

**SYNTHESIS, SPECTRAL CHARACTERISATION AND CRYSTAL
STRUCTURE OF NOVEL CHIRAL N₂O₂ SCHIFF BASE COMPLEXES**

Final Report of the Major Research Project
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SYNTHESIS, SPECTRAL CHARACTERISATION AND CRYSTAL STRUCTURE OF NOVEL CHIRAL N_2O_2 SCHIFF BASE COMPLEXES

1. Project Abstract

The basic strategy of this project is to develop few chiral N_2O_2 Schiff bases and their metal complexes. The steric and electronic properties of the chiral Schiff base metal complexes can be easily tuned by suitable alterations in the Schiff base portion. The heterocyclic aldehyde, 3-hydroxyquinoxaline-2-carboxaldehyde, will be used for the synthesis of chiral Schiff base ligands. Four new chiral Schiff base ligands, N,N' -bis(3-hydroxyquinoxaline-2-carboxalidine)- $R-(+)$ -2,2'-diamino-1,1'-binaphthyl, N,N' -bis(3-hydroxyquinoxaline-2-carboxalidine)- $S-(-)$ -2,2'-diamino-1,1'-binaphthyl, N,N' -bis(3-hydroxyquinoxaline-2-carboxalidine)- $(R,R')-(+)$ -1,2-diphenyl-1,2-diaminoethane and N,N' -bis(3-hydroxyquinoxaline-2-carboxalidine)- $(S,S')-(-)$ -1,2-diphenyl-1,2-diaminoethane has been synthesized. The present project resulted in the synthesis of new four chiral N_2O_2 Schiff bases by the condensation of 3-hydroxy quinoxaline 2-carboxaldehyde and chiral amines like 2,2'-diamino-1,1'-binaphthyl and 1,2-diphenyl-1,2-diaminoethane. We have developed a detailed three step synthetic procedure in the synthesis of 3-hydroxy quinoxaline 2-carboxaldehyde. We could not further go beyond this due to the lack of further financial assistance. However, we have synthesized and characterized a new copper complex of the Schiff base obtained by the condensation of 3-hydroxy quinoxaline 2-carboxaldehyde and 1,2 diamino benzene and results are published in a journal.

2. Project Description

2.1 Introduction:

Since the inception of Jacobsen and Katsuki's catalysts, the chiral N_2O_2 Schiff base transition metal complexes have attracted the researchers in the field of asymmetric catalysis [1]. However, little is known about quinoxaline chiral N_2O_2 Schiff base chelates. The steric and



electronic properties of the chiral Schiff base metal complexes can be easily changed by suitable alterations in the Schiff base portion. Now a day, construction of optically active metal centers has attracted much interest in main group chemistry also [2]. The chirality can be constructed by simply attaching different chiral ligands to the metal centre. The chiral ligands that modify intrinsically achiral metal atoms must possess suitable three-dimensional structures and functionality, to generate sufficient reactivity and the desired stereoselectivity [3]. The chiral Schiff base ligands formed by the condensation of 3-hydroxyquinoxaline-2-carboxaldehyde and chiral amines like (R,R')-(+)-1,2-diphenyl-1,2-diaminoethane, (S,S')-(-)-1,2-diphenyl-1,2-diaminoethane, R-(+)-2,2'-diamino-1,1'-binaphthyl and S-(-)-2,2'-diamino-1,1'-binaphthyl have not been reported yet. These fully aromatic chiral Schiff base ligands may exert strong steric and electronic influences on its metal complexes. It is therefore thought worthwhile to synthesize and characterize some new asymmetric Schiff base having quinoxaline rings and its metal complexes and to compare how effective would be these complexes when compared to those derived from salicylaldehyde.

2.2 Methodology

This research project involves the synthesis of novel Schiff bases and their metal complexes. New chiral Schiff base ligands will be prepared by the condensation of heterocyclic aldehyde, 3-hydroxyquinoxaline-2-carboxaldehyde, with chiral amines like 2,2'-diamino-1,1'-binaphthyl and 1,2-diphenyl-1,2-diaminoethane. The proposed synthetic routes to the chiral Schiff bases and their metal complexes involve the following steps.

