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Metallization of non-genotoxic direct dyes

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Dedicated to the memory of Professor Masaru Matsuoka

Abstract

Copper (II) salts were used as metallizing agents in the synthesis of new direct dyes for cotton. In this regard, direct dyes possessing *ortho*-propoxy, *ortho*′-hydroxy-substituted systems formed the corresponding dye–metal complexes. The complexes were characterized by neutron activation and spectrometric analyses and evaluated on cotton for color fastness.

Keywords: Metallization; Direct dyes; Neutron activation; Synthesis; Lightfastness

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1. Introduction

It is well known that the treatment of suitably substituted azo dyes with metal ions (e.g. Cr^{3+}, Cu^{2+}, Fe^{3+}) can improve lightfastness and washfastness properties [1–12]. In this regard, the dyes often form ligand–metal complexes that are less soluble in water than the starting ligands, which contributes to the observed improvement in washfastness. In the case of medially metallized azo dye complexes, enhanced lightfastness arises from protection of the azo bond through back bonding, which utilizes the empty d-orbitals of the transition metals employed.

The formation of copper complexes includes the metallization of direct dyes containing an *ortho*, *ortho*′-dihydroxyazo or *ortho*-methoxy-*ortho*′-hydroxyazo ligand system [5–12]. Well-known examples are C.I. Direct Blue 76 and C.I. Direct Blue 218, which are derivatives of C.I. Direct Blue 1 and C.I. Direct Blue 15, respectively (cf. Fig. 1). (It should be noted that, for simplicity, such metal complexes have been depicted throughout this paper in one isomeric form only, although in reality they will be produced as isomeric mixtures.)

In previous studies in our laboratories, a series of new direct dyes (cf. Fig. 2) was synthesized from non-genotoxic diamines and evaluated as potential alternatives to certain benzidine-based dyes [13]. Results from fastness testing indicated that the new dyes had comparable colors and intensities to structurally related commercial dyes but had low lightfastness. Bearing in mind that treatment with Cu^{2+} ions can improve the lightfastness of metallizable direct dyes, we examined the suitability of dyes **1–12** for metal complex formation.

