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Synthesis and Studies of Eco-friendly Acid Dye Metal Complexes and its Application on Woolen fabrics

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Abstract: *The acid dyes form a big class of dyes comprising compounds with various chemical constitutions. In this respect, metal complex acid dyes synthesized showed high affinity towards fabrics. These dyeing possess better wet-fastness property and have the advantage of the high light fastness.*

Our work focuses mainly on the synthesis and dyeing of eco-friendly acid dye metal complexes on wool fabrics which is one of the novel property . These dyes are eco-friendly having good washing fastness and so gives less residue in water effluent. This method produces substituted pyrazolone metal complex acid dyes in very high yield(85%), when aqueous metal solutions are reacted with 5-Bromo-2{[5-hydroxy-3-methyl]-1-{[2-methyl -5-sulfophenyl)- 1H- pyrazol-4-yl]diazenyl} benzoicacid (PC_3). Also along with the application of dye on fabrics, study of exhaustion of the dye-bath, study of fixation of dye on the fabrics and the study of the fastness properties of the dyed patterns was carried out. The color yield of the dye furnished over fibre was found to be excellent. All the synthesized compounds have been evaluated for antibacterial activity against Pseudomonas aeruginosa, Escherichia Coli and Staphylococcus aureus.

Keywords: *Metal complexes, dyeing, fastness properties, antibacterial.*

I. Introduction

Metallizable azo dyes containing one heterocyclic donor atom suitably located for formation of annulated chelate complex were the subject of numerous studies[1-3], the most common being those containing a hetero nitrogen atom in a position adjacent to the azo group [4,5,6] . Infact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts[7,8]. Copper, cobalt and chromium complex combinations with azo dyes prepared from 1-diazo-2-napthol-4-sulphonic, and 6-nitro-1-diazo-2-napthol-4-sulphonic acids by coupling with β-naphthol have showed moderate dyeing resistances on wool and polyamides[9]. 1,2-hydroxo phenyl azo dyes and their metal complex with chromium and cobalt salts synthesized showed dyeing protein and polyamide fibers with excellent light and wash fastness. These dyes are used in electrophotographic or sensor applications, lasers, electro-optical devices and ink-jet printers[10,11].

In recent years phase transfer catalysis has assumed a new importance in organometallic [12,13,14] and coordination metal chemistry[15-17] in particular as a useful approach to the preparation of ligands [18,19]. 5-pyrazolones are the most familiar heterocyclic coupling components used in the azo dye chemistry. They couple as 5-hydroxypyrazoles and are specially valuable for the production of yellow to red dyes[20]. These complexes are used in the dye industry to give desired properties to the dyes .In our present study a small library of hitherto unprepared metal complex acid dyes were synthesized on a preparative scale. The synthesis start with a substituted 2-amino-5-bromo benzoic acid that undergoes diazotization to give corresponding diazo compound**,** the latter undergoes reaction with 1-(2'-methyl,5'-sulfo)phenyl-3methylpyrazolone(0.01mole) to give the ligand 5-Bromo-2{[5-hydroxy-3-methyl]-1-{[2'-methyl -5'-sulfophenyl)- 1H- pyrazol-4-yl]diazenyl} benzoicacid (PC_3**)** promoted with aqueous metal solution yielding title metal complex dyes. The intermediates and the target compounds were isolated by IR and NMR. Also washing fastness and light fastness properties of all the dyed patterns were studied along with its antibacterial activities against gram positive and gram negative bacteria.

II. Experimental

All reagents, solvents and catalyst were of analytical grade and used directly. All the melting points were determined in open capillaries and are uncorrected. The purity of compounds was checked routinely by TLC (0.5mm) thickness using silica gel-G coated Al-plates (Merck) and spots were visualized by exposing the dry plates in iodine vapors. Fastness to light and washing was assessed in accordance with BS : 1006-1978 and 765-1979 respectively whereas rubbing fastness test was carried out with a Crockmeter (Atlas) in accordance with AATCC-1961

2.1.Methods of Synthesis

2.1.1. Synthesis of 2-Amino-5-bromo benzoic acid (2a)

2-Amino benzoic acid (20 g) was dissolved in glacial acetic acid(250ml) and cooled below 16°c. Bromine(9.5 ml) was added rapidly to it and the mixture was stirred for 2-3 hours vigorously. Reaction mixture consisting of 2-Amino-5-bromo benzoic acid and 2-Amino-3,5-dibromo benzoic acid and then filtered off. The solid mass was obtained was then boiled up with water(500 ml) containing concentrated hydrochloric acid (25 ml).The hot boiling solution was filtered rapidly and the filtrate obtained was cooled in ice-bath.The filtrates upon cooling yielded abundant precipitates of the 2-Amino-5-bromobenzoic acid (M.P 219°C) and insoluble residue consisted of the 2-Amino-3,5-dibromo benzoic acid(.M.P.235°C)

