



Synthesis of Metal Complexes of Some Formazans Drived From Cinnamaldehyde and Investigation of Their Dyeing Properties Using Different Methods

Fatma Erol², Nursabah Sarikavakli^{1*}

¹Department of Chemistry, Faculty of Sciences, and Arts, Aydin Adnan Menderes University, 09010 Aytepe/ Aydin, Turkey

²Gazi University, Technical Sciences Vocational School, 06374 Ostim/Ankara, Turkey

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Abstract

In this study, two formazans were synthesized by coupling cinnamaldehyde phenyl hydrazone obtained by activation of cinnamaldehyde with phenylhydrazine, with diazonium salts of anthranilic acid and sulfonilic acid. The complexes of Co⁺², Ni⁺², Cu²⁺ salts of these formazans were also synthesized. These compounds were characterized by elemental analysis, infrared (IR), ultraviolet-visible (UV-vis), ¹H nuclear magnetic resonance (¹H -NMR) and ¹³C- NMR spectral data. Investigation of these compounds as dyes were studied. In the present experimental approach, two methods were employed; The first one was direct dyeing with these complexes, and the other one was complex formation on the fibres. Finally fastness values (test) were calculated and significantly higher values are obtained.

Keywords: Formazans, Metal complexes, Dyeing, Fastness properties, Polyamide fibres

¹ Corresponding Author: Department of Chemistry, Faculty of Sciences, and Arts, Adnan Menderes University, 09010 Aytepe/ Aydin, Turkey, nsarikavakli@adu.edu.tr

