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Synthesis, Characterization and Dyeing Properties of Copper(II), Nickel(II) and Cobalt(III) Complexes of 2-Pyridylmethylene-1-Amino-2-Naphthol

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ABSTRACT

Synthetic methods for the preparation of the heterocyclic ligand 2-pyridylmethylene-1-amino-2-naphthol (PMAN) and its complexes with copper(II), nickel(II) and cobalt(III) are described. The structure of the ligand and of its metal complexes has been investigated by IR, UV/VIS and mass spectroscopy, and by elemental analysis. It has been found that the azomethine compound PMAN behaves as a tridentate ligand which forms various types of complexes. The Cu(II)–PMAN complex tends to form a chelate of ML type and with perchlorate as an anion. The Ni(II)–PMAN complex forms an ML_2 type of neutral complex, while the Co(III)–PMAN complex has the same ML_2 stoichiometry, but with perchlorate as an anion.

The dyestuffs have been used for wool dyeing under a controlled dyeing process. Parameters such as the optimal dyeing temperature, exhaustion with time and fixing on fabrics under acidic conditions have been determined.

1 INTRODUCTION

Schiff base ligands derived from 2-pyridinecarboxaldehyde and certain amines have wide application as spectrophotometric reagents in analytical chemistry due to their relatively stable complexes in the solutions. PMAN

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has been used as an indicator in the complexometric titration of Cu(II).[1] An analogous Schiff base derived from picolinealdehyde, 1-picolideneamino-2-naphthol has been used as a reagent for the extractive spectrophotometric determination of Zn(II).[2] Several other complexes of this ligand in solution have been used and investigated in analytical chemistry and spectrophotometric methods for the determination of V(V) and Ni(II) with the same ligand have been proposed.[3,4]

The syntheses of two solid complexes of 1-picolideneamino-2-naphthol with $Ni(NO_3)_2 . 6H_2O$ and $CoCl_2 . 6H_2O$ salts have been described and conductivity, solubility, magnetic and thermogravimetric behaviour, UV/VIS and IR spectra have been studied.[5] The solid Cu(II), Co(II), Ga(II), In(II) and Zn(II) complexes with the same ligand have also been prepared and characterized.[6]

Another interesting feature is the importance of certain types of metal complexes in the dye industry. The object of this investigation was to synthesize, isolate and characterize a Schiff base, 2-pyridylmethylene-1-amino-2-naphthol (PMAN), and its copper(II), nickel(II) and cobalt(III) complexes, and to investigate their application as wool dyes.

2 MATERIALS AND METHODS

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

The PMAN ligand was prepared by the reaction of 2-pyridinecarboxaldehyde with 1-amino-2-naphthol hydrochloride in ethanol in the presence of $CH_3COONa . 3H_2O$. A new series of Cu(II), Ni(II) and Co(II) complexes was synthesized and characterized.

Melting points were determined on a Koffler hot stage apparatus and they are given uncorrected. Samples for elemental analyses were dried for 6 h in vacuum, p 533 Pa (0·04 mmHg) at 100°C above phosphorus pentoxide. The IR spectra were recorded on a Perkin Elmer spectrometer (Model 257) using KBr pellets; UV/VIS spectra were measured in methanol solution on a Pye Unicam spectrophotometer (Model SP-1800); mass spectra were recorded on a Hitachi-Perkin Elmer spectrometer (Model RMU-60). A Linitest apparatus (Hanau) was used for the isothermal dyeing of wool.

2.1 2-Pyridylmethylene-1-amino-2-naphthol (PMAN)

This ligand was prepared by slight modification of an earlier method.[7] 1-Amino-2-naphthol hydrochloride (9·9 g) was dissolved in $EtOH/H_2O$ (1 : 1) (100 ml) and into this solution 2-pyridinecarboxaldehyde (5·4 g) was added with stirring, giving an orange coloured product. Subsequently a solution of $CH_3COONa.3H_2O$ (7·0 g) in water (20 ml) was added into the above mixture, which became yellow. The reaction mixture was heated for 1 h and after cooling, dark yellow crystals were obtained (m.p. 176°C). After three recrystallizations from benzene, thin yellow needles were obtained (m.p. 178°C).

