



Electronic And Spectral Studies of Some Five Coordinate Complexes of Copper (II)

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ABSTRACT

1-phenylazo-2-naphthol has been synthesized and used for complexation with Cu(II) metal ion along with pyridine, α -picoline, β -picoline, γ -picoline and water as secondary ligands. On the basis of elemental analysis and molar conductivity complexes were formulated as CuL_2X [Where L is the prime ligand i.e 1-phenyl-azo-2-naphthol and X is the secondary ligand i.e. pyridine, α -picoline, β -picoline, γ -picoline and H_2O .] The magnetic moment of these complexes (1.80-1.83 BM) indicates that these complexes are magnetically dilute. The appearance of 3 bands in the electronic spectra of complexes rules out the trigonal bipyramidal (D_{3h}) symmetry around Cu(II) ion in these complexes rather the electronic spectra favours square pyramidal (C_{4v}) symmetry of these five coordinate complexes. The highest value of $10Dq$ clearly indicates the greater coordinating ability of α -picoline than pyridine, β -picoline and γ -picoline.

Keywords: α -picoline, β -picoline, γ -picoline, trigonal bipyramidal [D_{3h}], square pyramidal [C_{4v}], Five coordinate complexes, Magnetically dilute.

INTRODUCTION

The well known story of blue proteins which have been extensively explored due to their involvement in oxygen and electron transfer in physiological reactions, is well documented¹⁻². Metal ions are electron deficient while most of biological molecules like proteins, DNA, etc, are of these opposing charges leads to a general tendency to form metal ions polymers³⁻⁴. Chemical nucleases based on the transition metal ions, cleave DNA hydrolytically or oxydatively with or without added reductant.

Cu(II) hypyrimol complex [Cu(Hypyrimol)Cl] has been reported to cleave ϕ X174 supercoiled DNA efficiently without any reductant and also showed high cytotoxicity toward L_{1210} murine Leukemia and A_{2780} human, ovarian carcinoma cancer cell lines⁵⁻⁶. Riboflavin binding protein responsible for active transport and storage of riboflavin in egg needed for developments also binds Cu⁷. Dinuclear complexes of copper are also well known artificial metalonucleases and metalloprotease⁸. Recently superoxide dismutase and antimicrobial activities of emidazolate bridged dinuclear complexes of Cu(II) have also been reported⁹.



Recently Day *et al.*,¹⁰ have reported five coordinate Cu(II) complexes with a N, O donor Schiff-base ligand which showed their effective participation in CT-DNA binding and pBR322 DNA cleavage activities.

The interest in five coordinate complexes took root in 1974 when M. Nonoyama¹¹ studied five coordinate Ni(II) and Cu(II) complexes and reported their magnetic moments, infrared and electronic spectra.

Albertin *et al.*,¹² have reported the synthesis and properties of five coordinate Cu(II) complexes with amine ligand. Milan Melnik *et al.*,¹³ have made a review in 2006 on five coordinate Cu(II) complexes. The review summarises the data over a good number of four and five coordinate Cu(II) complexes, mostly with square pyramidal symmetry. The interesting structural features of five coordinate complexes with either square pyramidal or trigonal bipyramidal symmetry invited our attention to five coordinate complexes. In continuation of our previous work¹⁴⁻¹⁷, in the present paper we report the synthesis and spectral properties of some five coordinate Cu(II) complexes with 1-phenylazo-2-naphthol (PANH) as prime ligand and α -picoline, β -picoline, γ -picoline and water as secondary ligand.

MATERIAL AND METHODS

All the reagents used were of AnalR grade and were used without further purification. Benzene diazonium chloride and 2-naphthol were procured from Marc. India and copper chloride hexa hydrate ($\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$) was purchased from Nice. The ligand 1-phenylazo-2-naphthol (PANH)

was prepared by heating the mixture of 0.01 mole (1.425 g) of benzene diazonium chloride and 0.01 mole (1.44 g) of 2-naphthol in ethanolic solution for one hour with stirring. On cooling the solution at room temperature, a brown precipitate appeared which was filtered and washed with alcohol several times. It was recrystallized in alcohol and dried in an electric oven at 90°C. The yield was found about 80% and its melting point was recorded 115°C. The ligand was used for complexation with Cu(II) by the usual method of reflux of the ethanolic solution of 0.01 mole of $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$, 0.02 mole of PANH and 0.01 of the secondary ligands pyridine or α -picoline or β -picoline or γ -picoline. Pyridine, α -picoline, β -picoline and γ -picoline were used as secondary ligand. Complexes were recrystallized in 1:1 ethanol-acetone solvent. The micro analysis of carbon, hydrogen and nitrogen in ligand as well as complexes were carried out by using micro analysis technique on Carbo Erba Micro Analyzer 1108. Copper content in complexes was determined iodometrically. The molar conductivity of the complexes was measured at room temperature with its DMSO solution of 10^{-3} M concentration using Toshniwal digital conductivity meter with deep type cell. The I. R. Spectra of the ligand, 1-phenylazo-2-naphthol and its Cu(II) complexes were recorded on PerkinElmer Model Arc RX1 Spectrophotometer. The magnetic susceptibility of the complexes was measured at room temperature by Gouy's balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant. The electronic spectra of complexes were recorded on Perkin-Elmer Lambda 950 Spectrophotometer. The analytical data, magnetic moment and molar conductivity have been presented in Table 1.

