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Synthesis and Properties of 1:1 Copper–Azo Dye Complexes Derived from 1-Phenyl-3-Methyl-5-Pyrazolone

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ABSTRACT

*A series of orange and red 1:1 copper–azo dye complexes, derived from 1-(3'-*N*-benzenesulphonamido)phenyl-3-methyl-5-pyrazolone, have been synthesized. The dyes were evaluated with respect to application, fastness and spectroscopic properties. Due to the presence of sulphonamide groups the dyes are suitable for dyeing polyamide fibres and wool from a weakly acidic dye bath; they have good application and end-use properties.*

1 INTRODUCTION

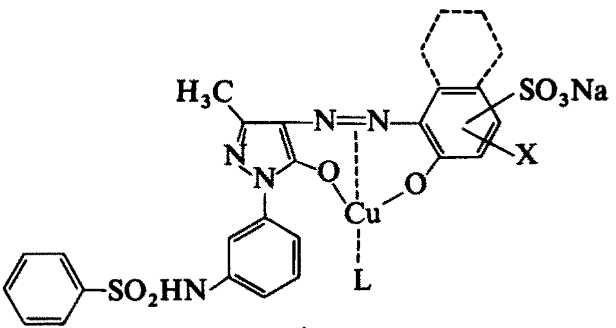
Both acid and 1:2 metal–azo dye complexes are used for the colouration of polyamide, wool, leather and silk. The dyes must satisfy high end-use and application requirements, particularly with regard to light and wet fastness and dyebath exhaustion. Many acid dyes have low light fastness. The main disadvantage of 1:2 metal–azo dye complexes, apart from their paler shades, is the possibility of environmental problems arising from the disposal of residual chromium and cobalt salts.

Copper complexes have not been widely applied in the dyeing of polyamide fibres and wool because of the requirement of dyeing from strongly acidic baths, low wet fastness of the dyeings, and possible unlevel colouration of polyamide fibres.[1]

The object of this investigation is the synthesis of some 1:1 copper–azo dye complexes suitable for application from weakly acidic baths (pH 5–6). The dyeings need to have high wet fastness and fulfilment of the objectives was based on the introduction of arylsulphonamide groups into the dye molecule, thus increasing its affinity for both polyamide and wool.

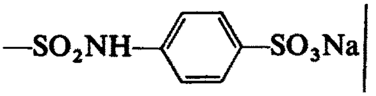
The subject of the investigation was a series of 1:1 copper–azo dye complexes derived from 1-(3'-*N*-benzenesulphonamido)phenyl-3-methyl-5-pyrazolone (**1**),[2] containing different numbers of sulphonamide groups, as shown in Formula **A**.

The diazo components used were 2-aminophenol-4-sulphoanilide-4'-sulphonic acid (**I**), 2-aminophenol-4-sulphonic acid (**II**), 2-amino-6-nitrophenol-4-sulphonic acid (**III**), 2-amino-4-nitrophenol-6-sulphonic acid (**IV**), 2-amino-6-chlorophenol-4-sulphonic acid (**V**), 6-nitro-2,1-naphthoquinone-diazide-4-sulphonic acid (**VI**) and 2,1-naphthoquinone-diazide-4-sulphonic acid (**VII**).



A

where: X = SO_3Na, H, Cl, NO_2



L = NH_3, H_2O.

For comparative studies, a 1:1 copper–azo dyes complex (**2**) not containing sulphonamide groups was synthesized.

2 EXPERIMENTAL

o-Aminophenolsulphonic and 2,1-naphthoquinonediazide-4-sulphonic acids were technical products. 1-Phenyl-3-Methyl-5-Pyrazolone was supplied by POCh, Poland.

1-(3'-*N*-Benzenesulphonamido)phenyl-3-methyl-5-pyrazolone was obtained by condensation of benzene sulphonyl chloride with 1-(3'-amino)-

phenyl-3-methyl-5-pyrazolone in water at pH 5·0–5·5 at 10–15°C in the initial stage, and 40–45°C in the final stage. Under these conditions, 1-(3'-*N*-benzenesulphonamido)phenyl-3-methyl-5-pyrazolone was obtained in high purity and yield exceeding 90%; after crystallization from 50% aq. ethanol the product had m.p. 145–147°C.

