

## Synthesis and Characterization of Complexes of Cobalt(II), Nickel(II) and Copper(II) with 2-Pyrrolidene-*m*-nitroaniline and 2-Pyrrolidene-*p*-nitroaniline Schiff Bases and Their Biological Activity

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Complexes of Co(II), Ni(II) and Cu(II) with the Schiff base ligands PPNA (pyrrole-2-carboxaldehyde and *p*-nitroaniline) and PMNA (pyrrole-2-carboxaldehyde and *m*-nitroaniline) were synthesised and characterized on the basis of the molar conductance, elemental analysis, IR, magnetic moment and electronic spectra. Complexes were also tested for antifungal activity. Complexes derived from PPNA are ionic, paramagnetic and octahedral, whereas complexes derived from PMNA are non-ionic, paramagnetic, tetrahedral [Co(II) and Cu(II)] and square-planar [Ni(II)].

### INTRODUCTION

The complexing behaviour of Schiff bases<sup>1</sup>, their biological activities<sup>2</sup> and industrial<sup>3</sup> applications have made them a widely studied subject. But an attempt has been made here to study the chelating behaviour of the Schiff base derived from the condensation of substituted heterocyclic aldehyde and substituted anilines.

The present paper reports the ligational behaviour of heterocyclic Schiff bases derived from pyrrole-2-carboxaldehyde, *p*-nitroaniline (PPNA) and pyrrole-2-carboxaldehyde, *m*-nitroaniline (PMNA) with Co(II), Ni(II) and Cu(II).

### EXPERIMENTAL

The elemental analysis was carried out by established method<sup>4</sup> and metal contents in complexes have been found gravimetrically<sup>5</sup>. The molar conductance was measured on Toshniwal Instrument type CL01-OTA using DMF as solvent. Electronic spectra (MeOH) were obtained on a Perkin-Elmer Spectrophotometer and IR spectra (KBr) on an Acculab-10 Spectrophotometer at CDRI, Lucknow. Magnetic susceptibility in the solid state was measured at room temperature by the Gouy's technique.

*Synthesis of Ligands:* 2-Pyrrolidene-*m*-nitroaniline (PPNA) was prepared by adding an ethanolic solution of pyrrole-2-carboxaldehyde (0.01 mol) to a methanolic solution of *m*-nitroaniline (0.01 mol) or *p*-nitroaniline (0.01 mol) in 1 : 1 ratio followed by reflux on a water bath for about 4 and 5 h respectively. The ligand 2-pyrrolidene-*p*-nitroaniline (light yellow coloured) and 2-pyrrolidene-*m*-nitroaniline (dull yellow coloured) were obtained and crystallised from methanol (m.p. 130 and 150°C respectively).

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**Synthesis of Complexes:** Methanolic solution of the respective metal sulphate (0.01 mol) was added to a methanolic solution of the ligand 2-pyrrolidene-*p*-nitroaniline or 2-pyrrolidene-*m*-nitroaniline and the mixture was refluxed on water bath for 4–5 h. The resulting complexes were washed with methanol and dried under reduced pressure over CaCl<sub>2</sub> and finally dried at 50°C in the oven.

Complexes were stable at room temperature and non-hygroscopic. complexes were soluble in methanol, ethanol, DMSO and dimethylformamide.

## RESULTS AND DISCUSSION

The analytical data of the ligands and their metal complexes have been summarised in Table-1. The analytical data are indicative of metal ligand stoichiometry for all the complexes as 1:2. The molar conductance values of complexes of 2-pyrrolidene-*p*-nitroaniline (in ethanol) at 10<sup>-3</sup> M have been observed in the range 180–230 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicative of electrolytic nature of complexes, whereas complexes formed with ligand 2-pyrrolidene-*m*-nitroaniline (in DMF) at 10<sup>-3</sup> M showed molar conductance in the range 19–25 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicative of non-electrolytic nature of these complexes.

TABLE-1  
ANALYTICAL DATA OF THE COMPOUNDS

Compound/complexes (Colour)	Decomp. Temp. (°C)	Analysis % Found (Calcd.)				Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	μ <sub>eff</sub> B.M.
		M	C	H	N		
C <sub>11</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub> (PPNA) (light yellow)	130	—	62.10 (61.39)	5.00 (4.18)	20.14 (19.53)	—	—
Co(PPNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O (brown)	235	10.01 (9.14)	41.51 (40.93)	4.00 (3.72)	13.48 (13.02)	212.00	4.93
Ni(PPNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O (light green)	218	10.21 (9.53)	39.64 (39.28)	3.92 (3.89)	13.93 (13.63)	30.00	3.00
Cu(PPNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O (light brown)	230	11.21 (10.96)	46.00 (45.55)	4.52 (4.14)	14.62 (14.49)	180.00	2.00
C <sub>11</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub> (PMNA) (dull yellow)	150	—	62.10 (61.39)	5.00 (4.18)	20.14 (19.53)	—	—
Co(PMNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O (light brown)	242	9.98 (9.14)	41.34 (40.93)	4.25 (3.72)	13.50 (13.02)	25.00	4.40
Ni(PMNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O (brown)	228	10.25 (9.53)	39.70 (39.28)	4.00 (3.89)	14.02 (13.63)	21.00	Diamg.
Cu(PMNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O (brownish)	235	11.16 (10.96)	46.00 (45.55)	4.63 (4.14)	15.00 (14.49)	19.00	2.15

