



Synthesis and Properties of Some Pyridone Chromium Complex Azo Dyes

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(Received 12 August 1990; accepted 26 September 1990)

ABSTRACT

*This paper reports the synthesis of some chromium complex dyes obtained from the reaction of *o,o'*-dihydroxyazo pyridone intermediates and ammonium chromium sulfate. The IR-, UV/Vis- and mass spectral data of the azo pyridone intermediates and the chromium complexes were studied and compared. Their structures were confirmed by elemental analysis, and the chromium content of the complexes was also determined. The fastness properties of the azo pyridone intermediates and of the chromium complexes on polyester and wool were assessed.*

1 INTRODUCTION

It is well known that metal complexes of azo dyes possess dyeing properties with excellent light and wash fastness, and the preparation of these dyes is of great interest for dye chemists. A number of metal complexes from heteroaromatic pyrazolone compounds have been studied,^{1–5} but the metal complexes of analogous pyridone azo dyes have not been developed.

In this paper we report the synthesis of some metal complexes of pyridone azo dyes from *o,o'*-dihydroxyazo pyridone intermediates, which were synthesized by coupling pyridone compounds with diazotized *o*-hydroxy-aniline derivatives. Comparison is made between the spectral characteristics of the *o,o'*-dihydroxyazo pyridone intermediates and their chromium complexes, and the dyeing properties of both types of dyes are also reported.

2 EXPERIMENTAL

2.1 General

All melting points are uncorrected. IR spectra were determined on a Jasco HC-12 FT/IR in KBr. The UV/Vis absorption spectra were recorded using a Shimadzu UV-240 spectrophotometer. The mass spectra were measured on a JMS-D-300 (JEOL) mass spectrometer.

o-Hydroxyaniline derivatives (**a–d**) were commercial products. The 1-substituted-5-cyano-2-hydroxy-6-pyridones **I–III** were prepared by known methods.^{6–9}

2.2 Preparation of intermediates **Ia–IIIId**

The *o*-hydroxyanilines (**a–d**) were diazotized in ice-cold aqueous hydrochloric acid at 0–5°C with sodium nitrite for 30 min and the resultant diazonium salts coupled at pH 3–4 with the pyridone compounds **I–III** dissolved in sodium carbonate solution, at pH 3–4. The precipitated **Ia–IIIId** were filtered, dried and recrystallized from acetone. Characterization data for these compounds are summarized in Table 1.

2.3 Preparation of azo pyridone chromium complexes **I'a–III'd**^{10,11}

The *o,o'*-dihydroxyazo pyridone intermediate **Ia** was heated with ammonium chromium sulfate and sodium acetate under reflux for 2–3 h in formamide solution, then cooled and poured into a saturated salt solution. The product was filtered and recrystallized from acetone as purple crystals.

The other metal complexes **I'b–III'd** were prepared by a similar method. Elemental analysis for the chromium complexes **I'a–III'd** are listed in Table 2.

2.4 Determination of chromium content¹²

Metal complex dye (0.1 g) was fused to decompose the complex. The resultant grey residue was cooled, and then oxidized with 5 ml conc. nitric acid and 0.5 g potassium chlorate. The solution was taken to dryness, 10 ml distilled water was added and the mass was dried again. The residue was dissolved in conc. sulfuric acid, diluted to 25 ml and the solution titrated with 0.1M-ferrous ammonium sulphate solution using *N*-phenylanthranilic acid as indicator. The chromium content was calculated using the relationship:

$$\text{Cr (\%)} = \frac{\text{vol. of 0.1M-Fe}_{\text{soln}}^{2+} (\text{ml}) \times 0.1\text{M of Fe}^{2+}}{3} \frac{\text{mol. wt of Cr}}{\text{wt of sample (g)}} 100 (\%)$$

TABLE 1
Elemental Analysis and Characterization Data of *o,o'*-Dihydroxyazo Pyridone Intermediates
Ia–IIId

