#### **ORIGINAL ARTICLE**



# Synthesis of Symmetric Bridged Bis-Pyrazolone Based Metal Complex Acid Dyes and their Applications on Leather

Muhammad Ayaz<sup>1</sup> • Muhammad Ayaz<sup>1</sup> • Farman Ali<sup>1</sup> • Aamer Saeed<sup>2</sup> • Asma Khurshid<sup>3</sup> • Ghulam Shabir<sup>2,4</sup> • Tanveer Ahmad<sup>4</sup> • Syed Asad Raza Kazmi<sup>4</sup> • Hassan Ali Khan<sup>4</sup>

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#### Abstract

Our present investigation aims at the synthesis and application of new, symmetric bridged bis-pyrazolone based acid dyes. The bis-pyrazolone compounds were accomplished from bis- hydrazine of 4,4'-Diaminostilbene-2,2'-disulfonic acid and ethyl acetoacetate. The bis-pyrazolones have been coupled with diazonium salts of *o*-hydroxyl aromatic amines which resulted in ligand dyes. The intermediate ligand dyes were treated with 3d transition metals to achieve the targeted metal complex acid dyes. The structures of investigated compounds were confirmed with the help of spectroscopic techniques. Dyes were applied on leather and their application parameters including their light fastness, wash fastness and rubbing fastness were determined.

Keywords Bis-Pyrazolone · Acid Dyes · Diazotization · Spectroscopic Techniques · Leather · Fastness

#### Introduction

Azo compounds and their metal complex dyes are continuously gaining much attention in scientific research because of variety of derivatives obtained by adopting a slight changing in dye intermediate structure [1–3]. Furthermore, azo dyes have been studied widely because of their excellent thermal and optical

properties in applications such as optical recording medium toner ink-jet printing and oil-soluble light fast dyes [4, 5]. Azo dyes are used in dyeing textile fibres, particularly cotton but also silk, wool, viscose and synthetic fibres. They are considered to be easy to use, relatively cheap and to provide clear, strong colors [6, 7]. Recently, azo compounds as organic dyes have also attracted attention due to their interesting electronic features in

Research Highlights

- Bis-pyrazolones were employed to couples with diazonium salts of *ortho*-hydroxy aromatic amines
- Ligand dyes have complexed with 3d metals and applied on leather.

Farman Ali farmanqau@gmail.com

Ghulam Shabir shabirg@yahoo.com

> Muhammad Ayaz mohammadayaz31@gmail.com

Muhammad Ayaz ayazanwar239@gmail.com

Aamer Saeed aamersaeed@yahoo.com

Asma Khurshid asmakhurshid2000@hotmail.com

Tanveer Ahmad arslansaleem557@gmail.com Syed Asad Raza Kazmi syedasadrazakazmi72@gmail.com

Hassan Ali Khan hassanalikhan@gmail.com

- <sup>1</sup> Department of Chemistry, Hazara University, KPK, Mansehra 21300, Pakistan
- <sup>2</sup> Department of Chemistry, Quaid-I-Azam University, Islamabad 45320, Pakistan
- <sup>3</sup> Department of Metallurgy and Material Engineering, PIEAS, PO Nilore, Islamabad 45650, Pakistan
- <sup>4</sup> Department of Chemistry, Govt. Gordon College Rawalpindi, Punjab, Pakistan

<sup>•</sup> Synthesis of symmetric bis-pyrazolones has been conducted.

connection with their application for molecular memory storage, nonlinear optical elements and organic photoconductors [8]. Because of their interesting electronic properties in concern to their application for molecular memory storage, wide variety of hues ranging from blue to red in the visible region of the electromagnetic radiation (EMR) spectrum have been synthesized.

Above all the medicinal importance of azo compound is well documented as antidiabetics, antiseptic, anti-neoplastic, antibacterial and antitumor [9-11]. Besides these, a number of biological reactions are there in which the azo compounds exhibit their role such as in protein synthesis, RNA synthesis and inhibition of DNA [12-17].

Keeping in view, the above mention facts, the main objective of this research is to develop and evaluate the bissymmetric bridged pyrazolone acid dyes having strong and bright shade which should have ability to show exhaust dyeing when applied on leather. In order to cope with this purpose, DASDA based bis-pyrazolone were prepared and their acid dyes and metal complexes have been synthesized and applied on leather.

#### Experimental

#### **Materials and Methods**

All compounds were purchased from Sigma-Aldrich. Analytical grade solvents were used and when necessary, were redistilled and dried by the standard methods. Stuart melting apparatus was used to determine the melting point of compounds. The FT-IR spectra were conducted on the single beam Nicolet IR 100 (Fourier-Transform); while UV of all the samples were taken in water using UV-Genesys spectrophotometer. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in DMSO-d<sub>6</sub> using NMR Bruker DPX 300 spectrophotometer operating at 300 MHz. TMS was used as internal standard with the deuterium signal of the solvent as the lock and chemical shifts  $\delta$  were recorded in ppm. The elemental analysis (C, H, N, S) of the compounds was performed using Flash EA 1112 elemental analyzer and the pH was measured employing portable pH Meter PHB4. Compounds were routinely checked by TLC on silica gel G plates using different eluting solvents keeping in view the solvent polarities. The different solvent systems which were employed in TLC separations are: petroleum ether: chloroform (9:1, v/v), petroleum ether: chloroform (6:4, v/v) and chloroform: methanol (9:1, v/v). The developed TLC plates were visualized using UV lamp to detect the presence of spots and Rf values were duly calculated. All crude products were isolated as solids and purified by a combination of column chromatography and re-crystallization. Color fastness to light, rubbing and washing was determined as per standard test method of EN ISO 105-B02, ISO 11640 [18] and ISO 765-1979 [19] respectively.