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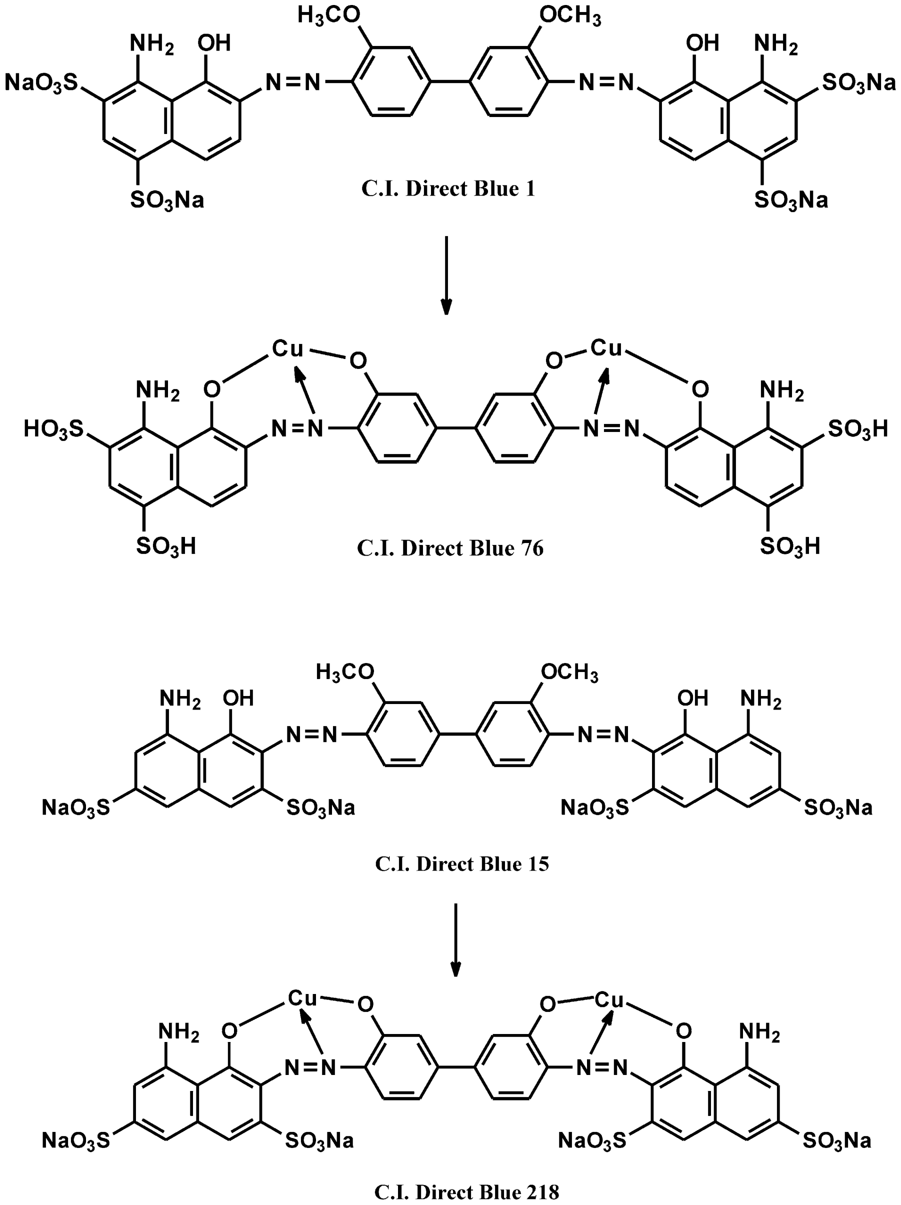
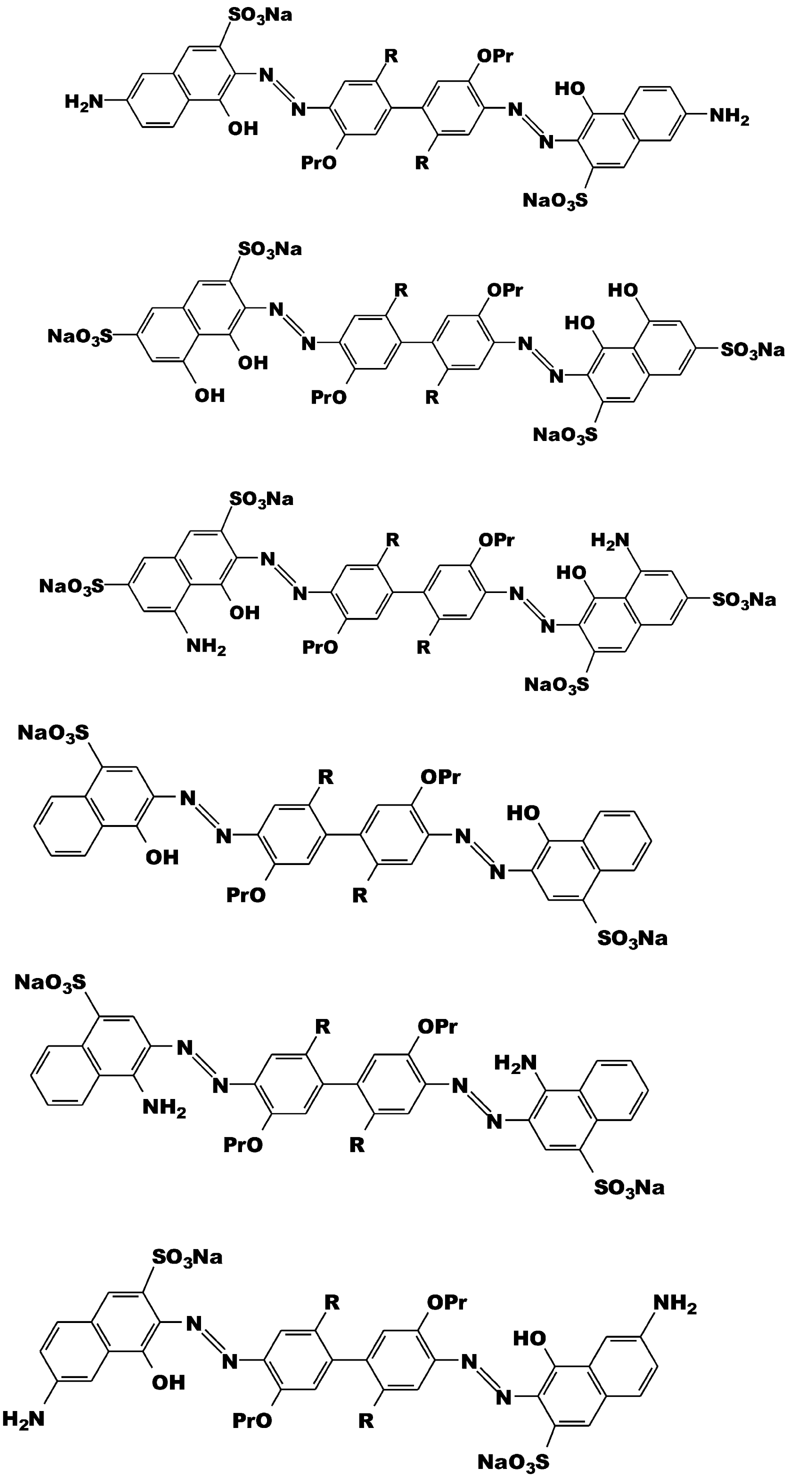


