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Research Article

**SYNTHESIS AND NMR STUDY OF HYDROXYQUINOXALINE
CARBOXALIDINE AMINO METHYL PHENOL COBALT (II)
METAL COMPLEX**

Daljeet Singh Manhas¹, Anuja Chauhan²

¹Assistant Professor, Department of Chemistry, Govt. College for Women,
Gandhi Nagar, Jammu (India).

²Associate Professor, Department of Chemistry, Arni University, Kathgarh, Indore,
Kangra (HP), India.

Abstract:

Transition metal complex of Schiff base formed by the condensation of quinoxaline-2-carboxaldehyde with 2-aminophenol or were synthesized and characterized by NMR spectroscopy. The phenolic OH and NH signals which are found at 12.85 and 11.52 ppm in the spectrum of the ligand are not seen in the spectrum of the Co (II) complex indicating the enolisation of the Schiff base in Co (II) complex and participation of the phenolic OH group in chelation with proton displacement

Keywords: *Condensation, carboxaldehyde, 2-aminophenol, Schiff base, NMR spectra*

Corresponding author:

Daljeet Singh Manhas,
Assistant Professor,
Department of Chemistry,
Govt. College for Women,
Gandhi Nagar, Jammu (India).
E-Mail: dalmanhas@gmail.com

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INTRODUCTION:

The Schiff base derived from salicylaldehyde and 2-aminophenol is well studied [1-5]. Several metal chelates coordinated through the Schiff base ONO donors have been studied as oxygen carriers and they are useful models for bioinorganic processes [8, 9]. Patel *et al.* [6-9] reported the crystal structures of the copper (II) complex of N-(salicylidene) anthranilic acid with imidazole, 2,2'-bipyridine or 1,10-phenanthroline as co ligands. These complexes were screened for superoxide dismutase activity. The ONO donor Schiff bases derived from salicylaldehyde and their transition metal complexes can be considered as non-enzymatic models for pyridoxal amino acid systems. The chemistry of the metal complexes of ONO donor Schiff bases is quite interesting because of their biological applications [10-12]. quinoxalines with ortho hydroxy groups are of particular interest due to their ability to form tautomers. They can form complexes in either neutral keto form or enolic form. Even though quinoxalines and their compounds have been extensively studied [13-15], the reports on the quinoxaline based Schiff bases are very scanty. The synthesis and characterization of quinoxaline-2-carboxaldehyde with 2-aminophenol was previously reported [16-17]. Our aim was to prepare new tridentate ONO donor Schiff base from 3-hydroxyquinoxaline-2-carboxaldehyde and 2-amino-5-methylphenol and study the nature of its complexes.

MATERIALS AND METHODS:

Cobalt (II) chloride hexahydrate (Merck), cobalt (II) acetate hexahydrate (Merck), 2-aminothiophenol, 2-amino-5-methylphenol were purchased from Sigma Aldrich Chemicals Private Limited,

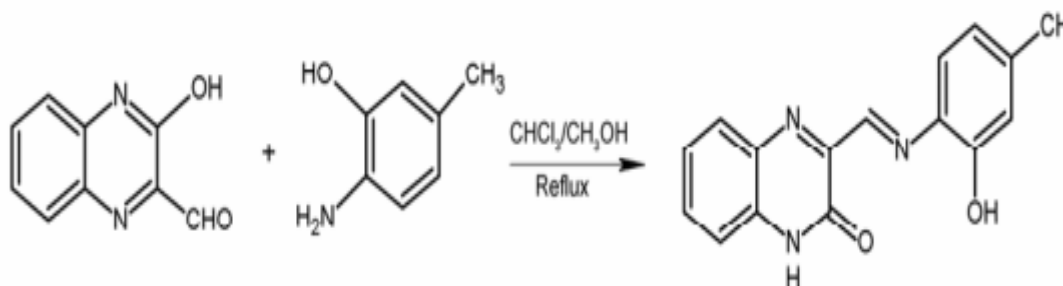
Delhi. Ortho-phenylenediamine (Lobachemie), D-glucose (SD Fine Chem Limited), sodium sulphate (Merck), sodium metaperiodate (Merck), glacial acetic acid, hydrazine hydrate (Qualigens), sodium bicarbonate (Sisco Research Laboratories Limited), bromine (Merck) and sodium pyruvate (Sisco Research Laboratories Limited) were used in the present investigation.

NMR analysis

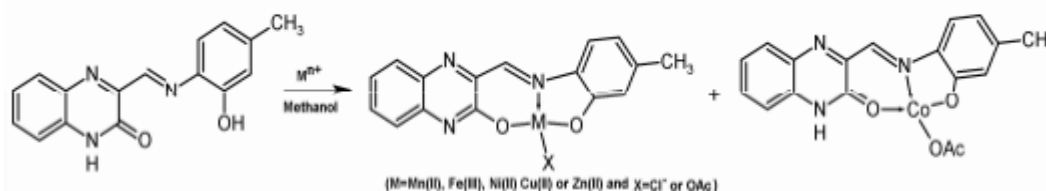
¹H NMR spectra were recorded in CDCl₃ or DMSO-d₆ on a Bruker AVANCE III 400 MHz -NMR spectrometer using TMS as the internal standard at the SAIF, Sophisticated Test and Instrumentation Chandigarh. NMR spectral data provide valuable information regarding the structure of Schiff bases. The NMR spectra of the Cobalt (II) complexes were also recorded to know the nature of binding of metal ion.