Dye	Formula (Mol. wt)	Yield (%)	M.p. (°C)	Crystal colour	Analysis (%): Calcd (Found)		
					C	H	N
Ia	C ₁₃ H ₁₀ N ₄ O ₃ (270.00)	81	288–289	Red–orange	57.8 (57.1)	3.7 (3.6)	20.7 (20.95)
Ib	C ₁₁ H ₁₂ N ₄ O ₃ (284.00)	91	280–281	Red–orange	59.15 (59.9)	4.2 (4.1)	19.7 (19.6)
Ic	C ₁₃ H ₉ ClN ₄ O ₃ (305.00)	85	291–292	Red–orange	51.15 (51.0)	2.95 (2.9)	18.4 (18.7)
Id	C ₁₃ H ₉ N ₅ O ₅ (315.00)	79	> 300	Yellow	49.5 (49.4)	2.9 (2.9)	22.2 (22.3)
IIa	C ₁₇ H ₁₈ N ₄ O ₃ (326.00)	86	248–249	Orange–yellow	62.6 (62.7)	5.5 (5.55)	17.2 (17.1)
IIb	C ₁₈ H ₂₀ N ₄ O ₃ (340.00)	90	266–267	Orange	63.5 (63.7)	5.9 (5.9)	16.5 (16.5)
IIc	C ₁₇ H ₁₇ ClN ₄ O ₃ (360.50)	88	> 300	Orange–yellow	56.7 (56.8)	4.7 (4.7)	15.6 (15.5)
IIId	C ₁₇ H ₁₇ N ₅ O ₅ (371.00)	92	> 300	Yellow	55.0 (55.15)	4.6 (4.7)	18.9 (18.9)
IIIa	C ₁₇ H ₁₈ N ₄ O ₃ (326.00)	89	262–263	Orange–yellow	62.6 (62.6)	5.5 (5.5)	17.2 (17.2)
IIIb	C ₁₈ H ₂₀ N ₄ O ₃ (340.00)	86	286–287	Orange	63.5 (63.8)	5.9 (5.85)	16.5 (16.5)
IIIc	C ₁₇ H ₁₇ ClN ₄ O ₃ (360.50)	85	296–297	Orange–yellow	56.7 (56.8)	4.7 (4.7)	15.6 (15.6)
IIId	C ₁₇ H ₁₇ N ₅ O ₅ (371.00)	90	> 300	Yellow	55.0 (55.1)	4.6 (4.6)	18.9 (18.9)

2.5 Dyeing of fabrics

2.5.1 Dyeing of polyester fabrics

The dyebath was prepared at a 30:1 liquor ratio containing 0.5% dye (on weight of fiber) and 1.0 g litre⁻¹ leveling agent (Coloursol Ace-65) and the pH was adjusted to 4–5 with acetic acid (10%). The polyester fabrics were wetted and entered into the dyebath at room temperature; they were maintained at this temperature for 20 min, the bath was then raised to 130°C over 50 min (2°C min⁻¹) and dyeing continued for a further 1 h. The dyeings were rinsed and reduction-cleared in a solution of sodium hydroxide (6 g litre⁻¹), soap (1 g litre⁻¹) and hydrosulfite (2 g litre⁻¹) at 70°C, and then finally washed and dried.