Found ($C_{16}H_{12}N_2O$): C, 77·56; H, 4·92; N, 14·40%.
Calcd: C, 77·40; H, 4·88; N, 11·28%.

2.2 2-Pyridylmethylene-1-amino-2-naphthol copper(II) perchlorate monohydrate, Cu(PMAN) $ClO_4.H_2O$

$Cu(CH_3COO)_2.H_2O$ (1·0 g) was dissolved in MeOH (20 ml) and mixed with a solution of PMAN (1·24 g) in EtOH (60 ml). The resulting mixture was refluxed for 30 min and a saturated solution of $NaClO_4$ was then added. After a few minutes dark green crystals precipitated; after isolation, these were recrystallized from EtOH: m.p. 231°C; yield 60%.

Found ($C_{16}H_{11}N_2OCuClO_4.H_2O$): C, 45·2; H, 3·2; N, 6·2; Cl, 8·0; Cu, 14·1%.
Calcd: C, 44·9; H, 3·0; N, 6·5; Cl, 8·3; Cu, 14·8%.

2.3 2-Pyridylmethylene-1-amino-2-naphthol nickel(II), $Ni(PMAN)_2$

PMAN (1·24 g) was dissolved in MeOH (60 ml) giving a yellow solution; a solution of $Ni(CH_3COO)_2.4H_2O$ (1·24 g) in MeOH (30 ml) was then added with stirring, giving a deep red coloured solution. This solution was stirred for 5 h at room temperature and then allowed to stand overnight. The precipitate was filtered and recrystallized from Me_2CO, giving dark needles with a metallic lustre, m.p. 336°C; yield 40%.

Found ($C_{32}H_{22}N_4O_2Ni$): C, 70·0; H, 4·1; N, 9·9; Ni, 10·8%.
Calcd.: C, 69·5; H, 4·0; N, 10·1; Ni, 10·6%.

2.4 2-Pyridylmethylene-1-amino-2-naphthol cobalt(III) perchlorate dihydrate, $Co(PMAN)_2$ $ClO_4.2H_2O$

An equimolar amount of PMAN and $Co(CH_3COO)_2.4H_2O$ was mixed by addition of PMAN (2·48 g) in MeOH (60 ml) to a solution of $Co(CH_3COO)_2.4H_2O$ (2·49 g) in MeOH (30 ml). A dark red coloured solution resulted; after stirring for 6 h at room temperature, a saturated methanolic solution of $NaClO_4$ was added and the resultant dark red precipitate filtered and recrystallized from Me_2CO, m.p. 322°C, yield 30%.

Found ($C_{32}H_{22}N_4O_2CoClO_4 . 2H_2O$): C, 55·4; H, 3·7; N, 7·9; Cl, 4·9; Co, 8·2%

Calcd: C, 55·8; H, 3·8; N, 8·1; Cl, 5·2; Co, 8·6%.

The dyeing properties of the Co-, Ni- and Cu-PMAN complexes were investigated on samples of wool from New Zealand ($d = 34{\cdot}6\ \mu m$). In order to determine the optimal dyeing conditions, bleached samples of wool (1 g) were treated with aqueous dye-liquor (1:60) containing 3% of dyestuff (o.w.f.) at pH 5·5 (ammonium acetate buffer). Dyeing was performed isothermally at 80°C and 100°C in a Linitest apparatus (Hanau). After dyeing for 5–60 min at these temperatures the wool was rinsed with cold and hot water until all dye not bound to the wool was washed off. The depth of dyeing was measured using a Datacolor Model DC 3890 and values of K/S, relative depth of dyeing calculated according to the Kubelka–Munk equation, $K/S = (1 - R)^2/(2R)$, are presented in Table 5 and Fig. 2. Washing fastness was examined at 95°C according to DIN 54011.[8]