The room temperature magnetic moment values of complexes derived from 2-pyrrolidene-*p*-nitroaniline are indicative of high spin octahedral complexes<sup>6</sup>, the complex of Co(II) derived from 2-pyrrolidene-*m*-nitroaniline is tetrahedral whereas Ni(II) and Cu(II) complexes are square-planar<sup>7</sup>.

The IR spectra of the ligands PPNA and PMNA showed bands in the range 1610–1587 cm<sup>-1</sup> which can be assigned to ν(C=N). The lowering of this absorption band by 40 ± 10 cm<sup>-1</sup> in the Co(II), Ni(II) and Cu(II) complexes derived from

PPNA and PMNA indicates the coordination between metal and the azomethine nitrogen<sup>8,9</sup>.

The bands appearing due to ring stretching vibrations of 2-substituted pyrrole in the ligand spectrum shift toward lower wave-numbers in the corresponding complex spectrum indicating the involvement of heterocyclic 'N' atom in the formation of complexes of Co(II), Ni(II) and Cu(II) with PPNA.

In the ligand PPNA, a band appearing in the range 3200–3127  $\text{cm}^{-1}$  may be assigned to  $\nu(\text{N—H})$  which shifted from their original value, in the corresponding spectrum of Co(II), Ni(II) and Cu(II) complexes. This gives an additional evidence of the involvement of N—M group of pyrrole ring in the complexation. Additional bands at  $3450 \pm 10$ ,  $1600 \pm 20$  and  $10 \pm 20 \text{ cm}^{-1}$  for all the complexes derived from PPNA due to stretching, bending and rocking modes respectively suggest coordinated mode of water molecules<sup>10</sup> but are found absent in the complexes derived from PMNA.

The appearance of a new band in the region 430–415 and 520  $\text{cm}^{-1}$  may be assigned to  $\nu_{(\text{M—N})}$  and  $\nu_{(\text{M—O})}$ , respectively. The vibrations of sulphate ion appeared at 1110–1100 and 615–605  $\text{cm}^{-1}$  respectively, indicating the non-coordinating nature of sulphate group in PPNA complexes.

Thus complexes of Co(II), Ni(II) and Cu(II) derived from PPNA show coordination through nitrogen of  $\nu_{\text{C=N}}$ , 'N' of 2-substituted pyrrole and oxygen of water molecule. Complexes of Co(II), Ni(II) and Cu(II) derived from PMNA exhibit bands at *ca.* 1050, *ca.* 980 and *ca.* 640  $\text{cm}^{-1}$  which may be tentatively assigned to coordinated bidentate sulphate moiety in the complexes<sup>7</sup>.

Bands appearing due to ring stretching vibrations of 2-substituted pyrrole in the ligand spectrum of PMNA in the range 3200–2953  $\text{cm}^{-1}$  do not show any change in the complexes of Co(II), Ni(II) and Cu(II) ruling out the involvement of heterocyclic 'N' atom in the coordination.

SALIENT FEATURES OF IR SPECTRA ( $\text{cm}^{-1}$ )  
OF LIGANDS AND COMPLEXES

Ligands/Complexes	$\nu(\text{N—H})$ ( $\text{cm}^{-1}$ )
PPNA	3200
Co(PPNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	2957
Ni(PPNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	3127
Cu(PPNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	2953
PMNA	3127
Co(PMNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ·SO <sub>4</sub> ·H <sub>2</sub> O	—
Ni(PMNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ·SO <sub>4</sub> ·H <sub>2</sub> O	—
Cu(PMNA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ·SO <sub>4</sub> ·H <sub>2</sub> O	—

Two additional bands were observed in the complexes derived from PMNA at 3440 and 1600  $\text{cm}^{-1}$  due to stretching and bending modes of water. The third and fourth bands were not visible. This rules out the possibility of coordination through oxygen atom of water molecule.

The electronic spectra of Co(II) complex derived from PPNA exhibited two

bands at 20500–20510 ( $\epsilon = 2.0$ – $2.4$ ) and 8700–8900 ( $\epsilon = 1.4$ – $2.0$ )  $\text{cm}^{-1}$  which have been assigned to the transition  ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$  and  ${}^4\text{T}_{2g} \leftarrow {}^4\text{T}_{1g}(\text{F})$ , respectively, of octahedral Co(II) complex<sup>11</sup>. The  $\nu_2$  band, since it involves a two-electron transition, has not been observed. Its position has been calculated using Koning equation<sup>12</sup>. The values of  $10\text{Dq}$ ,  $B$ ,  $\beta$ ,  $\nu_3/\nu_1$ ,  $\text{Dq}/B$  and LFSE have been observed to be  $8900\text{ cm}^{-1}$ ,  $830.08\text{ cm}^{-1}$ ,  $0.82$ ,  $2.3$  and  $90.19$  respectively. These values are in agreement with the predicted values of octahedral complex.

