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Synthesis and Serviceability of New Symmetric Bis-pyrazolone Metal Complex Acid Dyes

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Abstract—Synthesis of new symmetric bis-pyrazolone acid dye and its 3d transition metal complexes is studied. Bis-pyrazolone is synthesized from (*E*)-6,6'-(ethene-1,2-diyl)bis(3-hydrazinylbenzenesulfonic acid) and ethyl acetoacetate. The synthesized bis-pyrazolone is coupled with diazonium salt of 4-sulpho-2-aminophenol in alkaline medium targeting bis-pyrazolone ligand acid dye. Various metal complexes are obtained by treating a methanolic solution of metal salts with ligand acid dye in basic media. Structures of the synthesized ligand dye and its metal complexes are confirmed by UV-Vis, FTIR, and NMR spectra. The ligand acid dye and metal complex dyes demonstrate absorption in UV-Vis in the range of 400–600 nm. Ligand acid dye and its metal complexes demonstrate good to high value of light speed, washing fastness and rubbing fastness on leather.

Keywords: bis-pyrazolone, acid dyes, spectroscopic techniques, light fastness, rubbing fastness

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INTRODUCTION

Pyrazolones based azo dyes have been widely studied in oil-soluble light fast dyes and in optical recording medium toner ink inject printing due to their excellent thermal stability and optical characteristics [1, 2]. Ease of use and enhanced strong and clear colors stimulated their wide use in dyeing textile fibers like wool, viscose, silk, synthetic fibers, and particularly cotton [3, 4]. Depending upon structure of a medium and pH, azo dyes demonstrate a variety of colors [5, 6], and are also used on a broad scale in organic photoconductors, non-linear optical elements and molecular memory storages [7].

The objective of our study is synthesis of new bis-pyrazolone and its metal complexes for creating molecules with desired washing, light and rubbing fastness, and dyeing properties.

EXPERIMENTAL

All commercial materials were purchased from Sigma Aldrich. Analytical grade solvents were purified and dried by the standard methods. Melting points were determined on a Stuart melting point apparatus in open capillary tubes. FTIR (KBr) spectra were recorded on a Single beam Nicolet, IR 100 spectrophotometer. UV-Vis spectra were recorded by a Genesys spectrophotometer for water solutions. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX 400 spectrometer using D_2O as a solvent and TMS as an internal standard. CHNS analysis was carried out on a Flash EA 1112 analyzer. TLC was carried out on Silica Gel G plates using petroleum ether: chloroform (6 : 4, v/v), chloroform: ethanol (9 : 1, v/v), and petroleum ether: chloroform (9 : 1, v/v) as eluents and UV lamp for visualization. Fastness to light was assessed by a BS 1006-1978. Rubbing fastness was checked by an Atlas crock meter in accordance with AATCC TM 8-1961. Wash fastness was determined according to ISO: 765-1975 [8,9].

Synthesis of bis-hydrazine from 4,4'-diaminostilbene-2,2'-disulfonic acid. Symmetric bridged bis-pyrazolone reactive acid dyes were synthesis from a common bis-azo component, reactive system and coupler but a different bridging system.

