



Schiff base derived from phenylenediamine and salicylaldehyde as precursor techniques in Coordination Chemistry

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ABSTRACT

The coordination behavior of Schiff bases synthesized from phenylenediamine and carbonyl compounds can be justified and introduced in precursor technique in different applications. The investigation and the studies of such Schiff base have performed because not as coordination chemistry, metal ion uptake or in dyes techniques, but also because their chemistry interest and other applications such as titration analysis, anticorrosion and biological activity. The advantage of salicylaldehyde as a part in the synthesis of the Schiff base and chelate give the chemical compounds very great deal of reactivity, usefulness and as a clear goal of applications. The synthesis and characterization of phenylenediamine Schiff base was performing by different analytical methods. The chemical structures of the Schiff base and its copper chelate have been elucidated by different physiochemical methods such as elemental analysis, molar conductivity, Infrared EPR, NMR and mass spectroscopy. Moreover, all properties may lead to a wild use of such Schiff base.

Key words: Coordination Chemistry, Schiff bases, precursor, phenylenediamine, salicylaldehyde

INTRODUCTION

Aromatic amine that reacted with any carbonyl group produce a Schiff base. The Schiff bases containing active sites were prepared and spread in different directions of applications. Schiff bases introduced to metal ions uptake, which justified by coordination became a moiety and starting material to other chemical compounds or techniques. The simple and straight forward of preparation gave this kind of compounds advantages to be modified as model compounds for membrane techniques. The azomethine group mainly dominate and influence the reactivity of the Schiff bases as the most important part in the Schiff base body. The coordination binding ability of Schiff base prepared from 1,3-propenediamine and 1-hydroxy-2-acetonaphthone towards metal ions was investigated by using liquid-liquid extraction experiments to extract Cu(II), Ni(II), Co(II) and Zn(II) ions from nitrate solutions.[1-5]

The capability of Schiff bases in chelation give these special chemical compounds advantages to be introduced to coordination interaction with metals. In this aspect, the Schiff base considered be as bi , tri or tetradentate ligands and the characterization was facilitated by all modern tools, in particular, elemental analysis. infrared and other physical methods when necessary. When primary amine heated with aldehydes in appropriate solvents or even by using microwave techniques, the corresponding Schiff bases will be obtained. The phenomena of coordination can be introduced to the complexation and other scientific techniques. The transition metal ions play a good role in these fields, because of their chemicals, physical properties and their ability to form chelating molecules. The chelation of a series of Schiff bases containing various substituents such as OH, N(CH₃)₂ or CH₃ in different positions on the phenyl rings towards some metal ions has been studied with different tools [6-8].

Schiff bases, can be introduced for coordination reaction, specially, if they have either free lone pair of electrons such as nitrogen or oxygen or sulfur atoms with any unshared lone pair of electrons on atoms adjacent the azomethine group in order to form stable chelates with five or six membered rings. The formed chelates must gain appropriate geometry to be stable under normal conditions and to be handling in the chemical analysis. The electronic structures justify the coordination numbers, as well as the geometry of coordination units [9].

The ratio of metal to ligands (M:L) in most chelates, play a major factor and control. As long as there is limited concentration of the ligand, the chelates will be 1:1 ratio. However, increasing in ligand amount, lead to increase the ratio, which may produce 1:2 ratio. The increasing in the ratio controlled by the electronic structures of the metal ions and the type of the chemical geometry having electron withdrawing group in para-position, for example, nitrogen as azomethine and as amino groups, that give the indication of the type of coordination appeared. The Schiff base with a chemical formula $H_2L(C_{31}H_{26}O_6N_2)$ from a dialdehyde and 2-aminobenzoic acid as well as the corresponding metal chelates of Cu(II), Ni(II) and Co(II) as binuclear complexes have been synthesized and characterized [10].

