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Synthesis and Colour Properties of Some Copper Complexes of Tetradenate Formazan Dyes

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ABSTRACT

A series of copper complexes of tetradenate formazan dyes derived from 1-(2-carboxyphenyl)-3-phenyl-5-(2-hydroxyphenyl)formazan was prepared using two different methods. IR spectra and the colour properties of the dyes were determined and compared. It was found that the colours of the complexes obtained from a particular formazan varied considerably depending on the method of preparation, especially when substituent groups were present on the ortho *position of the 3-phenyl ring. The dyeing properties of the dyes are also reported.*

1 INTRODUCTION

Metal complexes of tetradenate formazan were first employed as dyes for the dyeing of wool by Ciba in 1947.[1] Since then many metal complexes of tetradenate formazans have been reported and they have become an important dye type, especially in the areas of reactive and acid dyes[2,3] although other applications have also been reported.[4–8] In addition to studies on their end-uses, investigations have been made with respect to synthetic methods, as well as on the relationships between applications, colour properties and chemical constitutions of the dyes.[9–12]

In the present paper, five copper complexes of tetradenate formazans derived from the 1-(2-carboxyphenyl)-3-phenyl-5-(2-hydroxy)phenyl formazan chromophore were synthesized using two different procedures and

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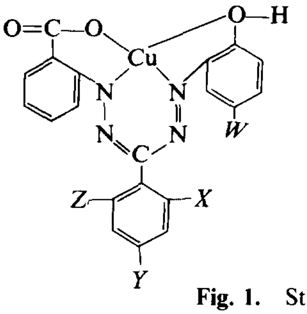


Dye no.	*X*	*Y*	*Z*	*W*
1	H	H	H	SO_2NH_2
2	H	H	H	SO_3H
3	Cl	Cl	H	SO_2NH_2
4	Cl	H	Cl	SO_2NH_2
5	SO_3H	H	H	NO_2
6	Cl	Cl	H	SO_3H

Fig. 1. Structures of synthesised dyes.

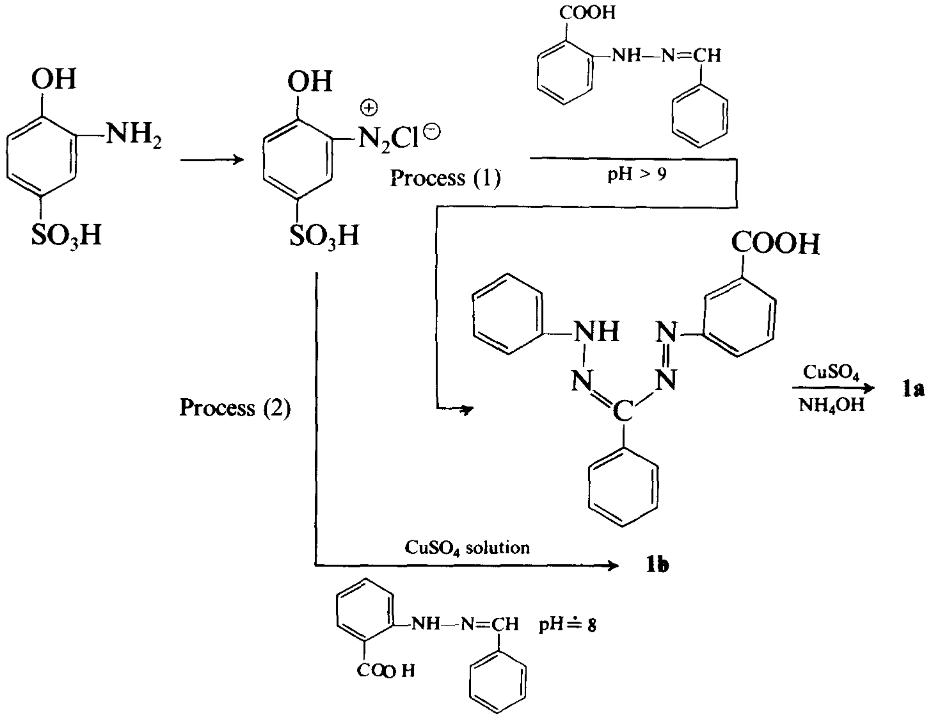
their structures investigated by IR; the colour and dyeing properties were also examined.

The five prepared dyes are shown in Fig. 1.

2 RESULTS AND DISCUSSION

2.1 Synthesis and colour properties of the dyes

The formazan dyes were prepared using two different methods, as outlined in Scheme 1.



Scheme 1. The synthetic processes.

