

## Synthesis, Spectroscopic Investigation and Biological Activity of 5-[(Z)-1-(2-hydroxyphenyl) ethylidene] amino -1, 2, 3, 4-tetrahydro-1, 4 -phthalazinedione Complexes

Abdsalam. M. A. Hamil<sup>1</sup>, Marei. M. El-ajaily<sup>2\*</sup>, Hamed.A.A Bogdadi<sup>3</sup>

1.Chemistry Department, Science Faculty, Sebha University, Sebha, Libya

2\*.Chemistry Department, Science Faculty, Benghazi University, Benghazi, Libya.

3. Botany Department, Science Faculty, Sebha University, Sebha, Libya.

### ABSTRACT

Two complexes of 5-[(Z)-1-(2-hydroxyphenyl) ethylidene] amino-1, 2, 3, 4-tetrahydro-1,4-phthalazinedione have been synthesized by the reaction of luminol and 2-hydroxyacetophenone with Co(II) and Ni(II) ions, and then some physical techniques were used to investigate the complexes, such as CHN elemental analyses, conductivity measurements, magnetic moments, infrared and electronic spectra. The CHN elemental analyses data showed the formation of 1:2 [M: L] ratio. The conductivity measurements exhibited the presence of non-electrolytic nature. The infrared spectral data revealed the coordination trends of the free compound towards the metal ions. The electronic spectral results showed the proper transitions of the free compound and its complexes. The geometrical structures of the complexes were confirmed according to the data which obtained from the electronic spectra. Also, the antibacterial activity of the free compound and its complexes were screened on some pathogenic bacteria, and showed the existence of an effect.

**KEYWORDS:** luminol, 2-hydroxyacetophenone, Complexes, Antibacterial Activity.

### INTRODUCTION

Acetophenone is the simplest aromatic ketone group, in industry; acetophenone is recovered as a by-product of the oxidation of ethylbenzene, which mainly gives ethylbenzenhydroperoxide for use in the production of propylene oxide. It is a raw material for the synthesis of some pharmaceuticals[1]. Ni (II) and Cu (II) ions tetradentate Schiff base complexes with N<sub>2</sub>O<sub>2</sub> and N<sub>2</sub>O donor sites have been synthesized and characterized[2,3]. Some chelates of Mn(II), Co(II), Cu(II) and Cr(III) ions with Schiff base formed from salicylaldehyde and thiourea have been prepared and investigated by several physicochemical techniques [4]. The Schiff base and its chelates showed a good effect for Mn(II) chelate,

moderate effect for Co(II) chelate and no effect for Cu(II) chelate on the pathogenic bacteria. The effect is increased with higher concentration.

The present investigation aims to synthesis, characterize and study the antibacterial activity of the Schiff base and its Co (II) and Ni (II) complexes on some pathogenic bacteria.

### EXPERIMENTAL Section

#### *Chemicals and techniques*

All chemicals and reagents used in this study were purchased from Aldrich. The melting point of the Schiff base was determined in capillary tube using griffin apparatus and the obtained m.p was

uncorrected. CHN elemental analyses of the Schiff base and its complexes under investigation have been carried out using 2400 elemental analyzer at micro Analytical center, Cairo university, Egypt. The infrared spectra of the Schiff base and its complexes were carried out by applying KBr disc technique using IF-25OPUS/IR (Bruker) spectrometer. Proton nuclear magnetic resonance spectrum of the Schiff base was achieved using Varian Gemini 200 MHz spectrometer. The used solvent was deuterated with DMSO ( $d^6$ -DMSO) and deuterium oxide ( $D_2O$ ). The spectrum was extended from 0 – 16 ppm using TMS as internal standard. The electronic spectra were measured by applying nujol mull as solvent using UV-Vis – NIR 3101 pc Shimadzu (Japan) using 1cm matched silica cells. The mass spectrum of Schiff base was carried out using a direct insertion probe at temperature 90 – 110°C.

