalative molecule to DNA is generally characterized by large hypochromism and significant red shift due to strong stacking interaction between the aromatic chromophore of the ligand and DNA base pairs with the extent of of hypochromism and red shift commonly consistent with the strength of intercalative interaction [31-33]. However, in the present case, the magnitude of hypochriomism and red shift observed for copper

complexes are lower than those observed for typical classical intercalators of partially intercalating complexes. To enable quantitative comparison of DNA binding affinities, the intrinsic binding constant $K_b$ of the complexes were obtained using equation(1). The complexes are found to show high binding constants( Table 5 ).

## CONCLUSION

Copper(II) complexes of four hydrazone ligands are synthesized and characterized based on analytical and spectral data. The present studies revealed that complexes bind DNA strongly . The complexes undergo quasi-reversible one electron reduction. The high binding constants suggest that the complexes bind DNA via intercalation which is a promising feature of anticancer drug like cis-platin.

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## REFERENCES

[1] Rollas S and Gunik SK, Molecules, 2007, 12, 1910
[2] Lakshminaryayan S. Young KS, .Sung OB and Varada Reddy A, E -Journal of Chem., 2012, 9, 1288.
[3] Ghazy , Mostafa HA, El-farra SA and Fouda AS, Indian J Chem Technol. 2004, 11. 787.
[4] Maurya MR, Halder C, Kumar A, Kuznestsov ML, Avecilla F and Costa JP, Dalton Trans, 2013, 42, 11941.
[5] Yadav J ,. Pandeya SN, and Singh S.P, J Chem. Pharma Res, 2010, 2, 558
[6] Lerman, LS., Journal of Molecular Biolology, 1961, 3, 18.
[7] Dutta RL and Hossain M M, J. Scientific Industrial Research , 1985. 33. 635.
[8] Shechter Y, Goldwash I, Micronchik M, Fridkin M and Gefel D, Coord Chem. Rev, 2003, 237, 3.
[9] Rehder D, Inorg Chem commun. 2003, 6, 604.
[10] Thompson KH and Orvig C, Coord. Chem. Rev, 2001, 219, 1033.
[11] Verquin G, Fourtane G, Bria M, Zhilinskaya E, Abi-Azad E, Aboukais, Baldeyron, Bailly C & Bernier JL, J. Biol Inorg. Chem, 9(2004) 345.
[12] Raman N, Kulandaisamy and Subramanian KJ, Synt React Inorg Met-Org Chem 2004, 34, 17.
[13] Jane A, Journal of Molecular Structure, 2013, 651, 19.
[14] Deweese JE, Peter FG, Burgin AB & Osherroff N, Biochenmistry , 2009, 48, 8940.
[15] Oliveira SCB Corduneanu O, Oliveira-Brett AM, Bioelectrochemistry, 2008, 71, 53.
[16] Pyle AM & Barton JK, Inorg. Chem 1990, 38, 413.
[17] Hussain Reddy K. Bioinorganic Chemistry (New Age International, New Delhi) 2003.
[18] Hari Babu P and Hussain Reddy K , Indian J Chem, 52A (2013) 327

[19] Pragathi M and. Hussain Reddy, Indian J Chem, 52A (2013) 845.
[20] Marmur J, Mol. Biol , 1968, 3, 208.
[21] Reichmann ME, Rice SA, Thomas CA, and Doty P, J Am Chem Soc 76(1954) 3047.
[22] Lever ABP Inorganic electronic spectroscopy, 2nd Edn (Elsevier, Amsterdam) 1984.
[23] Kivelson D and Newiman R , J Chem. Phys, 35(1961)149.
[24] Raman N, Kulandaisamy A and Jayesubramanian K, Indian J Chem, 2002, 41A 942.
[25] Mamdoush S M , AbouElenein SM and Kamel H M, Indian J Chem, 2002, 41A, 297.
[26] Jebbar-sid S D, Benali-Baitich O and Deloume JD, Polyhedron, 1997, 16, 2175.
[27] Bu X H, Zhang Z H, Cao X, Ma S & Tichen Y, Polyhedron, 1997, 16, 3525.
[28] Dhar S, Senapathi D, Das PKChattopadyay P, Nethaji M and Chakravarthy A R, J Am. Chem Soc, 2003, 125,12218.
[29] Khumbar A A, Padhye S B, West D X, and Libert A E, Trans Met Chem, 1991, 16, 276.
[30] Usha S and Palaniadavar M, J Chem Soc , Dalton Trans 1994, 2277.
[31] Barton JR, Danishefsky AT & Goldberg JM, J Am Chem Soc, 1984, 106, 2127.
[32] Tysose SA, Morgan RJ, Barker AD and Strekars TC, J Phys Chem , 1993;97, 1707.
[33] Kelly TM, Tossi AB, Mc Konnell DJ and Strekas TC, Nucleic acid Res , 1985, 13, 6017.