



STUDY OF NOVEL SCHIFF BASE LIGAND WITH RESPECT TO ITS ANALYTICAL APPLICATIONS

Dr. Akramullah Khan

Associate Professor, P.G. Dept. Of Chemistry, Purnea College, Purnea.

ABSTRACT:

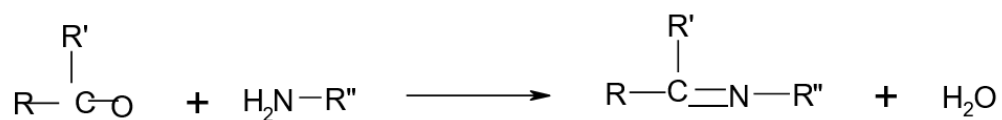
Novel Schiff bases were synthesized from substituted 2-hydroxy benzaldehydes and dihydrazide. These Schiff bases were used to prepare metal complexes. The complexes were distinctly coloured and stable to atmospheric conditions. Schiff bases are considered as privileged ligand in coordination chemistry as they easily form stable complexes with most transition metal complexes. Schiff bases were shown to behave as a tetradentate ligand. The metal complexes were proposed to square planar geometry and 1:1 metals to ligands ratio was suggested, One of the ligand was studied for spectrophotometric determination of Cu (II) (Extractive spectrophotometry), The stability constants of their complexes with Copper (II) ions and Nickel (II) ions, have been studied.

KEYWORDS: Schiff Base, Complexes, Metal Complexes, Ligands.

INTRODUCTION:

The Schiff base ligands and their metal complexes have special importance in the field of coordination chemistry. As the present work deals with the complexes of schiff base ligands, it is appropriate to include a brief general discussion on the chemistry of Schiff bases and their metal complexes.

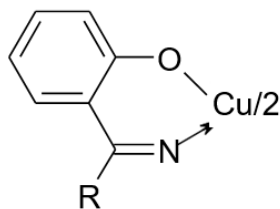
Hugo Schiff, a German chemist, isolated [1] the first condensed product of amines with carbonyl compounds, which he referred to as Schiff base. Thus the Schiff bases are the organic compounds containing azomethine $-R-C=N-$ group and are usually formed by the condensation of a primary amine with an active carbonyl compound. In general a Schiff base can be prepared as follows:



The above reaction is acid catalyzed and is generally carried out by refluxing the carbonyl compound and amine with an azeotroping agent if necessary and separating the water formed in the reaction.

The Schiff base metal complexes have an old history, in the beginning of the 18th century preceding the work of S. M. Jorgensen and Werner, Etting[2] in 1840 isolated a dark green crystalline

product from the reaction of cupric acetate, Salicylaldehyde and aqueous ammonia. This product was undoubtedly [bis(salicylaldehyde)Cu(II)]. In 1869 Schiff [3] established the 1:2 metal-ligand stoichiometry and later reported the complexes of Schiff base of urea and salicylaldehyde.



The synthesis and properties of Schiff base complexes are very often related to the associated metal and these aspects have been discussed in detail by Lindoy and Layer [4,5].

Uses of Schiff bases and their metal complexes

The Schiff base ligands and their metal complexes have special importance in the field of coordination chemistry. A survey of the literature shows that, in recent times, increasing number of studies has been devoted to the synthesis and structural studies. However, the utility aspects of the Schiff bases and their metal complexes have received their share of attention with an all round progress in the field of coordination chemistry. The importance of Schiff bases and their metal complexes with transition metals have been well emphasized by several researchers.

Materials and methodology

Chemicals used for this work like substituted hydroxyl benzaldehyde, hydrazine hydrate, diethyl malonate, metal salts, Ethanol, chloroform, methanol, distilled water, Acetone cobalt standard, Nickel standard etc were of analytical grade.

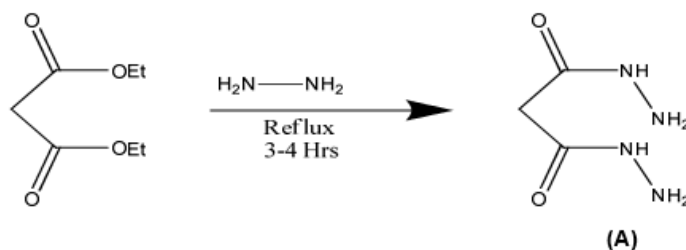
EXPERIMENTAL

General procedures:

Step 1: Preparation of compound A.