# (a) Procedure for the Synthesis Bis-Hydrazine from 4,4'-Diaminostilbene-2,2'-Disulfonic Acid

4,4'-Diaminostilbene-2,2'-disulfonic acid (7.4, 0.02 mol, 1) was suspended in 100 ml of distilled water in a round bottomed flask kept in ice bath and started stirring. It was added HCl (14.6 ml) followed by addition of NaNO<sub>2</sub> (2.8 g, 0.04 mol). Stirred the whole mixture for 1 h while keeping the temperature constant (0-5 °C) until the diazotization was completed which was observed by the paper chromatogram. The diazonium salt of 4,4'-Diaminostilbene-2,2'-disulfonic acid was filtered and precipitates were collected.

The cooled and wet diazonium salt was subjected to reduction. A saturated solution of 12 g of Na<sub>2</sub>SO<sub>3</sub>.7H<sub>2</sub>O (5.02 g, 0.04 mol) was prepared in 50 ml water and cooled the solution up to 0–5 °C. The diazonium salt was added slowly (within 1 h) into the well stirred solution of sodium thiosulfate Na<sub>2</sub>SO<sub>3</sub>.7H<sub>2</sub>O and further stirred the reaction mixture at 0-5 °C for more one hour. Then removed the mixture from ice jacket and heated up to 100 °C by gradual heating. It was slowly added concentrated HCl (30 ml) at 100 °C with constant stirring. The reaction mixture was then cooled to room temperature and was added a pinch of Zn dust. The precipitates of (E)-6,6'-(ethene-1,2-diyl) bis (3-hydrazinylbenzenesulfonic acid) (**3**) were settled down by keeping the reaction mixture overnight. The precipitates were filtered and dried in oven at 70 °C.

The above synthesized hydrazine (3, 4.0 g 0.01 mol) was dissolved in 30 ml H<sub>2</sub>O in 100 ml beaker by adding Na<sub>2</sub>CO<sub>3</sub> (2 g) and clear solution was obtained which was filtered to remove the undissolved materials. Few drops of HCl were added to neutralize the hydrazine solution. The hydrazine solution was poured in round bottomed flask and was refluxed at 100 °C with ethyl acetoacetate (0.02 mol) for 1 h at constant stirring and heating until completion of reaction was observed from TLC (methanol: chloroform, 9:1). The reaction mixture was cooled and added of HCl (10 ml) which resulted in the precipitation of pyrazolone (4) which was filtered and dried in oven at 70 °C. This synthesized pyrazolone (5.32 g, 0.01 mol) was coupled with separately prepared diazonium salt of 4-Chloro-2aminophenol (2.86 g, 0.02 mol) at 0-5 °C in alkaline medium (pH = 9.0). The synthesized ligand dye 7a was precipitated from aqueous solution by adding HCl (15 ml), that was then filtered and dried at 70 °C in oven. Similarly another dye 7b was synthesized by coupling the pyrazolone (4) with diazonium salt of 4-Nitro-2-aminophenol by employing the above conditions.

The ligand dye **7a** (0.84 g 0.001 mol) was dissolved in methanol and treated with CuSO<sub>4</sub>.5H<sub>2</sub>O (8a, 0.002 mol) in round bottomed flask at reflux temperature. The reaction mixture was then made basic by adding tri-ethylamine (pH = 9.5–10). The reaction mixture was stirred for 4 h till complex formation was completed. Methanolic solution of copper complex was kept at room temperature for the slow evaporation of methanol and precipitates of metal complex dyes were obtained. In this way all metal complex dyes 9a-f and 10a-f were synthesized by treating ligands 7a and 7b with different metal salts 8a-f. The characteristic physical and spectroscopic data of synthesized ligand dyes (**7a-b**) and their metal complexes (9a-f and 10a-f) is as follows.