3 RESULTS AND DISCUSSION

Ligand solubility was investigated and relevant data are given in Table 1, together with the solubility of the Cu(II), Ni(II) and Co(III) complexes. At room temperature, the Co–PMAN complex was very soluble in water, while the solubility of the Cu–PMAN complex had to be increased by heating at 60°C for use in the dyeing process. For the same purpose, the addition of a dispersing agent (1 g/litre) to the Ni–PMAN complex was necessary, because this dye was insoluble in water even at higher temperatures. This suggest that the Cu–PMAN and Co–PMAN are cationic complexes while the Ni–PMAN is a neutral complex with very weak hydrophilic character. The type of structure of the metal complex compounds, ionic or neutral, as suggested by solubility, is further confirmed by spectroscopic results obtained for solid state and solution samples.

The UV/VIS spectral data shown in Table 2 give an insight into the change of the structure as a consequence of the chelation. Table 2 shows the bathochromic shifts of the absorption maxima due to formation of the metal ion–ligand complex: 141, 125 and 189 nm for Cu(II), Ni(II) and Co(III) complexes, respectively, relative to the λ of A_{max} of the PMAN ligand.[9,10]

The position of the characteristic bands of the ligand PMAN and its Cu(II), Ni(II) and Co(III) complexes in the IR spectra (Table 3) are in the following regions: 3650–3200 cm^{-1} (—OH stretching vibrations),

TABLE 1
Solubilty of the PMAN Ligand and its Metal Complexes in Different Solvents

Solvent	*PMAN*			$[Cu(PMAN)]ClO_4 . H_2O$			$Ni(PMAN)_2$			$[Co(PMAN)_2]ClO_4 . 2H_2O$		
	Sol.		*Col.*	*Sol.*		*Col.*	*Sol.*		*Col.*	*So.*		*Col.*
	c.	*w.*		*c.*	*w.*		*c.*	*w.*		*c.*	*w.*	
Water	−	−	—	+ −	+ −	Oran.	−	−	—	+ −	+	Red.
Ethanol	+ +	+ +	Yell.	+ +	+ +	Red	+ −	+	Red	+	+ +	Red
Methanol	+ +	+ +	Yell.	+ +	+ +	Red	+ −	+	Red	+	+ +	Red
Acetone	+ +	+ +	Yell.	+ +	+ +	Red	+	+	Red	+ +	+ +	Viol.
DMF	+ +	+ +	Yell.	+ +	+ +	Red	+	+ +	Red	+ +	+ +	Viol. red
Petrolether	−	−		−	−		−	−		−	−	
Benzene	+ −	+ −	Gre.-yell.	−	−	Red	+ +	+ +	Viol. red	+ +	+ +	Viol. red
Chloroform	+ +	+ +	Yell.	+ +	+ +	Red	+ +	+ +	Viol. red	+ +	+ +	Viol. red
Pyridine	+ +	+ +	Yell.	+ +	+ +	Red	+ +	+ +	Dark red	+ +	+ +	Red
Acetic acid (glac.)	+ +	+ +	Oran.	+ +	+ +	Red	+ +	+ +	Yell.	+ +	+ +	Yell.
Sulphuric acid (conc.)	+ +	+ +	Brown	+ +	+ +	Red	+ +	+ +	Viol. red	+ +	+ +	Viol. red

Sol., solubility; c, cold; w., warm; Col., solution colour; −, insoluble; + −, slightly soluble; +, soluble; + +, very soluble; yell., yellow; gre., green; oran., orange; viol., violet.