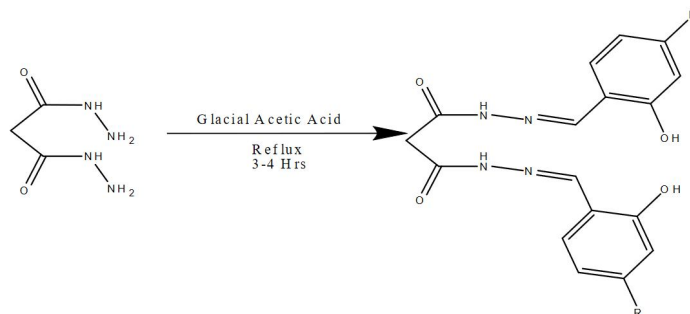
Diethyl malonate (0.1mol) & Hydrazine hydrate (0.2mol) were refluxed in a 3-necked round bottom flask fitted with water condenser for 4-5 hrs. Hydrazine hydrate was added in excess. White water-soluble residue precipitated out with exothermic reaction. The solid was filtered off. This is Compound A. It is recrystallized with hot absolute Alcohol (99%).

Reaction:



STEP 2: Preparation of compound (I). (Schiff Base Ligand)

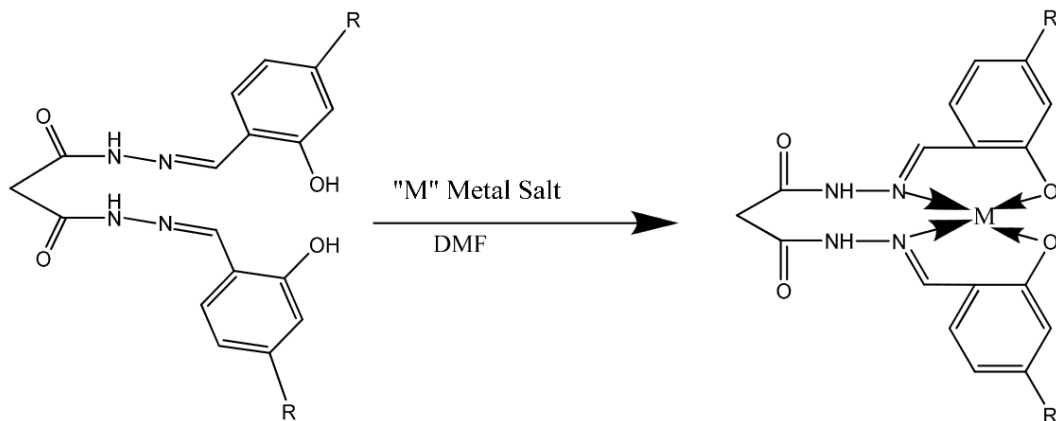
Compound A(0.1mol) was dissolved in glacial acetic acid. Substituted 2-hydroxy-1- benzaldehyde (0.1mol) was added to it & refluxed for 3-4hrs. The reaction was monitored by TLC On cooling the reaction mixture coloured solid compound precipitated out. The residue was filtered off and recrystallized using absolute alcohol. This is compound I. R= -H, -NO₂, -Br. [I (a), (b), (c).]



STEP 3: (I-a,b,c) Preparation of compound (II). (Schiff Base)

Compound I(a) - (c) (0.1mol) was dissolved in DMF (Dimethyl formamide). Metal salt was dissolved in DMF in test tube. Both the hot solutions were mixed in a round bottom flask and refluxed for 8-10 hrs. The solution on cooling was then dumped in cold water. Colored Solid compound precipitated out. It was then filtered off & recrystallized using absolute alcohol. Here M= Cu and Ni. Compounds [I,II (a)- (f)]

Reaction:



Applications

Extractive Spectrophotometry

Spectrophotometry facilitates the determination of the concentration of coloured substances in a solution and has been employed for the analysis of metals at the trace levels. Spectrophotometry is based on the quantitative study of absorption of radiation. Spectrophotometry can be classified, namely UV Spectrophotometry and Visible Spectrophotometry.

UV Spectrophotometric methods have been applied extensively for the identification of aromatic hydrocarbons, vitamins, steroids, heterocyclic and conjugated aliphatic compounds. In biochemical and pharmaceutical research, UV absorption spectra are often used to identify degradation products and to test purity. The detection of characteristic UV absorption bands of contaminant is used

as a guide to check the purity, while the constancy of molar absorptivity at a specific wavelength on additional purification steps is indicative of purity.

Solvent Extraction

Solvent extraction methods have been extensively investigated in the past few years as a promising alternative for the recovery, concentration and separation. The best evidence for the usefulness of the technique of solvent extraction in chemical science is the large number of research papers those appear in the literature, showing its analytical and industrial importance. Morrison and Freiser [6] have written a comprehensive monograph on solvent extraction chemistry. The solvent extractions of metal chelate complexes have been reviewed from the stand point of chemistry by Stary and Zolotov [7, 8]. Mercus and Kertes [9] have discussed the ion exchange and solvent extraction of metal complexes. The analytical use of solvent extraction of metals has been published by De. et al [10]. Two important articles on solvent extraction of inorganic substances have been reviewed by Dimond, Tuck and Marcus [11,12]. The chemical aspects, fundamentals and applications of solvent extraction have been compiled very elegantly by Sekine and Hasegawa [13].

