

Nickel(II) Chelate of Schiff Base Derived from 4-Dimethylaminobenzaldehyde with Cysteine

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Nickel(II) chelate of Schiff base derived from 4-dimethylamino-benzaldehyde and cysteine has been prepared and investigated by physico-chemical techniques such as elemental analysis, molar conductance measurements, infrared, electronic, mass and ^1H NMR spectra. The elemental analysis data of the chelate suggest the stoichiometry of 2 : 1 [M : L] ratio. The molar conductance measurements reveal the presence of non-electrolytic nature. Infrared spectral data exhibit that the chelation may take place through the nitrogen atom of azomethine, the 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 display the presence of square-planar geometry.

Key Words: Ni(II), Chelates, Schiff Base, Cysteine.

INTRODUCTION

The Co(II) and Fe(III) complexes of various Schiff bases derived from isatin with some amino acid have been synthesized and identified on the basis of elemental analysis, infrared and electronic spectra. All complexes are suggested to possess an octahedral geometry¹. 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 and investigated by different spectroscopic techniques. A square-planar structure for Ni(II), Cu(II) and Pd(II) chelates, whereas tetrahedral structure for Zn(II) chelate have been suggested².

Maihub *et al.*³ reported some transition metal complexes of Schiff bases, which were derived from salicylaldehyde and *o*-aminophenol or *o*-aminobenzoic acid. A square-planar geometry was predicted for these metal complexes. 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 geometry⁴. The aim of this study is to illustrate the chemical structure of the Ni-Schiff base chelate under investigation.

EXPERIMENTAL

All chemicals used in this investigation were laboratory pure, including

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$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{C}_2\text{H}_5\text{OH}$, DMSO, CHCl_3 , 4-dimethylaminobenzaldehyde and cysteine.

Preparation of Schiff bases: The Schiff base (Fig. 1) used was prepared by mixing an ethanolic solution (50 mL) of 4-dimethylaminobenzaldehyde (0.01 mol) with cysteine (0.01 mol) in the same volume of ethanol. The mixture was then refluxed with stirring for 2 h. The obtained precipitate was collected by filtration through Buchner funnel, washed and recrystallized from ethanol and then dried at room temperature in a desiccator over calcium chloride.

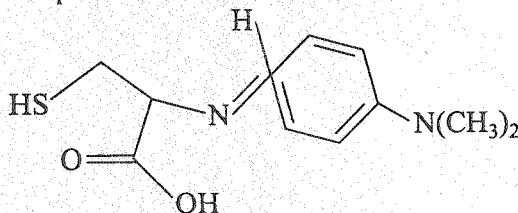


Fig. 1

Preparation of chelate: The nickel(II) chelate was prepared by mixing 25 mL hot ethanolic solution of the Schiff base (0.01 mol; 4.70 g) with 25 mL of the hot ethanolic solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol; 2.37 g). The reaction mixture was refluxed with stirring for 2 h. Thus, the formed complex was filtered, collected and then washed several times with hot ethanol until the filtrate becomes colourless. The chelate was dried in a desiccator over anhydrous calcium chloride under vacuum. The yield was estimated to be about 80%. The purity of the compound was confirmed by elemental analysis and TLC technique.

The present Ni(II) chelate was subjected to elemental analysis, molar conductance measurements and spectroscopic analysis at the Microanalytical Center, Cairo University, Egypt. The molar conductance measurement was 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 was measured in DMSO using a Perkin-Elmer Lambda 4 β spectrophotometer in 1 cm matched silica cells. The proton NMR spectrum of the complex was recorded on a Varian Gemini 200-200 MHz spectrometer using d^6 -DMSO as solvent, were measured in the 0–14 ppm range using TMS as reference.

RESULTS AND DISCUSSION

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 $[\text{NiL}(\text{OH})_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$. The 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 ($2.80 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) indicates a non-electrolytic nature⁵.

