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To cite this article: Nasir Abbas, Syed Ahmad Tirmizi, Ghulam Shabir, Aamer Saeed, Ghulam Hussain, Pervaiz Ali Channer, Rashid Saleem & Muhammad Ayaz (2017): Chromium (III) complexes of azo dye ligands: Synthesis, characterization, DNA binding and application studies, Inorganic and Nano-Metal Chemistry,

Accepted author version posted online: 30 Aug 2017.

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Chromium (III) Complexes of Azo Dye Ligands: Synthesis, Characterization, DNA Binding and Application Studies

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Research Highlights

- A series of metal complexes has been synthesized from 1-(*p*-sulphophenyl)-3-methyl-4-amino pyrazolone with different phenol derivatives at high temperature for chromium.
- Investigated metal complexes have been applied on leather which exhibit high light fastness, wash fastness and rubbing fastness.
- DNA interaction has also been accomplished.

Abstract

Chromium (III) complexes of Azo dyes ligands envisaged on novel synthesized 4-Amino-1-(*p*-sulphophenyl)-3-methyl-5-pyrazolone diazonium salt coupled with different phenolic couplers appended on diverse substituents. The complexes have been characterized by elemental analysis,

UV, FTIR and NMR studies. The DNA studies have been investigated for complexes by electronic absorption spectroscopy. The results have shown that chromium (III) complexes bind to DNA through intercalation mode. Synthesized Chromium complexes have been applied on leather to check their serviceability and they exhibited moderate to high values of light fastness and perspiration fastness (4-5).

Graphical Abstract

Key Words

Complexes, DNA binding, Intercalation mode, Electronic Spectroscopy

1. Introduction

Azo compounds are very important molecules and have attracted much attention in both academic and applied research [Nejati 2009]. Most azo dyes are prepared from Diazonium salts furthermore they constitute 60--70% of the industrial dyes used today. The obtained chromium complexed azo dyes are colored and have been widely used in many practical applications such as printing systems, coloring fibers, photo-electronic applications, optical storage technology as well as biological reactions and analytical chemistry [Vulpes 2009]. Also the importance of heterocyclic azo dyes and their metal complexes may stem from their biological activity [Gaber 2003]. Metal complexes of azo dyes ligand have extensive applications in electro-photographic toners as charge controlling agents, developers in power coating materials and in electrostatic separation process [Khalid 2015]. Azo derivatives and their complexes are very important pigments for synthetic leather and vinyl polymers [Nejati 2009]. Many azo dyes have been utilized as chromogenic reagents for colorimetric determinations and as indicators for complexometric titrations [sarigul 2016]. The azo metal complexes were applied on leather and their color fastness studies were performed.

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2. Experimental.

2.1. Materials and reagents.

All the chemicals and reagents used were analytical grade. Melting points were determined in open capillary tube on Gallencamp apparatus. UV of all the samples were determined in water using Shimadzu UV-1700 spectrophotometer. FT-IR spectra were run in Cary 630, Agilent Technologies, USA. The formation of complexes were analyzed progressively on silica gel TLC

using two different eluting solvents. The solvent systems were petroleum ether: chloroform (9:1, V/V) and chloroform and methanol (9:1, V/V). Under UV lamp the spots were visualized and their R_f values were compared. Fastness properties were obtained in accordance with BS 1006-- 1978. AtlasCrock meter in accordance with AATCC TM 8--1961 was employed to check the rubbing fastness properties. In accordance to ISO: 765--1979 the wash fastness were observed (Sakuma et al. 2012).

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2.2 General Procedure for the Synthesis of 1-(*p*-Sulphophenyl)-3-methyl-4-amino pyrazolone based Acid Dyes

Synthesis of acid dyes and their metal complexes involves three step procedure which is as follows:

a. Nitrosation of 1-(*p*-Sulphophenyl)-3-methyl-4-amino pyrazolone (SPMP)

1-(*p*-methylphenyl-3-methyl-5-pyrazolone (**1**) (25.4 g, 0.1 mol) was suspended in H₂O (250 ml). Hydrochloric acid (45 ml) was added to this well stirred suspension. The reaction mixture was cooled to 0--5 °C in an ice bath. A solution of NaNO₂ (6.9 g, 0.1 mol) in H₂O (25 ml) previously cooled to 0 °C, was then added over a period of half hour with stirring. The stirring was continued for an hour more maintaining the same temperature, with a positive test for nitrous acid. Later on the excess of nitrous acid was destroyed with required amount of sulphamic acid. The Nitroso compound (Tautomeric form is called Oxime) was filtered after salting out. Then oxime was reduced by stirring in 200 ml water containing 85 ml HCl and 23 g Zinc metal at boiling for 4 h. At the completion of reaction, pH of the reaction mixture

was raised to 9 with 6 N NaOH, and precipitated the 1-(*p*-sulphophenyl-3-methyl-4-amino pyrazolones.

