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Characterisation and applications of some *o,o′*-dihydroxyazo dyes containing a 7-hydroxy group and their chromium complexes on nylon and wool

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Abstract

The synthesis and characterisation of *o,o′*-dihydroxyazo dyes and their chromium complexes is described by IR, UV–VIS, ^{1}H NMR spectroscopic techniques, magnetic susceptibility, thin-layer chromatography and elemental analysis. The synthesized dyes and complexes were applied on wool and nylon fabric. Fastness to light, washing, and rubbing of the dyed fabrics were measured and discussed.

Keywords: *o,o′*-Dihydroxyazo; 2:1 Metal complexes; 1:1 Metal complexes; Fastness

1. Introduction

It is well known that dyes and their complexes have been most widely used in fields such as dyeing textile fibre, biomedical studies, advanced applications in organic synthesis and high technology areas like lasers, liquid crystalline displays, electro-optical devices, and ink-jet printers [1–3].

o,o′-Dihydroxyazo dyes and their metal complexes are principally used as chromium and cobalt complexes for dyeing properties of protein and polyamide fibres with excellent light and washing fastness [4,5] and in electrophotographic applications for photoconductors [2,6,7]. These chromium complexes obtained from *o,o′*-dihydroxyazo dyes have been investigated by a variety of spectroscopic techniques to identify their structures and dyeing properties [8] but metal complexes containing a 7-hydroxy group have yet to be described. We have previously reported the fastness properties and synthesis of some similar compounds and their complexes [9,10]. The 7-hydroxy derivatives of *o,o′*-dihydroxyazo dyes and metal complexes can be as important as chromium complexes for obtaining excellent dyeing properties, for use in electrophotography, and also for preparing dyes and pigments that have different groups in their molecules.

In this work, we report the synthesis of some novel *o,o′*-dihydroxyazo compounds and their chromium complexes, and we characterise them using IR, UV–VIS, ^{1}H NMR spectroscopic techniques, magnetic susceptibility, thin-layer chromatography and elemental analysis. We measure

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and discuss their fastness to light, washing and rubbing.

2. Experimental

2.1. General

Melting points were taken with a digital melting point apparatus and were uncorrected. IR spectra were determined on a Mattson 1000 FTIR spectrometer by preparing KBr pellets. The UV–VIS absorption spectra in acetone and dimethylformamide were recorded with a Unicam UV2-100 UV/VIS spectrometer. The ^{1}H NMR spectra were taken on a Bruker AC 200 Fourier Transform Spectrometer operating at 200 MHz in DMSO-d_6. Elemental analyses were performed by the Instrumental Analysis Laboratory of TUBITAK, Marmara Research Center. Magnetic susceptibility measurement was measured at room temperatures with a Sherwood Scientific MXI Model Gouy.

All dyeing were done in an EMKO ESM 9440 dyeing apparatus. Rubbing, washing, and light fastness were determined using standard methods of the ISO 105-X12, ISO 105 CO6 A2S and ISO 105 B02.

Substituted *o*-hydroxyanilines were obtained from Aldrich, Merck, and Sigma.

2.2. Preparation of diazotized o-hydroxyanilines

o-Hydroxyanilines were diazotized in aqueous hydrochloric acid at 0–5 °C with $NaNO_2$ solution. The nitro derivative of diazotized *o*-hydroxyanilines was directly precipitated out of the solution as a yellow solid. The other derivatives ($-H$, $-CH_3$, $-Cl$) were precipitated by adding a concentrated aqueous solution of ammonium hexafluorophosphate salt. The precipitate was filtered and washed with cold water and ether [11].

