

## Synthesis and Characterization of Metal Complex Dyes Using a Co (II) and Cu (II) As a Ligand

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### Abstract

*Metal complex azo dyes are more light-stable and allow for easier control of the wavelength through selection of suitable substituted group. Recently, azo metal chelates have been given increasing attention as some results of their fascinating geometrical and electronic properties which inform the possibility of their application in molecular memory usage. This research work aimed at synthesis of metal complex dyes using certain transition metal complexes as Ligand. Metallic salts of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  were dissolved in distilled water and appropriate amount of NaOH and Methanol were added to chelating agents. The mixture was heated to 80-90<sup>0</sup>C in a mantle for a specific period of time. The product obtained was filtered using filter paper and the residue dried in an oven for 35minutes. The percentage yield of the dried residue (metal orange II complex) was determined and physical properties such as colour, texture, solubility and melting point of the complexes were analysed using FTIR and UV-Vis spectrometric techniques. The maximum wavelength of absorption for all the three metals complexes synthesized occurred between 483.5nm and 550nm. Similarly, their frequencies of vibration also occur relatively similar peaks along their respective frequency bands. These suggest the fact that the metal orange II complexes synthesize possess similar structural formulae. The preparation of such metal complexes for both industrial and laboratory uses should be encouraged.*

**Key words:** Characterization, Synthesis, Metal-Complexes, Azo-Dyes

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## Introduction

Dyes are coloured compounds that absorb light in the visible region of the spectrum (400-700nm) and possess at least one colour bearing group (chromophore). Have a conjugated structural set-up (presence of alternating single and double bonds) and exhibit resonance of electrons. In addition to this feature, they also carry auxochromes, usually carboxylic acid, sulphonic acid, amino or hydroxyl groups. [1] The auxochromes are used to shift a colour of a colourant and often assist in influencing the solubility of the dye. The dye molecule is often described as chromogen. Azo compounds are very important class of chemicals compound receiving attention in scientific research; they are highly coloured and has been used as dyes and pigment for along times.

Azo groups are by far the most important and they represent the major and most versatile class of synthetic dyes. Azo dyes have been widely studied in recent years because of ease of availability, reasonable price and applied utilities. The wider application of these dyes results from a combination of the properties of azo groups and several types of the aromatic-substituted ligand that confer to them intense colour over the whole visible range. These dyes have been exploited for non-linear optical usage when they contain substituent groups on the aromatic rings with push-pull electron ability [1]. Quite a number of azo dyes have been studied by many researchers, as chelating agent and their metal chelates have been extensively used in textile industries. Azo dyes have a general structure  $R-N=N-R$ , where R and R are aryl, or heterocyclic groups. Monoazo dyes have only one  $N=N$  double bonds, while diazo and triazo dyes contain two to three  $N=N$  double bonds, respectively. The azo groups are generally connected to benzene and naphthalene rings. They are usually prepared through condensation of azo compounds with ketones or aldehydes. Synthesis of most azo dyes involves diazotization of a primary aromatic amine, followed by coupling with one or more nucleophiles. Amino- and hydroxyl- groups are commonly used coupling components [5]

Azo dyes have excellent thermal and optical properties and widely applied in areas such as optical recording medium, toner, inkjet printing and oil soluble light fast dyes. Recently azo metal chelates have been given increasing attention as a result of their fascinating geometrical and electronic properties which inform the possibility of their application in molecular memory usage. In comparison with dyes themselves metal complex azo dyes are more light-stable and allow for easier control of the wavelength through careful selection suitable substituent groups. This informs the fact that the thermal stability and the suitable absorption band of azo compound provide the essential properties for their application as high-density optical recording materials [1].

Vast quantity of dyes are annually produced and consumed in many different industries all over the world, which include pharmaceuticals, cosmetics, food, leather, paper, and textiles [2]. Worldwide production of organic dyes is currently estimated at nearly 450,000 tons, with 50,000 tons being lost of effluents during application and manufacture [3]. Transition metals azo complexes have played an important role in the development of coordination chemistry and have wide application in industry and biological system [4]. The three most common chemical groups used in the production of dyes are anthraquinone, phthalocyanine and azo groups.

