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The synthesis and spectroscopic characterization of Ni(II) complexes of 1-substituted phenyl-3,5-diphenylformazans

Habibe Tezcan*, Elif Uzluk

Department of Chemistry, Gazi University, Faculty of Gazi Education, Teknikokullar, 06500 Ankara, Turkey

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Abstract

Novel Ni(II) complexes of formazans containing $-NO_2$, $-COOH$, $-Cl$, $-Br$, $-CH_3$ groups in the *o*-, *m*-, *p*-positions of the 1-phenyl ring were synthesized. The dyes were characterized using elemental analysis, 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 broad absorption band was observed at 426–446 nm in CH_2Cl_2 at 25 °C. A linear correlation was obtained between Hammett substituent coefficients and λ_{max} values.

Keywords: Formazan dyes; Nickel complex dyes; Spectroscopy; Mass spectra; Substituent effect

1. Introduction

Formazans are colored compounds, owing to π bonds and contain azohydrazone conjugated double bonds (Scheme 1). Their color ranges from cherry red to red-violet. 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 were investigated [1,2]. Metal complexes of formazans are also colored compounds. Since the first nickel complexes of formazans were synthesized by Hunter–Roberts, numerous nickel complexes of formazans have been synthesized [3]. The ionization constants and stability constants of La(III) complexes have been determined and their synthesis have been accomplished [4]. Structural, TGA and DTA studies on 3-acetyl-1,5-diaryl and 3-cyano-1,5-diaryl formazan chelates with Ce(III), Th(IV) and U(VI) were carried out [5]. Crystal structures and magnetic properties of Fe and Mn complexes were determined [6]. IR, PMR and TG studies on substituted 1,3,5-triphenylformazan complexes with bivalent Co, Ni, Cu and Zn were carried out [7,8]. On the other hand synthesis of Fe complexes of 1,5-diaryl-3-cyanoformazans was accomplished and their spectral properties were determined, and dyeing rate and chrominance properties on wool and polyamide fibers were studied [9]. It was determined that the formation of Fe complexes was dependent upon the pH value and it was observed by the same researcher [10] that two different isomers were formed at pH 2 and pH 7–8. Synthesis of metal complexes of formazan and complex stability constant determination were investigated [11,12]. The latter study revealed that Fe complexes were less toxic than the corresponding Cr and Co complexes with the same structure [13]. Metal complex dyes are used widely on textile substrates as they provide shades of high fastness to light, wet treatments and other agencies [14].

Previous work focused 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. The electrochemical investigation of their nitro derivatives and quantum chemical calculations of bis-formazan were also carried out [15–20].

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* Corresponding author. Fax: +90 312 2227037.
E-mail address: habibe@gazi.edu.tr (H. Tezcan).

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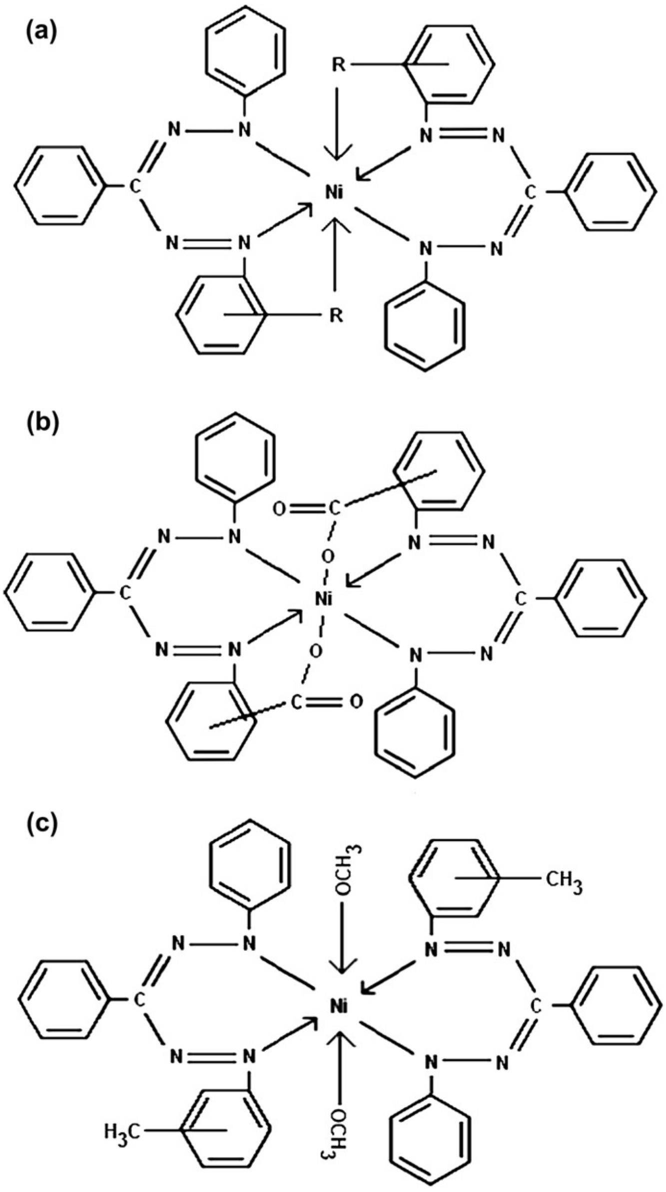
Despite the fact that metal complexes of formazans are widely used as dyes there are only a limited number of publications that concern the Ni(II) complexes of formazans. We decided to investigate the Ni(II) complexes of formazans because the formation of such complexes should be efficient due to smaller size of the nickel atom compared to other metals in the same group in the periodic table. Accordingly, 1-substituted phenyl-3,5-diphenylformazans were synthesized once more [15] and their Ni(II) complexes were synthesized and their structures were identified using elemental analyses, FTIR, ^{1}H NMR, ^{13}C NMR, UV–vis, and GC–mass spectral data. Since coloring property is dependent upon absorption λ_{max} value, the effect of substituents upon λ_{max} value was 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(II) complexes of formazan synthesized in this study were obtained using a Unicam UV2-100 UV–visible spectrophotometer equipped with 1 cm quartz cells in 10^{-5} mol L^{-1} CH_2Cl_2 in the range of 250–700 nm. IR spectra were recorded on a Mattson 100-FT-IR spectrophotometer between 4000 and 400 cm^{-1} using KBr pellets. ^{1}H NMR spectra were recorded on a Bruker Avance DPX-400 MHz and ^{13}C NMR spectra were performed on 100 MHz spectrophotometer using $CDCl_3$ and DMSO-d_6, 10^{-4} mol L^{-1}. Elemental analyses