2.1.2 Synthesis of diazonium salt of 2-Amino-5-Bromo benzoic acid: (2b)

2-Amino-5-bromobenzoic acid (0.01 moles) was suspended in water (50 ml), concentrated hydrochloric acid (3.0 ml, 0.025mole) was added drop-wise to the well stirred suspension and the resultant clear solution was cooled to 0-5°C in ice-bath. A solution of sodium nitrite(0.012 moles) in water (10 ml) previously cooled to 0°C was then added and the reaction mixture was stirred for an hour and the diazo was used for the subsequent coupling.

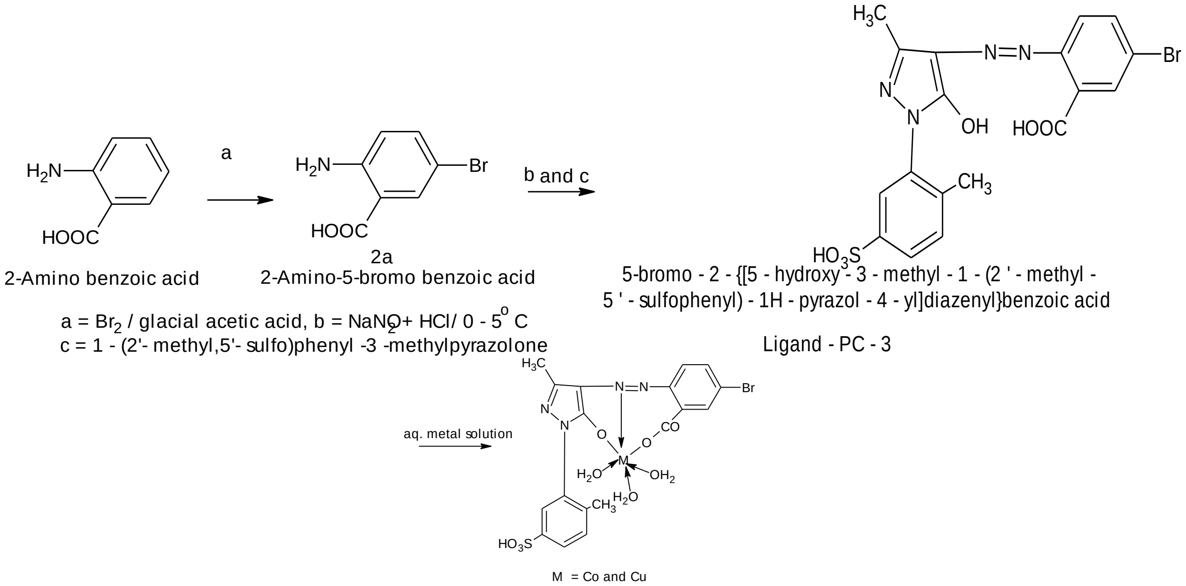
2.1.3 Synthesis of 5-Bromo-2{[5-hydroxy-3-methyl]-1-{[2'-methyl-5'-sulfophenyl)-1H-pyrazol-4yl]diazenyl} benzoicacid :(Ligand-PC$_3$)

1-(2'-Methyl,5'-sulfo)phenyl-3methylpyrazolone(0.01mole) was dissolved in Na_2CO_3 solution(10% W/V) and cooled to 0-5°C in and ice-bath. A well stirred diazonium solution of 2-Amino-5-Bromo-benzoic acid was added and stirring was continued for 3 hours at 0-5°C and pH was adjusted to 7 by adding Na_2CO_3 solution (10%W/V) . After the completion of reaction, NaCl solution (10% W/V) was added with stirring to precipitate out the solid material. It was then filtered and crystallized from DMSO to get orange yellow crystals Yield 80%, M.P above 300°C

2.1.4. Synthesis of metal complexes : TP-1(Co-PC$_3$) and TP-2(Cu-PC$_3$)

The hot aqueous solution of metal chloride (0.01) mole was added to 5-Bromo-2{[5-hydroxy-3-methyl]-1-{[2-methyl-5-sulfophenyl)-1H-pyrazol-4-yl]diazenyl}benzoic acid (0.01mole) dissolved in diaoxane slowly with constant stirring. Then a small amount of sodium acetate (0.5g) was stirred into it and the whole was set aside for about an hour. The solid metal complex precipitated was first filtered with small portion of hot distilled water and finally with dioxane. The Co(II) and Cu(II) complexes were crystallized from DMF.