b. Diazotization and Coupling with Phenol Derivatives

To the well stirred aqueous of 1-(*p*-sulphophenyl-3-methyl-4- amino pyrazolone (2.69 g) sodium nitrite solution (0.7 g in 2 mL water) was added after the addition of Conc. HCl (3.5 mL) at 0--5 °C. In order to obtain the diazonium salt of 1-(*p*-sulphophenyl)-3-methyl-4-amino pyrazolone, the reaction mixture was stirred for 1 h at the temperature aforesaid. A variety of dyes were prepared by coupling various compounds as couplers with prepared diazonium salt. Ipso-facto 1.285 g (0.010 mol) 4-Chlorophenol (5a) was dissolved in 200 mL water containing 0.45 g NaOH and coupled with prepared diazo. The coupling was facilitated using sodium carbonate as an acid binding agent. The reaction mixture was given 4--5 h to complete the coupling at 30--35 °C. The dye was cooled to room temperature. Its pH was reduced to 4.5 by HCl and filtered. The cake was dried in oven at 70--75 °C till constant weight. By adopting the same procedure other dyes 6b-f were prepared from couplers 5b-f as shown in (scheme-1).

c. Metallization of Acid Dyes.

For the synthesis of Chromium complex pH of 25 mL (0.005mole) of dye 6a was reduced to 6.5 with HCl. Then it was heated to 70°C and to it 5 mL (0.005 mole Cr³⁺) solution of chromium acetate Cr(CH₃COO)₃ was added drop wise. Mixing and heating at this temperature was continued for further 1.0 hour till the metallization was completed, as shown by the comparative

TLC. The dye was cooled to room temperature; its pH was reduced to 1.0 with conc. HCl. Then it was salted out with sodium chloride, filtered and dried in oven at 70 °C till constant weight.

In this way complexes **7a-f** were synthesized from respective dye ligands whose physical and spectroscopic data is as follows

6a (C₁₆H₁₃ClN₄O₅S)

Orange, (76%) $\lambda_{\max}$ (nm): 460. FTIR (KBr, cm⁻¹) $\nu_{\max}$: 3255 (OH str.), 3050 (C = C-H str.), 2927 (CH₂ str.), 1653 (C = O str.), 1595, 1541 (C = C aromatic, C = N), 1498 (N = N str.), 1422, 1340 (SO₃H str., CH₂ bend.), 1236, 1155 (C-C, C-O str.), 1000 (S = O str.), 833 (Ar-H), 790 (C-Cl str.). ¹HNMR (300 MHz, DMSO-d₆) δ : 8.07 (1 H, d J = 2.35 Hz), 7.95 (2 H, d J = 8.6 Hz), 7.83-7.90 (1 H, m), 7.68 (2 H, d J = 8.6 Hz), 6.65 (1 H, d, J = 9.1 Hz), 2.20 (3 H, s). ¹³C-NMR (75 MHz DMSO-d₆) δ (ppm): 158.54, 156.64, 147.93, 147.37, 143.21, 139.93, 125.43, 124.41, 119.45, 118.06, 116.22, 12.45. Anal. Calcd. For C₁₆H₁₃ClN₄O₅S: C, 47.01; H, 3.21; N, 13.71; S, 7.84 Found: C, 47.05; H, 3.30; N, 13.59; S, 7.79.

6b (C₁₆H₁₃N₅O₇S)

Dark Brown, (83%). $\lambda_{\max}$ (nm): 480. FTIR (KBr, cm⁻¹) $\nu_{\max}$: 3388 (OH str.), 2924 (CH₂ str.), 1666 (C = C str.), 1593 (C = C aromatic, C = C), 1498, 1476 (N = N, NO₂ str.), 1267, 1172 (C-O str.), 1034 (C-OC str.), 821 (Ar-H). ¹HNMR (300 MHz, DMSO-d₆) δ : 8.15 (1 H, d J = 2.4 Hz), 7.942 (2 H, d J = 8.7 Hz), 7.81-7.92 (1 H, m), 7.65 (2 H, d J = 8.7 Hz), 6.38 (1 H, d, J = 9.3 Hz), 2.27 (3 H, s). ¹³C-NMR (75 MHz DMSO-d₆) δ (ppm): 158.0, 155.28, 148.32, 147.57, 144.58, 138.72, 128.18, 126.86, 126.24, 118.19, 117.06, 116.17, 12.14. Anal.

