



## Spectral Characterization and Biological Activities of Metal Complexes of Cu(II), Ni(II) and Co(II) with Tridentate $\alpha$ -Amino-1-indole Propionic Acid Based Ligand

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Four novel Schiff base metal complexes of Cu(II), Ni(II) and Co(II) have been synthesized from a new Schiff base ligand derived from salicylaldehyde and  $\alpha$ -amino-1-indole propionic acid. The ligand and its complexes have been characterized on the basis of elemental analysis, magnetic susceptibility, UV, IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral studies, as well as conductivity data. On the basis of spectral studies, for Co(II) complex tetragonal and Cu(II) and Ni(II) complex, octahedral geometry has been proposed. The data indicate that most of the metal complexes have higher antimicrobial activity than the free ligand against *E. Coli*, *Salmonella*, *P. aeruginosa* and *S. aureus*.

**Key Words:** Metal(II) complexes,  $\alpha$ -Amino-1-indole propionic acid, Imine group.

### INTRODUCTION

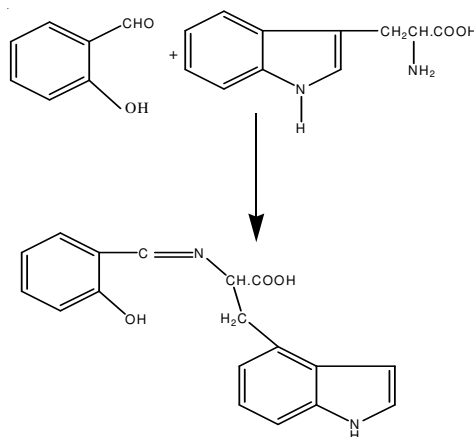
A large number of reports are available on the chemistry and the biological activities of transition metal complexes containing O, N and S donor atoms<sup>1</sup>. The presence of transition metals in human blood plasma indicates their importance in the mechanism for accumulation storage and transport of transition metals in living organisms<sup>2</sup>. Complexes of some divalent metal ions with Schiff base derived from salicylaldehyde and carbonyl group containing compounds are show various biological activities, in this paper we report the synthesis, structures and antimicrobial nature of four novel Schiff base metal complexes of Cu(II), Ni(II) and Co(II), synthesized from salicylaldehyde and  $\alpha$ -amino-1-indole propionic acid.

### EXPERIMENTAL

All chemicals used in this work were grade of BDH or Aldrich including NH<sub>4</sub>OH, CHCl<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, DMF NaOH, salicylaldehyde and tryptophan ( $\alpha$ -amino-1-indole propionic acid). Double distilled water were used throughout the experiment. which show its neutral pH and zero conductivity.

**Preparation of Schiff base:** The Schiff base under investigation was prepared by mixing an ethanolic solution of 1.22 g, 0.01 mol of salicylaldehyde with 1.08 gm, 0.01 mol of  $\alpha$ -amino-1-indole propionic acid in same volume of ethanol. Few drops of 10 % NaOH were added to adjust pH and the obtained mixture the refluxed with stirring for 2 h and then obtained precipitate was collected by filtration through

buchner funnel, recrystallized from ethanol and dried at room temperature with 65 % yield.



**Preparation of complexes:** The complexes under investigation were prepared by mixing ethanolic solution of Schiff base 2.12 g, 0.01 mol with same amount of ethanolic solution of metal salts. If complexes did not separate, few drops of ammonium hydroxide were added to adjust the pH = 8. The obtained mixtures were refluxed with stirring for extra 4 h and then filtered and washed with ethanol and dried under vacuum. (Yield = 60-75%)

**Antibacterial activity:** The strains of bacteria used were *E. coli*, *Salmonella*, *P. aeruginosa* and *S. aureus*. All strains were isolated from patients in L.L.R. medical college hospital.

The identity of all strains was confirmed. A bacterial pension was prepared and added to the sterilized medium before solidification. The media with bacteria was poured in to sterilized Petri dishes under aseptic condition. Different weights of Schiff base and Co(II), Ni(II) and Cu(II) complexes of Schiff base complexes: (1 mg, 5 mg and 10 mg) were placed on the surface of the culture and incubated at 37 °C for 24 h. After incubation the inhibition (mm) and average of inhibition zones recorded<sup>3,4</sup>.

## RESULTS AND DISCUSSION

Table-1 comprises that the found data are in good agreement with those theoretical ones and the obtained analytical analysis data indicate the formation of 1:1 [M:L] ratio. The conductance measurement of the prepared complexes were carried out in CHCl<sub>3</sub> solvent which show the non-electrolytic nature of complexes<sup>5</sup>.