TABLE 2
Elemental Analysis of Pyridone Chromium Complex Azo Dyes I'a-III'd

Dye	Formula (Mol. wt)	Analysis (%): Calcd (Found)				Crystal colour
		C	H	N	Cr	
I'a	C ₂₆ H ₁₆ N ₈ O ₆ CrNa (611·00)	51·1 (48·2)	2·6 (4·0)	18·3 (12·8)	8·5 (9·2)	Purple
I'b	C ₂₈ H ₂₀ N ₈ O ₆ CrNa (639·00)	52·6 (55·2)	3·1 (4·6)	17·5 (15·7)	8·1 (8·7)	Purple
I'c	C ₂₆ H ₂₄ Cl ₂ N ₈ O ₆ CrNa (680·00)	45·9 (46·3)	2·1 (3·4)	16·5 (14·6)	7·6 (8·3)	Purple
I'd	C ₂₆ H ₂₄ N ₁₀ O ₁₀ CrNa (701·00)	44·5 (43·4)	2·0 (3·4)	20·0 (17·7)	7·4 (7·9)	Purple
II'a	C ₃₄ H ₃₂ N ₈ O ₆ CrNa (723·00)	56·4 (55·9)	4·4 (4·4)	15·5 (15·6)	7·2 (7·3)	Purple
II'b	C ₃₆ H ₃₆ N ₈ O ₆ CrNa (751·00)	57·5 (57·4)	4·8 (4·8)	14·9 (15·0)	6·9 (7·0)	Purple
II'c	C ₃₄ H ₃₀ Cl ₂ N ₈ O ₆ CrNa (792·00)	51·5 (51·3)	3·8 (3·8)	14·15 (14·2)	6·6 (6·9)	Purple
II'd	C ₃₄ H ₃₀ N ₁₀ O ₁₀ CrNa (813·00)	50·2 (50·3)	3·7 (3·7)	17·2 (17·2)	6·4 (6·5)	Purple
III'a	C ₃₄ H ₃₂ N ₈ O ₆ CrNa (723·00)	56·4 (55·9)	4·4 (4·4)	15·5 (15·5)	7·2 (7·3)	Purple
III'b	C ₃₆ H ₃₆ N ₈ O ₆ CrNa (751·00)	57·5 (57·4)	4·8 (4·8)	14·9 (15·0)	6·9 (7·1)	Purple
III'c	C ₃₄ H ₃₀ Cl ₂ N ₈ O ₆ CrNa (792·00)	51·5 (51·55)	3·8 (3·8)	14·15 (14·1)	6·6 (6·85)	Purple
III'd	C ₃₄ H ₃₀ N ₁₀ O ₁₀ CrNa (813·00)	50·2 (50·3)	3·7 (3·65)	17·2 (17·3)	6·4 (6·4)	Purple

2.5.2 Dyeing of wool fabrics

The dyebath was set at a 30:1 liquor ratio containing 0·5% dye (on weight of fiber) and 2 g litre⁻¹ amphoteric leveling agent (Coloursol AC); the pH was adjusted to 5·5–6. The pre-wetted wool fabrics were entered into the dyebath at room temperature for 20 min, the temperature was raised to the boil over 40 min (2°C min⁻¹) and boiling continued for 1 h. The fabrics were finally cooled and treated in 2 g litre⁻¹ soap at 70°C for 30 min, then washed and dried.

All the dyeings were carried out on a Rapid Ltd dyeing apparatus. Lightfastness was determined on a Xenotest 150 (Hanau) according to AATCC Test method 117–1978. The wash fastness was assessed on a T.S.S. Tester (Yasuda Seiki Seisakusho Ltd) according to CNS 1494–64, A2 (CNS = Chinese National Standard).

3 RESULTS AND DISCUSSION

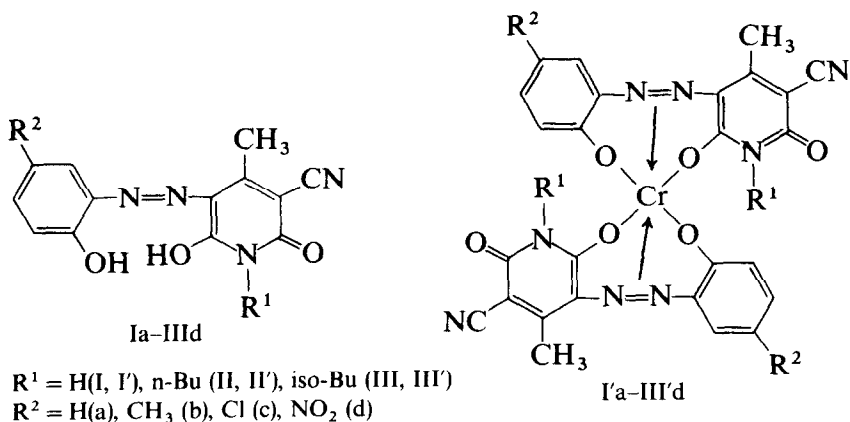
The purple azo pyridone chromium complexes **I'a-III'd** were readily synthesized by refluxing a mixture of ammonium chromium sulfate, sodium acetate and the appropriate *o,o'*-dihydrozyazo pyridone intermediates **1a-IIIId** for 2–3 h in formamide.

