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Constitution and Dyeing Properties of a 2:2 Copper Complex Azomethine Dye

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ABSTRACT

A copper(II) complex azomethine dye with a 2-(2-pyridylmethylene-amino)phenol (PMAP) ligand was prepared and characterized on the basis of IR, UV/VIS, MS, X-ray and elemental analysis. The structure comprised a dinuclear $[Cu_2L_2(O_2CMe)]^+$ *(L = deprotonated PMAP) cation and the well separated perchlorate anion. Both phenolate residues and the acetate moiety bridged the two copper(II) centers, giving a* $Cu_2(\mu\text{-}O)_2(\mu\text{-}1,3\text{-}MeCO_2)$ *core. The possibility of spectrophotometric determination of copper with this ligand was investigated, as was the possibility of wool dyeing with Cu–PMAP, and the stability of the dye–wool bonding at pH 4.5 and 5.5. The color hue changes on the dyeing samples with* a*, b* *coordinates (CIELAB diagram) are given. © 1997 Elsevier Science Ltd*

Keywords: 2-(2-pyridylmethyleneamino)phenol, copper(II) complex, azomethine dye, structure determination, wool dyeing.

INTRODUCTION

The possibility of employing metallizable azomethines in the dyestuffs field has been widely investigated. Spectrophotometric investigations of the

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tridentate ligand 2-(2-pyridylmethyleneamino)phenol (PMAP) have been well documented [1,2].

The synthesis, structure determination, solution properties, application as a dye and possibility of biodegradation of the Cr(III)–PMAP have been reported in our previous paper [3].

Cr complexes are mainly used as metal complex dyes in the world market, but on ecological aspects, it is now necessary to find alternatives to chromium. We have recently reported the preparation, structure characterization and dyeing properties of Mn(II) and Ni(II)–PMAP dyes [4,5].

In the present paper, the constitution of Cu(II)–PMAP dye is investigated by means of IR, UV/VIS, MS, X-ray and elemental analysis. The dyeing kinetics on wool fabric and the color hue changes on the dyeing samples were also studied.

MATERIALS AND METHODS

All chemicals and solvents were of reagent grade (Merck, Aldrich or Kemika) and were used without further purification.

The PMAP ligand was prepared according to the method described in the literature [6], and the Cu–PMAP complex was then synthesized and characterized.

Melting points were determined on a Koffler hot stage apparatus and are given uncorrected. Samples for elemental analyses were dried for 6 h in vacuum, *p* 533 Pa (0.04 mm Hg) at 100°C above phosphorous pentoxide.

IR spectra were recorded on a Perkin–Elmer (Model 257) spectrophotometer (KBr). The structure of the isolated Cu(II)–PMAP complex was determined by a Hitachi/Perkin–Elmer Model RMU-60 mass spectrometer. UV/VIS spectra were recorded on a Varian DMS-80 spectrophotometer, while the pH of the solutions was measured on a microprocessor controlled pH-meter, Iskra, Model MA 5740. X-ray data were collected using an automatic four-circle diffractometer, Philips PW1100 upgraded by Stoe [7].

Samples of wool (1 g) were treated in an aqueous dye–liquor (ratio 1:60) containing 3% of dye (44.1 μmol dye per gram of wet fabric) at pH 4.5 (acetate buffer) and pH 5.5 (ammonium acetate). A Linitest apparatus (Hanau) was used for the isothermal dyeing of wool at 100°C and two pH values. Dye exhaustion was monitored spectrophotometrically in the range 10 to 90 min. The stability of the wool–dye bond was confirmed using a hot solution of N,N-dimethylformamide. The concentration of the dye was determined spectrophotometrically. The color hue changes were measured on a Datacolor reflectance spectrophotometer.

