



**MIXED LIGAND COMPLEXES DERIVED FROM 4-(BENZENEAZO)  
SALICYLADEHYDE AND 2-AMINO-4-NITROPHENOL  
USING TRANSITION METAL IONS**

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**ABSTRACT**

This paper includes synthesis and characterization of mixed ligand complexes derived from 4-(Benzeneazo) salicylaldehyde and 2-amino-4-nitrophenol using transition metal ions such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). The synthesized complexes have been characterized with the help of molar conductance, magnetic susceptibility measurements, and spectral techniques such as IR, <sup>1</sup>H-NMR and electronic spectra. The synthesized complexes are also screened for their antibacterial activities. The studies made on these complexes proposed a six coordinated octahedral geometry for all these complexes.

**Key words:** Mixed ligand, 4-(Benzeneazo)salicylaldehyde, 2-Amino-4-nitrophenol, Transition metal ions, Antibacterial.

**INTRODUCTION**

Mixed ligand complexes differ from traditional complexes in the sense that they are having at least two different kinds of ligands associated with the same metal ion in a complex. The presence of more than one type of ligand in a complex increases chances of variation in properties expected for the complex. This makes the researcher interested in the synthesis of mixed ligand complexes with varying properties.

Synthesis and characterization of mixed ligand complexes is gaining importance day by day. The increased interest in this research area has motivated many researchers to get involved in this field. In recent years many publications are devoted to synthesis and characterization of mixed ligand complexes<sup>1-6</sup>.

Present work is continuation of our previous research work on synthesis and characterization of mixed ligand complexes<sup>7,8</sup>. In this paper, we report synthesis and characterization of a series of six mixed ligand complexes derived from 4-(Benzeneazo)salicylaldehyde and 2-amino-4-nitrophenol using transition metal ions such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). These complexes are then characterized using molar conductance, magnetic measurements and spectral techniques such as IR, <sup>1</sup>H-NMR and electronic spectra. These synthesized complexes are also screened for their antibacterial activities.

## EXPERIMENTAL

### Materials and methods

All the chemicals used in present study were of AR grade. 2-amino-4-nitrophenol and metal salts were procured from S. D. Fine Chemicals Limited and Spectrochem Private Limited, respectively. All the solvents used were distilled and dried using molecular sieves before use.

The molar conductance of complexes was measured by preparing  $10^{-3}$  M solutions in DMF solvent using Equiptronics conductivity meter with inbuilt magnetic stirrer Model (Eq-664) at room temperature.

Magnetic susceptibilities were determined on the SES instrument's magnetic susceptibility Guoy's balance (Model EMU-50) at room temperature using copper (II) sulphate as a standard. These magnetic susceptibility values were utilized to calculate magnetic moments using spin only formula  $\mu_{\text{eff}} = (n(n+2))^{1/2}$  for all the synthesized complexes.

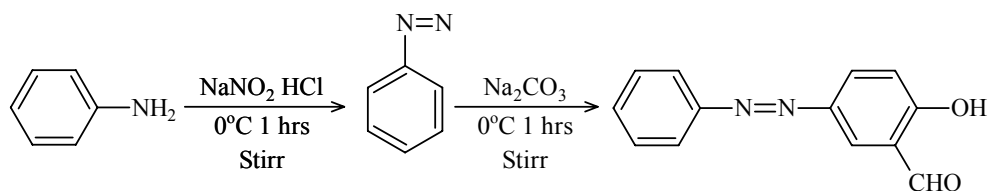
IR spectra were recorded as KBr pellets in the region of  $4000\text{-}400\text{ cm}^{-1}$  on a Perkin-Elmer Spectrophotometer. Electronic spectra were recorded in DMSO on a Shimadzu UV-1600 spectrophotometer.  $^1\text{H-NMR}$  spectra were recorded on Bruker Avance II 400 NMR spectrometer using DMSO  $d^6$  (spectroscopic grade) as a solvent.

All the synthesized mixed ligand complexes (0.5 mg/mL) were screened for their antibacterial activities against five bacteria (such as *Staphylococcus aureus* (ATCC 10832), *Bacillus subtilis*, *P. aeruginosa* (ATCC 14210), *Salmonella typhimurium* (ATCC 23564) and *Escherichia coli* (ATCC 33684)) by agar well diffusion assay method<sup>9</sup> using DMSO as control. The standard Tetracycline (0.05 mg/mL) antibiotics were used as an antibacterial agent. The inoculated plates were incubated at  $30^\circ\text{C}$  and  $37^\circ\text{C}$  temperature for 48 hours and inhibition zone was measured in mm.

### Synthesis of mixed ligand complexes

The synthesis of mixed ligand complexes was carried out in two steps. In the first step the ligand 4-(Benzeneazo)salicylaldehyde was prepared and it was then utilized in the second step to prepare the complexes using 2-amino-4-nitrophenol.

