



## Synthesis and characterization of Fe(II) and Co(II) complexes of Schiff base derived from 3,3'-diaminobenzidine and salicylaldehyde

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### ABSTRACT

Schiff base ligand derived from 3,3'-diaminobenzidine and salicylaldehyde and its divalent metal complexes (Fe(II) and Co(II)) were synthesized and characterized by using elemental analysis, thermal analyses, infrared and electronic spectral studies. Elemental and spectral data show that complexes are formed with 2:1 [M:L] molar ratio. Tetradentate Schiff base ligand with 2N2O2 donor atoms coordinates to transition metal to form the corresponding complexes ( $M_2L$ ). Antibacterial and antifungal activity of the synthesized ligand and its complexes was tested against selected pathogenic bacteria and fungi. The ligand and its complexes possess microorganism activity, the complexes showed higher microorganism activity than that of the free ligand.

**Keywords:** Synthesis and Characterization, Schiff base, 3,3'-diaminobenzidine and salicylaldehyde.

### INTRODUCTION

The complexes with salen ligands derived from the condensation of salicylaldehyde with diamine are widely studied. Schiff bases have been playing an important role in the development of coordination chemistry. The Schiff base metal complexes were studied extensively due to their attractive physical properties and wide applications in numerous scientific areas [1-3]. The mechanism of imine formation begins as nucleophilic addition to the carbonyl group, in this case the nucleophilic is the amine which reacts with the aldehyde or ketone to give an imines[4]. Iron(II) forms complexes with a variety of ligands [5]. As expected, in view of its smaller cationic charge, these are usually less stable than those of Fe(III) but the antipathy to N-donor ligands is less marked. Thus  $[Fe(NH_3)_6]^{2+}$  is known whereas the Fe(III) analogue is not; also there are fewer Fe(II) complexes with O-donor ligands such as acac and oxalate, and they are less stable than those of Fe(III). Many biologically applications of the Schiff bases have been reported in the literature possessing, antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant, antitumor and anti HIV activities [6-9]. Metal(II) complexes of the Schiff base derived from vanillin and DL- $\alpha$ -aminobutyric acid were also found to exhibit higher antibacterial activity compared to the free Schiff bases [10].

### EXPERIMENTAL SECTION

All materials and reagents used in this study were laboratory pure chemicals. They includes 3,3'-diaminobenzidine and salicylaldehyde. The solvents and metal salts are used as they received from the supplier without further purification. The synthesis of Schiff-base ligand and its complexes are based on the methods reported previously [11].

### Synthesis of the Schiff base ligand

3,3'-diaminobenzidine (1mole) was stirred with salicylaldehyde (4 moles) in 100 cm<sup>3</sup> dry ethanol for 1h. A yellow solid crude product is filtered off, wash several times with small portions of ethanol and finally with diethyl ether. Orange plate-shaped obtained and dried in desiccated over silica gel.

### Synthesis of Fe(II) Complex

The ligand (1 mole) was dissolved in (100 cm<sup>3</sup>) absolute methanol and added to another methanolic solution (50 cm<sup>3</sup>) of ferrous chloride salts (FeCl<sub>2</sub>.2H<sub>2</sub>O) (2 mole). The mixture was stirred at room temperature for one day. The green precipitate product is collected by filtration and washed several times with methanol and dried in desiccated over silica gel.

### Synthesis of Co(II) Complex

The ligand (1 mole) was dissolved in (100 cm<sup>3</sup>) absolute methanol and added to another methanolic solution (50 cm<sup>3</sup>) of cobaltous chloride salts (CoCl<sub>2</sub>.6H<sub>2</sub>O)(2 mole). The mixture was stirred at room temperature for one day. The reddish brown precipitate product is collected by filtration and washed several times with methanol and dried in desiccated over silica gel.