TABLE 1
The Colours and λ_{max} Values of the Synthesized Dyes in Water

Dye	*1a*	*1b*	*2a*	*2b*	*3a*	*3b*	*4a*	*4b*	*5a*	*5b*
λ_{max} (nm)	610		600		595	597	595		585	595
Colour	blue		reddish-blue		bluish-violet	greenish-blue	bluish-violet	greenish-blue	bluish-violet	greenish blue

Process (1) was carried out by coupling the diazonium salts at 5–10°C and pH > 9 with the hydrazone and then adding cuprammonium hydroxide for the complexing. In Process (2), the coupling and complexing were carried out at the same time. Using the two procedures, five pairs of dyes, i.e. **1a** and **1b**, **2a** and **2b**, **3a** and **3b**, **4a** and **4b**, **5a** and **5b**, were obtained.

From the results it was found that when a substituent was present on the *ortho* position of the 3-phenyl ring of the dyes (as in dyes **3**, **4** and **5**), Process (2) could be readily carried out with high yields, but Process (1) required a longer time to complete and gave lower yields; the colours of the dye species formed by the two processes were also different. On the other hand, when no *ortho* substituent was present, as in dyes **1** and **2**, both the processes could be readily accomplished and gave dyes which were slightly different in their colour properties (Table 1). This implies that the synthetic method used affects the properties of the resulting formazan dyes.

Dyeing experiments were carried out and the colour properties of wool dyeings measured in accord with ISO, and then compared; data are shown in Table 2. The results indicate that the colour properties of dyes

TABLE 2
Colour Properties of the Dyeings

	ΔE	L	C	h	Δh
1a		57·186	11·493	248·86	
1b	2·07	58·132	13·145	252·62	3·76
2a		57·326	11·517	253·96	
2b	1·11	57·242	12·417	257·03	3·07
3a		53·454	6·258	269·66	
3b	2·89	53·958	8·509	283·35	13·69
4a		55·865	8·618	258·33	
4b	2·88	54·983	9·598	276·43	18·10
5a		54·715	7·063	246·24	
5b	3·68	53·365	5·530	274·58	28·34

1a and **1b**, and of **2a** and **2b** are very similar in their brightness, chroma and hue respectively. Dyes **1a** and **1b** dyed wool in a bright blue shade and dyes **2a** and **2b** gave reddish-blues. However, dyes **3a** and **3b**, **4a** and **4b**, **5a** and **5b** exhibited large differences in shade. For example, **3a** gave bluish-violet dyeing and **3b** was greenish-blue. These results further confirm that the synthetic methods affect the colour properties of the formazan dyes, depending on whether substituent groups are present on the *ortho* position of the 3-phenyl ring.

2.2 Reasons for the colour differences

To investigate the effects of the synthetic methods on the properties of the synthesized dyes, the five pairs of dyes were purified using extraction, recrystallization and column chromatography techniques. Their IR and UV/Vis spectra were recorded and representative data are listed in Table 3. Comparison of the IR spectral data shows that similar results are obtained for dyes produced from both synthetic methods, irrespective of whether or not there are substituents on the *ortho* positions of the 3-phenyl rings (for example comparing **2a** and **2b** or **3a** and **3b**). This suggests that they have similar chemical structures, although different processes were employed in their synthesis. The colour differences are therefore not due to changes in the chemical structure of the dyes.

TABLE 3
IR Bands of Dyes **2a**, **2b** and **3a**, **3b** (cm^{-1})

	2a	**2b**	**3a**	**3b**
$\gamma_{C=O}$	1657	1655	1648	1648
γ_{C-H}	1406	1406	1408	1435
	920	924	929	951
γ_{C-O}	1256	1254	1269	1233
δ_{N-H}	1608	1609	1616	1599
	880	876	876	854
γ_{C-N}	1305	1302	1308	1331
$\gamma_{C=N=}$	1580	1578	1582	1583
$\gamma_{N=N}$	1608	1609	1616	1599
δ_{-OH}	1354	1352	1350	1376
	754	756	758	754
γ_{C-O}	1238	1238	1237	1233
γ_{O-H} (—COOH)	3464 (P)	3336 (P)	3378 (P)	3386 (P)
γ_{O-H} (—OH)	3656–3032	3656–3064	3624–3691	3624–3082
γ_{N-H}				

P = Highest peak.

If there are substituents on the *ortho* position, it has been noted that the synthetic method used does not change the structure of the dyes. Spatial factors must also be considered, and these will affect the formation and structure of the dyes; the colour differences may be caused by different stereoisomers being formed in the different synthetic processes. Such structural features may be a key factor influencing the colour properties of the dyes and these will be further investigated using single crystal X-ray diffraction.

