



SYNTHESIS, SPECTROSCOPIC INVESTIGATION AND ANTI-ANTIBACTERIAL ACTIVITY OF SCHIFF BASE COMPLEXES OF COBALT (II) AND COPPER (II) IONS

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ABSTRACT

Two complexes of Co(II) and Cu(II) with Schiff base derived from *o*-phenylenediamine and 2-hydroxyacetophenone have been synthesized by condensation in acidic medium. The synthesized complexes were investigated using different physical techniques such as elemental analysis (C, H and N), infrared, electronic and nuclear magnetic resonance spectroscopies. The geometrical structures of the synthesized complexes have been identified. The antibacterial activity of the Schiff base and their complexes have been also studied, showing that the complexes were of more antibacterial activity than the free Schiff bases

Keywords: Transition metal ions; Schiff base; complexes; pathogenic bacteria.

INTRODUCTION

Acetophenone compound is a bidentate ligand and it has a good ability to form several complexes with transition and non transition metal ions.¹ Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Cd complexes of ethylenediamine condensation with 4-(benzeazo)salicylaldehyde (1:2) [H₂L] were synthesized and characterized by elemental analysis, molar conductivity measurements, infrared and electronic spectra, the ligand and their Ni(II) and Zn(II) complexes were further identified using ¹H-NMR spectra. The results that metal is bonded to the ligand through the phenolic oxygen and the imino nitrogen.⁹ The three optically active Schiff-base ligands have been prepared by condensation of 2-hydroxyacetophenone with (1R,2R)-diaminocyclohexane, (1S,2S)-(-)-1,2-diphenylethylenediamine or R-(+)-2,2'-diamino-1,1'-binaphthalene, respectively. The products have been characterized by their IR, ¹H- and ¹³C-NMR spectra.^{3,4} Iron(III) and Osmium(III) chalets of Schiff bases derived from salicylaldehyde and anthranilic acid have been prepared and investigated using different techniques.⁵

EXPERIMENTAL

All chemicals used in this work were laboratory pure. All organic solvents were obtained as pure grade materials from BDH.

Preparation of the Schiff base:

The ligand of 2-[(2-[1-(hydroxyphenyl)ethyl]aminophenyl)ethanimidoyl]phenol was synthesized by mixing an ethanolic solution of 0.01 mole of *o*-phenylenediamine (1.08 g) with same solvent of 0.01 mole of 2-hydroxyacetophenone (1.36 g). The reaction mixture was refluxed for two hours, then the formed precipitate was filtered, washed several times with ethanol and dried in a desiccator over calcium hydroxide. The yield of the reaction was 73%. The following structure represents the formation of the Schiff base

Preparation of the complexes

Complexes of Co(II) and Cu(II) with 2-[(2-[1-(2-hydroxyphenyl)ethyl]aminophenyl)ethanimidoyl]phenol were synthesized by mixing ethanolic solutions (50 mL) of 0.01 mole (3.46 g) of the synthesized Schiff base with an ethanolic solution (50 mL) of the 0.01 mol of CoCl₂·6H₂O or CuCl₂·2H₂O salts (2.38 and 1.71 g), respectively, 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 left to cool and filtered by suction. The precipitates were washed several times with ethanol, then ether. The complexes were dried in desiccators over anhydrous calcium chloride. The yields were 75 and 78% respectively.