Electronic spectral data of the *o,o'*-dihydroxyazo pyridones **1a-IIIId** and of their chromium complexes **I'a-III'd** are summarized in Table 3.

The IR spectra of **1a-IIIId** showed a well-defined nitrile absorption band in the region of 2225–2250 cm^{-1} , a broad absorption band in the area of 3200–3600 cm^{-1} corresponding to the hydroxy group in the phenyl ring and

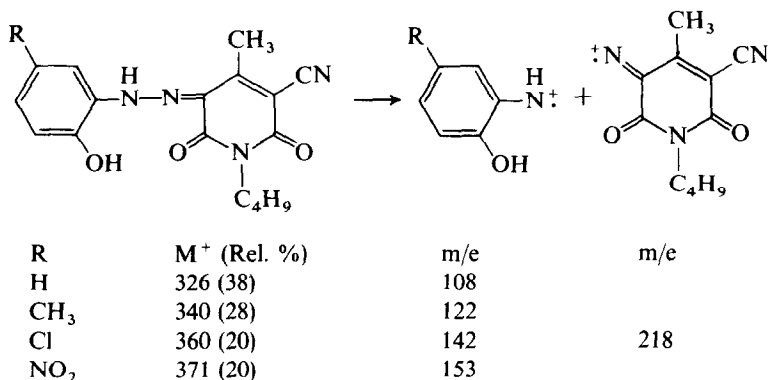
TABLE 3
Comparison of IR and UV/Vis Spectra of Pyridone Intermediates
1a-IIIId and Chromium Complexes **I'a-III'd**

<i>Dyes</i>	<i>Wavelength, λ_{max}, in DMF (nm)</i>		<i>Wavenumber, in KBr (cm^{-1})</i>	
	(log ϵ)		$\nu_{\text{C}\equiv\text{N}}$	$\nu_{\text{C}=\text{O}}$
Ia/I'a	480 / 529 (4.31) (4.51)		2235/2240	1665/1660 1650
Ib/I'b	485 / 537 (4.53) (4.39)		2240/2240	1670/1650 1640
Ic/I'c	478 / 527 (4.54) (4.51)		2230/2230	1670/1650 1650
Id/I'd	415, 550 / 510 (4.51) (4.52) (4.21)		2250/2230	1690/1670 1640
IIa/II'a	456, 474 / 525 (4.75) (4.91) (4.48)		2226/2221	1662/1642 1623
IIb/II'b	464, 478 / 530 (4.70) (4.75) (4.45)		2235/2221	1679/1640 1631
IIc/II'c	463, 481 / 536 (5.01) (5.03) (4.40)		2228/2224	1680/1643 1630
IIId/II'd	422, 590 / 515 (4.65) (4.78) (4.40)		2236/2227	1674/1644 1635
IIIa/III'a	456, 474 / 515 (4.74) (4.90) (4.46)		2225/2222	1664/1641 1629
IIIb/III'b	460, 478 / 532 (4.68) (4.70) (4.45)		2234/2222	1673/1641 1631
IIIc/III'c	464, 482 / 532 (4.76) (4.77) (4.44)		2237/2222	1681/1639 1630
IIId/III'd	420, 585 / 511 (4.62) (4.75) (4.41)		2238/2224	1681/1642 1635



