

(RESEARCH ARTICLE)



## Preparation, characterization and biological studies of azo dye Schiff base metal complexes derived from 2-aminothiophenol

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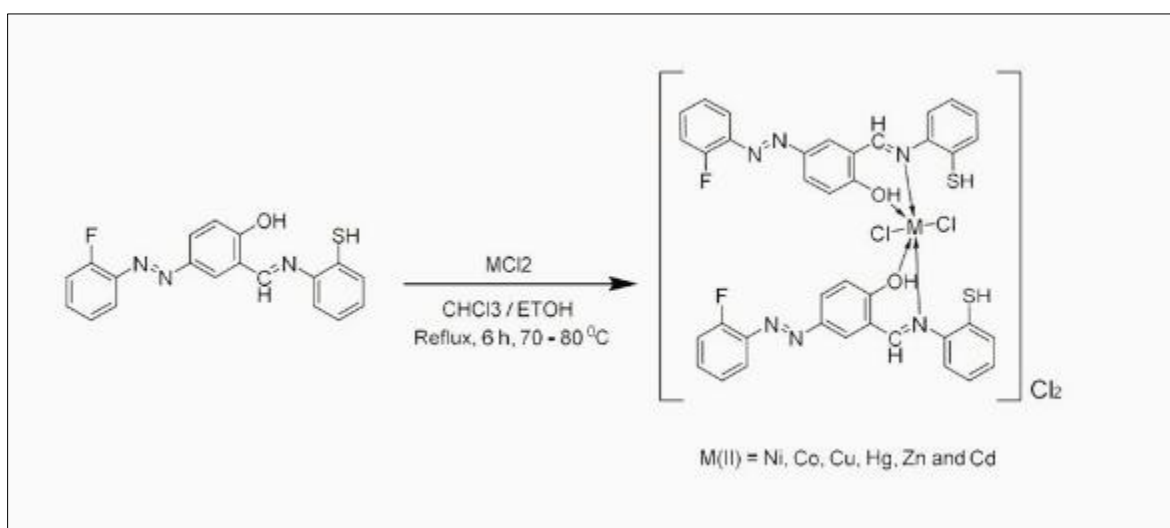
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### Abstract

The direct reaction of (E)-4-((2-fluorophenyl)diazanyl)-2-hydroxybenzaldehyde with 2-Aminothiophenol generated a azo dye ligand and its metal (II) complexes with the formula  $ML_2Cl_2$ , where M= Co, Ni, Cu, Zn, Cd, and Hg. Analytical, Infrared, <sup>1</sup>HNMR, <sup>13</sup>CNMR, and Mass spectra The Schiff base azo dye ligands and their metal complexes have been tested for their antimicrobial activity by MIC method.

**Keywords:** 2-Aminothiophenol, Schiff base; Metal complexes; Spectral studies, Biological activity; Molar conductance; Magnetic measurements and (E)-4-((2-fluorophenyl)-2-hydroxybenzaldehyde.

### Graphical abstract



### 1. Introduction

Metal complexes involving Schiff base ligands constitute a leading active and fertilize research area [1-3]. The literature is very rich in the published work on Schiff base complexes, and many studies reported wide-ranging applications of Schiff base metal complexes in many scientific areas particularly, the pharmaceutical and medicinal field [4-7]. The

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biological significance of the Schiff base complexes is of no doubt due to the presence of the azomethine group and the ability to design metal complexes containing model systems that able to mimic biological systems [8-10].

Investigating symmetrical and asymmetrical systems of Schiff base ligands for chelation with metal ions and assessing their biological application represent an important research issue in coordination chemistry[3,11-14]. The interest in designing and preparation of symmetrical and unsymmetrical Schiff bases derived from the ease of preparation using different molar ratio condensation reactions between different carbonyl and amine compounds. The interest in studying this type of compound is generated from their prospective applications in biologically active drugs and as models in bioinorganic chemistry [12,15,16]. Moreover, the attention for preparing metal complexes with unsymmetrical Schiff base ligands is because most of the coordinated ligands in natural systems around the central metal atom are unsymmetrical [11]. Unsymmetrical Schiff base ligands have an advantage over their symmetrical counterparts in the elucidation of compounds structure and prediction of geometry in the bioinorganic system [10,17].