2.3. Preparation of o,o′-dihydroxyazo dyes

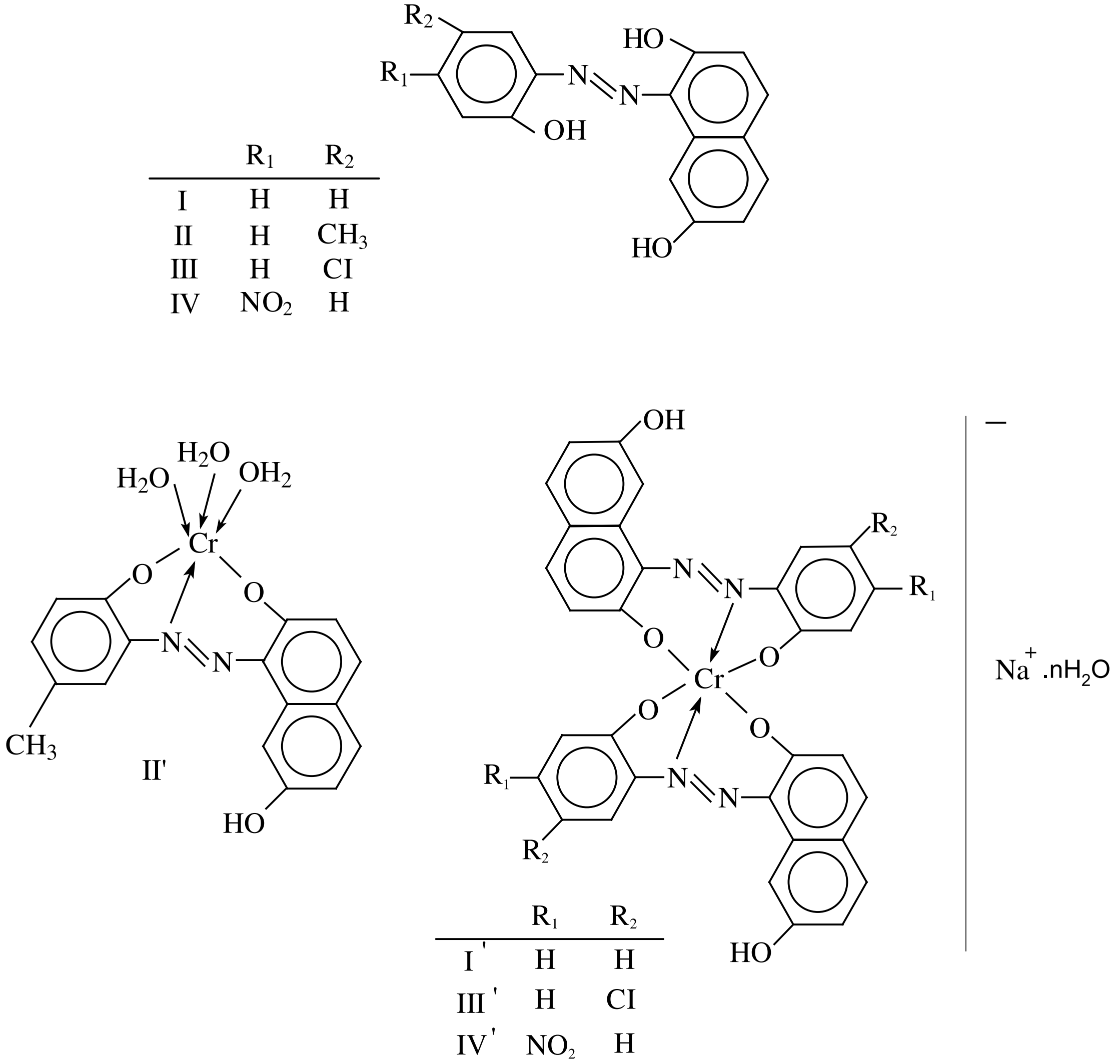
o,o′-Dihydroxyazo dyes were prepared by azo-coupling reaction of the 2,7-dihydroxynaphthalane with substituted 2-hydroxybenzenediazonium chloride according to the following procedure [11]: a mixture of freshly diazotized anilines (16 mmol) and 20 ml DMF was cooled by ice-water bath. A solution of naphthaline-2,7-diol (16 mmol) in 20 ml DMF was then added to the solutions, and solid sodium acetate was added to the resulting mixture. The mixture was stirred at 0–5 °C for 3 h and then at room temperature for 3 hours and quenched with ice-water or 0.2 M HCl. The coupling precipitate was filtered and washed with water, and then recrystallized by 10% water/ethanol. Purity was examined in a mixture of 5% water/ethanol by TLC with Kieselgel 60 HF_{254}.