#### Synthesis of 5 - [(Z) - 1 - (2 - hydroxyphenyl) ethylidene] amino - 1, 2, 3, 4 - tetrahydro-1, 4 - phthalazinedione

This compound was prepared by adding slowly with stirring 2-hydroxy-acetophenone (1.2 ml; 0.01mol.) to luminol (1.77 g; 0.01mmol) in 50 ml of absolute ethanol. The reaction mixture was refluxed for 2 hrs on hot plate at 80 °C, and then the pale brown crystals were isolated and recrystallized from ethanol. The obtained compound yields 75%.

#### Synthesis of complexes

Co(II) and Ni(II) complexes of 5-[(Z)-1-(2-hydroxyphenyl)ethylidene] amino-1,2,3,4-tetrahydro-1,4-phthalazinedione were prepared by mixing ethanol solution (50 mL) of 0.01 mole (3.46 gm) of the ligand ( $C_{16}H_{13}N_3O_3$ ) with the same solvent of the 0.01 mol (2.38 gm) of  $CoCl_2 \cdot 6H_2O$  and  $NiCl_2 \cdot 6H_2O$  (2.37 gm) and few drops of ammonia solution were added to adjust the pH until the complexes isolated. The reaction mixtures were refluxed for three hours, and then left to cool and filtered by suction. The precipitates were washed several times with chloroform, then ether. The complexes were dried in desiccator over anhydrous calcium chloride under vacuum. The yield was 79 and 75% respectively, some physical properties of the ligand and its complexes are listed in Table 1.

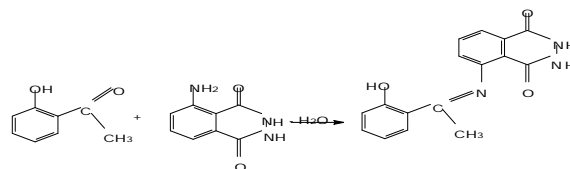
#### Bacterial assay

The Schiff base and its Co(II) complex under investigation were dissolved in 1,4-dioxane, and stock solutions of compounds were sterilized by filtration using a Millipore membrane filter of 0.2  $\mu m$  poresize[5,6]. Two gram positive (*Bacillus cereus* and *Staphylococcus aureus*) and one gram negative

(*Escherichia coli*) bacteria species were used in this study, antibacterial activity was determined by the well (6 mm diameter) diffusion method. Petri dishes containing Mueller Hinton agar medium were seeded with a 24 h culture of the bacterial species. Each well (6 mm diameter) was filled with 50  $\mu l$  of the solutions. Solvents were used as a negative control. Inoculated plates were incubated at 37 °C for 24 h[7]. The assessment of antibacterial activity was based on measurement of the diameter of inhibition formed around the well.

#### RESULTS AND DISCUSSION

The reaction between 2-hydroxyacetophenone and luminol undergoes one compound which is a Schiff base under investigation.



#### Elemental analysis and molar conductivity

The CHN elemental analysis data of the synthesized compounds are in a good agreement with the calculated values. The obtained data showed the formation of 1:2 [M: L] complexes. The molar conductance measurements of the complexes were dissolved in DMF solvent, and the obtained data revealed that the complexes are non electrolytes in nature[8], table.

#### Infrared spectra

The spectra of Co(II) and Ni(II) complexes displayed two bands 3414 and 3409  $cm^{-1}$  which could be assigned to the presence of water molecules in the complexes[9], table 2, Figures.1-3. Three bands in the range of 1621-1654  $cm^{-1}$  due to  $\nu_{H-C=N}$  vibration, the change of these bands to higher intensity in comparison with free compound (1654  $cm^{-1}$ ) indicating the involvement of the azomethine group in chelation via nitrogen atom[10]. New bands at 568, 618, 482 and 475  $cm^{-1}$  which are not exist in the free compound attributed to  $\nu_{M-O}$  and  $\nu_{M-N}$  vibrations[11,12]. The appearance of these bands supported the involvement of nitrogen and oxygen atoms in complexation.