Diazotization of the amines was performed in the usual way; coupling of the diazo compounds and quinone diazides with 1-(3'-*N*-benzenesulphonamido)phenyl-3-methyl-5-pyrazolone was carried out in a basic environment at pH 9·0–9·5 at 0–5°C.

To form the 1:1 copper–azo dye complexes, alkaline dye solutions were complexed with $(Cu(NH_3)_4)^{+2}$ at 35–40°C for 3–4 h. The reaction was controlled chromatographically on Whatman 3 paper using pyridine : 20% ammonia : 1% brine (1 : 1 : 8 by vol.) as eluent. The dyes were isolated by salting out with sodium chloride and were then dried at 60–70°C. The sodium chloride content in the products was determined using the potentiometric method. In all cases yields of dyes were over 90%. The purity of the dyes was confirmed by paper chromatography on Whatman 3 paper, using *n*-butyl acetate : pyridine : water (3 : 5 : 3 by vol.) as eluent. Dye structures, quantitative determination and R_f values are given in Table 1.

The absorption maxima of dyes were measured in water and in 50% aq. ethanol at pH values ranging from 2 to 12, using a Specord M-40 (Zeiss-Jena, Germany) at concentrations ranging from 1×10^{-6} to 2×10^{-4} mol/dcm³. Results obtained for the concentration 2×10^{-5} mol/dcm³ at pH 7·0 are given in Table 2.

TABLE 1

Structure, Quantitative Determination and R_f Values

Dye no.	*Active component*	*Coupling component*	*Paper Chromatography*		*NaCl content (%)*	*Colour*
			R_{f1}	R_{f2}		
D-1	I	1	0·86	0·89	19·8	Orange
D-2	II	1	0·70	0·81	12·2	Orange
D-3	III	1	0·59	0·85	9·5	Orange
D-4	IV	1	0·40	0·86	8·7	Orange
D-5	V	1	0·43	0·86	8·7	Orange
D-6	VI	1	0·55	0·86	5·1	Red
D-7	VII	1	0·32	0·84	6·2	Bluish red
D-8	II	2	0·62	0·75	16·3	Orange

R_{f1}, Whatman 3 paper, using pyridine : 20% ammonia : 1% brine 1 : 1 : 8 (by vol.) as eluent.
R_{f2}, Whatman 3 paper, using *n*-butyl acetate : pyridine : water 3 : 5 : 3 (by vol.) as eluent.

TABLE 2
Spectrophotometric and Application Properties of the Dyes

Dye no.	*Spectrophotometry*				*Application*			
	Water		*50% ethanol*		*Dyebath exhaustion (%)*			
	λ_{max} *(nm)*	ε_{max} *(mol/(dcm^3 cm))*	λ_{max} *(nm)*	ε_{max} *(mol/(dcm^3 cm))*	*pH 4·0*	*pH 5·0*	*pH 6·0*	*pH 7·0*
D-1	460·4	18 900	469·9	19 200	100	99·6	98·1	94·0
D-2	462·1	18 600	470·8	19 200	90·9	87·6	69·1	34·6
D-3	482·6	19 000	487·3	20 200	99·4	99·0	96·9	69·9
D-4	484·5	18 000	494·1	18 800	99·5	99·1	98·9	93·8
D-5	470·8	17 000	479·8	20 300	98·6	98·3	96·2	80·7
D-6	495·1	20 000	501·0	22 000	99·5	99·3	98·6	95·3
D-7	502·0	21 300	503·1	21 800	98·8	98·0	95·4	90·7
D-8	466·1	18 600	473·6	18 900	30·0	27·5	9·5	2·0

To evaluate end-use fastness, dyeings on knitted polyamide fabric were carried out to a strength of 1/1 of reference standard; fastness to water, acid and alkaline perspiration, washing at 40°C, and dry and wet rubbing was tested according to accepted standards; the light fastness determinations were carried out on Xenotest 150S (Heraus Hanau, Germany). The results of the tests are given in Table 3.