Reaction Scheme



The procedure through which wool fabrics was treated is divided into four major sections

2.2 An application of acid dyes on wool fabrics
2.3. Exhaustion of dye-bath
2.4. Fixation study of the dyed wool fabrics
2.5. Study of light and washing fastness

2.2. <u>An application of acid dyes on wool fabrics</u> :

Dyeing with acid dye is carried out by following the procedure given below :

2.2.1. Pre-treatment of the fabric: Knitted woolen fabric (2.5 gm) was scoured in a solution containing 2g/L soap solution, ammonia (0.1 mL) and water (100 mL). It was then boiled for 15 minutes. The fabric was removed from the bath and rinsed several times with water. It was then rinsed, dried and conditioned for two days in atmospheric condition and subsequently used for dyeing.

2.2.2 Adjustment of pH of fabrics to a required value: In order to study of dyeing at a certain pH, it is necessary to adjust pH of the suspended fabrics and solution forming dye-bath to a required value. In order to obtain evenness of pH throughout the material before it enters the dye liquor. A weighted amount of previously treated wool fabrics was heated for 5 minutes at 95-100°C in a solution which was adjusted to pH 3.0 by adding with acetic acid (10% w/v) solution. The wool fabrics were removed and squeezed as far as possible to make it free from adhering mother liquor.

2.2.3. Dyeing procedure: Dye solution (10 ml, 0.4% w/v) was taken in a dye-bath. Glauber's salt solution (7 ml., 20% w/v) was added to it. The pH of the dye-bath was adjusted to 3.0 by adding acetic acid solution (3.5 ml., 10% w/v) solution . The total volume of the dye-bath was adjusted to 80 ml by adding required amount of water. The wool fabric previously adjusted to pH 3.0 was introduced into the dye-bath with stirring. The content of the dye-bath was stirred for 30 minutes at room temperature. The temperature was then gradually raised to 95°C over period of 30 minutes and maintained for 20 minutes. The dye-bath was kept rotating during the process of dyeing. After this, the dye liquor was taken in 250 ml volumetric flask. The fabric was washed with cold water and the combined solution of dye liquor and washings was then further diluted to 250 ml with water. 5 ml of this solution was further diluted to 250 ml with water and the absorbance of this solution was measured.

The above pattern was further rinsed, washed and dried and a part of it was mounted on shade cards.

2.3. Exhaustion of dye-bath: The combined solutions of the dye liquor and the washings were diluted to 250 ml with water. 5 ml of this solution was further diluted to 25 ml with water. The percentage dye-bath exhaustion was calculated by measuring the absorbance of the above solution and reading the corresponding concentration on the calibration curve. The results of percentage exhaustion of dye-bath are shown in Table-3.

2.4. Fixation study of the dyed wool fabrics: This involves two steps : construction of calibration curve and estimation of dye which is fixed on the fabric by extraction method using boiling acidic solution of pyridine containing pyridine (10% w/v), 90% formic acid (20% w/v) and water (to 100% vol) instead of water. The data is presented in Table-2

2.4.1. Estimation of fixation of dye: Dyed wool fabric (0.1 gm) was place in corning tube and acidic solution of pyridine (10 mL) till the dye was completely extracted from the fabric. The combined extract was diluted to 50 mL with acidic solution of pyridine. The percentage fixation of the dye was then calculated by measuring the absorbance of this solution and reading the corresponding concentration on the calibration curve. A solution of undyed wool fabric in acidic solution of pyridine was used as reference solution in colorimetric estimation.

2.4.2. Color yield on dyed wool fabrics: Measurement of color yield was used as a known technique to ascertain the commercial viability of the prepared dyes for dyeing synthetic fibre and their blends. Further, results obtained might clarify the mode of interaction between the prepared dyes and test fibres.

Farag et al[1] had described the measurement of color yield over the fabrics. Color yield was formulated as,

Color yield = Z/A x 10,

Where, Z represents the amount of dye fixed on the fibres and A is the initial amount of dye applied on the fabrics.

