

Experimental techniques and synthesis of aldehydes

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2.1 INTRODUCTION

Details about the general reagents used, preparation of the aldehydes and various analytical and physicochemical methods employed in the characterization of ligands and complexes are discussed in this chapter. Procedural details regarding the synthesis of ligands and metal complexes and characterization of ligands and complexes are given in the appropriate chapters.

2.2 REAGENTS

The following metal salts were used:

Manganese(II) chloride tetrahydrate (Merck), manganese(II) acetate tetrahydrate (Merck), anhydrous ferric(III) chloride (Qualigens), cobalt(II) chloride hexahydrate (Merck), cobalt(II) acetate hexahydrate (Merck), nickel(II) chloride hexahydrate (Merck), nickel(II) acetate hexahydrate (Qualigens), copper(II) chloride dihydrate (Merck), copper(II) acetate dihydrate (Merck) and zinc(II) acetate dihydrate (Merck).

The amines, 2-aminothiophenol, 2-amino-5-methylphenol and L-histidine, were purchased from Sigma Aldrich Chemicals Private Limited, Bangalore. Orthophenylenediamine (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.

Hydrogen peroxide (30 % w/v, Merck), cyclohexane (Qualigens), phenol (Merck) and benzyl alcohol (SRL) were used for the catalytic activity studies using metal complexes. Gas cylinders containing oxygen, nitrogen or hydrogen (Sterling gases, Cochin) were also used for the catalytic activity studies. All other reagents were of analytical reagent grade and the solvents employed were either of 99 % purity or purified by known procedures [1].

2.3 SYNTHESIS OF ALDEHYDES

The aldehydes selected were quinoxaline-2-carboxaldehyde and 3-hydroxyquinoxaline-2-carboxaldehyde. The synthetic steps for the preparation of aldehydes are given below:

2.3.1 Synthesis of quinoxaline – 2– carboxaldehyde

The following procedure was adopted to synthesize quinoxaline –2–carboxaldehyde [2, 3]. Refluxing D-glucose (36 g, 0.2 mol) with orthophenylenediamine (21.6 g, 0.2 mol) in the presence of hydrazine hydrate (5 mL, 0.1 mol) and glacial acetic acid (6 mL) on a boiling water bath under carbon dioxide atmosphere (provided by the addition of a pinch of sodium bicarbonate) for 5 hours gave the compound, 2(D-arabinotetrahydroxybutyl)quinoxaline. This product was purified by recrystallisation from hot water. The recrystallised 2(D-arabinotetrahydroxybutyl)quinoxaline (5 g, 0.02 mol) was dissolved in water (300 mL) containing glacial acetic acid (10 mL) and sodium metaperiodate

(13 g, 0.06 mol) and was kept at room temperature (28 ± 2 °C) with controlled stirring for 16 hours. It was then filtered and the filtrate was neutralised with sodium bicarbonate. The neutral solution was then extracted with ether. The ether extract was dried with anhydrous sodium sulphate. It was then filtered and evaporated to dryness. The resulting residue was recrystallized from petroleum ether to give pure quinoxaline-2-carboxaldehyde (Figure 2.1) (Yield: 60%, M.P.: 107 °C).

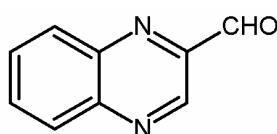


Figure 2.1: Structure of quinoxaline-2-carboxaldehyde

2.3.2 Synthesis of 3-hydroxyquinoxaline – 2– carboxaldehyde

A procedure different from that of Ohle [2] was used to synthesize 3-hydroxyquinoxaline-2-carboxaldehyde, as it can be used directly for preparation of Schiff base ligands without further purification. Figure 2.2 gives the structure of 3-hydroxyquinoxaline-2-carboxaldehyde.