Scheme 1. The structure of: (**a**) the Ni(II) complexes (**1a**–**4a**, **8a**–**13a**) of formazan derivatives; (**b**) the Ni(II) complexes (**5b**–**7b**) of formazan derivatives ; (**c**) the Ni(II) complexes of (**14c**–**16c**) formazan derivatives.

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 (**1–16**) were synthesized by the reaction of benzaldehyde (1.06 g, 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. [15].

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

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

2.3.1. Preparation of bis (1,3,5-triphenylformazanato)nickel(II) complex (*1a*)

1,3,5-Triphenylformazan (**1**) (1.500 g, 0.005 mol) obtained as described in Ref. [15] was dissolved in dioxane (20 mL). In another flask, $Ni(CH_3COO)_2 \cdot 4H_2O$ salt (0.0025 mol, 0.625 g) was dissolved in ethanol (25 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 washed with 10 mL 0.5 M NaOH, water and methanol. The compound was dried in stove at 40 °C for 24 h and recrystallized from methanol.

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

Compounds **2–4** (0.690 g, 0.002 mol) obtained as in Section 2.2 were dissolved in ethanol (15 mL)–dioxane (10 mL) mixture. In separate flasks, $Ni(CH_3COO)_2 \cdot 4H_2O$ (3×0.001 mol, 3×0.250 g) was dissolved in ethanol (3×10 mL) to which were added the formazan solutions. The mixtures were stirred at 30–35 °C under reflux for 8 h and kept in the dark for 3 days. The light pink-brown colored (**2a**), yellow-brown colored (**3a**) and violet-black colored (**4a**) compounds were filtered, washed with water and methanol, recrystallized from methanol and dried in stove at 40 °C for 24 h. Elemental analysis for $NiC_{38}H_{28}N_{10}O_4$ (comp. **3a**): calcd. (%): C, 61.23; H, 3.49; N, 18.79. Found (%): C, 61.17; H, 3.21; N, 18.49. Calcd. mass: 744.70 for compound **3a**. Found mass, *m*/*z* (eV): 744.30. Other peaks: 404.20, 345.10, 299.10, 194.15, 105.10.

2.3.3. Preparation of bis [1-(o-, m-, p-carboxyphenyl)-3,5-diphenylformazanato]nickel(II) complexes (*5b*, *6b*, *7b*)

Compounds **5–7** (0.688 g, 0.002 mol) prepared as in Section 2.2 were dissolved in ethanol (10 mL)–dioxane (10 mL) mixture. In separate flasks, $Ni(CH_3COO)_2 \cdot 4H_2O$ (3×0.001 mol, 3×0.250 g) was dissolved in ethanol (3×10 mL) to which were added the formazans. Following a similar procedure to that recounted in Section 2.3.2, purple colored (**5b**), yellow colored (**6b**) and brown colored (**7b**) compounds were obtained. Each compound was recrystallized from methanol. Elemental analysis for $NiC_{40}H_{30}N_8O_4$ (comp. **5b**): calcd. (%): C, 64.62; H, 3.77; N, 15.08. Found (%): C, 64.07; H, 4.01; N, 14.82. Calcd. mass: 742.70 for compound **5b**. Found mass, *m*/*z* (eV): 743.50. Other peaks: 403.40, 344.10, 299.10, 194.50.