The measured absorbance at λmax was used to determine the amount of dye present in the dissolved form in the solvent. The results of the colour yield study of dyes are presented in Table-4

2.5. Study of light and washing fastness :

Study of light and wash fastness properties of dyed wool fabrics

2.5.1. Study of light fastness :

The light fastness of a dyed pattern is one of the most important properties desired of a dye. The dye textiles are often exposed to light and here it is essential that the color should not fade on exposure to light. So the study of light fastness of dyes becomes essential.

To study light fastness property of a dyed fabric automatic device known as fadeometer are available. The light fastness study can also be carried out using sunlight microscal MBTF, microscal MB/U source etc.

Park and Smith had examined a number of sources with particular reference to the testing of materials with high light fastness. The authors have indicated several light sources that are suitable for carrying out fastness test on textiles. They have also compared the results of different light sources and their have good correlation.

To study the light fastness property of dyed patterns; microscale light fastness tester was used with the straight mercury vapor lamp (MB/U 400w.). This gives satisfactory results in light fastness evaluation and is especially useful, in that the time required for fading patterns of high fastness is considerably less than with other commonly used fading lamps.

The dyed fabrics were exposed to light along with the standard dye fabrics of specific rating. Such standard samples are blue wool standards developed and produced in Europe and are identified by the numerical designation 1-8. Higher the rating better, is the light fastness.The light fastness study was carried out using Microscale light fastness tester having MB/U mercury lamp. The dyed fabrics along with eight standard samples were routed on test holder. Part of the dyed fabric is exposed to light and part of it is covered. After definite intervals of time, the exposed and unexposed portions of test fabrics were examined and compared with the standard fabrics. Suppose at a given time the test fabric has not faded and the standard pattern rated at 7 has not faded then the light fastness is said to be excellent. Now at the next consecutive inspection if the test pattern has faded but the standard pattern of rating 3 has not faded then the test fabric, has the fair light fastness.

Following the above procedure the light fastness properties of dyes TP-1(Co-PC_3) and TP-2 (Cu-PC_3) wool was evaluated and assessed. The results are tabulated in Table-4.

2.5.2. Study of wash fastness: The wash fastness of the dyed fabrics is another important property desired off. The dyed textile materials are very often washed with soap and detergents and become necessary that the color should not fade on washing. Therefore to study the wash fastness, five test methods are developed by Indian Standards.[7] The results of wash fastness study of dye TP-1 and TP-2 on wool are presented in Table-4.

(a) Shade: Visual observation of the shade cards TP-1 and TP-2 reveals the excellent range of shades over the wool fabrics. The deep yellow and brown to orange shades were obtained.

(b) Fastness properties: The examination of data presented in Table-4 reveals following metal complex acid dyes show very good light fastness. The wash fastness was appeared to be excellent fastness for each dyes.The results of light and wash-fastness properties on the wool fabrics are presented inTable-4

III. Results and discussion

Ligand : PC_3

^{1}H NMR (DMSO, 400 MHz) δ 2.29 (s,3H, Ar-CH_3), 2.33 (s,3H,Ar-CH_3),14.66(s, 1H,Ar-COOH), 8.13 (s, 1H,Ar-OH), 14.2(s, 1H, Ar-SO_3H), 7.27-7.98 (m, 6H, Ar-H) ; IR (KBr, cm^{-1}) alkane 1217.12 (C-H) str , aromatic 3084.85 (C-H)str., 1449.81(C=C)str., 3502 (C-OH)str., Pyrazole 1529.60 (C=N)str., 1045.45 (C-N)str., Carboxylic 1320.10 (M-COOH), 590.13 (M-O), 460.00 (M-N), Sulphonic 2750.81 (-SO_3H), Halide 709.83(-C-Br); Yield: 82%

TP-1 :

^{1}H NMR (DMSO, 400 MHz) δ 2.34 (s,3H, Ar-CH_3), 2.54 (s,3H,Ar-CH_3), 14.67 (s, 1H, Ar-SO_3H), 7.31-8.13 (m, 5H, Ar-H) ; IR (KBr, cm^{-1}) alkane 1230.64 (C-H) str , aromatic 3019.71 (C-H)str., 1459.33 (C=C)str., 3264.15 (C-OH)str., Pyrazole 1413.44 (C=N)str., 1363.52 (C-N)str., Carboxylic 1329.10 (M-COOH), 590.13 (M-O), 450.00 (M-N), Sulphonic 2735.22 (-SO_3H), Halide 699.74(-C-Br); Yield: 80%

TP-2 :