Azo dyes are capable of providing high intensity of colour, about twice that of the anthraquinone, and reasonably bright colours. They are capable of providing reasonable to very good technical properties, for example fastness to light, heat, water and other solvents. Although in this respect

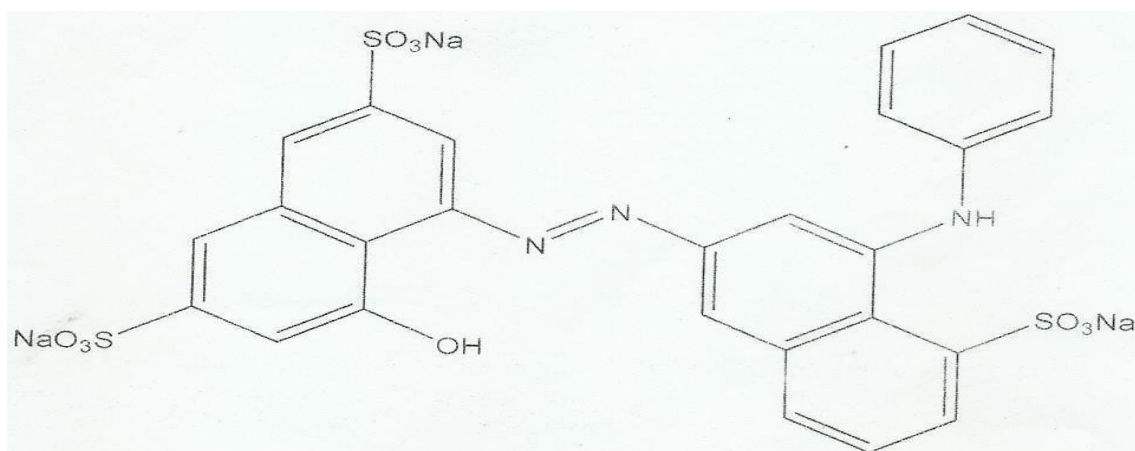
they are often inferior to other chemical classes, for example carbonyl and phthalocyanine dyes, especially in terms of light fastness. The prime reason for the commercial importance of azo dyes is that they are the most cost-effective of all the chemical classes of organic dyes and pigments. Many transition metals form complexes with azo dyes as ligands and were widely studied in different application such as biological stud, coordination polymers, textile industry, solvent extraction and spectrophotometric determination. Azo dyes usually react with metal ion as bidentate ligands or as tridentate in the field of coordination chemistry. The research work aimed at synthesis of metal complex dyes using certain transition metal complexes as Ligand. [5] The coordination complexes of transition metals with azo-ligands are of current attraction due to the interesting physical, chemical, photophysical and photochemical, catalytic and different material properties. The p-acidity and metal binding ability of azo nitrogen have drawn attention to the exploration of the chemistry of metal complexes incorporating azo-ligands [7]. The coordination chemistry of transition metals with azo ligands is being studied clue to the of several interesting properties. Facile metal-carbon bond formation and the subsequent reactions of some orthometallated azobenzene and related molecules demonstrated their importance in C-H bond activation [8].

The pharmaceutical importance of compounds including an arylazo group has been reported the literature. (2-amino-5-chlorophenyl) phenyl methanone and its derivatives are used as an intermediate to produce pharmaceuticals especially for a class of benzodiazepines (anxiolytics and hypnotics) such as chlorodiazepoxide and diazepam.

The Aim of This Study is to Synthesized and Characterized Metal Complex Dyes derived from Co (II) and Cu (II) ion as a ligand

### Acid Dyes

These are acidified basic dyes, intended for use on protein fibres but can be used on nylon and acrylics. They have a fair light fastness but poor wash fastness.