2-(2-Pyridylmethyleneamino)phenol copper(II), Cu–PMAP

The Cu–PMAP complex was prepared by mixing equimolar amounts of $Cu(CH_3COO)_2 \cdot H_2O$ and the ligand PMAP in methanol for 6 h at room temperature. A brown powder precipitated from this solution after 12 h; it was filtered and recrystallized from methanol/water (3:7) with addition of a saturated methanol solution of $NaClO_4 \cdot H_2O$. After 12 h green crystals with a metallic lustre were filtered and dried in vacuum over $CaCl_2$.

M.p. 242°C; yield 65%.

Found ($C_{26}H_{21}N_4O_8ClCu_2$): C, 45.50; H, 3.00; N, 8.02; Cu, 18.45%. Calcd.: C, 45.92; H, 3.12; N, 8.24; Cu, 18.69%.

RESULTS AND DISCUSSION

The Cu–PMAP complex was very soluble in polar solvents and the solubility decreased with decrease in the polarity of the solvent (Table 1). This suggests that the Cu–PMAP is a cationic type of complex.

Five notable changes of the infra red spectrum of Cu–PMAP are produced in chelation (Table 2). The band attributed to OH vibrations in the spectrum of the ligand PMAP at 3360 cm^{-1} disappears in the spectrum of its copper complex [8]. In the Cu–PMAP complex, the C–O frequencies shift to the higher wavenumbers, indicating that the phenoxide O atom is involved in bonding [9]. The high intensity band at 1630 cm^{-1} in the PMAP ligand, attributable to the C=N stretching, is shifted to lower frequencies in the spectrum of the complex (1610 cm^{-1}). The C=N vibration frequency is lowered by chelation, by 20 cm^{-1}; this decrease of the vibration frequency

TABLE 1

Solubility of the Cu–PMAP Complex in Different Solvents

Solvent	ε_0	*Solubility*	*Color*
Petroleum ether	1.8	–	—
Carbon tetrachloride	2.2	–	—
Benzene	2.3	–	—
Ether	4.3	–	—
Chloroform	4.8	+	pink
Acetic acid	6.2	+	yellow
Pyridine	1.4	+ +	violet–red
Acetone	20.7	+	orange
Ethanol	24.6	+	orange
Methanol	32.7	+	orange
Dimethylformamide	36.7	+ +	red
Water	80.2	+	orange

+ +, Very soluble; +, soluble; –, insoluble.

can be explained by a resonance through the metal in the chelation ring [10] and by the electron attracting properties of the metal ion. According to the literature [11] C=N frequencies undergo a substantial shift to lower wavenumbers in non-heterocyclic Schiff bases on chelation to metals. The shifts observed in copper complexes of the heterocyclic analogues are much smaller. The azomethine electrons in the heterocyclic Schiff bases are more delocalized. This reduces the electron density on the azomethine N atom. The appearance of a weak band at 1220 cm^{-1}, which is absent in the spectrum of the ligand, is a strong indication [12] that the hetero N atom is involved in bonding to the metal ions. The IR spectrum of Cu–PMAP shows two strong bands at 1550 and 1410 cm^{-1}, assignable to $\nu(C=O)$ and $\nu(C–O)$ of the carboxylate vibrations, respectively. The position of these bands, and the $\Delta\nu$ value (138 cm^{-1}), indicate the presence of a bridging acetate group in the molecule of this complex [13]. A broad band in the 1090 cm^{-1} region, as well as a sharp band at 625 cm^{-1}, indicates the presence of the perchlorate ion [14].

TABLE 2

Selected IR Bands (cm^{-1}) for the Ligand PMAP and its Complex Cu–PMAP

Compound	$\nu(O\text{–}H)$	$\nu(C=N)$	$\nu(C\text{–}O)$	$\nu(COO)$	$\nu(Cl\text{–}O)$
PMAP	3360 s	1630 m	1250 s	—	—
Cu–PMAP	—	1610 m	1270 m	1550, 1410 s	1090 s, 625 m

s = strong, m = medium.