2.3.4. Preparation of bis [1-(o-, m-, p-chlorophenyl)-3,5-diphenylformazanato]nickel(II) complexes (*8a*, *9a*, *10a*)

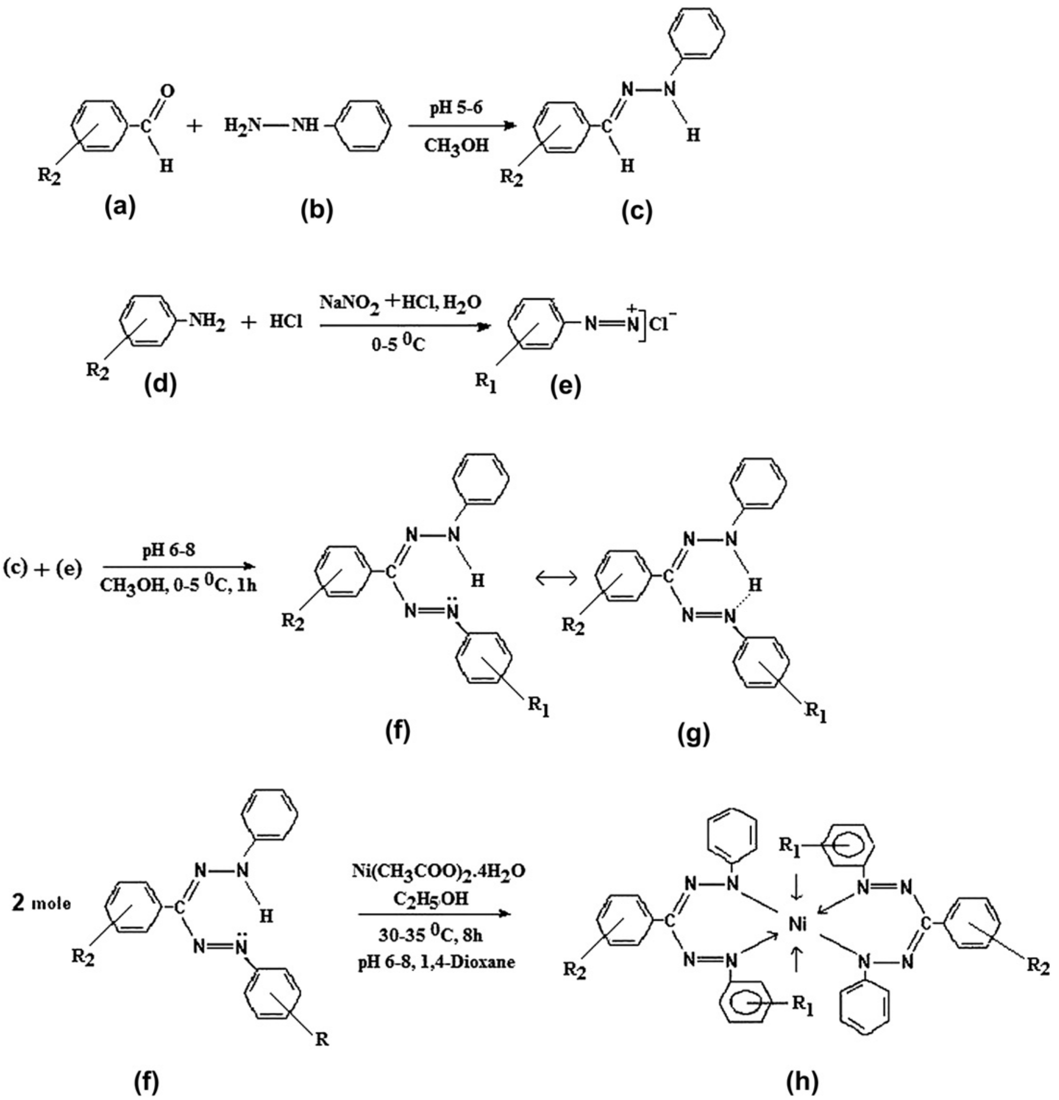
Compounds **8–10** (0.688 g, 0.002 mol) prepared as in Section 2.2 were dissolved in ethanol (15 mL)–dioxane (20 mL) mixture. In separate flasks, $Ni(CH_3COO)_2 \cdot 4H_2O$ (3×0.001 mol, 3×0.250 g) was dissolved in ethanol (3×10 mL) to which were added the formazan solutions. Following a similar procedure to that recounted in Section 2.3.2, light pink-brown colored (**8a**), light green colored (**9a** and **10a**) compounds were obtained. Each compound was recrystallized from methanol. Elemental analysis for $NiC_{38}H_{28}N_8Cl_2$ (comp. **9a**): calcd. (%): C, 63.09; H, 3.59; N, 15.49. Found (%): C, 63.28; H, 3.23; N, 15.12. Calcd. mass: 722.70 for compound **9a**. Found mass, *m*/*z* (eV): 722.90. Other peaks: 394.30, 335.00, 301.10, 194.10.

2.3.5. Preparation of bis [1-(o-, m-, p-bromophenyl)-3,5-diphenylformazanato]nickel(II) complexes (*11a*, *12a*, *13a*)

Compounds **11–13** (0.758 g, 0.002 mol) prepared as in Section 2.2 were dissolved in ethanol (15 mL)–dioxane (10 mL) mixture. 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 were added the formazan solutions. Following a similar procedure to that recounted in Section 2.3.2, light pink-brown colored (**11a**), yellow-green colored (**12a**) and light brown colored (**13a**) compounds were obtained. Each compound was recrystallized from methanol. Elemental analysis for $NiC_{38}H_{28}N_8Br_2$ (comp. **12a**): calcd. (%): C, 56.10; H, 3.19; N, 13.78. Found (%): C, 55.80; H, 2.89; N, 13.20. Calcd. mass: 812.70 for compound **12a**. Found mass: *m*/*z* (eV): 813.00. Other peaks: 437.20, 379.00, 299.00, 195.00.

2.3.6. Preparation of bis [1-(o-, m-, p-tolylphenyl)-3,5-diphenylformazanato]nickel(II) complexes (*14c*, *15c*, *16c*)

Compounds **14–16** (0.628 g, 0.002 mol) prepared as in Section 2.2 were dissolved in ethanol (4 mL)–dioxane (8 mL) mixture. In separate flasks, $Ni(CH_3COO)_2 \cdot 4H_2O$ (3×0.001 mol, 3×0.250 g) was dissolved in ethanol (3×10 mL) to which were added the formazan solutions. Following a similar procedure to that recounted in Section 2.3.2, yellow-green colored (**14c**), green-brown colored (**15c**) and light green colored (**16c**) compounds were obtained. Each compound was recrystallized from methanol. Elemental analysis for $NiC_{42}H_{42}N_8O_2$ (comp. **14c**): calcd. (%): C, 70.03; H, 4.68; N, 16.40. Found (%): C, 69.38; H, 4.23; N, 16.08. Calcd. mass: 746.70 for compound **14c**. Found mass, *m*/*z* (eV): 747.00. Other peaks: 599.60, 314.20, 299.10, 195.00.