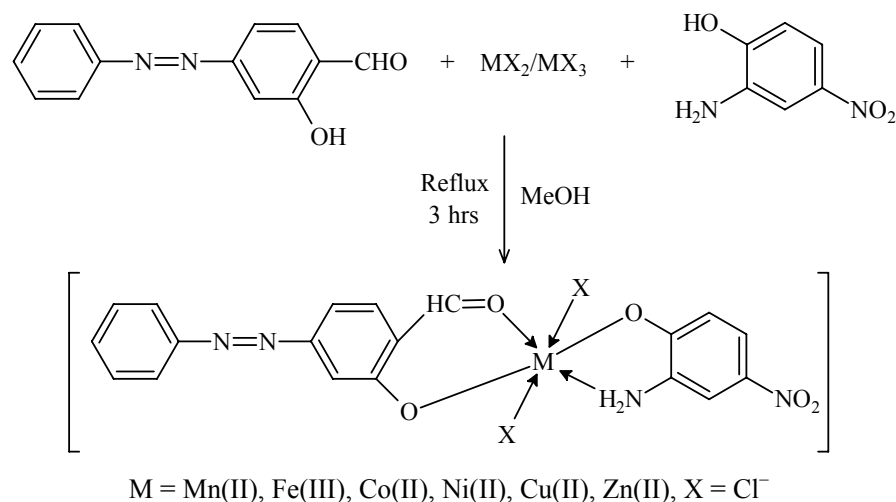
**(a) Preparation of 4-(Benzeneazo)salicylaldehyde:** 4-(Benzeneazo)salicylaldehyde was prepared as per the procedure reported earlier by Liu et al.<sup>10</sup>



**Scheme 1: Preparation of 4-(Benzeneazo)salicylaldehyde**

**(b) General procedure for the synthesis of mixed ligand complexes:** Synthesis of mixed ligand complexes was carried out using template method. A hot methanolic solution (10 mL) of respective transition metal salt (1 mmol) was mixed with a hot solution (1 mmol) of 2-amino-4-nitrophenol and 4-(benzeneazo)salicylaldehyde (1 mmol). Few drops of Conc. HCl were added to the mixture. The resulting mixture was then left under reflux for 4 hours. After refluxing for 4 hrs appropriate complexes were precipitated out on cooling the reaction mixture. Those were then filtered, washed with methanol and

recrystallized from ethanol. The purity of the complexes was checked by taking TLC [solvent system (9:1)  $\text{CHCl}_3 + \text{MeOH}$ ]. The synthesized complexes were obtained in 60-70% yield. The general scheme (**Scheme 2**) for the synthesis of mixed ligand complexes is given as below.



**Scheme 2: Synthesis of mixed ligand complexes**

## RESULTS AND DISCUSSION

The general composition of the synthesized mixed ligand complexes can be represented as  $[\text{M}(\text{C}_{19}\text{H}_{13}\text{N}_4\text{O}_5)\text{X}_2]$  (where M = Mn(II), Co(II), Ni(II), Cu(II) & Zn(II)) and  $[\text{M}(\text{C}_{19}\text{H}_{13}\text{N}_4\text{O}_5)\text{X}_2]\text{X}$  [where M = Fe(III)]. All the synthesized complexes were thermally stable and colored. Observations such as colour, melting point, % yield, solubility behavior for all the complexes were recorded. Table 1 shows physicochemical data recorded along with molar conductance and magnetic moments for all the synthesized complexes.

**Table 1: Physicochemical data of mixed ligand metal complexes**

S. No.	Molecular formula	Colour	Melting point (°C)	Yield (%)	Molar conductance ( $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ )	Magnetic moment ( $\mu_{\text{eff}}$ B. M.)
1	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{MnN}_4\text{O}_5$	Dark brown	200	65	12	5.84
2	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{FeN}_4\text{O}_5$	Light yellow	210	68	82	5.38
3	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{CoN}_4\text{O}_5$	Black	200	62	25	4.29
4	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{NiN}_4\text{O}_5$	Light Red	220	69	21	2.81
5	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{CuN}_4\text{O}_5$	Blue	200	70	18	1.85
6	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{ZnN}_4\text{O}_5$	Dark green	210	59	10	Diamagnetic

### Solubility behaviour

Solubility behaviour of all the synthesized complexes was checked using different solvents such as water, methanol, ethanol, chloroform, acetone, acetonitrile, DMSO and DMF. All the synthesized complexes were found to be insoluble in water and partially soluble in methanol, ethanol, acetone and ethyl acetate. All the complexes were found to be soluble in DMF and DMSO. In acetonitrile three of the complexes of Mn(II),

Fe(III) and Cu(II) were soluble and the remaining were found to be partially soluble. The results obtained are shown in Table 2 as below.