Fig. 1. Metallization of C.I. Direct Blue 1 and C.I. Direct Blue 15.

Though it is well known that the treatment of dyes such as C.I. Direct Blue 15 with $CuSO_4$ gives simultaneous cleavage of the methyl groups and Cu-complex formation [11,14], it has not been shown that the propyl groups of dyes such as **1–12** can be removed in the same way. The closest reported analog involves a direct dye of the type shown in Fig. 3, in which a single ethyl group is reported to undergo cleavage in an after-treatment process [6].

In preparation for the current study, we conducted MO calculations on dye **11** and the corresponding methoxy analog (**11′**; Fig. 4) as model compounds for comparing the C–O bond strain in propoxy and methoxy-substituted benzidines. Using the MOPAC-based PM3 semi-empirical



1 (R=CH$_3$)
2 (R=H)

3 (R=CH$_3$)
4 (R=H)

5 (R=CH$_3$)
6 (R=H)

7 (R=CH$_3$)
8 (R=H)

9 (R=CH$_3$)
10 (R=H)

11 (R=CH$_3$)
12 (R=H)

Fig. 2. Structures of direct dyes used in this study.

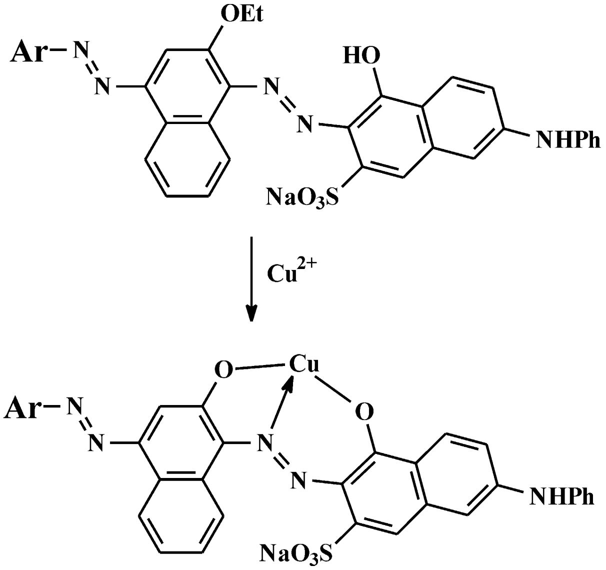


Fig. 3. Cu-complex formation involving the cleavage of an *O*-ethyl group.