**Infrared spectra:** The infrared band assignment of the Schiff base complexes of Ni(II), Cu(II) and Co(II) complexes exhibit a broad band at 3400 cm<sup>-1</sup> which indicate the presence of a water molecule<sup>6</sup>. The presence of bands in the range of 1619 cm<sup>-1</sup> indicate the presence of azomethine group (C=N group) and the change of this band (1612 cm<sup>-1</sup>) from its position, on coordination suggest that the participation of azomethine group in coordination with metal ions<sup>7</sup>. The new bands in the range of 490 cm<sup>-1</sup> and 455 cm<sup>-1</sup> show the  $\nu$ (M-N) and  $\nu$ (M-O) vibrations<sup>8</sup>, respectively. The appearance of these bands show that the N and O atom of Schiff base is involved in coordination with metal ions (Table-2). The band in the range of 1760 cm<sup>-1</sup>

indicates that -COOH group is not participate in coordination with metal ions under investigation<sup>9</sup>. The IR spectral data (Table-2) of ligand show a sharp absorption around 3200 cm<sup>-1</sup> attributed to the presence of NH group, this band show a change in the position of the signal show the involvement of the indolic N atom in the coordination with metal<sup>10</sup>. The band appears in the range of 3210-3160 cm<sup>-1</sup> assigned to the stretching vibration of ring (N-H).

**Electronic spectra:** The electronic spectral data of the Schiff base and its complexes were recorded in chloroform and their assignments are listed in Table-3. The spectral data of Schiff base show three bands at 559 nm and 334 nm due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions.

The electronic spectra of cobalt(II) complex display the *d-d* transition in the region 9,746-10,441, 15,247-19,493 and 18,621-22371 cm<sup>-1</sup>. These transitions may be assigned to the  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ .

These transitions correspond to the tetragonal geometry of the complex<sup>11</sup>. The absorption spectra of Nickel(II) complex display three d-d transitions in the range of 11,135-12,108, 18,621-19,416 and 21,413-27,322 cm<sup>-1</sup> these bands corresponds to  ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ ,  ${}^4A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ . These transitions reveal that the nickel complex possess an octahedral geometry of complex<sup>12</sup>.

The copper(II) complex show *d-d* transition in the range of 12,188-15,149, 18,621-19,132 and 24,402-27,322 cm<sup>-1</sup> corresponds to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  transitions<sup>13</sup>.

TABLE-1  
SOME PHYSICAL PROPERTIES OF SCHIFF BASE AND ITS METAL COMPLEXES

Schiff base/ complexes	m.p.	$\Lambda_m^*$	Elemental analysis (%): Calcd. (found)			
			C	H	N	M
C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	159	00	70.12 (71.01)	5.19 (5.12)	9.09 (9.05)	-
[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]Co	160	00	59.00 (59.03)	4.13 (4.08)	7.65 (7.55)	16.13 (16.09)
[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]Cu	162	00	58.23 (58.29)	4.08 (4.09)	7.45 (7.55)	17.16 (17.14)
[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]Ni	165	00	59.05 (59.09)	4.13 (4.13)	7.63 (7.65)	16.12 (16.04)

TABLE-2  
IR SPECTRAL DATA OF SCHIFF BASE AND ITS METAL COMPLEXES

Schiff base /complexes	$\nu$ (COOH) (cm <sup>-1</sup> )	$\nu$ (C=N) (cm <sup>-1</sup> )	$\nu$ (M-O) (cm <sup>-1</sup> )	$\nu$ (M-N) (cm <sup>-1</sup> )	Indolic group (cm <sup>-1</sup> )
C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	1760	1619 s	-	-	3200 s
[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]Co	1760	1612 ms	455 w	490 s	3122 s
[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]Cu	1760	1611 s	450 m	489 mw	3010 s
[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]Ni	1760	1614 s	453 ms	487 m	3115 s

Abbreviations; s = strong, w= weak, mw=medium weak, sh=sharp

TABLE-3  
ELECTRONIC SPECTRA OF SCHIFF BASE AND ITS METAL COMPLEXES

Schiff base/complexes	$\lambda_{max}$ (nm/cm <sup>-1</sup> )	Transition	Geometry	$\mu_{eff}$ (B.M.)
C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	559, 334	$\pi \rightarrow \pi^*$ and $n \rightarrow \pi$		
[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]Co	9,746-10,441, 15,247-19,493, 18,621-22371	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$	Tetragonal	4.98
[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]Cu	12,188-15,149, 18,621-19,132, 24,402-27,322	${}^2B_{1g} \rightarrow {}^2A_{1g}$ ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Octahedral	3.55
[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]Ni	11,135-12,108, 18,621-19,416 21,413-27,322	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Octahedral	1.91

