

## SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF Cu(II), Co(II) AND Ni(II) COMPLEXES WITH SCHIFF BASE DERIVED FROM N- AMINO RHODANINE AND SALICYLALDEHYDE

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### ABSTRACT

The Schiff base ligand was prepared from the N-amino rhodanine and salicylaldehyde. Ligand are characterized by elemental analysis, IR, mass, <sup>1</sup>H NMR and electronic spectra. The Cu(II), Co(II) and Ni(II) complexes of the ligand were prepared and characterized by the analytical and spectroscopic methods. In addition, the magnetic susceptibility and molar conductance measurements have been made. Octahedral geometrical structure was proposed for Cu(II), Co(III) and Ni(II). The free ligand and their metal complexes were screened for their antimicrobial activities. The results indicated that the ligands do not have any activity, whereas their complexes showed more activity against the same organisms under identical experimental conditions.

**Keywords:** Synthesis, Characterization, Biological activity, Transition Metal, Complexes, Rhodanine

### INTRODUCTION

Schiff bases are the compounds with a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group, not hydrogen<sup>1</sup>. They are important class of ligands due to their synthetic flexibility, their selectivity and sensitivity towards the central metal atom, structural similarities with natural biological substances and also due to the presence of imine group (N=CH-)<sup>2</sup>. Interest in these ligands has been driven, that they have been studied for a considerable period of time for their biological properties.

Rhodanine derivatives are known to possess biological activities such as anticonvulsant, antibacterial, antiviral and antidiabetic. Many researchers reported rhodanine derivatives as hepatitis C virus (HCV) protease inhibitor. On the other hand, it is known that rhodanine plays an important role in biological reactions, i.e., in the inhibition of mycobacterium tuberculosis. Chemical properties of rhodanine and its derivatives are of interest due to coordination capacity and their use as metal extracting agents<sup>3</sup>. Many transition elements have been extensively investigated with regard to their potential quality as anticancer agents.

### MATERIALS AND METHODS

#### Materials and General Procedures

All the chemicals were procured commercially and were used without further purification. The IR spectra of the compounds were recorded on a Nicolet FT-IR 560 Magna spectrometer using KBr. The Bruker 300 MHz NMR spectrometer was used to obtain the <sup>1</sup>H NMR spectrum of the ligand. Elemental analysis was obtained from vario-micro cube elemental analyzer. The electronic spectra of the complexes were recorded on a UV-2601. EPR spectra were recorded on an EPR spectrometer (JEOL FE - 1X) operating in the X-band frequencies with a modulation frequency of 100 kHz. The magnetic field was scanned from 2200 to 4200 G, with a scan speed of 250 Gmin<sup>-1</sup>. 100mg of powdered metal complex was taken in a quartz tube for EPR measurements.

#### Synthesis of the Schiff base ligand

Hot solution (~ 55°C) of salicylaldehyde (4.9 g, 40 mmol) was mixed with hot solution (5.94 g, 40 mmol) of 3-aminorhodanine (5.94g, 40 mmol), in 100 ml of hot mixture (~ 55°C) of ethanol-chloroform (1:1). The resulting mixture was left under reflux for an hour and the formed solid product was separated by filtration, purified by

crystallization from ethanol-chloroform mixture, washed with diethylether and dried in a vacuum desiccator over anhydrous calcium chloride. The yellow product is produced in 76.6% yield.

#### Synthesis of the Metal Complexes

The complexes obtain on mixing the warm solution (~ 50°C) of the appropriate metal chloride or nitrate (3 mmol) in an ethanol water mixture (1:1, 10ml) with a warm suspension (~ 50°C) of the Schiff base. The resulting mixture was stirred under reflux for two hours. The solid complexes did not separate on standing but when a few drops of aqueous ammonia solution (1:10) were slowly added with stirring until the pH reached 4-5, the solid metal chelates precipitated. In case of the preparation of all the complexes, the precipitates were collected by filtration and washed with a 1:1 ethanol-water mixture and diethylether and dried over anhydrous CaCl<sub>2</sub>.

### RESULT AND DISCUSSION

#### Schiff Bases Characterization

The Schiff bases are subjected to elemental analyses. The results of elemental analyses are tabulated in the table-1. The results obtained are in good agreement with those calculated for the suggested empirical formulae (C<sub>5</sub>H<sub>4</sub>NSO). The formulae of these Schiff bases are also confirmed by IR and <sup>1</sup>H NMR spectra, which will be discussed later with metal complexes<sup>4</sup>.