Calcd. For **C₁₆H₁₃N₅O₇S**: C, 45.83; H, 3.12; N, 16.70, S, 7.64; Found: C, 45.78; H, 3.20; N, 16.58, S, 7.57.

6c (C₁₆H₁₄N₄O₈S₂)

Orange, (84%). $\lambda_{\max}$ (nm): 460. FTIR (KBr, cm^{-1}) $\nu_{\max}$: 3389 (OH str), 3086 (C = C-H str.), 1638 (N-H bend.), 1619, 1597 (C = C aromatic), 1541 (N = N str.), 1500 (N-Hbend.), 1340 (SO₃H, CH₂ str.), 1185 (C-O str.), 818 (Ar-H). ¹HNMR (300 MHz, DMSO-d₆) δ : 11.87 (1 H, s, O-H), 8.10 (1 H, d J = 2.6 Hz), 7.93 (2 H, d J = 8.6 Hz), 7.79-7.90 (1 H, m), 7.67 (2 H, d J = 8.6 Hz), 6.90 (1 H, s, SO₃H), 6.58 (1 H, d, J = 9.5 Hz), 2.27 (3 H, s). ¹³C-NMR (75 MHz DMSO-d₆) δ (ppm): 159.12, 156.48, 147.72, 147.17, 145.23, 141.33, 138.62, 125.68, 124.42, 117.19, 116.96, 116.43 11.81. Anal. Calcd. For **C₁₆H₁₄N₄O₈S₂**: C, 42.29; H, 3.11; N, 12.33, S: 14.11 Found: C, 42.24; H, 3.20; N, 12.21, S: 14.04.

6d (C₁₆H₁₃N₅O₁₀S₂)

Orange, (81%). $\lambda_{\max}$ (nm): 520. FTIR (KBr, cm^{-1}) $\nu_{\max}$: 3449 (OH str.), 3050 (C = C-H str.), 1653 (C = C str. NH bend), 1619, 1541 (C = C aromatic), 1498 (N = N str.), 1338 (SO₃H, CH₂ str.), 1183 (C-O str.), 1008 (S = O), 840 (Ar-H). ¹HNMR (300 MHz, DMSO-d₆) δ : 11.33 (1 H, s, O-H), 8.15 (1 H, d J = 2.4 Hz), 7.99 (1 H, d J = 2.4 Hz), 7.922 (2 H, d J = 8.7 Hz), 7.63 (2 H, d J = 8.7 Hz), 2.23 (3 H, s). ¹³C-NMR (75 MHz DMSO-d₆) δ (ppm): 157.05, 156.28, 149.25, 147.63, 144.28, 142.76, 140.92, 127.16, 125.54, 119.19, 116.56, 115.20 12.14. Anal. Calcd. For **C₁₆H₁₃N₅O₁₀S₂**: C, 38.48; H, 2.62; N, 14.02; S, 12.84; Found: C, 38.37; H, 2.69; N, 13.96; S, 12.88.

6e (C₃₂H₂₆N₈O₁₂S₃)

Orange, (80%). $\lambda_{\max}$ (nm): 420. FTIR (KBr, cm^{-1}) $\nu_{\max}$: 3395 (, OH, NH str.), 3050 (C = C-H str.), 2926 (CH_2 str.), 1619, 1586 (C = C aromatic, C = N), 1498 (N = N str.), 1125 (C-O str.), 1008 (S = O), 872 (Ar-H). $^1\text{H-NMR}$ (300 MHz, DMSO-d_6) δ : 11.67 (1 H, s, O-H), 7.91 (2 H, d, $J = 8.7$ Hz), 7.81-7.92 (1 H, m), 7.69 (2 H, d $J = 8.7$ Hz), 6.90 (1 H, d, $J = 9.4$ Hz), 6.78 (1 H, s), 6.62 (1 H, s, SO_3H), 6.59 (1 H, d, $J = 9.4$ Hz), 2.51 (3 H, s), 1.469 (6 H, s). $^{13}\text{C-NMR}$ (75 MHz, DMSO-d_6) δ (ppm): 157.56, 154.89, 148.97, 154.64, 144.47, 143.44, 142.29, 141.31, 138.88, 137.90, 129.96, 128.05, 127.74, 126.78, 119.85, 118.63, 117.64, 115.79, 115.64, 115.13, 115.02, 41.19, 30.83, 11.59. Anal. Calcd. For $\text{C}_{32}\text{H}_{26}\text{N}_8\text{O}_{12}\text{S}_3$: C, 47.40; H, 3.23; N, 13.82; S, 11.86; Found: C, 47.46; H, 3.31; N, 13.56; S, 11.80.