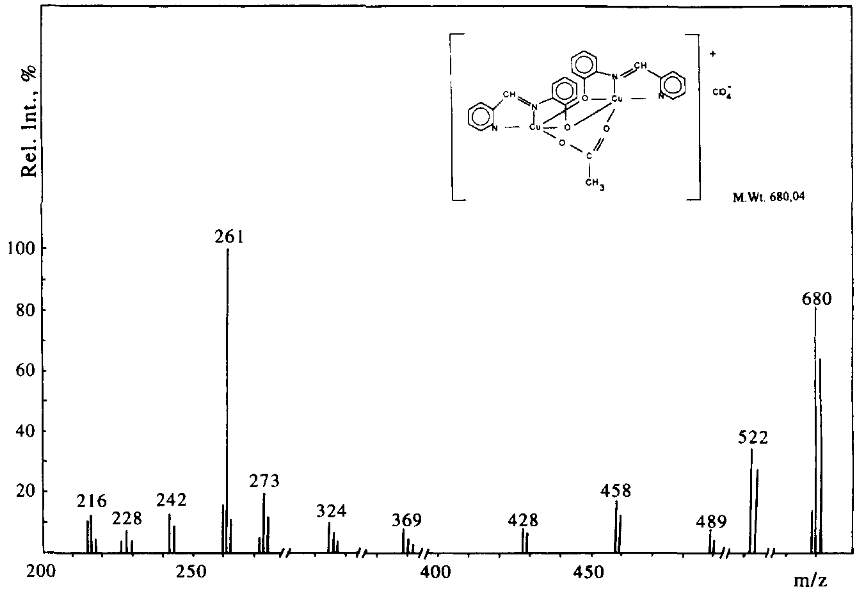

Fig. 1. Mass spectrum of the Cu–PMAP complex.

The mass spectrum of the Cu–PMAP (Fig. 1) shows a molecular ion at *m/z* 680. The ion at *m/z* 522 results from the elimination of acetate and perchlorate, and confirms the 2:2 (metal/ligand) stoichiometry. Most of the fragmentation products are due to loss of the copper ion and the ligand from the Cu–PMAP complex structure. Ions at *m/z* 458 and 324 originate from copper and ligand losses from the ionic species at *m/z* 521, and they show 1:2 and 2:1 type structure, respectively. The ion at *m/z* 261, which represents a 1:1 fragmentation product, is a base peak; this latter ion originates from the ions at *m/z* 521 (by symmetrical cleavage), *m/z* 458 (by loss of ligand) and *m/z* 324 (by loss of copper ion).

The mass spectrum of the ligand PMAP together with its fragmentation pattern have been reported in the literature [15].

The solution properties of the PMAP ligand at different pH in methanol–water have also been reported [1]. The absorption spectra of Cu–PMAP complexes are presented in Fig. 2. The mixed methanol–water medium, (methanol) = 0.1, has been used due to the lower solubility of the PMAP ligand and its metal complexes in water. The volume of methanol was kept as low as possible, because the addition of methanol decreased the absorption of the complexes [16]. The spectra were recorded at constant temperature, t = (25 ± 1)°C, and at constant ionic strength, I = 0.5 M, adjusted with KNO_3.