#### 5-(4-((E)-(5-Chloro-2-Hydroxyphenyl)Diazenyl) -5-Hydroxy-3-Methyl-1H-Pyrazol-1-Yl)-2 ((E)-4-(4-((E) -(5-Chloro-2-Hydroxyphenyl)Diazenyl) -5-Hydroxy-3-Methyl-1H-Pyrazol-1-Yl) 2-Sulfostyryl) Benzenesulfonic Acid (C<sub>34</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>10</sub>S<sub>2</sub>, 7a)

Brown crystal (76%)  $\lambda_{max}$  (nm, log  $\varepsilon$ ): 450 (5.80). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3360 br (OH, NH), 3055 (C=C-H), 1731 (C=O), 1690 (C=O, amide), 1665, 1585, 1510 (C=C aromatic), 1270 (S=O), 1050 (C-O), 760 (C=C bend). <sup>1</sup>H-NMR (300 MHz, DMSO)  $\delta$ : 2.32 (6H, s, CH<sub>3</sub>), 6.98 (1H, d), 7.04 (1H, d), 7.54 (1H, s), 7.74 (2H, d, J=7.5), 7.95 (2H, dJ=7.5), 8.12 (1H, s), 8.44 (1H, s), 11.15 (2H, br, SO<sub>3</sub>H), 13.44 (1H, br, O-H). <sup>13</sup>C NMR (75 MHz, DMSO)  $\delta$ : 157.45, 148.95, 146.25, 145.53, 136.34, 131.97, 130.44, 129.30, 127.32, 126.72, 125.86, 124.40, 118.35, 117.61, 117.11, 114.05, 12.05. Anal. Calcd. For C<sub>34</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>10</sub>S<sub>2</sub>; C, 48.52; H, 3.11; N, 13.31; S, 7.62; Found: C, 48.30; H, 3.15; N, 12.80; S, 7.75.

# $C_{40}H_{46}Cl_2Cu_2N_8O_{16}S_2$ (9a)

Dark brown, (81%).  $\lambda_{max}$  (nm, log  $\varepsilon$ ): 505 (5.97). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3047 (-C=C-H), 1635, 1558 (C=C benzene), 1417 (-CH<sub>2</sub>), 1339 (CH<sub>2</sub> bend), 1274 (S=O), 1171 (C-N), 1074 (C-O), 812 (Ar-H), 560 (N-Cu). Anal. Calcd. For C<sub>40</sub>H<sub>46</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>16</sub>S<sub>2</sub> C, 41.53; H, 4.01; N, 9.69; S, 5.54; Found: C, 41.44; H, 4.11; N, 9.54; S, 5.63.

# $C_{40}H_{46}Cl_2Fe_2N_8O_{16}S_2$ (9b)

Reddish brown, (80%).  $\lambda_{max}$  (nm, log ε): 455 (5.90). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3190 (C-H), 1603, 1565 (C=C benzene), 1424 (-CH<sub>2</sub>), 1072 (C=O), 609 (C-Cl), 514 (O-Fe). Anal. Calcd. For **C**<sub>40</sub>**H**<sub>46</sub>**Cl**<sub>2</sub>**Fe**<sub>2</sub>**N**<sub>8</sub>**O**<sub>16</sub>**S**<sub>2</sub> C, 42.09; H, 4.06; N, 9.82; S, 5.62; Found: C, 42.02; H, 4.12; N, 9.74; S, 5.68.

# $C_{40}H_{46}CI_2Ni_2N_8O_{16}S_2$ (9c)

Grey (80%).  $\lambda_{max}$  (nm, log  $\varepsilon$ ): 495 (6.10). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3154 (C-H, str), 1635, 1560 (C=C aromatic), 1453 (N=N, str), 1320 (C-H, bend), 1240 (S=O str), 1056, C-O), 880 (C=C, bend). Anal. Calcd. For  $C_{40}H_{46}Cl_2Ni_2N_8O_{16}S_2$  C, 41.88; H, 4.04; N, 9.77; S, 5.59 Found: C, 41.82; H, 4.14; N, 9.70; S, 5.65.

# $C_{40}H_{46}Cl_2Co_2N_8O_{16}S_2$ (9d)

Dark brown (81%).  $\lambda_{max}$  (nm, log  $\epsilon$ ): 490 (6.16). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3120 (C-H), 1643, 1590, 1518 (C=C aromatic),

1242 (S=O), 1176 (C-N Amines Aromatic), 1079 (C-O), 824 (C=C bending), 545 (N-Co). Anal. Calcd. For  $C_{40}H_{46}Cl_2Co_2N_8O_{16}S_2$ : C, 41.86; H, 4.04; N, 9.76; S, 5.59 Found: C, 41.75; H, 4.09; N, 9.63; S, 5.65.

#### $C_{40}H_{46}Cl_2Cr_2N_8O_{16}S_2$ (9e)

Dark brown (81%).  $\lambda_{max}$  (nm, log  $\varepsilon$ ): 497 (6.20). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3155 (C-H), 1643, 1590, 1518 (C=C aromatic), 1447 (N=N), 1220 (S=O), 1060 (C-O), 1176 (C-N), 1090 (C-O), 855 (C=C bending), 595 (O-Cr). Anal. Calcd. For C<sub>40</sub>H<sub>46</sub>Cl<sub>2</sub>Cr<sub>2</sub>N<sub>8</sub>O<sub>16</sub>S<sub>2</sub> C, 42.37; H, 4.09; N, 9.88; S, 5.66; Found: C, 42.30; H, 4.15; N, 9.80; S, 5.71.