The coordination compounds of Cd(II), Zn(II) and Pb(II) ions with chemical formula $[ML(OH)_2(H_2O)_2]$ in which the primary amine was phenylenediamine have been synthesized and characterized, using elemental analysis, molar conductance, magnetic susceptibility measurements, thermal analysis and some spectral studies were considered as common tools of analysis. All conducted studies support the formation of the chelation phenomena between the positively charged metal ions and the Schiff bases. The reaction of salicylaldehyde with 2-aminophenol or any other amino compounds has been studied in terms of coordination chemistry. The solubility in different chemical solvents gives a lot of indications about the nature of the chelates and can be examined to be electrolytic or non-electrolytic nature. Most bases containing nitrogen atom as well as salicylaldehyde moiety are of significant importance in their chelation or in the other uses. The shade of light of the applications of the Schiff bases give the importance of the nature of the ligands [11-16]. All isomers of phenylenediamine, can be used in preparation of Schiff bases. The chelation may occur, with one or more metal ions depending on the amount used and the geometrical structure of the bases [17,18].

Our aim in this study is to prepare and investigate the structure of the Schiff base derived from salicylaldehyde and m-phenylenediamine and its Cu(II) chelate by using physical and spectral techniques, including elemental analysis, conductivity measurements, IR,UV/Visible, proton NMR, EPR and mass spectroscopy.

EXPERIMENTAL SECTION

Chemicals and Reagents

All chemicals used were reagent grade. Including, m-Phenylenediamine, salicylaldehyde $CuCl_2 \cdot 2H_2O$, absolute ethanol, DMSO and KBr. The double distilled water was used.

Preparation of the Schiff Base

The Schiff base was prepared by mixing 50 ml hot ethanolic solution of m-phenylenediamine (M.Wt=108) (1.08g ; 0.01mol) with 50 ml hot ethanolic solution of salicylaldehyde (M.Wt=122) (2.44g ; 0.02mol). The obtained mixture then refluxed with stirring for 2-3 hrs. The produced precipitate was collected by filtration through Buchner funnel, recrystallized from ethanol and dried at room temperature in desiccator over anhydrous calcium chloride. The purity of the product was carried out by using TLC technique with the yield of 75%..

Preparation of Copper(II) Chelate

The synthesis of the Cu(II) chelate was carried out by adding 50 ml hot ethanolic solution of Schiff base (M. Wt.= 316; 3.16 g ; 0.01mol) to 50 ml hot ethanolic solution of $CuCl_2 \cdot 2H_2O$ (M. Wt.= 170; 1.71 g ; 0.01mol), stepwise. Then few drops of dilute ammonium hydroxide solution were added to adjust the pH, at which the solid chelate will start precipitate. The obtained mixture then refluxed with stirring for 2-3 hrs. The precipitate were collected by filtration through Buchner funnel, washed several times with hot ethanol until the color of the filtrate becomes clear. The product was dried at room temperature in desiccator over anhydrous calcium chloride. The obtained yielded 75%.

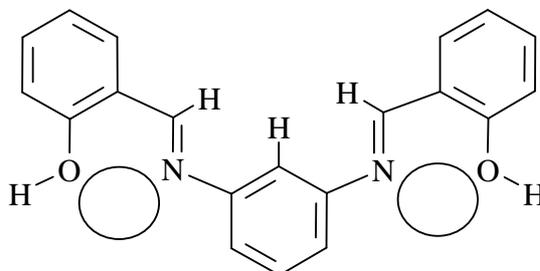
Physical measurements

The synthesized Schiff base and its Cu(II) chelate were subjected to; CHN elemental analyses using 2400 elemental analyzer. The molar conductance measurement was carried out in DMF solvent using digital conductivity meter CMD-650, Benghazi University. The magnetic moment measurement was measured using magnetic susceptibility balance Sherwood Scientific England. The electronic spectra of the Schiff base and its Cu(II) chelate were measured in DMSO solvent using UV/Visible, NIR-101 PC. The IR spectra were obtained by using KBr disk

technique on IFS-25 DPUS/IR spectrometer (Bruker) in the range of 400-4000 cm^{-1} . The proton-NMR (300MHz) also used to analyze the Schiff base. The analyses were done at the Micro analytical center-Cairo University, Giza, Egypt.