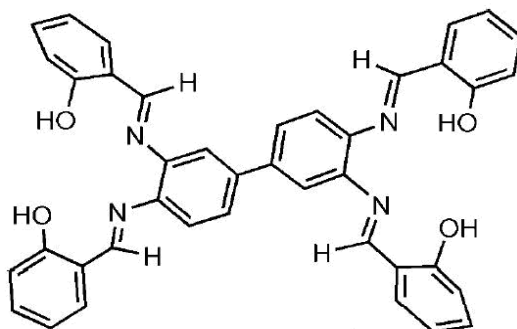
### Measurements

The Schiff base ligand and its complexes under investigation were subjected to (C, H and N) elemental analysis which performed using 2400 elemental analyzer at the Micro-Analytical Center, Faculty of Science, Assiut University, Assiut, Egypt. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the Schiff base complexes were carried out using Shimadzu DTH-60H thermal analysis at thermal analysis unit of central laboratory of Assiut University (Egypt). The melting point of ligand and its complexes were measured in capillary tubes Philip Haris, Shenston-England serial NO.B/A-211, at Chemistry Department, Faculty of Science, University of Benghazi. The IR spectra of the Schiff base ligand and its complexes were recorded as KBr discs on a Shimadzu IR400-91527, at the Faculty of Pharmacy, Assiut University, Assiut, Egypt. The electronic spectra of the Schiff base ligand and its complexes were measured by the applying dimethylformamide (DMF) as solvent using UV-Vis-NIR 3101pc Shimadzu at Chemistry Department, Faculty of Science University of Benghazi. The strains of bacteria and fungi were used are *Escherichia coli*, *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Micrococcus spp.*, *Pseudomonas Aeruginos*, *Klebsiella pneumonia*, *Salmonella typhimurium*, *Aspragillus niger* and *Candida albicans*. They were grown overnight at 37°C in Mueller-Hinton Broth at pH 7.4 [12-13], this study was done in faculty of pharmacy, microbiology Department, Zagazig university, Egypt. Yeast and mould extract agar was used for testing antifungal activity and the above method as for bacteria were adopted [14]. Sensitivity test of the ligand and its complexes on the bacteria and fungi were compared with sensitivity to common antibiotics (Cefotaxime, Amoxicillin, Nystatin and Amphotericin B). The antibiotics were placed on the surface of the culture medium which contains the same bacteria and fungi used in this study.

## RESULTS AND DISCUSSION

The Schiff base ligand under investigation was formed by the condensation of 3,3'-diaminobenzidine and salicylaldehyde (1: 4 molar ratio) and it was investigated by several techniques such as elemental analysis, Infrared and UV-Visible spectroscopy to identify its structure.

The structure of Schiff base ligand is shown below.

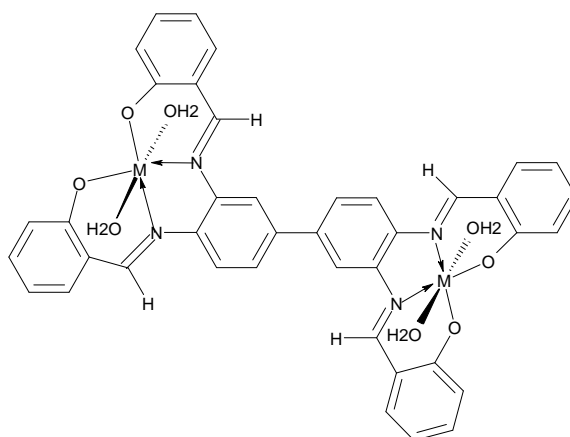


### Elemental analysis

Physical characteristics and elemental analysis of C, H and N of the compounds considered are listed in Table 1. The results of C, H and N percentage are in accordance with the composition suggested for the ligand and the complexes.

**Table 1: Elemental analysis and some physical properties of the ligand and its complexes**

Compound	Formula Weight	M.P./ °C	Microanalysis (Calc.)		
			%C	%H	%N
H <sub>4</sub> L	630	240	76.18 (75.25)	4.79 (4.76)	8.88 (8.40)
[Fe <sub>2</sub> L.4H <sub>2</sub> O]2H <sub>2</sub> O	737.69	230	53.0 (52.28)	3.52 (3.70)	7.59 (6.13)
[Co <sub>2</sub> L.4H <sub>2</sub> O]4H <sub>2</sub> O	743.86	225	54.06 (53.99)	4.73 (4.10)	6.36 (6.88)



The complex structures (M= Fe or Co)

