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Synthesis and Characterization of Water Soluble Analytical Reagent like 2-[(5-Hydroxy-3-Methyl-1-(4-Sulfophenyl)-1H-Pyrazolyl)Diazenyl] Benzene-1,4-Disulfonic acid Spectrophotometric reagent for Ni (II)

Anil V. Patil, Ravindra L. Aavhare and Ketan C. Desai*

Department of Chemistry, Sir PT Sarvajanik College of Science, Surat, Gujarat, **INDIA**
Email: raviaware27@gmail.com

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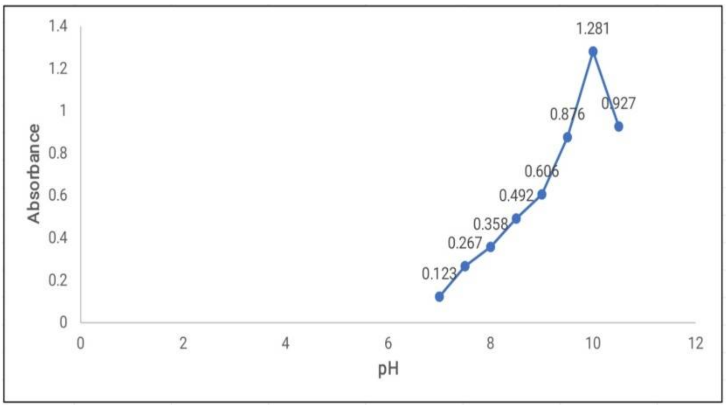
ABSTRACT

The pyrazolone azo dye containing bidentate donor ligand 2-[(5-hydroxy-3-methyl-1-(4-sulfophenyl)-1H-pyrazol-4-yl)diazenyl]benzene-1,4-disulfonic derived from aniline-2,5-disuphonic acid and 4-(5-hydroxy-3-methyl-1H-pyrazol-1-yl)benzene-1-sulfonic acid (pyrazolone) as a coupler by the diazotization reaction. The diazonium salt solution of aniline-2,5-disulphonic acid reacting with pyrazolone as a coupling compound in solution. The metal complexes series of the same were prepared with Ni(II), Co(II), Cu(II), Mn(II) and Fe(III).The synthesized ligand structures was identified and confirmed via various spectroscopic techniques which is UV-Visible, ^{1}H NMR, Fourier-transform Infrared (FTIR). The physical properties of the ligand have been studied via check its melting point. The formation of metal complexes in proper condition have been studied the prepared metal ion complexes where identified via UV- visible and FT-IR spectra and also check by biological activities of all metal ion complexes and ligand.

Graphical Abstract:



Effect of pH on absorbance values of Ni chelate complex.

Keywords: Heterocyclic acid dyes, Metal complexes, Spectral studies, Physico-chemical studies, Antibacterial activity.

INTRODUCTION

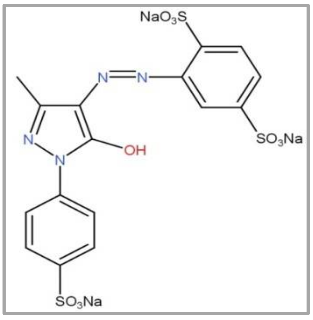
The dyes bearing pyrazolone containing ligands and its derivatives are also used as intermediate in the dyestuff industry although they are known to possess many biological activities [1-3]. The biological active molecules can be obtained by increasing the number of functional groups on azo compounds including heteroaromatic structures [4-14].

In this work, two different heterocyclic azo dyes with two different aromatic amines where synthesized. These heterocyclic azo dyes (Phenylazo-5-pyrazolone) have been synthesis used as analytical reagents for determination of variety of metal ions using different physico-chemical techniques. The ligands have been used as gravimetric and spectrophotometric reagent for Co(II), Cu(II), Ni(II), Mn(II) & Fe(III). The conditions of pH have been established and effects of diverse ions have been studied. The molar ratio of the metal ions to ligands [M/L] was is studied spectrophotometrically using molar ratio and continuous variation methods and also determined using the Job's method.