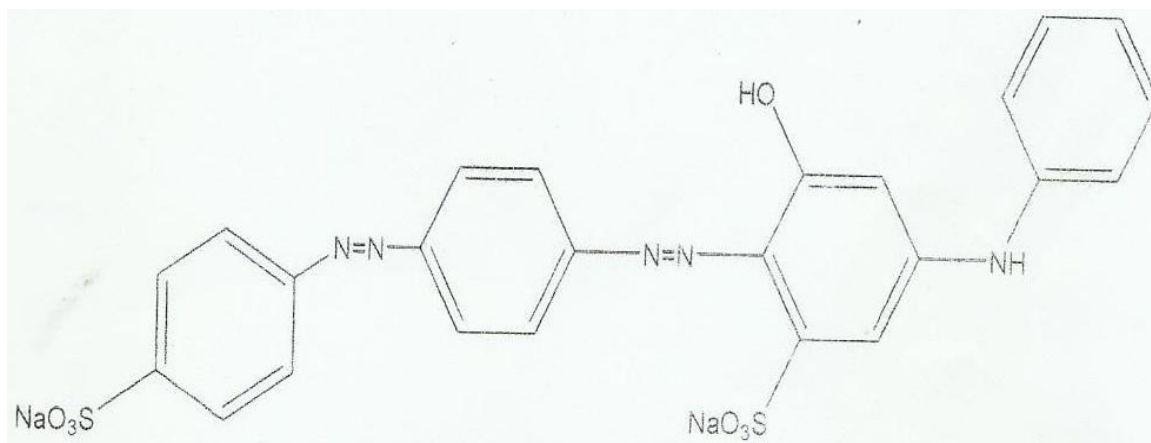


sodium (*E*) – 4 – hydroxyl – 5 – ((4 – (phenylamino) – 5 – sulfonatophthalen – 2 – yl) diazenyl) naphthalene – 2, 7 – disulfonate

Figure 1: Structure of acid dyes

## Direct Dyes

These substantive dyes colour cellulose fibres directly in a hot dye bath without a mordant to give bright colours. They are not very fast to light or to washing. Direct dyes are generally any dyes which use salt as their only fixative e.g. Dylon dyes (not to be confused with reactive dyes which use salt plus other chemicals).

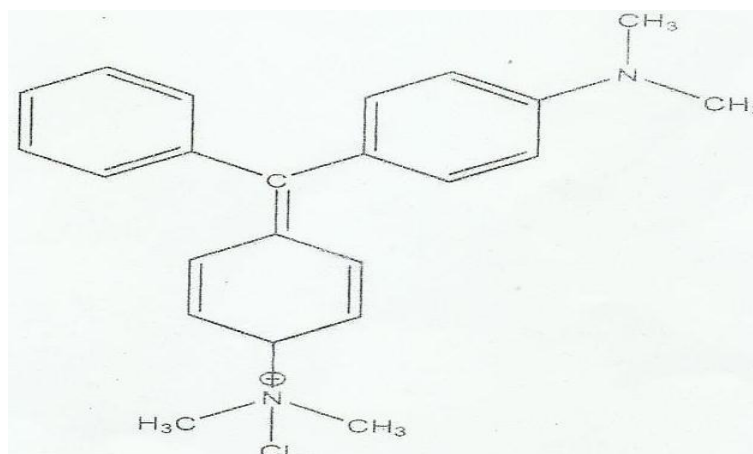


sodium 3 – hydroxyl – 5 – (phenylamino) – 2 – ((4 – ((4 – sulfonatophenyl) diazenyl) phenyl) diazenyl) benzenesulfonate

Figure 2: Structure of direct dyes

## Basic Dyes

The colours are very bright but not very fast to light, washing- perspiration. Fastness is improved if they are given an after treatment or steaming e.g French silk dyes are basic dyes and should be steamed to fix.

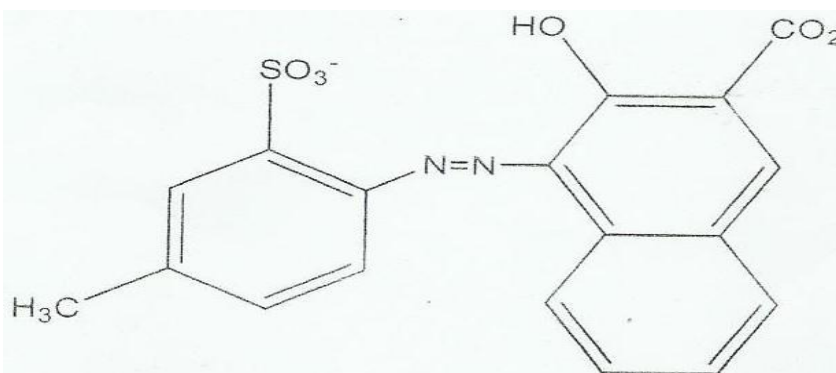


N – chloro – 4 – ((4 – (dimethylamino) phenyl) (phenyl) methylene) – N, N – dimethylcyclohexa – 2, 5 – dien – 1 – aminium