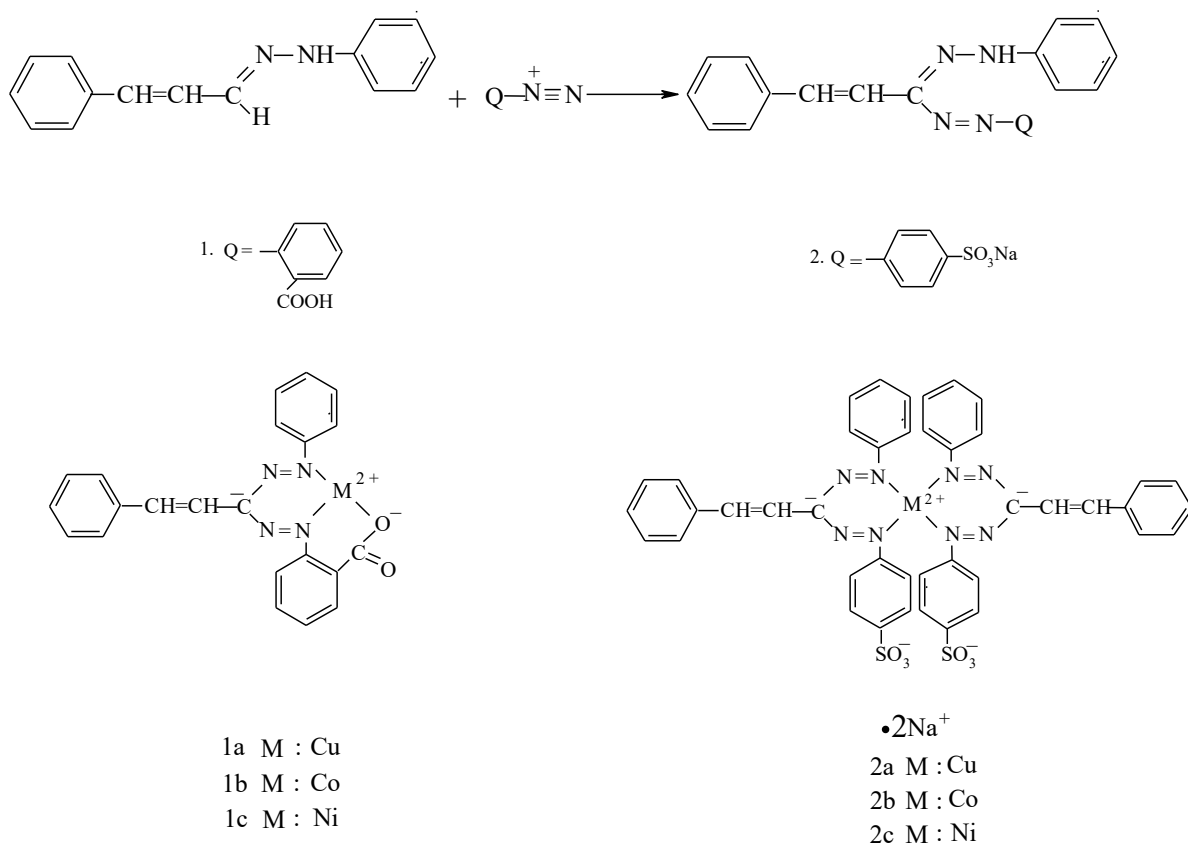
1. Introduction

The formazans are azohydrazone (-N=N-C=N-NH-) containing group have intense colour. The colour of these formazan derivatives may be due to $\pi \rightarrow \pi^*$ transitions. In these chromogenic compounds, the terminal groups play a crucial role in determining the physical and chemical properties of the compound. Numerous formazans have been synthesized and structurally characterized.

Their tautomeric and photochromic isomers have also been studied [1,2]. Several derivatives bearing electron donating and withdrawing group attached to 1,3,5-phenyl ring were synthesized and the effects of substituents on the absorption values i.e. λ_{\max} were examined [3,4]. Formazans forms complexes with a variety of metal ions. These complexes are formed by coordinating metal atom to 1 and 5 positions of the formazans [5-13]. The metal complexes of formazans are used widely on textile substrates since they provide shades of high fastness to light, They are also used in paint industries [14-17].

In recent years, formazans have been very important to be able to use as a reactive dye. The reactive formazan dyes are

environmental friendly dyes due to their water-solubility. Generally they contain sulfonamide, alkylsulfonyl, or sulfonic acid groups possessing high affinity for protein and polyamide fibers [18-22]. Although there are number of reports on the use of formazans and their complexes for dyeing purposes but the method of complex formation on the fibers has not been reported in the literature [18-22]. In the present study, two different formazans from cinnamaldehyde and their cobalt(II), nickel(II), copper(II) complexes have been synthesized (Scheme 1). Their structures were elucidated by elemental analyses, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FTIR and also by UV-vis spectral data. Since colouring property is dependent upon the absorption (λ_{\max}) value, therefore, the effect of substituents with (λ_{\max}) value was investigated. The process of dyeing of polyamide fabric with the complex compounds was performed by using two different methods that were water dispersion of complexes and the synthesizing of complexes on the fabric. We also compared these two methods to obtain the better fastness properties for the present samples.



Scheme 1

2. Materials and Methods

2.1. Materials

All the chemicals were purchased from the reputed agencies (Aldrich and Merck) at Ankara, Turkey and were used without purification. The solvents were pure of spectroscopic grade. The elemental analyses were carried out by using LECO-CHNS-932 elemental analyzer in our laboratory. The Infrared spectra of the samples were carried by using MATT-SON 100-FT-IR

spectrophotometer between 4000 and 400 cm^{-1} using KBr pellets. Further, the $^1\text{H-NMR}$ spectra were performed in deuterated dimethylsulfoxide (DMSO- d_6) and deuterated water (D_2O) solvents by using Bruker AVANCE DPX-400 MHz spectrophotometer. The $^{13}\text{C-NMR}$ spectra were recorded on 100 MHz spectrophotometer by using D_2O , and DMSO- d_6 , with a concentration of 10^{-4} mol/L^{-1} . The UV-vis spectra were obtained with Unicam UV2-100 spectrophotometer equipped with 1 cm quartz cells in 10^{-5} mol/L^{-1} dimethyl formamide and toluene in the range of 200–800 nm. The light and the treatment

fastness tests of formazans and their M(II) complexes were performed by using Xenon Arc Lamp Method (Atlas, Electric Type, Turkey) and Crock Meter Method (Atlas, Electric Type, Turkey), respectively.