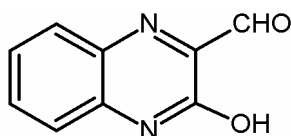
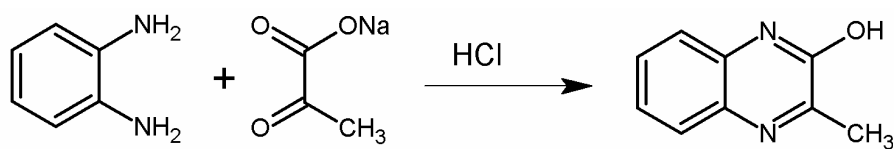


Figure 2.2: Structure of 3-hydroxyquinoxaline-2-carboxaldehyde

2.3.2.1 3-Hydroxy-2-methylquinoxaline

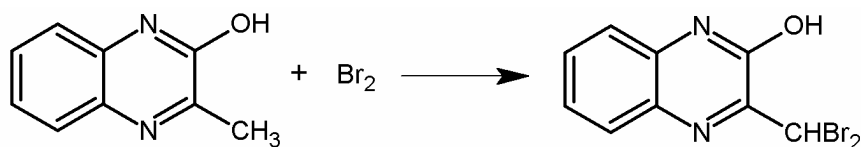
O-Phenylenediamine (0.1 mol, 10.8 g) and sodium pyruvate (0.1 mol, 11 g) were dissolved in 250 mL water. A slight excess of con. HCl was needed to convert sodium pyruvate to pyruvic acid. The solutions were then mixed and stirred for 30 minutes. The precipitated yellow compound (Scheme 1) was then filtered and dried over anhydrous calcium chloride. (Yield: 90 %, m.p.: 255 °C)



Scheme 1

2.3.2.2 3-Hydroxy-2-dibromomethylquinoxaline

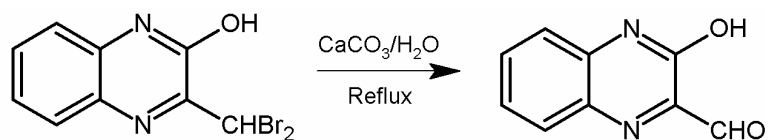
3-Hydroxy-2-methylquinoxaline (0.1 mol, 16.2 g) was dissolved in glacial acetic acid (200 mL). To this, 10% (v/v) bromine in acetic acid (110 mL) was added and kept in sunlight for 1 hour with occasional stirring. The solution was then diluted to 1 L with water and the precipitated dibromo derivative (Scheme 2) was filtered and purified by recrystallisation from 50% alcohol (Yield: 95 %, m.p.: 246 °C).



Scheme 2

2.3.2.3 3-Hydroxyquinoxaline-2-carboxaldehyde

The dibromo compound (0.0157 mol, 5 g) was thoroughly mixed with 20 g of precipitated calcium carbonate. This was taken in a 3 L round bottom flask containing water (1.5 L). The solution was kept on a water bath with timely stirring for 3 hours. The aldehyde formed remains in aqueous solution (Scheme 3). This yellow solution was collected by filtration is very stable and can be used to prepare the Schiff bases.



Scheme 3

The aldehyde and the compounds involved in the preparation of the aldehyde are characterized by various physicochemical and spectral studies. The details of the characterizations are given in a paper published from our group [4], and the data agrees with that for the present compounds.

2.4 PREPARATION OF SCHIFF BASES

We have synthesized three new Schiff base ligands by taking quinoxaline-2-carboxaldehyde or 3-hydroxyquinoxaline-2-carboxaldehyde. The amines chosen were 2-aminothiophenol, L-histidine and 2-amino-5-methylphenol. The ligands synthesized are:

1. quinoxaline-2-carboxalidine-2-amino-5-methylphenol (qamp)
2. 3-hydroxyquinoxaline-2-carboxalidine-2-aminothiophenol (hatp)
3. 3-hydroxyquinoxaline-2-carboxalidine-2-amino-5-methylphenol (hamp)

The ligand qamp is monoprotic. The ligands, hatp and hamp, are diprotic and exhibit tautomerism, and hence they coordinate with metal center either in keto form or in enol form in neutral condition. We could not isolate the Schiff base quinoxaline-2-carboxalidine-L-histidine (qlh), hence complexes of this ligand were prepared using template method. The formation of Schiff base complexes through the rearrangement of benzothiazoline is also studied. The details regarding synthesis of the Schiff bases are given in respective chapters.

