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Dyes and Pigments 76 (2008) 733–740

DYES and PIGMENTS

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The synthesis and spectral properties of 1,3-substituted phenyl-5-phenylformazans and their Ni(II) complexes

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Received 7 September 2006; received in revised form 25 January 2007; accepted 26 January 2007
Available online 4 February 2007

Abstract

Novel, 1:2 Ni(II) complexes of 1,3-substituted phenyl-5-phenylformazans were synthesized. The formazans contained $-NO_2$, $-Cl$, $-Br$, $-CH_3$ $-OCH_3$ groups at the *o*-, *m*-, *p*-positions of the 1-phenyl ring and $-NO_2$ and $-OCH_3$ groups at the *m*- and *p*-positions of the 3-phenyl ring. Their structures were identified by elemental analyses, FTIR, ^{1}H NMR, ^{13}C NMR, UV–vis and GC–mass spectra. UV–vis spectra indicated that their λ_{max} was shifted to an extent that depended upon the type and position of the substituent on the ring. A linear correlation was obtained between Hammett substituent coefficients and λ_{max} values.

Keywords: Formazans dyes; Nickel complexes dyes; Spectroscopy; Substituent effect

1. Introduction

Formazans are colored compounds, owing to π bonds and contain azohydrazone conjugated double bonds (Scheme 1). Since the first formazans were synthesized by Von Pechmann, numerous formazans have been synthesized and their structural properties as well as their tautomeric and photochromic isomers have been investigated [1–5].

Metal complex dyes are used widely on textile substrates as they provide shades of high fastness to light, wet treatments and other agencies [6]. The synthesis, structure, complex stability, spectroscopic characterization, spectrophotometry, extraction and stripping behaviour, *Salmonella* mutagenicity as well as the design of *o*-substituted formazan metal complexes have been studied [7–18].

Previous work focussed on formazans and bis-formazans with electron donating and withdrawing groups attached to the 1,3,5-phenyl ring and the effects of substituents on λ_{max} were investigated [19–22]; the electrochemical investigation of their nitro derivatives and quantum chemical calculations of bis-formazan were also carried out [23,24].

Despite the fact that metal complexes of formazans are widely used as dyes there are only a limited number of publications that concern the Ni-complexes of formazans. We decided to investigate the Ni-complexes of formazans because the formation of such complexes should be efficient due to the smaller size of the Ni atom compared to other metals in the same group in the periodic table. Accordingly, 1,3-substituted phenyl-5-phenylformazans and their Ni-complexes were synthesized and their structures were identified using FTIR, ^{1}H NMR, ^{13}C NMR, UV–vis and GC–mass spectral data; the effect of substituents upon λ_{max} was also investigated. The proposed structures of the complexes are given in Scheme 1.

2. Experimental

2.1. General

All chemicals were purchased from Merck and Sigma–Aldrich and used without further purification. The UV–vis spectra of the Ni-complexes of formazan synthesized in this study

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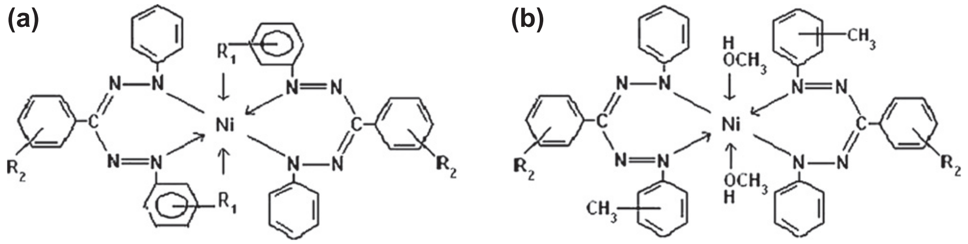
doi:10.1016/j.dyepig.2007.01.016



No	Formazans (a)	R_1	R_2	Ni complexes (b)
1	**1a**	H	H	**1b**
2	**2a**	*o*-NO_2	*m*-NO_2	**2b**
3	**3a**	*m*-NO_2	*m*-NO_2	**3b**
4	**4a**	*p*-NO_2	*m*-NO_2	**4b**
5	**5a**	*o*-Cl	*m*-NO_2	**5b**
6	**6a**	*m*-Cl	*m*-NO_2	**6b**
7	**7a**	*p*-Cl	*m*-NO_2	**7b**
8	**8a**	*o*-Br	*m*-NO_2	**8b**
9	**9a**	*m*-Br	*m*-NO_2	**9b**
10	**10a**	*p*-Br	*m*-NO_2	**10b**
11	**11a**	*o*-CH_3	*p*-OCH_3	**11b**
12	**12a**	*m*-CH_3	*p*-OCH_3	**12b**
13	**13a**	*p*-CH_3	*p*-OCH_3	**13b**
14	**14a**	*o*-OCH_3	*p*-OCH_3	**14b**
15	**15a**	*m*-OCH_3	*p*-OCH_3	**15b**
16	**16a**	*p*-OCH_3	*p*-OCH_3	**16b**

Scheme 1. The structure of (a) the Ni-complexes of formazan derivatives (**1b–10b**, **14b–16b**); (b) derivatives of the Ni-complexes of formazan (**11b–13b**).

were obtained using a Unicam UV2-100 UV–vis spectrophotometer equipped with 1 cm quartz cells in 10^{-5} mol L^{-1} DMSO in the range 250–700 nm. IR spectra were recorded on a Mattson 100-FT-IR spectrophotometer between 4000 and 400 cm^{-1} using KBr pellets. ^1H NMR spectra were recorded on a Bruker Avance DPX-400 MHz and ^{13}C NMR 100 MHz spectrophotometer using $CDCl_3$ and DMSO-d_6, 10^{-4} mol L^{-1}. Elemental analyses were carried out using a LECO-CHNS-932 elemental analyzer and mass spectra were recorded on an Agilent 1100 MSD LC/MS spectrometer.