#### Mass Spectra of the Ligands

Mass spectral data of the ligands indicated by the peaks corresponding to their molecular mass. The presence of mass spectral peak at 251 confirms the formulation of the ligand. A set of peaks observed in the range 78, 85, 91, 104, 118 and 133 are assigned to various fragments, confirms the stability of the ligand<sup>5</sup>. The interpretation of the ligands fragmentation is shown in figure 1.

The isolated complexes of Cu(II), Co(II) and Ni(II) with the Schiff base ligand were subjected to elemental analyses (C, H, N, S and metal content). The results of elemental analyses are shown in the table 1 below.

#### <sup>1</sup>H NMR:

The <sup>1</sup>H NMR spectra of the ligands in DMSO solutions with assignments are collected in Table (2). The <sup>1</sup>H NMR spectra of the

free ligands showed the azomethane proton at 8.1 and 8.9. The

phenolic OH proton has a signal at 10.7 ppm (fig-2).

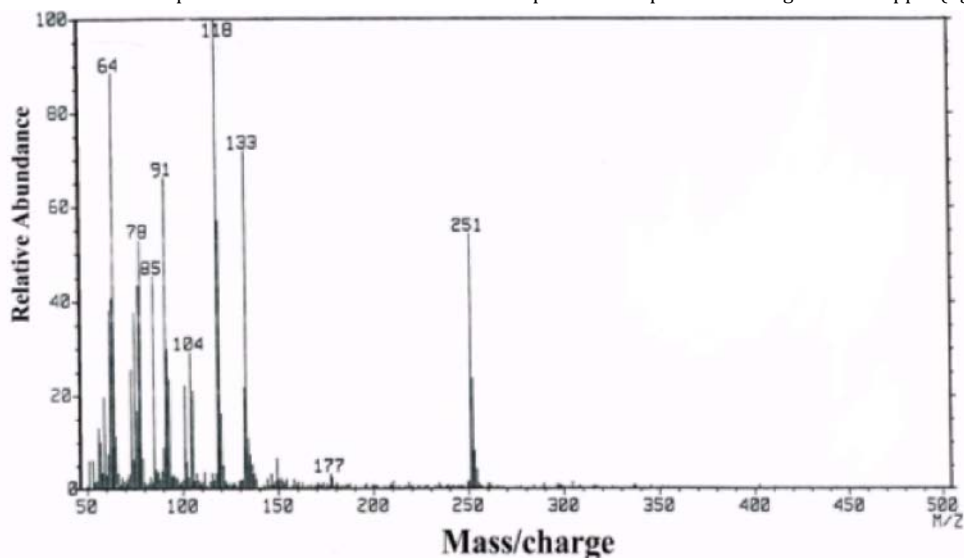


Fig. 1: Mass spectra of the ligand

Table 1: Result of elemental analysis for ligand and its complex:

Ligands and Their Complexes	M:L	Colour	Analysis, (Found)					% Molar %M	Magnetic Conductance $\mu\text{m} (\Omega^{-1}\text{cm}^2 \text{mol}^{-1})$	Magnetic Moment BM
			%C	%H	%N	%S	%Cl			
Ligand	1:1	Yellow	48.14	2.46	11.19	25.18	-	-	-	-
[Cu(L)Cl(H <sub>2</sub> O) <sub>2</sub> ]	1:1	Greenish	23.89	4.39	5.68	13.32	7.49	13.42	13.54	1.82
[Co(L) Cl(H <sub>2</sub> O) <sub>2</sub> ]	1:1	Brown	28.58	3.42	6.79	15.25	8.58	14.10	12.00	4.87
[Ni(L) <sub>2</sub> ]	1:2	yellow	36.77	3.78	8.69	19.56	-	8.85	13.80	3.18

Table 2: <sup>1</sup>HNMR data for the ligands L1 and HL2 in DMSO solution ( $\delta$  ppm)

Ligand	Phenolic OH	$\delta$ CH <sub>2</sub> (of the ring)	NH (Indole)	CH (Indole)	CH=N (azomethine)	Aromatic protons
L	10.7	4.3	-	-	8.9	6.9-7.8