MATERIALS AND METHODS

All the required chemicals and solvents used for the synthesis of heterocyclic azo dye ligands and their metal complexes are analytical grade (AR) and pure grade are purchased from Loba, BDH, Merk, Spectrochem and Sigma-Aldrich chemical companies. The synthesized azo molecules melting points are recorded by open capillary method. The 1H NMR spectra were carried out on a Bruker Avance III 400 MHz FT-NMR spectrometer using DMSO-d6 as solvent for measurement and using TMS as an internal standard reference. Fourier Transform Infrared (FT-IR) spectra were recorded on a Shimadzu model 8400s FT-IR spectrometer scanning at range between (4000-400 cm^{-1}) via a KBr pellets. The UV-Visible spectra were measured on a Shimadzu model UV-1650 UV-Visible spectrophotometer Double beam scanning at range of (200-1100 nm) using water as solvent for measurement.

General procedure for synthesis of the azo dye ligand 2-[(5-hydroxy-3-methyl-1-(4-sulfophenyl)-1H-pyrazol-4-yl)diazenyl]benzene-1,4-disulfonic acid (HMSPDABDS): The aniline-2,5-disulphonic acid (0.01 mmol) where dissolve in 30 mL distilled water and concentrated HCl (2 mL, 0.02 mmol). This well stirred suspension solution were cooled 0-5°C in ice-salt bath. A solution of $NaNO_2$ (0.01 mmol) previously cooled to 0-5°C were added. The reaction mass was stirred for an hour at 0-5°C. The completion of diazotization reaction was checked by thin layer chromatography (TLC) in different solvent system. The 4-(5-hydroxy-3-methyl-1H-pyrazol-1-yl) benzene-1-sulfonic acid (pyrazolone) (0.01 mmol) was dissolved in Na_2CO_3 solution (10% W/V) and cooled to 0-5°C in an ice bath. To this well stirred solution, the above solution of diazonium salt was added constant stirring was continued for 2-3 h at 0-5°C and the pH was adjusted



Azo dye ligand

to 7 by adding Na_2CO_3 solution (20% w/v). After the completion of reaction, NaCl solution (10% w/v) was added with stirring to precipitate out the coloured solid product. The reaction progress was monitored by TLC as developing different solvent system. It was then filtered off and recrystallized from mixture of DMF and acetone. The orange-yellow crystals soluble in water and DMF, slightly soluble in methanol, ethanol and insoluble in acetone and chloroform.

General method for the synthesis of metal ion complex: The synthesis of metal ion complex was prepared by The azo ligand HMSPDABDS (0.002 mmol) dissolved in minimum quantity of water was added in dropwise with constant stirring to (0.001 mmol) amount of M:L (1:2) for metal salts dissolved in 30 mL buffer solution, at proper pH in boiling water bath for about 2 h. The pH was adjusted to using suitable buffer solution. The solid complex was separated, filtered and recrystallized from mixture of DMF and Acetone. The analytical and physical data of ligand and its metal complexes are collected in table 1.

Table 1. Physical properties and Analytical data of ligand (HMSPDABDS) and their complexes

Compound Colour	Melting Point	Molecular Formula
Orange-yellow	> 280	$C_{16}H_{11}N_4Na_3O_{10}S_3$
Yellowish green	>300	$C_{32}H_{22}N_8Na_6O_{20}S_{6Ni}$

Determination of Nickel in German silver: The standard sample of German silver (0.3971 gm) was dissolved in nitric acid (1: 2) by heating for 30 to 40 minutes on a water-bath. The solution was evaporated to a volume of 5 mL on a water bath, but not to dryness, and the excess nitric acid was removed. Using deionized water, the solution was prepared up to 250 mL in a volumetric flask. In a volumetric flask, 10 mL of this solution was diluted to 100 mL. An aliquot of the aforementioned diluted solution (4.0 mL) was obtained and placed in a 25 mL beaker. The pH of the solution was then adjusted to 10.0 using buffer solution. After that, 1.0 mL of HMSPDABDS reagent solution (0.01 M) was added. The solution was diluted to 50 ml. In a volumetric flask, the solution was diluted to 50 mL with deionized water. At 450 nm, the absorbance was compared to a reagent blank. The results are listed in the table below.