Scheme 2. Synthesis of formazans and their Ni(II) complexes.

Table 1
Experimental and ^{1}H NMR data of Ni(II) complexes of formazans (**1a**–**4a**, **5b**–**7b**, **8a**–**13a**, **14c**–**16c**) investigated

Comp.	Color	Mp/°C (lit)	Yield % (lit)	^{1}H NMR[a]		
				Aromatic-H δ (ppm)	Methyl-H δ (ppm)	Solvent (CH_3OH) δ (ppm)
1a	Light brown	300 (300)	82 (9)	8.18–7.45 (30H)	–	1.6
2a	Light pink-brown	274–275	70	8.58–7.14 (28H)	–	1.6
3a	Yellow-brown	291–292	61	8.52–7.10 (28H)	–	3.7, 1.6
4a	Violet-black	294–295	50	8.45–6.98 (28H)	–	2.8, 1.6
5b	Violet	268–269	50	8.45–7.36 (28H)	–	3.5, 2.5
6b	Yellow	281–282	45	8.12–7.10 (28H)	–	3.3, 2.6
7b	Brown	298–299	47	8.28–6.98 (28H)	–	3.2, 2.6
8a	Light pink-brown	247–248	65	8.24–7.09 (28H)	–	1.6
9a	Light green	276–277	60	8.25–7.00 (28H)	–	1.6
10a	Light green	289–290	62	8.18–6.90 (28H)	–	3.7, 1.5
11a	Light pink-brown	264–265	66	8.29–7.05 (28H)	–	1.6
12a	Yellow-green	275–276	65	8.28–6.98 (28H)	–	3.8, 1.6
13a	Light brown	282–283	40	8.22–7.12 (28H)	–	3.8, 1.6
14c	Yellow-green	299–300	70	8.10–6.91 (28H)	2.58 (6H)	3.8, 1.6
15c	Green-brown	272–273	66	8.22–6.84 (28H)	2.28 (6H)	2.3, 1.6
16c	Light green	282–283	61	7.90–6.59 (28H)	2.52 (6H)	3.4, 2.5

[a] The ^{1}H NMR spectra were recorded with 400 MHz (in $CDCl_3$ and DMSO-d_6).

Table 2
^{13}C NMR data of the Ni(II) complexes of formazans (**1a**–**4a**, **5b**–**7b**, **8a**–**13a**, **14c**–**16c**) investigated (100 MHz, in $CDCl_3$ and DMSO-d_6)

Comp.	δ ppm	
	Imino-C (C=N)	Other explicit carbons
1a	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)
2a	152.80	143.96, 140.76, 137.09, 135.98, 135.00, 133.97, 133.58, 130.52, 129.48, 129.15, 127.21, 126.35, 125.43, 123.24, 122.61, 116.86
3a	174.50	160.02, 153.57, 151.07, 150.36, 146.07, 144.28, 142.86, 139.28, 136.07, 133.21, 131.78, 129.80, 128.57, 126.07, 124.64, 121.71, 119.64, 116.78
4a	175.10	170.46, 167.50, 162.81, 151.72, 147.97, 143.28, 140.62, 135.16, 134.56, 132.35, 129.86, 128.12, 122.50, 112.38
5b	175.18	160.04, 157.81, 156.87, 154.37, 153.12, 149.68, 148.12, 145.94, 142.18, 133.75, 130.10, 126.25, 123.75, 122.50, 120.05, 116.87, 115.00, 111.25
6b	175.50	160.03, 157.50, 153.33, 151.67, 144.30, 142.64, 139.17, 137.50, 136.53, 135.56, 133.33, 132.64, 130.00, 139.17, 120.00, 117.22, 114.86, 113.34
7b	175.10	160.03, 157.06, 150.48, 145.29, 144.90, 144.11, 141.76, 137.35, 133.53, 132.94, 127.35, 124.11, 119.12, 116.76
8a	152.50	150.00, 149.40, 148.47, 147.35, 146.60, 143.85, 142.30, 136.80, 131.00, 130.42, 129.14, 128.75, 127.15, 126.27, 123.50, 121.24, 116.15
9a	163.80	154.18, 152.90, 151.51, 147.21, 145.69, 137.28, 136.19, 132.61, 130.54, 130.11, 129.53, 129.28, 127.07, 125.65, 124.37, 124.03, 121.30, 119.78
10a	151.58	150.30, 149.75, 148.72, 147.11, 139.00, 137.50, 128.79, 128.18, 127.09, 125.75, 124.76, 124.36, 122.75
11a	151.23	149.53, 147.56, 146.28, 145.11, 143.03, 139.65, 133.72, 133.64, 130.56, 129.37, 129.33, 128.69, 126.81, 126.12, 121.80, 117.04, 114.76
12a	175.16	152.00, 151.40, 150.31, 149.37, 148.75, 144.37, 143.75, 141.87, 137.03, 136.25, 135.10, 129.06, 128.59, 125.10, 124.06, 120.47, 120.07, 118.28
13a	175.28	154.03, 152.11, 150.38, 148.84, 147.88, 145.96, 144.42, 139.24, 130.12, 125.10, 121.50, 118.23, 116.10, 111.00
14c	175.28	161.43, 160.21, 156.43, 154.85, 153.57, 148.50, 144.50, 139.80, 138.10, 136.50, 133.00, 129.75, 128.00, 125.10, 124.80, 123.00, 119.85, 116.00
15c	171.05	167.37, 164.74, 157.37, 155.26, 149.47, 147.36, 145.79, 144.73, 143.16, 137.37, 135.79, 132.63, 131.05, 125.256, 123.68, 122.56, 117.10
16c	174.00	165.10, 161.00, 158.75, 156.00, 147.00, 146.50, 144.85, 142.00, 141.50, 134.50, 129.90, 127.50, 122.50, 120.50