#### $C_{40}H_{46}Cl_2Zn_2N_8O_{16}S_2$ (9f)

Grey (78%).  $\lambda_{max}$  (nm, log  $\varepsilon$ ): 470 (6.01). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3140 (N-H), 1578 (C=C Aromatic), 1389 (SO<sub>3</sub>H), 1335 (SO<sub>3</sub>H), 1285 (C-C stretch), 1177 (C-O stretch), 1079 (-CH-OH), 1020 (S=O), 507 (Zn). Anal. Calcd. For C<sub>40</sub>H<sub>46</sub>Cl<sub>2</sub>Zn<sub>2</sub>N<sub>8</sub>O<sub>16</sub>S<sub>2</sub>: C, 41.39; H, 4.00; N, 9.65; S, 5.52; Found: C, 41.32; H, 4.06; N, 9.63; S, 5.52.

#### 5-(5-Hydroxy-4-((E)-(2-Hydroxy-5-Nitrophenyl)Diazenyl) -3-Methyl-1H-Pyrazol-1-Yl)-2-((E)-4-(5-Hydroxy-4-((E) -(2-Hydroxy-5-Nitrophenyl)Diazenyl) -3-Methyl-1H-Pyrazol-1-Yl)-2-Sulfostyryl)Benzenesulfonic Acid (C<sub>34</sub>H<sub>26</sub>N<sub>10</sub>O<sub>14</sub>S<sub>2</sub> 7b)

Yellowish brown crystal, (72%).  $\lambda_{\text{max}}$  (nm, log  $\varepsilon$ ): 460 (6.05). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{\text{max}}$ : 3365 br (OH), 3080 (C=C-H), 1720 (C=O), 1685 (C=O, amide), 1620, 1585, 1510 (C=C aromatic), 1484.7 (C-H scissoring), 1277 (S=O), 1070 (C-O), 780 (Ar-H). <sup>1</sup>H-NMR (300 MHz, DMSO)  $\delta$ : 2.25 (6H, s, CH<sub>3</sub>), 6.98 (2H, d), 7.35 (2H, d), 7.71 (2H, s), 7.849–7.95 (4H, m), 8.11(2H, s), 8.29 (2H, s), 8.44 (2H, s), 11.15 (2H, br, SO<sub>3</sub>H), 13.67 (1H, br, O-H), 14.67 (1H, br, O-H). <sup>13</sup>C NMR (75 MHz, DMSO)  $\delta$ : 161.87, 157.96, 148.82, 147.07, 146.47, 140.85, 136.61, 131.94, 128.57, 115.49, 112.96, 100.56, 12.30. Anal. Calcd. For C<sub>34</sub>H<sub>26</sub>N<sub>10</sub>O<sub>14</sub>S<sub>2</sub>; C, 47.33; H, 3.04; N, 16.24; S, 7.43; Found: C, 47.13; H, 3.14; N, 15.95; S, 7.48.

# $C_{40}Cu_2H_{46}N_{10}O_{20}S_2$ (10a)

Pink violet (75%).  $\lambda_{max}$  (nm, log ε): 515 (6.25). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3080.5 (=C-H Stretch), 1610, 1570, 1515 (C=C aromatic), 1484.7 (C-H scissoring), 1277.1 (S=O), 1161.2(C-O Alcohol). Anal. Calcd. For C<sub>34</sub>H<sub>26</sub>N<sub>10</sub>O<sub>14</sub>S<sub>2</sub>; C, 40.78; H, 3.94; N, 11.89; S, 5.44 Found: C, 40.70; H, 3.99; N, 11.89; S, 5.49.

# $C_{40}Fe_2H_{46}N_{10}O_{20}S_2$ (10b)

Yellowish brown (76%).  $\lambda_{max}$  (nm, log  $\epsilon$ ): 460 (6.14). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3308.2(N-H), 2879.4(C-H Aliphatic),

1579.3(C=C benzene ring), 1474.8(N-H), 1277.1 (C-O stretch), 1171.1(C-N amides), 1058.6(c-o), 828.2(C=C aromatic ring bending), 613.7(N-Fe), 505.4 (O-Fe). Anal. Calcd. For  $C_{34}H_{26}N_{10}O_{14}S_2$ ; C, 41.32; H, 3.99; N, 12.05; S, 5.51; Found: C, 41.22; H, 4.06; N, 11.97; S, 5.59.

#### $C_{40}H_{46}N_{10} Ni_2O_{20}S_2$ (10c)

Pink Violet (74%).  $\lambda_{max}$  (nm, log  $\varepsilon$ ): 407 (6.12). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3188.5 (N-H), 1605, 1581.3(C=C benzene ring), 1478.3 (N-H bend), 1424.3(-CH<sub>2</sub>), 1285.7(C-O stretch), 1174.2(C-N Amines-Amides), 1072.0(C-O), 824.5(C=C bending aromatic ring), 616.9(N-Ni), 509.5(O-Ni). Anal. Calcd. For C<sub>34</sub>H<sub>26</sub>N<sub>10</sub>O<sub>14</sub>S<sub>2</sub>; C, 41.12; H, 3.97; N, 11.99; S, 5.49; Found: C, 41.02; H, 3.99; N, 11.82; S, 5.55.