2.2. General synthesis of formazans

Formazans **1a–16a** were synthesized by the reaction of benzaldehyde or substituted benzaldehyde (0.01 mol), phenylhydrazine (1.08 g, 0.01 mol), aniline or substituted aniline (0.01 mol), concentrated HCl and sodium nitrite in methanol, at 0–5 °C as described in Ref. [28].

2.3. General synthesis of Ni(II) complexes of formazan

By the reaction of 1-(*o*-, *m*-, *p*-substituted phenyl)-3-(*m*-, *p*-substituted phenyl)-5-phenylformazans with the metal salt [$Ni(CH_3COO)_2 \cdot 4H_2O$], 16 different complexes were obtained.

2.3.1. Synthesis of bis(1,3,5-triphenyl formazanato)-nickel(II) complexes (*1b*)

1,3,5-Triphenylformazan (**1a**) (1.500 g, 0.005 mol) obtained as described in Ref. [20] was dissolved in dioxane (20 mL). In another flask, $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.0025 mol, 0.625 g) was dissolved in ethanol (22 mL) under reflux with constant stirring at 25 °C to which was added the formazan solution gradually with constant stirring at pH 6–7 and 30–35 °C. There was no color change or precipitation observed during this process; precipitation commenced after 1 h and the color turned from red to orange after 2 h and to brown after 3 h. The mixture was stirred for 8 h and the color remained brown. The mixture was kept in the dark for 4 days. The light-brown colored precipitate was filtered and then washed with 10 mL 0.5 M NaOH, water and methanol. The compound was dried at 40 °C for 24 h and recrystallized from methanol.

Note: when 5, 10, 15, 20, 25 mL, 0.5 M NaOH was added to bis(1,3,5-triphenyl formazanato)nickel(II) solution the color of the mixture changed, respectively, to brown, light brown, light brown, yellow, yellow. These color changes may be the indication of the isomerism of bis(1,3,5-triphenyl formazanato)-nickel(II) complex. This aspect will be discussed in a later paper.

*2.3.2. Synthesis of bis[1-(o-, m-, p-nitrophenyl)-3-(m-nitrophenyl)-5-phenyl formazanato]nickel(II) complexes (**2b**, **3b**, **4b**)*

Compounds **2a–4a** (0.780 g, 0.002 mol) obtained as in Section 2.2 were dissolved in dioxane (20 mL). In separate flasks $Ni(CH_3COO)_2 \cdot 4H_2O$ (3 × 0.001 mol, 3 × 0.250 g) was dissolved in ethanol (3 × 15 mL) to which was added the formazan solution. The mixtures were stirred at 30–35 °C under reflux for 8 h and kept in the dark for 3 days. The brown colored (**2b**), green-black colored (**3b**) and green-black colored (**4b**) compounds were filtered, washed with water and methanol, recrystallized from methanol and dried at 40 °C for 24 h. Elemental analysis for $NiC_{38}H_{26}N_{12}O_8$, Calc. (%): C, 54.50; H, 3.10; N, 20.08. Found (%): C, 54.45; H, 3.17; N, 20.03. Calc. mass: 836.70. Found mass: *m/z* (eV): 836.70. Other peaks: 447.15, 389.10, 241.00, 150.15, 170.25.

*2.3.3. Synthesis of bis[1-(o-, m-, p-chlorophenyl)-3-(m-nitrophenyl)-5-phenyl formazanato]nickel(II) complexes (**5b**, **6b**, **7b**)*

Compounds **5a–7a** (0.760 g, 0.002 mol) synthesized as in Section 2.2 were dissolved in dioxane (25 mL). In separate flasks $Ni(CH_3COO)_2 \cdot 4H_2O$ (3 × 0.001 mol, 3 × 0.250 g) was dissolved in ethanol (3 × 15 mL) to which was added the formazan solution. Following a similar procedure to that recounted in Section 2.3.2, brown colored (**5b**), light green colored (**6b**) and brown colored (**7b**) compounds were obtained. Each compound was recrystallized from methanol. Elemental analysis for $NiC_{38}H_{26}N_{10}O_4Cl_2$, Calc. (%): C, 55.97; H, 3.19; N, 17.18. Found (%): C, 55.93; H, 3.25; N, 17.11. Calc. mass: 814.70. Found mass: *m/z* (eV): 814.70. Other peaks: 437.20, 378.05, 240.05.

*2.3.4. Synthesis of bis[1-(o-, m-, p-bromophenyl)-3-(m-nitrophenyl)-5-phenyl formazanato]nickel(II) complexes (**8b**, **9b**, **10b**)*

Compounds **8a–10a** (0.848 g, 0.002 mol) prepared as in Section 2.2 were dissolved in ethanol (10 mL) and dioxane (25 mL). In separate flasks $Ni(CH_3COO)_2 \cdot 4H_2O$ (3 × 0.001 mol, 3 × 0.250 g) was dissolved in ethanol (3 × 15 mL) to which was added the formazan solution. Following a similar procedure as in Section 2.3.2 the brown colored (**8b**), light green-brown colored (**9b**) and brown colored (**10b**) compounds were filtered and recrystallized from dioxane. Elemental analysis for $NiC_{38}H_{26}N_{10}O_4Br_2$, Calc. (%): C, 50.40; H, 2.87; N, 15.47. Found (%): C, 50.46; H, 2.95; N, 15.42. Calc. mass: 904.70. Found mass: *m/z* (eV): 904.10. Other peaks: 481.15, 423.90, 240.90.