2.4. Preparation of chromium complexes of o,o′-dihydroxyazo dyes

o,o′-Dihydroxyazo dyes (0.52 mmol) were heated with chromium(III) sulphate (0.13 mmol) and sodium acetate under reflux overnight in 20 ml DMF and then cooled and poured into a saturated NaCl solution with ice. The precipitate was filtered and washed with water and dried. Purity was examined in a mixture of 5% water/DMSO by TLC with Kieselgel 60 HF_{254}.

2.5. Dyeing of nylon fabrics

The dyebath was prepared at a 20:1 liquor ratio containing 0.5% dye for methyl and nitro substituents, 2.5% for proton substituent and 1.0% dye for chloride substituent. Then 1.2 ml (10%) Setacid VS-N(egalisator) was added as an acidic buffer (pH 5–5.5), along with 0.6 ml (10%) Setalan PM-7 (levelling agent) and 0.6 ml (10%) Setalub ACA (anticrease agents) to prevent fibres breaking during processing. The nylon fabrics (272 g/m^2) were wetted and immersed into dyebath at 40 °C and maintained at this temperature for 10 min. The bath temperature was then raised to 102 °C over 15 min and maintained there for 30 min. After cooling the dyebath, the dyed fabrics were rinsed and reduction-cleared twice with water at 40 °C for 15 min, then fixed at a 20:1 liquor ratio containing 1.5% Setafix-S (fixing agent). The pH was adjusted to 5–5.5 with acetic acid. The nylon fabrics were immersed into this liquor at 50 °C for 30 min and then rinsed with water and dried.



	R_1	R_2
I	H	H
II	H	CH_3
III	H	CI
IV	NO_2	H

	R_1	R_2
I'	H	H
III'	H	CI
IV'	NO_2	H

Fig. 1. The structures of the 7-hydroxy-*o,o'*-dihydroxyazo dyes and their chromium complexes.

2.6. Dyeing of wool fabrics

The dyebath was prepared in a similar manner to that described above for nylon fabrics: 1.8 ml (10%) ammonium sulphate and 0.3 ml amphoteric levelling agent Setalan IW were added and the pH was adjusted to 3.0 with formic acid. The wool fabric (457 g/m^2) was immersed in the dyebath at room temperature, then the temperature was raised to 98 °C for 40 min and maintained at this temperature for 60 min. The dyed fabrics were finally rinsed and washed with water at 40 °C twice for 10 min and then dried and reduction-cleared in a solution of 1 g L^{-1} Setalan BNH at 40 °C for 20 min. Afterwards, wool fabrics were washed with water and dried.

Rubbing, washing, and light fastness were determined using the ISO 105-X12, ISO 105 and BS 1006 B01 methods and the data were summarized in Table 2.

Table 1
The spectroscopic magnetic susceptibility data of the dyes and their complexes

Dyes/ complexes	Wavelength in DMF	λ_{max} (nm) in acetone	IR (cm^{-1})		^{1}H NMR	Magnetic susceptibility (BM)
			O–H	Cr–O	OH	
I	493 (5.520) 429^a (4.321)	482 (5.185) 425^a (4.051)	3687–2745	–	15.07	–
II	530 (5.278) 505 (5.281)	486 (5.310) 420^a (3.703)	3682–2555	–	15.62	–
III	498 (5.074) 434 (3.343)	486 (3.809) 434^a (3.644)	3481–2572	–	16.08	–
IV	446^a (3.220) 505 (5.149) 596^a (3.857)	495 (5.017) 420^a (4.007)	3695–2945	–	16.03	–
I′	–	536 (4.523) 490 (4.525)	3660–2695^b	554	–	3,53
II′	–	570 (4.210) 510^a (3.416)	3607–2659^a	541	–	2,87
III′	–	621^a (4.376) 580 (4.885) 549^a (4.501)	3677–2591^a	542	–	3,12
IV′	–	642^a (3.934) 605 (3.987) 557^a (3.941)	3674–2659^a	567,523	–	3,47

Concentrations in DMF and acetone: 1.07×10^{-5}–2.23×10^{-5} M, 1.11×10^{-5}–1.27×10^{-4} M.

[a] Shoulder peak.

[b] H_2O in complexes.

