

## SPECTROSCOPIC STUDIES, BIOLOGICAL ACTIVITY AND CRYSTAL STRUCTURE OF SCHIFF BASE AND ITS NI (II)-COMPLEX

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### **ABSTRACT**

*Schiff's bases was fabricated and the composition was illustrated by X-rays demonstrating the formation of the molecule, which indicated that the compound was crystallized in monoclinic  $C2/c$  with  $a = 16.0116 (5)$ ,  $b = 6.0215 (2) \text{ \AA}$ ,  $c = 29.0082 (10) \text{ \AA}$ ,  $\alpha = 90.10^\circ$ ,  $\beta = 101.956 (2)^\circ$ ,  $\gamma = 90.10^\circ$ ,  $V = 2759.3 (2) \text{ \AA}^3$ ,  $Z = 8$  and  $R_{int} = 0.032$ . Mass spectroscopy,  $^1\text{H NMR}$ , X-ray, UV-VIS, and infrared. Also, the Ni complex was prepared and its structure was elucidated in the bases for primary analysis, electronic measurements, infrared spectra, and conduction measurements. Also, the biological activity of Schiff's base and its nickel complex is biologically active.*

**KEYWORDS:** *Biological Activities, Schiff Base, Spectroscopic; X-Ray Single Crystal*

### **INTRODUCTION**

Schiff's base is well-known for their biological applications such as antibacterial, antifungal, anticancer and antiviral agents (1, 2). Also, Schiff's basic mineral complexes have been extensively studied because they have industrial, anti-fungal, anti-bacterial applications, anti-cancer herbicides (3), anti-TB activities (4) and chelating capabilities that attract remarkable attention (5). Benzocaine was prepared by direct esterification of p-aminobenzoic acid with absolute ethanol, in the presence of sulfuric acid as a drying agent (6).

Schiff base compounds containing azomethane (imine) ( $-\text{RC}=\text{N}-$ ) which are usually prepared by condensation of a primary amine with an active carbonyl complex (7).

It has often been used as chelating agents (bonds) in the field of coordination chemistry and their mineral complexes are of great interest for many years. O, N, and S atoms are known to play a major role in the active sites of many vital mineral particles in coordination with the minerals (8).

In the present work, the nickel Schiff base and its compound were prepared and the crystal structure of X-rays studied. The Schiff base structure and its nickel compound were matched on the basis of molar ratio methods, UV-VIS and IR methods.

### **EXPERIMENTAL**

#### **Instruments**

The infrared spectrum of Schiff's base (I) and its Ni (Ia) compound was recorded in KBr CDEX medium using a shimadzu 8400 S FT-IR spectrophotometer in the number of waves in the range (4000-400)  $\text{cm}^{-1}$ . The electron spectra were measured absolutely ethanol As a (10-4M) solvent in the (200-1100) nm range using UV-Visb. T80-PG Spectro photometer.

H-NMR spectra were recorded on a Bruker 500 MHz spectroscopy model using DMSO-d<sub>6</sub> as the solvent and TMS as an internal standard. The mass spectra were obtained from Shimadzu Agilent Technologies 5973C at 70e and MSD using straight probe input (Acq 10 watt power method) at 90-110 °C

### Synthesis of Schiff Base (I)

Schiff bases were prepared by means of a condensation reaction (9), in which 2-hydroxybenzaldehyde (0.1 mol) was wisely added to the amine (4-aminobenzoic acid) (0.1 mol) with constant stirring, (drops of glacial acetic acid) (10) Added). After complete addition, the reaction mixture was heated under vapor condensation for three hours. The products (imines) were separated after cooling at room temperature by filtration. The isolated compound was purified by recrystallization from ethanol. After one week, the orange leaflets for compound (I) were obtained (Scheme 1). The melting point of Schiff's base was found at 88 °C.

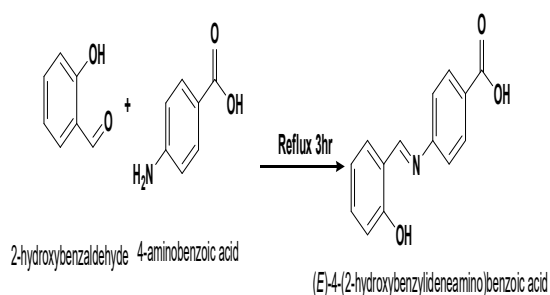


Figure 1: Synthesis of Schiff Base (I).