*2.3.5. Synthesis of bis[1-(o-, m-, p-tolylphenyl)-3-(p-methoxyphenyl)-5-phenyl formazanato]nickel(II) complexes (**11b**, **12b**, **13b**)*

Compounds **11a–13a** (0.690 g, 0.002 mol) obtained as in Section 2.2 were dissolved in dioxane (15 mL). In separate flasks $Ni(CH_3COO)_2 \cdot 4H_2O$ (3 × 0.001 mol, 3 × 0.250 g) was dissolved in ethanol (3 × 15 mL) to which was added the formazan solution. Following the procedure described in Section 2.3.2, green-brown colored (**11b**), orange-brown colored (**12b**) and light green-brown colored (**13b**) compounds were obtained. Each compound was recrystallized from methanol. Elemental analysis for $NiC_{42}H_{38}N_8O_2$, Calc. (%): C, 64.89; H, 4.89; N, 14.42. Found (%): C, 64.85; H, 4.95; N, 14.35. Calc. mass: 744.70. Found mass: *m/z* (eV): 744.80. Other peaks: 419.15, 359.10, 225.00.

*2.3.6. Synthesis of bis[1-(o-, m-, p-methoxyphenyl)-3-(p-methoxyphenyl)-5-phenyl formazanato]nickel(II) complexes (**14b**, **15b**, **16b**)*

Compounds **14a–16a** (0.690 g, 0.002 mol) prepared in Section 2.2 were dissolved in dioxane (15 mL). In separate flasks $Ni(CH_3COO)_2 \cdot 4H_2O$ (3 × 0.001 mol, 3 × 0.250 g) was dissolved in ethanol (3 × 15 mL) to which was added the formazan solution. Following the procedure outlined in Section 2.3.2 pink-brown colored (**14b**), green colored (**15b**) and green colored (**16b**) compounds were obtained. Each product was recrystallized from methanol. Elemental analysis for $NiC_{42}H_{38}N_8O_4$, Calc (%): C, 70.72; H, 5.33; N, 15.71. Found (%): C, 70.65; H, 5.28; N, 15.67. Calc. mass: 776.70 Found mass: *m/z* (eV): 777.03. Other peaks: 401.80, 345.20, 225.10.

3. Results and discussion

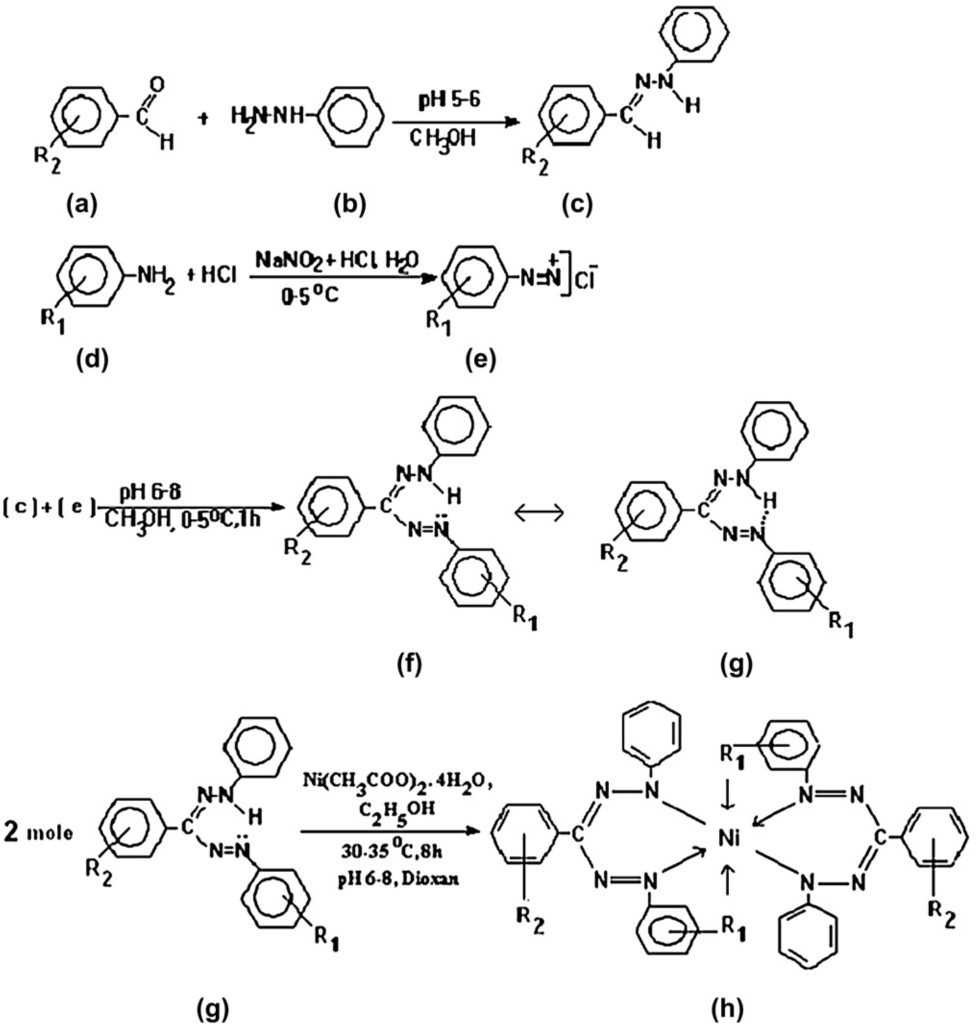
This study was carried out in four steps. In the first and second steps, formazans and their Ni(II) complexes were synthesized; in the third step, their structures and spectroscopic properties were elucidated by elemental analysis, FTIR, ^1H NMR, ^{13}C NMR, UV–vis and GC–mass spectral data whilst in the fourth step, the effects of substituents on the structural properties and the absorption properties of the compounds were investigated. The reaction scheme is provided in Scheme 2 and the experimental data are tabulated in Table 1.