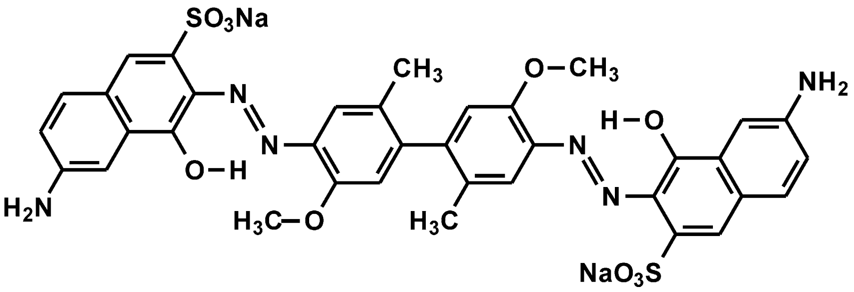


Fig. 4. Structure of dye **11′**.

method, we found that the C–O bond strain in dye **11** was at least twice that in dye **11′**. Interestingly, we also found that the bond strain was the same at both C–O bonds in dye **11′** (0.010kcal/mol) but different at the C–O bonds in dye **11** (0.022 vs. 0.044kcal/mol).

In the present study, the metallization of dyes **1–12** was undertaken. The effectiveness of Cu complex formation was judged with the aid of atomic absorption, neutron activation, and spectroscopic analyses and the fastness properties of the resultant dyes were assessed on cotton.

2. Experimental

2.1. General

All of the chemicals used in this work were obtained from Aldrich Chemical Co., Milwaukee, WI, USA. The mercerized cotton fabric was obtained from Test Fabrics, Inc., Pittston, PA, USA, and the style number was 400M. The equipment used to dye cotton fabric was an Ahiba Texomat dyeing machine. Washfastness and lightfastness properties were measured by using an

Atlas Launder-ometer and an Atlas 3SUN Hi35 high irradiance xenon weather-ometer, respectively.

Absorption spectra were recorded on a Varian Cary 3 UV-visible spectrophotometer and thin layer chromatography (TLC) was conducted using Whatman 250 μm silica gel 60 plates. Perkin Elmer Analyst 300 and Pulstar pneumatic terminus instruments were used to record atomic absorption and neutron activation data, respectively. L^*, a^*, b^* and K/S values were measured using a Data Color International spectrophotometer equipped with Color Tools QC software (version 1.2.4) for color quality control.

2.2. Synthesis of Cu-complexed dyes

The required dye ligands (**1–12**) were prepared as described previously [13]. For the metallization step, cuprammonium sulfate [$Cu(NH_3)_4SO_4$] was prepared by dissolving $CuSO_4$ (3.2 g, 20 mmol) in NH_4OH (13 ml) and precipitating the product by the addition of ethanol (10 ml) [15].

The unmetallized dyes (2.0–2.3 mmol) were dissolved in water (20 ml) at 60 °C, $Cu(NH_3)_4SO_4$ (4.0–4.6 mmol) and piperidine (0.01 g) were added, and the reaction mixture was stirred under reflux for 15 h. The progress of the reactions was followed by TLC using $BuOH:EtOH:NH_4OH$:pyridine/4:1:3:2.2 or $BuOH:EtOH:NH_4OH:H_2O$/3:1:0.5:1.5, and the dyes were isolated by adding NaCl to effect precipitation. The precipitated dyes were collected by filtration and dried.

2.3. Post-metallization of dyed fabric

A 1% dyeing (owf) of cotton was carried out at pH 7 using a 60:1 liquor ratio. In this regard, mercerized cotton fabric (5 g) was wet out with hot water and added to dyebaths consisting of dye (0.05 g) and water (270 ml) at 60 °C. The temperature was raised to 95 °C and maintained for 30 min. Na_2SO_4 solution (10%, 15 ml) was added to the dyebath and dyeing was continued for 30 min. The dyebath temperature was cooled to 80 °C, $CuSO_4$ (2 mmol/mmol dye) in water (15 ml) was added, and the bath was held at 100 °C for 45 min. The dyed fabric was removed, rinsed with water, and air-dried.