RESULTS AND DISCUSSION

The reaction of m-phenylenediamine with salicylaldehyde produces the Schiff base in 1:2 [amine: aldehydes] as shown below.



Physical properties, elemental analysis and molar conductivity

The physical properties of the Schiff base and its Cu(II) chelate in term of the color appear to have characteristic dark blue and dark orange, respectively. The Schiff base and its Cu(II) chelate were subjected to (CHN) elemental analyses. The obtained CHN data (table-1) reveal that the calculated values are in a good agreement with the experimental data. Molar conductivity of the chelate was carried out in DMF solvent and found to be non electrolyte nature because the zero value exhibits the high purity of the chelate [19].

Table-1: Molecular weights, Elemental analysis, Molar conductance, Magnetic moment and Electron paramagnetic resonance

| Schiff base/ chelate | M.Wt | %C | %H | %N | \wedge | $\mu\text{s(B.M)}$ | EPR |
|--|--------|------------------|----------------|----------------|----------|--------------------|---------|
| HL | 316.34 | 75.86 (76.05) | 5.06 (4.92) | 8.91 (9.10) | - | - | - |
| [CuL(OH)(H ₂ O) ₃].H ₂ O | 467.89 | 51.29 (50.80) | 5.13 (4.93) | 6.03 (6.02) | 7.63 | 1.95 | 2.08581 |

() = calculated %, \wedge = molar conductance($\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)

Electronic spectra and magnetic moment

The electronic spectrum of the Schiff base was measured in DMF solvent. The most important bands in this spectrum are 266 nm (37594cm^{-1}) and 348nm (28736cm^{-1}) assigned to $\pi \rightarrow \pi^*$ (phenyl ring) and $n \rightarrow \pi^*$ ($-\text{H}-\text{C}=\text{N}$) transitions, whereas, the electronic spectral data of the Cu(II) chelate exhibit two bands at 303 nm (33003cm^{-1}) and 401nm (24938cm^{-1}) due to charge transfer and ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transitions. The nature of the electronic absorption bands and the magnetic moment value (1.95 B.M) support the existence of an octahedral geometrical structure of the chelate [20-23].

Infrared spectra of the Schiff base and its Cu(II) chelate

The infrared spectral data of the Schiff base exhibit $\nu(\text{OH})$, $\nu(\text{HC}=\text{N})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{OH})$ groups at 3398, 1612, 1458 and 1284cm^{-1} , respectively. The infrared spectrum of the Cu(II) chelate shows bands at 3425, 1630, 1272cm^{-1} due to the presence of hydrated and coordinated water molecules, $\text{HC}=\text{N}$ and $\text{C}-\text{OH}$ vibrations [24, 25] New bands at 581 and 462cm^{-1} which are not present in the free Schiff base attributed to $\text{M}-\text{O}$ and $\text{M}-\text{N}$ vibrations [24, 25].