2.5 CHARACTERIZATION TECHNIQUES

2.5.1 CHN analysis

Microanalysis for carbon, hydrogen, nitrogen and sulphur in the synthesized ligands and complexes were carried out on an Elementar model Vario EL III at Sophisticated Analytical Instrument Facility (SAIF), Sophisticated Test and

Instrumentation Centre (STIC), Kochi. These results give an idea about the structure of the ligands and complexes.

2.5.2 Estimation of metal ions

In all the cases, the organic part of the complexes was completely eliminated before the estimation of metal ions. The following procedure was adopted for this purpose in the case of all the complexes. A known weight (0.2–0.3 g) of the metal complex was treated with concentrated sulphuric acid (5 mL) followed by concentrated nitric acid (20 mL). After the reaction has subsided, perchloric acid (5 mL, 60 %) was added. This mixture was kept aside until the colour of the solution changes to that of the metal salt. The clear solution thus obtained was evaporated to dryness on water bath. After cooling, concentrated nitric acid (15 mL) was added and was again evaporated to dryness on a water bath. The residue was dissolved in water and this neutral solution was used for the estimation of metals. The estimation of metals was carried out on a Thermo Electron Corporation, M series Atomic Absorption Spectrophotometer.

2.5.3 Estimation of chloride

Chlorine present in the complexes was converted into soluble sodium chloride by the peroxide fusion. An intimate mixture of the complex (0.2 g) sodium carbonate (3 g) and sodium peroxide (2 g) was fused on a nickel crucible for nearly two hours. It was then treated with concentrated nitric acid. Chloride was then volumetrically estimated by Volhard's method [5]. Chloride was precipitated as silver chloride by the addition of a known volume of standard silver nitrate solution. The excess silver nitrate was titrated against standard ammonium thiocyanate solution using ferric alum as indicator.

2.5.4 Conductance Measurements

Molar conductance values of the complexes were measured using a systronic conductivity bridge type 305. The solvent used was methanol, DMF or dimethyl sulphoxide. The molarity of the solution was 10^{-3} M.

2.5.5 Electronic spectra

Electronic spectroscopy is a valuable tool for coordination chemists to draw important information about the structural aspects of the complexes. The ligands, which are organic compounds, have absorption in the ultraviolet region and in some cases these bands extend to higher wavelength region due to conjugation. Upon complexation with transition metal ions, changes will take place in the electronic properties of the system. New features or bands in the visible region due to d-d absorption and charge transfer spectra from metal to ligand (M→L) or ligand to metal (L→M) can be observed and this data can be processed to obtain information regarding the structure and geometry of the complexes. The electronic spectra of the complexes in solution phase (0.0005 molar) were recorded in the region 200-1100 nm on a Thermoelectron Nicolet evolution 300 UV-Vis spectrophotometer. In the solution phase some important d-d bands, which are important in assuming geometry, were obscured. In such cases, the spectra were also taken in the solid state using the mull technique [6].

2.5.6 IR Spectra

The vibrational states of a molecule can be probed in a variety of ways. The most direct way is infrared spectroscopy because vibrational transitions typically require an amount of energy that corresponds to the infrared region of the spectrum between 4000 and 400 cm^{-1} (wavenumbers). The IR spectra provide valuable information regarding the structure of the complex and the nature of the functional groups present. Hence it can be used as an effective tool to confirm the formation of the complexes and to determine the mode of coordination of ligands to the

transition metals. Infrared spectra of the ligands and simple complexes were recorded using Jasco-8000 Fourier Transform Infrared Spectrophotometer.