Scheme 1

two strong, sharp absorption bands in the range $1623\text{--}1690\text{ cm}^{-1}$, which are attributed to the carbonyl group in the heteroaromatic pyridone ring. The mass spectra of **IIa–IIId** showed the relevant molecular peak and fragments due to the cleavage of the azo linkage. Characteristic fragments appeared at m/e 108 (**IIa**), 122 (**IIb**) and 142 (**IIc**) as base peaks and at m/e 153 (**IIId**) (35% relative abundance). Other characteristic peaks were at m/e 164, 177 and 218 with relative abundance varying from 20 to 100% (Scheme 2).



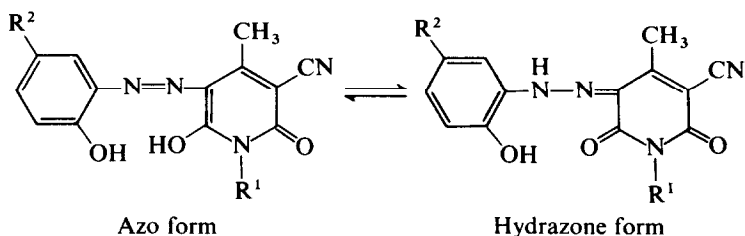
Scheme 2

The electronic absorption spectra in DMF of **Ia**, **Ib** and **Ic** showed only one absorption maximum in the range 478–485 nm, whilst **Id**, **IIa–IIId** and **IIIa–IIIId** showed two absorption maxima in the range of 415–464 nm and 474–590 nm, the latter band having the higher molar extinction coefficient.

Compounds **Id**, **IIId** and **IIIId**, which contain a nitro group, absorbed in the range 415–422 nm and 550–590 nm, and the different absorptions of these compounds can probably be attributed to solvent interactions.

The spectral data generally lead to the conclusion that the tautomeric

equilibrium of the *o,o'*-dihydroxyazo pyridones **Ia–III'd** is inclined to the hydrazone form and not to the azo form (Scheme 3).



Scheme 3

Table 2 gives the elemental analyses of the chromium complexes **I'a–III'd** and show a satisfactory stoichiometry, the results corresponding to a ligand:metal ratio of 2:1.

In the IR spectral data of **I'a–III'd**, the nitrile band absorbs at lower frequency than in **Ia–III'd**. Figure 1 shows a comparison of the carbonyl absorption bands of the chromium complexes **II'a–II'd** and of the precursor intermediates. The complexes show one strong single carbonyl absorption in the region $1639\text{--}1670\text{ cm}^{-1}$. The second carbonyl absorption band, which appears in the spectra of the intermediates, was not observed in the spectra of the complexes. This can be explained by the metal ion being bonded to the oxygen atom of the second carbonyl group in the pyridone ring.

The electronic absorption spectra of the chromium complexes **I'a–III'd** in DMF shows only one absorption maximum in the range of $511\text{--}537\text{ nm}$, i.e. a bathochromic shift of $40\text{--}55\text{ nm}$, with exception of **I'd**, **II'd** and **III'd**.