### Synthesis of Complex

Conductivity measurement calibration is performed by titrating 10 mL of  $1 \times 10^{-3}$  M Ni (II) ion solution while increasing the volume of a  $1 \times 10^{-3}$  M complex agent solution to Schiff's base, using DMF as solvent, and the conductivity was then recorded after stirring the solution for 2 minutes. Through a plotting the conductance value against milliliter of reagent was added, and by applying the least squares equation the ratio was 1: 1 as shown in Figure 2 (11)

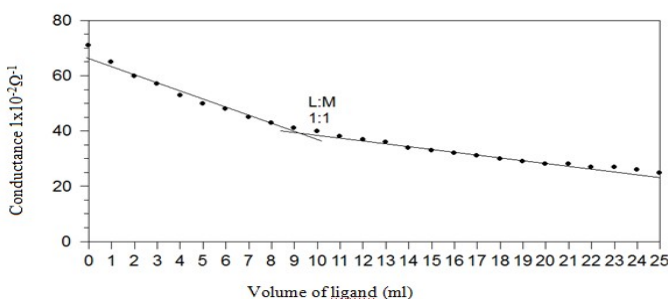


Figure 2: Conduct Metric Titration of Schiff Base (I) ( $1 \times 10^{-3}$  M) with  $(\text{CH}_3\text{COO})_2 \cdot \text{Ni} \cdot \text{H}_2\text{O}$  ( $1 \times 10^{-3}$  M) System.

### Spectroscopic Molar Ratio Testing

In the current study, the concentration of 2 mL of Ni + 2 ion solution was kept constant at  $1 \times 10^{-3}$  M, while the bonds were regularly varied from  $0.2 \times 10^{-3}$  to  $2 \times 10^{-3}$  M using DMF as the solvent. The absorbance of the mixed solutions was measured and plotted against the molar ratio of [ligand] / [metal ion]. The results obtained are graphically represented in Figure 3

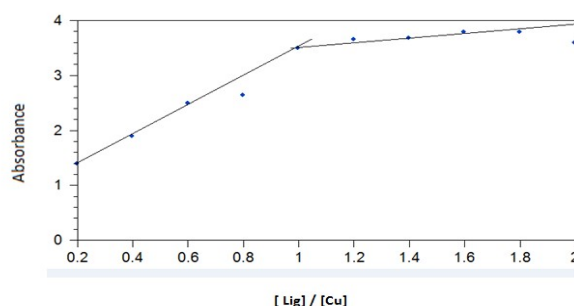


Figure 3: Absorption Spectra of Ni (II) Complex Molar Ratio Method.

### Preparation of Schiff-Base Metal Complexes

The absorption diagram is represented as a function of the ion / ligand molar ratio by two parts indicating the composition of a 1: 1 compound. Therefore, a solution of copper acetate monohydrate  $(\text{CH}_3\text{COO})_2 \cdot 2\text{Ni} \cdot \text{H}_2\text{O}$  (0.001 mol) was added in 25 mL of drip-release ethyl alcohol to stir a quantity Equality of Schiff base (I). After complete addition of the mineral salt, the reaction mixture was heated under reflux for about three hours. Then the product is immediately separated, and recrystallized from DMF to give solid (Ia) products (Figure 4).

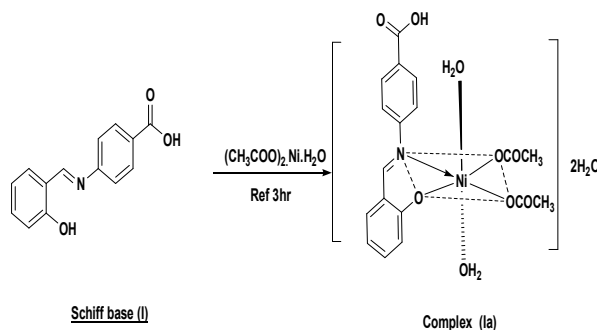


Figure 4: Synthesis of Ni-Complex (I<sub>a</sub>).

## RESULTS AND DISCUSSIONS

### Electronic Spectra of Schiff Base

The electron spectrum (UV-VIS) is present in (DMF) where the solvent displays the absorption band structure at  $\lambda_{\text{max}} = 267 \text{ nm}$  corresponds to the  $\pi \rightarrow \pi^*$  shifts of the  $\text{C} = \text{N}$  group. The broadband at  $\lambda_{\text{max}} = 332 \text{ nm}$  corresponds to the  $n \rightarrow \pi^*$  transformations of groups. azomethine and carbonyl.

