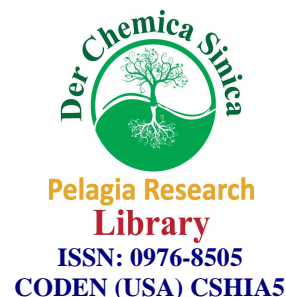




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Synthesis and characterization of mixed ligand complexes derived from 4-(benzeneazo)salicylaldehyde and 2-amino-4-nitrophenol using transition metal nitrates

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ABSTRACT

Mixed ligand complexes of transition metal ions such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized using 4-(Benzeneazo)salicylaldehyde, 2-amino-4-nitrophenol and nitrates of respective metal ions. The synthesized complexes have been characterized with infra red (IR), electronic, and ¹H-NMR Spectra, molar conductance and magnetic susceptibility measurements at room temperature. Based on the results obtained an octahedral geometry has been proposed for all these complexes. The synthesized complexes were also screened for their antibacterial activity.

Keywords: Mixed ligand complexes, 4-(Benzeneazo)salicylaldehyde, 2-amino-4-nitrophenol, Octahedral, Antibacterial.

INTRODUCTION

The area of research including synthesis of mixed ligand complexes has gained tremendous interest in recent years. The growing interest in this area of research has prompted many researchers to work in this area and as a result a vast amount of literature has been published in this area [1-6].

Classical complexes normally include one type of ligand molecules attached to the metal. The number of ligands attached however differs depending on the nature of metal ion and geometry of the complex formed. Mixed ligand complexes differ from classical complexes in the sense that they are having more than one type of ligands attached to the same metal atom in a complex. This involvement of more than one type of ligands in a metal complex creates a chance of alteration in properties expected for the complex due to structural variations. This may lead to variety of applications and thus keep the researchers interested.

Present investigation deals with synthesis and characterization of mixed ligand complexes of transition metal ions such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) using 4-(benzeneazo)salicylaldehyde and 2-amino-4-nitrophenol and respective metal nitrates and is a continuation of systematic research program related to synthesis and characterization of mixed ligand complexes going on in my laboratory [7-9].

The synthesized complexes are then characterized using molar conductance, magnetic susceptibility measurements at room temperature and spectral techniques such as infra red (IR), electronic and $^1\text{H-NMR}$ spectra. The complexes are also scanned for their antibacterial activity against five bacterial pathogens.

MATERIALS AND METHODS

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

Analytical methods and measurements:

Molar conductance values of synthesized mixed ligand complexes were measured by preparing their 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 a Bruker Avance II 400 MHz NMR spectrometer using DMSO-d^6 (spectroscopic grade) as a solvent.

Antibacterial assay of mixed ligand complexes:

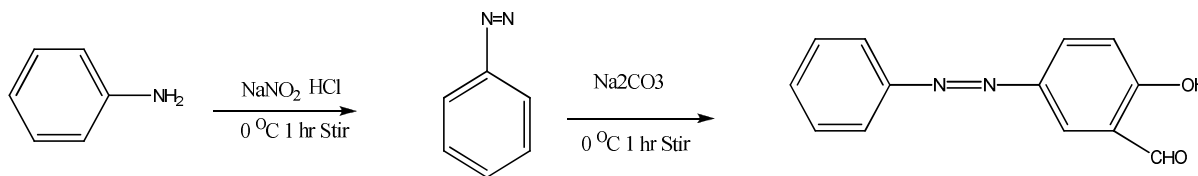
All the synthesized mixed ligand complexes (0.5 mg/mL) were screened for their antibacterial activities against five bacterial pathogens such as *S. aureus* (ATCC 10832), *B. subtilis*, *P. aeruginosa* (ATCC 14210), *S. Typhimurium* (ATCC 23654) and *E. coli* (ATCC 33684) by agar well diffusion assay method [10] using DMSO as a control. The standard tetracycline (0.05 mg/mL) antibiotic was used as an antibacterial agent. The inoculated plates were incubated at 30°C and 37°C temperature for 48 hours and inhibition zone was measured in mm.

Synthesis of mixed ligand complexes

Synthesis of mixed ligand complexes was carried out in two steps. In the first step primary 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 by diazotizing aniline and reacting the diazo product with salicylaldehyde. The procedure used for preparation of 4-(Benzeneazo)salicylaldehyde was reported earlier by Liu et. al [11].