2.4. Colorfastness assessment [16]

The washfastness of dyed fabrics was evaluated using AATCC test method 61-1996 No. 2A and the resultant fabrics were evaluated for color change and staining of adjacent multifiber fabric. Lightfastness was evaluated using AATCC test method 16-1998 option E. For the assessments, a rating scale of 1 (poor) to 5 (excellent) was used.

3. Results and discussion

3.1. Reaction yields

The isolated reaction yields, R_f values, and λ_{max} data for the products produced from the treatment of dyes **1–12** with $Cu(NH_3)_4SO_4$ are shown in Table 1 and the target structures are shown in Fig. 5. The yields were fair to good and the colors were in the red to blue region. We also found that introducing a Cu moiety significantly diminished water solubility.

3.2. Atomic absorption and neutron activation analysis

To establish the Cu levels in the dyes obtained, atomic absorption analysis was attempted. However,

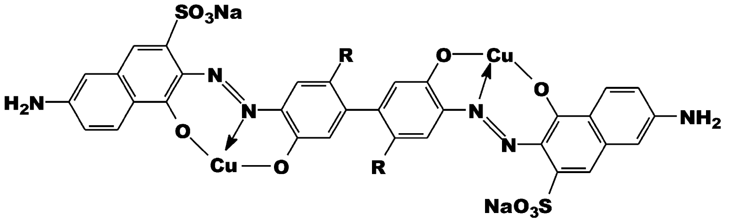
Table 1
Key experimental data recorded on the products from the metallization of dyes **1–12**

Dye	Yield (%)	R_f	λ_{max}(DMSO) (nm)
13	82	0.23[a]	522
14	77	0.24[a]	516
15	85	0.23[b]	568
16	75	0.22[b]	568
17	71	0.21[b]	577
18	69	0.25[b]	568
19	72	0.19[a]	510
20	79	0.26[b]	588
21	–[c]	0.18[a]	–[c]
22	–[c]	0.16[a]	–[c]
23	82	0.20[a]	553
24	74	0.19[a]	547

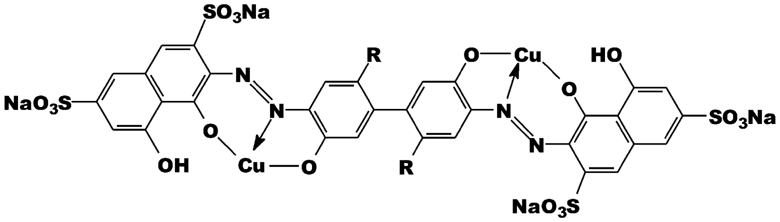
[a] $BuOH:EtOH:NH_4OH:H_2O$/3:1:0.5:1.5.

[b] $BuOH:EtOH:NH_4OH$:pyridine/4:1:3:2.2.

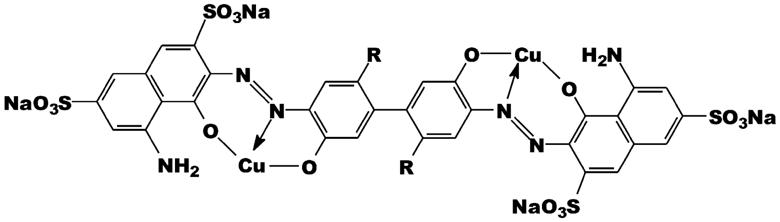
[c] Dye degradation occurred.



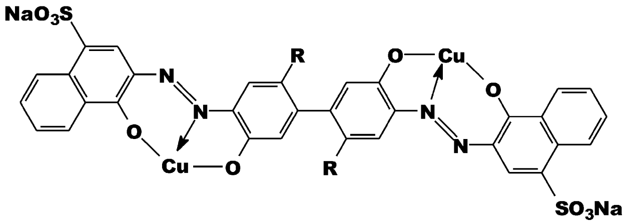
13 (R=CH$_3$)
14 (R=H)



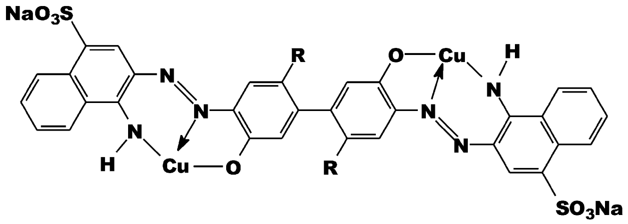
15 (R=CH$_3$)
16 (R=H)