Figure 3: Structure of basic dyes

## Azoic Dyes

These are another sort of direct dyes but ones that are extremely fast to washing, bleach and light. They are intended for cellulose fibres and can be used successfully protein fibres although the colours are different. These dyes are widely used all over Asia and Australia for batik and direct application. They can be used to give interesting texture colour effects on fabric, thread or paper. Their use for straight silk painting is minimal because of the difficulty in achieving evenness of painted colour. The discovery of azo dyes led to the development of other dyeing techniques. Azo dyes are formed from an azoic diazo component and a coupling component. The first compound, aniline, gives a diazonium salt upon treatment with nitrous acid: this salt reacts with the coupling component to form a dye, many of which are used as direct and disperse colorants. These dyes can be generated directly on the fabric.



3 - hydroxyl - 4 - ((4 - methyl - 2 - sulfonatophenyl) diazenyl) - 2 - naphthoate

Figure 4: Structure of azo dyes

## Disperse Dyes

Originally developed for acetate fibres, these are now major dyes for synthetics. They are not soluble in water, but in the actual fibres themselves. They require a carrier to swell the fibres so that the finely ground particles can penetrate. They are dyed hot like direct dyes but do not use salt. Disperse dyes are widely used for heat transfer printing (polysol) [10]. Dye is printed onto paper and heat pressed onto fabric. Prints have excellent light and wash fastness and strong bright colours. Their major disadvantage is that only synthetic fabrics can be used.

## Vat Dyes

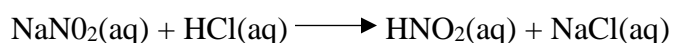
Vat dyes are the fastest for cellulose fibres. The dye is made soluble with alkali, put in a "vat" with a reducing agent usually sodium hydrosulphite, which removes all oxygen from the liquid and the fabric is dyed then oxidized in the air to achieve the true colour. Synthetic indigo is a characteristic vat dye but there are many colours available.

## AZO COMPOUNDS

Today's experiments deal with a class of compounds called Azo dyes, compounds that contain two aromatic fragments connected by a  $\text{N}=\text{N}$  double bond. You may have encountered these in

chemistry experiments as they are typical pH indicators. Methyl yellow, methyl orange, methyl red, Congo red and alizarine yellow are some of the examples. They are straightforward to make and of industrial importance. Azo dyes are prepared in a two-step reaction, the first being the synthesis of an aromatic diazonium ion from an aniline derivative. The next step is coupling of the diazonium salt with an aromatic compound. A practical example is when Phenylamine reacts with a solution of sodium nitrate (III) and hydrochloric acid at a temperature below 5°C (remember keeping that test-tube in ice) to produce benzene diazonium chloride. This type of reaction is known as diazotisation.

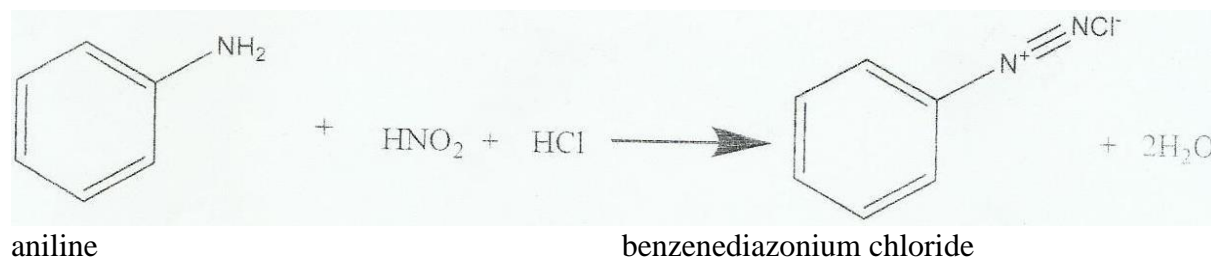
The hydrochloric acid first reacts with sodium nitrate (III) to form unstable nitrous acid.