3.1. Synthesis of formazanato Ni(II) complexes

The intermediate hydrazones (**c**) were synthesized at pH 5–6 and the syntheses of the formazans were carried out at pH 9–12. The Ni-complexes were synthesized at pH 6–7 according to Ref. [16] in order to prevent the formation of different isomers.

As seen in Table 1 the yield of the Ni-complexes of *o*-substituted formazans on the 1-phenyl ring was higher than that of the dyes substituted at the *m*- and *p*-positions. These results are not in accordance with Ref [18] and can be explained by the fact that the substituents at the *m*- and *p*-positions were further away from the d-orbitals of Ni^{++} compared to substituents at the *o*-position; the general decrease in yield on going from the *m*- to the *p*-positions verifies this assumption.

The synthesis of the Ni-complexes of –Cl and –Br substituted formazans were particularly difficult (**6b**, **7b**, **9b**, **10b**) and the resulting products were plastic-like, resinous and non-crystallizable, being obtained in powder forms after recrystallization from ethanol–dioxane mixture. The compounds substituted with $-CH_3$ and $-OCH_3$ in the *p*-position on the 1-phenyl ring (**13b**, **16b**) were much easier to prepare in crystallized form compared to other compounds.



Scheme 2. Synthesis of formazans and their Ni-complexes.

Table 1
Experimental and ^{1}H NMR data of Ni-complexes formazans

Compound	Color	Mp (°C)	Yield %	^{1}H NMR[a]			
				Aromatic-H δ (ppm)	Methyl-H δ (ppm)	Methoxy-H δ (ppm)	Solvent (CH_3OH) δ (ppm)
1b	Light brown	300	82	8.02−7.28 (30H)	−	−	3.72, 1.58 (2H)
2b	Brown	239−240	72	9.00−6.92 (26H)	−	−	4.02, 1.58 (2H)
3b	Green-black	299	65	8.80−6.81 (26H)	−	−	3.90, 1.22 (2H)
4b	Green-black	321	61	8.95−6.81 (26H)	−	−	3.30, 2.41 (2H)
5b	Pink-brown	240	79	8.82−7.30 (26H)	−	−	3.30, 1.28 (2H)
6b	Light green	305	65	8.45−7.12 (26H)	−	−	3.74, 1.61 (2H)
7b	Brown	310	63	8.78−7.22 (26H)	−	−	3.32, 1.22 (2H)
8b	Pink-brown	260	82	8.84−7.24 (26H)	−	−	3.32, 1.22 (2H)
9b	Light green	281.5	63	8.50−7.02 (26H)	−	−	3.70, 1.60 (2H)
10b	Brown	298	60	8.62−7.30 (26H)	−	−	3.30, 1.22 (2H)
11b	Light green-brown	244−245	69	8.23−6.92 (26H)	2.50 (6H)	3.80 (6H)	3.82, 1.22 (2H)
12b	Orange-brown	238	63	8.45−6.83 (26H)	2.45 (6H)	3.80 (6H)	3.83, 1.22 (2H)
13b	Light green-brown	295	61	8.15−6.38 (26H)	2.50 (6H)	3.70 (6H)	3.74, 1.39 (2H)
14b	Pink-brown	225−226.5	73	8.28−6.41 (26H)	−	4.02 (12H)	3.90, 1.24 (2H)
15b	Green	273	64	8.42−6.80 (26H)	−	3.92 (12H)	3.90,1.25 (2H)
16b	Green	271−272	60	8.21−6.68 (26H)	−	3.89 (12H)	3.83,1.59 (2H)

[a] The ^{1}H NMR spectra were recorded with 400 MHz (in $CDCl_3$).

3.2. Spectral properties

The results of the elemental analysis and mass spectra are in agreement with the proposed structures (Scheme 1).

3.2.1. ^{1}H NMR

Table 1 shows that the aromatic-H peaks of the substituted Ni-complexes generally shifted to lower fields compared to Ni−TPF complex (**1b**). The extent of this shift decreased in the order: $NO_2 > Br > Cl$, in accord with the electron withdrawing power of the substituent insofar as NO_2 is a stronger electron withdrawing group than Cl and Br. Although there was a shift towards lower fields in the case of electron donating groups, such as CH_3 and OCH_3 this was not of the same magnitude as that of the electron withdrawing groups. This can be explained by the fact that the electron donating effects of CH_3 and OCH_3 were negated by the strong electron withdrawing effect of Ni^{++}.

When the aromatic-H peaks of the Ni-complexes are compared with the corresponding formazans there was observed a shift towards lower fields in accordance with the fact that the electrons in the structure were withdrawn as a result of the insertion of Ni^{++} into the formazan structure [8,26]. In contrast, there was a slight shift towards higher fields in the complexes substituted with Cl and Br.

The N−H peak observed at 2.68−1.18 ppm in the formazans was not present in the Ni-complexes. This is a further proof that the metal ion was inserted in place of the proton of N−H group. The peaks at 4.02−1.22 ppm were attributed to the solvent (CH_3OH). Other CH_3−H and OCH_3−H peaks in the Ni-complexes were found to be at lower fields compared to the formazans, as expected. These data are supported by the IR results.