4,4'-Diaminostilbene-2,2'-disulfonic acid (DASDA) was treated with concentrated HCl and stirred at 0–5°C. A solution of $NaNO_2$ was added within 30 min to the cooled solution of DASDA upon stirring which was continued for 1 h more. The diazonium salt was filtered off and slowly added to Na_2SO_3 solution at 0–5°C upon stirring within 1 h. The mixture was removed from an ice jacket and heated up to 100°C. Hydrochloric acid was added upon stirring drop wise within 1 h at 100°C. The mixture was cooled down to room temperature and a small portion of Zn dust was added for completing reduction. The reaction mixture was stored overnight at room temperature. The precipitate of hydrazinium hydrochloride was collected and dried. The synthesized hydrazine **3** (4.0 g, 0.01 mol) was dissolved in H_2O (30 mL) and Na_2CO_3 (2 g) was added to the mixture to make a clear solution. The residue was filtered off. Few drops of HCl were added to neutralize the hydrazine solution, which was then refluxed at 100°C with ethyl acetoacetate (0.02 mol) for 1 h upon constant stirring and heating till completion of the process (TLC, methanol–chloroform, 9 : 1). The reaction mixture was cooled down. Following addition of HCl (10 mL) resulted in precipitation of pyrazolone **4** which was filtered off and dried in an oven at 70°C. Thus synthesized pyrazolone (5.32 g, 0.01 mol) was coupled with diazonium salt of 4-sulpho-2-aminophenol (3.78 g, 0.02 mol) prepared at 0–5°C in alkaline medium (pH = 9.0). The synthesized ligand dye **7** was precipitated from aqueous solution by adding HCl (15mL), filtered off and dried at 70°C in an oven. Dry ligand dye **7** (0.932 g, 0.001 mol) was dissolved in methanol and treated with $CuSO_4 \cdot 5H_2O$ (**8a**, 0.002 mol), mole ratio 1 : 2, upon refluxing. The reaction mixture was then made basic by adding TEA (pH = 9.5–10) and stirred for 4 h till complex formation was completed. Methanol was evaporated slowly at temperature, and precipitates of metal complex dyes were obtained. All metal complex dyes **9a**–**9h** were synthesized similarly by treating ligand **7** with different metal salts **8a**–**8h**.

2-[(*E*)-4-{5-hydroxy-4-[(*E*)-(2-hydroxy-5-sulfophenyl)diazenyl]-3-methyl-1*H*-pyrazol-1-yl}-2-sulfostyryl)-5-{5-hydroxy-4-[(*E*)-(2-hydroxyphenyl)-diazenyl]-3-methyl-1*H*-pyrazol-1-yl}benzenesulfonic acid] [ligand acid dye, $C_{34}H_{28}N_8O_{16}S_4$ (7)]. Brown compound, yield 75%. FTIR spectrum, ν, cm^{-1}: 3338 br (OH, NH), 1548 (C=C aromatic), 1388 (S=O), 1120 (C–O), 1029 (C–O), 839 (C=C bend). ^{1}H NMR (DMSO-d_6) spectrum, δ, ppm: 2.24 s (6H, CH_3), 6.67 s (1H), 6.96 d (1H), 7.34 d (1H), 7.71 d (1H), 7.84 s (1H), 7.907 s (1H), 7.95 d (2H, *J* = 7.5), 8.98 s (1H), 8.08 s (1H), 8.12 d (1H), 8.29 s (1H), 8.45 s (1H), 11.06 br (2H, SO_3H), 13.69 br (1H, O–H), 14.33 br (1H, O–H). ^{13}C NMR (DMSO-d_6) spectrum, δ, ppm: 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. Found, %: C 43.65; H 3.08; N 11.90; S 13.88. $C_{34}H_{28}N_8O_{16}S_4$. Calculated, %: C 43.77; H 3.03; N 12.01; S 13.75.

$C_{40}H_{48}Cu_2N_8O_{30}S_6$ (9a). Reddish brown complex, yield 73%. FTIR spectrum, ν_{max}, cm^{-1}: 3344 (OH), 1534 (C=C benzene), 1387 (CH_2 bend), 1115 (C–N), 1031 (C–O), 840 (Ar-H), 532 (N–Cu). Found, %: C 33.30; H 3.40; N 7.65; S 13.43. $C_{40}H_{48}Cu_2N_8O_{30}S_6$. Calculated, %: C 33.36; H 3.36; N 7.78; S 13.36.

$C_{40}H_{48}Fe_2N_8O_{30}S_6$ (9b). Brown complex, yield 77%. FTIR spectrum, ν_{max}, cm^{-1}: 3325 (OH), 2876 (C–H), 1645 (C=C benzene), 1439 (CH_2), 1357 (CH_2 bend), 1039 (C=O), 871 (Ar-H). Found, %: C 39.15; H 2.40; N 10.65; S 12.41. $C_{40}H_{48}Fe_2N_8O_{30}S_6$. Calculated, %: C 39.25; H 2.32; N 10.77; S 12.32.