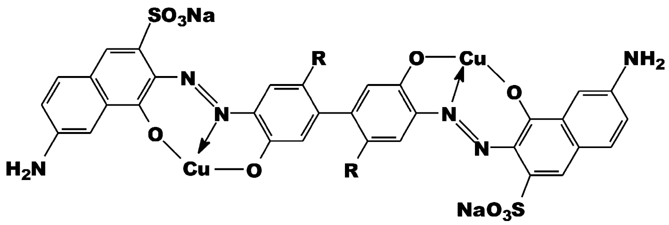
17 (R=CH$_3$)
18 (R=H)



19 (R=CH$_3$)
20 (R=H)



21 (R=CH$_3$)
22 (R=H)



23 (R=CH$_3$)
24 (R=H)

Fig. 5. Target Cu-complexed dyes.

due to the very low water solubility of the Cu^{2+} complexes, useful data was obtained only for dye **24**. In this case, the measured amount of copper (15.2 ppm) was very close to the calculated amount (14.38 ppm).

When neutron activation analysis was employed, dyes **13–15**, **19**, and **24** gave measured Cu levels that were comparable to the theoretical values. The results from dyes **21** and **22**, in which *ortho*-propoxy groups are combined with *ortho*-amino groups, indicated that Cu-complex formation had not occurred. For dyes **16**, **18**, **20** and **23** it appears that only one Cu^{2+} ion was incorporated into these molecules. This may have occurred because the resultant 1:1 complexes precipitated before the second Cu^{2+} ion could be inserted. Three of the four dyes have $R = H$, which suggests that linearity facilitated dye crystallization. However, differences in bond strain at the two ether groups probably also contribute to these results. The results of neutron activation analysis are shown in Table 2.

Table 2
Summary of data from determining Cu levels using neutron activation analysis

Dye	Measured (%)	Calculated (%)
13	11.04	13.94
14	12.29	14.88
15	10.44	11.37
16	7.21	11.66
17	1.16	11.39
18	6.41	11.68
19	11.29	14.41
20	9.01	14.89
21	0.53	14.49
22	0.24	14.96
23	7.69	13.94
24	14.05	14.38

3.3. *Post-metallization*

We found that the low water solubility of the Cu complexes prevented satisfactory exhaustion from a dyebath. Since the unmetallized precursors possessed higher solubility, we elected to apply them to cotton before metallization and to treat the resultant fabrics with $CuSO_4$, as an alternative to exhausting the premetallized forms. The observed fabric color changes are indicated in Table 3. While darker colors appeared on the cotton fabrics, the λ_{max} values of the metallized dyes reflected hypsochromic shifts in most cases. Notable exceptions were dyes **9** and **10**, which were derived from naphthionic acid. For gamma acid based dyes **23** and **24**, relatively broad absorption bands were produced.

L^*, a^*, b^* values are reported in Table 4. In general, the lightness/darkness value (L^*) increased following Cu^{2+} treatment. Fabrics dyed with dyes **1–8** and **11–12** became lighter and acquired a more yellow character than the corresponding untreated dyed fabrics. Fabrics dyed with naphthionic acid based dyes **9–10** had greener and bluer shades after Cu^{2+} treatment than the corresponding untreated dyed fabrics. Fabrics dyed with **2**, **4**, **6**, **8**, **10** and **12**, in which 5,5′-dipropoxybenzidine ($R = H$) was used, had a greener character (lower a^* values), before and after Cu^{2+} treatment, compared to fabrics dyed with **1**, **3**, **5**, **7**, **9** and **11** which employed 2,2′-dimethyl-5,5′-dipropoxybenzidine ($R = CH_3$).