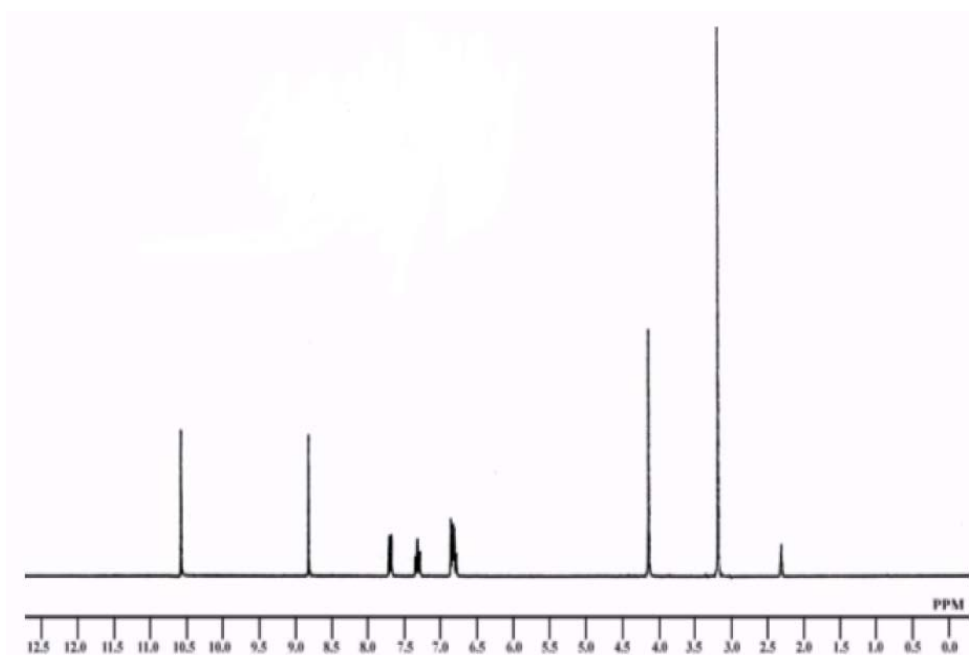


Fig. 2: <sup>1</sup>HNMR spectra of ligand

### Infrared Spectra

The significant IR bands of the ligands and their metal complexes and their assignments are given in Table (3). The spectra of all studied complexes show a broad band in the range 3157-3500 cm<sup>-1</sup> assigned to ν(OH), suggesting the presence of water molecules. The bands due to ν(CS) and ν(CS) + ν(CN) at 673-889 cm<sup>-1</sup> and 1023-1049 cm<sup>-1</sup> respectively, in the free ligand are either shifted, split, or

weakened in all of their complexes indicating the participation of the S atom in complex formation. Moreover, coordination of the azomethine N to the metal ion is suggested by the shift of the ν(C=N) band. The N-bonding is also indicated by the shift of the strong bands at 1234 and 1272 cm<sup>-1</sup> in case of ligand and too high or lower frequencies in their complexes. The strong phenolic ν(C-O) band at 1202 cm<sup>-1</sup> in the free ligand is shifted towards lower wave numbers in its complexes.

Table 3: IR Spectra (cm<sup>-1</sup>) of the ligand and their metal complexes

Compounds	ν(OH)(H <sub>2</sub> O)	ν(C=O)	ν(C=N)	ν(CNC)	ν(C=S)	ν(CS)+ν(CN)	ν(C-O) <sub>phenolic</sub>
L	-	1716	1597	-	767	-	-
[Cu(L) Cl(H <sub>2</sub> O) <sub>2</sub> ]	3417	1730	1602	1199	811	1022	1151
[Co(L) Cl(H <sub>2</sub> O) <sub>2</sub> ]	3426	1728	1599	1293	876	1027	1162
[Ni(L) <sub>2</sub> ]	3335	1767	1595	1240	875	1034	1139

### Molar Conductivity

The molar conductivity values of ligand and their complexes in DMF solutions confirmed the non-electrolytic nature of these complexes<sup>6</sup>.