$C_{40}H_{48}Ni_2N_8O_{30}S_6$ (9c). Greyish brown complex, yield 74%. FTIR spectrum, ν_{max}, cm^{-1}: 3345 (OH), 2880 (C–H), 1660 (C=C benzene), 1374 (CH_2 bend), 1177 (C–N), 1082 (C–O), 1027 (C–O), 841 (Ar-H), 598 (Ni). Found, %: C 39.08; H 2.38; N 10.58; S 12.43. $C_{40}H_{48}Ni_2N_8O_{30}S_6$. Calculated, %: C 39.03; H 2.31; N 10.71; S 12.26.

$C_{40}H_{48}Co_2N_8O_{30}S_6$ (9d). Greyish brown complex, yield 75%. FTIR spectrum, ν, cm^{-1}: 3456 (OH), 1665 (C=C aromatic), 1559 (C=C benzene), 1409 (CH_2), 1180 (C–N amines aromatic), 1029 (C–O), 973, 845 (C=C bend), 587 (N–Co). Found, %: C 39.06; H 2.36; N 10.53; S 12.33. $C_{40}H_{48}Co_2N_8O_{30}S_6$. Calculated, %: C 39.02; H 2.31; N 10.71; S 12.25.

$C_{40}H_{48}Cr_2N_8O_{30}S_6$ (9e). Violet brown complex, yield 77%. FTIR spectrum, ν, cm^{-1}: 3341 (OH), 1647 (C=C benzene), 1433 (OH), 1355 (CH_2 bend), 1044 (C=O), 874 (Ar-H), 585 (Cr). Found, %: C 39.58; H 2.38; N 10.76; S 12.52. $C_{40}H_{48}Cr_2N_8O_{30}S_6$. Calculated, %: C 39.54; H 2.34; N 10.85; S 12.42.

$C_{40}H_{48}Zn_2N_8O_{30}S_6$ (9f). Greyish brown complex, yield 73%. FTIR spectrum, ν, cm^{-1}: 3375 (OH), 1557 (C=C aromatic), 1407 (N=N), 1182 (C–N), 1083, 1028 (C–O), 838 (C=C bending). Found, %: C 38.63; H 2.33; N 10.47; S 12.22. $C_{40}H_{48}Zn_2N_8O_{30}S_6$. Calculated, %: C 38.54; H 2.28; N 10.58; S 12.10.

$C_{40}H_{48}Cd_2N_8O_{30}S_6$ (9g). Yellowish brown complex, yield 76%. FTIR spectrum, ν, cm^{-1}: 3371 (OH str), 1386

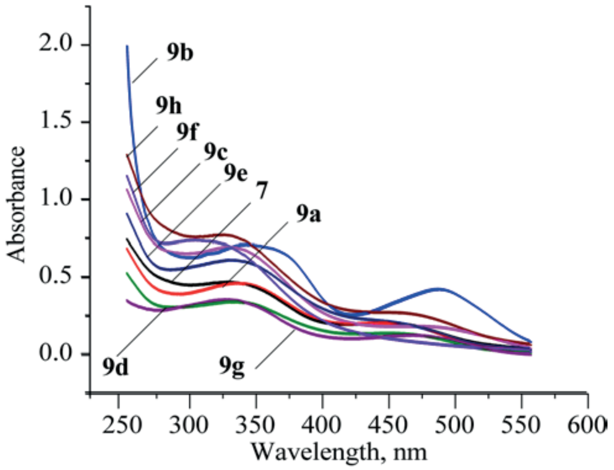


Fig. 1. Combined UV-Vis spectra of the ligand acid dye **7** and its complexes **9a–9h.**

(C–H bend), 1175 (C–N), 1026 (C–O), 854 (C=C bend), 599 (O-Cd). Found, %: C 35.46; H 2.16; N 9.62; S 11.19. $C_{40}H_{48}Cd_2N_8O_{30}S_6$. Calculated, %: C 35.40; H 2.10; N 9.71; S 11.12.