3.2.2. ^{13}C NMR

As seen from Table 2 the δ value for the C═N carbon of Ni−TPF complex (**1b**) was 174.81 ppm. The attachment of a second electron withdrawing group to the 1-phenyl ring

Table 2
^{13}C NMR data of the Ni-complexes formazans investigated (100 MHz, in $CDCl_3$ and DMSO)

Compound	δ (ppm)	
	Imino-C (C═N)	Other carbons
1b	174.81	163.97, 161.86, 158.67, 157.90, 155.03, 153.47, 152.20, 150.21, 149.01, 148.61, 142.21, 139.03, 130.42, 127.90, 126.33, 120.59, 118.50 (total 18C)
2b	172.50	152.40, 149.60, 148.80, 147.60, 147.40, 146.20, 145.20, 143.20, 142.00, 141.60, 140.40, 139.20, 137.80, 136.40, 135.20, 134.20, 134.00, 133.60, 132.80, 131.40, 130.60, 130.00, 128.80, 128.00, 126.80, 126.00, 124.40, 122.80, 122.60, 121.20, 120.04, 118.80, 116.80 (total 34C)
3b	174.80	161.70, 151.33, 149.33, 147.50, 146.33, 145.00, 144.00, 142.67, 141.00, 138.83, 138.00, 136.33, 134.33, 133.50, 132.67, 132.00, 131.67, 130.18, 129.00, 128.00, 127.00, 126.00, 124.33, 123.00, 122.17, 121.00, 120.33, 18.33, 116.67, 113.70, 113.00, 110.50, 109.25 (total 34C)
4b	175.22	165.50, 150.31, 148.44, 147.50, 145.63, 144.37, 142.81, 141.87, 140.62, 139.37, 138.12, 137.81, 136.25, 134.06, 132.81, 131.25, 130.00, 129.06, 128.12, 126.87, 125.62, 123.75, 122.50, 120.31, 118.75, 117.81, 116.56, 115.00, 92.30 (Total 30C)
5b	175.31	167.81, 163.90, 150.94, 149.69, 147.96, 146.72, 145.62, 144.53, 143.75, 143.12, 141.72, 141.09, 140.62, 139.75, 137.75, 137.00, 134.50, 133.25, 132.75, 131.25, 130.00, 128.75, 127.00, 126.25, 125.10, 124.50, 123.00, 122.50, 122.00, 120.15, 116.00, 113.50, 108.20 (total 34C)
6b	175.36	172.06, 164.80, 160.00, 153.05, 149.44, 148.89, 148.33, 147.22, 145.56, 144.17, 143.33, 142.50, 141.39, 140.00, 139.17, 137.50, 136.39, 135.28, 134.44, 133.89, 132.50, 131.11, 130.00, 128.06, 127.67, 125.10, 124.17, 123.33, 122.78, 121.67, 121.39, 119.78, 116.28 (total 34C)
7b	174.80	172.36, 163.85, 149.44, 148.33, 146.67, 145.00, 144.44, 143.33, 142.22, 141.11, 139.89, 137.78, 136.67, 135.47, 134.44, 133.89, 132.78, 131.11, 130.23, 129.79, 128.89, 127.78, 125.56, 122.22, 120.38, 119.44, 117.22, 115.00, 110.00 (total 30C)
8b	172.38	164.87, 163.32, 150.15, 149.61, 149.00, 148.65, 147.11, 146.15, 145.38, 144.42, 143.07, 141.73, 140.96, 140.19, 139.42, 137.88, 135.70, 135.00, 134.42, 133.27, 131.92, 130.96, 129.42, 128.65, 127.50, 126.54, 125.00, 124.04, 122.50, 121.54, 118.85, 115.58, 107.52 (total 34C)
9b	175.02	170.38, 164.86, 152.86, 151.07, 148.57, 146.43, 145.71, 144.98, 143.57, 142.14, 141.07, 139.29, 138.57, 136.43, 135.10, 134.28, 133.57, 131.78, 130.71, 130.00, 129.28, 127.78, 127.50, 126.79, 126.07, 125.00, 120.00, 119.28, 117.14, 115.00, 112.88, 111.07, 108.57 (total 34C)
10b	174.96	167.47, 156.50, 149.38, 149.00, 148.17, 147.50, 146.53, 145.97, 145.00, 144.50, 143.25, 142.80, 141.53, 140.82, 140.10, 139.50, 139.38, 138.50, 136.65, 135.00, 134.81, 129.17, 126.10, 124.64, 122.50, 120.00, 117.22, 113.90, 110.88 (total 30C)
11b	186.87	175.28, 167.63, 164.47, 160.00, 155.10, 151.75, 150.28, 149.47, 148.64, 148.29, 147.27, 146.14, 145.00, 144.54, 143.97, 143.41, 140.57, 138.97, 133.65, 130.18, 129.25, 128.51, 128.24, 127.93, 126.35, 125.74, 123.38, 121.90, 114.73 (total 30C)
12b	185.87	177.60, 174.68, 167.55, 164.53, 163.21, 160.92, 158.25, 157.59, 155.23, 151.08, 149.54, 147.40, 145.68, 143.75, 142.97, 140.27, 138.30, 132.45, 131.85, 130.28, 128.87, 127.54, 126.00, 125.56, 124.02, 120.05, 119.45, 118.30, 117.05 (total 30C)
13b	174.80	169.11, 168.21, 167.86, 164.91, 160.00, 158.21, 156.25, 152.32, 149.28, 147.50, 145.53, 143.93, 140.10, 138.22, 136.78, 134.88, 131.25, 130.07, 129.28, 127.85, 123.21, 120.07, 120.00, 119.11, 118.21 (total 26C)
14b	186.67	175.02, 167.78, 165.00, 163.78, 157.62, 153.33, 150.00, 145.07, 144.33, 142.17, 140.83, 138.67, 135.67, 134.33, 133.00, 132.33, 130.83, 129.50, 127.67, 126.17, 126.00, 124.17, 122.33, 121.43, 120.67, 119.33, 117.67, 116.00, 115.00 (total 30C)
15b	185.56	177.42, 175.05, 168.98, 165.47, 163.50, 161.32, 160.85, 158.65, 156.52, 154.74, 151.65, 150.75, 149.00, 148.91, 147.75, 146.03, 144.56, 143.07, 141.52, 140.96, 138.32, 135.65, 128.85, 126.14, 120.26, 118.10, 116.25, 115.12, 113.32 (total 30C)
16b	182.62	175.24, 168.33, 167.38, 164.28, 161.19, 157.14, 155.24, 152.14, 149.76, 149.04, 145.95, 143.33, 142.62, 141.43, 140.24, 137.38, 135.71, 134.28, 130.95, 129.76, 128.33, 125.95, 122.62, 120.12, 117.38 (total 26C)