3. Results and discussion

This study was carried out in four stages. 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 analyses, FTIR, ^{1}H NMR, ^{13}C NMR, UV–vis, GC–mass spectral data; in the fourth step, the effects of the substituents on the structural properties and the absorption properties of the compounds were also 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 formazans were carried out at pH 9–12. The Ni(II) complexes were synthesized at pH 6–7 according to Ref. [10] in order to prevent the formation of different isomers.

As seen from Table 1, the yield of Ni(II) complexes of *o*-substituted formazans on the 1-phenyl ring was higher than that of the dyes substituted at the *m*- and *p*-positions. This can be explained by the fact that the substituents at the *m*- and *p*-positions were further away from the d-orbitals of Ni^{2+} compared to the substituent at the *o*-position. It is much more difficult for the d-orbitals of a metal ion to overlap with the orbitals of the ligand. It also may be the result of the various solubilities of synthesized isomers in the solvents used during their preparation and purification. The general decrease of the yield on going from the *m*- to the *p*-positions verifies this assumption.

The syntheses of the Ni(II) complexes of –COOH substituted formazans (comps. **5b**–**7b**) were particularly difficult and the resulting products were plastic-like, being obtained in powder form after recrystallization from ethanol–dioxane mixtures.

The compounds substituted with $-CH_3$ (comps. **14c**–**16c**) in the *o*-, *m*-, *p*-positions of the 1-phenyl ring were much easier to prepare in crystallized form compared to other products.

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(II) complexes generally shifted to lower fields compared to Ni-TPF complex (**1a**). The extent of this shift decreased in the order: $NO_2 > COOH > Br > Cl > CH_3$, in accord with the electron withdrawing and donating power of the substituents. Since NO_2 and COOH groups are electron withdrawing as regards to both resonance and inductive effects, their effect on the shift of aromatic-H peak to the lower field is relatively large. Since NO_2 group is a stronger electron withdrawing group than COOH group, its shifting power is much higher. Cl and Br are electron withdrawing as regards to inductive

Table 3
The IR spectral data of the Ni(II) complexes of formazans (**1a–4a**, **5b–7b**, **8a–13a**, **14c–16c**) (KBr, cm^{-1})

Comp.	Solvent (CH_3OH)	Aromatic C–H	Aromatic C=C	C=N	N=N	C=O	$-CH_3$	–C–O–Ni	CNNC struc. vibr.
1a	–	3098–3025	1600	1500	1410	–	–	–	780–550
2a	–	3071–3048	1660	1589	1357	–	–	–	750–598
3a	–	3070–3040	1660	1580	1357	–	–	–	750–600
4a	–	3070–3035	1630	1570	1357	–	–	–	725–620
5b	–	3063–3018	1660	1527	1375	1589	–	3410–3375	750–652
6b	–	3070–2975	1678	1553	1392	1598	–	3410–3375	750–642
7b	–	3120–3052	–	1526	1365	1580	–	3402–3375	750–598
8a	–	3027–3000	1630	1571	1339	–	–	–	750–598
9a	–	3053–2998	1651	1580	1348	–	–	–	760–643
10a	–	3053–3000	1598	1495	1378	–	–	–	803–625
11a	–	3035	1607	1498	1321	–	–	–	767–630
12a	–	3053–3017	1553	1446	1380	–	–	–	755–625
13a	–	3027–2973	1589	1446	1339	–	–	–	750–678
14c	3661	3036–2998	1580	1455	1125	–	1250	–	750–589
15c	3732	3035–3010	1616	1455	1120	–	1260	–	678–553
16c	3750	3053–3017	1600	1455	1120	–	1260	–	687–625

effect but electron donating as regards to resonance effect, their effect upon the system is the summation of these two opposite effects. That is why their effect in shifting aromatic-H peak to lower field is much lower than those of NO_2 and COOH. This findings are as expected [22]. There was a shift towards the lower fields in the case of electron donating groups, such as CH_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 effect of CH_3 was negated by the strong electron withdrawing effect of Ni^{2+}.