### Electronic Spectra and Magnetic Susceptibility

The observed magnetic moment of the Co (II) complexes fall in the range 4.7-4.87 BM. The electronic spectra of these complexes display two electronic spectral bands at 525 nm and 420-445 nm, assignable to <sup>4</sup>T<sub>1</sub> g (F) → <sup>4</sup>A<sub>2</sub> g (F) and <sup>4</sup>T<sub>1</sub> g (F) → <sup>4</sup>T<sub>1</sub> g (p)

transitions, respectively, characteristic of octahedral geometry<sup>7</sup>. The Ni (II) complex shows electronic spectral band at 410 nm attributable to <sup>3</sup>A g (F) → <sup>3</sup>T g (F) transition. This complex has magnetic moment value of 3.18 BM which indicates that it is of high-spin octahedral type. The Cu (II) complex is a non-electrolyte with a magnetic moment of 1.82 BM. The magnetic moment of this complex at room temperature, given in Table (1), lie in the range normally observed for octahedral Cu (II) complexes corresponding to one unpaired electron<sup>8</sup>. This indicates that this complex is monomeric in nature and the absence of metal-metal interaction<sup>9-11</sup>.

Table 4: Electronic Absorption Spectral Bands of the Ligand and their Complexes:

Ligands and their Complexes	Intra ligand& Transfer bands (nm)	d-d Bands (nm)
Ligand	215,290,350	-
[Cu(L) Cl(H <sub>2</sub> O) <sub>2</sub> ]	210,230,345	420,455
[Co(L) Cl(H <sub>2</sub> O) <sub>2</sub> ]	210,230,345	420
[Ni(L) <sub>2</sub> ]	210,220,310,330,390	410

### Biological Activity

The antibacterial activities of both ligand and its metal complexes were studied by usual cup-plate agar diffusion method<sup>12-14</sup>. The bacterial species used in the screening were *Klebsiella pneumonia*, *Escherichia coli*, (gram negative) and *Staphylococcus aureus* *Bacillus subtilis* (gram-positive). Stock cultures of the test bacterial species were maintained on *Nutrient Agar media* by sub culturing on petri dishes. The media were prepared by adding the components as per manufacturer's instructions and sterilized in the autoclave at 121°C temperature and 15 lbs pressure for 15 minutes and then cooled to 45-60 °C. 20 mL of each medium was poured in a Petri dish and allowed to solidify. After solidification, Petri plates with media were

spread with 1.0 mL of bacterial suspension, which is prepared in sterile distilled water. The wells were bored with cork borer and the agar plugs were removed. 100 µl of the compound reconstituted in DMF (Dimethyl formamide) in concentrations of 1.0 mg/mL was added to the agar wells. DMF was used as a negative control and antibiotics such as ampicillin and tetracycline were used as positive control standards. The plates were incubated at 37°C for 24 hours and then the plates were observed for the growth inhibition zones. The presence of clear zones around the wells indicated that the compound is active<sup>15-17</sup>. The diameter of the zone of inhibition was calculated in millimeters. The well diameter was deducted from the zone diameter to get the actual zone of the inhibition diameter and the values have been tabulated.

Table 3: Antibacterial activity of ligands and its complexes

Compound	<i>K. pneumoniae</i>	<i>E. coli</i>	<i>B. subtilis</i>	<i>S. aureus</i>
Ligand (L)	-	-	-	-
[Cu(L) Cl(H <sub>2</sub> O) <sub>2</sub> ]	9	12	11	10
[Co(L) Cl(H <sub>2</sub> O) <sub>2</sub> ]	6	-	-	-
[Ni(L) <sub>2</sub> ]	8	11	9	11
Ampicillin	43	40	43	42
Tetracycline	32	33	30	32

### CONCLUSION

Complex formation reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor

groups and possible electron delocalization over the whole chelate ring. Such chelation could also enhance the lipophilic character of the central metal atom, which subsequently favours its permeation through the lipid layer of the cell membrane<sup>19-22</sup>. We conclude that

the complexes show more anti-bacterial activity and the ligands do not have any activity against some organisms under identical experimental conditions<sup>23-25</sup>.

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#### Abbreviations

<sup>o</sup>C = centigrade

% = percentage

nm = nano meter

mmol = milli molar

IR= Infrared

<sup>1</sup>H NMR= proton nuclear magnetic resonance

KBr= potassium bromide

DMF = Dimethyl formamide

DMSO = Dimethyl sulfoxide

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