The nitrous acid then reacts with the amine.

### Equation of Reaction

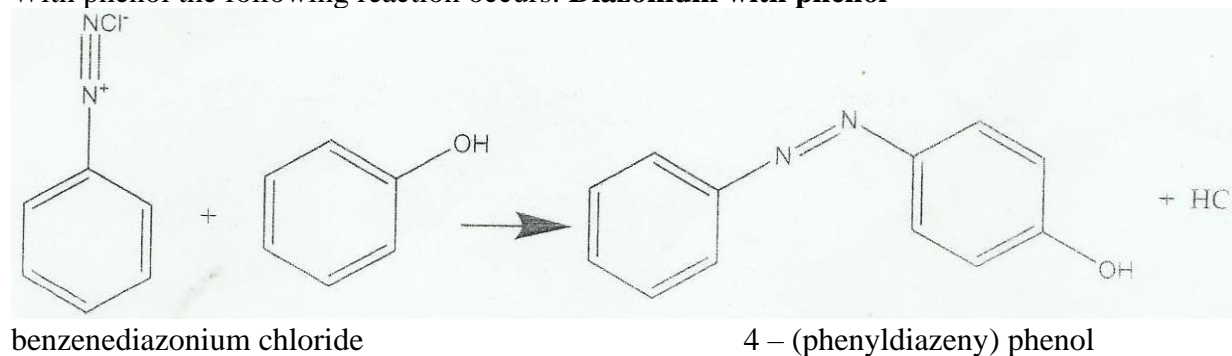
Reaction of nitrous acid with amine



Scheme 1: Reaction of aniline with nitrous acid

If the temperature is allowed to rise above 5°C, the benzenediazonium chloride decomposes to form phenol and nitrogen gas is given off. If the benzenediazonium chloride IS reacted with another compound containing a benzene ring, called a coupling agent, an azo compound is produced. The diazonium salt acts as an electrophile. Phenols and amines are often used as coupling compounds. Many of the products are important dyes.

With phenol the following reaction occurs: **Diazonium with phenol**



Scheme 2: formation of 4-(phenyldiazeny) phenol

The colours of azo dyes include different shades of yellow, red, orange. Brown, and blue. All coupling compounds contain a benzene ring that performs the coupling because it stabilises the delocalised electron structure. Without a coupled benzene ring the compound would remain

### Chromophore

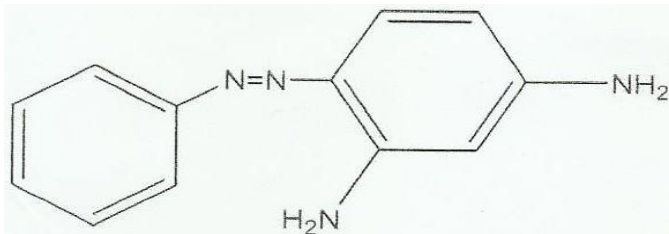


Figure 5: Structure of 4 – (phenyldiazenyl) benzene – 1, 3 - diamine

Other functional groups may be added which can modify or enhance the colour of the dye make the dye more soluble in water attach the dye molecule to the fibres of the cloth.

All azo dyes contain the R-N=N-R arrangement.

### Materials and Method

#### Materials

The materials that were used for this research work are of analytical grade not industrial grade which are free from impurities and as are follows:

Copper (II) sulphate ( $\text{CuSO}_4$ ), Cobalt (II) Chloride ( $\text{CoCl}_2$ ), Aniline, Sodium nitrite ( $\text{NaNO}_2$ ), 2-naphthol, Sodium hydroxide ( $\text{NaOH}$ ), Methanol, Filter paper, drying oven, conical flask, measuring cylinder, stirring rod, beaker, thermometer, melting point apparatus, heating mantle, Melting point decomposition, FTIR, UV Visible spectroscopy etc.