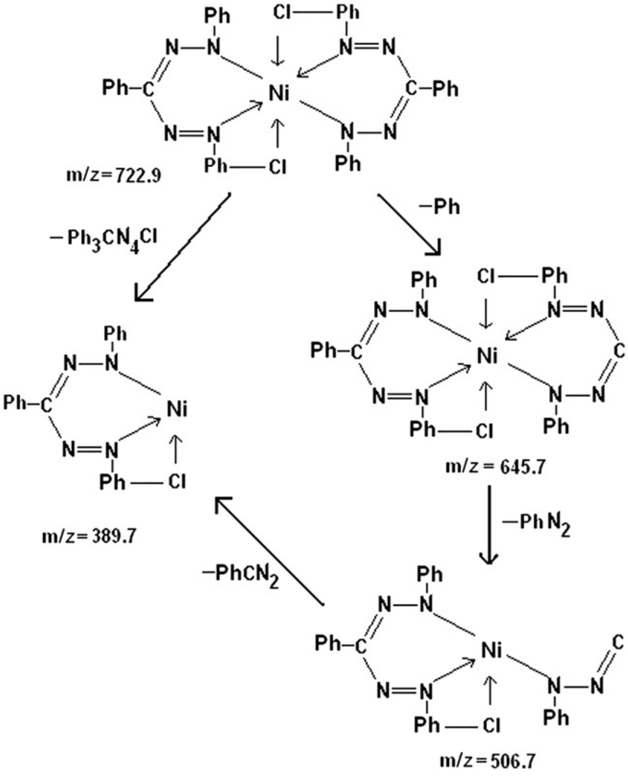
The peaks for the proton of COOH group observed at 12.00–8.00 ppm and the N–H peaks observed at 2.68–1.18 ppm in formazans disappeared in the Ni(II) complexes. This is a further proof that the metal ion was inserted in place of the protons of N–H group and COOH group. These results confirm the proposed formula given in Scheme 1.

The peaks at 3.8–3.2 ppm and 1.6–1.3 ppm were attributed to the solvent. This was an expected outcome. These data are supported by the IR results.

3.2.2. ^{13}C NMR

As seen from Table 2 the δ values for the C=N carbon were observed between 174.00 and 175.00 ppm in Ni(II) complexes of formazans generally. But these results showed the effect of changing the type and the position of the substituent on the rings.

For instance there was a shift in C=N peaks towards higher field when the 1-phenyl ring is substituted with NO_2, COOH



Scheme 3. Proposed fragmentation pattern of compound **8a**.

Table 4
UV–visible absorption maxima of the formazans (**1–16**) and their Ni(II) complexes (**1a–4a**, **5b–7b**, **8a–13a**, **14c–16c**) (CH_2Cl_2, 10^{-5} mol L^{-1})

Formazans	λ_{max1} (nm) (Abs)	Ni-Complexes	λ_{max1} (nm) (Abs)	λ_{max2} (nm) (Abs)	Chemical shift $\Delta\lambda_{max1}$
1	482.0	**1a**	442.0 (0.283)	361.0 (0.252)	–
2	487.0	**2a**	429.0 (0.640)	300.0 (1.250)	13
3	478.0	**3a**	440.0 (0.383)	300.0 (1.325)	2
4	480.0	**4a**	444.0 (0.548)	276.0 (0.546)	−2
5	478.0	**5b**	431.0 (0.347)	295.0 (1.415)	9
6	480.0	**6b**	426.0 (0.265)	301.0 (1.037)	16
7	481.0	**7b**	446.0 (0.356)	302.0 (0.649)	−4
8	486.0	**8a**	435.0 (0.708)	300.0 (1.250)	7
9	486.0	**9a**	435.0 (0.355)	300.0 (1.475)	7
10	489.0	**10a**	438.0 (0.375)	310.0 (1.435)	4
11	487.0	**11a**	436.0 (0.286)	300.0 (0.495)	6
12	487.0	**12a**	436.0 (0.208)	310.0 (0.710)	6
13	489.0	**13a**	437.0 (0.678)	325.0 (2.000)	5
14	489.0	**14c**	426.0 (0.454)	306.0 (1.511)	16
15	488.0	**15c**	430.0 (0.407)	305.0 (1.390)	12
16	487.0	**16c**	429.0 (0.371)	303.0 (1.221)	8

Column 6: $\Delta\lambda_{max} = \lambda_{max1}$ (Ni-TPF) − λ_{max1} (substituted Ni(II) complexes of formazan).

and Br compared with unsubstituted Ni-TPF (**1a**) while there was a shift towards lower fields when 1-phenyl ring is substituted with Cl. In the case of CH_3 substitution there was a shift towards higher fields for *o*- and *p*-positions and a shift towards lower fields for *m*-position. It is clear that the location of C=N peak changes according to the type and the position of the substituents. The fact that this peak was observed at higher frequencies verifies that the complex forms a stabile structure [6].

3.2.3. IR

As seen from Table 3 ν(C=N) bands observed between 1545 and 1500 cm^{-1} in the formazans were shifted to 1589–1446 cm^{-1} in Ni(II) complexes. The general evaluation of ν(C=N) peaks showed no significant changes. However, the ν(C=N) values of **2a–4a**, **6b**, **8a**, **9a** showed an increase [6,21] while ν(C=N) values of **1a**, **5b**, **7b**, **10a–13a**, **14c–16c** showed a decrease [10,11,23] compared with Ni-TPF (**1a**). This supports the fact that the stability of the complex changes according to the type and the position of the substituents and the observation of this peak at higher frequencies verify that the complex forms a stabile structure [6].

The ν(N=N) bands observed at 1455–1410 cm^{-1} in the formazans were shifted to 1440–1120 cm^{-1} in the Ni(II) complexes. There was generally a decrease in this frequency in the compounds. These results are in agreement with Refs. [5,8].