The unsymmetrical Schiff base ligands containing soft-hard donor atoms (N, O, and S) have been reported to increase the chelation ability forming highly stable versatile complexes with different structures and having different applications in bioinorganic, medicinal, optical, and thermal fields [1,18-20]. In view of the facts mentioned above, we are encouraged and considered interesting to design new Schiff base ligand compounds in a trial to develop chemical compounds with different scaffolds in one structure, which may lead to interesting biologically active agents. Therefore, we hereby report to synthesis and characterization of azo dye of 2-Aminothiophenol and its synthesizing complexes and as well as screening their biological activity.

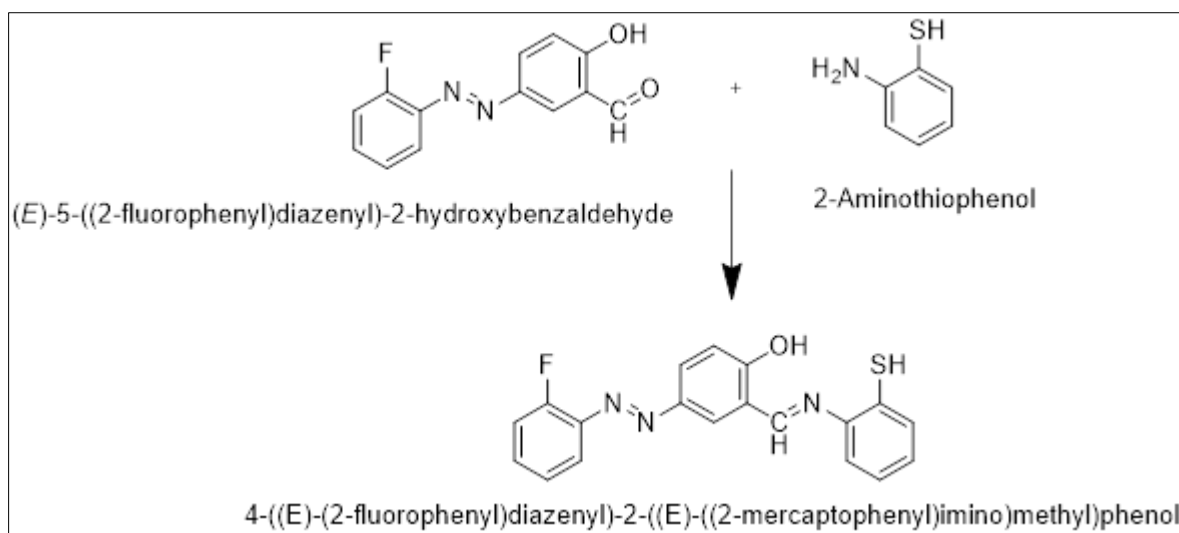
## 2. Material and methods

### 2.1. Experimental

All of the synthesis was conducted out with analytical reagent grade chemicals of the utmost purity commercially available. The basic component, (E)-5-((2-fluorophenyl)diazenyl)-2-hydroxybenzaldehyde has been synthesized using a method reported in the literature. The metal and chloride content were determined using well-established techniques.[21, 22]

### 2.2. Synthesis of Schiff base ligand 4-((E)-(2-fluorophenyl) diazenyl)-2-((E)-((2- mercaptophenyl) imino) methyl)phenol (L4)

A mixture of (E)-5-((2-fluorophenyl)diazenyl)-2-hydroxybenzaldehyde (0.1 mol) and 2-Aminothiophenol (0.1 mol) in ethanol (30 ml) were refluxed on water bath for about 5-8 hrs. in presence of few drops of glacial acetic acid. The product which was separated out as crystalline solid on cooling was collected and recrystallized from ethanol.



**Figure 1** Synthesis of Ligand (L4)

### 2.3. Preparation of metal complexes:

The Complexes were prepared by adding appropriate amount of the ethanolic metal salt (10 ml), namely, Co (II), Ni (II) and Cu (II) hydrated metal chloride and anhydrous Zn (II), Cd (II) and Hg (II) chloride and (4 mmol) to an ethanol/chloroform (1:1 v/v) solution containing 8 mmol of the ligand (LH) and the mixture was refluxed for 6 hr. The obtained solution was left at room temperature and the resulting precipitates were filtered off, washed with ethanol and then recrystallized from ethanol / chloroform (1:3 v/v) solvent mixture.