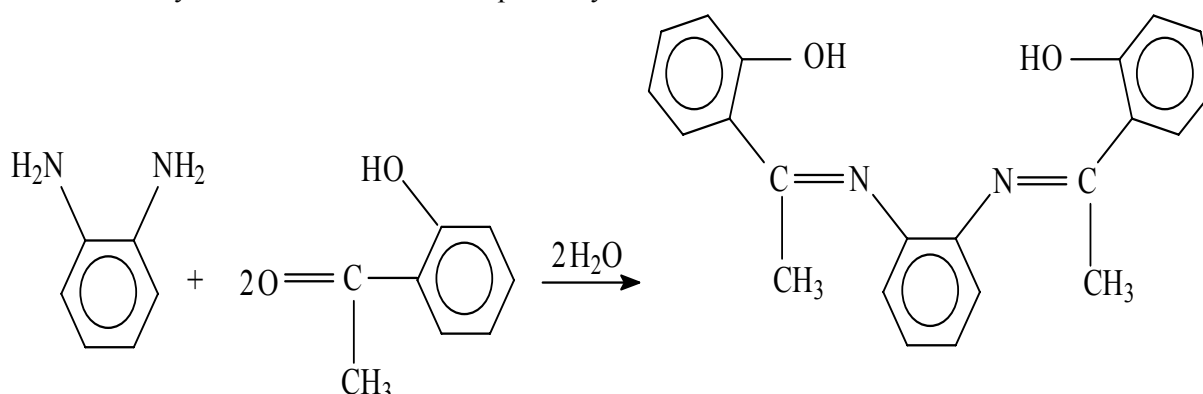


Table-1: Elemental analysis and some physical properties of Schiff base and its complexes

Schiff base/ Complexes	M.Wt	M.P. °C	Color	%C		%H		%N	
				Calc.	Found	Calc.	Found	Calc.	Found
C ₂₂ H ₂₀ N ₂ O ₂	344	103 - 105	Brown	86.72	77.11	5.85	5.63	8.19	8.23
[Co(C ₂₂ H ₁₈ N ₂ O ₂)]H ₂ O	419	>250	Black	63.07	63.05	4.77	4.85	6.68	6.95
[Cu(C ₂₂ H ₁₈ N ₂ O ₂)]H ₂ O	658	>250	Black	40.12	39.92	3.04	3.48	4.26	4.91

Table-2: Infrared and UV-Vis spectra of Schiff base and its complexes

Schiff base/ and Complexes	IR (cm ⁻¹)				UV - Vis. nm	¹ H-NMR ppm
	_{Bv} OH	_{Bv} C=N	_{Bv} M-O	_{Bv} M-N		
C ₂₂ H ₂₀ N ₂ O ₂	3344-3450	1610			280,390	15 (OH), 6.6-7.87 (Phenyl group), 2.29 - 2.2 (CH ₃ group)
[Co(C ₂₂ H ₁₈ N ₂ O ₂)]H ₂ O	3160	1608	862	748	280,370,580	-
[Cu(C ₂₂ H ₁₈ N ₂ O ₂)]H ₂ O	3151	1609	757	584	326,407,511	-

Measurements

The synthesized Schiff base and its complexes were subjected to CHN elemental analyses using 2400 elemental analyzer at Micro-Analytical Center, Cairo University, Giza, Egypt. Infrared spectra were obtained by KBr disc technique by using IFS-25DPUS/IR Spectrometer (Bruker) in the range of 4000-400 cm⁻¹. Electronic absorption spectra were measured in nujol mull using a Perkin-Elmer-Lambda β-spectrophotometer. The ¹H-NMR spectra were recorded using a Varian Gemini 400 MHz Spectrometer using d⁶-DMSO solvent and TMs as reference. Mass spectrum was carried out using Q1000 EX GC-MS Shimadzu spectrometer at 70 eV and AM energy using a direct insertion probe at temperature 90-100 °C.

RESULTS AND DISCUSSION

The reactions of o-phenylenediamine with 2-hydroxyacetophenone yields one Schiff base compound which is 2-[(2-[1-(2-hydroxyphenyl)ethyl] aminophenyl) ethanimidoyl]phen- ol. The reaction of the Schiff base with Co(II) and Cu(II) ions leading to the formation of complexes.

Microanalysis:

The elemental analyses (C, H and N) of the Schiff base and its complexes are listed in table 2. The obtained elemental analysis data were in a good agreement with the calculated values and display the formation of 1:1 [M:L] ratio.

Infrared spectra:

Infrared spectral data of the Schiff base (Fig. 1) shows several bands at 3344, 3450 and 1610 cm^{-1} due to OH and C=N of the free Schiff base.^{6,7} These bands are shifted to lower frequency on complexation with Co(II) and Cu(II) ions (Table-1)^{8,9}. New vibrations at 584-748 and 757-862 cm^{-1} which are not present in the free Schiff base are attributed to the existence of ν (M-O) and ν (M-N)^{10,11}. The appearance of these vibrations confirmed the involvement of nitrogen and oxygen atoms in chelation^{12,13}.