3.4. K/S *determination*

Absorption measurements were conducted on dyed cotton before and after treatment with Cu^{2+}, to provide K/S values and the results are summarized in Table 5. There was a hypsochromic

Table 3
Colors generated on cotton before and after Cu^{2+} treatments

Dye[a]	Before Cu^{2+} treatment	After Cu^{2+} treatment
1 (13)	Purple	Pale violet
2 (14)	Violet	Deep violet
3 (15)	Sky blue	Pale gray
4 (16)	Mid blue	Sky blue
5 (17)	Steel blue	Pale blue
6 (18)	Bright blue	Mid blue
7 (19)	Pale purple	Pinkish red
8 (20)	Royal blue	Bright blue
9 (21)	Orange	Pink
10 (22)	Red	Violet
11 (23)	Pale violet	Reddish gray
12 (24)	Navy blue	Bluish gray

[a] Numbers in parentheses are for the Cu-complexed dyes.

Table 4
L^*, a^*, b^* values for cotton fabrics containing dyes **1–12** before and after Cu^{2+} treatment

Dye	L^*	a^*	b^*
1	36.12	33.41	−13.54
13	41.53	20.10	−8.88
2	27.86	12.40	−19.27
14	31.38	16.29	−17.93
3	61.34	2.85	−20.41
15	75.62	7.41	−5.70
4	45.99	−4.60	−25.39
16	63.89	−5.55	−15.35
5	59.03	0.74	−20.22
17	77.17	0.21	−5.58
6	42.99	−3.18	−31.89
18	62.90	−6.37	−15.49
7	52.50	27.45	−14.48
19	56.17	30.17	0.80
8	33.50	8.52	−31.06
20	40.07	5.75	−23.25
9	63.43	28.25	24.95
21	74.14	16.79	−0.38
10	35.80	40.36	9.61
22	34.05	13.57	−19.26
11	43.31	8.30	−11.31
23	56.62	8.55	−3.84
12	30.53	−0.60	−16.29
24	36.16	3.10	−7.99

Table 5
Absorption spectral data for dyeings generated on cotton

Dye	Before Cu^{2+} treatment		After Cu^{2+} treatment	
	λ_{max} (nm)	K/S	λ_{max} (nm)	K/S
1	550	8.201	530	4.541
2	565	10.141	540	8.682
3	595	1.083	550	0.315
4	605	3.620	610	1.021
5	602	1.613	580	0.298
6	615	6.050	610	1.210
7	560	2.425	510	2.276
8	580	8.202	575	5.024
9	495	2.016	520	0.476
10	520	10.329	560	6.897
11	578	3.127	550	1.398
12	603	9.260	580	5.548

shift following metallization of dyes **1**–**3**, **5**–**8** and **11**–**12**, but the spectra of dye **4** and naphthionic acid based dyes **9** and **10** underwent a bathochromic shift following Cu^{2+} treatment. The former dyes possess *ortho*-propoxy, *ortho′*-hydroxy groups as ligands around the azo bonds, while dyes **9** and **10** have *ortho*-propoxy, *ortho′*-amino groups as ligands. The results from **9** and **10** are noteworthy because it was clear from neutron activation experiments that these dyes gave quite unsatisfactory results following Cu^{2+} treatment in solution. It is now clear, however, that both dyes did interact with Cu on cotton fabric.

The results in Table 5 indicate that the linear dyes ($R = H$) gave appreciably higher K/S values on cotton before and after Cu treatment than the corresponding twisted structures ($R = CH_3$). It is also evident that chromotropic acid gave the lowest K/S values when the twisted or linear diamine was used.

3.5. Fastness properties

The results in Table 6 show the lightfastness and washfastness ratings for unmetallized dyes **1**–**12** on cotton before and after Cu^{2+} treatment. As expected, an improvement in lightfastness occurred, which was especially true for dyes **2**, **8** and **12**. Improvements in lightfastness were also observed with dyes **1**, **3** and **11** but not with dyes **9** and **10**. In the latter cases, an *ortho*-propoxy group was combined with an *ortho′*-amino group. This observation was consistent with the results from neutron activation studies, which showed that the corresponding pre-metallized dyes were less stable than the other complexes.