Table 1: Percentage Composition (%) Found/Calculated, Molar Conductivity and Magnetic Moment

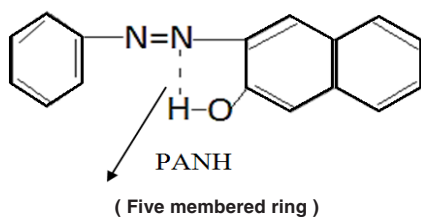
Compounds	Colour	m.p.	Metal	C	H	N	λ_m ($\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	μ_s BM
1. 1-phenylazo-2-naphthol(PANH)	Brown	1150C	--	77.64/77.42	4.53/4.84	11.10/11.29	--	--
2. $[\text{Cu}(\text{PAN})_2(\text{H}_2\text{O})]$	Green	259°C	10.96/11.03	66.82/66.72	4.00/4.14	9.61/9.73	24	2.00
3. $[\text{Cu}(\text{PAN})_2(\text{Py})]$	Light Green	265°C	9.81/9.98	69.91/69.76	4.13/4.24	10.84/11.00	20	1.80a
4. $[\text{Cu}(\text{PAN})_2(\alpha\text{-Pico})]$	Light Green	278°C	9.66/9.76	70.30/70.10	4.28/4.46	10.62/10.76	22	1.83
5. $[\text{Cu}(\text{PAN})_2(\beta\text{-Pico})]$	Dull Green	258°C	9.64/9.76	70.35/70.10	4.26/4.46	10.66/10.76	20	1.82
6. $[\text{Cu}(\text{PAN})_2(\gamma\text{-Pico})]$	Bright Green	259°C	9.62/9.76	69.32/70.10	4.32/4.46	10.58/10.76	18	1.82

RESULT AND DISCUSSION

The molar conductivity of complexes falls in the range of 18-24 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, which is indicative of non electrolytic nature of complexes¹⁸⁻²².

On the basis of elemental analytical data and molar conductivity the complexes have been formulated as $[\text{Cu}(\text{L}_2)\text{X}]$ where L is 1-phenylazo-2-naphthol (PANH) and X is H_2O , pyridine, α -picoline, β -picoline and γ -picoline. Out of cumbersome infrared spectra

of the free ligand and complexes, some important bands of interest have been discussed here. The IR spectrum of the free ligand displays a broad band at 3200 cm^{-1} which may be assigned to intramolecular hydrogen bonded phenolic group vibration.²³⁻²⁵ The possibility of intramolecular H-Bond formation in the ligand may be seen from its structure.



This band disappears in the spectrum of all the complexes of Cu(II) indicating the deprotonation of phenolic O-H group and subsequent coordination through it²⁶⁻²⁸. This supposition is further confirmed by red shift in the absorption frequency of $\nu_{\text{Ar-C-O}}$ stretching vibration, from 1040 cm^{-1} in the spectra of free ligand to $1050\text{-}1055\text{ cm}^{-1}$ in the spectra of complexes²⁹⁻³¹. The bands appearing at 1610 cm^{-1} (weak and sharp), 1525 cm^{-1} (strong and sharp) and 1480 cm^{-1} (medium and sharp) may be assigned to aromatic ring vibration³²⁻³³. The weak and broad band appearing at 1455 cm^{-1} in the spectra of free ligands as well as complexes is assigned to the ring vibration of two condensed ring system i.e. naphthalene³⁴⁻³⁵. Thus the presence of both benzene and naphthalene rings in the ligand and complexes is confirmed. A very weak band appearing at 1410 cm^{-1} in the IR spectra of free ligand has reasonably been assigned to $\nu_{\text{-N=N-}}$ stretching vibration³⁶. This band is found to have undergone blue shifts in the spectra of complexes wherein it absorbs at $1380\text{-}1385\text{ cm}^{-1}$. This negative shifting in stretching vibration of -N=N- (azo) group is indicative of its involvement in coordination to Cu (II) in complexes³⁷⁻³⁸. This coordination may further be substantiated by an increase in absorption frequency of $\nu_{\text{-C-N}}$ stretching which shifts from 1290 cm^{-1} in the IR spectrum of free ligand to $1295\text{-}1300\text{ cm}^{-1}$ in the spectra of all the complexes. A tacit support from such proposition may be brought out more clearly from far infrared range wherein two new vibration bands appear in the range of $490\text{-}510\text{ cm}^{-1}$ due to $\nu_{\text{-Cu-N}}$ and at $410\text{-}420\text{ cm}^{-1}$ due to $\nu_{\text{-Cu-O}}$ ³⁹⁻⁴¹. In addition to these bands some new bands also appear in spectra of complexes. A broad band appearing at 1400 cm^{-1} with another band at 910 cm^{-1} are the diagnostic