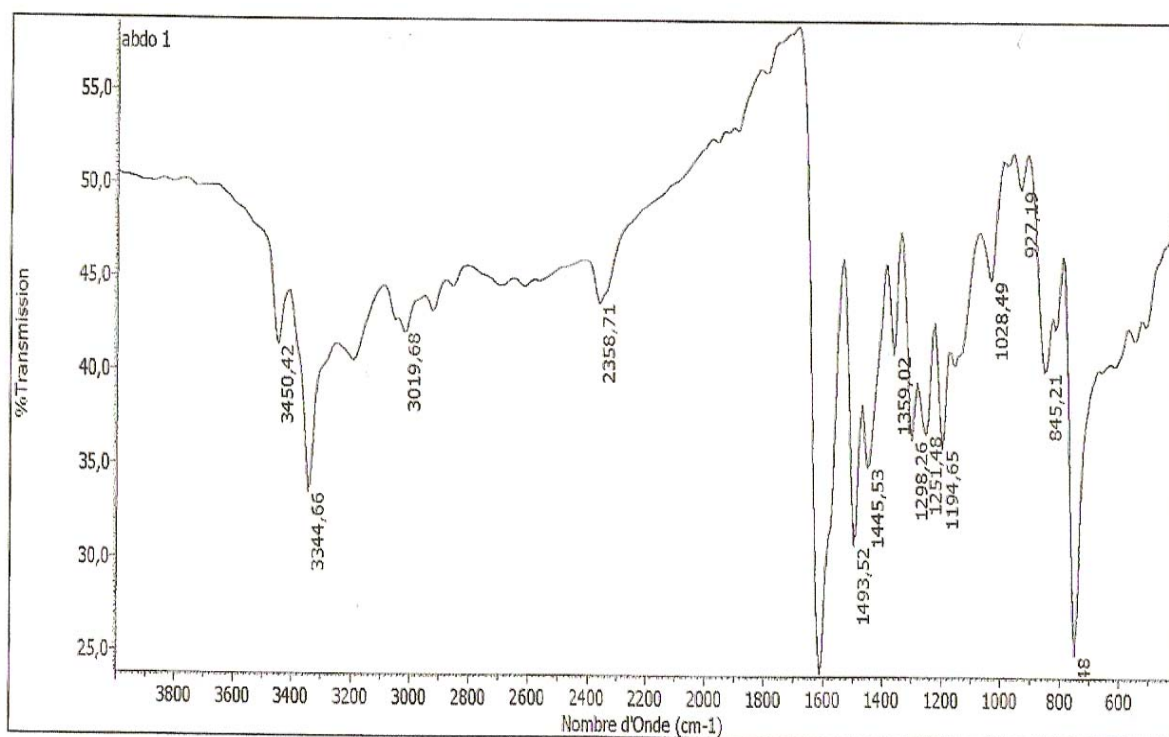


Fig.-1: IR spectrum of the free Schiff base

Electronic spectra:

The electronic absorption spectra of the ligand show two bands at 280 and 390 nm which are due to $\pi \rightarrow \pi^*$ (phenyl ring) and $n \rightarrow \pi^*$ (-C=N), respectively. The electronic spectra of Co(II) and Cu(II) complexes display three bands each at 280, 370, 580 nm and 326, 407, 511 nm, respectively, which are due to d-d and charge transfer transitions. A square planar geometry was suggested for both complexes.¹⁴

Proton nuclear magnetic resonance spectrum of the Schiff base:

¹H-NMR spectral data of the Schiff base was recorded in d⁶-DMSO (Figure 2) show bands at 15, 6.60 – 7.87 and 2.29 – 2.40 ppm, due to OH, phenyl protons and CH₃ groups, respectively¹⁵.