Table 3
The IR spectral data of the Ni-complexes formazans **1b−16b** (KBr, cm^{-1})

Compound	Aromatic C−H	Aromatic C=C	C=N	−NO$_2$	−CH3 and −OCH3	N=N	CNNC structural vibration
1b	3098−3025	1600	1500	−	−	1410	780−550
2b	3500−3410	1660	1517	1482	−	1357	893−678
3b	3500−3410	1607	1526	1520	−	1348	803−652
4b	3500−3428	1669	1527	1455	−	1348	812−661
5b	3482−3384	1589	1527	1339	−	1241	813−652
6b	3482−3428	1607	1563	1339	−	1276	830−679
7b	3480−3410	1607	1536	1348	−	1277	857−679
8b	3491−3411	1598	1527	1339	−	1232	813−652
9b	3490−3464	1580	1536	1348	−	1214	800−650
10b	3490−3411	1571	1527	1339	−	1276	813−643
11b	3480−3410	1580	1518	−	1241	1027	839−589
12b	3475−3410	1580	1500	−	1241	1027	840−590
13b	3419−3366	1598	1500	−	1241	1027	857−544
14b	3490−3455	1607	1509	−	1223	1027	839−616
15b	3480−3420	1580	1500	−	1240	1027	835−620
16b	3464−3410	1580	1500	−	1268	1054	821−536

while the 3-phenyl ring contained an electron withdrawing *m*-NO$_2$, did not cause a significant change in the δ values. However, the attachment of an electron donating group to the 1-phenyl ring such as CH$_3$ and OCH$_3$ caused the δ values to increase slightly. The C=N carbon peaks of the Ni-complexes were at lower field compared with those of the corresponding formazan. The C=N peaks normally observed between 148.80 and 164.50 ppm in the formazans were shifted to 172.50−186.67 ppm in the Ni-complexes. This result is in accord with the insertion of the electron withdrawing group Ni^{++} into the system. Other C peaks can also be evaluated in a similar manner [7].

3.2.3. IR

As seen from Table 3 ν(C=N) bands observed between 1530 and 1495 cm^{-1} in the formazans were shifted to 1536−1500 cm^{-1} in the Ni-complexes, in accordance with the formation of a more stable chelate structure by the insertion of Ni^{++} into the structure [8,25,27].

The ν(N−H) bands observed at 3100−2800 cm^{-1} in the case of the formazans were generally not present in the complexes. However, new peaks emerged, as exemplified by the peaks at 3089−2937 cm^{-1} which can be attributed to ligand−metal peaks. This is verification of the formation of Ni-complexes as a result of insertion of Ni^{++} in place of an H atom in N−H [12] and confirms the proposed formula given in Scheme 1. However, the N−H band was weakly observed in compounds **6b**, **13b** and **16b**; these results are in agreement with the literature [7,14].

The ν(N=N) bands normally observed at 1450−1010 cm^{-1} in the formazans were shifted to 1410−1027 cm^{-1} in the Ni-complexes while there was a slight increase seen for the remaining compounds **12b−14b**, **16b**. These results are in good agreement with the literature [12]. Other aromatic C−H, C=C, CNNC skeleton stretching peaks and NO$_2$, CH$_3$, OCH$_3$ vibration bands in the compounds were observed in their expected regions. Examples of the changes in the bands belonging to C=N, N−H and N=N groups of **9a** and **9b** are shown in Fig. 1.

3.3. Substituent effects on the UV−vis absorption λ_{max} values

As seen from Table 4 there were three peaks observed in the UV−vis spectra of the Ni-complexes of the formazans. λ_{max1} for the Ni-complexes, λ_{max2} for formazans and λ_{max3} for the hydrazones were attributed to the absorption peaks [8,20,21]. It is not appropriate to compare the UV−vis peaks of the formazans with that of their Ni-complex counterparts, as the spectra of the formazans were recorded using acetone while the spectra of the Ni-complexes were recorded using DMSO as the complexes were not entirely soluble in acetone. However, it is apparent that the λ_{max1} values of the complexes were significantly shifted towards higher wavelengths. These results are in compliance with the literature [7,8,10,11,16,18].

When the $\Delta\lambda_{max}$ values are considered according to the nature of the substituent, it is evident that the size of the shift was small when the 1-phenyl ring had been substituted with

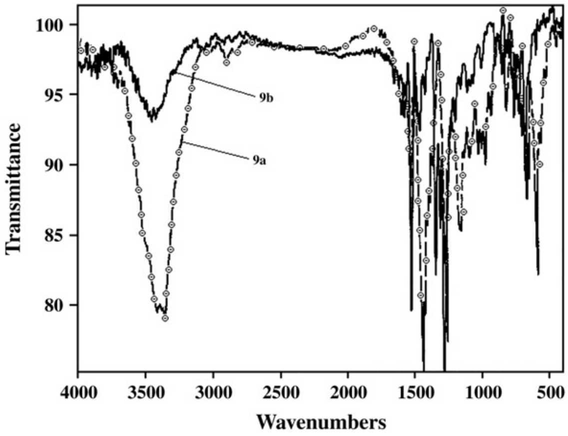


Fig. 1. Comparison of the IR bands of compounds **9a** and **9b**.

