

Synthesis of Cobalt-Complex Azo Dye from 2, 2[Benzen-1, 3-diyl di-(E)-diazene-2, 1-diyl] bis (4-nitroaniline)

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Abstract: The aim of this investigation is to carry out the synthesis of bisazo dye 2, 2[benzene-1, 3-diyl di (E) diazene 2, 1-diyl] bis (4-nitroaniline). The synthesis was conducted through the diazotization and coupling of *m*-phenylene diamine with 4-nitroaniline leading to the production of azo metal (II) complex of Cobalt. Characterization of the ligand and the metal complex was carried out using various physico-chemical techniques. The metal chelates have a metal to ligand ratio of 1:1. The synthesized azo metal (II) complex dye had a potential application for high density optical recording media due to their good absorption spectra and high thermal stability.

Key Words: Azo dye, Ligand, Metal Complex, UV-Visible Spectroscopy

I. Introduction

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 [1]. Dyes are coloured compounds, they 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 [2]. In addition to these features they also carry auxochromes, usually carboxylic acid, sulphonic acid, amino, or hydroxyl groups. The auxochromes are used to shift the colour of a colourant and often assist in influencing the solubility of the dye.

The three most common chemical groups used in the production of dyes are anthraquinone, phthalocyanine and azo groups [3]. Azo groups are by far the most important and they represent the major and most versatile class of synthetic dyes [4]. Azo dyes have been widely studied in recent years because of ease of availability, reasonable price and applied utilities [5]. The wider applications of these dyes result 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 [6]. Azo dyes have excellent thermal and optical properties and widely applied in areas such as optical recording medium [7], toner [8], inkjet printing [9] and oil soluble light fast dyes [10].

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 storage [7]. In comparison with dyes themselves metal complex azo dyes are more light-stable and allow for easier control of the wavelength through careful selection of suitable substituent groups [11]. 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.

Literature survey suggests that quite a number of azo dyes have been studied by many workers [8], as chelating agents and their metal chelates have been extensively used in the textile industries. Azo dyes have a general structure R-N=N-R, where R and R are aryl, alkyl, or heterocyclic groups. They are usually prepared through condensation of azo compounds with ketones or aldehydes. Numerous researches have been carried out on the synthesis of mono azo dyes as reported in the reviews but very little comparative investigations were conducted on diazo dyes.

In the present investigation the synthesis of bisazo dyes derived from *m*-phenylene diamine and 4-nitroaniline as coupling components and its metal complex is described. The spectral observations and physico-chemical analysis of the synthesized compounds are discussed.

Experimental

All the chemicals and the solvents used were of analytical grade and therefore need no further purification.

Synthesis of the Ligand

1.08g/0.01mol of m-phenylene diamine was dissolved in a mixture of 5cm³ of water and 10cm³ of concentrated hydrochloric acid. While 20ml of concentrated hydrochloric acid was diluted with about 60g of crushed ice to which 2.5g of sodium nitrite dissolved in 10ml of water was added. The m-phenylene diamine hydrochloric acid solution was then added immediately. The mixture was stirred continuously over a period of one hour until a dark yellow coloured (tetra azo) solution is obtained. The coupling agent (p-nitro aniline) dissolved in 0.02mol DMF cooled with ice blocks to a temperature of 5⁰C is slowly added with continuous stirring to the tetra azo solution. A solution of sodium acetate is then stirred in to the mixture until neutralization was achieved. The dye is washed thoroughly with water and collected by filtration [12].

Synthesis of the Metal (II) complex

4mmol of metal acetate solution in 10ml of methanol was added to methanol-chloroform (1:1v/v) solution containing 8mmol of ligand and was refluxed for 2hours and kept at room temperature. The precipitated complex was filtered, washed with methanol and then recrystallized from 1:3v/v methanol-chloroform mixture and dried.

UV-Visible Spectroscopy

The electronic spectra were measured by means of a Shimadzu 1601 Spectrophotometer in the region 200–800nm [13].

II. Results and Discussion

The proposed synthetic scheme for the metal complex and its precursor ligand is outlined below:

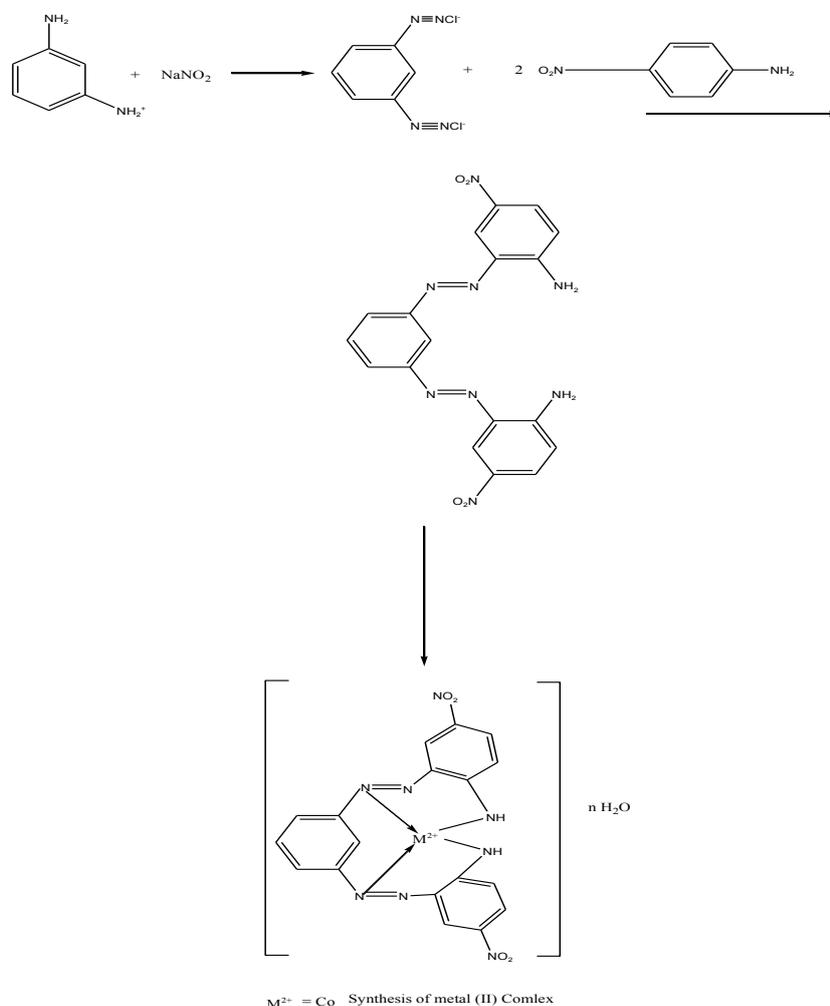


Figure 1: General Routes for Synthesis of the Ligand

The table below shows the micro-analytical investigation results for the synthesized ligand and the metal complex.

Table 1: Micro analytical data of ligand and metal complexes

Name of compound	Yield %	Colour	M.P. °C	Decomposition Temperature (°C)
Ligand (L)	68	Reddish brown	94	130
L-Co ²⁺	72	Deep brown	280	250

The synthesized compound was an intensely amorphous solid. The ligand and the metal complex decompose at 130 and 250 °C respectively. It was found that the thermal stability of the metal complex was higher than that of the ligand. Azo dyes possess good thermal stability,

Solubility of the Synthesized Compounds

The solubility test results of the synthesized ligand and the metal complex is presented in the table below:

Table 2: Solubility Test

Solvent	Ligand (L)	L-Co ²⁺
Methanol	Soluble	Not soluble
Chloroform	Soluble	Not soluble
DMSO	Soluble	Soluble
DMF	Slightly soluble	Soluble
Water	Slightly soluble	Not soluble

The ligand was soluble in methanol, chloroform and dimethylsulfoxide but the metal complex was not in methanol but soluble in dimethylsulfoxide and dimethylformide. The good solubility of the azo-metal chelates makes them suitable for use as optical medium [14].

UV-Visible Spectroscopy

This technique was employed in order to determine the wavelength of maximum absorption (λ_{max}) for the synthesized dyes. Results obtained are presented in table below.

Table 3: UV-VIS Spectra in DMSO

Compound	Ligand(L)	L-Co ²⁺
λ_{max} (nm)	264.47 397.97	270.01 399.58
Absorbance	0.335	0.776

The λ_{max} of the ligand was around 264nm and 398nm while that of the metal complex was 270nm and 398nm.

The UV-VIS spectra of synthesized azo dye and its metal complexes showed two bands between 264-398nm and 270-398nm. The first band maybe due to π - π^* transition within the aromatic ring and the second band would be due to n - π^* transition of N=N group. The formation of metal (II) azo complexes was also confirmed by their UV-VIS spectra. It can be seen that λ_{max} of azo dye was at around 264 and 398nm. While the λ_{max} of complexes were slightly blue shifted which arise from the energy change of intense π - π^* and n - π^* transition of the conjugated chromophore due to the chelation between metal ions and azo ligand. The complexation of the dye with the metal ion was responsible for a significant hypochromic shift at both π - π^* and n - π^* transition region [15]. In metal chelates, the light absorption is believed to take place in the UV region as a result of absorption arising from electronic transition in a conjugated system, where a metal may or may not participate. These types of absorptions are referred to as K type and have been studied by a number of workers [16]. Absorption bands in the UV region due to forbidden transitions and the ligand K type band characteristics in visible region have been extensively studied by researchers [17].

III. Conclusion

It can be concluded that the synthesized azo metal (II) complex has potential application for high density optical recording media due to their good absorption spectra and high thermal stability. The result from the elemental analysis and spectral observation indicated that the ligand is coordinated to the metal atom as monodentate in the ratio of 1:1.

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