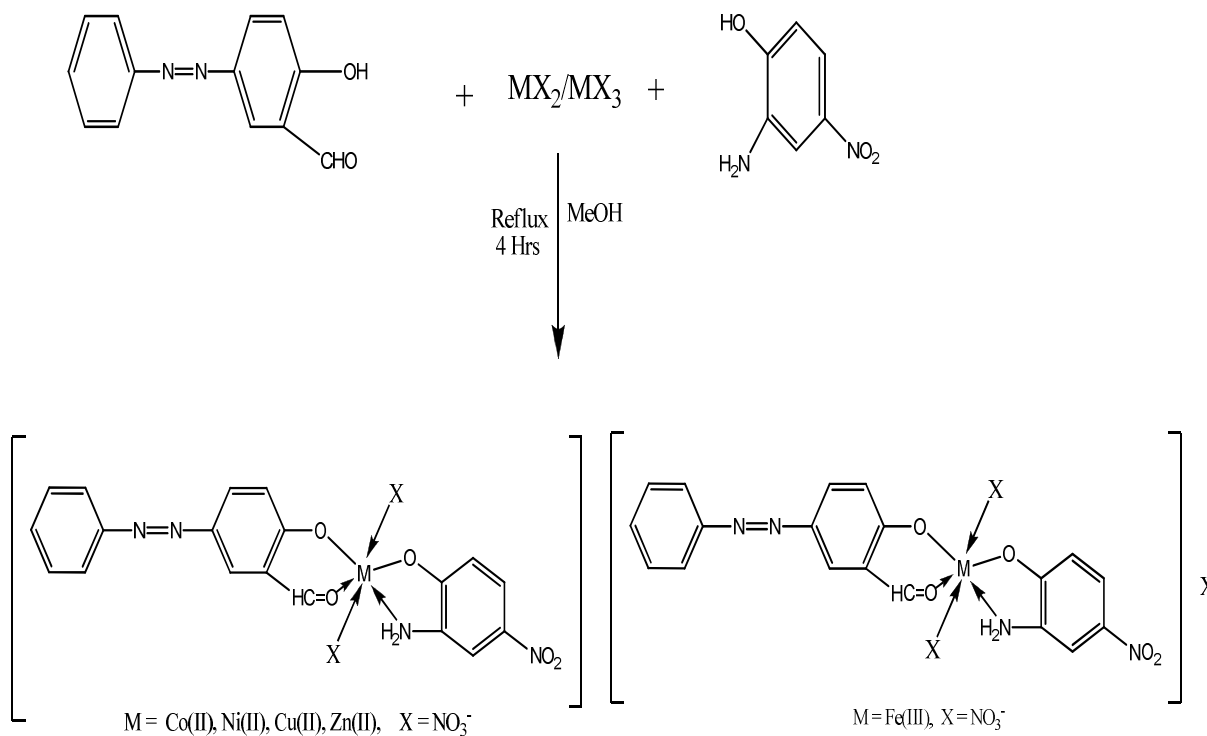
Scheme 1: Preparation of 4-(Benzeneazo)salicylaldehyde

(b) General procedure for synthesis of mixed ligand complexes:

A hot methanolic solution (10 mL) of respective transition metal nitrates (1 mmol) was mixed with a hot methanolic solution of 2-amino-4-nitrophenol (1 mmol) and 4-(Benzeneazo)salicylaldehyde (1 mmol). Few drops of Conc. HCl were added to the reaction mixture. The resulting mixture was then left under reflux for 4 hours.

The progress of the reaction was checked by taking TLC [solvent system (9:1) $\text{CHCl}_3 + \text{MeOH}$] after every 30 minutes. After refluxing for 4 hours, appropriate complexes were precipitated out on cooling the reaction mixture.

Those were then filtered, washed with methanol and recrystallized from ethanol. The synthesized complexes were obtained in 60-70 % yield. General scheme for the synthesis and proposed structures of complexes is given below.



Scheme 2: Synthesis and proposed structures of mixed ligand complexes

RESULTS AND DISCUSSION

The general composition of synthesized mixed ligand complexes can be represented as $[\text{M}(\text{C}_{19}\text{H}_{14}\text{N}_4\text{O}_5)\text{X}_2]$ [Where $\text{M} = \text{Mn(II), Co(II), Ni(II), Cu(II), Zn(II)}$] and $[\text{M}(\text{C}_{19}\text{H}_{14}\text{N}_4\text{O}_5)\text{X}_2]\text{X}$ (Where $\text{M} = \text{Fe(III)}$ $\text{X} = \text{NO}_3^-$ in both the cases). All the synthesized complexes were thermally stable and colored.