#### $C_{40}Co_2H_{46}N_{10}O_{20}S_2$ (10d)

Pink Violet (70%).  $\lambda_{max}$  (nm, log  $\varepsilon$ ): 400 (6.18). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3174.7(N-H), 1580.5(C=C benzene ring), 1478.4(N-H bend amides), 1427.3(-CH<sub>2</sub>), 1287.9 (C-O stretch), 1177.4 (C-N Amines), 1072.2(-C=O), 1018.2(C-O), 825.0 (C=C bending), 516.3(N-Co). Anal. Calcd. For C<sub>34</sub>H<sub>26</sub>N<sub>10</sub>O<sub>14</sub>S<sub>2</sub>; C, 41.10; H, 3.97; N, 11.98; S, 5.49; Found: C, 41.00; H, 4.04; N, 11.76; S, 5.53.

#### $C_{40}Cr_2H_{46}N_{10}O_{20}S_2$ (10e)

Reddish violet (74%).  $\lambda_{max}$  (nm, log  $\varepsilon$ ): 403 (6.20). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3084(C=C-H Aromatic), 1594, 1536 (benzene ring), 1487 (N-H bend), 1336 (C-H bending), 1294(S=O), 1072(C=O), 1015(C=O), 823 (C=C aromatic bending), 616 (N-Co), 509(O-Co). Anal. Calcd. For C<sub>40</sub>Cr<sub>2</sub>H<sub>46</sub>N<sub>10</sub>O<sub>20</sub>S<sub>2</sub>; C, 41.60; H, 4.01; N, 12.13; S, 5.55; Found: C, 41.38; H, 4.12; N, 12.01; S, 5.62.

#### $C_{40}H_{46}N_{10}O_{20}S_2Zn_2$ (10f)

Yellowish brown (75%).  $\lambda_{max}$  (nm, log  $\varepsilon$ ): 405 (6.28). FTIR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3323.5(N-H), 3202.1(O-H), 1590.8 (C=C benzene ring), 1478.8 (N-H bend), 1403.2 (CH<sub>2</sub>), 1177.0 (C-N, amines), 1072.6(C-O), 1018.2(C-O), 826.7(C=C bend), 627.2(C-X), 509.4(O-Zn). Anal. Calcd. For C<sub>40</sub>H<sub>46</sub>N<sub>10</sub>O<sub>20</sub>S<sub>2</sub>Zn<sub>2</sub>; C, 40.66; H, 3.92; N, 11.85; S, 5.43; Found: C, 40.32; H, 3.96; N, 11.56; S, 5.52.

#### **Dyeing Method**

Dyeing was conducted in dye bath containing 0.4% of dye solution (10 ml, 0.4% w/v) in the presence of 20% sodium sulfate solution (Na<sub>2</sub>SO<sub>4</sub>.7H<sub>2</sub>O, 7 ml. 20% w/v). Acetic acid solution was used to set the pH of the dye-bath at 6.5 (1.0 ml. 10% w/v). The total volume of the dye-bath was adjusted to

100 ml by adding required amount of water. The leather fabric was introduced into the dye-bath with stirring. Dye bath containing dye solution and leather pieces was stirred at 45-50 °C for 1 h. The temperature was then gradually raised to 80 °C over period of 1/2 h and adjusted at 80 °C for 3 h. The dyebath was kept rotating during the process of dyeing and was added formic acid 2.0 ml to lower the pH value of dyeing solution upto 2.0. After dyeing the leather, the dye liquor was poured in volumetric flask. Then dyes leather piece was washed with cold water and washing solution was stored and the combined with dye liquor. The combined dye solution was diluted to 250 ml with water. From this diluted solution, 1 ml was further diluted to 50 ml with water and the absorbance of this solution was measured to observe the dye exhaustion leather. The dyed leather piece was dried and mounted on shade card. In order to measure the percentage fixation of dye, a weighed amount of dyed leather was stirred in boiling acidified pyridine. The unfixed dye was dissolved in pyridine and from the absorbance of this pyridine solution percentage fixation was determined.

#### **Results and Discussion**

# Synthesis of Acid Dyes 7, 8 and their Metal Complexes (10a-H, 11a-H)

The synthesis of acid dyes 7a-b based on bis pyrazolone (4) and their Copper (II), Iron (II), Nickel (II), Cobalt (II), Chromium (III) and Zinc (II) complexes (9a-f and 10a-f) were achieved by following a multistep procedure which involved the diazotization of 4,4'-Diaminostilbene-2,2'-disulfonic acid (DASDA) with NaNO<sub>2</sub> and HCl at low temperature 0-5 °C and its reduction with Na<sub>2</sub>SO<sub>3</sub>.7H<sub>2</sub>O to produce its hydrazine (3). The synthesized hydrazine (3) was condensed with ethylacetoacetate under neutral conditions and reaction mixture was refluxes which produced pyrazolone nucleus on both sides of the hydrazine. Reaction mixture on acidification with HCl provided the precipitates of the symmetric bis-pyrazolone (4). The symmetric pyrazolone (4) were coupled with separately prepared diazonium salt of 4-Chloro-2-aminophenol (6a) and achieved the ligand acid dyes 7a-b. Coupling was conducted in alkaline medium to do the reaction at active methylene centre and was accomplished in 2.5 h with continuous stirring at 0-5 °C. By following the same condition, the bis-pyrazolone was also coupled with diazonium salt of 4-Nitro-2-aminophenol (6b) to obtain the dye 7b. Synthesized dyes 7a-b were precipitated on completion of reaction by changing the pH of solution to acidic at 4.0 with HCl. Dyes were dried and purified by recrystallization in ethanol. Metallization of above synthesized dyes was done by treating the alkaline solution of dyes with FeSO<sub>4</sub>.7H<sub>2</sub>O, CuSO<sub>4</sub>.5H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)<sub>2</sub>.4H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, Cr<sub>2</sub>(OOCCH<sub>3</sub>)<sub>2</sub>. 2H<sub>2</sub>O and ZnCl<sub>2</sub> with continuous stirring and heating the reaction