### The Structure of Schiff Base (I) was Elucidated on the Bases of

#### Elemental Analysis

The ratio of C, H, and N was found to Schiff's base ((E)-4-(2-hydroxybenzylideneamino) benzoic acid) (69.70, 4.60, and 5.81, respectively) that corresponds to those required (69.20, 4.40 and 5.31, respectively).

#### IR Spectra

The infrared spectrum of Schiff's base (I) shows a wide band at  $3254 \text{ cm}^{-1}$  characteristic of the expansion vibrations of the phenolic O-H group. The amplitude of this band indicates the presence of hydrogen bonds between OH and azomethine N. The band at  $1608 \text{ cm}^{-1}$  can be designated as a  $\nu\text{-CH} = \text{N}$  expansion mode for the vibration of the azomethine group (13,

14). The sharp peak at 1703  $\text{cm}^{-1}$  is due to the expansion mode of the vibrations  $\text{C} = \text{O}$ . The aromatic vibrations  $\text{C} = \text{C}$  extend at 1454 and 1567  $\text{cm}^{-1}$ . Finally, the bands at 2971, 2751, and 1354  $\text{cm}^{-1}$  can be designated as  $\nu$  C-H aromatic, aliphatic C-H, and C-N, respectively (15).

### **<sup>1</sup>H-NMR Spectra**

The <sup>1</sup>H-NMR spectrum of the linker in DMSO shows signals at 1111.10 (w), 8.657 (w), 4.50 (p), and 1.30 (t) ppm, attributed to OH, CH = N-, CH<sub>2</sub> and -CH<sub>3</sub> protons respectively. Multiple signals within the range at = 6.91-7.78 (m) ppm assigned to the aromatic protons of both rings.

### **The Structure of Ni Complex of Schiff Base (I) was Elucidated on the Bases of**

#### **Elemental analysis**

The preliminary analysis showed that C = 43.77 %, N = 2.84 % and Ni = 12.87 % which is compatible with the required (43.27 %, N = 2.44%, Ni = 12.87 %). Found that; Yield = 54.73 % (0.28 g) and m.p = 180 ° C.

#### **IR Spectra of Schiff Base Complex**

The Schiff base spectra (I) show a wide band at 3254  $\text{cm}^{-1}$  in the ligand (I) that designated the OH group bound to intramolecular hydrogen (15), indicating that the OH group acts as the covalent site. Complex (Ia) shows a broad band at 3540  $\text{cm}^{-1}$  appearing simultaneously with bands at 888  $\text{cm}^{-1}$  attributed to coordinated water molecules (17, 18).

Shows the range of the azomethene group ( $\text{C} = \text{N}$ ) extended at 1608  $\text{cm}^{-1}$ , which is shifted to a lower wavelength; 1600  $\text{cm}^{-1}$  of the Ia complexes, indicating that the nitrogen of the azomethene group is homogeneous with the metal ion (13, 14). New bands appear in the region 510-582  $\text{cm}^{-1}$  and 450-470  $\text{cm}^{-1}$  in the spectra of the Ia complexes that can be attributed to the  $\text{M} \leftarrow \text{N}$  and  $\text{M} \rightarrow \text{O}$  vibrations, respectively. The range resulting from  $\text{C} = \text{O}$  at approximately 1704 is reported at about the same locus in the complexes and indicates that this group does not participate in complexity, finally bands at 2978 instead of 2973 and 1390  $\text{cm}^{-1}$  instead of 1361  $\text{cm}^{-1}$  may be designated as  $\nu$  CH Ar And CN, respectively (15).

#### **Electronic Spectra of Schiff Base Complex**

Electron spectra of Schiff base complexes were performed in DMF solutions at a concentration of 3-10 M. The spectrum of the complex displays absorption bands at  $\lambda_{\text{max}} = 266$  nm corresponding to  $\pi \rightarrow \pi^*$  transitions of  $\text{C} = \text{N}$  range. The acute range at  $\lambda_{\text{max}} = 318$  nm corresponds to the  $n \rightarrow \pi^*$  transitions of the acetate group. The acute range at  $\lambda_{\text{max}} = 359$  nm corresponds to the  $n \rightarrow \pi^*$  transitions of the azomethine group. Where the range at  $\lambda_{\text{max}} = 367$ -451 corresponds to a d-d transition copper metal. The magnetic moment of the compound (Ia) was observed at 1.80 BM in the range of 1.7-1.85 BM of the octahedral Cu (II) compound (16).