German silver solution: 0.3971 gm German silver in 250 mL stock solution. The 5.0 mL stock solution contains 7.94 mg german silver; 5.0 mL aliquot contained 0.3971 mg German silver.

Reagent solution: 1.0 mL (0.01M)
pH : 10.0
Final volume : 50 mL
Wavelength : 450 nm
From the above experiment, absorbance was found to be 0.494, which corresponds to 0.1809 mg Nickel in 4.0 mL finally diluted solution of brass.
Nickel found in German silver sample = 25.87 %
Reported nickel in German silver sample = 25.00 %
% Relative error = 0.87 %

RESULTS AND DISCUSSION

Physical and Chemical properties of azo dye ligand (HMSPDABDS): The synthesized azo dye ligand is amorphous and a fine orange-yellow powder. After crystalline its shows a micro needle shaped crystals, giving the orange yellow colour when dissolve with DMF and reappear by acetone. This azo dye ligand is easily soluble in water and DMF, but slightly soluble in methanol, ethanol and insoluble in acetone and chloroform. This compound was synthesized by diazotization reaction between aromatic amines (Aniline-2,5-disuphonic acid) and pyrazolone derivative (4-(5-hydroxy-3-methyl-1H-pyrazol-1-yl)benzene-1-sulfonic acid) as coupling component at 0-5°C in good yield. The azo dye ligand was characterized by various spectroscopic and analytical techniques. The purity of the ligand was confirmed by thin layer chromatography (TLC) technique using different solvent system. The ligand absorbed a single yellow spot on alumina silica chromatography plates. The synthesized metal ion complexes and azo ligand was stable in air.

Effect of pH: The azo dye reagent HMSPDABDS is soluble in water and shows maximum absorbance at 410 nm. The reagent HMSPDABDS forms green coloured complex with Ni (II) in pH range 7.0 to 10.5. To study the effect of pH, a solution was prepared for metal salts 2 mL 0.005 M Ni (II) solution was mixed with 5 mL 0.01 M solution of azo ligand in water. The pH of solution was adjusted to 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0 and 10.5 with suitable buffer solution. All solutions was diluted to 50.0 mL in volumetric flask and the absorbance was measured between 400 nm to 600 nm against blank reagent. The absorbance spectra shown in figure 1 shows that maximum absorbance is found at 450 nm in all cases. The maximum complex formation occurs at pH 10.0. The absorbance spectra of the reagent show λ_{max} at 410 nm. At 450 nm where complex shows maximum absorbance (Figure 1) the reagent does not absorb much and hence 450 nm wavelength was used in further studies. It was observed that the absorbance increased with increasing pH upto optimum pH and then decreased with increasing pH.

Mole ratio [Metal : Ligand]: The equimolar ratio method were used in order to identify spectrophotometrically formation of metal ion complexes and finding possible structural formula of prepared metal ion complexes. The mole ratio method is based on the measurement of absorbance of each complexes solution at optimum pH and concentration at the maximum absorbance wavelength. The solution of prepared metal ion complexes intensity of the color was increase as approach point of intersection [M:L] ratio and the continued stability of the colour after the point of intersection indicating on formation of the metal complexes [18]. The mole ratio found to be [1:2] for all formation of metal ion complexes and maximum absorbance was obtained in pH range.

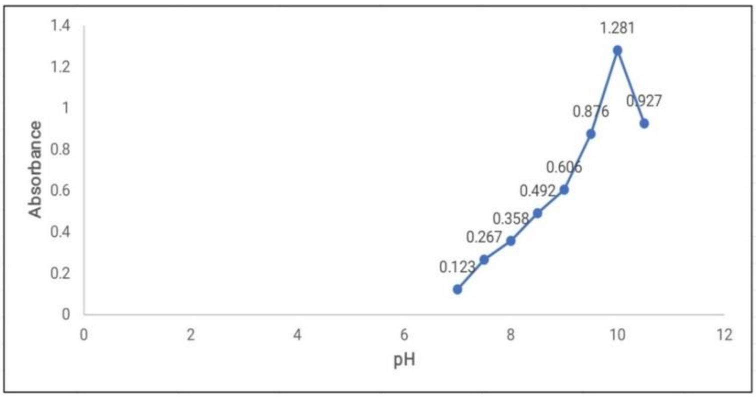


Figure 1. Effect of pH on absorbance values of Ni chelate complex.