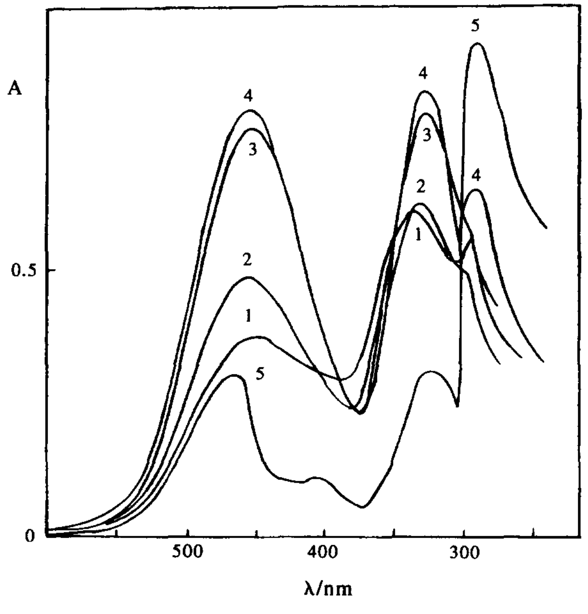

Fig. 2. Absorption spectra of Cu–PMAP complexes at different pH. c(Cu) = 0.05 mM; c(PMAP) = 2 mM; φ(methanol) = 0.1; t = (25 ± 1)°C. time = 5 min. (1) pH 4; (2) pH 6; (3) pH 8; (4) pH 10; (5) pH 10, time = 60 min.

The results obtained show one absorption maximum in the visible region, at 450 nm, and two absorption maxima in the UV region, at 280–288 nm and 316–330 nm. The absorption of the Cu–PMAP complexes is strongly influenced by pH. Increase of pH causes a hypsochromic shift in the UV region of the absorption spectra. The absorption maxima at 450 nm increases with increase of pH. The formation of the complexes is instantaneous, and the absorption up to pH 8 remains constant over 1 h. At pH 10, the absorption of the complex decreases with time, having after 60 min one third of the initial value, while the absorption maximum at 280 nm increases, indicating the change in ratio of the different complex species present in the solution. Due to the relatively high molar absorption coefficients obtained (Table 3), the validity of Beer's law was examined.

Linear calibration diagrams show that better sensitivity can be obtained at higher pH values, but special care has to be taken at pH 10 due to lower stability with time. The adherence of calibration graphs to Beer's law in the range between 0 and 5 µg/ml is validated by the high value for the correlation coefficients of the regression equations (Table 4).

TABLE 3

Influence of pH on Molar Absorption Coefficients of Cu–PMAP Complexes

pH	λ_{max} *(nm)*	ε *(*M^{-1} cm^{-1}*)*
4	288	11440
	330	13030
	450	7730
6	288 shoulder	—
	320	14050
	450	10280
8	288 shoulder	—
	316	18000
	450	15680
10	280	17800
	320	17160
	450	16530

TABLE 4

Regression Lines of Calibration Diagrams $A = a + b\gamma$ for Spectrophotometric Determination of Cu with PMAP at Different pH, γ (Cu) = 0.5 to 5.0 µg/ml and γ (PMAP) = 2.0 mM

pH	*a ± std. error*	*b ± std. error*	r^2
4	$(6 \pm 9) \times 10^{-3}$	(0.127 ± 0.002)	0.9997
6	$(5 \pm 8) \times 10^{-3}$	(0.157 ± 0.002)	0.9998
8	$(1 \pm 5) \times 10^{-3}$	(0.246 ± 0.001)	0.9998
10	$-(12 \pm 8) \times 10^{-3}$	(0.279 ± 0.002)	0.9997

A = absorbance; γ = mass concentration (µg/ml); a = Y axis intercept in absorbance units; b = slope; r^2 = squared correlation coefficient.

The lowest detection limit for the determination of Cu is 0.1 μg/ml at pH 8, which is recommended for possible spectrophotometric determination of copper.

Structure determination of $[Cu_2(\mu\text{-}MeCO_2)(PMAP)_2]ClO_4$

Dark red crystals were grown from a methanol solution and that used had dimensions 0.20×0.15×0.36 mm^3. Of the 7453 data collected in the 2θ range 4–60° using the ω-scan technique, 3618 unique data had $I \geq 2\sigma(I)$, and only these were used for structure solution and refinement. An empirical absorption correction was applied using a method based upon azimuthal scan data.

Crystal data for $C_{26}H_{21}N_4O_8ClCu_2$, $M_r = 680.0$, monoclinic, space group $P2_1/c$, $a = 13.849(3)$, $b = 10.996(4)$, $c = 17.527(5)$ Å, $\beta = 101.73(3)°$; $V = 2613(1)$ $Å^3$; $D_x = 1.728$ g cm^{-3}; $Z = 4$; $F(000) = 1376$; Mo $K\alpha$ radiation; $\mu = 17.916$ cm^{-1}.