2.2. Methodology

2.2.1. Preparation of Dyes

2.2.1.1. Synthesis of Cinnamaldehyde phenylhydrazone

The Cinnamaldehyde (0.02 mol) dissolved in 2 mL, the cinnam oil and phenylhydrazone were dissolved in 15 mL of ethanol and were mixed for 30 minutes at room temperature to obtain a preceptate. It was filtrated and washed with ethanol, dried and recrystallized from ethanol. The percentage yield was recorded 91% and mp. was 168-169 °C [23].

2.2.1.2. Synthesis of 1-(2'carboxyphenyl)-5-phenyl-3-strylformazan(dye 1)

0.002 mol of aniline derivative was dissolved in a mixture of 3 mL hydrochloric acid and 1 mL water and was cooled until 0 °C in the ice bath. After that 0.002 moles of sodium nitrate dissolved in 1 mL of water and was cooled to 0 °C, it was added to aniline solution drop by drop in 30 minutes. The mixture was stirred regularly upto 1 hour and at temperature 0-5 °C.

The Cinnamaldehyde phenylhydrazone (0.004 moles) and sodium hydroxide (1g) were dissolved in 150 mL of methanol and cooled upto 0 °C in ice bath. The dizaonium salt of anthranilic acid was added to hydrazone solution drop by drop at 0 °C. The mixture was stirred regularly until 3 hours. In the same time, the mixture was stabilized at the pH values of 10-11 by adding little portions of sodium carbonate simultaneously. The precipitate was filtrated and washed with water. Then, it was dried and recrystallized from aqueous acetic acid. This method is different from literature [24]. The yield percentage was recorded 37% and mp. was 216-217 °C.

2.2.1.3. Synthesis of 1-(4'sulfophenyl)-5-phenyl-3-strylformazan(dye 2)

The same procedure was carried out as in the synthesis of 1-(2'carboxyphenyl)-5-phenyl-3-strylformazan for the synthesis of dye 2. The recrystallization of dye 2 from n-propanol and ethanol was done and the yield percentage was found 33%.

2.2.2. Synthesis of Complexes

2.2.2.1. Synthesis of M(II)complexes of 1-(2'carboxyphenyl)-5-phenyl-3-strylformazan (1a,1b,1c)

The solution of 1-(2'carboxyphenyl)-5-phenyl-3-strylformazan in hot dioxane of 20 mL was added to the solution of Cu(CH₃COO)₂ in hot methanol slowly. The mixture was refluxed upto 3 hours. After that the dark blue-coloured precipitate of compound (1a) was filtered, it was washed several times with hot water and hot toluene and later on it has been dried. This method is different from literature [24]. The yield percentage was observed 62% and mp. was 212-213 °C

The same procedure was carried out for the synthesis of compounds (1b) and (1c), as it was done for the synthesis of compound (1a). And the yield percentage of these two new compounds (1b,1c) were 78% and 57% respectively and the mp.were 218-219 °C and 234-235 °C respectively.

2.2.2.2. Synthesis of M(II)complexes of 1-(4'sulfophenyl)-5-phenyl-3-strylformazan (2a, 2b, 2c)

The solution of 1-(4'sulfophenyl)-5-phenyl-3-strylformazan in hot ethanol of 20 mL was added to the solution of M(II) in hot methanol slowly. The mixture was refluxed for 3 hours. After that the dark-coloured precipitate was filtered, it was washed several times with hot water and hot dimethylformamide (DMF) and it was dried. The yield percentage was found in between 53% to 66%.

2.2.3. Dyeing Method

The polyamide fabric was dyed according to the procedures as given in Table 1 at our laboratory, Department of Chemistry, Faculty of Sciences, Adnan Menderes University, Aydin 09010, Turkey.