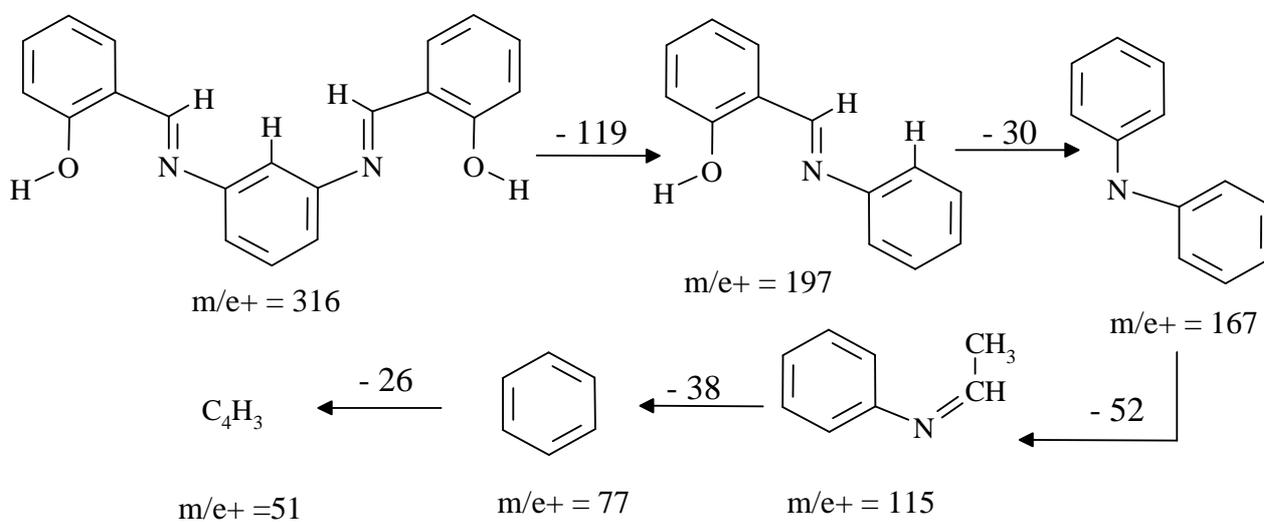
¹HNMR spectrum of the Schiff base

The proton NMR spectrum which performed in DMSO as a solvent indicates the molecule as symmetrical molecule, so the proposed chemical structure of the Schiff base contains the most important bands which represent groups; OH, $\text{CH}=\text{N}$, H(aromatic) as included. Therefore the ¹HNMR (300 MHz, DMSO- d_6): δ [ppm] 12.98 (s,1H, Ar-OH), 9.06 (s,1H, $\text{HC}=\text{N}$), 7.69-7.00 (m,11H,Ar-H), 6.98 (s,1H, Ar-H) and 2.51-2.49 (s, DMSO- d_6) [26].

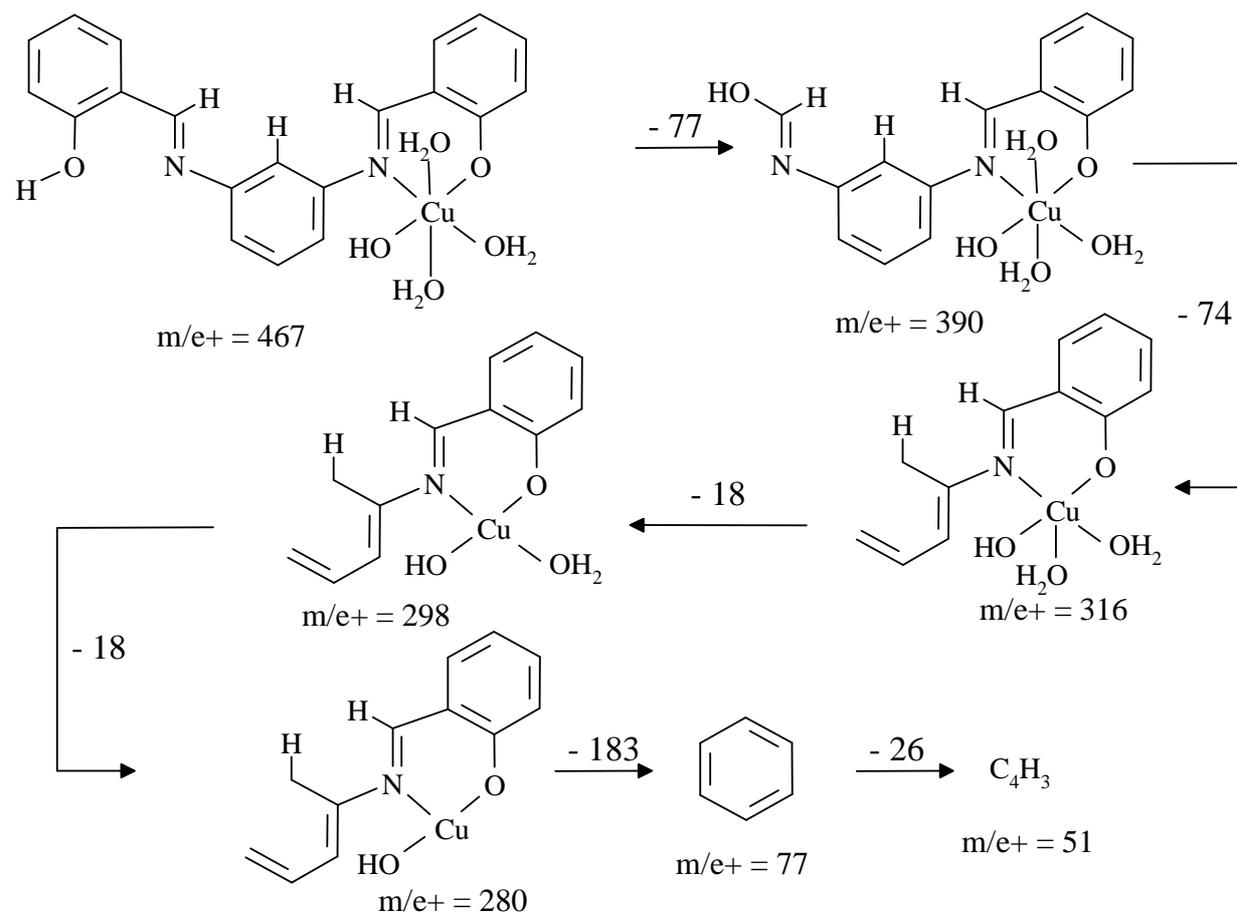
Mass spectrum of the Schiff base and the chelate

