

## **Nickel (II) Chelate of Schiff Base Derived from 4-dimethylamino-benzaldehyde with cysteine**

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**Summary.** Nickel (II) chelate of Schiff base derived from 4-dimethylamino-benzaldehyde and cysteine has been prepared and investigated by elemental analysis (C, H, N and S), molar conductance measurements, and spectroscopic methods, in particular; infrared, electronic spectra, <sup>1</sup>H-NMR and mass spectra. The elemental analysis data suggested the stoichiometry of 2:1[M: L] ratio. The molar conductance measurements revealed the presence of non-electrolytic nature. Infrared spectral data exhibited the chelation sites, which are through the nitrogen atom of the azomethine, oxygen atom of the hydroxyl group of the carboxyl group and the sulphur atom of the thio group of the cysteine moiety. The electronic spectral data displayed the presence of square planar geometry. The integration between mass spectrums with the other analysis data confirms the final conclusion of the investigation. As well, the <sup>1</sup>H-NMR spectral data exhibited the important signals that coordinated to the metal ion.

### **Introduction**

A Series of 6-aryl-5-hexene-2,4-diones and their chelates with Ni(II), Cu(II), Zn(II) and Pd(II) of composition  $Ml_4$  have been prepared investigated by different spectroscopic techniques. A square planar structures was suggested for Ni(II), Cu(II) and Pd(II) chelates, whereas tetrahedral suggested for Zn(II) chelate.<sup>(1)</sup> New complexes of Schiff bases which derived from Salicylaldehyde and o-aminophenol or o-aminobenzoic acid have been prepared and characterized by using different techniques in particular; infrared, electronic spectra and molar conductance measurements. A square planar geometry was predicted for the metal complexes.<sup>(2)</sup> Ternary complexes of Ni(II) with 1,2-diaminopropane, 1,3-diaminopropane-cysteine, o-Penicillamine and L-cysteic acid have been synthesized and characterized by using elemental analysis and spectral methods. The obtained complexes have a square planar geometry.<sup>(3)</sup>

The aim of this study is to illustrate the chemical structure of the Ni-Schiff base chelate under investigation.

## Experimental

### Chemicals

All chemicals used in this investigation were laboratory pure, including  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , DMSO,  $\text{CHCl}_3$ , 4-dimethylaminobenzaldehyde and cysteine.

### Preparation of Schiff base

The Schiff base used was prepared by mixing an ethanolic solution (50ml) of 4-dimethyl-aminobenzaldehyde (0.01mol) with cysteine (0.01mol) in the same volume of ethanol. The mixture then refluxed with stirring for two hours. The obtained precipitate collected by filtration through Buchner funnel, washed and recrystallized by using ethanol and then dried at room temperature in a desiccator over calcium chloride.

### Preparation of complexes

The Schiff base chelate with Nickel ion was prepared by mixing 25ml hot ethanolic solution of the Schiff base (0.01mole) with 25ml of the hot ethanolic solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.01mol, 2.37g). The obtained mixture was refluxed with stirring for two hours. Thus, the formed complex was filtrated, collected, and then washed several times with hot ethanol until the filtrate becomes colorless. The complex dried in a desiccator over anhydrous calcium chloride under vacuum. The yield estimated to be about 80%.

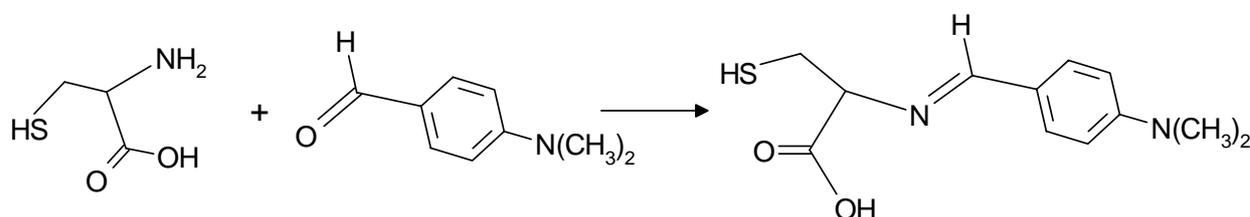
### Physical tools

The prepared metal chelate was subjected to elemental analysis, Molar conductance measurements and spectroscopic analysis at the Microanalytical Center, Cairo University, Egypt. The elemental analysis (C, H, N and S) The Molar conductance measurement carried out in DMSO solvent using conductivity meter model CMD650 digital. Infrared spectra were obtained by using IFS-25DPUS/IR spectrometer (Bruker) 1998Y. The electronic absorption spectrum measured in DMSO

using a Perkin-Elmer lambda 4 $\beta$ -spectrophotometer in 1Cm matched silica cells. The proton NMR spectrum of the complex recorded on a Varian Gemini 200MHz Spectrometer using d6-DMSO as solvent measured in a range of 0-14 ppm using TMS as internal standard.