The structure was solved by a combination of heavy method and Fourier techniques, and refined by block-diagonal least-squares using the CRYSRULER program package [17]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bonded to the methyl group and to ligands were included in the calculation with fixed positions, with overall isotropic thermal parameters U_{iso} of 0.189 and 0.054 $Å^2$, respectively. Final $R = 0.034$ with a unique weight. Maximum and minimum heights in the final difference Fourier map were 0.575 and −0.575 $e^- Å^{-3}$, respectively.

The crystal structure of the complex is shown in Fig. 3. Selected bond lengths and angles are in Table 5, and atomic coordinates in Table 6 (relevant bond lengths and angles, Table 7, anisotropic thermal parameters for non-hydrogen atoms, Table 8, hydrogen atomic coordinates and isotropic thermal parameters, Table 9, are deposited material. Copies are available from the Editor on request).

The binuclear core consists of two Cu–L units in which the ligand is tridentate and deprotonated, stacked adjacent to one another, such that the phenolate oxygens bridge the copper atoms giving a Cu_2O_2 unit. The axial interaction to the bridging phenolate oxygens of the adjacent CuL fragment are 2.293(3) and 2.377(3) Å. Apart from the N,N,O donor set of L, the basal square coordination plane of each copper(II) ion is completed by coordination of an acetate oxygen atom. The very similar square-pyramidal coordination of the copper was observed in the structure of the complex $[Cu_2L_2(\mu\text{-}MeCO_2)][PF_6]\cdot 1.5CH_2Cl_2$ [18] [L = protonated 6-(2-hydroxyphenyl)-2,2′-bipyridine] containing the $Cu_2(\mu\text{-}O)_2$ core with an additional bridging acetate. The Cu(II)···Cu(II) separation is 3.013(1) Å. The dihedral angle between the nearly planar ligand is 31.59(6)°.

The dyeing properties of the Cu–PMAP complex on wool were investigated. Wool, as a protein fiber, changes its ionic character with the pH of the solution. At lower pH, wool has a cationic character, while at higher pH it is anionic [20],[21]. As the solubility, constitution and stability of the Cu–PMAP were experimentally established, it could be predicted under the experimental conditions used (pH 4.5 and 5.5) that the dye will be bound to the wool with van der Waals and ionic forces. At pH 5.5, the negatively charged carboxyl groups of wool will be more attracted to the positively charged Cu cationic complex ion. The dye will be bound to the wool with van der Waals and ionic forces [22]. At pH 4.5, the dye will be bound principally with van der Waals forces. Very low values of dyebath exhaustion were indicated in the first 20 min of dyeing for both pH values (Fig. 4). The dye exhaustion increases more rapidly at pH 5.5 (curve 1) than at pH 4.5 (curve 2), which can be related to the morphological structure of the wool more than to the dyeing properties of the Cu–PMAP complex. In order to investigate the stability of the dye–wool bond, the stability to hot