$C_{40}H_{48}Mn_2N_8O_{30}S_6$ (9h). Greyish brown complex, yield 72%. FTIR spectrum, ν, cm^{-1}: 3456 (OH str), 1445 (N=N str), 1380 (C–H bend), 1178 (C–N), 1027 (C–O), 845 (C=C bending), 505 (O-Mn). Found, %: C 39.37; H 2.38; N 10.63; S 12.43. $C_{40}H_{48}Mn_2N_8O_{30}S_6$. Calculated, %: **C** 39.32; H 2.33; N 10.79; S 12.35.

Dyeing process. A dye solution (10 mL, 0.4 % w/v) was prepared and charged in a dye bath. The content of the dye bath was stirred throughout the following processes. A $NaNO_2$ (7 mL, 20% w/v) solution was added to the dye solution maintaining pH in the dye bath at 6.5 by adding 1.0 mL of 10% w/v acetic acid solution. The total amount of the solution was adjusted to 100 mL by water. The leather fabric was introduced into the dye bath at 45–50°C. The dye bath solution was stirred for 1 h while rising temperature gradually up to 80°C which was maintained for 3 h more. pH of the dye-bath solution was adjusted to 2.0 by adding 2.0 mL of formic acid. The dye liquor was separated and the dyed fabric was washed with cold water. The dye liquor solution combined with washing was then further diluted with 250 mL of water. 1 mL Of the dye was further diluted by water to 50 mL. For determining the exhaustion of dye on the fabric, the characteristic absorbance of this solution was measured. The dyed fabric was then dried and mounted on a shade card. The percent of fixation of this solution was deduced from the absorbance when a weighed amount of leather fabrics was stirred in boiling acidified pyridine, which was able to remove the unfixed dye from the fabric.