Surprisingly, it was found that dyes **5a** and **5b** could interchange with each other during purification. When **5a** and **5b** were separated by column chromatography, **5b** was formed from the separated **5a** after a short time, and **5a** was also formed from the separated **5b**, i.e. **5a** $\rightleftharpoons$ **5b**. This may imply that there is tautomerism or a complex change existing between the two species obtained from different synthetic methods.

2.3 Dyeing properties

Some of the dyes were evaluated for the dyeing of wool using established procedures; representative fastness properties of the dyeings are listed in Table 4. Coloration properties were generally very good and all dyeings had very good fastness to light; other fastnesses were moderate.

TABLE 4
Fastness Properties of the Dyes on Wool

	2a	**2b**	**3b**	**5a**	**6b**
Light	6	6	5	6	5
Washing with water	4–5	4–5	4	4–5	4–5
Wool staining	3–4	3–4	4	3–4	4–5
Cotton staining	3–4	3	4–5	4	4–5
Washing with soap	4–5	4–5	4–5	4–5	4
Wool staining	4–5	4–5	4	4–5	4–5
Cotton staining	3	3	3–4	4–5	4–5
Perspiration	4–5	4–5	4	4–5	4–5
Wool staining	2–3	2–3	4–5	2–3	3–4
Cotton staining	2	2	4–5	4–5	4–5
Rubbing dry	4–5	4–5	2–3	4–5	3–4
wet	4–5	4–5	3–4	4–5	4–5
Stoving	4	4	4–5	—	—
Cotton staining	4	4	4–5	—	—

3 EXPERIMENTAL

3.1 Synthesis method

Process (1)
The amines (0·1 mole) were diazotized at pH 5·6, temperature of 0–5°C and with a slight excess of nitrous acid during the procedure (starch/KI test). The pH of the diazotized solutions was adjusted to 3–4 with sodium acetate and residual nitrous acid destroyed with urea prior to coupling. The hydrazones (0·1 mol) were dissolved in aqueous sodium hydroxide (pH 8) with slight heating and then cooled to 5–10°C. The diazonium solution was added to the stirred hydrazane solution whilst maintaining the pH slightly higher than 9. When the coupling was completed, the solution was stirred for 2 h and then filtered. The filtrates were then added to stirred cuprammonium hydroxide (which was obtained by adding 40 ml 26–28% aq. ammonia to a solution of 0·1 mol copper sulfate in 60 ml water) at 50–60°C for 2 h. During this process, the deep red colour of the solution turned to bluish violet. The end of the reaction was monitored using paper chromatography with *n*-butanol : pyridine : aq. ammonia (25%) : water = 1 : 1 : 1 : 1 as developing solvent. When the reaction was complete, the solutions were cooled to room temperature and HCl added to bring the pH of the solution to 5–6; 10–15% (w/v) salt was added and the products filtered.

Process (2)
The diazonium solutions were prepared by the same procedure as in Process (1). When diazotisation was complete, residual nitrous acid was destroyed with urea and the pH value of the solutions was adjusted to 3–4 with sodium acetate. A solution of copper sulfate (0·1 mole) in 60 ml water was added at 0–5°C. The appropriate hydrazones (0·1 mole) were dissolved in aqueous sodium hydroxide with stirring and slight heating at pH 8–9, and then cooled to 15°C. The diazonium solutions were added to the stirred hydrazone solution for coupling and complexing at 15–20°C, maintaining the pH at 8–9 by addition of 20% aq. sodium hydroxide. When reaction was complete, the solution was heated to 40–50°C, a moderate amount of salt added and the product filtered. The residue was washed with 10% aq. salt solution until the colour of the residual liquor was pale blue.

3.2 Dyeing method

Wool pieces were immersed in a dyebath containing the dye solution, 10% sodium sulphate and 5% ammonium acetate at a liquor to goods ratio of 50 : 1 at room temperature. The bath was heated to 90–95°C over 30–40 min and then heated to boiling in 5 min and maintained at the boil for 10 min. The dyeing was then rinsed and dried at room temperature.

3.3 Instrumental measurements

Infrared spectra (KBr) were recorded on a Nicolet FT-IR5DX Spectrometer (USA) and the UV/Vis on an acs Spectro-Sensor and a Carl Zeiss Jena Specord instrument (Germany). Colour measurements were made using a Macbeth Colour-Eye type instrument (Hong Kong).

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