2.2.3.1. Direct Dyeing with Formazans and Their Complexes

The dye and dyeing agents were taken in different proportions as depicted in Table 1. These dyes and dyeing agents were heated upto 60 °C temperature. After, 15 min. the polyamide fabric was kept into the dye bath and this bath was boiled regularly for 1 hour. The dyeing process was finished by mixing at room temperature, and then the fabric that was picked up from the bath was washed with cold and hot water several times. The dyed material was boiled in 1% soap solution for 30 minutes. After that the fabric was shaken up within water, and then it was dried in the air.

Table 1. The dyeing equipment for all the dyes

Dye	Fabric(g)	Material:Dye	Material:Liquor	Na ₂ CO ₃ (g/L)	Na ₂ SO ₄ (g/L)	Urea (g/L)
Dye 1	2,5	100:5	1:100	1	15	10
Dye 2	2,5	100:5	1:100	15	10	-
1a,1b,1c 2a,2b,2c	2,5	100:5	1:100	1	15	10
1a*,1b*,1c*	2,5	100:5	1:100	1	15	10
2a*,2b*,2c*	2,5	100:5	1:100	15	10	-

*The complexes were formed on the fabric

2.2.3.2. Dyeing Through the Formation of Complexes on Fabric

The temperature of polyamide fabric was raised to 40 °C in the 250 mL of M(II) solution. Then, the material removed from this solution and was kept into the dyeing bath containing formazan and dyeing agents. The dyeing bath was boiled for 1 hour. The dyeing process was finished after the bath was stirred for one hour at room temperature. The polyamide fabric was removed from dye bath and it was washed with cold and hot water several times.

The dyed material was boiled in 1% of soap solution upto 30 minutes and then it was shaken with water and dried in the air.

3. Results and Discussion

The solvent 1-(2'carboxyphenyl)-5-phenyl-3-strylformazan (dye 1) is soluble in aqueous acetic acid, toluene, DMSO and DMF. The Na⁺ salt of 1-(4'sulfophenyl)-5-phenyl-3-strylformazan (dye 2) is stable in the said organic solvent, but soluble in water and DMF. All the complexes are stable in air, and in anhydrous EtOH and MeOH, but soluble in DMSO and DMF. An attempt has been made to propose the structure of the isolated complexes and its result with full investigation were presented the following steps.

3.1. Elemental Analyses

The elemental analyses data were listed in Table 2, which shows that 1-(2'carboxyphenyl)-5-phenyl-3-strylformazan complexes and 1-(4'sulfophenyl)-5-phenyl-3-strylformazan complexes were formed in a ratio of 1:1 and 1:2 type structure respectively.

Table 2. The elemental analyses of the formazans and metal coplexes

Dye	Formula (Mol. Wt.)	Yield(%)	C%		H%		N%		S%	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
1	C ₂₂ H ₁₈ O ₂ N ₄ (370)	37	71.35	71.84	4.86	4.51	15.14	13.67	-	-
1a	C ₂₂ H ₁₆ O ₂ N ₄ Cu (431.5)	62	61.18	61.43	3.70	4.45	12.97	12.27	-	-
1b	C ₂₂ H ₁₆ O ₂ N ₄ Co (427)	78	61.82	61.21	3.74	4.43	13.11	13.58	-	-
1c	C ₂₂ H ₁₆ O ₂ N ₄ Ni (427)	57	61.82	61.56	3.74	4.54	13.11	13.69	-	-
2	C ₂₁ H ₁₇ O ₃ N ₄ Sa (428)	33	58.87	59.27	3.97	3.62	13.08	13.46	7.47	6.71
2a	C ₄₂ H ₃₂ O ₆ N ₈ S ₂ Na ₂ Cu (917.5)	66	54.93	55.45	3.48	3.21	12.20	12.78	6.97	7.36
2b	C ₄₂ H ₃₂ O ₆ N ₈ S ₂ Na ₂ Co (913)	59	55.20	55.77	3.50	3.72	12.26	11.63	7.00	7.22
2c	C ₄₂ H ₃₂ O ₆ N ₈ S ₂ Na ₂ Ni (913)	53	55.20	55.60	3.50	3.22	12.26	11.40	7.00	6.75