6f ($\text{C}_{35}\text{H}_{32}\text{N}_8\text{O}_{10}\text{S}_2$)

Brown, (83%). $\lambda_{\max}$ (nm): 450. FTIR (KBr, cm^{-1}) $\nu_{\max}$: 3464 (OH, NH str.), 2963 (CH_2 str.), 1653, 1593 (C = C aromatic), 1490 (N = N str.), 1338 (SO_3H str.), 1213, 1153, 1120 (C-C str.), 1002 (S = O), 872 (Ar-H). $^1\text{H-NMR}$ (300 MHz, DMSO-d_6) δ : 11.30 (1 H, s, O-H), 7.94 (2 H, d $J = 8.7$ Hz), 7.82-7.93 (1 H, m), 7.67 (2 H, d $J = 8.7$ Hz), 6.98 (1 H, d, $J = 9.4$ Hz), 6.81 (1 H, s), 6.58 (1 H, d, $J = 9.4$ Hz), 6.42 (1 H, s, SO_3H), 2.47 (3 H, s). $^{13}\text{C-NMR}$ (75 MHz, DMSO-d_6) δ (ppm): 158.77, 155.9, 147.61, 145.61, 143.86, 143.25, 141.63, 139.81, 136.75, 130.25, 127.91, 125.78, 119.80, 118.31, 116.73, 115.94, 115.23, 11.59. Anal. Calcd. For $\text{C}_{35}\text{H}_{32}\text{N}_8\text{O}_{10}\text{S}_2$: C, 53.29; H, 4.09; N, 14.21; S, 8.13; Found: C, 53.35; H, 4.13; N, 14.04; S, 8.20.

7a ($\text{C}_{32}\text{H}_{23}\text{Cl}_2\text{CrN}_8\text{O}_{10}\text{S}_2$)

Maroon/Yellowish Red, (66%) $\lambda_{\max}$ (nm): 464. FTIR (KBr, cm^{-1}) $\nu_{\max}$: 3050 (C = C-H str.), 1642 (C = O str.), 1583, 1537 (C = C aromatic, C = N), 1485 (N = N str.), 1417, 1335 (SO_3H str., CH_2

bend.), 1226, 1145 (C-C, C-O str.), 1012 (S = O str.), 830 (Ar-H), 785(C-Cl str.). Anal. Calcd. For **C₁₆H₁₃ClN₄O₅S**: C, 44.35; H, 2.68; N, 12.93; S, 7.40; Found: C, 44.43; H, 2.58; N, 12.83; S, 7.50.

7b(C₃₂H₂₃CrN₁₀O₁₄S₂)

Reddish orange, (73%). λ_{max} (nm):483. FTIR (KBr, cm^{-1}) ν_{max} : 1676 (C = C str.), 1587 (C = C aromatic, C = C), 1495, 1471 (N = N, NO₂str.), 1267, 1172 (C-O str.), 1039 (C-OC str.), 829 (Ar-H). Anal. Calcd. For **C₁₆H₁₃N₅O₇S**: C, 43.30; H, 2.61; N, 15.78; S, 7.22; Found: C, 43.20; H, 2.70; N, 15.89; S, 7.34.

7c(C₃₂H₂₅CrN₈O₁₆S₄)

Brown/Reddish orange, (74%). λ_{max} (nm):489. FTIR (KBr, cm^{-1}) ν_{max} : 3076 (C = C-H str.), 1623 (N-H bend.), 1621, 1599 (C = C aromatic), 1539 (N = N str.), 1498 (N-Hbend.), 1354 (SO₃H, CH₂ str.), 1174 (C-O str.), 814 (Ar-H). Anal. Calcd. For **C₁₆H₁₄N₄O₈S₂**: C, 40.13; H, 2.63; N, 11.70; S, 13.39; Found: C, 40.33; H, 2.54; N, 11.73; S, 13.41.