### **Biological Activity**

#### **Antifungal Activity**

Schiff's base (I) and its copper complex (Ia) were separately examined in the laboratory for their antifungal activity against various fungi (*Aspergillus fumigatus* (RCMB 002003), *Geotrichum candidum* (RCMB 052006), *Candida albicans* (RCMB 005002) and *Syncephalastrum racemosum* (RCMB 005003). On Saborad Dextrose agar plates the fungicide culture was purified by single spore isolation technique and the antifungal activity of the agar method was well spread (19) using clotrimazole and itraconazole as standard antifungal drugs.

### Antibacterial Activity

The antibacterial efficacy has been studied using the agar-well diffusion method (19). The activity of Schiff's base (I) and its copper complex (Ia) was studied against *Staphylococcus aureus* (RCMB 000106) and *Bacillus subtilis* (RCMB 000107) (as Gram positive bacteria) while *Pseudomonas aeruginosa* (RCMB 000102) and *Escherichia coli* (RCMB) 000103) (as bacteria). Gram-negative), using penicillin G and streptomycin as standard antibacterials. All the selected strains showed sensitivity to I and Ia, which showed good activity against all tasteless bacteria and fungi except for *Syncephalastrum racemosum* (RCMB 005003).

**Table 1: Crystallographic Details for Schiff Base (I)**

$C_{16}H_{15}NO_3$ $C_{16}H_{15}NO_3$ $M_r = 269.300$ Monoclinic $C2/c$ $a = 16.0956 (5)\text{\AA}$ $b = 6.0415 (2)\text{\AA}$ $c = 29.1072 (10)\text{\AA}$ $\alpha = 90.20^\circ$ $\beta = 101.886 (2)^\circ$ $\gamma = 90.10^\circ$ $V = 2755.4 (2)\text{\AA}^3$ $Z = 8$ <b>Data Collection</b> Kappa CCD Absorption correction: none 5846 measured reflections 3902 independent reflections 921 observed reflections Criterion: $I > 3.00 \text{ sigma}(I)$ $R_{int} = 0.032$	$D_x = 1.299 \text{ Mg m}^{-3}$ Density measured by: not measured fine-focus sealed tube Mo $K\alpha$ radiation $\lambda = 0.71083$ Cell parameters from 2935 $\theta = 2.920\text{--}27.495^\circ$ $\mu = 0.09 \text{ mm}^{-1}$ $T = 297 \text{ K}$ needle pale orange Crystal source: Local laboratory $\theta_{max} = 27.49^\circ$ $h = -21 \rightarrow 21$ $k = -8 \rightarrow 8$ $l = -38 \rightarrow 38$ $h = 0 \rightarrow 21$ $k = 0 \rightarrow 8$ $l = -37 \rightarrow 37$
<b>Refinement</b> Refinement on $F^2$ fullmatrix least squares refinement $R(\text{all}) = 0.278$ $R(\text{gt}) = 0.063$ $wR(\text{ref}) = 0.112$ $wR(\text{all}) = 0.175$ Only coordinates of H atoms refined Calculated weights sigma $\Delta/\sigma_{max} = 0.004$ $\Delta\rho_{max} = 0.73e\text{\AA}^3$	$wR(\text{gt}) = 0.111$ $S(\text{ref}) = 2.504$ $S(\text{all}) = 2.129$ $S(\text{gt}) = 2.538$ 916 reflections 180 parameters 0 restraints $\Delta\rho_{min} = -0.78e\text{\AA}^3$ Extinction correction: none Atomic scattering factors from Waasmaier & Kirfel, 1995

Data collection: Kappa CCD

Cell refinement: HKL Scalepack (Otwinowski & Minor 1997) <sup>(20)</sup>

Data reduction: Denzo and Scalepak (Otwinowski & Minor, 1997) <sup>(21)</sup>

Program(s) used to refine structure: maXus (Mackay et al., 1999) <sup>(22)</sup>

Molecular graphics: *ORTEP* (Johnson, 1976) Software used to prepare material for publication: maXus(Mackay et al., 1999) <sup>(24)</sup>

### CONCLUSIONS

Ethyl4- (2-hydroxy-benzylideneamino) benzoate (Schiff base (I)) was synthesized from the condensation of benzocaine and o-hydroxybenzaldehyde, and the Schiff base (I) reacted with the monohydrate monohydrate as a binary compound of hydroxyl and the other of nitrogen azomethene to form an octal structure Surfaces.