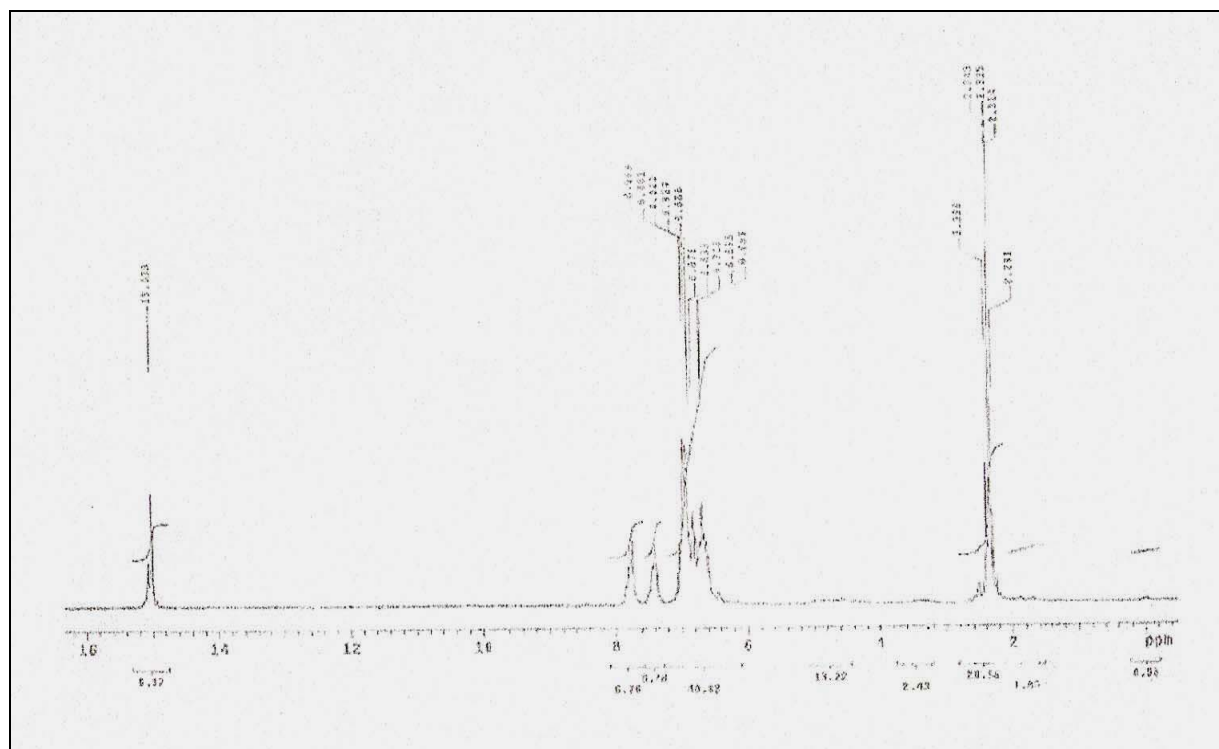


Fig.-2: $^1\text{H-NMR}$ spectrum of the free Schiff base

Mass spectral fragmentation of the Schiff base:

The mass spectrum of Schiff base (Fig.3) shows a base peak m/e^+ at 344 which is due to the original molecular weight of the prepared compound (Schiff base). This means that the condensation of the reactant substances gave pure compound.