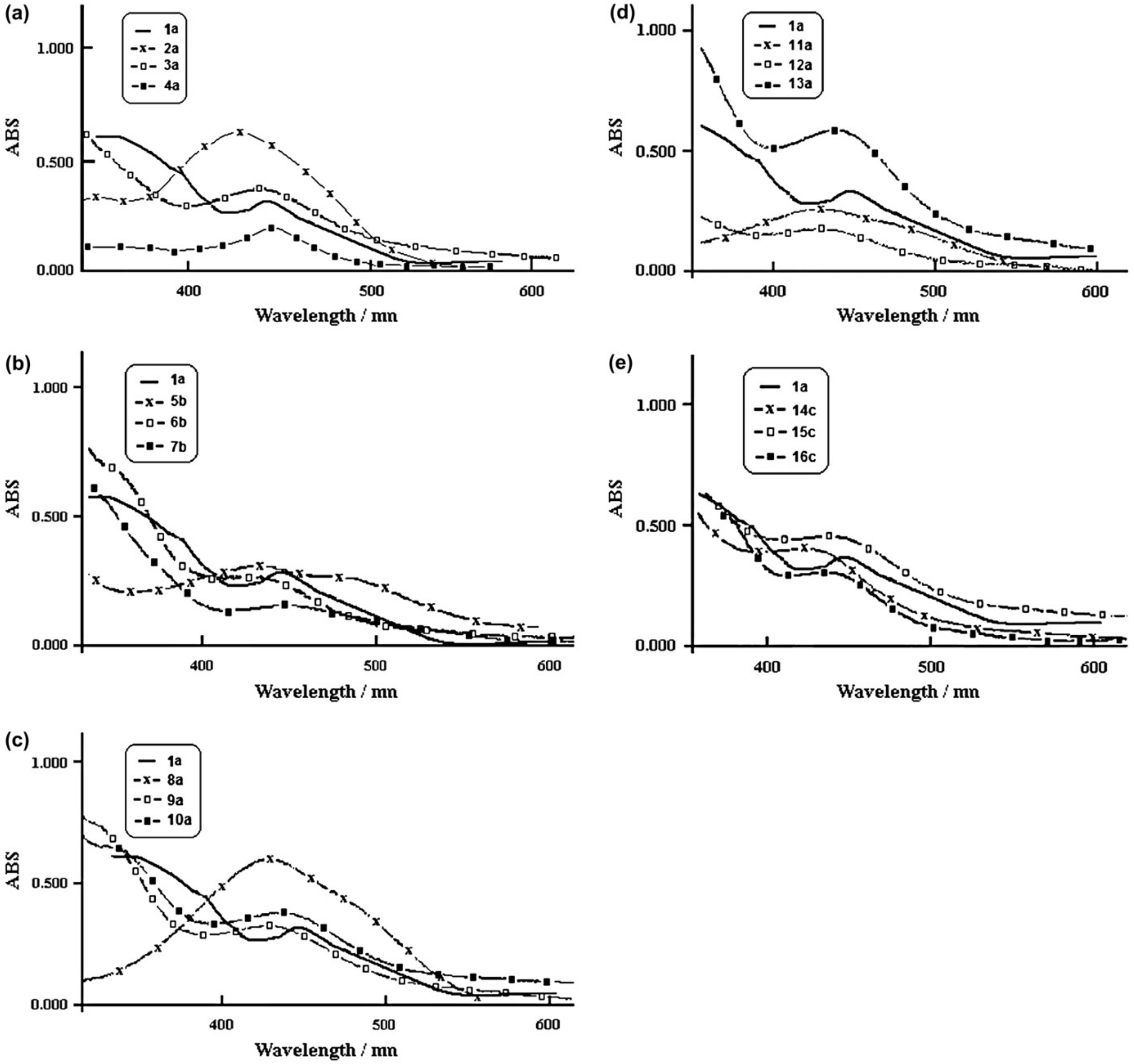


Fig. 1. UV–vis spectra of: (a) compounds **2a–4a** compared to **1a**; (b) compounds **5b–7b** compared to **1a**; (c) compounds **8a–10a** compared to **1a**; (d) compounds **11a–13a** compared to **1a**; (e) compounds **14c–16c** compared to **1a**.

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(II) complexes as a result of insertion of Ni^{2+} in place of an H atom in N–H [5,6,8]. The bands observed at 650–450 cm^{-1} are assigned to Ni–N, Ni–Cl, Ni–Br bending vibrations, supporting the ligands such as NO_2, Cl, Br and Ni(II) ion coordination. These results confirm the proposed formula given in Scheme 1a.

ν(C=O) stretching bands observed at 1700–1615 cm^{-1} for –COOH group in substituted formazans (**5–7**) were shifted to lower frequencies (1598–1580 cm^{-1}) in their respective Ni(II) complexes (**5b–7b**) [4]. This can be taken as an evidence for the non-participation of COOH groups in chelation [4–6,8]. Also OH stretching bands observed at 3400–3300 cm^{-1} in the case of formazans disappeared in the Ni(II) complexes and were replaced by new peaks at 3410–3375 cm^{-1}. This proves that OH group takes part in the formation of C–O–Ni bond. These results are in accordance with Refs. [4,5,8,11] and confirm the structure given in Scheme 1b.

OH stretching bands of the solvent (CH_3OH) were observed at 3661 cm^{-1} (**14c**), 3732 cm^{-1} (**15c**) and 3750 cm^{-1} (**16c**) in the Ni(II) complexes [5]. This is the indication that solvent takes part in the formation of the complex (Scheme 1c).

Other aromatic C–H, C=C, CNNC skeleton stretching peaks and CH_3 vibration band in the compounds were observed in their expected regions.