Following Cu^{2+} treatment, lightfastness (color change) was generally better when $R = H$ (**2**, **6**, **8**, **12**). In terms of couplers used, dye lightfastness was generally better when J-acid (cf. **1**, **2**), Nevile-Winther acid (cf. **7**, **8**) and gamma acid (cf. **11**, **12**) were used, while naphthionic acid (cf. **9**, **10**) gave dyes with the poorest lightfastness.

Cu^{2+} treatments did not give a significant improvement in the change in color component of the washfastness test. This was surprising, since water solubility was appreciably lower following metallization. On the other hand, washfastness ratings for staining of cotton and wool were improved by Cu^{2+} treatment. Also, as would be anticipated, staining on cotton was lower after Cu^{2+} treatment when the non-linear dyes **1**, **3**, **5**, **7**, **9** and **11** were used.

Table 6
Fastness properties in before and after Cu^{2+} treatment

Dye	Color change				Washfastness			
	Lightfastness		Washfastness		Staining of cotton		Staining of wool	
	Before treatment	After Cu^{2+} treatment	Before treatment	After Cu^{2+} treatment	Before treatment	After Cu^{2+} treatment	Before treatment	After Cu^{2+} treatment
1	2	3	1–2	1	2	3	3	4–5
2	3	4	3–4	2–3	2	2	5	5
3	2	3	1	1–2	5	5	5	5
4	2	2–3	2	2	3	4–5	5	5
5	1–2	2	1	1–2	4	5	5	5
6	2–3	2–3	1–2	1–2	2–3	4	5	5
7	1	2–3	1	2	3	3	3	4–5
8	2–3	4	2–3	1–2	2	4	5	5
9	1	1	1	1	3–4	4–5	4	5
10	2	1	3	2	2	3	4	5
11	2	3–4	1	1–2	3	4–5	5	5
12	3–4	4–5	3–4	2	2	3–4	5	5

4. Conclusion

The results of this investigation demonstrate that it is possible to prepare Cu complexes of disazo direct dyes containing propoxy groups *ortho* to the azo bonds, indicating that Cu^{2+} can cleave propyl groups in the essential step for metal-complex formation. Although the low water solubility of the premetallized Cu^{2+} complexes prevents direct application to cotton, post-treatment of the unmetallized dyes on cotton is a viable alternative approach to the desired dyes. As expected, post-metallization improves lightfastness but, unexpectedly, enhanced washfastness (color change) is not improved.

Acknowledgements

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References

[1] Wilcock CC, Tattersfield CP. J Soc Dyers Colour 1943; 59:119.
[2] Matthews JM. Application of dyestuffs. New York: John Wiley; 1947.
[3] Schmitz A. J Soc Dyers Colour 1955;71:910.
[4] Venkataraman K. The chemistry of synthetic dyes, chapter XIV, vol. I. New York: Academic Press; 1952.
[5] Trotman ER. Dyeing and chemical technology of textile fibers, 5th ed.. London: Charles Griffin; 1975.
[6] Zollinger H. Color chemistry; syntheses, properties and application of organic dyes and pigments. VCH; 1991.
[7] Jones F. The chemistry and property of metal-complex dyes. In: Shore J, editor. Organic chemistry and application properties. Society of Dyers and Colourists; 1990. pp. 196, 218.
[8] Crossley ML. Am Dyest Rep 1938;27(3):124.
[9] Varghese J, Bhattacharyya N, Sahasrabdhe AS. Colourage 1989;3:16.
[10] Preston C. The dyeing of cellulosic fibers. Dyer's Company Publication Trust; 1986.
[11] Shore J. Cellulosic dyeing. Society of Dyers and Colourists; 1995.
[12] Perkins WS. Textile coloration and finishing. Durham, North Carolina: Carolina Academic Press; 1996.
[13] Bae J, Freeman HS. AATCC Review 2001;1(9):67.
[14] Prival MJ, Bell SJ, Mitchell VD, Peiperl MD, Vaughan VL. Mutation Res 1984;136:33.
[15] Sax NI, Lewis RJ. Hawley's condensed chemical dictionary. New York: Van Nostrand Reinhold; 1987.
[16] Technical Manual. Research Triangle Park; NC: American Association of Textile Chemists and Colorists, 2000.