The mass spectral fragmentations of the Schiff base and its Cu(II) chelate are shown in schemes-1,2. For the Schiff base; base peak at $m/e+ = 316$ is attributed to the original molecular weight. Meanwhile, the peak at $m/e+ = 197$ is analogous to the loss of $\text{C}_7\text{H}_5\text{NO}$ from the Schiff base. The loss of CH_2O gives a peak at $m/e+ = 167$. The peak at $m/e+ = 115$ due to loss of C_4H_4 . The same spectrum shows a peak at $m/e+ = 77$ corresponding to loss of C_2N . A peak at $m/e+ = 51$ is due to the appearance of C_4H_3 . For Cu(II) chelate, the spectrum exhibits a peak at $m/e+ = 390$ due

to the loss to C_6H_5 . The peak at $m/e+ = 316$ corresponding to the loss of C_2H_2ON and H_2O . The peak at $m/e+ = 298$ assigned to the loss of H_2O molecule. The same spectrum shows a peak at $m/e+ = 280$ due to the loss of H_2O molecule. The appearance of a peak at $m/e+ = 77$ attributed to the loss of $C_6H_2NO_2Cu$. A peak at $m/e+ = 51$ is analogous to the appearance of C_4H_3 [27].



Scheme-1: Mass spectral fragmentations of the Schiff base



Scheme-2 : Mass spectral fragmentations of the Cu(II) chelate

Electron paramagnetic resonance spectrum of Cu(II) chelate

This technique is used to illustrate the deviation of the ideal value (2.0023) during the chelate formation. In the present chelate, the obtained g_{eff} (2.08581). This obtained deviation supports the existence of an octahedral geometry around the Cu(II) chelate [28].

CONCLUSION

From the previous analysis data, we can establish the geometrical structure of the Cu(II) chelate as shown in fig 1.

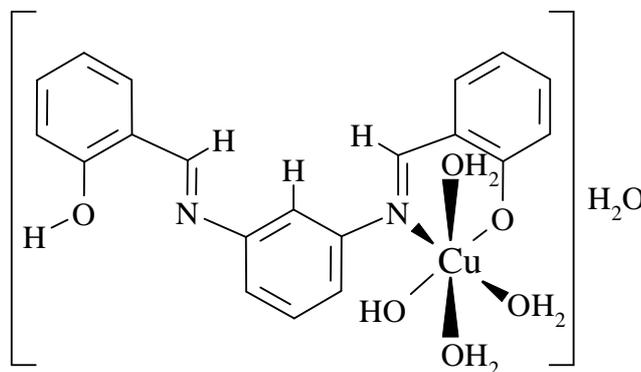


Fig-1: Geometrical structure of Cu(II) Schiff base chelate

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