The Ni(II) complex exhibited bands at 25550–23330 ( $\epsilon = 5.2$ – $5.6$ ), 15730–13980 ( $\epsilon = 2.0$ – $2.6$ ) and 8650–8400 ( $\epsilon = 1.0$ – $1.1$ )  $\text{cm}^{-1}$ . These are assigned to  ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\nu_3)$ ,  ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\nu_2)$  and  ${}^3\text{T}_{2g} \leftarrow {}^3\text{A}_{2g}(\nu_1)$  transitions respectively, expected from octahedral Ni(II) complexes. Out of these three, the low energy band ( $\nu_1$ ) has been equated to  $10\text{Dq}$ . The spectral parameters  $10\text{Dq}$ ,  $B$ ,  $\beta$ ,  $\nu_2/\nu_1$  and LFSE have been observed to be  $8650\text{ cm}^{-1}$ ,  $870\text{ cm}^{-1}$ ,  $1.6$  and  $160.82$  respectively. The lowering in the value of  $B$  from the free-ion value for Ni(II) ( $1040\text{ cm}^{-1}$ ) suggest covalent character of nickel-ligand band<sup>12</sup>. The Cu(II) complex gives a single broad band at 13600–13400  $\text{cm}^{-1}$  ( $\epsilon = 10.0$ – $11.3$ ) corresponding to the transition  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  characteristic of octahedral geometry<sup>13</sup>.

The room temperature magnetic moment values of Co(II), Ni(II) and Cu(II) complexes derived from PPNA show magnetic moment values 4.93, 3.00 and 2.00 B.M. respectively. These values are consistent with the values reported for octahedral complexes<sup>11</sup>. The small increase in the magnetic moment value of the Cu(II) complexes can be ascribed to spin-orbit coupling<sup>14</sup>.

The electronic spectra of the Co(II) complexes of PMNA shows one band at  $15860\text{ cm}^{-1}$  ( $\epsilon = .8$ ) corresponding to the transition  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$  transition. The room temperature magnetic moment value of Co(II) complex is observed to be 4.4 B.M. suggestive for tetrahedral geometry of this complex.

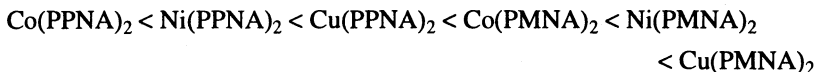
The electronic spectra of the Ni(II) complex with PMNA exhibits bands at  $17530$  ( $\epsilon = 1.00$ ) and  $27500$  ( $\epsilon = 2.33$ )  $\text{cm}^{-1}$  corresponding to the transitions  ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$  and  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$  respectively. The room temperature magnetic moment value shows diamagnetic behaviour. These findings suggest square-planar structure of this complex.

The Cu(II) complex exhibits two peaks around  $9000$  and  $12450\text{ cm}^{-1}$  respectively. The crystal field theory of tetrahedral Cu(II) complex predicts only one transition  ${}^2\text{T}_2 \rightarrow {}^2\text{E}$  which occurs below  $10000\text{ cm}^{-1}$ . However, for pseudo-tetrahedral Cu(II) complexes three peaks at  $8500$  ( $\epsilon = 48$ ) and  $13600$  ( $\epsilon = 52$ ) and  $21000\text{ cm}^{-1}$  ( $\epsilon = 58$ ) have been reported<sup>15</sup>. Therefore energy peaks observed in the present Cu(II) complexes may be assigned in conformity with the earlier observations<sup>16</sup> to a pseudo-tetrahedral configuration.

The magnetic moment values of Cu(II) complex have been observed to be 2.15 B.M. Large orbital contribution to magnetic moment has been used as an evidence for tetrahedral Cu(II) complex<sup>14, 17</sup>.

**Antifungal activity:** The fungicidal<sup>18</sup> activity of ligands and complexes was tested against the fungi causing damage to vegetative plants at different concentrations in the form of solutions or suspensions. The solutions and suspensions of ligands and complexes were prepared in ethanol. The metal complexes were found

more fungitoxic than the free ligands. It has already been observed<sup>19, 20</sup> that polarity of metal ions gets reduced upon complexation, which increases the lipophilicity of the metal complexes facilitating them to cross the cell membrane easily. It has been observed that four-coordinated complex of Co, Ni and Cu with PMNA is more toxic than six-coordinated complex of Co, Ni and Cu with PPNA. It may be due to unsaturation of coordination number. So, the increasing order of antifungal activity of complexes of PPNA and PNMA may be:



From studies with various aquatic organisms, it has been found that cation toxicity also follows the sequence of natural stability order for complexes, in the case of the transition metal ions, viz., Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) and this order also applies for a group of enzymes such as urease and diastase. This obviously shows that the metal ion toxicity is connected with chelation process.

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