

## Studies on Cobalt(II) and Copper(II) Schiff Base Complexes

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Co(II) and Cu(II) Schiff base complexes derived from salicylaldehyde and anthranilic acid (L) have been prepared and characterized by using elemental analysis, thermogravimetric analysis, magnetic analysis, infrared and electronic spectra. The theoretical elemental analysis data of the prepared Schiff base and its complexes are in a good agreement with those found data and show the formation of 1:1 [M:L] ratio. Thermogravimetric analysis reveals the presence of hydrated and coordinated water molecules. The magnetic moment values show the existence of three unpaired electrons for Co(II) complex and one unpaired electron for Cu(II) complex. The infrared spectral data display the coordination sites of the Schiff base towards the Co(II) and Cu(II) ions. The electronic absorption spectra exhibit  $\pi \rightarrow \pi^*$  (phenyl ring) and  $n \rightarrow \pi^*$  (HC=N) transitions and the expected geometrical structures of the prepared complexes.

**Key Words:** Cobalt(II), Copper(II), Schiff base complexes.

### INTRODUCTION

Salicylaldehyde and anthranilic acid compounds are bidentate ligands and have a large applications in chemistry and medicine. The present ligands have a good ability to form large number of chelates with most transition and non-transition metal ions of periodic table. Ben Saber *et al.*<sup>1</sup> prepared some transition metal chelates with Schiff base derived from salicylaldehyde and (*o*-aminophenol or *o*-amino benzoic acid). The chemical investigation of these chelates were carried out by elemental analysis, molar conductivity, thermal analysis and spectroscopic studies. Some new transition metal complexes of the Schiff base quinoxaline-2-carboxalidine-2-aminophenol (HQAP) have been synthesized and characterized by elemental analysis, molar conductance measurements, magnetic moments and spectroscopic studies<sup>2</sup>. The complexes have an empirical formulae of [Mn(QAP)<sub>2</sub>], [Mn(QAP)<sub>2</sub>Cl], [Ni(QAP)<sub>2</sub>] and [Cu(QAP)<sub>2</sub>]. Tetrahedral geometries have been suggested for Mn(II), Co(II), Ni(II) and Cu(II) complexes. An octahedral dimeric structure has been assigned for Fe(III) complex. It has been found that the HQAP acts as a bidentate ligand. Hassan<sup>3</sup>

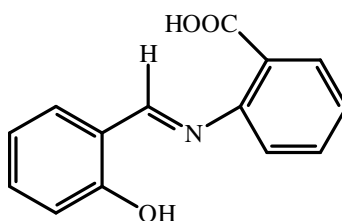
synthesized some Co(II) and Fe(III) Schiff base complexes derived from isatin and some  $\alpha$ -amino acids. The synthesized complexes were identified by chemical analysis and physical studies.

In this paper, the synthesis and characterization of cobalt(II) and copper(II) Schiff base complexes derived from salicylaldehyde and anthranilic acid are reported.

### EXPERIMENTAL

All chemicals used in this investigation were reagent pure of BDH or Aldrich. All organic solvents were obtained as pure grade materials from BDH. Double distilled water was used throughout.

**Preparation of Schiff base:** The Schiff base was prepared by mixing an ethanolic solution of 0.01 mol of salicylaldehyde (1.22 g) with 0.01 mole of anthranilic acid (1.37 g) in the same solvent. After 2 h, yellow crystals appeared. The crystals were filtered and washed with ethanol, recrystallized from hot methanol to give yellow crystals and dried at room temperature with 80 % yield and its purity was confirmed by TLC technique.



Structure of the Schiff base

**Preparation of Schiff base complexes:** Co(II) and Cu(II) Schiff base complexes under investigation were prepared by mixing 25 mL of ethanol of the Schiff base (1.22 g) with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (2.38 and 1.70 g) and few drops of ammonia solution were added to adjust the pH. The reaction mixtures were refluxed for 3 h and then the residues were left to cool and filtered by suction. The final products were recrystallized from ethanol.

The elemental analyses of the prepared complexes estimate the percent of carbon, hydrogen and nitrogen. These analyses have been performed at chemistry laboratory of Ras-Lanouf oil company-Libya, using Perkin-Elmer 2400 CHN elemental analyzer. The infrared spectra of the complexes in the range of  $4000\text{-}500\text{ cm}^{-1}$  were recorded as KBr disk using IFS-25DPUS/IR spectrometer (Bruker) 1998Y. The electronic spectra of the complexes under study were measured in  $\text{CHCl}_3$  solvent using a Perkin-

Elmer lambda 4B spectrophotometer. The mass spectra were carried out to show the possible fragmentations of the complexes. The TLC technique was used to confirm the purity.