### Thermal analysis

The thermal investigation results are tabulated in Table 2. Ligand [H<sub>4</sub>L] shows endothermic peak at 40 °C which is due to broken of hydrogen bonding, another endothermic peak appears at 90 °C may due to phase transformation. Endothermic peak observed at 231 °C, assigned to melting point. Exothermic peaks appeared at 255, 295, 345, 365 and 385 °C with weight loss 59.3 % (Calc. 59.4 %), corresponding to loss of 4 C<sub>6</sub>H<sub>5</sub>O group. The final exothermic peak observed at 435 °C with weight loss of 37.91 % (Calc. 37.21 %) may be due to loss of 2 CO<sub>2</sub>. The Fe<sub>2</sub>(L) complex shows endothermic peak at 65 °C, corresponding to loss of two hydrated water [15-16] with weight loss of 4.17 % (Calc. 3.92 %). Exothermic peaks at 325, 340 and 380 °C with weight loss of 50.0 % (Calc. 50.89 %) is due to loss of 4 C<sub>6</sub>H<sub>5</sub>O group. Melting point of the complex observed at 350 °C as endothermic peak. Oxidative thermal decomposition occurs at 500°C with endothermic peak leaving Fe<sub>2</sub>O<sub>3</sub> with weight loss of 44.79 % (Calc. 55.57 %). Co<sub>2</sub>(L) complex shows endothermic peak at 70 °C with weight loss of 7.92 % (Calc. 8.11 %) corresponding to loss of four hydrated water molecules, another endothermic peak appeared at 180 °C with weight loss of 8.91 % (Calc. 8.82 %) is attributed to the lost of four coordinated water [15-16]. Endothermic peak observed at 310 °C, may be due to melting point. Elimination of 4 C<sub>6</sub>H<sub>5</sub>O group occurred at 240, 280, 360 and 425 °C with exothermic peaks accompanied with weight loss of 49.5 % (Calc. 50.0 %). Oxidative thermal decomposition occurs at 450 °C with exothermic peak leaving Co<sub>2</sub>O<sub>3</sub> weight loss of 44.55 % (Calc. 44.62 %).

**Table (2): Thermal analysis of complexes**

complexes	Water of hydration weight loss %	No. of water molec.	Water of coord. weigh loss	No. of water coord.	4C <sub>6</sub> H <sub>5</sub> O groups weight loss	Temp. °C	M O weight loss	Temp. °C
[Fe <sub>2</sub> L.4H <sub>2</sub> O]2H <sub>2</sub> O	(4.17) (3.92)	2	-	4	(50.0) (50.89)	310- 380	(44.79) (55.57)	500
[Co <sub>2</sub> L.4H <sub>2</sub> O]4H <sub>2</sub> O	(7.92) (8.11)	4	(8.91) (8.82)	4	(49.5) (50.0)	240- 425	(44.55) (44.62)	450

### The infrared study

The important IR absorption frequencies of the prepared Schiff base complexes are given in Table (3). The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation. The band at  $1603\text{ cm}^{-1}$  is characteristic of the azomethine presents in the free ligand. The lowering in this frequency region ( $1600\text{--}1590\text{ cm}^{-1}$ ), observed in all the complexes, indicates the involvement of the azomethine in the coordination to the metal(II) ion [17-18]. The complexation process takes place through two nitrogen atoms of the imine groups and the two hydroxyl group of the salicylaldehyde, i.e., the ligand is tetradentate. Abroad bands in the range  $3510\text{--}3220$  and  $3250\text{--}3020\text{ cm}^{-1}$  confirms the presence of water molecules [19]. Characteristic absorption bands for (M-N) and (M-O) of the complexes appear respectively in the region of  $545\text{--}510\text{ cm}^{-1}$  and  $590\text{--}554\text{ cm}^{-1}$ . The C-OH stretching modes of the ligand appears at  $1265\text{ cm}^{-1}$ , these bands shift to higher or lower wave numbers as a result of coordination through the hydroxyl oxygen atoms.

Table (3) Infrared band assignments ( $\text{cm}^{-1}$ ) of the ligand and its complexes

Compound	$\nu(\text{OH}) / \text{H}_2\text{O} / \text{H-bond}$	$\nu(\text{C}=\text{N})$	$\nu(\text{C-OH}) / \nu(\text{C-O})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{Ar})$
$\text{H}_4\text{L}$	3460 3520 – 2980 2970 - 2350	1603	1265	–	–	1556, 820 1545, 720
$[\text{Fe}_2\text{L}.4\text{H}_2\text{O}]2\text{H}_2\text{O}$	3435 3525 – 3050 3040 - 2560	1600	1182	535	580	1556, 805 1545, 742
$[\text{Co}_2\text{L}.4\text{H}_2\text{O}]4\text{H}_2\text{O}$	3460 – 3220 3210 - 3050	1592	1186	530	585	1555, 801 1540, 748