mixture at 70-80 °C for 4-5 h in triethylamine at pH 9–10 until the completion of reaction was observed by taking the TLC of reaction mixture in 9:1 chloroform and methanol. Dyes 9a-f and 10a-f were precipitated with addition of HCl, filtered and dried in oven at 70 °C. Dyes were again re-crystallized from ethanol, dried, weighed and determined the percentage yield.



Table 1Exhaustion and fixationdata of the dyes 7a-b and theirmetal complexes (9a-f and 10a-f)

Dye	Shade on leather	$\lambda_{max}$ (nm) in ethanol	Log ε	Exhaustion % (C)	Fixation % (C)
7a	Brown	450	5.80	72.80	83.38
9a	Dark brown	505	5.97	74.46	84.23
9b	Reddish brown	455	5.90	75.42	92.35
9c	Grey	495	6.10	76.76	79.63
9d	Dark brown	490	6.16	74.45	82.23
9e	Dark brown	497	6.20	73.28	81.25
9f	Grey	470	6.01	75.77	82.54
7b	Yellowish brown	460	6.05	75.55	87.18
10a	Pink violet	510	6.25	76.88	78.40
10b	Yellowish brown	460	6.14	77.64	80.49
10c	Pink Violet	407	6.12	78.43	80.54
10d	Pink Violet	400	6.18	77.79	85.15
10e	Reddish violet	403	6.20	78.32	80.57
10f	Yellowish brown	405	6.28	77.91	86.34

#### **Spectral Properties of Dyes**

Dyes were synthesized and properly characterized by UVvisible, FTIR and NMR spectroscopic techniques to confirm the structures of newly synthesized dyes. The UV visible studies of synthesized dyes 7a-b, 9a-f and 10a-f were recorded in distilled water and are shown in Table 1 and Figs. 1 and 2. UV-visible study provided us the presences of chromophores and the conjugation framework of dyes. The ligand dyes 7a and 7b showed  $\lambda_{max}$  at 450 and 460 nm respectively. The synthesized compounds (dyes) showed two absorption maxima, one absorption maxima which is common in all dyes fall in the UV range due to  $\pi$ - $\pi$ \* transition of C=C present in the aromatic moiety of the dyes, the second one lies in visible region and is due to  $\pi$ - $\pi$ \* of azo linkage because of N=N of dyes. The metal complex dyes 9a-f and 10a-f exhibited  $\lambda_{max}$  in the range 455-505 nm and 405-515 nm respectively. From the Figs. 1 and 2, it is clear that the  $\lambda_{max}$  (absorption maxima) values have a direct relation to the nature, position and electronic power of the substituents on the aromatic rings of the diazo component and the coupler as well. The copper complexes (**9a** and **10a**) of



Fig. 1 Combined UV spectrum of Ligand Acid Dye 7a and it complexes 9a-f



Fig. 2 Combined UV spectrum of Ligand Acid Dye 7b and it complexes 10a-f



Fig. 3 FTIR Spectrum of Ligand Acid Dye 7a

ligand dyes **7a-b** exhibited largest bathochromic shift as compared to ligand dyes. Change in  $\lambda_{max}$  after metal complex formation depends upon electron accepting or donating ability of d-orbitals either they are in stable or unstable state

of electronic configuration and also on the geometry of molecule achieved after complex formation.

The FTIR spectra of the pyrazolones acid dyes derivatives (7a-b) exhibited absorption due to O-H, Ar-H, C=O,



Fig. 4 FTIR Spectrum Cu (II) complex (9a) of Acid Dye 7a



Fig. 5 <sup>1</sup>H NMR spectrum of ligand acid dye 7a

C=C, N=N, S=O, C-O at 3365-3360, 3055-3080, 1731-1720, 1690-1685, 1428-1450, 1277-1270, 1070-1050, 780-760. Specifically taking into consideration FTIR spectrum of 7a it showed broad band in the range of  $3000-3500 \text{ cm}^{-1}$  due to H-bonding of O-H group present in the molecule (Fig. 3). The absorption bands at 1665,



Fig. 6 <sup>13</sup>C NMR spectrum of ligand acid dye 7a



Fig. 7 <sup>1</sup>H NMR spectrum of ligand acid dye 7b

1585, 1510, 760 depicted the presence of C=C stretching and bending vibrations of aromatic double bonds respectively. Amide carbonyl peak was observed at 1690 cm<sup>-1</sup>. A prominent peak at 1270 cm<sup>-1</sup> is due to S=O bond of SO<sub>3</sub>H present in dye 7a. Similarly the functional groups in dye 7b have been correlated with the peaks in the FTIR spectrum.