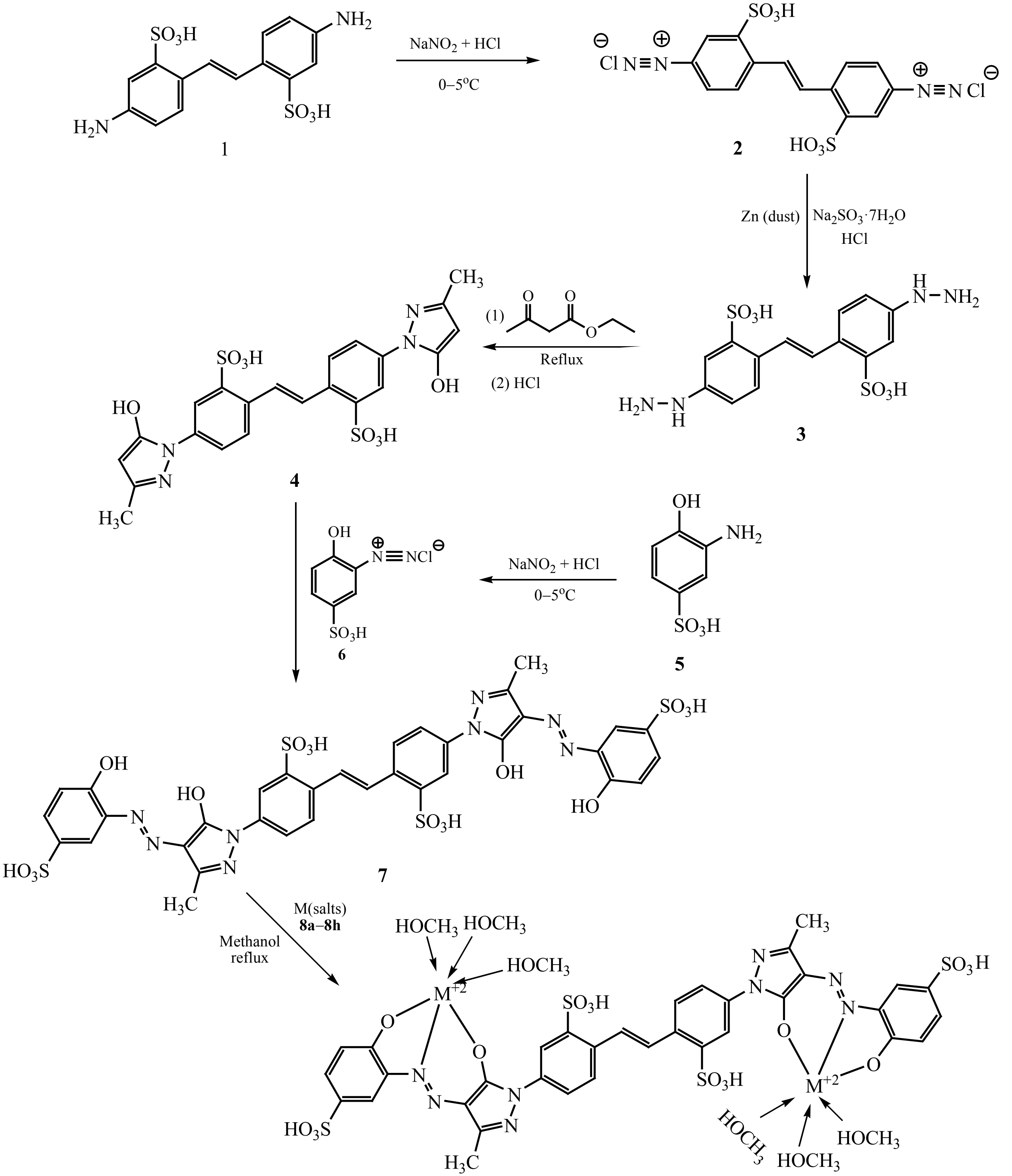
RESULTS AND DISCUSSION

Synthesis of acid dyes and their metal complexes 10a–10h. Diazotization of 4,4'-diaminostilbene-2,2'-disulfonic acid (DASDA) by $NaNO_2$ and HCl at 0–5°C was followed by reduction with $Na_2SO_3{\cdot}7H_2O$ which gave hydrazine **3** (Scheme 1). The synthesized hydrazine **3** was condensed with ethyl acetoacetate upon refluxing forming pyrazolones nucleus on both sides of the hydrazine. The symmetric bis-pyrazolone **4** was precipitated upon acidification of the reaction mixture by HCl. The prepared diazonium salt of 4-sulpho-2-aminophenol **6** was coupled with bis-pyrazolone derivative **4** upon stirring for ca 3 h

Table 1. Exhaustion and fixation data for the dye **7** and its metal complexes **9a**–**9h**

Dye	Shade on leather	$\lambda_{max,}$ nm (in ethanol)	log ε	Exhaustion, % (C)	Fixation, % (C)
7	Brown	408	6.0	70.31	75.32
9a	Reddish brown	455	6.10	77.78	80.67
9b	Violet brown	490	6.20	73.46	82.23
9c	Greyish brown	432	6.10	73.42	90.35
9d	Greyish brown	438	6.20	75.77	78.63
9e	Violet brown	473	6.25	75.45	80.23
9f	Greyish brown	437	6.25	77.28	86.25
9g	Yellowish brown	440	6.05	75.47	80.54
9h	Greyish brown	430	6.27	75.30	87.18

Scheme 1. Synthesis of acid dye **7** and its metal complexes **9a**–**9h**.