Infrared spectral data of the chelate of the type $[\text{NiL}(\text{OH})_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ display a broad band at 3433 cm^{-1} due to the presence of water molecules in the chelate⁶. Bands at 1690 and 1620 cm^{-1} that are attributed to $\nu(\text{C}=\text{O})$ of the

$\nu(-\text{COOH})$ and $\nu(\text{C}=\text{N})$ stretching frequencies respectively in the spectrum of the free ligand (Schiff base, L) shift to lower values in the spectrum of metal chelate, 1621 and 1585 cm^{-1} suggesting that $-\text{COOH}$ and the azomethine nitrogen are coordinated to the metal ion^{7, 8}.

The appearance of the two bands at 2916 and 3024 cm^{-1} is assigned to $-\text{CH}_3$ and $-\text{CH}$ groups in the spectrum of the metal chelate compared with their position in the free ligand. This suggests that these groups are not involved in chelation with the metal ion⁹. The disappearance of $\delta(\text{OH})$ and $\nu(\text{C}-\text{OH})$ (1350 and 850 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 cm^{-1} attributed to the appearance of $\nu(\text{Ni}-\text{N})$ and $\nu(\text{Ni}-\text{O})$ vibrations^{10, 11}. Finally, the data exhibit a band at 300–360 cm^{-1} that can be attributed to the appearance of $\nu(\text{Ni}-\text{S})$ vibrations¹².

The electronic spectral data of the chelate under investigation which are recorded in chloroform, show one band at 707 nm (14144 cm^{-1}) ascribed to ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ transition, suggesting a square-planar geometry¹³.

${}^1\text{H}$ NMR spectral data of the chelate of the form $[\text{NiL}(\text{OH})_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ recorded in DMSO and $\text{CH}_3\text{CO}_2\text{H}$ shows signals at 2.30 and 1.35 ppm corresponding to $-\text{CH}_3$ and $-\text{CH}_2$ groups respectively and normally are not involved in the coordination. The multiplet signal at 8.2 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 disappeared. The $-\text{SH}$ signal is shifted and appears at 10.50 ppm (high field). These data support the involvement of these two groups in chelation. However, the $-\text{NH}_2$ group disappears on chelation formation, indicating the presence of azomethine group¹⁴.

The mass spectrum of the Ni(II)-Schiff base chelate shows some peaks illustrating the fragmentation of the chelate. The peak at m/e 283 corresponds to loss of the $\text{C}_{10}\text{H}_{12}\text{NO}$ fragment from the original chelate of molecular weight (470.4 g/mol). The peak at m/e 197 is due to the loss of the CONi fragment. The peak at m/e 107 gives 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

The elemental analysis data exhibit the formation of 2 : 1 [M : L] ratio of the formula $[\text{NiL}(\text{OH})_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$. The molar conductance value reveal the presence of non-electrolytic compound with no inorganic anion outside the coordination sphere. The spectral data exhibit the chelation sites of the chelate formation, confirming that chelation takes place through oxygen, nitrogen and sulphur atoms of the different parts of the Schiff base as shown in Fig. 2. Also these data show that the chelate has a square-planar geometry.

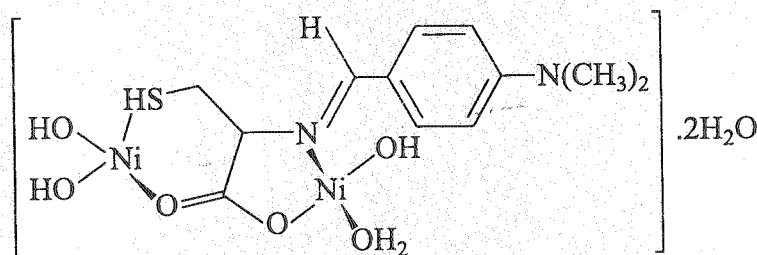


Fig. 2. The proposed structure of the chelate

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