2.2.1. Synthesis of chiral Schiff ligands.

Novel chiral Schiff base ligands, N,N'-bis(3-hydroxyquinoxaline-2-carboxalidine)-R-(+)-2,2'-diamino-1,1'-binaphthyl, N,N'-bis(3-hydroxyquinoxaline-2-carboxalidine)-S-(-)-2,2'-



diamino-1,1'-binaphthyl, N,N'-bis(3-hydroxyquinoxaline-2-carboxalidine)-(R,R')-(+)-1,2-diphenyl-1,2-diaminoethane and N,N'-bis(3-hydroxyquinoxaline-2-carboxalidine)-(S,S')-(-)-1,2-diphenyl-1,2-diaminoethane, synthesized by adopting the following synthetic methods.

2.2.1a. Synthesis of 3-hydroxyquinoxaline-2-carboxaldehyde.

The aldehyde, 3-hydroxyquinoxaline-2-carboxaldehyde, has been synthesized by the procedure of V. Arun *et al.* [4]. This synthesis involved a three-step procedure starting from o-phenylenediamine and sodium pyruvate.

2.2.1b. Condensation of 3-hydroxyquinoxaline-2-carboxaldehyde with chiral diamines.

Synthesized 1:2 condensation products between chiral diamine ((R,R')-(+)-1,2-diphenyl-1,2-diaminoethane, (S,S')-(-)-1,2-diphenyl-1,2-diaminoethane, R-(+)-2,2'-diamino-1,1'-binaphthyl and S-(-)-2,2'-diamino-1,1'-binaphthyl) and 3-hydroxyquinoxaline-2-carboxaldehyde (Figures 1 and 2). The attempts to grow single crystals of these chiral Schiff bases not successful yet.

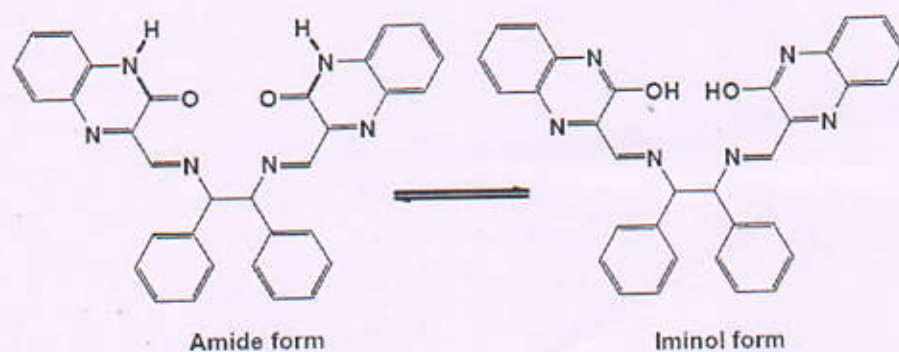


Figure 1: Expected general structure of the chiral Schiff base ligands form (R,R')-(+)/(S,S')-(-)-1,2-diphenyl-1,2-diaminoethane.



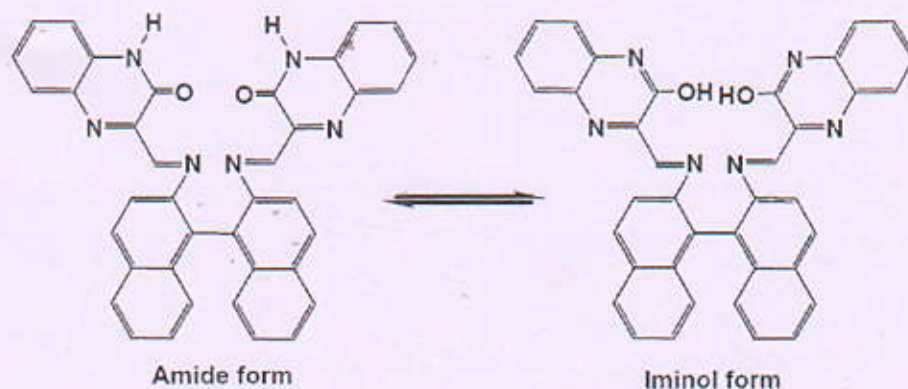


Figure 2: Expected general structure of the chiral Schiff base ligands form R-(+)/S-(-)-2,2'-diamino-1,1'-binaphthyl.

3. Results

At this stage, in the year 2016, the project was stopped as the UGC not released the balance sanctioned amount of the Project. We could not proceed further because of the cost of chemicals and characterizations techniques. However, I have synthesized and characterized a new copper complex of the Schiff base obtained by the condensation of 3-hydroxy quinoxaline 2-carboxaldehyde and 1,2 diamino benzene and results are published in a journal (*DOI: 10.5958/2320-320X.2021.00015.7*).

4. References

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