TABLE-4  
<sup>1</sup>H NMR SPECTRAL DATA OF SCHIFF BASE AND METAL COMPLEXES

Schiff base /complexes	δ(OH) (ppm)	δ(CH) (ppm)	δ(CH) aromatic (ppm)	δ(NH) (ppm)	δ(COOH) (ppm)
C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	12.18 (1H)	6.93 (H)	6.93-7.60 (7H)	10.09 (1H)	11
Co[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]	-	6.92 (H)	6.83-7.70 (7H)	10.10 (1H)	11
Cu[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]	-	6.93 (H)	6.90-7.77 (7H)	10.08 (1H)	11
Ni[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]	-	6.82 (H)	6.93-7.60 (7H)	10.07 (1H)	11

TABLE-5  
 ANTIBACTERIAL ACTIVITIES OF SCHIFF BASE AND METAL COMPLEXES

Schiff base /complexes	<i>E. coli</i>			<i>Salmonella</i>			<i>P. aeruginosa</i>			<i>S. aureus</i>		
	1 mg	5 mg	10 mg	1 mg	5 mg	10 mg	1 mg	5 mg	10 mg	1 mg	5 mg	10 mg
Wt. of Schiff base /complexes	1 mm	3 mm	3 mm	0 mm	1 mm	1 mm	1 mm	1 mm	1 mm	2 mm	3 mm	3 mm
C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	8 mm	11 mm	22 mm	5 mm	5 mm	9 mm	1 mm	2 mm	4 mm	6 mm	11 mm	21 mm
Co[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]	5 mm	12 mm	22 mm	4 mm	10 mm	12 mm	1 mm	7 mm	18 mm	6 mm	14 mm	23 mm
Cu[C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> ]	6 mm	11 mm	22 mm	5 mm	12 mm	21 mm	6 mm	11 mm	21 mm	1 mm	5 mm	16 mm

**<sup>1</sup>H NMR spectra:** The <sup>1</sup>H NMR spectra of ligands and their metal complexes have been recorded in TMS. The <sup>1</sup>H NMR spectra of the ligands show a signal at 10.10 ppm for the hydrogen atom of Indolic group this signal is not changed in complex, which indicate non-deprotonation of indole group nitrogen during complexation with metal. The presence of a signal at 11.00 ppm show the presence of proton of carboxylic group and this signal remain same in complexes, which exhibit the non-involvement of this group in coordination with metal ions. The ligand show a proton signal at 3.88 ppm indicates the presence of azomethine proton in ligand this signal shift up-field in the spectra of complexes (4.39 ppm), which is attributed to the donation of lone pair of the electron by azomethine nitrogen to the metal (Table-4).

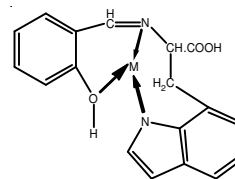
The ligand show a singlet at 5.0 ppm due to the presence of phenolic -OH group this signal shift downfield in the spectra of metal complexes indicating the donation of lone pair of the electron by phenolic O-atom to the metal<sup>14</sup>.

**<sup>13</sup>C NMR spectra:** The <sup>13</sup>C NMR spectral data of Schiff base and its corresponding metal complexes are reported<sup>15</sup>. The shifting of position of resonance of carbon attached to the phenolic -OH group suggested the bonding of oxygen to metal atom. Further the shifting of azomethine carbon signal in the spectra of complexes as compared to ligand clearly indicates that azomethine group has been involved in coordination. The <sup>13</sup>C NMR spectrum display the signals corresponding to azomethine carbon atom of Schiff base at δ 132.5 ppm, 124.4 ppm (indole group carbon atom), 67.1 (α-carbon atom attached with carboxylic group), 177.5 ppm (carbon atom of carboxylic group). The spectrum show signals at 121.5, 132.5, 116.0, 161.1, 124.6, 130.6 ppm corresponding to aromatic carbon atom of substituted ring<sup>16,17</sup>.

**Antibacterial activity:** Table-5 exhibit the zone of bacterial growth inhibition of the Schiff base and its metal complexes of Ni(II), Cu(II) and Co(II) against the tested bacteria. Norfloxacin is used as reference drug in this testing. (ZI = 25 mm at 10 mg) Schiff base display a weak activity against all bacteria. On complexation with metals the antibacterial activity of Schiff base is increased. Different weight of metal complexes (1, 5 and 10 mg) are used to identify the zone of inhibition of each metal complexes. The Ni(II) complexes are weakly active against *Salmonella* (ZI = 9 mm) and *P.*

*aeruginosa* (ZI = 4 mm) and show strong activity against *E. coli* and *S. aureus* (ZI= 22 mm and 23 mm). The Cu(II) complex show strong activity against *E. coli* and *S. aureus* (ZI = 22 mm and 21 mm) The Co(II) complex show its strong activity against *E. coli*, *Salmonella* and *P. aeruginosa* ((ZI = 22 mm, 21 mm and 21 mm) while this complex show a moderate activity against *S. aureus* (ZI = 16 mm)

The following structure of metal complexes are proposed



where, M= Co(II), Cu(II) and Ni(II)

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