band for coordinated water⁴²⁻⁴³. The appearance of new bands at $755\text{-}795\text{ cm}^{-1}$ is the signature of the presence of coordinated pyridine, α -picoline, β -picoline and γ -picoline in complexes number 3, 4, 5 and 6 respectively.⁴⁴⁻⁴⁵ The graphs of FTIR spectra of the ligand as well as its complexes have been given in Figure 1-5.

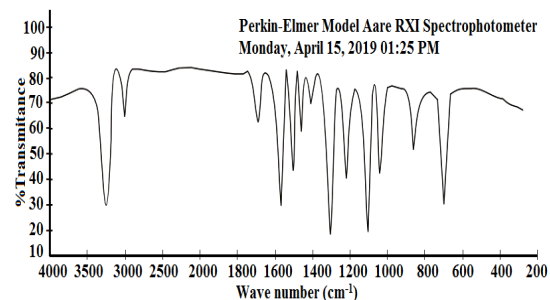


Fig. 1. IR Spectrum of 1-Phenylazo-2-Naphthol, (PANH)

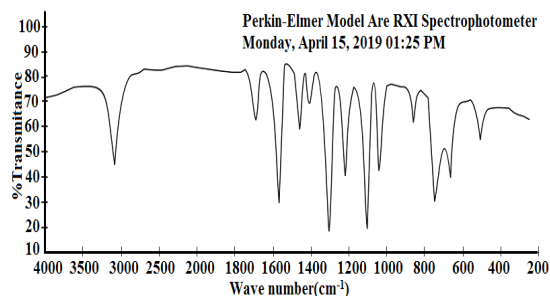


Fig. 2. IR Spectrum of $\text{Cu(PAN)}_2\text{Py}$

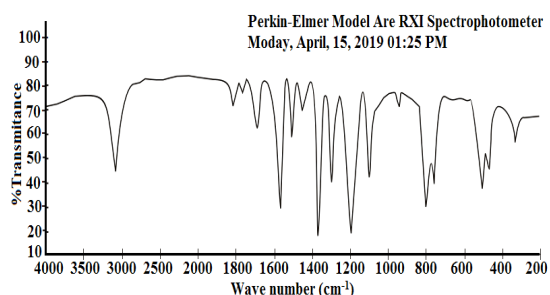


Fig. 3. IR Spectrum of $\text{Cu(PAN)}_2(\alpha\text{-Pico})$

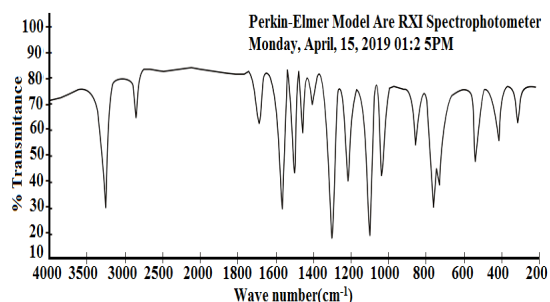


Fig. 4. IR Spectrum of $\text{Cu(PAN)}_2(\beta\text{-Pico})$

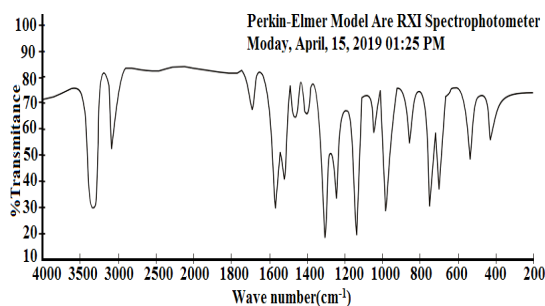
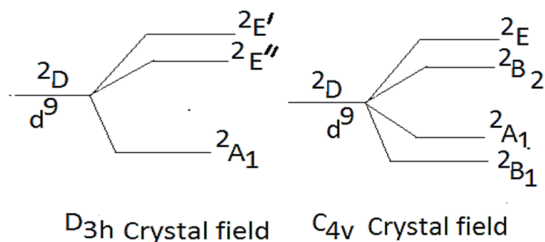


Fig. 5. IR Spectrum of $\text{Cu(PAN)}_2(\text{H}_2\text{O})$

The magnetic moment values of complexes fall in the range of 1.80-2.00BM, which is greater than μ_s for 1-unpaired electron in d^9 System i.e., 1.732BM. It shows that all the complexes are magnetically dilute. The values however couldn't predict the geometry of complexes⁴⁶⁻⁴⁸.