### Results and Discussion

The condensation of 4-dimethylaminobenzaldehyde with cysteine in boiling ethanol yields one Schiff base compound. The chemical equations concerning the formation of the Schiff base and the complex represented as following:



#### Elemental analysis and Molar conductance measurements:

The elemental analysis data of the prepared Schiff base chelate [C% 30.50(29.54), H% 5.37(4.42), N% 10.75(10.4) and S% 6.75(6.55)] reveal that the chelate is formed in 2:1[M:L] ratio of the type [Ni<sub>2</sub>L(OH)<sub>3</sub>(H<sub>2</sub>O)].2H<sub>2</sub>O. The separated chelate is air stable and insoluble in most common organic solvents, but easily soluble in DMF and DMSO. The low molar conductance value of the chelate (2.80 Ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) indicates a non-electrolytic nature.<sup>(4)</sup>

#### Infrared spectrum

The infrared spectral data of the chelate of the type [Ni<sub>2</sub>L(OH)<sub>3</sub>(H<sub>2</sub>O)].2H<sub>2</sub>O display a broad band at 3433cm<sup>-1</sup> is due to the presence of water molecules in the chelate.<sup>(5)</sup> Bands at 1690 and 1620cm<sup>-1</sup> attributed to  $\nu_{(C=O)}$  of the -COOH and  $\nu_{(C=N)}$  stretching frequencies, respectively, in the spectrum of the free ligand(Schiff base; L) shift to lower values in the spectrum of metal chelate; 1621cm<sup>-1</sup> and 1585cm<sup>-1</sup> suggesting that -COOH and the azomethine nitrogen are coordinated to the metal ion.<sup>(6,7)</sup> The appearance of the two bands<sup>(6)</sup> at 2916 and 3024cm<sup>-1</sup> assigned to -CH<sub>3</sub> and -CH groups in the spectrum of the metal chelate compared with their position in the

free ligand. This is suggesting these groups are not involved in chelation with the metal ion.<sup>(8)</sup> The disappearance of  $\delta_{(\text{OH})}$  and  $\nu_{(\text{C-OH})}$  ( $1350$  and  $850\text{cm}^{-1}$ ) of vibrations, respectively support the participation of oxygen atom in the coordination with metal ion. The chelate exhibits two bands at  $453$  and  $539\text{cm}^{-1}$  attributed to the appearance of  $\nu_{(\text{M-N})}$  and  $\nu_{(\text{M-O})}$  vibrations.<sup>(9,10)</sup> Finally the data exhibit a band at  $300\text{-}360\text{cm}^{-1}$  can be attributed to the appearance of  $\nu_{(\text{M-S})}$  vibrations.<sup>(11)</sup>

### Electronic absorption spectrum

The electronic spectra data of the chelate under investigation which recorded in chloroform, show one band at  $707\text{nm}$  ( $14144\text{cm}^{-1}$ ) ascribed to  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$  transition, suggesting a square planar geometry.<sup>(12)</sup>

### ${}^1\text{H-NMR}$ spectrum

${}^1\text{H-NMR}$  spectral data of the  $[\text{Ni}_2\text{L}(\text{OH})_3(\text{H}_2\text{O})].2\text{H}_2\text{O}$  chelate were recorded in DMSO and show signals at  $2.30$  and  $1.35\text{ppm}$  corresponding to  $-\text{CH}_3$  and  $-\text{CH}_2$  groups respectively, and normally did not involve in the coordination. The multiplet signal at  $8.2\text{ppm}$  is due to aromatic protons, which is broadened and shifted to the lower field, suggesting that the complexation perturbs the electron density distribution through the phenyl ring to some extent. The  $-\text{OH}$  of the carboxyl group has been disappeared. The  $-\text{SH}$  signal is shifted and appeared at  $10.50\text{ppm}$  (higher field). These data support the involvement of these two groups in chelation. However the  $-\text{NH}_2$  group is disappeared on chelation formation, indicating the presence of azomethine group.<sup>(13)</sup>

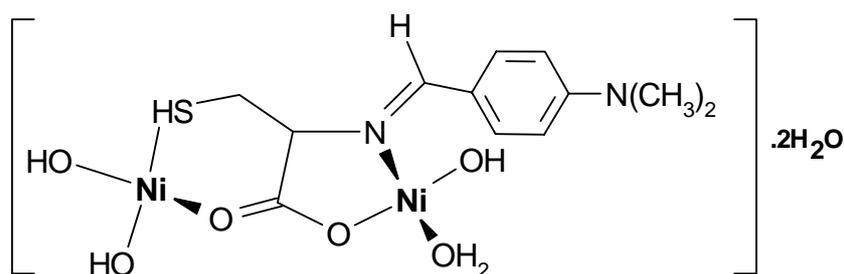
### Mass spectrum

Mass spectrometry permits the elucidation of the molecular formula. The interpretation of the mass spectrum requires an understanding of the ionization processes that occur before the ions reach the collector. The mass spectroscopy has proved extremely valuable for the estimation of accurate molecular weight, obtained molecular formulae, ionization potential and bond strength.<sup>(14)</sup> The mass spectrum of the Ni(II)-Schiff base chelate show some peaks illustrate the fragmentation of the chelate. The peak at  $(m/e^+ 283)$  corresponding to loss  $\text{C}_{10}\text{H}_{12}\text{NO}$  fragment from the original chelate of molecular weight ( $432.4\text{g/mol}$ ). The peak at  $(m/e^+ 197)$  is due to the

loss of CO-Ni fragment. The peak at ( $m/e^+$  107) gives the information about the fragmentation of NiS from the chelate. The peak at ( $m/e^+$  56) is attributed to the presence of three water molecules and two hydrogen atoms in the chelate.

### Conclusion

From the previous data (elemental analysis, molar conductance measurements, spectral techniques) one can conclude the proper geometrical structure of the Schiff base chelate under investigation. The elemental analysis data exhibit the formation of 2:1[M:L] ratio of the formula  $[\text{Ni}_2\text{L}(\text{OH})_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ . The molar conductance value reveals the presence of non-electrolytic compound. The spectral data exhibited the chelation sites of the chelate formation. In addition, these data show that the chelate has a square planar geometry. Moreover, the proper fragmentation of the chelate was suggested based on the literature.



**Figure:-** The proposed chemical structure of the chelate

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