#### Methods

##### Synthesis of azo dyes

2.88g of 2- naphthol was weighted and dissolved in 20ml of 1m NaOH in conical flask, the mixture was stirred until it completed dissolution and the solution was cooled with an ice water bath at a very low temperature. 3.5g of sulphanilic acid was added into 20ml of 1m NaOH in an Erlenmeyer flask. the mixture was warmed on a steam bath for 15 minutes and a sample grey solution was formed. the flask content was cooled in an ice water bath, 0.35g of  $\text{NaNO}_2$  (1M) was added in 5ml of distilled water, the solution of sodium nitrate that was prepared in was transferred into the solution prepared. 10g of crushed ice was placed in a beaker and 2ml of concentrated HCl was added and the solution was transferred into 500ml beaker containing a solution of sulphanilic acid and sodium nitrate prepared and was stirred the solution was poured into the solution the mixture was stirred was stirred well for several minutes and most of the solid was dissolved. A dark red colour of the dissolved product dye appeared, the product was filtered dried and weighted

### Synthesis of Co (II) complex

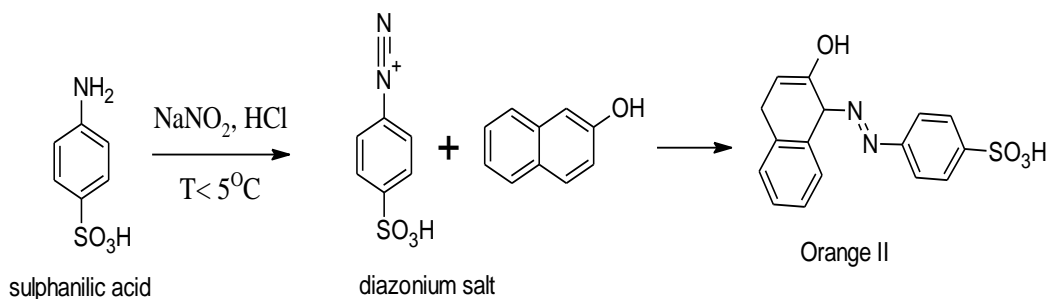
3g of orange II was dissolved in 40ml of distilled water in 250ml beaker A, 1.2g of  $\text{CoCl}_2$  was also dissolved in 20ml of methanol in a 100ml beaker B. Solution was placed on a hot plate and was heated with a heating mantle to  $80^\circ\text{C}$ . While heating solution A, solution B was carefully transferred into a beaker A on the hot plate. 10ml of 0.1M NaOH was added to the mixture and heated and stirred at  $80^\circ\text{C}$  for about two hours (2 hrs). The solution was allowed to cool on a bench top and filtered using filter paper. The residue was washed with methanol and allowed to dry at room temperature for two days. The metallized dye synthesized was dried, weighed and characterized.

### Synthesis of Cu (II) complex

1.4g of azo dye was dissolved in 20ml of distilled water in a 250ml beaker A. 0.6g of  $\text{CuCl}_2$  was also dissolved in 10ml of methanol in a 100ml beaker B. The solution in beaker A was placed on a hot plate and heated to about  $70\text{-}80^\circ\text{C}$  until the azo dye dissolved completely. While heating and stirring with glass rod, the Cu (II) solution in beaker B was carefully transferred into beaker A on the hot plate. The mixture was heated and stirred for about 5-10 minutes. 5ml of 0.1M NaOH was poured into the mixture and was heated and stirred at  $80^\circ\text{C}$  for two hours (2hrs). The mixture was allowed to cool on a bench top and was filtered using suction filtration. The precipitate obtained was the complex dye and was allowed to dry at room temperature for two days.