The result of all previous physiochemical measurements shows that the structure of a 1: 1 complex can be represented as in diagram (2). Finally, I and Ia show more biological activity both bacterial and fungal than the basic drug (benzocaine).

## REFERENCES

1. D. Venegas-Yazigi, D. Aravena, E. Spodine, E. Ruiz, S. Alvarez, *Coord. Chem. Rev.* 254 (2010) 2086.
2. E. Ruiz, S. Alvarez, A. Rodríguez-Forteza, P. Alemany, Y. Pouillon, C. Massobrio, in: J.S. Miller, M. Drillon (Eds.), *Electronic Structure and Magnetic Behavior in Polynuclear Transition-Metal Compounds*, vol. 2, Wiley-VCH, Weinheim, 2001, p. 227.
3. S. Anbu, M. Kandaswamy, *Polyhedron* 30 (2011) 123.
4. R. Vafazadeh, B. Khaledi, A.C. Willis, M. Namazian, *Polyhedron* 30 (2011) 1815.
5. (a) A. Jana, S. Mohanta, *Inorg. Chim. Acta*, 405, (2013) 265; (b) S. Saha, A. Sasmal, C. R. Choudhury, C. J. Gómez-García, E. Garribba, S. Mitra, *Polyhedron* 69 (2014) 262.
6. D. Gatteschi, O. Kahn, R.D. Willet, *Magneto structural Correlations in Exchange Coupled Systems*, Reidel, Dordrecht, 1984.
7. V.H. Crawford, H.W. Richardson, J.R. Wasson, D.J. Hodgson, W.E. Hatfield, *Inorg. Chem.* 15 (1976) 2107.
8. L. Merz, W. Haase, *J. Chem. Soc., Dalton Trans.* (1980) 1594.
9. T.N. Doman, D.E. Williams, J.F. Banks, R.M. Buchanan, H.-R. Chang, R.J. Webb, D.N. Hendrickson, *Inorg. Chem.* 29 (1990) 1058.
10. G. Dutta, R. K. Debnath, A. Kalita, P. Kumar, M. Sarma, R. B. Shankar, B. Mondal, *Polyhedron* 30 (2011) 293.
11. O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993.
12. J.-P. Launay, M. Verdaguer, *Electrons in Molecules: From Basic Principles to Molecular Electronics*, 1st Edn, OXFORD University Press, Oxford, UK, 2014, Chapter 2, p. 145.
13. L.K. Thompson, S.K. Mandal, S.S. Tandon, J.N. Bridson, M.K. Park, *Inorg. Chem.* 35 (1996) 3117.
14. E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *Inorg. Chem.* 36 (1997) 3683.
15. E. Safaei, A. Wojtczak, E. Bill, H. Hamidi, *Polyhedron* 29 (2010) 2769.
16. S. Gupta, A. Mukherjee, M. Nethaji, A. R. Chakravarty, *Polyhedron* 24 (2005) 1922.
17. A. Mukherjee, R. Raghunathan, M.K. Saha, M. Nethaji, S. Ramasesha, A.R. Chakravarty, *Chem.-Eur. J.* 11 (2005) 3087.
18. S. G. Naik, A. Mukherjee, R. Raghunathan, M. Nethaji, S. Ramasesha, A. R. Chakravarty, *Polyhedron* 25 (2006) 2135.
19. P. Bhowmik, N. Aliaga-Alcalde, V. Gómez, M. Corbella, S. Chattopadhyay, *Polyhedron* 49 (2013) 269.

20. N.E. Borisova, A. Kostin, T.V. Magdesieva, M.D. Reshetova, O. Nikitin, V. Paredes-García, M.T. Garland, P. Hermosilla-Ibáñez, W. Cañon-Mancisidor, A. Rodionov, D. Venegas-Yazigi, E. Spodine, *New J. Chem.* 38 (2014) 709.
21. S. Khanra, T. Weyhermüller, P. Chaudhuri, *Dalton Trans.* (2009) 3847.
22. C.R. Bhattacharjee, P. Goswami, H.a.R. Pramanik, P.C. Paul, P. Mondal, *Spectrochim. Acta A78* (2011) 1408.