Metal salts = $CuSO_4{\cdot}5H_2O$ (**8a**), $FeSO_4{\cdot}7H_2O$ (**8b**), $Ni(CH_3COO)_2{\cdot}4H_2O$ (**8c**), $Co(NO_3)_2{\cdot}6H_2O$ (**8d**), $Cr_2(CH_3CO_2)_4(H_2O)$ (**8e**), $ZnCl_2$ (**8f**), $CdCl_2{\cdot}2.5H_2O$ (**8g**), $MnCl_2{\cdot}4H_2O$ (**8h**); M = Cu^{+2} (**9a**), Fe^{+2} (**9b**), Ni^{+2} (**9c**), Co^{+2} (**9d**), Cr^{+3} (**9e**), Zn^{+2} (**9f**), Cd^{+2} (**9g**), Mn^{+2} (**9h**).

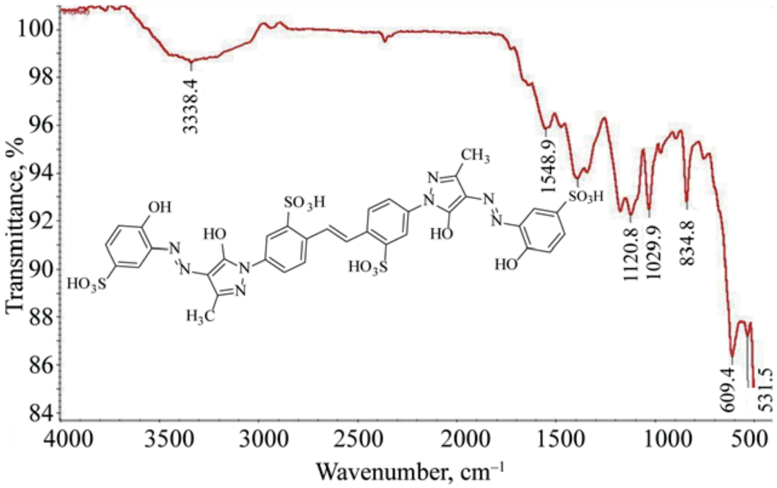


Fig. 2. FTIR spectrum of the ligand acid dye **7**.

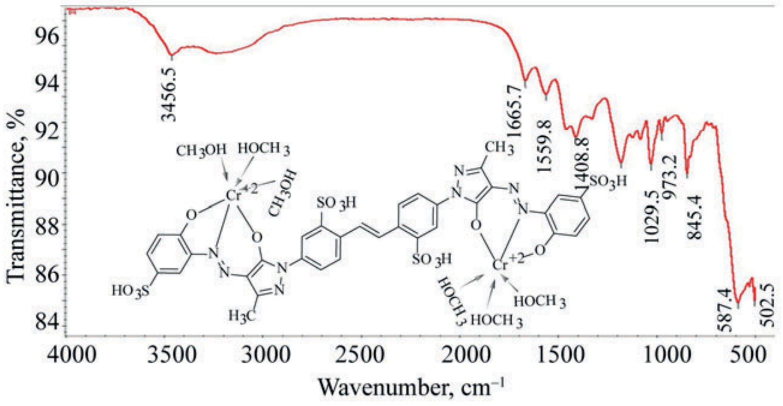


Fig. 3. FTIR spectrum of Cr(II) complex **9e** of the acid dye **7**.

at 0–5°C in an alkaline medium to give the ligand acid dye **7**. The coupling was achieved at active methylene center of bis-pyrazolone. The dye **7** was precipitated upon addition of HCl to adjust pH 4.0 of the mixture. The dye **7** was dried and recrystallization from ethanol.

Metal complexes of the dye 7 (Scheme 1). Upon continuous stirring at 70-80°C one of metal salts **8a**–**8h** was added to the solution of dye **7** in TEA at pH 9–10. Completion of the reaction was monitored by TLC using 9 : 1 chloroform - methanol solution. Upon following addition of HCl the corresponding dye **9a**–**9h** was precipitated, filtered off and dried in an oven at 70°C. The dyes were re-crystallized from ethanol.