7d(C₃₂H₂₃CrN₁₀O₂₀S₄)

Brown/Reddish orange, (81%). λ_{max} (nm):505. FTIR (KBr, cm^{-1}) ν_{max} : 3056 (C = C-H str.), 1648 (C = C str. NH bend), 1622, 1539 (C = C aromatic), 1492 (N = N str.), 1343 (SO₃H.), 1173 (C-O str.), 1010 (S = O), 856 (Ar-H). Anal. Calcd. **C₃₂H₂₃CrN₁₀O₂₀S₄**: C, 36.68; H, 2.21; N, 13.37; S, 12.24; Found: C, 36.73; H, 2.27; N, 13.39; S, 12.20.

7e(C₆₄H₄₆Cr₂N₁₆O₂₄S₆)

Beige/Yellowish orange, (70%). $\lambda_{\max}$ (nm):584. FTIR (KBr, cm^{-1}) $\nu_{\max}$: 3048 (C = C-H str.), 1621, 1574 (C = C aromatic, C = N), 1496 (N = N str.), 1122 (C-O str.), 1011 (S = O), 869 (Ar-H). Anal. Calcd. For **C₃₂H₂₆N₈O₁₂S₃**: C, 47.48; H, 3.27; N, 13.86; S, 11.85; Found: C, 47.44; H, 3.33; N, 13.52; S, 11.81.

7f(C₇₀H₅₈Cr₂N₁₆O₂₀S₄)

Tan/Reddish orange, (73%). $\lambda_{\max}$ (nm):479. FTIR (KBr, cm^{-1}) $\nu_{\max}$: 1645, 1589 (C = C aromatic), 1485(N = N str.), 1341 (SO₃H str.), 1210, 1150, 1118 (C-C str.), 999 (S = O), 875 (Ar-H). Anal. Calcd. For **C₃₅H₃₂N₈O₁₀S₂**: C, 45.81; H, 3.02; N, 18.53; S, 12.34. Found: C, 45.85; H, 3.09; N, 18.56; S, 12.38.

2.3 Dyeing Method.

Dye solution (10 ml, 0.4% w/v) was taken in a dye-bath. The pH of the dye-bath was adjusted to 6.5 by adding acetic acid solution (1.0 ml, 10% w/v) solution. The total volume of the dye-bath was adjusted to 100 ml by adding required amount of water. The leather swatches were immersed into the dye-bath with stirring. The content of the dye-bath was stirred for 1 h at 25--30°C. The temperature was then gradually raised to 55°C over period of half hour and this temperature was maintained for one hour. The dye-bath was kept rotating during the process of dyeing. Then 2.0 ml formic acid was added to adjust pH to 2.0 for dye fixation. After this, the spent dye liquor was taken in 250 ml volumetric flask. The swatches were washed with cold water and the combined solution of dye liquor and washings was then further diluted to 250 ml with water. In order to find out the exhaustion of dye on leather the absorbance of the solutions were recorded. The dyed swatches were dried and mounted on shade card. A weighed amount of

leather swatch was stirred in boiling acidified pyridine which dissolves the unfixed dye from swatch and from the absorbance of this solution percentage fixation was checked.

2.4 DNA binding.

The concentrations of the complexes and DNA were determined spectroscopically using molar extinction co-efficient. The DNA binding experiments were performed in distilled Water using 2% solution of metal complexes. The concentration of the DNA was determined from the absorption intensity at 261.5 nm with a ϵ value (Jayaseelan et al, 2011) of $6600 \text{ M}^{-1} \text{ cm}^{-1}$. Experiments were performed by using different concentration of SS Fish Salmon sperm DNA [10, 20, 30 up to 100 μM], keeping the concentration of the complex constant, with due correction for the absorbance of the SS Fish Salmon sperm DNA itself. Before recording the spectra the samples were equilibrated.

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3. Results and Discussion

3.1 Synthesis and spectral characterization of ligand acid dyes and their metal complexes

Synthesis of Acid dyes and their (Cr, III) complexes were achieved accordingly as represented in scheme 1. Reactant 1 was nitrosated at 0--5°C using NaNO_2 and HCl , and filtered to remove the remove the suspended impurities as described by Knorr. The clarified nitroso intermediate was salted out by common salt. Reduction of nitroso was carried at 100--105°C using Zinc and HCl . The oxime and zinc dust were successively added in small portions in boiling HCl solution. A small amount of additional zinc dust was also added to prevent aerial oxidation on cooling.