3. Results and discussion

o,o′-Dihydroxyazo dyes (I–IV) shown in Fig. 1, were synthesized by azo-coupling reactions of o-hydroxyphenylazodiazonium salts and their derivatives with 2,7-dihydroxynaphtaline and then their chromium complexes (I′–IV′) by refluxing a mixture of chromium sulphate, sodium acetate and the appropriate o,o′-dihydroxyazo dyes overnight in DMF. The structures of o,o′-dihydroxyazo dyes and their chromium complexes are shown in Fig. 1. The synthesized dyes and their complexes were applied to nylon and wool fabrics.

Spectroscopic, magnetic susceptibility, and analytical data for the o,o′-dihydroxyazo dyes and their complexes are summarized in Tables 1 and 2. Fastness values to light, washing and rubbing of dyed fabrics are given in Tables 3 and 4.

Table 2
Elemental analysis and characterisation data of 7-hydroxy-o,o′-dihydroxyazo dyes and their complexes

Dye	Formula	Yield (%)	Mp (°C)	Crystal colour	R_f (acetone)	Analysis (%) Calculated (found)		
						C	H	N
I	$C_{16}H_{12}N_2O_2$	90.72	239–240	Dark pink	0.73	68.57 (68,61)	4,59 (4,04)	10,00 (9,54)
II	$C_{17}H_{14}N_2O_2$	73.21	238–239^a	Dark red	0.74	69.39 (68,78)	4,76 (4,43)	9,52 (9,03)
III	$C_{16}H_{11}N_2O_2Cl$	57.69	272–274^a	Brown	0.81	61,05 (60,66)	3,49 (3,30)	8,90 (8,44)
IV	$C_{16}H_{11}N_3O_4$	67.29	>300	Dark red	0.71	59,08 (58,32)	3,38 (3,36)	12,92 (12,13)
I′	$NaC_{32}H_{20}N_4O_6Cr\cdot4.5H_2O$	11.81	>300	Black	0.48^b	53,83 (53,97)	4,07 (3,72)	7,86 (7,20)
II′	$C_{17}H_{12}N_2O_3Cr\cdot4H_2O$	44.52	>300	Black	0.76^b	47.72 (48.20)	4.68 (4.32)	6.55 (6.36)
III′	$NaC_{32}H_{18}N_4O_6Cl_2Cr\cdot2H_2O$	60.29	>300	Black	0.57^b	52,17 (52,90)	2,99 (3,59)	7,61 (7,74)
IV′	$NaC_{32}H_{18}N_6O_{10}Cr\cdot2.5H_2O$	46.71	>300	Black	0.79^b	50,13 (50,86)	3,00 (3,80)	10,97 (11,04)

[a] Decomposed.

[b] DMSO/H_2O.

Table 3
Fastness properties of the dyes and their complexes on nylon

Dye	Colour code [14]	Light fastness	Washing fastness						Rubbing fastness	
			Acetate	Cotton	Nylon	PES	Acrylic	Wool	Dry	Wet
I	$S_{07}O_{50}M_{07}$	3	3/4	4	2/3	5	5	3	4/5	4/5
II	$S_{07}O_{99}M_{99}$	3	3/4	3/4	2	5	5	3/4	4/5	4
III	$S_{04}O_{99}M_{50}$	3	3/4	3/4	2	5	5	3/4	4/5	4/5
IV	$S_{50}O_{50}M_{99}$	3	4	3/4	2	5	5	4	4	4/5
I′	$S_{41}O_{33}Y_{04}$	4	5	5	5	5	5	5	4	4
II′	$S_{07}O_{99}M_{99}$	> 6	5	5	5	5	5	5	4	4
III′	$S_{80}V_{60}M_{80}$	> 6	5	5	5	5	5	5	4	4/5
IV′	$S_{80}V_{80}C_{02}$	> 6	5	5	5	5	5	5	4	4/5

We investigated the UV–VIS spectral behaviour of 7-hydroxy-*o*,*o*′-dihydroxyazo dyes and their complexes in acetone and dimethylformamide depending on their solubility. Comparing the UV spectral data in acetone, we found that all dye spectra showed a strong absorption band in the range of 420 and 495 nm, had at least two individual absorption peaks, one of which was a shoulder. These peaks are characteristic for the azo and hydrazone forms [9,12–14]. The shoulder peak in the region 420–435 nm represents the azo form and the peak at 482–495 nm corresponds to the hydrazone form. In DMF, the dyes had very similar spectra but with another shoulder at 596 nm in nitro derivative. As Table 1 shows, the absorption maximum of the complexes demonstrated a bathochromic shift between 54 and 110 nm in comparison with the dyes inconsistent with the literature values [9,10,15].