3.2.4. Mass spectra

The mass spectra of complexes were recorded and their molecular ion peaks confirm the suggested formula of these complexes. The calculated and found values of the molecular weights of some complexes are given in Sections 2.3.2–2.3.6. Scheme 3 demonstrates the proposed paths of the decomposition steps for the investigated complex **8a**. The spectrum shows numerous peaks representing successive degradation of the molecule. The observed peak at *m*/*z* 722.90 (calcd. 722.70) represents the molecular ion peak of the complex with 50.4% abundance. One of the strongest peaks (base peak) at *m*/*z* 389.70 represents the stable species $NiC_{19}H_{14}N_4Cl$. Elemental analysis and mass spectroscopic data also corroborated the structures proposed in Scheme 1.

Table 5
The total σ and related λ_{max} values

Substituent position	Comp.	Abbreviation	σ' s	λ_{max1} (nm)
m-	**1a**	H	0	442.0
	3a	*m*-NO_2	0.71	440.0
	6b	*m*-COOH	0.35	426.0
	9a	*m*-Cl	0.37	435.0
	12a	*m*-Br	0.37	436.0
	15c	*m*-CH_3	−0.06	430.0
p-	**4a**	*p*-NO_2	0.81	444.0
	7b	*p*-COOH	0.44	446.0
	10a	*p*-Cl	0.24	438.0
	13a	*p*-Br	0.26	437.0
	16c	*p*-CH_3	−0.14	434.0

3.2.5. Substituent effect on the UV–vis absorption λ_{max} values

As seen from Table 4, there were two peaks observed in the UV–vis spectra of the Ni(II) complexes [7]. The characteristic broad peak observed at 478–479 nm in the formazans was observed to disappear in the complexes and was replaced by a broad peak which appeared at 426–446 nm (λ_{max1}). This peak was attributed to the complex formation [4,21]. The second peak which appeared at 276–361 nm (λ_{max2}) was related to the π–π* transition of the hydrazone part in the structure of the complex [16,17].

λ_{max1} values were observed to increase by 2–4 nm in *p*-substituted electron withdrawing groups such as –NO_2 and –COOH of the 1-phenyl ring compared to Ni-TPF (**1a**). λ_{max1} values were observed to decrease with all other substituents (Table 4).

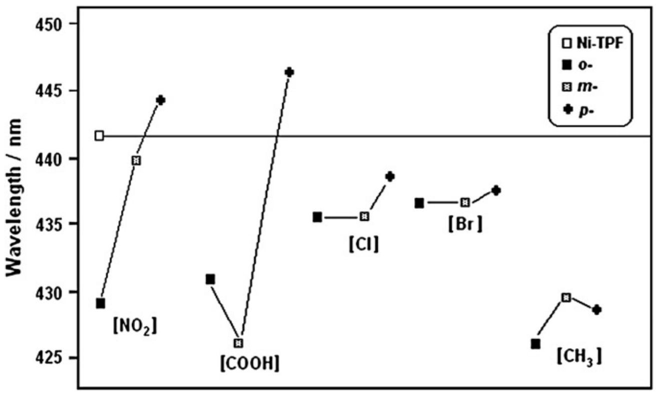


Fig. 2. Comparison of λ_{max} values of the Ni(II) complexes of formazans (**2a–4a**, **5b–7b**, **8a–13a**, **14c–16c**) with **1a**.

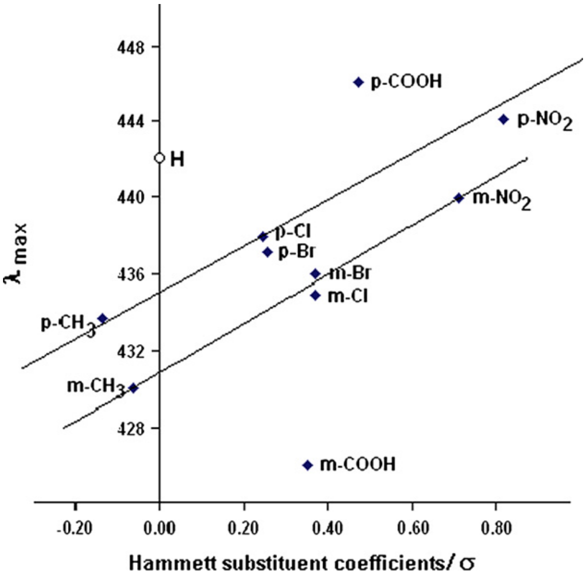


Fig. 3. The λ_{max} values against σ.

When we look at the effect of the substituents on the absorption value according to their respective positions of the 1-phenyl ring we see that $-NO_2$ and $-COOH$ groups shift the absorbance values to higher wavelengths at the *p*-position compared to *m*- and *o*-positions (Fig. 1a and b). On the other hand in the case of Br and Cl substitutions the absorption value shifted to lower wavelength in the *o*-, *m*-, *p*-positions. However, the shift in the *p*-position was less than that in the other two positions (Fig. 1c and d). In the case of $-CH_3$ group the shift in the absorbance values is more extensive than that in the other groups (Fig. 1e). All these shifts (λ_{max}) are illustrated in Fig. 2.

3.2.6. The relation between the λ_{max} values and Hammett substituent coefficients-σ

In previous work the effects of substituents on the absorption properties of the formazans were investigated. A linear correlation between Hammett substituent coefficients-σ and λ_{max} values was determined [15–17]. This study investigated the effects of substituents on the absorption properties of the Ni(II) complexes of formazans.

In order to investigate the existence of any correlation between the Hammett substituent coefficients and λ_{max} values, σ values and λ_{max} values are tabulated in Table 5 and plotted in Fig. 3. As seen from Fig. 3 there was a linear correlation between the σ and λ_{max} values, showing that it is possible to use the summation of Hammett substituent coefficients-σ to evaluate the absorption properties of the compounds.

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