3.2. IR Spectra

The IR spectral data of formazans and metal coplexes were listed in Table 3. One can find out from this Table 3, that the C=N stretching bands were found at 1530, 1543 cm⁻¹ and the N-H bands were observed at 3367, 3345 cm⁻¹ respectively for the formazans (1 and 2) but they were not observed in the complexes [8,25]. These results confirm the formula which is depicted in Scheme 1. The N=N bands observed at 1405-1398 cm⁻¹ in the formazans (1 and 2) and were observed to shift to 1249-1267 cm⁻¹ and 1267-1272 cm⁻¹ in M(II) complexes. The

results are consistent with the literature [8, 25]. The C=O stretching band was observed at 1682 cm⁻¹ for -COOH group in formazan 1, but it was shifted to lower frequencies (1591-1603 cm⁻¹) in M(II) complexes [26-27]. The OH stretching band was observed at 3400-3300 cm⁻¹ in the formazan 1 and it was disappeared in the M(II) complexes. This proves that OH group takes part in the formation of C-O-M bond. These results are in good accordance with the literature [5,8,11,26] and confirm the structure given in Scheme1. Some, other aromatic C-H, SO₂, S-O stretching peaks and -C-O-M vibration band in the compounds were observed in their expected regions.

Table 3. List of the IR spectral data of the formazans and metal complexes (in KBr, m/cm⁻¹)

Comp.	-NH	Arom.C-H -CH=CH-	C=O	Arom.C=C Alift.C=C	C=N	N=N	OH	SO ₂	S-O	-C-O-M
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1	3367	3053-3018	1682	1660-1570	1530	1405	3400-3300	-	-	-
1a	-	3022-2982	1591	1580-1500	-	1249	-	-	-	3400-3372
1b	-	3053-3018	1603	1590-1500	-	1267	-	-	-	3405-3380
1c	-	3061-3029	1591	1580-1500	-	1249	-	-	-	3402-3375
2	3345	3063-3037	-	1690-1600	1543	1398	-	1230,1060	684	
2a	-	3061-3018	-	1645-1550	-	1267	-	1157,1010	646	
2b	-	3054-3022	-	1645-1550	-	1272	-	1165,1019	653	
2c	-	3053-3029	-	1645-1550	-	1269	-	1150,1010	641	

3.3. ¹H-NMR Spectra

The ¹H-NMR spectra data of formazans and metal complexes were listed in Table 4. From this Table 4 one can find that the aromatic C-H peak for formazans (**1** and **2**) were observed at $\delta=8.20-7.11$ and $\delta=8.47-7.50$ ppm [4,8,12,25-30]. On the other hand, in the M(II) complexes of formazan **2** (**2a**, **2b**, **2c**) the aromatic C-H signals were shifted respectively towards lower fields in comparison to the complexes of formazan **1** (**1a**, **1b**, **1c**). This shows a good agreement with the electron withdrawing properties of $-\text{SO}_3\text{H}$ and $-\text{COOH}$ substituents. These groups are electrons withdrawing with regards to both resonance and inductive effects, but the effect of

$-\text{SO}_3\text{H}$ group is relatively large. On comparing all these corresponding formazans, it has been found that the aromatic C-H peaks of M(II) complexes were observed to shift towards the lower fields. This is in accordance with the fact that the electrons in the structure are withdrawn with the insertion of M(II) into formazans structure [28]. The peak for the proton of COOH group was observed at 12.25 ppm [4,8] and the N-H peaks were observed at 14.10-14.55 ppm [4,28,29] in formazans but they disappeared in the M(II) complexes [8,25]. This is a further proof that the metal ion was inserted in place of the protons of N-H group and COOH group. These results confirm that the proposed formula given in Scheme 1 is valid.