## RESULTS AND DISCUSSION

The obtained elemental analysis data of the Schiff base and its complexes (Table-1) are in a good agreement with the theoretical values and display the formation of 1:1 [M:L] ratio. Thermogravimetric analysis data of  $[\text{CoL}\cdot\text{H}_2\text{O}]\text{H}_2\text{O}$  and  $[\text{CuL}\cdot\text{H}_2\text{O}]\text{H}_2\text{O}$  complexes show a mass-losses at 213 and 276°C attributed to loss one water molecule of hydration during the complex drying process, whereas, the second mass-losses at 368 and 335°C is due to the loss of one water molecule of coordination. The residual metal oxide percentage coincides fairly with the theoretical value (Table-2).

**Infrared spectra of the Schiff base and its complexes:** The infrared spectrum of the Schiff base shows a band in the range of 3068-2500  $\text{cm}^{-1}$  due to COOH group, a strong band at 1683  $\text{cm}^{-1}$  is assigned to (C=O) of the carboxylic group in anthranilic acid compound and the other band appears at 1552  $\text{cm}^{-1}$  region could be due to HC=N bond formation<sup>4</sup>. The infrared spectral data of Co(II) and Cu(II) complexes under investigation exhibit a broad band at 3434  $\text{cm}^{-1}$  assigned to the existence of water molecules<sup>5,6</sup> and the bands which attributed to  $\nu(\text{H-C}=\text{N})$  and  $\nu(\text{COOH})$  vibrations were shifted to lower frequency suggesting their participation in complexation through nitrogen and oxygen atoms with the metal ion<sup>7</sup>. The same spectra show bands at 423-419 and 566-563  $\text{cm}^{-1}$  due to  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$  vibrations<sup>8,9</sup>. The appearance of these bands support the involvement of azomethine and hydroxyl group of the salicylaldehyde and carboxylic group of the anthranilic acid in coordination (Table-1).

**Electronic spectra and magnetic moments:** The electronic spectral data and the magnetic moment values of the complexes are listed in the Table-1. The spectral data of the Schiff base under investigation display three bands at 250 nm (40000  $\text{cm}^{-1}$ ), 223 nm (44843  $\text{cm}^{-1}$ ) and 334 nm (29940  $\text{cm}^{-1}$ ) bands corresponding to  $\pi \rightarrow \pi^*$  (phenyl ring) and  $n \rightarrow \pi^*$  (HC=N) transitions<sup>10</sup>. The magnetic moment values of Co(II) and Cu(II) complexes reveal the presence of unpaired electrons. The electronic absorption spectrum of the  $[\text{CoL}\cdot\text{H}_2\text{O}]\text{H}_2\text{O}$  complex displays three bands at 555 nm (18018  $\text{cm}^{-1}$ ), 626 nm (15974  $\text{cm}^{-1}$ ) and 774 nm (12920  $\text{cm}^{-1}$ ) assigned to  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ , whereas, the Cu(II) complex shows bands at 564 nm (17730  $\text{cm}^{-1}$ ), 587 nm (17036  $\text{cm}^{-1}$ ) and 604 nm (16557  $\text{cm}^{-1}$ ) due to  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  transitions. On the basis of obtained data, a square planar structure was suggested for Co(II) and Cu(II) complexes<sup>11</sup>.