2.5.7 NMR spectra

^1H NMR spectra were recorded in CDCl_3 or DMSO-d_6 on a Bruker AVAVCE III 400 MHz -NMR spectrometer using TMS as the internal standard at the SAIF, Sophisticated Test and Instrumentation Centre, Kochi. NMR spectral data provide valuable information regarding the structure of Schiff bases. The NMR spectra of the zinc(II) complexes were also recorded to know the nature of binding of metal ion.

2.5.8 EPR spectra

EPR spectroscopy is a reliable method to determine the geometry and electronic structure of the complexes. The EPR spectra of the complexes in DMF were recorded on Varian E-112 X/Q band spectrophotometer at liquid nitrogen temperature and the standard used was tetracyanoethylene (TCNE) with a g value of 2.0027. The EPR spectra of transition metal complexes contain a wealth of information about their electronic structures. The interpretation of the EPR spectra of these complexes can be done on the basis of the ligand field theory. The degeneracy of the d orbitals and the presence of the unpaired electrons give rise to orbital contributions as a result of which anisotropic g values are obtained.

2.5.9 Magnetic susceptibility measurements

The magnetic susceptibility measurements were done at room temperature (28 ± 2 °C) on a simple Gouy-type balance. The Gouy tube was standardized using $\text{Co}[\text{Hg}(\text{SCN})_4]$ as standard as recommended by Figgis and Nyholm [7]. The effective magnetic moments were calculated using the equation.

$$\mu_{\text{eff}} = 2.84 (\chi_m T)^{1/2} \text{ B.M.}$$

Where T is the absolute temperature and χ_m is the molar susceptibility corrected for diamagnetism of all the atoms present in the complex using pascals constants [8-10]. The magnetic susceptibility measurements were done on a Magway MSB Mk 1 Magnetic Susceptibility Balance.

2.5.10 Thermogravimetric analysis

Thermogravimetric analysis is an effective tool to study the nature of decomposition of the metal complexes. The thermal stability of the synthesized complexes can be determined using this method. In this technique, the sample under consideration is heated at a controlled rate in an atmosphere of nitrogen and the mass of the substance is recorded as a function of temperature. The major advantage of this method is that it can directly give idea about the upper limit of thermal stability of a material. The thermograms obtained are characteristic for a given sample due to the unique sequence of physico-chemical reactions occurring over definite temperature ranges which in turn depends upon the structure of the molecule. The changes in weight occur as a result of the rupture or formation of various physical and chemical bonds at elevated temperatures. This may lead to the evolution of volatile products or the formation of heavier reaction products. TG analyses were carried out on a Perkin Elmer, Diamond thermogravimetric analyser at a heating rate of 10 °C per minute in an atmosphere of nitrogen.

2.5.11 Single crystal XRD

The diffraction/scattering of X-ray radiations by array of atoms in a single crystal of a compound is exploited to establish the structure and geometry of the complexes. At present this versatile technique is valued as the final word by many chemists for establishing the accurate structure of the complex compounds. X-ray crystal structure determination was performed with a Bruker SMART APEX CCD X-ray diffractometer at University of Hyderabad and at CSMCRI Gujarat using graphite monochromated MoK α radiation ($\lambda=0.71073$ Å, φ and ω scans). The data was reduced using SAINTPLUS [11] and a multiscan absorption correction using

SADABS was performed [12]. The structure was solved using SHELXS-97 and full matrix least squares refinement against F^2 was carried out using SHELXL-97 in anisotropic approximation for non-hydrogen atoms [13]. All hydrogen atoms were assigned on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms.

2.5.12 Gas Chromatography

The analysis of the reactants and products of the different catalytic reactions was conducted using a Chemito 8510 Gas Chromatograph. In gas chromatography, the separation is carried out in a tubular column made of metal and an adsorbent which serves as the stationary phase is filled in this column. The carrier gas serving as the mobile phase is made to flow continuously through the column. The instrumentation consists of a tank of carrier gas, an injection port for introducing the sample, the column and a detector. The various components in the reaction mixture were separated using an OV-17 or carbowax column. The peaks appearing on the recorder are characteristic of the different components. The peak area is found to be proportional to the amount of the component present in the mixture.

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