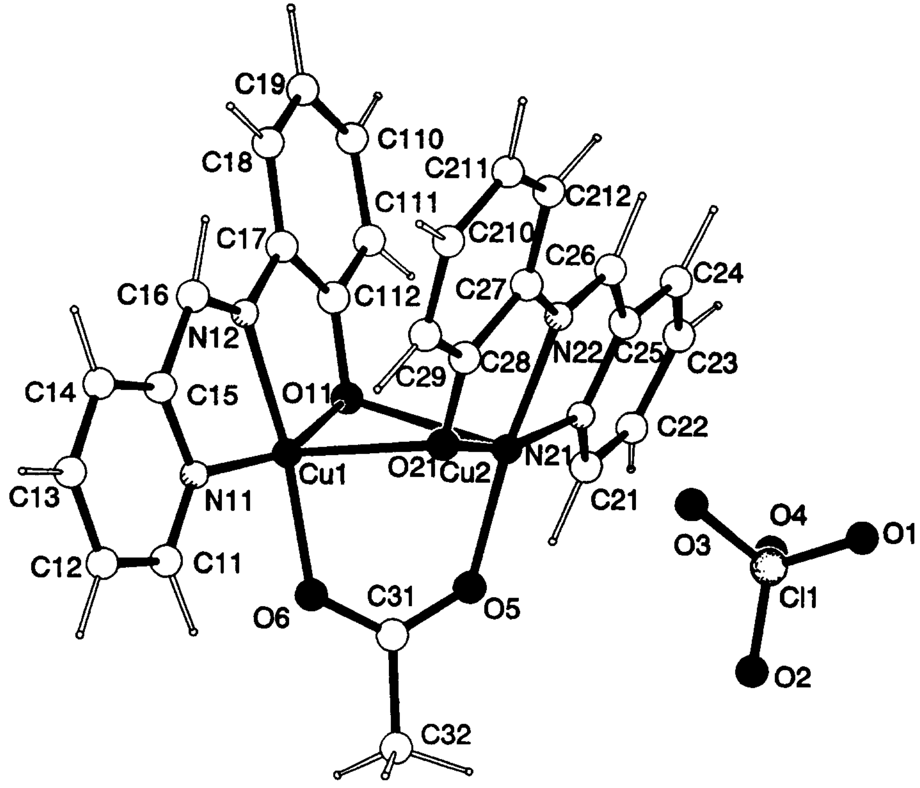

Fig. 3. A PLUTON [19] perspective view of the complex $[Cu_2(\mu\text{-}MeCO_2)(PMAP)_2]ClO_4$ showing atomic numbering.

N,N′-dimethylformamide was carried out. The small amount of the removed dye, although at somewhat higher pH 5.5, confirms the stable dye–fibre bond, and implies very good washing fastness. The results obtained for the

TABLE 5
Selected Bond Distances (Å) and Bond Angles (°) in the Structure of $C_{26}H_{21}N_4O_8ClCu_2$

Cu1–Cu2	3.013(1)
Cu1–O6	1.936(3)
Cu1–O11	1.953(3)
Cu1–N11	2.022(3)
Cu1–N12	1.954(3)
Cu1–O21	2.293(3)
Cu2–O5	1.930(3)
Cu2–O11	2.377(3)
Cu2–O21	1.967(3)
Cu2–N21	2.021(3)
Cu2–N22	1.946(3)
N12–Cu1–O21	98.5(2)
N11–Cu1–O21	102.0(1)
N11–Cu1–N12	80.9(2)
O11–Cu1–O21	88.6(1)
O11–Cu1–N12	83.5(1)
O11–Cu1–N11	162.2(1)
O6–Cu1–O21	88.6(1)
O6–Cu1–N12	172.7(2)
O6–Cu1–N11	96.2(2)
O6–Cu1–O11	98.3(1)
Cu2–Cu1–O21	40.8(1)
Cu2–Cu1–N12	107.5(1)
Cu2–Cu1–N11	142.0(1)
Cu2–Cu1–O11	52.0(1)
Cu2–Cu1–O6	78.9(1)
Cu1–Cu2–N22	106.7(1)
Cu1–Cu2–N21	133.7(1)
Cu1–Cu2–O21	49.6(1)
Cu1–Cu2–O11	40.4(1)
Cu1–Cu2–O5	77.9(1)
N21–Cu2–N22	81.0(2)
O21–Cu2–N22	84.0(1)
O21–Cu2–N21	164.8(2)
O11–Cu2–N22	98.1(1)
O11–Cu2–N21	93.8(1)
O11–Cu2–O21	86.0(1)
O5–Cu2–N22	172.9(1)
O5–Cu2–N21	99.8(2)
O5–Cu2–O21	95.4(1)
O5–Cu2–O11	88.9(1)
Cu1–O11–Cu2	87.6(1)
Cu1–O21–Cu2	89.7(1)

color hue changes, measured by reflectance spectrophotometry, are given with coordinates *a**, *b** (Fig. 5) [23]. At pH 4.5 the hue (point 2) became more yellow than at pH 5.5 (point 1), which confirms the sensibility of the