A class of organic compounds, Schiff base, also known as anil, azomethine or imine, has acquired a place of prime importance due to their varied applications when utilized as a ligand in the formation of metal complexes. In the polydentate Schiff base ligands, along with main functional group azomethine, the other donor sites contain various electronegative atoms such as oxygen, nitrogen and sulphur. The Schiff bases have been effectively used as an analytical reagent⁴⁷⁻⁴⁹ for extractive / direct spectrophotometric determination of metal ions, as they possess excellent ligational properties. Looking at the importance of the different classes of ligands, we have tried to explore the property of Schiff base ligand as an analytical reagent for extractive and / or direct spectrophotometric determination of heavy metal ions in trace levels.

The respective reagent reacts with copper (II) to give colored complex, which is extracted into organic solvent. Various experimental parameters like pH, equilibrium time, reagent concentration, stability etc. have been studied and optimized. The nature of extracted species has been determined by Job's variation method and mole ratio method, further confirmed by the slope ratio method. The effect of foreign ions on the extraction has been studied and their tolerance limits have been determined. The proposed method has also been employed for estimation of copper in various synthetic.

RESULTS AND DISCUSSION

Copper (II) and Nickel (II) Forms colored complex with derived Schiff bases ligands, which was quantitatively extracted in chloroform in the alkaline medium. The extraction of metal complex from the aqueous phase into organic phase was studied over wide range of experimental conditions. The results obtained during various studies are discussed below.

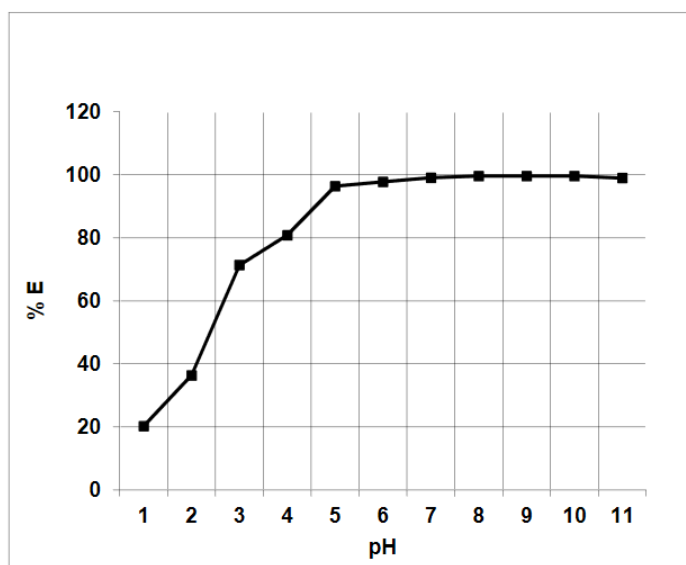
Effect of pH

The extraction of copper (II) was carried over the pH range of 1.0 to 11.0 [Table.1].

Table 1: The relative caution selectivity and PH

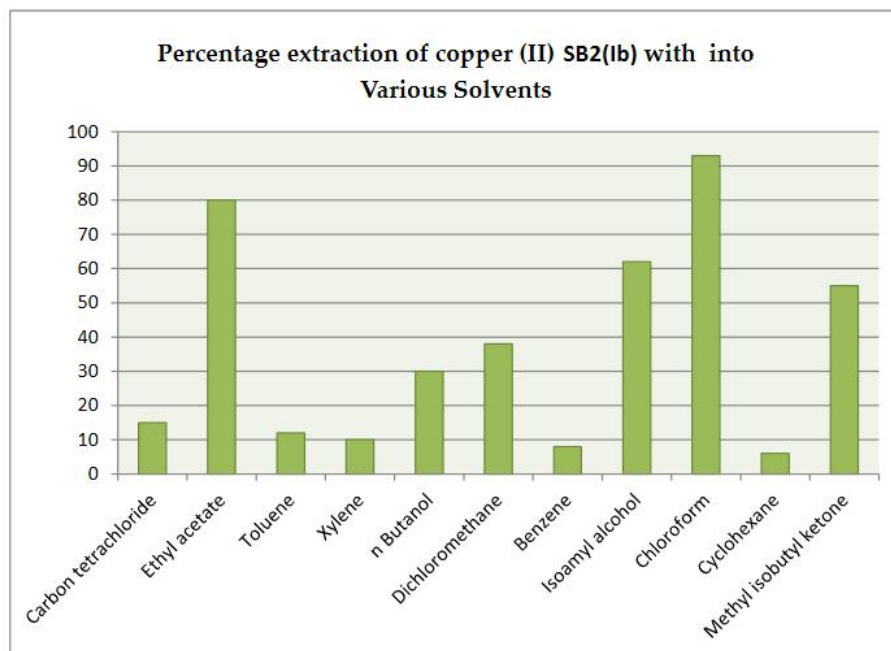
pH	Selectivity	
	Cu ⁺² / Ni ⁺² CHLOROFORM	Cu ⁺² /Ni ⁺² ETHANOL
6.2	56.5	41.5
7.2	3.5	7.50
7.5	3	3.5
8.2	4.2	4.0
8.5	13	1.6