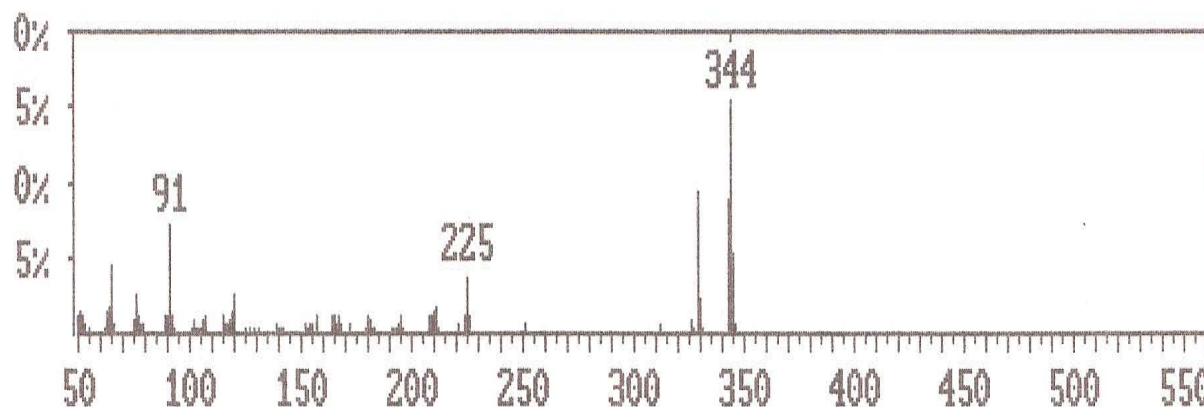


Figure 3: Mass spectra of the Schiff base

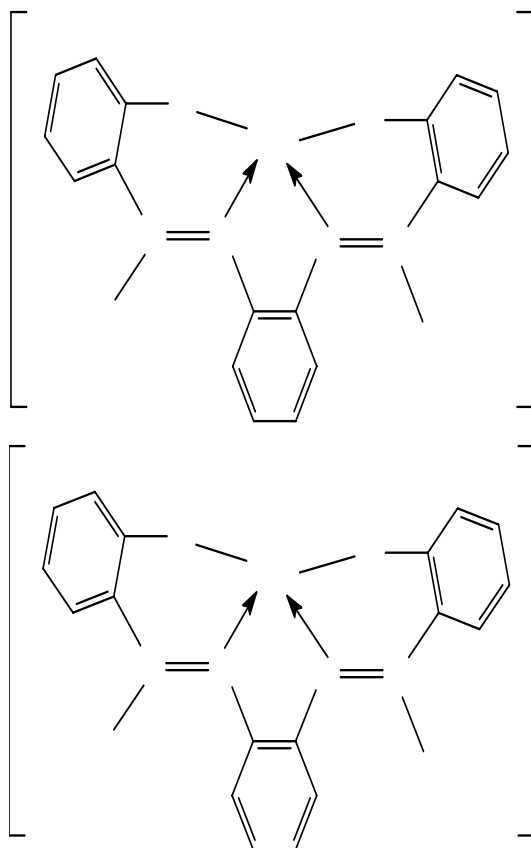
Antibacterial activity:

The three species of bacteria were streaked on nutrient agar (Oxford, England) plates, so that the streaking covered the surface of the plane, The 2-hydroxyacetophenon (sample 1), o-phenylenediamine sample 2), Schiff base compound (sample 3) and Co(II) and Cu(II) complexes (4,5)

were applied on the streaked nutrient agar plate as powder, taking an area not more than 6mm (size of an antibiotic paper disc) and leaving enough distances between them. The plates were then inverted and incubated at 37 °C for 24 h. The inhibition zones were then increased in millimeters and recorded. The two strains of bacteria (*Bacillus cereus* *Staphylococcus aureus* and *E. Coli*) were tested by Mueller-Hinton agar plates. The acetophenone, o-phenylenediamine, Schiff base compounds were applied on the plate by disc paper 6mm, the plates were then inverted and incubated at 37 °C for 24 h. In an attempt assess, the resistance and inhibitor diameters of *Klebsiella sp.* bacteria for 2 different ions in 3 chemical compounds, the inhibitor diameters were recorded between 10 – 30 mm. inhibitor diameter for *sta. spp.* was between 5 – 34 mm. Sample (4) was given best results with diameters (30 mm), due to the entrance of Co(II) ion. For *E. coli resistance* sample 1 was given best results due to the presence of hydroxyl group (2OH) in the compound. For sample 5 with biological effect less than sample 2 due to the presence of (Cu²⁺) ion.

CONCLUSION

Form the previous analysis we can conclude that the complexes have a octahedral and square planar structure in which the ligand coordinated to the metal ion as a tetra dentate via two nitrogen and tow oxygen atoms. The suggested geometrical structure is shown below:



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