Physicochemical data:

Observations such as colour, melting point, percentage yield, solubility behavior were recorded for all the synthesized complexes. Table 1 includes physicochemical data such as colour, melting point, percentage yield along with molar conductance and magnetic susceptibility values for all the synthesized mixed ligand complexes.

Table 1: Physicochemical data of synthesized mixed ligand complexes

Sr. No.	Proposed Molecular Formula	Colour	Melting Point (°C)	Percentage Yield (%)	Molar conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)	Magnetic Susceptibility (μ_{eff} B. M.)
1	$\text{C}_{19}\text{H}_{14}\text{MnN}_6\text{O}_{11}$	Dark Brown	210	65	15	5.86
2	$\text{C}_{19}\text{H}_{14}\text{FeN}_6\text{O}_{11}$	Light black	200	64	73	5.32
3	$\text{C}_{19}\text{H}_{14}\text{CON}_6\text{O}_{11}$	brown	240	69	17	4.20
4	$\text{C}_{19}\text{H}_{14}\text{NiN}_6\text{O}_{11}$	Red	220	66	14	2.73
5	$\text{C}_{19}\text{H}_{14}\text{CuN}_6\text{O}_{11}$	Light blue	230	70	19	1.73
6	$\text{C}_{19}\text{H}_{14}\text{ZnN}_6\text{O}_{11}$	Brown	250	62	15	Diamagnetic

Solubility behaviour:

All the synthesized mixed ligand complexes were checked for their solubility behaviour using different solvents such as water, methanol, ethanol, acetone, ethyl acetate, acetonitrile, DMF and DMSO. All the complexes were found to be insoluble in water, partially soluble in methanol, ethanol, acetone, ethyl acetate and acetonitrile and freely soluble in DMF and DMSO.

Table 2: Solubility behaviour of synthesized mixed ligand complexes

Sr. no.	Complex	Water	MeOH	EtOH	Acetone	Ethyl-acetate	CH ₃ CN	DMF	DMSO
1	C ₁₉ H ₁₄ MnN ₆ O ₁₁	I	P	P	P	P	P	S	S
2	C ₁₉ H ₁₄ FeN ₆ O ₁₁	I	P	P	P	P	P	S	S
3	C ₁₉ H ₁₄ CON ₆ O ₁₁	I	P	P	P	P	P	S	S
4	C ₁₉ H ₁₄ NiN ₆ O ₁₁	I	P	P	P	P	P	S	S
5	C ₁₉ H ₁₄ CuN ₆ O ₁₁	I	P	P	P	P	P	S	S
6	C ₁₉ H ₁₄ ZnN ₆ O ₁₁	I	P	P	P	P	P	S	S

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

Molar conductance:

Based on the solubility behaviour observed, it was decided to record molar conductance values of all the synthesized complexes by preparing their solutions in DMF. Thus appropriate quantities of complexes were dissolved in DMF so as to prepare their 10⁻³ M solutions. These solutions were then used for recording molar conductance values.

Low values (14-19 ohm⁻¹ cm² mol⁻¹) of molar conductance were recorded for complexes with divalent metal ions whereas quite a high value (i.e 73 ohm⁻¹ cm² mol⁻¹) of molar conductance was observed for Fe(III) complex.

The observed molar conductance values for divalent metal ion complexes indicate towards their non-electrolytic behavior whereas that for Fe(III) complex indicate towards its 1:1 electrolytic nature [12-13]. The molar conductance values observed for all the complexes are reported in Table 1 along with the physicochemical data of the complexes.

Magnetic moments:

The obtained magnetic moment values of all the synthesized mixed ligand complexes are reported in Table 1 along with physicochemical data of the complexes. Mn(II) and Fe(III) complexes showed magnetic moment values of 5.90 and 5.32 B.M. respectively. These values indicate towards high-spin d⁵ configuration and presence of five unpaired electrons in these complexes [14].

The magnetic moment value observed for Co(II) complex (4.20 B.M.) corresponds to three unpaired electrons in an octahedral environment [14]. The observed magnetic moment value for Ni(II) and Cu(II) complexes are 2.73 and 1.73 B.M. respectively corresponding to two and one unpaired electrons in these complexes [14].

Zn(II) complex has been found to be diamagnetic indicating towards d¹⁰ completely filled configuration [14].