TABLE 2
UV/VIS Spectra Data for the PMAN Ligand and its Metal Complexes (in MeOH)

Compound	λ_{max} *(nm)*
PMAN	236; 281; 379
Cu(PMAN) ClO$_4$.. H$_2$O	337; 520
Ni(PMAN)$_2$	248; 283; 35; 504
Co(PMAN)$_2$ ClO$_4$. 2H$_2$O	392; 568

TABLE 3
IR Spectral Data of the PMAN Ligand and its Metal Complexes

Absorption band wavenumbers (cm^{-1})				*Assignments*
PMAN	*Cu–PMAN*	*Ni–PMAN*	*Co–PMAN*	
3 650–3 200 s	3 200 broad	—	—	—OH st
3 040 w	3 030 w	3 030 w	3 030 w	ar C—H st
1 630 m	1 590 s	1 610 m	1 610 m	C=N st
1 580 s	1 530 w	1 550 m	1 560 m	—
—	—	1 530 m	1 530 w	—
1 490 s	1 480 s	1 470 m	1 480 m	=CH ip
1 470 m	1 450 s	1 440 s	1 450 m	—
1 440 s	1 430 s	—	1 430 w	—
1 320 s	1 300 m	1 390 m	1 390 w	C—N st, C—O st
1 260 s	1 250 m	1 300 m	1 290 m	—
1 220 m	1 200 m	1 250 m	1 260 m	—
—	—	1 200 m	1 200 w	—
1 170 m	1 150 m	1 130 s	1 140 s	C—C δ
1 060 s	1 130 m	1 070w	1 090 s	—
1 000 s	1 040 w	1 000 m	1 000 m	—
—	1 090 s	—	—	—
—	1 000 m	—	—	—
—	960 w	—	—	$\delta(H_2O)$
950 s	920 w	820 w	930 m	ar C—H δ op
870 w	850 w	740 m	850 m	—
800 s	810 m	630 w	820 m	—
750 s	730 m	—	730 m	—
650 m	625 m	—	625 m	—

ip, in plane; op, out of plane; s, strong; m, medium; w, weak; ar, aromatic; st, stretching vibrations; δ, deformation vibrations.

3060–3030 cm^{-1} (aromatic C—H stretching vibrations), 1630–1580 cm^{-1} (C=N stretching vibrations), 1480–1430 cm^{-1} (=CH deformation vibrations in the plane), 1300–1200 cm^{-1} (C—N, C—O stretching vibrations), 1200–1020 cm^{-1} (C—C deformation vibrations) and 900–650 cm^{-1} (out of plane aromatic C—H deformation vibrations).[11] A broad band between 3650 and 3200 cm^{-1} in the spectrum of the free ligand was absent in the spectra of the Co(III) and Ni(II) complexes. This may confirm the formation of a covalent bond between the oxygen of the OH group and metal ions. A broad band in the spectrum of the Cu(II) complex at 3200 cm^{-1} and the weak band at 960 cm^{-1} are due to OH stretching and H_2O rocking, respectively, and confirm the presence of water within the coordination sphere.[12,13] The C=N stretching absorption band of the azomethine group was found in the spectrum of the ligand[14] at 1630 and 1580 cm^{-1}. These bands in the spectra of the metal complexes are shifted to lower frequencies. This slight shift confirmed coordination of a nitrogen of the azomethine group with the metal ion. Coordination through the nitrogen of the pyridine ring was shown by the shift of the C—N stretching vibrations from 1320 cm^{-1} (for ligand) to 1300 cm^{-1} (for Cu complex) and 1390 cm^{-1} (for Co and Ni complexes). 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 in the spectra of the following compounds:

$$\mathrm{Cu(PMAN)ClO_4.H_2O} \quad \text{and} \quad \mathrm{Co(PMAN)_2ClO_4.2H_2O}^{15}$$

Mass spectrometry has been established as a suitable method for the investigation of the stoichiometry of metal complex compounds.[16] Mass spectral data are given in Table 4.