^{1}H NMR (DMSO, 400 MHz) δ 2.34 (s,3H, Ar-CH_3), 2.62 (s,3H,Ar-CH_3), 14.77 (s, 1H, Ar-SO_3H), 7.28-8.20 (m, 5H, Ar-H) ; IR (KBr, cm^{-1}) alkane 1245.92 (C-H) str , aromatic 3036.26 (C-H)str., 1464.48(C=C)str., 3289.12 (C-OH)str., Pyrazole 1499.54 (C=N)str., 1377.98 (C-N)str., Carboxylic 1397.45 (M-COOH), 566.23 (M-O), 455.90 (M-N), Sulphonic 2763.63 (-SO_3H), Halide 675.22(-C-Br); Yield: 86%

Table-1: Calibration data for Exhaustion study of Acid Dyes TP-1 toTP-2

Substrate for dyeing :Wool (2.0 gm) Medium of spectral study : Aqueous

Dye Code No.	Wave length λ_{max} nm	Absorbance of the dye solutions at specified wavelength conc. x 10^{-3} mg.m^{-1}				Slope of linear plot K*
		4.0 Ab.	8.0 Ab.	12.0 Ab.	16.0 Ab.	
TP-1	**422**	0.090	0.140	0.210	0.160	10.00
TP-2	450	0.120	0.210	0.235	0.310	19.375

Table-2 : Calibration data for Fixation study of Acid dyes: TP-1 to TP-2

Dyed pattern for fixation study: Wool fabric(0.1 gm)

Medium of spectral study :Acidic pyridine

Dye Code No.	Wave length λ_{max} nm	Absorbance of the dye solutions at specified wavelength conc. x 10^{-3} mg.m^{-1}				Slope of linear plot K*
		4.0 Ab.	8.0 Ab.	12.0 Ab.	16.0 Ab.	
TP-1	422	0.160	0.320	0.450	0.550	34.375
TP-2	450	0.120	0.240	0.360	0.470	29.375

Table-3: Result of Exhaustion and Fixation study of Acid dyes TP-1 to TP-2

Substrate for dyeing : Wool fabric (2.0 gm)

Dyed pattern for fixation study: Wool fabric (0.1 gm)

Medium of spectral study: Aqueous-exhaustion, acidic pyridine-fixation study.

Amount of dye under study : 40 g

Dye Code No.	Amount of dye remain-ed in dye bath (X mg)	Amountof exhausted from dyebath (40-X) = Y mg	% ExhaustionYmg/ 40mg x 100	Amount of dye in 0.1 gm of dyeing a mg.	Amount of dye in 2.0 gm of dyeing (total weight 20a=Z mg)	Fixation=(Zmg/Ymg) x 100%
TP-1	9.02	30.98	77.45	1.26	25.2	81.34
TP-2	8.62	31.38	78.45	1.31	26.2	83.49

Table-4 :Shade, colour yield and fastness properties of Acid dyes on Wool fabrics.

Dye Code No.	Compound	Shade on Wool	λmax nm	Coloryield = (Zmg / 40mg) x 100	Light	Wash
TP-1	**Co-PC$_3$**	Dark yellow	520	63.0	6	5
TP-2	**Cu-PC$_3$**	Dark brown	530	65.5	5	4

IV. Antibacterial activity

The synthesized compounds were screened against Pseudomonas Aeruginosa, Escherichia Coli and Staphylococcus Aureus bacteria were studied and results presented in table 5.

Table 5 : Antibacterial activity of TP-1 and TP-2

Compound	Gram negative E.c ATCC 25922	Gram negative P.a ATCC 27853	Gram positive S.a ATCC25923
TP-1	-	++	+++
TP-2	+	++	++++

Zone of Inhibition of Standard drug (µg/ml)

Streptomycin	-	-	-
The inhibition diameter in mm: (-) < 6, (+) 7-9, (++)10-15, (+++) 16-22			
S.a-Staphylococcus aureus, **P.a**- Pseudomonas aeruginosa, **E.c**-Escherichia Coli			

V. Conclusion:

In conclusion, acid dye metal complexes TP-1 and TP-2 were synthesized .The pharmacological study was undertaken to evaluate the effects of substituents on the antibacterial activities. All synthesized compounds exhibited good antibacterial activity towards Gram positive bacteria. These compounds also showed promising activity towards Gram negative bacteria.Its activity increased from ligand to complexes. The washing fastness was appeared to be excellent fastness for each dyes thus proved to be eco-friendly.

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