The reagent (0.005 M) and equimolar metal ions were utilised in this procedure. A series of solutions were created by maintaining the concentration of reagent solution (6.0 mL, 0.005 M) constant while altering the quantity of metal ion solution from 0.5 mL to 5.0 mL and 0.005 M with increments of 0.5 mL.

The pH of the solutions was adjusted to pH 10.0 by using buffer solution and the content was diluted to 50 mL in volumetric flask by using deionised water. At 450 nm wavelength absorbances of these solutions were recorded and plotted against the ratio of metal ion concentration to reagent concentration. The results are show in the graph. It is evident from the graph that the absorbance gradually increases up to the molar composition of metal to the reagent and after that it becomes constant indicating 1 : 2 (M : L) stoichiometry of the complex.

Infrared spectra: The FT-IR spectra of the azo dye ligand and the complexes were recorded in the form of their KBr pellets and are given in table 2. The FT-IR spectrum of the free ligand and complexes shows a number of variable absorbance bands in them is due to this transitions responsible for FT-IR bands are due to molecular vibrations. These absorbance bands that appeared on FT-IR spectrum were due to active functional groups present [28-30]. The IR spectra of ligand and metal complexes of an important absorption bands observed in figure 2 and 3.

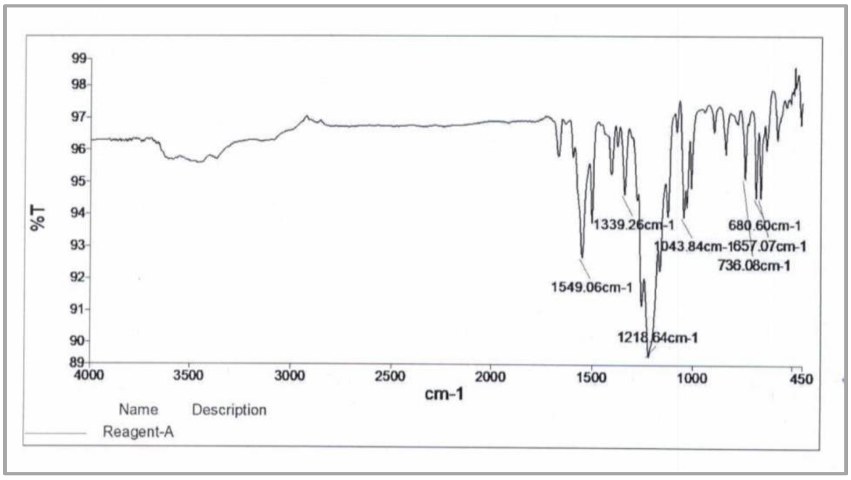


Figure 2. IR of azo dye ligand (HMSPDABDS).

Table 2. IR data of azo dye ligand (HMSPDABDS) and Ni(II) complex

Compounds	-OH Stretching cm^{-1}	N = N cm-1	C-O-H banding of –OH in Pyrazolone cm^{-1}	S = O Stretching in $–SO_3H$ group cm^{-1}
Ligand	3512	1549.06	1339.26	1218.64,1043.84
Ni(II) complex	-	1607.23	1387.27	1188.58,1040.69

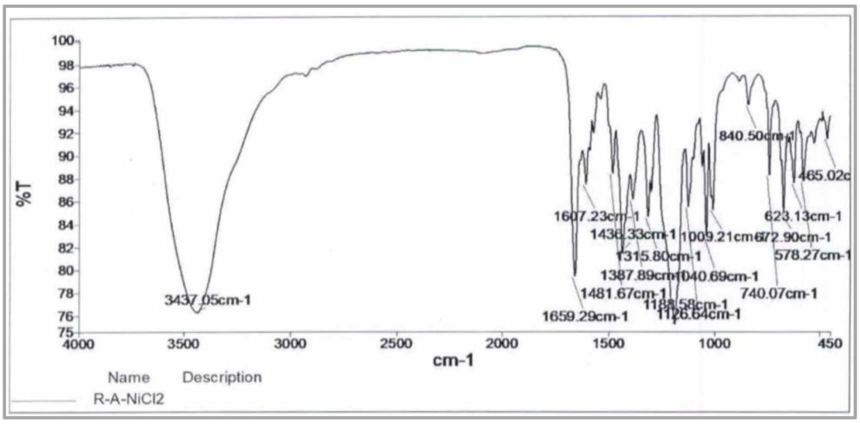


Figure 3. IR of Nickel metal complex of azo dye ligand (HMSPDABDS).