#### Electronic spectra and magnetic moments

The electronic spectral data of the 5-[(Z)-1-(2-hydroxyphenyl) ethylidene] amino-1,2,3,4-tetrahydro-1,4-phthalazinedione exhibited two bands at 350 and 380 nm (28571 and 26315  $cm^{-1}$ ) due to  $\pi \rightarrow \pi^*$  (phenyl ring) and  $n \rightarrow \pi^*$  ( $-HC=N$ ) transition[13], meanwhile, the spectra of the

synthesized complexes showed several bands in the range of 355 – 385 nm ( $28169\text{--}25974\text{ cm}^{-1}$ ), Table 2, Figures.4-6.

These bands suggested that the complexes have octahedral structure[14]. The magnetic moment values revealed that both Co(II) and Ni(II) complexes have paramagnetic character.

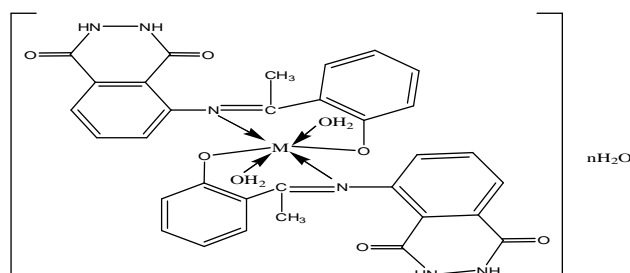
#### Antibacterial activity

The obtained antibacterial activity results of  $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_3$  and its Co(II) and Ni(II) complexes are shown various inhibitory effects (12 to 18 mm) against three tested bacterial species, The inhibition zones vary depending on bacteria species and type of

compound. Gram positive bacteria are more sensitive than gram negative bacteria to compounds. The largest zone of inhibition was observed for Co(II) and Ni(II) complexes against *S.aureus* (18 mm and 17 mm). The lowest zone of inhibition was observed for Co(II) and Ni(II) complexes against *E. coli* (12 and 13 mm). Co(II) and Ni(II) complexes showed an effect against *B. cereus* (14 and 17 mm). No effect was detected by  $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_3$  compound against all bacteria species[15].

#### CONCLUSION

The obtained data showed the formation of 1:2 [M: L] complexes and suggested the following structure.



Where M = Co (II) and Ni (II)

n= 2 for Co(II) complex

#### The suggested chemical structures of the complexes

**Table 1. Elemental analysis and some physical data of the Schiff base and its complexes**

Schiff base/ Complexes	Color	M.wt.	M.P. °C	Found ( calc. ) %			Λ	μ
				C%	H%	N%		
$\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_3$ (L)	Yellow	295.30	209	64.97 (65.08)	4.41 (4.44)	14.35 (14.23)	-	-
$[\text{Co}(\text{C}_{16}\text{H}_{12}\text{N}_3\text{O}_3)_2]2\text{H}_2\text{O}$	Gray	683.54	>250	55.93 (56.23)	4.44 (4.13)	12.45 (12.29)	6.45	3.87
$[\text{Ni}(\text{C}_{16}\text{H}_{12}\text{N}_3\text{O}_3)_2]$	Dark brown	647.27	>250	59.51 (59.38)	3.41 (3.74)	12.35 (12.98)	7.01	2.93

μ = BM, Λ = molar conductance.

Table 2. Spectroscopic data for the Schiff base and its complexes

Schiff base/ Complexes	IR (cm <sup>-1</sup> )					<sup>1</sup> HNMR (ppm)
	vH <sub>2</sub> O	vOH	vC=N	vM-O	vM-N	
C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub>	-	3518	1654	-	-	OH(11.64), NH(3.8), CH <sub>3</sub> (2.06)
[Co(C <sub>16</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub> ) <sub>2</sub> ]2H <sub>2</sub> O	3550	3414	1621	568	482	-
[Ni(C <sub>16</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub> ) <sub>2</sub> ]	3542	3409	1623	618	475	?