TABLE 6

Atomic Coordinates and Equivalent Isotropic Thermal Parameters (×10^4) with E.s.d.s in Parentheses in the Structure $C_{26}H_{21}N_4O_8ClCu_2$

Atom	*x*	*y*	*z*	U_{eq}
Cu1	0.4194(1)	0.3052(1)	0.5505(1)	332(2)
Cu2	0.2765(1)	0.0972(1)	0.5446(1)	334(2)
O5	0.5021(2)	0.0169(3)	0.5768(2)	426(10)
O6	0.5074(2)	0.1747(3)	0.5941(2)	391(10)
C31	0.4849(3)	0.0642(4)	0.6022(2)	336(13)
C32	0.5644(3)	−0.0163(4)	0.6468(3)	459(18)
O11	0.3474(2)	0.2198(2)	0.4587(2)	363(10)
N11	0.4879(3)	0.4370(3)	0.6220(2)	373(11)
N12	0.3450(3)	0.4458(3)	0.5020(2)	338(11)
C11	0.5652(3)	0.4286(4)	0.6803(3)	426(16)
C12	0.6027(4)	0.5289(5)	0.7265(3)	459(16)
C13	0.5558(4)	0.6391(5)	0.7102(3)	503(18)
C14	9.4752(4)	0.6491(4)	0.6496(3)	480(18)
C15	0.4436(3)	0.5467(4)	0.6061(3)	374(15)
C16	0.3612(3)	0.5476(4)	0.5392(3)	423(16)
C17	0.2771(3)	0.4166(4)	0.4342(2)	369(14)
C18	0.2112(4)	0.4959(5)	0.3885(3)	482(17)
C19	0.1545(4)	0.4547(5)	0.3197(3)	545(19)
C110	0.1622(4)	0.3346(5)	0.2972(3)	549(18)
C111	0.2248(3)	0.2542(5)	0.3434(3)	450(15)
C112	0.2850(3)	0.2933(4)	0.4127(2)	349(13)
C11	0.1894(1)	−0.1815(1)	0.6422(1)	446(4)
O1	0.1044(3)	−0.2115(4)	0.6718(2)	729(16)
O2	0.2737(3)	−0.2225(4)	0.6962(3)	820(16)
O3	0.1925(3)	−0.0512(3)	0.6334(2)	582(13)
O4	0.1836(4)	−0.2379(4)	0.5689(2)	840(21)
O21	0.3069(2)	0.2327(3)	0.6189(2)	357(9)
N21	0.2115(3)	−0.0176(3)	0.4595(2)	346(11)
N22	0.1448(2)	0.1675(3)	0.5227(2)	310(11)
C21	0.2509(3)	−0.1092(4)	0.4261(3)	416(15)
C22	0.1973(4)	−0.1721(4)	0.3630(3)	514(18)
C23	0.0994(4)	−0.1451(5)	0.3364(3)	545(20)
C24	0.0572(4)	−0.0520(5)	0.3716(3)	502(16)
C25	0.1159(3)	0.0114(4)	0.4319(3)	369(15)
C26	0.0814(3)	0.1165(4)	0.4697(2)	383(13)
C27	0.1373(3)	0.2723(4)	0.5664(2)	351(13)
C28	0.2268(3)	0.3022(4)	0.6165(2)	328(13)
C29	0.2307(4)	0.4074(4)	0.6630(3)	445(15)
C210	0.1458(4)	0.4779(4)	0.6568(3)	537(20)
C211	0.0594(4)	0.4480(5)	0.6068(3)	578(21)
C212	0.0526(4)	0.3446(4)	0.5608(3)	467(16)

$U_{eq} = 1/3\ E_iE_jU_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$.