^{1}H-NMR spectra: The ^{1}H-NMR spectra of azo dye ligand was obtained in DMSO-d6 as a solvent with TMS as an internal reference (300MHz). The NMR spectra of the ligand give the the multiplate between 7.4-7.9 d ppm for aromatic protons, singlet at 3.4 d ppm for -OH and singlet at 2.3 to 2.5 d ppm due to the aliphatic $-CH_3$ group protons. The spectrograph which is illustrated in figure 4.

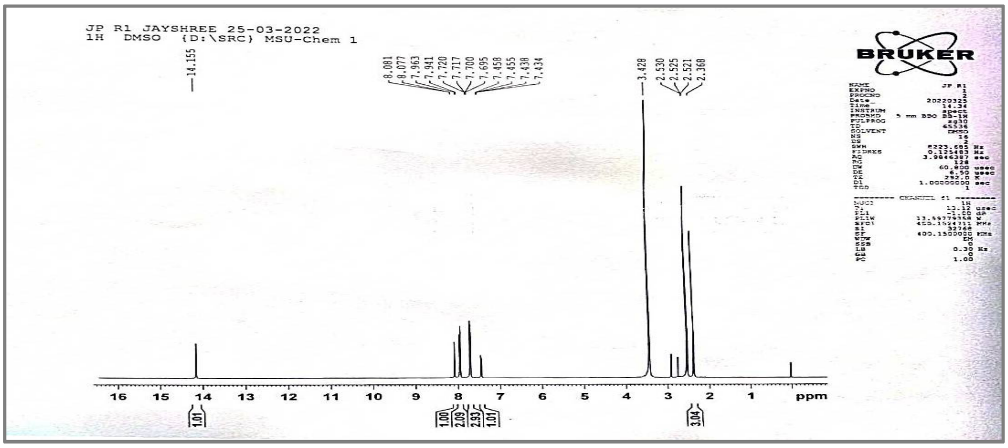


Figure 4. ^{1}H-NMR of azo dye ligand (HMSPDABDS).

Antimicrobial activity of complexes: The results show that the Ni (II) has higher action than the ligands against majority of the plant pathogenic pathogens investigated. In comparison to the ligands, the other metal complexes showed no significant increase in activity. The findings imply that variations in structure on coordination alter microorganism growth and may lead to inhibitory or reduced metal ion toxicity towards particular species. The zone of inhibition was measured the data for selected cultures are given table 3.

Table 3. Antibacterial Activity

Name of Azo dye Compound	Zone of Inhibition in mm		
	Staphylococcus Aureus	Bacillus Megaterium	Escherichia coli
Ni (II) – Complex	55	80	70

APPLICATION

The dye produces intensely coloured complexes with Ni (II) and a few other metal ions that are entirely soluble in water, eliminating the need for extraction. This helps to reduce the use of expensive and hazardous solvents. Its selectivity, however, is harmed as a result. Long-term stability of the dye solution and compounds As a metallochromic indicator, it works well. It is soluble in water rather than ethanol like many other metallochromic indicators. It has a high degree of precision for analysing alloys and pharmaceutical samples.

CONCLUSION

The dye produces intensely coloured complexes with Ni (II) and a few other metal ions that are entirely soluble in water, eliminating the need for extraction. This helps to reduce the use of expensive and hazardous solvents. Its selectivity, however, is harmed as a result. Long-term stability of the dye solution and compounds As a metallochromic indicator, it works well. It is soluble in water rather than ethanol like many other metallochromic indicators. It has a high degree of precision for analysing alloys and pharmaceutical samples.

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