The spectrum of the ligand PMAN is dominated by an intense parent ion peak at *m/z* 248, with the base peak at *m/z* 219. Loss of OH (*m/z* 231), of CHN (*m/z* 219), of the pyridine group (*m/z* 170) and of the naphthol group (*m/z* 105) are the major process in the fragmentation of the ligand. The mass histogram of PMAN is shown in the Fig. 1.

In the spectrum of the Cu(II)–PMAN complex, the parent peak was not observed, but there was a peak at *m/z* 312, due to the parent ion minus perchlorate and water, confirming the ML stoichiometry of the chelate complex. The signal at *m/z* 248 corresponds to the mass of the ligand. Further, the spectrum shows similar fragments to those of the ligand itself.

The mass spectrum of the Ni(II)–PMAN complex shows the parent ion at *m/z* 553, confirming the ML_2 type of neutral chelate molecule, as was indicated previously from the solubility data.

The signal of the mass spectrum of the Co(III)–PMAN complex at *m/z* 556 corresponds to the mass of two ligands; the ML_2 type of chelate structure is therefore confirmed.

TABLE 4
Mass Spectral Data for the PMAN Ligand and its Metal Complexes

Compound	M_r	*m/z (Rel. int. (%))*
PMAN	248·28	248(86), 231(34), 219(100), 192(3), 170(88), 143(12·5), 128(6), 115(61), 105(13), 79(53)
$Cu(PMAN)ClO_4 . H_2O$	428·28	312(22), 248(80), 220(50), 173(30), 170(40), 141(63), 127(35), 121(30), 120(45), 78(100)
$Ni(PMAN)_2$	553·26	553(18), 326(15), 248(30), 220(100), 170(25), 192(40), 143(30), 130(35), 115(42), 78(45)
$Co(PMAN)_2ClO_4 . 2H_2O$	689·00	556(60), 496(38), 450(20), 403(8), 370(85), 310(30), 260(9), 246(100), 220(65), 190(60), 165(20), 140(70), 123(72), 91(60), 78(55)

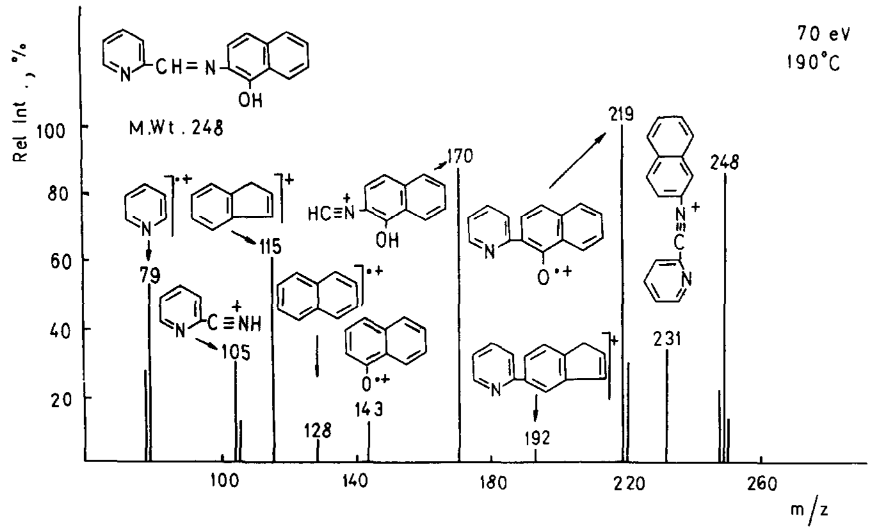
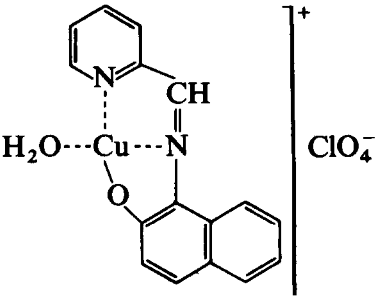


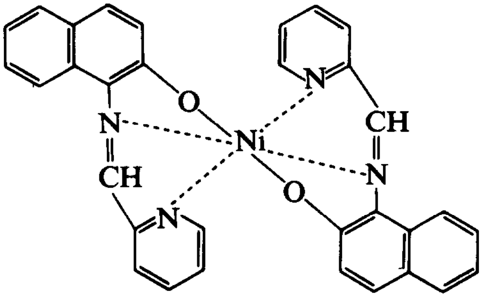
Fig. 1. Mass histogram of 2-pyridylmethylene-amino-2-naphthol.