NaNO₂ (6.9 g dissolved in 250 ml of solution) and HCl at -5 to -2°C to avoid the formation of Rubazoic acid, which results due to oxidizing action of nitrous acid, formed in situ. The diazonium salt prepared in this way was coupled with different para substituted phenols, like, *p*-Chlorophenol, *p*-Nitrophenol, phenol-4-sulphonic acid, 2-Nitrophenol-4-sulphonic acid and bisphenols (Bisphenol S and Bisphenol A). The coupling was carried out in alkaline medium at pH 8--9. The synthesis of this diazo has been confirmed from X-ray structure of its crystal. Coupling in alkaline medium occurred at ortho position to the hydroxyl groups of phenol and bisphenol derivatives, as para positions were blocked. The synthesized dyes 6a-e were precipitated on completion of reaction by lowering the pH of solution to 1.0 with HCl. The filtered dyes were dried and purified in ethanol. Metallization of these dyes was done by treating their alkaline solution with Cr(CH₃COO)₃ at 65--70°C. It took about 4--5 hours for completion of metallization which was observed by taking the TLC of reaction mixture in 9:1 chloroform and methanol. Dyes (7a-f) were precipitated with addition of HCl, filtered and dried in oven at 80°C. These dyes were again recrystallized from ethanol, dried, weighed and calculated their percentage yield. These unmetallized dyes 6a-e are tridentate ligands which formed complexes with Chromium (Cr, III) through 1:2 metal and ligand ratio. In Chromium (III) complexes lone pairs of electrons are donated by two oxygen atoms and one nitrogen atom of the diazo linkage. The complex formation pattern has been verified by the UV-visible spectrophotometric studies of these dyes 7a-f. The infrared spectra of the synthesized acid dyes and their metal complexes exhibited IR absorption peaks due to O-H, Ar-H, C-H, C = O, C = C, N = N, SO₃H, C-O and O-M stretching and bending vibrations at 3399, 3050, 2926, 1550, 1472, 1272, 1164, 1004, 834

610 cm^{-1} as depicted from their FTIR spectra (Figure 1). Similarly other metal complexes have been confirmed from their respective IR spectra.

^1H -NMR and ^{13}C -NMR spectra were taken for ligand dyes which showed characteristic signals for different protons and carbons at different positions which evidenced the synthesis of dyes. In case of compounds 6b signal for hydroxyl group was absent due to exchangeable proton with DMSO. The doublet signal of mutually coupled set of four protons of phenyl group substituted with sulfonic group at present 7.95 and 7.68 ppm having coupling constant respectively signals 8.6 Hz. The multiplet signal for one proton of aromatic ring of coupling moiety is present at 7.83-7.90 ppm while the same ring bearing another single proton shows signal at 8.07 ppm with coupling constant 2.35 Hz which evidenced the meta relationship with another proton at the same ring. The methyl group present at pyrazolone ring exhibited singlet signal at 2.20 ppm (Figure 2). In ^{13}C -NMR spectrum the signal for methyl group is present at 12.14 ppm. There are ten signals in the range 117.06-158.00 ppm for different carbon nuclei in the compound (Figure 3). In this way other ligand acid dyes were confirmed from their respective ^1H -NMR and ^{13}C -NMR spectra. When the ^1H -NMR spectra of metal complexes were conducted but they showed very broad and distorted signals due to paramagnetic nature of Chromium used for complexation and the so the NMR study of complexes did not prove fruitful for structure elucidation but on the other hand distorted broad signals evidenced the complexation when the ^1H -NMR of ligands acid dyes and complexes were compared.

3.2 Dyeing properties of substituted ligand acid dyes and their metal complexes (6a-f and 7a-f)

The dyeing properties of *p*-substituted phenols and bis phenol dyes have been found to be very attractive. Almost all properties have been found to be of very high value (4-5). Ligand dyes had low values as per our expectation due to the presence of free hydroxyl groups. The dyeing properties of these dyes are given in Table 2.

Almost all un-metalized *p*-substituted phenol dyes have been found to be different; both in 2% and 5% dyed leathers, along with a variation of depth of Shades. This can be attributed to the difference of chromophoric systems in all dyes. However, it is clear from shades that this difference is due to the difference of *p*-substituents in different phenols. All of the phenol homologues had dark and redder shades except *p*-sulphophenol substituted dyes. The variation of the depth can be attributed to the participation of peripheral group's variation in different phenols.