Synthesis of 3-{(E)-[(2-hydroxy-4-methylphenyl) imino] methyl} quinoxalin-2(1H)-one

To an aqueous solution of 3-hydroxyquinoxaline-2-carboxaldehyde (1.742 g, 10 mmol, in 500 mL distilled water), 3-4 drops of conc. HCl was added. To this solution was added drop wise 2-amino-5-methylphenol (1.231 g, 10 mmol) in methanol (20 mL). The solution was stirred for 6 hours. The red coloured Schiff base formed was filtered, washed with water and dried over anhydrous calcium chloride. The crude product was recrystallized from absolute ethanol. Formation of 3-{(E)-[(2-hydroxy-4-methylphenyl) imino] methyl} quinoxalin-2(1H)-one is presented in scheme 1. (Yield: 75 %, MP: 220 °C)



Scheme 1: Formation of 3-{(E)-[(2-hydroxy-4-methylphenyl) imino] methyl} quinoxalin-2(1H)-one



Scheme II: The formation of metal complexes

Preparation of Complexes

The Schiff base, amp, (0.01 mol, 0.279 g) was dissolved in 50 mL methanol. To this solution a solution of metal compound (0.01 mol: manganese acetate tetrahydrate 0.245 g, ferric chloride 0.162 g, cobalt acetate hexa hydrate 0.249 g, zinc acetate 0.219 g, cupric acetate 0.198 g or nickel acetate 0.249 g) in methanol (30 mL) was added. The solution was then refluxed for an hour and was then kept at room temperature (28 ± 2 °C) after reducing its volume by evaporation. The precipitate formed was filtered, washed with methanol and kept in a desiccator. The formation of metal complexes is given below scheme II.

RESULT AND DISCUSSION:

The complexes are stable in air and non-hygroscopic. They are soluble in common solvents like ethanol, methanol, acetonitrile and DMF. The analytical data shows that the carbon, hydrogen, Nitrogen, Chlorine, and Metal content of Schiff base and metal complex is found and calculated values are 69.15, 4.50, 14.00 for Carbon, Hydrogen, Nitrogen respectively while the found values are 68.8, 4.69, and 13.95 respectively. The analytic data found and calculated for Schiff base Cobalt metal complex is 47.96, 4.71, 9.15, and 13.11 for C, H, N, and M respectively. While the found values are 48.01, 4.70, 9.33, 13.05 respectively. Reveal that the complex is formed in metal: ligand ratio of 1:1.

NMR Study

The ^1H NMR spectrum of amp and that of the Co (II) complex shows low solubility in CDCl_3 , the NMR spectra of the Schiff base and Co (II) complex were made in deuterated DMSO. The spectral features suggest that the compound exist as keto tautomer. The co-existence of the tautomers is not observed. The broad singlet observed at 12.85 ppm is due to phenolic -OH proton. The broadness of the band indicates considerable hydrogen bonding in the Schiff base. The peak observed at 11.52 ppm is due to NH proton [18-24]. The azomethine proton

resonates at 9.15 ppm which is a singlet [25]. The multiplet observed around 6.40-8.30 ppm is due to aromatic protons of quinoxaline ring and phenolic ring. The peak due to methyl protons is observed at 2.26 ppm as a singlet. The phenolic OH and NH signals which are found at 12.85 and 11.52 ppm in the spectrum of the ligand are not seen in the spectrum of the Co(II) complex indicating the enolisation of the Schiff base in Co(II) complex and participation of the phenolic OH group in chelation with proton displacement [26-27]. The signals due to azomethine proton are shifted upon complexation, which is probably due to the donation of the lone pair of electrons by the nitrogen to the central metal atom [28]. ^1H NMR spectrum gives the aromatic and quinoxaline protons as a number of complex multiplets in the region 7.10–7.98 ppm. The methyl group attached to the phenolic ring is observed at 2.22 ppm as a singlet. The broad singlet in the region 3.51– 3.80 ppm indicates the presence of a water molecule in the complex.

CONCLUSION:

A new Schiff base derived from 3-hydroxy quinoxaline-2-carboxaldehyde and 2-amino-5-methylphenol and its complex Co (II) have been synthesized and characterized. Based on the physicochemical and spectroscopic studies we propose the following structures for the complex. The multiplet observed around 6.40-8.30 ppm is due to aromatic protons of quinoxaline ring and phenolic ring. The peak due to methyl protons is observed at 2.26 ppm as a singlet.

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