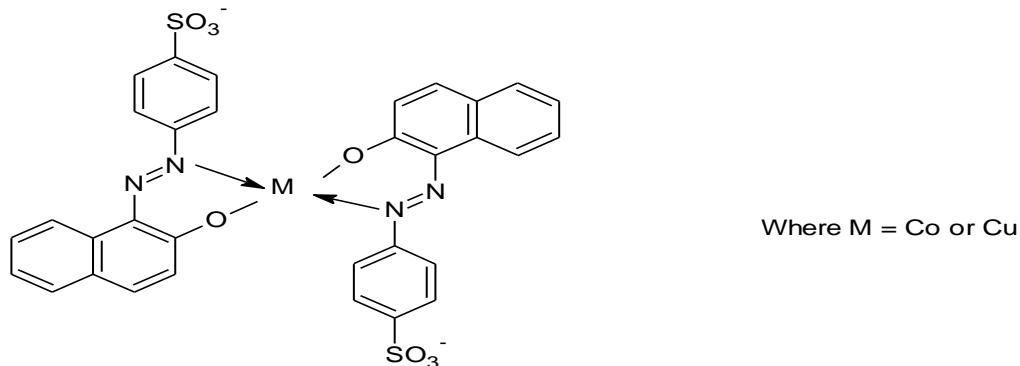
### Results and Discussion

Reaction scheme showing the synthesis route for Orange II azo dye



Scheme 3: Diazotization and Coupling reaction of sulphanilic acid





Proposed metal complex azo dye structure

Figure 6: Proposed structure of metal complex dyes

**Table Physical Properties of Dyes.**

NAME OF DYE	COLOUR	TEXTURE	MOLECUAR WEIGHT g/mol	PERCENTAGE YIELD %	MELTIN-G POINT °C
Orange II Azo dye	Orange	Powdery	350.3	56	163
Co II complex Azo dye	Brown	powdery	349.2	47	196
Cu II complex Azo dye	Dark brown	powdery	219.8	62	189

**Table Solubility of complexes formed.**

Name of complex synthesized	Water	Methanol	Acetone	Chloroform
Orange II	Sparingly Soluble	Sparingly Soluble	Sparingly Soluble	Sparingly Soluble
Co II complex Azo dye	Sparingly Soluble	Soluble	Soluble	Soluble
Cu II complex Azo dye	Slightly Soluble	Soluble	Soluble	Soluble

**Table FTIR corresponding vibrational frequency peaks for all two complexes formed.**

Functional group	Experimental Peak range (cm <sup>-1</sup> )	Literature (cm <sup>-1</sup> )	References
N=N	1450	2000-1500	Table of characteristic frequencies of vibration(www.orgchem Colorado.edu) June 28,2004
O-H	3618	4000-2500	Table of characteristic frequencies of vibration(www.orgchem Colorado.edu) June 28,2004
C=C	1682	2000-1500	Table of characteristic frequencies of vibration(www.orgchem Colorado.edu) June 28,2004

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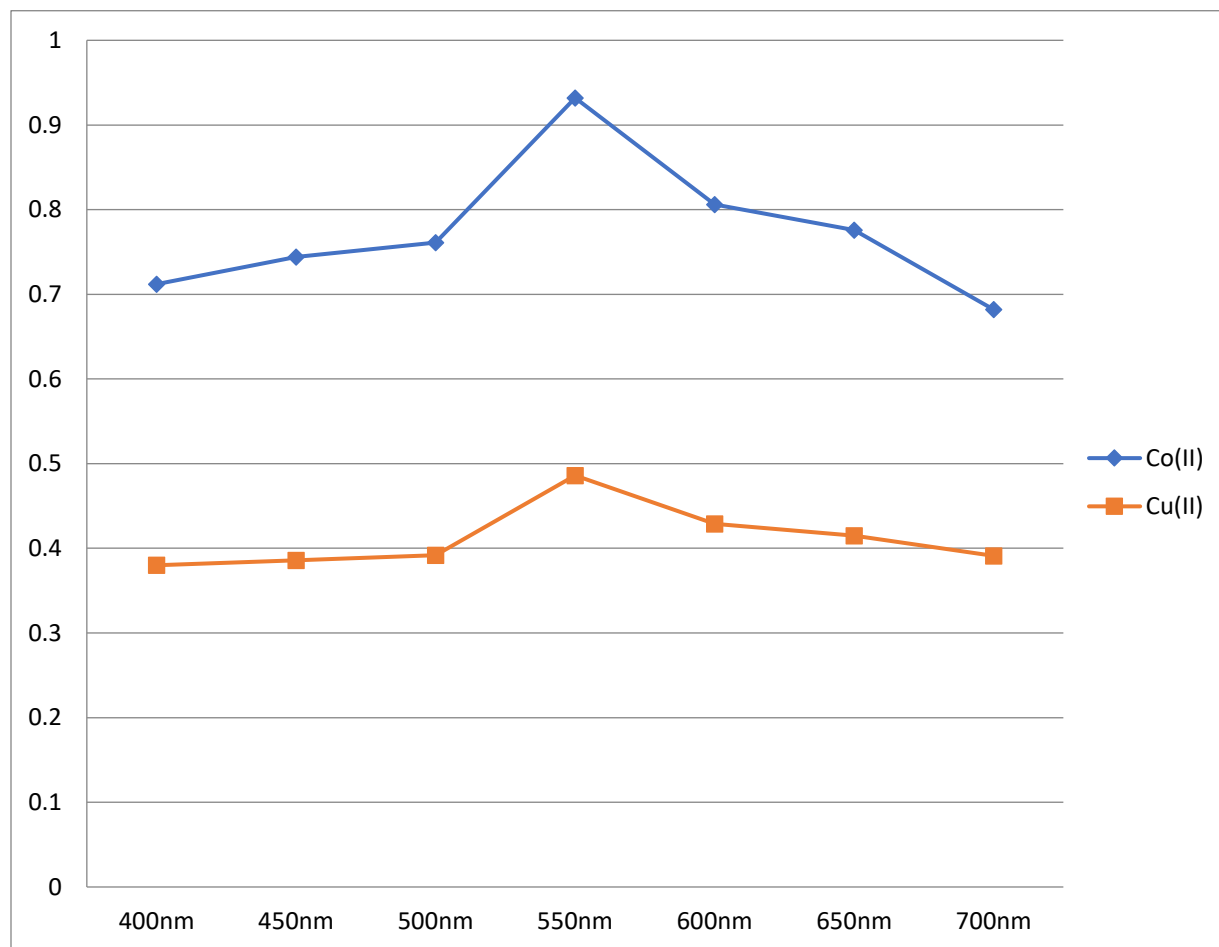
C-N	1257	1030-1230	Table of characteristic frequencies of vibration(www.orgchem Colorado.edu) June 28,2004
C-H	3063	4000-2500	Table of characteristic frequencies of vibration(www.orgchem Colorado.edu) June 28,2004