Almost all Chromium-metalized Phenol dyes had been found to be of Olive color; both in 2% and 5% dyed leathers with a little variation of depth in Shades. All the phenol homologues had dark and redder shades except *p*-sulphophenol. Both nitro phenols had similar shades with yellowish tone. The dyeing properties of Bis-phenols dyes have been found to be very good and attractive. Almost all properties have been found to be of very high value (4-5). The dyes with Bisphenol-A has been found to be much darker as compared to the dyes of Bisphenol-S. This can be attributed to the $n \rightarrow \pi^*$ electronic transitions occurring in sulphone group of Bisphenol-S.

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As it is clear from dye shades among the un-metalized Bisphenol dyes, the dye with Bisphenol-A had a high color value while Bisphenol-S dye gave a low color yield on Leather. This difference can be ascribed to the participation of Sulphone group present in Bisphenol-S.

complex with ligand acid dye based on bisphenol-S had a low color value while bisphenol-A dye provided a darker shade and high color yield on leather along with a much redder effect. This difference can be attributed to the participation of sulphone group in bisphenol-S (Table 3 and 4).

3.3 Optical Studies of Dyes

In case of optical studies, dyes were conducted their UV-visible studies to observe the changes rendered by metal complex formation. The UV-visible data presented in table-2 is supported by combined UV-visible spectra of ligand acid dyes 6a-f. The un-metalized dye-6a was an orange dye with $\lambda_{\max}$ 460 nm while on metallization of this with Chromium Olive Brown dye (Dye-7a) was produced with $\lambda_{\max}$ 490 nm undergoing a bathochromic shift of 30 nm along with hypochromic effect.

The unmetallized dye 6b was an Orange dye with $\lambda_{\max}$ 480 nm which developed tan/ dye on complexation with chromium (Dye 7b) with $\lambda_{\max}$ 500 nm. It also showed bathochromic shift of 20 nm along with hyperchromic effect. Chromium (III) complexes of ligands 6c and 6d showed hypsochromic effect which is attributed to electron withdrawing groups attached to couplers.

In the bisphenol series two dyes were prepared. For this purpose two different Bisphenols, namely 4,4'-dihydroxy biphenyl sulphone (BPS), 4, 4'-dihydroxy biphenyl propane (BPA), were used as couplers. The un-metalized dye 6e was a Reddish Orange dye with $\lambda_{\max}$ 420 nm Its metallization with Chromium produced a Reddish brown dye (Dye 7i) with $\lambda_{\max}$ 430 nm and a red shift of 10 nm was seen. From the detailed UV-visible study of dyes it was gathered that metal complexes of ligand dyes bearing electron withdrawing groups showed hypsochromic shift

and those having electron donating groups showed bathochromic shift in absorbance which is in accordance with well-established UV-visible absorption pattern of compounds (Figure 5 and 6). This UV-visible also established the octahedral geometry for the synthesized metal complexes [Yildiz 2013].

3.4 DNA Binding Studies.

The binding Characteristics of metal complexes with DNA can be emphasized by employing electronic spectroscopy (Table, 5). The absorption spectra of some representative metal complexes 7a, 7b, 7d and 7f in the presence and absence of SS Fish Salmon Sperm shown in figure 7. In UV and visible region, the intense band at 370 nm attributed to the ligand to metal charge transfer absorption and another at 265 nm which is assigned to the π - π^* transition of aromatic chromophore. Polarity of the ligand, coordination geometry, ligand donor atom type and metal ion type (Jayaseelan et al, 2011) dictate the chelating ability of the complex. Strong stacking interaction between an aromatic chromophore and the base pairs of DNA results in the Red shift while the cause of hypochromism is intercalative mode of DNA binding. Similarly the hyperchromism is actually due to non-intercalative or electrostatic mode of DNA binding.

Strong π - π^* stacking interaction between the aromatic chromophore ligand of metal complex and base pairs of DNA exhibit significant hypochromism and red shift (Terenzi et al, 2009). Intercalative binding between DNA and metal complex is responsible in hypochromism with slight red shift (Bathochromic shift).

By increasing the concentration 10 μ M to 100 μ M at lambda shift to red/blue nearly 3,3,2,2 nm respectively (Colak et al, 2010).

4. Conclusions

New acid dye ligands and their Chromium (III) complexes based on 4-Amino-1-(*p*-sulphophenyl)-3-methyl-5-pyrazolone diazonium salt and phenolic couplers were prepared and characterized by physico-chemical methods. The octahedral geometry was observed by UV visible spectrophotometric studies and was attributed to Cr (III) coordination with nitrogen of azo group and oxygen of pyrazolone ring hydroxyl groups. The DNA binding studies showed that metal complexes have good binding constant and spontaneity as compared to ligands and intercalation DNA binding mode was observed as shown in table 5.