**Table 2: Solubility of mixed ligand metal complexes**

S. No.	Compound	Water	MeOH	EtOH	Acetone	EA	CH <sub>3</sub> CN	DMF	DMSO
1	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> MnN <sub>4</sub> O <sub>5</sub>	I	P	P	P	P	S	S	S
2	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> FeN <sub>4</sub> O <sub>5</sub>	I	P	P	P	P	S	S	S
3	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> CoN <sub>4</sub> O <sub>5</sub>	I	P	P	P	P	P	S	S
4	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> NiN <sub>4</sub> O <sub>5</sub>	I	P	P	P	P	P	S	S
5	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> CuN <sub>4</sub> O <sub>5</sub>	I	P	P	P	P	S	S	S
6	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> ZnN <sub>4</sub> O <sub>5</sub>	I	P	P	P	P	P	S	S

\*P = Partially, S = Soluble, I = Insoluble

### Molar conductance

Molar conductance for all the complexes was measured by preparing their 10<sup>-3</sup> M solutions in DMF as a solvent. Low values (13-27 ohm<sup>-1</sup> cm<sup>-2</sup> mol<sup>-1</sup>) for complexes with divalent metal ions such as Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) and high value i.e. 82 ohm<sup>-1</sup> cm<sup>-2</sup> mol<sup>-1</sup> for Fe(III) complex was recorded. The low values recorded for divalent metal ion complexes indicate towards nonelectrolytic behavior of these complexes whereas that for Fe(III) complexes indicate towards its 1:1 electrolytic nature<sup>11-12</sup>.

### Magnetic properties

The observed magnetic moment values for Mn(II) and Fe(III) complexes are 5.84 and 5.38 B.M., respectively indicating towards d<sup>5</sup> configuration and five unpaired electrons present in these complexes. This means these complexes are having an octahedral geometry. Magnetic moment of Co(II) complex is 4.29 B.M. corresponding to three unpaired electrons in an octahedral environment. The observed magnetic moment value for Ni(II) and Cu(II) complexes are 2.81 and 1.85 B.M., respectively corresponding to two and one unpaired electrons in these complexes. Zn(II) complex has been found to be diamagnetic<sup>13</sup>. The magnetic moment values of all the synthesized complexes are reported in Table 1.

### IR Spectra

IR spectra of all the synthesized complexes have been recorded in the range 4000-400 cm<sup>-1</sup>. The spectra are interpreted considering few main peaks observed. The presence of peaks in the region around 3400 cm<sup>-1</sup> indicates towards the presence of -NH<sub>2</sub> group in the complexes.

The bands observed around 1440-1450 cm<sup>-1</sup> and 2854-3100 cm<sup>-1</sup> were assigned to  $\nu$ (C=C) and  $\nu$ (C-H) aromatic stretching, respectively<sup>6</sup>. The peaks observed in the region 1600-1650 cm<sup>-1</sup> for all the complexes are due to >C=O group present in complexes. The peaks observed around 1515-1535 cm<sup>-1</sup> can be assigned due to -N=N- group present in the complexes. Similar observation was reported by Rao and Shaw<sup>14</sup>. In their paper, they have reported a peak at 1535-1560 cm<sup>-1</sup> for -N=N- group in complexes.

Identification of peaks for  $\nu$ (M-O) and  $\nu$ (M-N) is difficult as these can be observed at any value between 400-800 cm<sup>-1</sup>. Many authors have defined peaks at different values for these signals<sup>15-18</sup>. In the present case, the peaks of weak intensity observed in the region 500-650 cm<sup>-1</sup> can be assigned to  $\nu$ (M-O) and

$\nu(\text{M-N})$  present in the complexes. The  $\nu(\text{M-Cl})$  band is usually reported to be observed below  $400\text{ cm}^{-1}$  region<sup>19,20</sup>. Due to instrument limitation, the said region was not scanned for present investigation. The results obtained from the IR spectra are listed in Table 3.

**Table 3: IR spectroscopic data ( $\text{cm}^{-1}$ ) of the synthesized mixed ligand metal complexes**

S. No.	Molecular formula	N-H str	C=O str	M-O str	M-N str
1	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{MnN}_4\text{O}_5$	3433	1631	632	505
2	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{FeN}_4\text{O}_5$	3421	1604	648	509
3	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{CoN}_4\text{O}_5$	3429	1604	651	524
4	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{NiN}_4\text{O}_5$	3444	1627	636	509
5	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{CuN}_4\text{O}_5$	3433	1612	648	532
6	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{ZnN}_4\text{O}_5$	3433	1627	632	509

### <sup>1</sup>H-NMR Spectra

<sup>1</sup>H-NMR spectrum for Ni(II) complex was recorded as a sample study to confirm the skeleton of metal complex. The spectrum shows three peaks out of which a peak observed in the region 2.5-2.6 ppm was due to the residual protons of the solvent DMSO- $d_6$ <sup>21</sup>. The well resolved multiplet at  $\delta$  7.20-7.7 ppm corresponding to aromatic protons in mixed ligand complexes and the singlet broad peak observed at  $\delta$  4.5 ppm corresponds to NH protons.