IR Spectra:

IR spectra recorded for ligands as well as complexes is normally helpful to confirm the proposed structure of complexes. The part of IR spectral study normally deals with comparison of IR spectra of synthesized ligand and metal complexes. Such kind of comparison helps researchers to identify the presence or absence of functional groups in the synthesized ligands and complexes and thus supports to confirm the formation of metal complexes. Interpretation of IR spectra normally includes consideration of few main peaks observed in the spectra.

For present investigation, IR spectra of all the synthesized mixed ligand complexes have been recorded in the range 4000-400 cm⁻¹. The presence of peaks in the region around 3400 cm⁻¹ indicates towards the presence of -NH₂ group in the complexes. The bands observed around 1440-1450 cm⁻¹ and 2854-3100 cm⁻¹ were assigned to ν (C=C) and ν (C-H) aromatic stretching respectively [6].

The peaks observed in the region 1600-1630 cm⁻¹ for all the complexes are due to >C=O group present in complexes. The peaks observed around 1515-1535 cm⁻¹ can be assigned due to -N=N- group present in the

complexes. Similar observation was reported by Rao and Shaw [15]. In their paper they have reported a peak at 1535-1560 cm^{-1} for $-\text{N}=\text{N}-$ group in complexes.

Identification of peaks for $\nu(\text{M-O})$ and $\nu(\text{M-N})$ is difficult as these peaks may be present at any value between 400-800 cm^{-1} . Peaks at different positions for these stretching vibrations have been reported by different researchers [16-19]. In present case, the peaks of weak intensity observed in the region 440-685 cm^{-1} can be assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ present in the complexes.

Nitrate ion is an ambidentate ligand. It may be attached to the metal in unidentate or bidentate fashion. It is well established that the bands present in the region 1408-1440, 1290-1320 and 1010-1030 cm^{-1} in IR spectra of complexes indicate that nitrate group is bonded to the metal ion in unidentate fashion [20-21]. The same is observed in present investigation. The results obtained from the IR spectral study are listed in Table 3.

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

Sr. No.	Complex	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
1	$\text{C}_{19}\text{H}_{14}\text{MnN}_6\text{O}_{11}$	3420	1615	668	498
2	$\text{C}_{19}\text{H}_{14}\text{FeN}_6\text{O}_{11}$	3419	1603	688	506
3	$\text{C}_{19}\text{H}_{14}\text{CON}_6\text{O}_{11}$	3431	1616	675	524
4	$\text{C}_{19}\text{H}_{14}\text{NiN}_6\text{O}_{11}$	3414	1621	685	484
5	$\text{C}_{19}\text{H}_{14}\text{CuN}_6\text{O}_{11}$	3425	1626	672	448
6	$\text{C}_{19}\text{H}_{14}\text{ZnN}_6\text{O}_{11}$	3415	1630	678	479

Electronic spectra:

Electronic spectra for all the synthesized mixed ligand complexes were recorded in DMSO solvent. Normally two to three bands are reported for azo compounds by different workers [22-24]. 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 transitions of $-\text{N}=\text{N}-$ group. A shift in the positions of these bands is observed when these azo compounds are engaged in complex formation with metals through $-\text{N}=\text{N}-$ group.

In present investigation these two bands are observed in the same region and they are almost undisturbed as the azo ($-\text{N}=\text{N}-$) 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 all the synthesized mixed ligand complexes

Sr. No	Complex	Wavelength (λ_{max})	Electronic Transitions
1	$\text{C}_{19}\text{H}_{14}\text{MnN}_6\text{O}_{11}$	665 nm	$6A_{1g} \rightarrow 4E_g$
2	$\text{C}_{19}\text{H}_{14}\text{FeN}_6\text{O}_{11}$	670 nm	$6A_{1g} \rightarrow 4T_{2g}$
3	$\text{C}_{19}\text{H}_{14}\text{CON}_6\text{O}_{11}$	560 nm	$4T_{1g}(\text{F}) \rightarrow 4T_{1g}(\text{P})$
		680 nm	$4T_{1g}(\text{F}) \rightarrow 4A_{2g}(\text{F})$
4	$\text{C}_{19}\text{H}_{14}\text{NiN}_6\text{O}_{11}$	580 nm	$3A_{2g}(\text{F}) \rightarrow 3T_{1g}(\text{F})$
5	$\text{C}_{19}\text{H}_{14}\text{CuN}_6\text{O}_{11}$	580 nm	${}^2E_g \rightarrow {}^2T_{2g}$
6	$\text{C}_{19}\text{H}_{14}\text{ZnN}_6\text{O}_{11}$	-----	-----

$^1\text{H-NMR}$ Spectra:

$^1\text{H-NMR}$ spectrum recorded for synthesized complex compound normally helps researchers to confirm the skeleton of metal complex by identifying protonic arrangement present in it. In present investigation $^1\text{H-NMR}$ spectrum for Ni(II) complex was recorded as a sample for study. The spectrum recorded showed three peaks out of which a peak observed in the region 2.5-2.6 ppm may be assigned to residual protons of the solvent DMSO- d_6 [25].