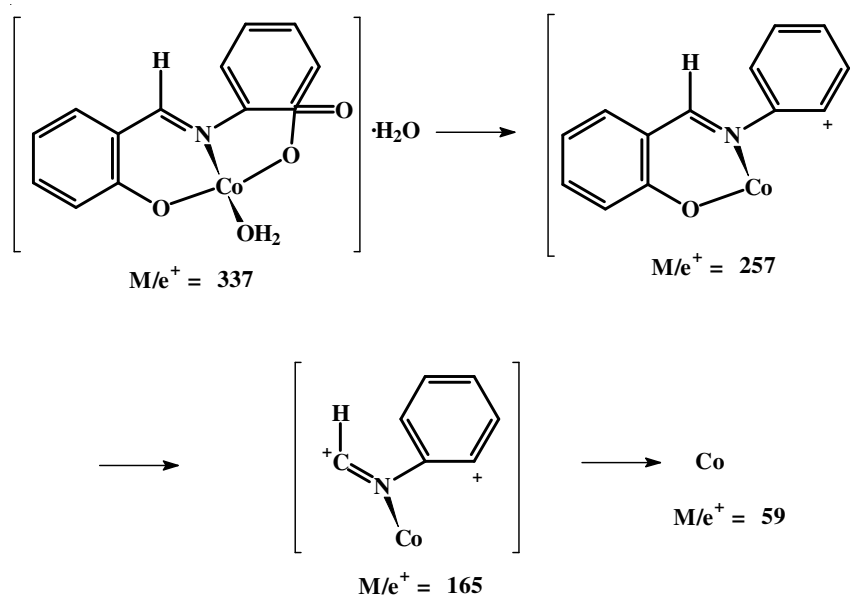
TABLE-1  
SOME PHYSICAL PROPERTIES OF SCHIFF BASE AND ITS Co(II) AND Cu(II)

Schiff base Complex	m.w.	Calc. (Found) %			$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\lambda_{\text{max}}$		$\mu$ (BM)
		C	H	N						nm	$\text{cm}^{-1}$	
(C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> N	241.0	69.70 (69.71)	4.73 (4.56)	6.04 (5.81)	-	1552	1683	-	-	334 250 223	29940 40000 44843	-
[CoLH <sub>2</sub> O]·H <sub>2</sub> O	333.9	49.4 (50.3)	3.86 (4.49)	7.71 (7.19)	3422	1592	1615	563	419	774 626 555	12920 15974 18018	4.13
[CuLH <sub>2</sub> O]·H <sub>2</sub> O	338.5	50.11 (49.60)	3.47 (4.14)	8.25 (8.14)	3446	1555	1606	566	423	604 587 564	16557 17036 17730	1.82

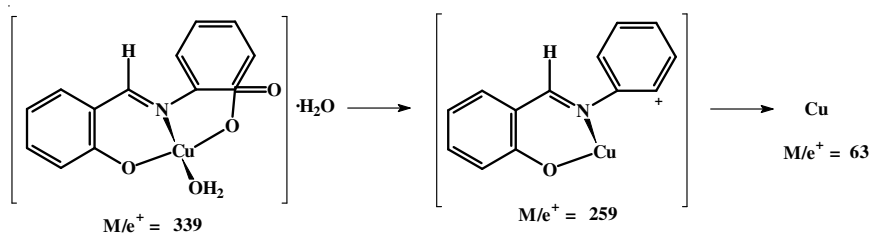
TABLE-2  
THERMOGRAVIMETRIC ANALYSIS DATA OF Co(II) AND Cu(II) COMPLEXES

Complex	Water of hydration weight loss (%)	No. of water molecules	Temp. (°C)	Water coordination weight loss (%)	No. of water molecules	Temp. (°C)	MO* weight loss (%)	Temp. (°C)
[CoLH <sub>2</sub> O]·H <sub>2</sub> O	5.39 (5.00)	1	213	5.70 (6.02)	1	335	26.40 (24.90)	653
[CuLH <sub>2</sub> O]·H <sub>2</sub> O	5.31 (5.50)	1	276	5.62 (5.20)	1	368	24.30 (24.75)	678

The mass spectra of the Schiff base complexes Cu(II), Co(II) support their structures, which are given in **Schemes I and II**. For Cu(II) Schiff base complex, the base peak at  $m/e^+$  339 is corresponding to the molecular weight of the complex. In all cases there is a constant weight with increasing of temperature regarding to the presence of the metallic oxide residue. However, the cobalt complex is in a similar state to Cu(II) complex.

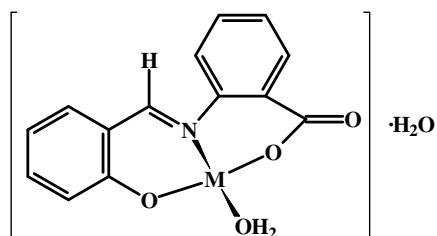


**Scheme-I** Mass spectrum of Co(II) Schiff base complex



**Scheme-II** Mass spectrum of Cu(II) Schiff base complex

On the basis of foregoing evidences, the following general structure has been proposed for present complexes.



[M = Co(II) or Cu(II)]

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