Table 2 Fastness properties data of the dyes 7a-b and their metal complexes (9a-f and 10a-f)

Dye	Light fastness	Wash fastness	Rubbing fastness	
			Dry	Wet
7a	6/7	4/5	4	3
9a	6/7	4/5	4	3
9b	6/7	4	5	4
9c	5/6	4/5	4/5	3/4
9d	5/6	4/5	4/5	3/4
9e	5/6	3/4	4/5	3/4
9f	5/6	4	4	3/4
7b	5/6	4	4/5	3/4
10a	5/6	5	4/5	3/4
10b	5/6	4/5	4/5	3/4
10c	5/6	4/5	4/5	3/4
10d	5/6	4/5	4/5	3/4
10e	5/6	4/5	4/5	3/4
10f	5/6	4/5	4/5	3/4

The metal complexes (9a-f, 10a-f) of ligand dyes 7a and 7b also have been correlated with spectra especially for peaks of N-M and O-M which are present in the range  $504-614 \text{ cm}^{-1}$  (Fig. 4).

The <sup>1</sup>H NMR spectrum of ligand acid dye 7a (Fig. 5) showed signals down field at 13.47 and 11.15 ppm due to OH and SO<sub>3</sub>H groups present in the coupling and azo components of dye and are highly deshielded due to H-bonding. A set of doublet signals at 6.98 and 7.04 ppm are due to two ortho protons present in the coupling partner of ligand dye. A similar set of doublet signals at 7.74 and 7.95 ppm is exhibited by those ortho protons which are present at the DASDA component of dye and these are deshielded due to electron withdrawing nature of SO<sub>3</sub>H group. A singlet signal for alkenic proton sandwiched between two phenyl rings is present 7.54 ppm and is deshielded by two aromatic rings. The singlet signals at 8.11 and 8.41 ppm are due to isolated protons present on the benzene rings of azo and coupling component of dyes. A singlet signal at 2.35 ppm is showed by methyl present at the pyrazolone moiety of coupling component of ligand dye 7a. <sup>13</sup>C NMR spectrum of 7a (Fig. 6) showed twelve signals in the unsaturated region at 157.45, 148.95, 146.25, 145.53, 136.34, 131.97, 130.44, 129.30, 127.32, 126.72, 125.86, 124.40, 118.35, 117.61, 117.11, 114.05 due to twelve non equivalent carbons and one signal at 12.05 ppm due to methyl carbon attached at pyrazolone nucleus. Both <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra confirmed the structure of synthesized ligand dye 7a. Similarly the ligand acid dye 7b has also been confirmed for its structure the respective <sup>1</sup>H NMR



Fig. 8 <sup>13</sup>C NMR spectrum of ligand acid dye 7b

and <sup>13</sup>C NMR spectra as presented in Figs. 7 and 8 respectively. NMR structure study of metal complex dyes was no conducted due to paramagnetic nature of metals in complexes which caused the overlapping and broadness of signals. The metal to ligand ratio in the metal complex acid dyes was determined from UV visible studies.

#### **Dyeing Properties of Dyes**

All the dyes 7a-b and their metal complexes 9a-f, 10a-f were applied at 2% depth (Figs. 6 and 7) on leather according to the standard procedure.

#### **Exhaustion and Fixation Study**

Exhaustion and fixation values are determined by the application of dyes at 2% dyeing on leather fabric. Exhaustion and fixation values are shown in Table 1. An exhaustion deals with the amount of dye transferred from dye bath to fiber and is articulated as percentage of the quantity of dye originally placed in the dye bath. Fixation of a dye is concerned with the amount of dye fixed with the fiber. Driving force for exhaustion is concentration of dye in two phases and for fixation is the physical as well as chemical interaction with fiber. In order to acquire high degree of exhaustion, assisting salt Na<sub>2</sub>SO<sub>4</sub> was added in the dye bath to perk up exhaustion by increasing the electrostatic interactions of dyes with fiber.

The percentage exhaustion and percentage fixation of 2% dyeing on leather ranges from 72 to 78% and 78–92% respectively as it is represented in the Table 1. All the dyes have good exhaustion and fixation values which are probably due to the rapid diffusion of the dye molecule within the fabric under dyeing conditions and physical as well as chemical interactions of polar groups present in diazo and coupling components. From the applications of dyes on leather it appears that metal complexes of the dyes have high exhaustion and