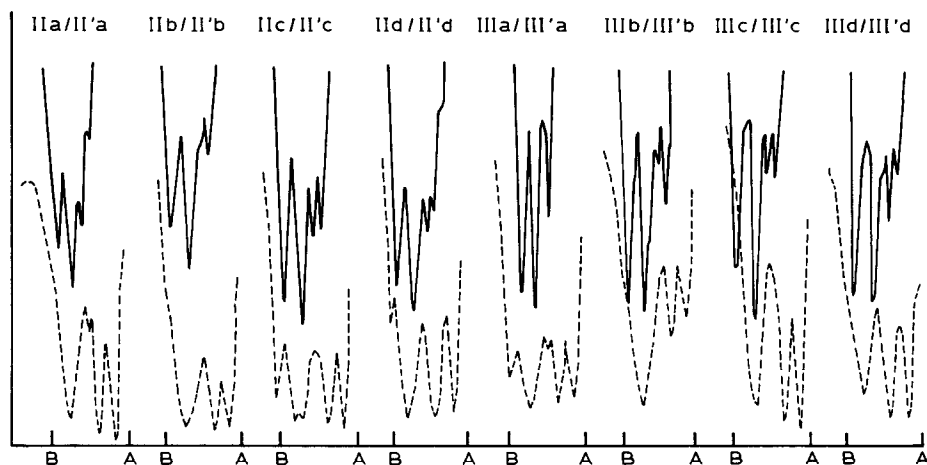


Fig. 1. Comparison of carbonyl absorption band of intermediates **IIa–III'd** (—) and chromium complexes **II'd–III'd** (---) in the region $1500\text{--}1700\text{ cm}^{-1}$. A–B: $1500\text{--}1700\text{ cm}^{-1}$.

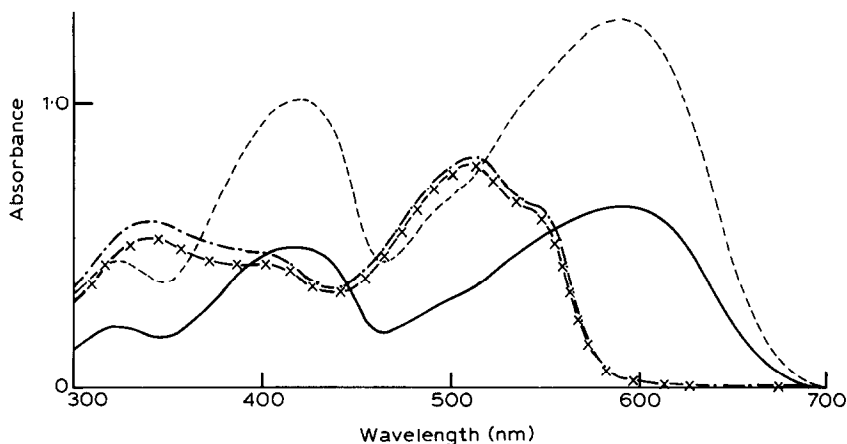


Fig. 2. Comparison of electronic absorption band of intermediates **II'd** (—) **III'd** (---) and chromium complexes **II'd** (- - -), **III'd** (- x - x $\sqrt{}$).

Figure 2 shows the absorption maximum of the chromium complexes **II'd** and **III'd**, demonstrating a hypsochromic shift of 77 nm in comparison with **II'd** and **III'd**. This is presumably due to the influence of the solvent polarity on the ionic system of the complexes.

The *o'o'*-dihydroxyazo pyridone intermediates **Ia–IIId** were applied to

TABLE 4
Fastness Properties^a of Intermediates **Ia–IIId** and Chromium Complexes **I'a–II'd**

Dye	Fastness on polyester fabrics		Dye	Fastness on wool fabrics	
	Washing ^b	Light ^c		Washing ^b	Light ^c
Ia	3	2–3	I'a	4–5	7
Ib	3	2–3	I'b	4–5	7
Ic	3–4	2	I'c	4–5	6–7
Id	3–4	2	I'd	4–5	6–7
IIa	5	2	II'a	5	7–8
IIb	5	2–3	II'b	5	7
IIc	5	1–2	II'c	4	7
IIId	5	1	II'd	4–5	7
IIIa	5	2	III'a	5	7
IIIb	5	2–3	III'b	5	6–7
IIIc	5	2	III'c	4	7
IIId	5	1	III'd	4	7–8

^a On dyeing at 0.5% depth (o.w.f.).

^b Washing fastness: CNS 1494–64, A2.

^c Lightfastness: AATCC test method 117–1978.

polyester and their chromium complexes to wool fabrics. The fastness properties are given in Table 4. Intermediates **Ia–III'd** showed good washing fastness, but very poor lightfastness, whilst the chromium complexes **I'd–III'd** showed excellent washing fastness and lightfastness.

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