### Electronic spectra

An electronic spectrum for all the synthesized complexes was recorded in DMSO solvent. Normally two to three bands are reported for azo compounds by different workers<sup>22-24</sup>. Out of these, the first band expected around 220 nm is assigned to  $\Pi \rightarrow \Pi^*$  of the benzenoid moiety and the second one expected around 425 nm is assigned to  $n \rightarrow \Pi^*$  electronic transition of  $-\text{N}=\text{N}-$  group. A shift in positions of these bands is observed when these azo compounds are engaged in complex formation with metals through  $-\text{N}=\text{N}-$  group.

In the present case, these two bands are observed in the same region and they are almost undisturbed as the  $-\text{N}=\text{N}-$  group is not taking part in bond formation with the metal ion. Apart from these bands some specific bands are also observed in case of metal complexes which are listed as below in Table 4.

**Table 4: Electronic spectral data (in nm) of the synthesized mixed ligand metal complexes**

S. No.	Molecular formula of complex	Wavelength (nm)	Transition
1	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{MnN}_4\text{O}_5$	650 nm	${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$
2	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{FeN}_4\text{O}_5$	660 nm	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$
3	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{CoN}_4\text{O}_5$	560 nm	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$
		680 nm	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$
4	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{NiN}_4\text{O}_5$	580 nm	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$
5	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{CuN}_4\text{O}_5$	580 nm	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$
6	$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{ZnN}_4\text{O}_5$	-	-

### Antibacterial activity

All the mixed ligand complexes exhibited antibacterial activity against various bacterial pathogens tested at 0.5 mg/ml concentration. Among the tested pathogens *S. aureus*, *E. coli* and *P. aeruginosa* are found to be more sensitive, whereas *Bacillus subtilis* and *Salmonella typhimurium* found to be comparatively less sensitive as shown in Table 5.

The Cu(II) complex showed efficient broad spectrum of activity against *B. subtilis*, *P. aeruginosa*, *S. aureus* and *E. Coli* with inhibition zone of diameter ranging from 18-24 mm. Positive control tetracycline produced maximum inhibition zone diameter on bacterial lawn plate used for comparative study. However, DMSO, which is used as negative control produced no observable inhibitory effect against any of the test pathogen tested.

**Table 5: Antibacterial activity (in mm) of synthesized mixed ligand complexes**

S. No.	Compounds	<i>B. subtilis</i>	<i>P. aeruginosa</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>S. typhimurium</i>
1	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> MnN <sub>4</sub> O <sub>5</sub>	20 ± 0.5	12 ± 1.0	13 ± 0.5	14 ± 0.5	12 ± 1.0
2	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> FeN <sub>4</sub> O <sub>5</sub>	12 ± 0.5	11 ± 1.0	14 ± 1.0	12 ± 0.5	11 ± 1.0
3	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> CoN <sub>4</sub> O <sub>5</sub>	10 ± 1.0	14 ± 1.0	20 ± 1.0	11 ± 1.0	10 ± 1.0
4	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> NiN <sub>4</sub> O <sub>5</sub>	10 ± 0.5	12 ± 0.5	12 ± 0.5	12 ± 0.5	12 ± 0.5
5	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> CuN <sub>4</sub> O <sub>5</sub>	24 ± 1.0	18 ± 1.0	22 ± 0.5	18 ± 1.0	11 ± 1.0
6	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> ZnN <sub>4</sub> O <sub>5</sub>	16 ± 0.5	10 ± 1.0	12 ± 1.0	14 ± 1.0	10 ± 1.0
7	Tetracycline	20 ± 0.5	23 ± 0.5	22 ± 0.5	24 ± 0.5	23 ± 0.5

### CONCLUSION

In present paper, we have reported a series of six mixed ligand complexes synthesized by reacting 4-(Benzeneazo)salicylaldehyde and 2-Amino-4-nitrophenol with respective metal chlorides in methanolic medium. These synthesized complexes have been characterized with the help of molar conductance, magnetic susceptibility measurements and spectral techniques such as IR, <sup>1</sup>H-NMR and electronic spectra. On the basis of studies made a six coordinated octahedral geometry has been proposed for all these complexes.

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