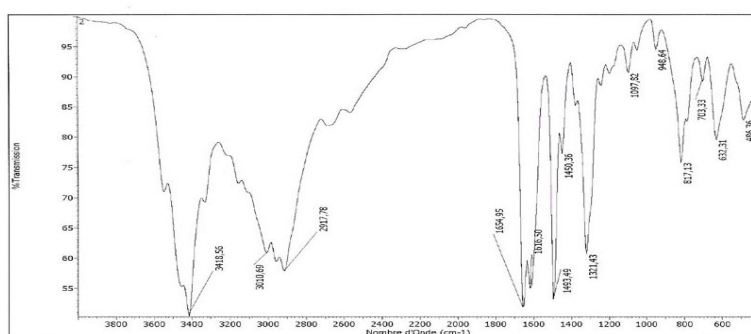


Figure 1. IR spectrum of the Schiff base.

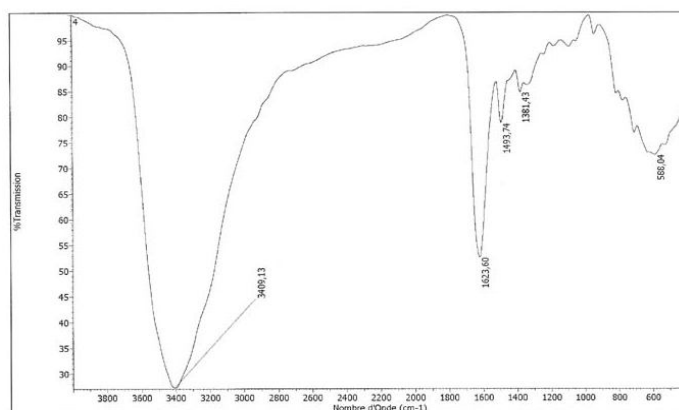


Figure 2. IR spectrum of Co(II) complex.

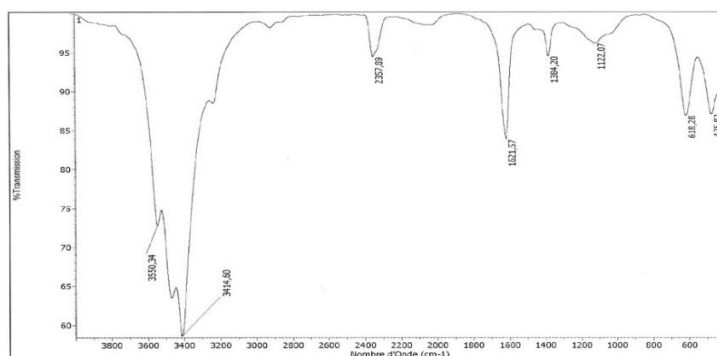


Figure3. IR spectrum of Ni(II) complex.

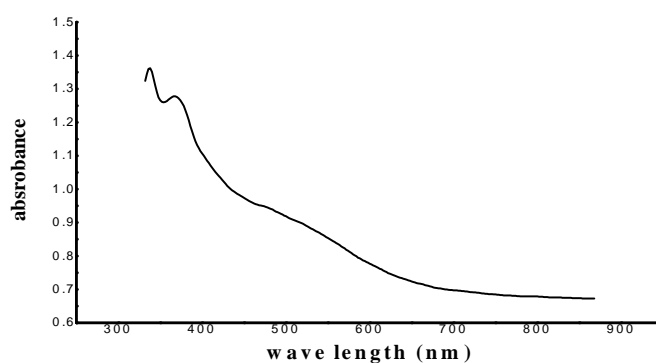


Figure 4. Ultraviolet spectrum of the Schiff base.