Out of remaining two peaks, the well resolved multiplet observed in the region 7.20-7.80 ppm corresponds to aromatic protons present in the skeleton of mixed ligand complexes and the singlet peak observed at δ 4.5 ppm corresponds to $-\text{NH}$ protons.

Antibacterial activity:

All the synthesized mixed ligand complexes were tested for their antibacterial activity against five bacterial pathogens viz. *B. subtilis*, *P. aeruginosa*, *S. Aureus*, *E. Coli* and *S. Typhimurium* and all the complexes exhibited antibacterial activity against all these tested bacterial pathogens at concentration of 0.5 mg/ml.

Fe(III) and Ni(II) complexes showed significant to good activity against four out of five tested pathogens viz. *B. Subtilis*, *P. aeruginosa*, *E. Coli* and *S. aureus* with inhibition zone of diameter ranging from 17-22 mm and 16-20 mm respectively. Both these complexes showed moderate activity against *S. typhimurium* with inhibition zone of diameter 13 mm and 11 mm respectively.

Cu(II) complex has showed good activity with inhibition zone of diameter 18 and 17 mm respectively for *B. subtilis* and *S. aureus* whereas for remaining pathogens moderate activity is observed with inhibition zone of diameter 14 mm. Zn(II) complex has showed good activity against *B. subtilis* with inhibition zone of diameter 16 mm whereas for all remaining pathogens moderate activity with inhibition zone of diameter ranging from 12-14 mm was observed.

Mn(II) and Co(II) complexes showed moderate activity against all the tested pathogens with inhibition zone of diameter ranging from 12-14 mm and 10-14 mm respectively. Positive control tetracycline produced maximum inhibition zone of diameter ranging from 20-24 mm on bacterial lawn plate used for comparative study. However, DMSO which is used as negative control has produced no observable inhibitory effect against any of the tested pathogens. The zone of inhibition observed for all the complexes against tested pathogens are represented in Table 5.

Table 5: Zone of inhibition (in mm) of synthesized mixed ligand complexes

Sr. No.	Complex	<i>B. Subtilis</i>	<i>P. aeruginosa</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>S. typhimurium</i>
1	C ₁₉ H ₁₄ MnN ₆ O ₁₁	12 ±0.5	12±1.0	13 ±0.5	14 ±0.5	12±1.0
2	C ₁₉ H ₁₄ FeN ₆ O ₁₁	20 ±0.5	18 ±1.0	22 ±0.5	17 ±0.5	13 ±1.0
3	C ₁₉ H ₁₄ CON ₆ O ₁₁	12 ±0.5	10 ±1.0	14 ±1.0	12 ±1.0	10 ±1.0
4	C ₁₉ H ₁₄ NiN ₆ O ₁₁	16 ±1.0	17 ±1.0	20 ±1.0	16 ±1.0	11 ±1.0
5	C ₁₉ H ₁₄ CuN ₆ O ₁₁	18 ±0.5	14 ±1.0	17 ±0.5	14±1.0	14 ±1.0
6	C ₁₉ H ₁₄ ZnN ₆ O ₁₁	16 ±1.0	14 ±1.0	14 ±0.5	12±1.0	14 ±1.0
7	Tetracycline	20 ±0.5	23 ±0.5	22 ±0.5	24 ±0.5	23 ±0.5

CONCLUSION

In present investigation synthesis of mixed ligand complexes derived from 4-(Benzeneazo)salicylaldehyde and 2-amino-4-nitrophenol using nitrates of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) have been reported. These synthesized complexes have been characterized with the help of infra red (IR), electronic and ¹H-NMR spectra, molar conductance and magnetic susceptibility measurements at room temperature. Based on the results obtained six coordinated octahedral geometry has been proposed for all these complexes. The synthesized complexes were also screened for their antibacterial activities against five bacterial pathogens and the results obtained are discussed.

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