Table 4
UV–vis absorption maxima of the Ni-complexes formazans **1b–16b** (DMSO, 10^{-5} mol L^{-1})

Compound	Abbreviation	λ_{max1}/nm (Abs)	λ_{max2}/nm (Abs)	λ_{max3}/nm (Abs)	Chemical shift ($\Delta\lambda_{max}$)
1b	Ni–TPF	611.0 (0.067)	448.0 (0.493)	275.0 (0.772)	–
2b	Ni-*o*-NNF	607.0 (0.079)	481.0 (0.684)	303.0 (1.510)	4
3b	Ni-*m*-NNF	613.0 (0.045)	417.8 (0.119)	–	2
4b	Ni-*p*-NNF	617.0 (0.030)	446.0 (0.505)	–	6
5b	Ni-*o*-CNF	621.0 (0.032)	481.0 (0.740)	305.0 (1.338)	10
6b	Ni-*m*-CNF	619.0 (0.063)	415.6 (0.548)	-	8
7b	Ni-*p*-CNF	624.0 (0.058)	426.0 (0.402)	275.0 (1.423)	13
8b	Ni-*o*-BNF	622.0 (0.054)	479.0 (0.617)	304.0 (1.176)	11
9b	Ni-*m*-BNF	618.0 (0.064)	413.4 (0.452)	298.0 (1.164)	7
10b	Ni-*p*-BNF	625.1 (0.047)	415.8 (0.354)	355.0 (0.648)	14.1
11b	Ni-*o*-MMOF	654.0 (0.046)	458.0 (0.338)	307.0 (1.159)	43
12b	Ni-*m*-MMOF	647.0 (0.053)	454.0 (0.467)	299.0 (1.146)	36
13b	Ni-*p*-MMOF	644.0 (0.046)	452.0 (0.087)	–	33
14b	Ni-*o*-MOF	661.0 (0.032)	460.0 (0.366)	311.0 (1.557)	50
15b	Ni-*m*-MOF	649.0 (0.042)	464.0 (0.527)	322.0 (1.254)	38
16b	Ni-*p*-MOF	642.0 (0.030)	456.0 (0.177)	274.0 (1.391)	31

Column 6: $\Delta\lambda_{max} = \lambda_{max1}$(Ni–TPF) – λ_{max1} (substituted Ni-complexes formazans).

electron withdrawing groups (NO_2, Cl, Br) and high when electron donating groups (CH_3 and OCH_3) were attached to the 1-phenyl ring. These results are depicted in Fig. 2a,b. When the λ_{max} values are considered according to the positions of the substituents on the 1-phenyl ring, the shift observed for the complexes containing NO_2, Cl, Br followed the order: *p*- > *o*- > *m*-positions. This result was expected due to the inductive and resonance effects of the electron withdrawing NO_2 group and the inductive effects of electron withdrawing and resonance effects of the electron donating Br and Cl substituents. In the complexes containing CH_3 and OCH_3 the size of the shift observed in absorption values ($\Delta\lambda_{max}$) followed the order: *o*- > *m*- > *p*-positions. This may be explained by the decreasing inductive effect on going from the *o*- to the *p*-position (Fig. 3).

It is noteworthy that in the literature it was claimed that the λ_{max} values of the complexes were shifted towards lower wavelengths [9]. When UV–vis data were recorded using CH_2Cl_2 the peaks located around 600 nm were seen to disappear and the peaks between 415 and 481 nm became dominant. Since it is a common fact that λ_{max} values change with solvent, it is not appropriate to say that the complexes underwent a hypsochromic change based upon a single experiment. This issue will be investigated in future studies.

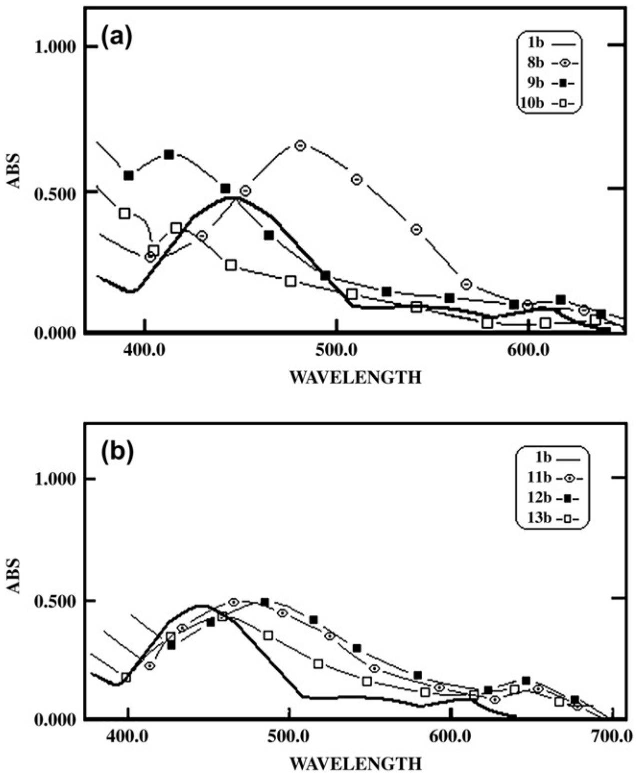


Fig. 2. UV–vis spectra of: (a) compounds **8b–10b** compared to **1b**; (b) compounds **11b–13b** compared to **1b**.