Spectroscopic study of bis-pyrazolones based acid dye 7 and its metal complexes 9a–9h. The synthesized dyes were characterized by UV-Vis, FTIR and NMR spectra. The ligand dye **7** demonstrated λ_{max} at 408 nm, π–π* transition of C=C (Fig. 1). The second absorption maxima was recorded in the visible range due to π–π* of the N=N linkage. The metal complex dyes **9a**–**9h** exhibited λ_{max} in the range of 430–473 nm (Fig. 1). The iron complex **9h** was characterized by the largest bathochromic shift as compared to the ligand dye **7**.

FTIR spectra of the acid dye **7** and all its metal complexes **9a**–**9h** exhibited a broad band in the range of 3000–3500 cm^{-1} which evidenced formation of the strong H-bond (Figs. 2, 3).

Because of paramagnetic nature of the metals involved in the synthesized complexes, ^{1}H and ^{13}C NMR spectra were not measured.

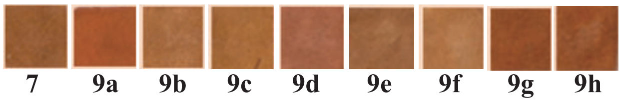


Fig. 4. 2 % Shade of dye **7** and its metal complexes **9a**–**9h** on leather.

Table 2. Fastness data for the dye **7** and its metal complexes **9a**–**9h**

Dye	Light fastness	Wash fastness	Rubbing fastness	
			dry	wet
7	5–6	4	4	4
9a	6–7	6–7	4	3
9b	6–7	4–5	4	4
9c	5–6	4–5	4–5	3–4
9d	6–7	4–5	4–5	3–4
9e	6–7	6–7	4	3–4
9f	6–7	4–5	4–5	3–4
9g	5–6	4–5	4–5	3–4
9h	5–6	5	4–5	3–4

Exhaustion and fixation study. Fixation exhaustion values were determined for application of dyes on cotton fibers at 2% (Table 1). Symmetric bis-pyrazolones were used as reagents towards cellulose fibers. In alkaline media the electron deficient carbon atoms attached to the sulphonic group could interact efficiently with cotton fibers. Percent of fixation of 2% dyeing and the percent of exhaustion [9] on cotton ranged within 70–90 and 65–72% (Table 1). Due to polar groups, physical and chemical interactions of dyes with fibers could lead to good exhaustion and fixation effects.

Fastness properties. The synthesized dyes fastness properties were also assessed (Table 2). The degree at which a dye resists fading is called light fastness, which is different for different dyes. For all sort of dyes, light fastness in the range of 4–5 is considered to be high. The resistance of dye fibers to retain colors when washed by detergents and soaps is called wash fastness.

Light fastness of the ligand acid dye **7** was in the range of 5–6 while its metal complexes exhibited high light fastness 6–7. Ligand dye **7** and its metal complexes exhibited high rubbing fastness 4–5. Improved properties like wash fastness can be easily tested by rubbing fastness. According to rubbing fastness values all synthesized dyes had high fixation on leather fabrics (Fig. 4).

Thermogravimetric analysis of acid dyes 7 and metal complexes 9a–9h. TGA was carried out for ligand **7** and its metal complexes **9a**–**9h**. Water molecules loss (12–13%) occurred in the range of 0–100°C. In the range of 100–400°C 9% weight loss could be attributed to N_2 gas formed from the azo fragments. The loss of gases CO, CO_2, and SO_2 occurred in the range of 400–800°C. Iron metal complex was more stable than other metal complexes.

CONCLUSIONS

A new series of bis-pyrazolone metal complex acid dyes **9a**–**9h** has been synthesized in high yield from bis-pyrazolone **4.** As compared to other metal complexes of acid dyes, iron and chromium metal complexes **9a** and **9e** exhibit higher bathochromic shift in UV-Vis spectra. The synthesized dyes applied on leather and show high wash fastness, light fastness and rubbing fastness. As compared to ligand dye, all metal complexes demonstrate high quality of exhaustion and fixation on leather. Due to strong metal binding with nitrogen and oxygen, metal complexes dyes exhibit thermal stability higher than the ligand dye.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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