On the basis of the analytical and spectroscopic data the structures of metal complexes have been proposed:



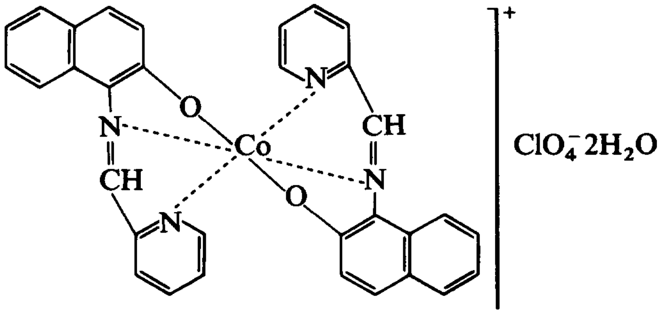
(1)

Cu(PMAN)ClO$_4$. H$_2$O



(2)

Ni(PMAN)$_2$



(3)

Co(PMAN)$_2$ClO$_4$. 2H$_2$O

PMAN is a tridentate ligand. Coordination can occur through the nitrogen of the pyridine group and the azomethine group, and through the oxygen atom of the hydroxy group.

The Cu(II) complex forms a chelate ML molecule with perchlorate as an anion; the coordination number of copper is 4.[2] The Ni(II) complex shows a ML$_2$ type of neutral metal complex structure; the coordination number of nickel is 6.[3]

The cobalt complex of PMAN was prepared by adding Co(II) acetate to a solution of the azomethine compound. Although the coordination of Co(II) ion was expected the analytical and spectroscopic data point to the presence of a Co(III) ion. Due to the negative standard reduction potential of the system Co(III)/Co(II), the Co(II) ion is easily oxidized by oxygen (from air) to the Co(III) ion.[2,17] It is important to point out that the reaction was carried out under normal conditions. Thus, oxidation of Co(II) to Co(III) was expected. The Co(III) ion with ligand PMAN forms an ML_2 type of cation complex with perchlorate as an anion; the coordination number of cobalt is 6.[4]

In the complex compounds of Cu(II) and Co(III) the presence of water was established. In the Co(III) complex, the crystalline water was determined from the mass loss by heating the complex in an oven at 180°C for 6 h. This loss of mass was not observed for the Cu(II) complex. The presence of water within the coordination sphere in the hydrated Cu(II) complex is supported by IR spectral data (Table 3) and by loss of water together with perchlorate ion, recorded at m/z 312 in the mass spectrum. Water in metal complexes of similar Schiff bases has also been determined by other authors.[13,18,19]

The dyeing properties of the Cu(II)-, Ni(II)- and Co(III)-PMAN complexes were investigated on wool. On the basis of the established structures of the complexes, it could be predicted that the attraction forces between the dyes and the wool would be van der Waals adsorption and ionic types. The large neutral dye molecules of $Ni(PMAN)_2$ are firmly held by fibre molecules because of non-polar van der Waals forces, whilst ionic links will be more pronounced between positively charged $Co(PMAN)_2^+$ or $Cu(PMAN)^+$ ions and the negatively charged carboxyl groups of wool. As the ionic link is easily broken, it needs to be supplemented by other van der Waals forces of attraction between dye and fibre. Wool, as a natural protein fibre, can change its polarity due to the pH of the dyebath.[20-23] Positively charged amino groups in wool attract the anions of acid dyes, while negatively charged carboxyl groups attract basic dyes. Therefore, all investigations were performed at pHs higher than that of the isoelectric point (pH 5·5), where the anionic character of the wool fibres is more pronounced. The results obtained for depth of staining, measured by reflectance spectrophotometry, are given in Table 5 and Fig. 2.