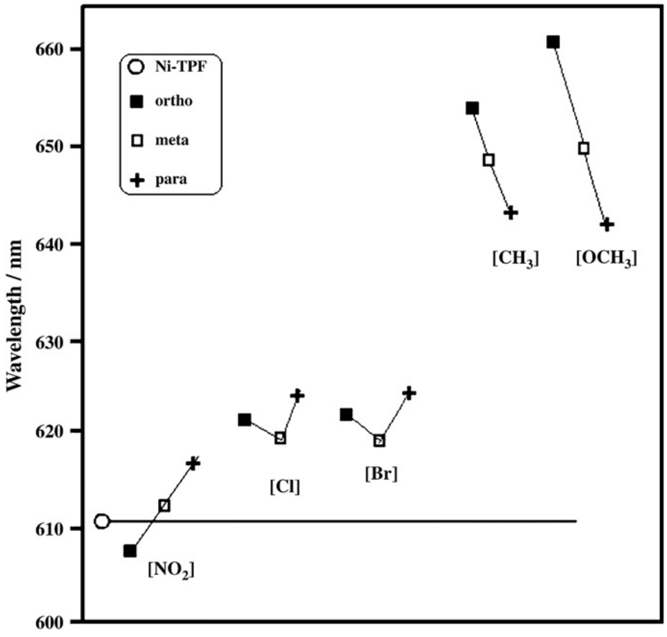


Fig. 3. Comparison of λ_{max} values of Ni-complexes formazans (**2b–16b**) with **1b**.

Table 5
The total σ_T ($\sigma_1 + \sigma_2 = \sigma_T$) and related λ_{max} values

Substituent position	Compound	Abbreviation	σ's	σ_T (total effect)	λ_{max1} (nm)
m-	**1b**	H	H: 0	0	611.0
	3b	*m*-NO_2, *m*-NO_2	*m*-NO_2: 0.71; *m*-NO_2: 0.71	1.42	613.0
	6b	*m*-Cl, *m*-NO_2	*m*-Cl: 0.37; *m*-NO_2: 0.71	1.08	619.0
	9b	*m*-Br, *m*-NO_2	*m*-Br: 0.37; *m*-NO_2: 0.71	1.08	618.0
	12b	*m*-CH_3, *p*-OCH_3	*m*-CH_3: -0.06; *p*-OCH_3: −0.12	−0.18	647.0
	15b	*m*-OCH_3, *p*-OCH_3	*m*-OCH_3: 0.10; *p*-OCH_3: −0.12	−0.02	649.0
p-	**4b**	*p*-NO_2, *m*-NO_2	*p*-NO_2: 0.81; *p*-NO_2: 0.71	1.52	617.0
	7b	*p*-Cl, *m*-NO_2	*p*-Cl: 0.24; *p*-NO_2: 0.71	0.95	624.0
	10b	*p*-Br, *m*-NO_2	*p*-Br: 0.26; *p*-NO_2: 0.71	0.97	625.0
	13b	*p*-CH_3, *p*-OCH_3	*p*-CH_3: −0.14; *p*-OCH_3: −0.12	−0.26	644.0
	16b	*p*-OCH_3, *p*-OCH_3	*p*-OCH_3: −0.12; *p*-OCH_3: −0.12	−0.24	642.0

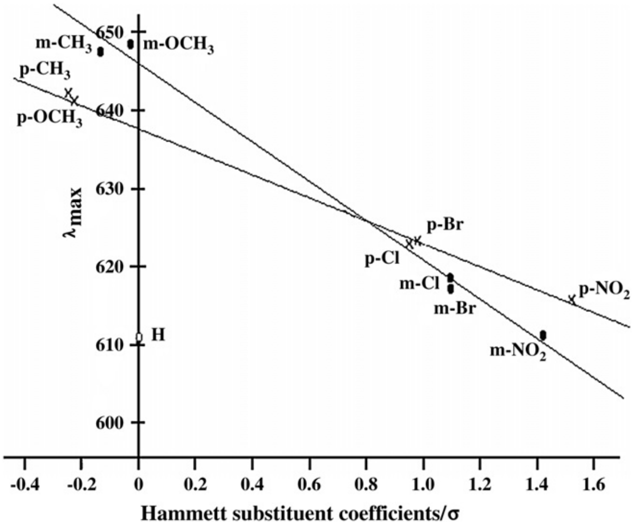


Fig. 4. The λ_{max} values against the σ.

4. Conclusions

4.1. The relation between the λ_{max} values and Hammett substituent coefficients (σ)

Hammett substituent coefficients (σ) are used to evaluate the effect of substituents on the rate of a chemical reaction whose mechanism is known. Hammett substituent coefficients (σ) have generally been related to λ_{max} values for only one substituent thus far. This study investigated whether or not the Hammett substituent coefficient (σ) could be used to evaluate the total effect of σ_T ($\sigma_1 + \sigma_2 = \sigma_T$) of two different substituents upon λ_{max} and, thus, color. The relationship between total σ_T ($\sigma_1 + \sigma_2 = \sigma_T$) and λ_{max} are tabulated in Table 5 and are plotted in Fig. 4.

As seen from Fig. 4 there was a linear correlation between Hammett substituent coefficient, σ_T and λ_{max}, showing that it is possible to use the summation of Hammett substituent coefficients σ_T ($\sigma_1 + \sigma_2 = \sigma_T$) to evaluate the absorptional properties of the compounds.

Acknowledgement

We are very grateful to the Gazi University Research Fund for providing financial support for this project (no. 04/2004-13).

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