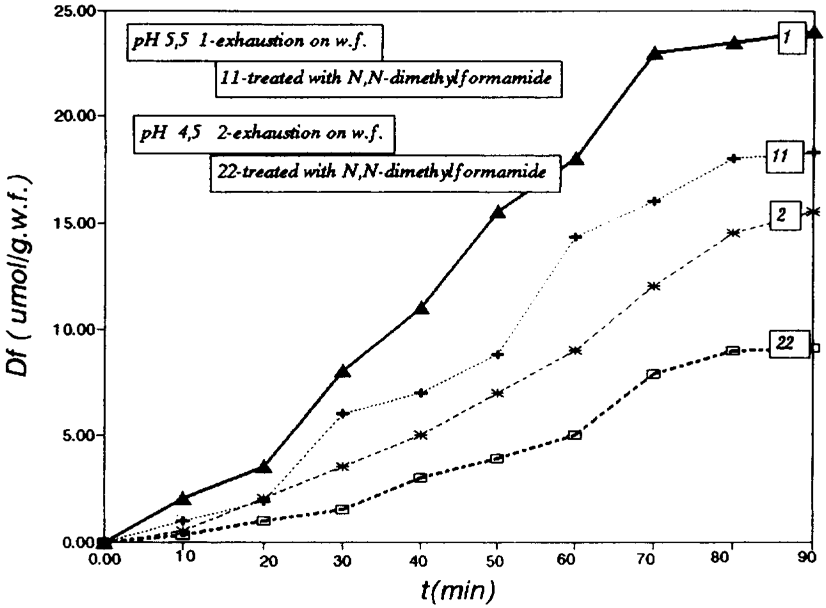

Fig. 4. Exhaustion of the Cu–PMAP complex on wool fabric at different pH values.

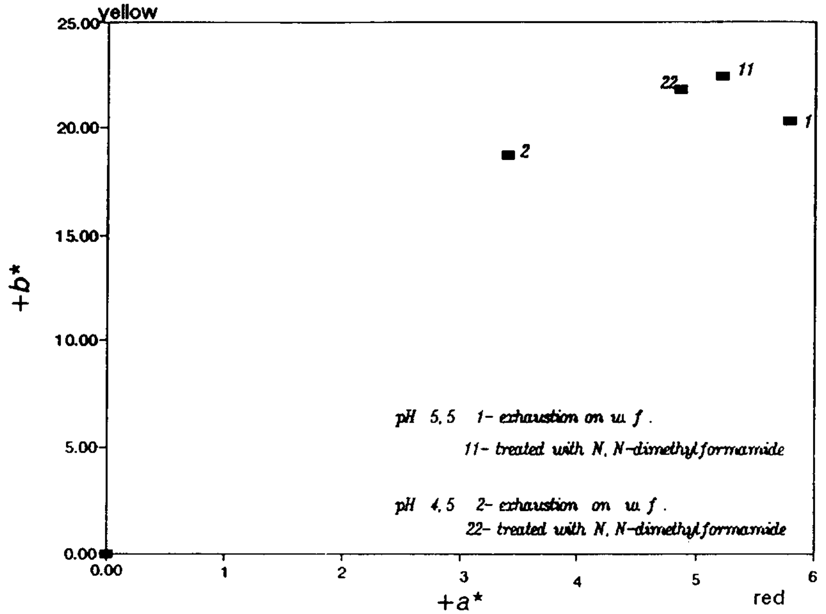

Fig. 5. The values a^*, b^* in the CIELAB diagram.

Cu–PMAP complex to the pH. Both dyed samples treated with N,N′-dimethylformamide have similar hue (points 11, 22). These experiments confirmed that the dye complex Cu–PMAP can be applied to wool fiber, but at pH above the fiber izoelectric point.

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