### 2.4. Physical data

Using traditional KBr pellet techniques, the IR spectra of the ligand and its metal complexes were collected On PerkinElmer IR E S Version 10.6.1 FTIR spectrophotometer in the (3800-650)  $\text{cm}^{-1}$  range, A dip-type conductivity cell with a platinum electrode was used to test molar conductivity on an Elico CM-180 Conductivity Bridge in dimethylformamide (10-3 M) solvent. Magnetic susceptibility studies were done on a Gouy balance at room temperature utilizing Hg [Co(NCS)<sub>4</sub>] as the calibrant.

## 3. Results and Discussion

### 3.1. Infrared spectral analysis of azo dyes

The IR spectra provided valuable information regarding the nature of functional group attached to the metal atom. The infrared spectral data of the Schiff base ligand show a medium intensity absorption band at  $3444 \text{ cm}^{-1}$  due to  $\nu(\text{O-H})$  stretching and Further the appearance sharp band at  $1483 \text{ cm}^{-1}$  indicate the presence of  $\nu(\text{N=N})$  stretching. Moreover, the appearance medium intensity band at  $1612 \text{ cm}^{-1}$  is, due to  $\nu(\text{C=N})$  a vibration of azomethine linkage. However, A broad absorption band is appeared at  $3436 \text{ cm}^{-1}$  in the IR spectra of the complexes of cobalt(II) chloride, nickel(II) chloride, and copper(II) chloride due to the  $\nu(\text{O-H})$  stretching of associated water molecule. The  $\nu(\text{C=N})$  detected at  $1613 \text{ cm}^{-1}$  remains in same place in the case of metal complexes. Finally, the IR spectra of complexes exhibited new non-ligand bands in the range of  $546\text{--}511 \text{ cm}^{-1}$ ,  $493\text{--}419 \text{ cm}^{-1}$  and  $391\text{--}342 \text{ cm}^{-1}$  assigned as  $\nu(\text{M-O})$ ,  $\nu(\text{M-N})$  and  $\nu(\text{M-Cl})$  stretching vibrations, This result makes it clear that both "N" atoms of the  $\nu(\text{C=N})$  linkage are coordinated to a metal atom in chloride complexes [23-25].

**Table 1** Physical properties and elemental analysis of azo ligand (L4) and their metal complexes, Including molar conductance and magnetic susceptibility

Compound	Mol. Wt	M.P $^{\circ}\text{C}$	Yield %	Formula	Formula Found (Caled) %								$\mu_{\text{eff}}$ (B.M)	Conductivity S.mol <sup>-1</sup> . cm <sup>2</sup>
					C	H	N	O	F	Cl	S	M		
L4	351.40	178	82	C <sub>19</sub> H <sub>14</sub> FN <sub>3</sub> OS	64.94	4.02	11.96	4.55	5.41	----	----	----	----	----
HAL4 Co	832.63	228	80	CoC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	54.82	3.39	10.09	3.84	4.56	8.52	7.70	7.08	4.31	12.01
TAL4 Cu	837.24	246	75	CuC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	54.51	3.37	10.04	3.82	4.16	8.47	7.66	7.59	1.57	11.32
THL4 Ni	832.39	280	71	NiC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	54.83	3.39	10.10	3.84	4.56	8.52	7.70	7.05	3.02	16.31
TCL4 Zn	839.08	260	82	ZnC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	54.40	3.36	10.02	3.81	4.53	8.45	7.64	7.79	Dia	9.20
TTL4 Cd	886.11	294	62	CdC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	51.51	3.19	9.48	3.61	4.29	8.00	7.24	12.69	Dia	8.62
MHL4 Hg	974.29	210	71	HgC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	46.85	2.90	8.63	3.28	3.90	7.28	6.58	20.59	Dia	10.02

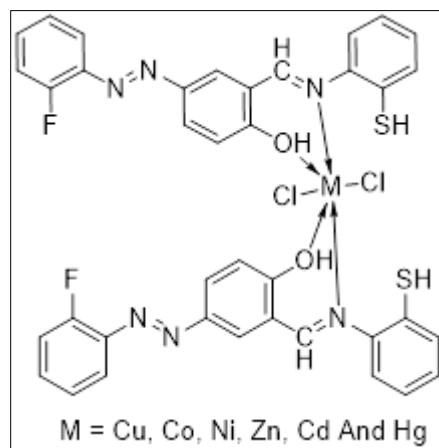
### 3.2. Magnetic measurements

The high spin magnetic moment value of Co (II) complex has a magnetic moment of 4.31 B.M in the high spin state which is in agreement with the reported value for octahedral Co (II) complexes [26]. The present Ni (II) complex showed a magnetic moment value of 3.02 B.M within the range 2.9–3.3 B.M for a high-spin Ni (II) complex depended on the magnitude of the orbital contribution [27] suggested an octahedral environment. The Cu (II) complex shows a magnetic moment value of 1.57 B.M monomeric and consistent with a distorted octahedral geometry. The Zn (II), Cd (II) and