From the stoichiometric formula derived from elemental analysis and molar conductivity it may be inferred that Cu(II) complexes are five coordinated, which may either be of trigonal bipyramidal symmetry (D_{3h}) or square pyramidal geometry (C_{4v}).⁴⁹ It has been reported that though a trigonal bipyramidal structure is eventually favoured for a five coordinate species, the energy difference between the two is in general rather small. So square pyramidal symmetry for five coordinate complexes may actually be favoured especially when ligands are large and bulky⁵⁰⁻⁵¹.

The other major point to predict the symmetry of a five coordinate complex is that for a complex of D_{3h} symmetry the electronic spectral bands at 10, 500-14, 600 cm^{-1} are observed with greater absorption intensity of the lower energy.⁵²⁻⁵³ The five coordinate complexes of C_{4v} symmetry display electronic spectral bands in the range of 11400-15000 cm^{-1} with greater absorption intensity of the band of higher energy. Secondly the splitting pattern of 2D -term of d^9 system. Under the perturbation of D_{3h} crystal field and C_{4v} crystal field may be given as below:-



Thus in the Cu(II) complexes of D_{3h} system only two bands are expected while for complexes of C_{4v} symmetry, three bands are expected in their electronic spectra. Here in our study the five

coordinate Cu(II) complexes display three bands in their electronic spectra which are given below in Table 2 with their assignment.

Assignment of these bands may be given as below:-

$$v_1 = {}^2B_1 \rightarrow {}^2A_1$$

$$v_2 = {}^2B_1 \rightarrow {}^2B_2$$

$$v_3 = {}^2B_1 \rightarrow {}^2E$$

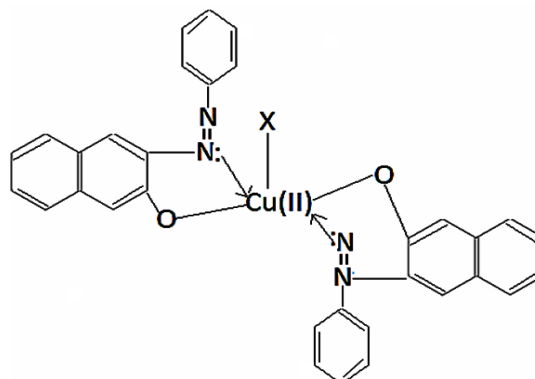
Table 2: Electronic spectral band in cm^{-1}

Compounds	v_1	v_2	v_3
1. $[\text{Cu(PAN)}_2(\text{H}_2\text{O})]$	11,580	14,250	14,700
2. $[\text{Cu(PAN)}_2(\text{Py})]$	11,500	14,000	14,800
3. $[\text{Cu(PAN)}_2(\alpha\text{-Pico})]$	11,550	14,150	14,900
4. $[\text{Cu(PAN)}_2(\beta\text{-Pico})]$	11,600	14,050	15,000
5. $[\text{Cu(PAN)}_2(\gamma\text{-Pico})]$	11,540	14,020	14,940

Since the v_2 is the measure of $10Dq$. So $10Dq$ values of these complexes $[\text{Cu(PAN)}_2(\text{H}_2\text{O})]$, $[\text{Cu(PAN)}_2(\text{Py})]$, $[\text{Cu(PAN)}_2(\alpha\text{-Pico})]$, $[\text{Cu(PAN)}_2(\beta\text{-Pico})]$ and $[\text{Cu(PAN)}_2(\gamma\text{-Pico})]$ are 14,250, 14,000, 14,150, 14,050 and 14,020 cm^{-1} respectively. Since the planner ligand PANH is the same producing the same crystal field the change in Dq value has been caused by the comparable strength of the ligand along Z-axis. The values are in good arrangement with the values reported for Cu(II) complexes of square pyramidal geometry⁵⁴⁻⁵⁶.

CONCLUSION

On the basis of the forgoing study of electronic spectra of complexes whole the Cu(ii) complexes have been found to possess square pyramidal (C_{4v}) symmetry. The tentative structure is given as below.



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Conflicts of Interest

The authors declare no conflict of interest.

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