5. References.

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Table-1; Fastness properties of ligand acid dyes (6a-f) and their metal complexes (7a-f)

Dye	2%Shade on Leather	5%Shade on Leather	Penetration	Washing Fastness	Light Fastness	Perspiration Fastness
6a	Yellowish Orange	Reddish Orange	2	2-3	2-3	3-4
7a	Olive	Dark Olive	5	4-5	5	5
6b	Orange	Yellowish Orange	2	2-3	2-3	3-4
7b	Yellowish Orange	Reddish Brown	3	3-4	3-4	4-5
6c	Yellowish Orange	Yellowish Orange	3	3-4	2-3	3-4
7c	Olive	Dark Olive	5	4-5	5	5
6d	Tan	Yellowish Brown	3	3-4	3-4	3-4
7d	Yellowish Orange	Yellowish Brown	3	3-4	3-4	4-5
6e	Greenish Beige	Reddish Beige	2	2-3	2-3	3-4
7e	Light Olive	Dark Olive	5	4-5	5	5
6f	Golden Yellow	Yellowish Orange	3	3-4	3-4	4-5
7f	Yellowish Orange	Yellowish Orange	4	3-4	3-4	4-5

Table-2; Dyeing properties of ligand acid dyes (6 a-f)

Dyes		6 a	6b	6 c	6 d	6e	6f
Shades on Leather	2% Shade
	5% Shade

Table-3; Dyeing properties of Chromium complex dyes (7a-f)

Dyes		7a	7b	7c	7d	7e	7f
Shades on Leather	2% Shade
	5% Shade

Table-4, UV-Visible data of ligand acid dyes (6a-f) and their Cr (III) complexes (7a-f)

Dye	Molecular formula	Molecular Mass	Powder/Solution Color	$\lambda_{\max}$ (nm)
6a	$C_{16}H_{13}ClN_4O_5S$	408.82	Orange/ Reddish Orange	460
7a	$C_{32}H_{23}Cl_2CrN_8O_{10}S_2$	866.60	Olive/Olive Brown	490
6b	$C_{16}H_{13}N_5O_7S$	419.37	Dark Brown / Reddish Orange	480
7b	$C_{32}H_{23}CrN_{10}O_{14}S_2$	887.71	Tan/Reddish Violet	500
6c	$C_{16}H_{14}N_4O_8S_2$	454.43	Orange/ Yellowish Orange	460
7c	$C_{32}H_{25}CrN_8O_{16}S_4$	957.83	Gray/Yellowish Brown	440
6d	$C_{16}H_{13}N_5O_{10}S_2$	499.43	Orange/ Reddish Orange	520
7d	$C_{32}H_{23}CrN_{10}O_{20}S_4$	1047.82	Tan/Reddish Yellow	460
6e	$C_{32}H_{26}N_8O_{12}S_3$	810.78	Orange/ Reddish Orange	420
7e	$C_{64}H_{46}Cr_2N_{16}O_{24}S_6$	1719.51	Olive Brown/ Yellowish Brown	430
6f	$C_{35}H_{32}N_8O_{10}S_2$	788.81	Brown/Yellowish Orange	450
7f	$C_{70}H_{58}Cr_2N_{16}O_{20}S_4$	1675.56	Brown/Yellowish Orange	460

Table-5, data of ligand acid dyes (6a-f) and their Cr (III) complexes (7a-f)

Sample Code	λ_{max} (nm)	Absorption of Free Complex	Absorption with DNA	Binding Constant (KJ mol ⁻¹)	Wavelength Shift(nm)
7a	464	0.603	0.556	-24.77	3
7b	483	1.142	0.960	-29.80	3
7c	489	1.521	-	-	-
7d	505	0.692	0.615	-29.82	2
7e	584	0.101	-	-	-
7f	479	0.437	0.386	-29.82	2

Figure 1, FTIR spectrum of Chromium complex of dye 6b.

Figure 2, ^1H -NMR spectrum of ligand acid dye 6b.

Figure 3, ¹³C-NMR spectrum of ligand acid dye 6b.

Figure 4, Expanded ^1H -NMR of Ligand acid dye 6b.

Figure 5, UV-Visible spectrum of ligand acid dyes **6 a-f**.

Figure 6, UV-Visible spectrum of Chromium (III) complex dyes **7a-f**.

Figure 7, DNA binding studies of Chromium (III) complex dyes 7a-f.

Scheme 1, Synthesis of ligand acid dyes and their Cr (III) complexes (7a-f)