Table 4. The ¹H-NMR and ¹³C-NMR data δ (ppm)

Compd.	¹ H - NMR				¹³ C- NMR		
	HC=CH	Arom. H	N-H	COOH	COOH	C=N	C= C and Arom. C
1	6.70, 5.54 (1H,d) (1H,d)	8.20-7.11 (14H,m)	14.10 (1H,s)	12,25 (1H,s)	187.33	144.03	140.90-114.02
1a	6.93, 5.68 (1H,d) (1H,d)	8.55-7.20 (14H,m)	-	-	201.74	68.17	164.46-124.79
1b	6.87, 5.69 (1H,d) (1H,d)	8.51-7.32 (14H,m)	-	-	193.21	60.88	166.51-119.72
1c	6.91, 5.70 (1H,d) (1H,d)	8.52-7.20 (14H,m)	-	-	197.65	67.53	167.43-123.63
2	6.80, 5.67 (1H,d) (1H,d)	8.47-7.50 (14H,m)	14.55 (1H,s)	-	-	151.17	146.88-122.96

2a	6.82, 5.47 (2H,d) (2H,d)	8.63-6.95 (28H,m)	-	-	-	74.45	166.43-130.87
2b	6.96, 5.72 (2H,d) (2H,d)	8.59-7.08 (28H,m)	-	-	-	75.21	168.89-128.32
2c	6.91, 5.68 (2H,d) (2H,d)	8.58-6.98 (28H,m)	-	-	-	77.63	171.22-129.01

s:singlet, d:doublet, m:multiplet

3.4. ¹³C- NMR Spectra

The ¹³C-NMR spectra data of formazans and metal complexes were listed in Table 4. Therefore, we draw conclusions from Table 4 that the C=N peaks observed at 144.03 and 151.17 ppm in formazans (**1** and **2**) [4,30] and shifted towards high fields in the M(II) complexes. This result confirms the structure given in Scheme 1. The peaks for the aromatic "C" and alifatic C=C of the M(II) complexes (120-171ppm) shifted to lower fields as compared to formazans (114-146 ppm). This result is in accordance with the replacement of an electron withdrawing M(II) into the system [12,25]. The peak of COOH group in formazan 1 and M(II) complexes (**1a**,**1b**,**1c**) can also be evaluated in a similar manner as it was in the literature [8,12].

3.5. UV-vis Spectra

The UV-vis spectra of formazans and metal complexes were listed in Table 5. It is clear from the Table 5, that there were

three peaks observed in the UV-vis spectra for the M(II) complexes of formazans. The absorptions peaks were such as attributed; $\lambda_{\max 1}$, was for the M(II) complex unit, $\lambda_{\max 2}$ was for the formazan unit and $\lambda_{\max 3}$, was for the hydrazone unit [25, 31]. The observed λ_{\max} value at 533.6 nm for the formazan 1, shifted to the 570.0–593.4 nm, and in the M(II) complexes λ_{\max} value observed at 503 nm for the formazan 2 and was shifted to 556.0–580.6 nm. This is an expected outcome as a result of the replacement of the M(II) ion in the structure. These results are consistent with the literature [6-8, 31]. When the λ_{\max} values of the formazans were compared according to the type of the substituents, it was found that the formazan 2 showed lower wavelength, which is known as hypsochromic effect. This is also an expected outcome since SO₃H group is a stronger electron withdrawing group than COOH group. When the λ_{\max} values of M(II) complexes were compared according to the type of the metals, It was found in such order Co>Ni>Cu. This result is found in good agreement with the electron withdrawing properties of M(II) into the system.