From the results presented it can be concluded that all three complex dyes have affinity for wool, affinity increasing with increase in temperature. The K/S values obtained for the first 10 min, regardless of temperature, for all three azomethine dyes were very low. This relates to the morphological structure of the wool,[22] more than to the dyeing properties of the dyes. The results given in Table 5 indicate that the dyeing time has to be longer than 20 min.

TABLE 5
Depth of Dyeing for Azomethine Dyes Used for Dyeing of Wool

t (min)	*K/S*					
	Cu(PMAN)ClO$_4$.H$_2$O		*Ni(PMAN)$_2$*		*Co(PMAN)$_2$ClO$_4$.2H$_2$O*	
	80°C	*100°C*	*80°C*	*100°C*	*80°C*	*100°C*
5	0·29	0·86	0·07	0·11	0·32	0·74
10	2·00	2·13	0·33	0·37	2·03	2·03
20	10·00	15·68	1·05	1·66	10·11	12·82
30	18·50	24·80	6·80	8·31	17·53	20·31
60	24·00	30·31	9·82	12·71	24·02	26·21

Very low values for exhaustion of dye were obtained for the Ni(PMAN)$_2$ complex, confirming that this complex is of a neutral type and bound to wool only by van der Waals forces (Fig. 2, curve 2). Higher exhaustion and better depth of dyeing were obtained for the Co–PMAN complex (curve 3), because the cationic dye also bound to the fibres with ionic links. The highest *K/S* values obtained for Cu–PMAN complex, can be explained by the

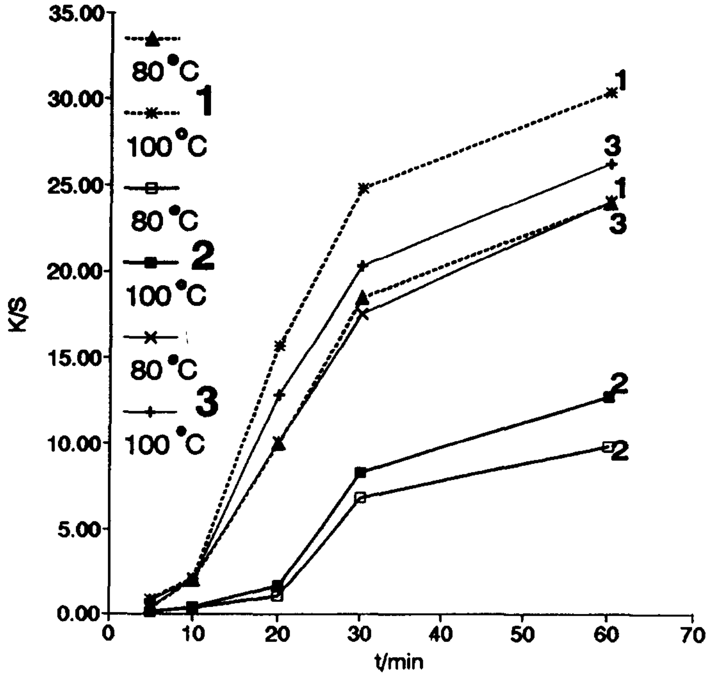


Fig. 2. Determination of *K/S* values with time for azomethine dyes: 1, Cu(PMAN)ClO$_4$.H$_2$O; 2, Ni(PMAN)$_2$; 3, Co(PMAN)$_2$ClO$_4$.2H$_2$O.

dimension of the molecule (one azomethine ligand is bound to one metal atom). The influence of temperature on the dyeing process with this dye is more pronounced and dyeing has to be performed at 100°C.