The elemental analysis of the chromium dye complexes containing physisorbed water between 2.0–4.5 mol gave satisfactory results with a corresponding ligand:metal ratio of 2:1 but 1:1 for complex II′ with coordination water. Magnetic susceptibility of the chromium complexes I′–IV′ agrees well with the usual range of 2.87–3.53 BM and the calculated value of 3.87 BM for Cr^{3+} with $[Ar]3d^3$ structure. These values are in accord with the structures shown in Fig. 1.

In the IR spectra of the dyes, characteristic stretches for OH groups were observed as broad signals between 3690 and 2500 cm^{-1} together with aromatic =C–H bonds. The broadening of this peak shows that these dyes have strong intramolecular hydrogen bonding between the hydroxyl group and the azo nitrogen. Because azo–hydrazone form can be seen forming UV–VIS spectra, in ^1H NMR spectra of the dyes, a broad signal near 15.07–16.08 ppm corresponds to imine NH proton resonance of the hydrazone form [15]. This state was confirmed by very low field signal at 177 ppm in ^{13}C NMR spectrum which are typical for C=O group of the hydrazone of the dye III. As Table 1 shows, the Cr–O peaks of the chromium complexes were

Table 4
Fastness properties of the dyes and their complexes on wool

Dye	Colour code [14]	Light fastness	Washing fastness						Rubbing fastness	
			Acetate	Cotton	Nylon	PES	Acrylic	Wool	Dry	Wet
I	$S_{60}O_{41}Y_{80}$	3	3	4	2	5	5	3	3	3/4
II	$S_{33}O_{60}Y_{02}$	3	2/3	3	1/2	5	5	2/3	3	3/4
III	$S_{41}O_{80}Y_{26}$	3	2	2	1	5	5	3	3	3/4
IV	$S_{33}O_{50}Y_{07}$	3	2/3	1/2	1/2	5	5	2/3	2	2/3
I′	$S_{41}O_{15}Y_{04}$	5	5	5	4/5	5	5	5	4/5	4/5
II′	$S_{80}V_{50}M_{99}$	5	5	5	3/4	5	5	5	3	3/4
III′	$S_{80}V_{80}M_{99}$	> 6	5	5	3/4	5	5	5	4	4
IV′	$S_{60}V_{90}C_{90}$	> 6	5	5	3/4	5	5	5	3	3/4

observed in the 523–567 region as expected in the IR spectra.

The dyes and their chromium complexes were applied to nylon and wool fabrics in different dyeing percentages because of colour shades. The fastness values of dyed fabrics to light, washing and rubbing are given in Tables 3 and 4. Although the fabrics dyed with the dyes showed poor light fastness, good rubbing and various washing fastness with different standards as shown in Tables 3 and 4, the complexes had excellent light and washing fastness, and good rubbing fastness on both nylon and wool fabrics. Fastness values observed for the chromium complexes I′–IV′ were similar to the values of complexes of Acid Black 63 (CI 12195), Acid Brown 29 (CI 12197), and acryloyloxy-*o*,*o*′-dihydroxyazo dyes [9,10,16]. The presence of a hydroxy group in the 7-position of the complexes has not much effect on the fastness properties of the dyes.

As Tables 3 and 4 show, the colour codes of the dyed fabric were determined from Farbenatlas [17]. While the colour of nylon fabric dyed was bright, the other wool fabrics were dull.

4. Conclusion

The *o*,*o*′-dihydroxyazo dyes and their chromium complexes have been synthesized and applied to nylon and wool fabrics and the substituted dyes and their complexes are characterized by IR, UV–VIS, ^{1}H NMR spectroscopic techniques, magnetic susceptibility, and elemental analysis. We can conclude from both UV–VIS and IR spectra that dyes I–IV have strong intramolecular hydrogen bond between the hydroxyl group and the azo nitrogen.

We have also measured the fastness values of the dyed fabrics to light, washing and rubbing. While chromium complexes showed excellent results for all the fastness properties, the lightness and some washing fastness of the dyes exhibited poor properties. The similar fastness properties have previously been obtained according to the literature [10,16].

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