Hg(II) are diamagnetic and according to the empirical formulae of complexes, an octahedral geometry was proposed [28]. Based on the above results, we can deduce the probable structures of the complexes as shown in Fig. 4.

### 3.3. Molar conductivity measurement

Molar conductance of the metal complexes was measured in DMSO as a solvent at room temperature. All chelate complexes prepared in this work showed conductivity values were ranged from 8.62 to 16.31 S.mol<sup>-1</sup>.cm<sup>2</sup> that were non-electrolyte and no conductive species [29]. According to these results, the structural formulas of this ligand and chelate complexes can be proposed as in



**Figure 2** The proposed Structure of Complexes

**Table 2** Characteristic IR absorption bands of the ligand (L4) and its metal complexes in cm<sup>-1</sup> units

S.No	Chemical formula	$\nu$ (O-H)	$\nu$ (C=N)	$\nu$ (N=N)	$\nu$ (M-N)	$\nu$ (M-O)	$\nu$ (M-Cl)
01	L4= C <sub>19</sub> H <sub>14</sub> FN <sub>3</sub> OS	3444	1612	1483	----	----	----
02	CuC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	3449	1606	1492	493	546	391
03	CoC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	3431	1604	1483	451	531	360
04	NiC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	3436	1613	1483	419	523	342
05	ZnC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	3428	1600	1480	485	511	363
06	CdC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	3422	1592	1472	471	532	361
07	HgC <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	3418	1587	1476	490	538	350

### 3.4. 1 H-NMR spectrum of azo dye

The <sup>1</sup>H spectra analysis was carried out for some prepared Schiff bases and their respective metal complexes due to the high cost of analysis and the inconvenience. In the <sup>1</sup>H NMR spectra of the ligand, a sharp singlet appeared at 9.18 ppm due to the azomethine protons (CH=N) and confirmed its formation. The multiplets in  $\delta$  7.19–8.36 ppm. All of the protons were found to be in their expected regions and numbers.



its metal complexes showed that the complexes have higher growth inhibiting property than the azo dye Schiff base[30,31].

**Table 3** Antimicrobial activity

Comp No	Pathogenic bacteria						Pathogenic fungi					
	<i>S. aureus</i>			<i>E. coli</i>			<i>A. Nizer</i>			<i>A. flavus</i>		
	25	50	100	25	50	100	25	50	100	25	50	100
L4	6	8	10	6	11	14	9	8	11	7	11	12
HAL4 Co	6	7	11	5	10	13	8	10	11	8	10	11
TAL4 Cu	6	8	11	6	9	10	9	11	12	9	12	10
THL4 Ni	5	8	10	7	9	12	8	10	13	10	11	9
TCL4 Zn	5	7	9	5	8	12	9	8	11	8	10	11
MHL4 Hg	7	9	13	9	13	15	10	11	17	13	17	18
TTL4 Cd	7	9	14	9	12	16	11	12	16	12	16	19
Std II	08	10	15	10	14	18	12	13	18	14	18	23

Values represent Zone of Inhibition in mm

#### 4. Conclusion

The Schiff base ligand (L4) is a neutral bidentate ligand that's been synthesized. The metal ion is coordinated by the azomethine group's amide oxygen and nitrogen. Analytical data, spectral data, molar conductance and magnetic studies all support the metal's bonding to the ligand. The antimicrobial activity results displayed that Cd(II) and Hg(II) complexes exhibit higher activity compared to Co(II), Ni(II) and Cu(II) complexes. We established octahedral molecular arrangements for Cobalt (II), Nickel(II), and Copper(II), Zinc(II), Cadmium(II), and Mercury(II) complexes.

#### Compliance with ethical standards

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##### Disclosure of conflict of interest

The authors declare that they have no conflict of interest.

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