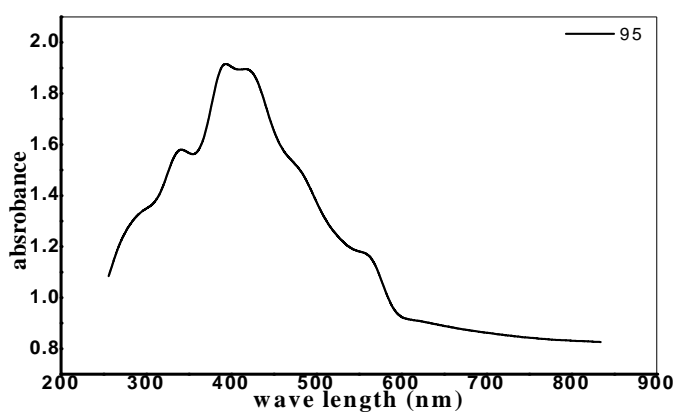


Figure 5. Electronic spectrum of Co(II) complex.

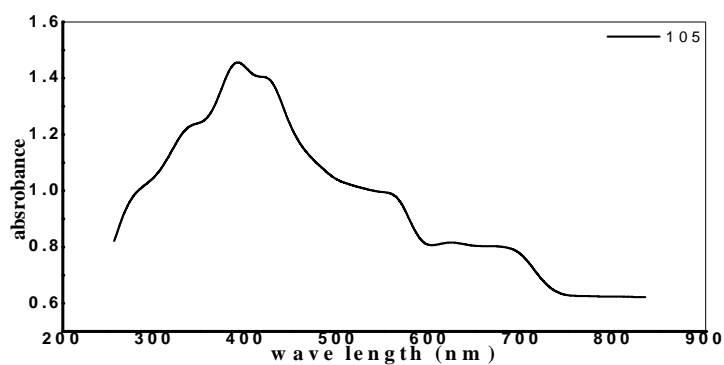


Figure 6. Electronic spectrum of Ni(II) complex.

## REFERENCES

1. Nagpal P. and Singh RV. Appl. Organomet. Chem., 2004; 18: 221.
2. Hamill A M, Khalifa KM, AL-Houni A and El-ajaily MM, Rasayan J. Chem., 2009; 2(2): 261.
3. Singh N P, Tyagi VP, and Ratnam B. J. Chem. Pharm. Res, 2010; 2(1): 473.
4. Baiu SH, El-ajaily MM, and El-Barasi NM. Asian. J. Chem., 2009; 21(1): 5.
5. Wu CY, Chen LH, Hwang WS, Chen HS and Hung CH. J. Organomet. Chem., 2004; 689: 2192.
6. Singh HL, Varshney S and Varshney AK, Appl. Organomet. Chem., 1999; 13: 637.

7. Maurya, R.C.; and Patel, P.; Spectrosc. Lett. 1999, 32(2), 213.
8. Jain, M.;Gaur, S.;Singh, V.P.; and Singh, R.V.;Appl. Organomet. Chem.,2004,18, 73.
- 9.Sobola AO and Warkins GM, Journal of Chemical and Pharmaceutical Research, 2013;5(10): 147-154.
- 10.Bansol A, and Singh R V. Indian J. Chem. Sec.,2002; A 40:9.
- 11.Wölfle H, Kopacka H, Wurst K, Preishuber P and Bildstein B. J. of Organomet. Chem., 2009; 694 (16): 2493.
- 12.Bogdadi HA, Kokoska A, Havlik L, Kloucek J, Rada PV and Vorisek K. Phar. Bio.,2007;45 (5): 386.
- 13.Sunitha M, Jogi P, Ushalah and Gyonakmri C, Journal of Chemical and Pharmaceutical Research, 2012; 4(3): 1553-1561.
- 14.Saghatforoush LA, Mehdizadeh R and Chalabian F, Journal of Chemical and Pharmaceutical Research, 2011; 3(2): 691-702.
- 15.Sule IO and Agbabiaka TO. Ethno. Leaf. 2008; 12: 1035.