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**Table 4.4 Absorbance against various wavelengths**

wavelengths	Co <sup>2+</sup> Absorbance	Cu <sup>2+</sup> Absorbance
400nm	0.712	0.380
450nm	0.744	0.386
500nm	0.761	0.392
550nm	0.932	0.486
600nm	0.806	0.429
650nm	0.776	0.415
700nm	0.682	0.391

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**Figure 4.1 graph of absorbance against wavelength**

Orange II azo dye was synthesized by coupling diazotised sulphuric acid with 2-naphthol. Its cobalt and copper complexes were formed by reacting the orange II with cobalt (II) chloride and copper (II) sulphate. From the various peaks obtained during the FTIR analysis of the two complexes synthesized, it can be seen that for all two complexes, the vibrational frequencies of the N=N, O-H, C-H and C=C, C-N and C-H bonds occurred at very similar peaks. This explains the fact that the reaction process follows a similar route and the product obtained in the two complexes of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  are most likely to have very similar molecular structures. From the FTIR results, it can be noted that the N=N bond for all two samples synthesized occurred at exactly 1450 which is at the extremes of the range for such a bond. This situation can be used to suggest delocalization of the N=N double bond in all the complexes formed.

The azo dye exhibits an absorption maximum at 483.5nm, upon binding with metal, forming the complex, the maximum absorption band was shifted to 550nm suggesting an interaction of the metal with the ligand. The percentage yield of the azo dye calculated was found to be 56% while the Cobalt and Copper were 47% and 62% respectively.

## CONCLUSION

Azo metal complexes dye was successfully synthesized with the physical properties such as the colour, and molecular weight. The dyes were further characterized using FTIR and UV – Vis spectrophotometer. The melting point and percentage yield were also determined. The results show that azo metal complex dye can be recommended for industrial application.

## RECOMMENDATIONS

The importance of complexes formed from interaction of most organic based ligands and metals especially within the transition series cannot be over emphasized in many chemical and biochemical industries today. Therefore;

- i. The production of such complexes for both industrial and laboratory uses should be encouraged.
- ii. Transition metal complexes are mainly used as precursors to many catalysts; this is why they should not be in short supply in both institutional and industrial laboratories.
- iii. Further similar research should be carried out on other transition metals using various ligands.

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