Fig. 9 2% shade of dyes 7a-b and their metal complexes 9a-f and 10a-f on leather



Compound	Temperature °C	TG Weight loss (%)	
7a	0–100	13	
	100-400	9	
	400-800	51	
9a	0–100	10	
	100-400	23	
	400-800	25	
9b	0–100	10	
	100-400	12	
	400-800	24	
9c	0–100	9	
	100-400	14	
	400-800	23	
9d	0–100	9	
	100-400	16	
	400-800	43	
9e	0–100	7	
	100-400	20	
	400-800	43	
9f	0–100	4	
	100-400	24	
	400-800	31	
7b	0–100	12	
	100-400	9	
	400-800	49	
10a	0–100	7	
	100-400	12	
	400-800	24	
10b	0–100	5	
	100-400	13	
	400-800	23	
10c	0–100	6	
	100-400	14	
	400-800	25	
10d	0–100	5	
	100-400	16	
	400-800	29	
10e	0–100	9	
	100-400	15	
	400-800	37	
10f	0–100	8	
	100-400	16	
	400-800	34	

Table 3TGA data of Ligand dyes 7a-b and their metal complexes 9a-fand 10a-f

fixation as compared to unmetallized dyes. Chromium (III) complexes of dyes have high fixation as compared with iron (II) and copper (II) complexes.

#### **Fastness Properties**

Fastness properties of dyes were assessed after application of 2% dye with respect to leather fabric as represented in Table 2. These were light fastness, wash fastness and rubbing fastness which provided the clear picture regarding quality of dye.

Light fastness is the property to which a dye resists fading due to light exposure. Different dyes have different degrees of resistance to fading by light. Light fastness of ligand acid dyes **7a-b** was in range 5–6 and their metal complex showed have high light fastness 6–7. These dyes

have very little susceptibility to phtochromisim, due to involvement of electrons in complex formations. Wash fastness is the resistance offered by dyed fabric to retain color when washed by soaps and detergents. Wash fastness of dyes was in range 4–5 and was high in case of Copper and Chromium complexes.

Rubbing fastness is the most important test which is always required for every colored fabric either it is printed or dyed. Rubbing fastness was planned to determine the degree of color which may transfer from the surface of a colored fabric to a particular test cloth for abrasion. Rubbing fastness of ligand acid dyes 7a-b and their metal complexes was very high 4–5. Rubbing fastness gives clue about other improved properties like wash fastness, substantively and sturdiness in use of dyed fabric [20, 21]. It is obvious from rubbing fastness value that all these dyes have high fixation on leather fabric (Fig. 9).

#### Thermogravimetric Analysis of Acid Dye and its Metal Complexes

Thermogravimetric analysis is one of the most useful methods for investigating the thermal degradation of dyes and polymeric materials. The results obtained from thermal analysis can be used to describe its thermal stability and to determine the temperature range in which they can be used without changes in its properties, colour and composition. Thermal degradation of ligand acid dyes 7a-b and their metal complexes was conducted in argon atmosphere using a Netzsch TG 209 thermogravimetric analyzer within temperature range of 0-800 °C in flowing Argon atmosphere employing  $Al_2O_3$ as reference material.

From the TGA profiles (Table 3) the onset temperature  $(T_0)$  of ligand acid dyes was found at 80 °C and three stages decomposition occurs and maximum weight loss was observed in the range 400-800 °C. The total weight loss in 7a was 73% and in 7b was 70% which indicates that ligand dye 7a was less stable than 7b. Weight loss in the range 0-100 °C was 12-13% which is most probably due to H<sub>2</sub>O molecules trapped in dye molecules. The weight loss in the rage 100-400 °C is 9% in both dyes is due to loss of N<sub>2</sub> gas formed by the decomposition of azo linkages. The maximum weight loss in the range 400-800 °C is due to breakage of intermediates formed after the removal of azo linkage. In this range loss of SO<sub>2</sub>, CO and CO<sub>2</sub> gases occurs. Ligand dyes 7b is more stable because it contains the coupling component which is 4-Nitro-2-aminophenol which is more stable than 4-Chloro-2-aminophenol because Cl<sub>2</sub> is released more easily than NO<sub>2</sub> because of strong C-N and N-O bonds in 4-Nitro-2aminophenol. These bonds have character between single and double bond. When metal complexes TGAs of Ligand dyes 7a and 7b are considered it appears that Iron



Fig. 10 TGA Thermogram of metal complex acid dye 9c

complexes are more stable than other metals. Moreover, the all metal complexes exhibit the less total weight loss

than ligand acid dyes and more residue is obtained at 800 °C (Figs. 10 and 11). This is due to M-N and M-O



Fig. 11 TGA Thermogram of metal complex acid dye 10c

strong bonds formed during complex formation [22–24]. In all complexes weight loss during the temperature range 0-100 °C is comparatively less than ligand dyes and is 5-10%.

#### Conclusions

A series of bis-symmetric acid dyes **7a-b** and their metal complexes **9a-f** and **10a-f** has been synthesized in high yields from bis-pyrazolone **4**. Copper complexes dyes **9a** and **10a** showed more bathochromic shift in absorption maximum as compared to other metal complexes of acid dyes. Application of dyes was made on leather where they showed high light fastness, rub fastness and wash fastness. All metal complexes of dyes exhibited high exhaustion and fixation on leather in comparison to ligand dyes. Metal complex dyes showed more thermal stability than ligand dyes due to strong metal to nitrogen and oxygen bonds.

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