Washing fastness tests were carried out and the high values obtained (4–5) confirm that the affinity for wool of these metal complex dyes is satisfactory.

Since the Co–PMAN complex has very good solubility and affinity for wool at low temperatures, it can be used for the analytical determination of basic groups in wool. Preliminary investigations show that the Co–PMAN dye has higher affinity for wool damaged by hydrolysis. Due to the hydrolysis, the peptide link in wool breaks and the number of carboxyl groups increases. It can be assumed that at pH 5·5, free carboxyl groups in wool have an anionic character. The positively charged $[Co(PMAN)_2]^+$ complex will react quantitatively with the $—COO^-$ groups in wool, and by measuring the exhaustion of the dye, the degree of hydrolytic damage of wool can be determined.

For analytical use, the experimental conditions for this need to be optimized, and investigations are in progress in this respect.

REFERENCES

1. Isagai, Ka., Isagai, Ki. & Yamasaki, K., *Bunseki Kagaku*, **30** (1981) 731.
2. Otomo, M., Fukui, K. & Kodama, K., *Bull. Chem. Soc. Japan*, **47** (1974) 455.
3. Jimenez Ruedas, M. & Millan Gomez, R., *Afinidad*, **37** (1980) 133.
4. Jimenez Ruedas, M. & Merino Gutierrez, R., *Bol. Soc. Quim. Peru*, **47** (1981) 109.
5. Jimenez Ruedas, M. & Prieto, T., *Biol. Soc. Quim. Peru*, **46** (1980) 85.
6. Jimenez Ruedas, M. & Merino Gutierrez, R., *Bol. Soc. Quim. Peru*, **47** (1981) 27.
7. Levi, T. G., *Gaz. Chim. Ital.*, **59** (1929) 544.
8. *DIN Farbechtheitsnormen.* Beuth-Vertrieb, Gmbh, Berlin, 1966.
9. Mahmoud, R. M. & El-Haty, M. T., *J. Inorg. Nucl. Chem.*, **42** (1980) 349.
10. El-Haty, M. T. & Adam, F. A., *Bull. Soc. Chim.*, **11–12** (1983) 253.
11. Shindo, H., Walter, J. L. & Hooper, R. J., *J. Inorg. Nucl. Chem.*, **27** (1965) 871.
12. Furniss, B. S., Hannaford, A. J., Smith, P. W. G & Tatchell, A. R., *Vogel's Textbook of Practical Organic Chemistry*, 5th edn. Longman, London, 1989, p. 1416.
13. Abu El-Reash, G. M., Ibrahim, K. M. & Bekheit, M. M., *Bull. Soc. Chim. Fr.*, **128** (1991) 149.
14. Kimura, M., Suzuki, S., Mori, W. & Nakahara, A., *Inorg. Chim. Acta*, **56** (1981) 83.
15. Costes, J. P., *Transit. Met. Chem.*, **10** (1985) 185.
16. Betteridge, D.& John, D., *Talanta*, **15** (1968) 1227.
17. Mochizuki, K., Imamura, T., Ito, T. & Fujimoto, M., *Bull. Chem. Soc. Japan*, **51** (1978) 1743.
18. Geary, W. J., Nickless, G. & Pollard, F. H., *Anal. Chim. Acta*, **27** (1962) 74.
19. Muto, Y., *Bull. Chem. Soc. Japan*, **31** (1958) 1917.

20. Asquith, R. S., *Chemistry of Natural Protein Fibres.* John Wiley, New York, 1977.
21. Schieche, H., *Wölle als Textilen Rohstoff.* Schiele Schon, Berlin, 1979.
22. Peters, R. H., *Textile Chemistry III. The Physical Chemistry of Dyeing.* Elsevier, Amsterdam, 1975.
23. Bird, C. L., *The Theory and Practice of Wool Dyeing.* The Society of Dyers and Colourists, Bradford, UK, 1972.