Table 5. The UV-vis absorption maxima and Fastness values of the formazans and M(II) complexes

Dye	Colour	Fastness			UV-vis			
		Light	Treatment		Washing	$\lambda_{\max 1}$ (nm)	$\lambda_{\max 2}$ (nm)	$\lambda_{\max 3}$ (nm)
			Wet	Dry				
1	Dark red	1-2	5	5	5	-	533.6	335.0
1a	Dark blue	3	5	4	5	570.0	340.4	241.2
1b	Dark brovn	5	5	5	5	593.4	368.0	244.0
1c	Green	4	5	4	5	581.0	345.0	240.0
2	Yelow	1-2	5	5	5	-	503.0	294.8
2a	Dark yellow	3	5	5	5	556.0	325.6	223.6
2b	Brovn	5	5	5	5	580.6	362.2	248.0
2c	Brovn	3	5	5	5	568.0	354.0	235.0
1a*	Blue	1-2	5	4	5	-	-	-
1b*	Black	5	3	2	5	-	-	-
1c*	Dark green	1-2	4	2	5	-	-	-
2a*	Dark yellow	1-2	5	5	5	-	-	-
2b*	Dark yellow	1-2	5	5	5	-	-	-
2c*	Dark yellow	1-2	5	5	5	-	-	-

3.6. Fastness Tests

The fastness values were determined according to the International Standards; the specific tests used were ISO 105 C06/C1S (washing fastness), ISO 105X12 (treatment fastness) and ISO 105 B02 (light fastness). The light fastness tests were assessed according to the international blue scale (1-8), the treatment and washing fastness tests were assessed according to the international grey scale (1-5), with scales 8 and 5, respectively, to find the best rank, while scale 1 was the most inferior. All fastness values of dyes were depicted in the Table 5.

It is clear from the Table 5, that the washing and treatment fastness values of the formazans were good but light fastness values were low. All these values of formazans were similar. These results showed that the effect of changing the type of the substituent on the rings upon fastness values was not existent. In the comparison of the fastness values of the formazans with their M(II) complexes, it was observed that light fastness values of the M(II) complexes were higher than those of formazans and other fastness values were found the same or very close to each other. This result is consistent with that of the studies in the literature [14-17]. On the other hand on the comparison of the fastness values obtained from dyeing directly of Cu²⁺ complex of formazan 1 with the fastness values obtained from the formation of the complex on the fabric, the light fastness value of compound 1a was higher than the compound of 1a*. Other fastness values of compound 1a and the compound 1a* were found in the same order.

In the comparison of the fastness values of the compound 1b with those of compound 1b*, it was found that treatment fastness values of compound 1b were higher than compound 1b*. Other fastness values of compound 1a and compound 1a* were found in the same order.

In comparison of the fastness values of compound 1c with compound 1c*, it was observed that light and treatment fastness values of compound 1c were higher than those values of compound 1c*, but the washing fastness values of compounds 1c and 1c* respectively were found in the same order. In addition, the comparison of the fastness values of compounds 2a, 2b, 2c with those of compounds 2a*, 2b*, 2c*, it was found that light fastness values of compounds 2a, 2b, 2c were higher than compounds 2a*, 2b*, 2c*. And other fastness values of compounds 2a, 2b, 2c and 2a*, 2b*, 2c* respectively were in the same order.

4. Conclusion

The formazans and their M(II) complexes were prepared and characterized. Their absorption and fastness properties were discussed. Therefore, based on the present experimental research work one can concluded the followings:

The absorption values (λ_{\max}) of the formazans showed the changing behavior / effect with different type of the substituent's rings. As well as the λ_{\max} values of the M(II) complexes also showed the effect of changing the type with the metal.

An investigation was carried out of which fastness values were higher and which method would be better according to the fastness values. Therefore, depending on the fastness tests in according to the International Standards/ISO, we applied to the

dyeing polyamide fabrics and it was found that light fastness values of M(II) complexes were higher than those of formazans.

The fastness values of complexes at direct dyeing were found normal and also were higher than the fastness values of complexes formed on the fabricator.

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