### The electronic spectra

The electronic spectra of Schiff base complexes are performed in DMF solvent and the band assignment are shown in Table (4). The electronic spectrum depends on the energy of metal d orbital, degeneracy and the number of electrons distributed. These features are in turn controlled by the oxidation state of the metal, number and kind of the ligand and the geometry of the complex. Only one broad band is observed at ( $2020\text{ cm}^{-1}$ ) in the electronic spectrum of the Fe(II) complex assigned to  ${}^5\text{T}_2\text{g} \rightarrow {}^5\text{E}_\text{g}$  transition which is in conformity with octahedral geometry [20-21]. The electronic spectrum of the Co(II) complex showed two spin allowed transition (designated as  $\nu_2$  and  $\nu_3$  absorption bands respectively) at ( $18382\text{ cm}^{-1}$  and  $19230\text{ cm}^{-1}$ )  ${}^4\text{T}_1\text{g}(\text{F}) \rightarrow {}^4\text{A}_2\text{g}(\text{F})$  and  ${}^4\text{T}_1\text{g}(\text{F}) \rightarrow {}^4\text{T}_1\text{g}(\text{P})$  transitions respectively, which clearly indicate that the complex has six coordination octahedral geometry[22].

Table (4): Electronic spectral data (nm,  $\text{cm}^{-1}$ ) of the complexes

ligand / complexes	$\lambda_{\text{max}}$	
	nm	$\text{cm}^{-1}$
$[\text{Fe}_2\text{L}.4\text{H}_2\text{O}]2\text{H}_2\text{O}$	495	20202
$[\text{Co}_2\text{L}.4\text{H}_2\text{O}]4\text{H}_2\text{O}$	520, 544	19230, 18382

Table 5: Microbiological activity against the Gram-positive bacteria and Gram-negative bacteria

Sample	Diameter (mm) of inhibition zones against the corresponding standard microorganisms						
	Gram-positive bacteria			Gram-negative bacteria			
	<i>Staphylococcus aureus</i> ATCC 6538	<i>Staphylococcus epidermidis</i> ATCC 12228	<i>Micrococcus spp.</i> ATCC 10240	<i>Pseudomonas aeruginosa</i> ATCC 9027	<i>Klebsiella pneumoniae</i> ATCC 27736	<i>salmonella typhimurium</i> ATCC 14028	<i>Escherichia coli</i> ATCC 10536
Ligand	17	16	16	20	21	17	19
$\text{Fe}_2\text{L}$	18	17	14	16	21	17	19
$\text{Co}_2\text{L}$	21	20	23	21	22	20	21
Cefotaxime (control)	34	33	43	30	37	36	35
Amoxicillin (control)	35	34	40	-	-	29	30
Nystatin (control)	-	-	-	-	-	-	-
Amphotericin B (control)	-	-	-	-	-	-	-
DMF (control)	-	-	-	-	-	-	-

**The antimicrobial activities**

The antimicrobial results are represented in Table (5,6), which is revealed the inhibition zones of bacteria and fungi growth of the Schiff base and its complexes Co(II) and Fe(II) against *Escherichia coli*, *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Micrococcus* spp., *Pseudomonas Aeruginos*, *Klebsiella pneumonia*, *Salmonella typhimurium*, *Aspragillus niger*, *Candida albicans*, *acidophilus*. The Sample (Co<sub>2</sub>L) complex showed more activity than the iron sample. Also the samples (Co<sub>2</sub>L) showed the more antifungal activity than iron sample. The samples (Co<sub>2</sub>L) has more antifungal activity than antibacterial activity and the microorganism activity of the complexes is higher than that of the free ligand

**Table 6: Microbiological activity against the Fungi**

Sample	Diameter (mm) of inhibition zones against the corresponding standard microorganisms	
	Fungi	
	<i>Aspragillus niger</i> ATCC 16404	<i>Candida albicans</i> ATCC 10231
Ligand	15	20
Fe <sub>2</sub> L	20	21
Co <sub>2</sub> L	23	21
Cefotaxime (control)	-	-
Amoxicillin (control)	-	-
Nystatin (control)	25	20
Amphotericin B (control)	16	22
DMF (control)	-	-

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