The results obtained from the pH studies indicate that the quantitative extraction (99.6%) of copper(II) as a complex occurs in the pH range of 8.0 to 10.0 [Figure 1]. The degree of separation was measured in terms of separation factor of metal ion phases, which is defined as the ratio of distribution of metal ion between two solvents.

**Figure 1: Effect of PH on extraction of Cu (II)**

Solvent study

A variety of solvents were tried to achieve maximum extraction of copper (II). From the study, chloroform was found to be the most suitable solvent. The extraction of Cu (II)- Schiff base complex was found to vary from a minimum of 8.57 % to maximum 92.053 % for the solvents cyclohexane < xylene < benzene < Toluene < Carbon tetrachloride < n-Butanol < Dichloromethane < Methyl isobutyl ketone < Isoamyl alcohol < Ethyl acetate < Chloroform. Moreover, stability of metal complex may be affected by various factors like nature of central metal ion, Ligands and chelating affect, etc.



Absorption spectra

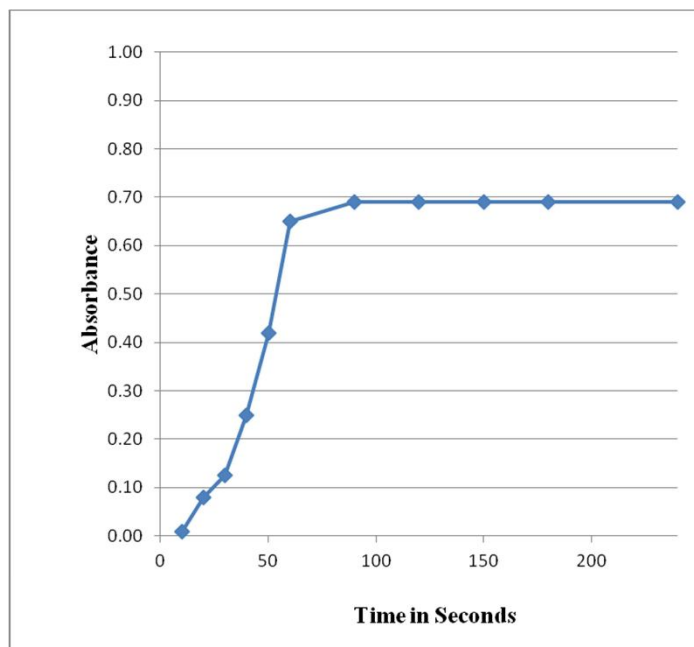
The absorption spectra of the extracted species, i.e. copper (II)- complex into chloroform Vs reagent blank shows absorption maxima at 440 nm, where absorption due to reagent was found to be negligible.

Reagent concentration

The effect of variation of Schiff bases ligand in the range of 0.01 % to 0.50 % was studied for quantitative extraction of 50 µg of copper (II). 1 ml of 0.1 % was found to be sufficient concentration for the maximum extraction and spectrophotometric determination of 50 µg copper (II)

Equilibration time and stability

Extraction of copper (II) with Schiff bases ligand as a function of equilibration time was studied for the shaking time of 10 to 240 s. The study reveals that the time of 90 seconds was found to be sufficient for quantitative extraction of copper (II) and prolong shaking had no adverse effect on extraction and spectrophotometric determination of copper (II).

**CONCLUSION:**

In conclusion, the highlights of the method developed for extractive spectrophotometric determination of Co (II) and Ni (II) are as follows:

1. These methods are simple, rapid, and sensitive.
2. The extraction of the copper metal was quantitative with the analytical reagent used without the use of any synergetic agent.
3. No pre-equilibration of phases is required; also scrubbing or back washing is.
4. These methods have also been satisfactorily applied for determination of copper in synthetic mixtures.
5. These methods are relatively free from interference due to commonly associated cations and anions.

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