3 DISCUSSION

By coupling the diazotized *o*-aminophenolsulphonic acids and 2,1-naphthoquinone-diazide-4-sulphonic acids with 1-(3'-*N*-benzenesulphonamido)-phenyl-3-methyl-5-pyrazolone, and then complexing with bivalent copper salts, a series of orange and red dyes were obtained. They gave bright shades when dyed on polyamide and wool from a weakly acidic dyebath.

Table 1 shows the beneficial influence of the arylsulphonamide group on the degree of absorption of the dyes, dyes containing such groups showing practically a quantitative uptake at pH 4–6. The reference dye (**D-8**) without any arylsulphonamide groups showed a considerably lower dye uptake at this pH and cannot therefore be practically used for dyeing polyamide from a weakly acidic dyebath. The influence of other substituents in the diazo component is also evident, e.g. the presence of a nitro group (**D-3**, **D-4**) or of a chlorine atom (**D-5**) increases the absorp-

TABLE 3
End-Use Fastness of 1:1 Copper Complexes

Dye no.	*Fastness*														*Light fastness*
	Water			*Washing*			*Acid perspiration*			*Alkaline perspiration*			*Rubbing*		
	1	*2*	*3*	*1*	*2*	*3*	*1*	*2*	*3*	*1*	*2*	*3*	*Dry*	*Wet*	*1/1*
D-1	5	5	5	5	5	5	5	5	5	5	5	5	5	5	7
D-2	5	3–4	3–4	4–5	5	5	4–5	3–4	4–5	4–5	4	4	5	5	6–7
D-3	5	4	4–5	4–5	5	5	4–5	4	4–5	4–5	4–5	5	5	5	6–7
D-4	4–5	4–5	5	4–5	5	5	4–5	4–5	5	4–5	5	5	5	5	8
D-5	4–5	4	5	4–5	5	5	4–5	4	5	4–5	4–5	5	5	5	8
D-6	5	5	5	5	5	5	4–5	5	5	5	5	5	5	5	6–7
D-7	5	5	5	5	5	5	5	5	5	5	5	5	5	5	6–7
D-8	4–5	3	3–4	4–5	5	5	4	2	2–3	4–5	3	3–4	5	4	6–7

1, Change of shade of dyed fabric; *2*, staining nylon; *3*, staining wool.

tion with respect to dye **D-2** at pH 4 by about 8–9%, and at pH 6·0 by about 27–29%. However, the effect of sulphonanilide groups is very significant in the dyes tested.

It should be emphasized that, although having high affinity for polyamide fibres, the 1:1 copper complexes containing arylsulphonamide groups give level dyeings on these fibres, and that the presence of sulphonamide groups also advantageously influences the fastness of the dyeings.

The 1:1 copper-azo dye complexes have good (**D-2** to **D-5**) or very good (**D-1**, **D-6**, **D-7**) wet fastness (to water, washing at 40°C, perspiration and rubbing), showing very significant improvements over the fastness of the reference dye not containing sulphonamide groups. The light fastness of the dyes is also very high (6–7 to 8).

Spectrophotometric studies of dye solutions in 50% ethanol at different pH values (varying from 2 to 12) showed a constant absorption band in the visible range. No effect of pH on the values of λ_{max} and ε_{max} was observed, indicating full complexation of the azo dyes and a high stability of the chelates over a wide range of pH. This is a significant advantage of the dyes. In aqueous solution, a very slight decrease of molar absorption occurs, probably due to partial aggregation of the dyes.

It should also be noted that the 1:1 copper–azo dye complexes are more environmentally friendly, because of the quantitative formation of the complexes and the lower toxicity of copper salts.

4 CONCLUSIONS

A series of orange and red 1:1 copper–azo dye complexes derived from 1-(3'-*N*-benzenesulphonamido)phenyl-3-methyl-5-pyrazolone containing one or two arylsulphonamide groups in a molecule were synthesized. The dyes are very suitable for dyeing polyamide and wool from weakly acidic dyebaths. The presence of the arylsulphonamide group increases the affinity of the dyes for polyamide and has a beneficial influence on end-use fastness (to water, perspiration, wet rubbing). The light fastness of the dyeings is also very high, ranging from 6–7 to 8 in the series of dyes investigated.

Spectroscopic data in 50% aq. ethanol and water at pH varying from 2 to 12 showed one absorption band in the visible region, confirming the stability of the chelates over a wide range of pH values.

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