Synthesis and characterization of Ni(II) and Cu(II) complexes derived from novel phenolic Mannich bases

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Abstract: The novel phenolic Mannich bases 2,2'-(2-hydroxy-4,5-dimethylbenzylazanediyl)diethanol (**1**) and 2-((2-(4-(2-hydroxy-4,5-dimethylbenzyl)piperazin-1-yl)ethylamino)methyl)-4,5-dimethylphenol (**2**) have been synthesized in good yield by using a microwave-induced technique from 3,4-dimethylphenol and corresponding amines in the presence of formaldehyde. Metal complexes of **1** and **2** for Ni(II) (**3** and **5**) and for Cu(II) (**4** and **6**) have also been prepared and all compounds have been characterized by elemental and spectral analyses. Thermal, magnetic, and electronic studies have also been reported for metal complexes. Electronic spectra and magnetic susceptibility measurements suggested tetrahedral geometry for Ni(II) (**3**), square planar geometry for Cu(II) (**4**) complexes of **1**, and octahedral geometries for both Ni(II) (**5**) and Cu(II) (**6**) complexes of **2**.

Key words: Mannich base, 3,4-dimethylphenol, piperazine, microwave irradiation, metal complexes

1. Introduction

Metal complexes of Mannich bases have been studied extensively in recent years due to selectivity and sensitivity of the ligands toward various metal ions.[1−3] The new ligand systems for transition metals have drawn considerable interest to chelating amino and hydroxy compounds. The compounds containing phenolic Mannich base components have a strong tendency to form metal complexes[4−7] and exhibit significant anticancer and antimalarial properties.[8,9] The classical Mannich reaction has limited applications and has a number of serious disadvantages. Therefore, numerous novel Mannich reactions have been developed[10,11] to overcome the drawbacks of the classical method and to avoid environmental problems using catalyst in combination with surfactant in aqueous medium.[12−21]

In view of these facts and following the research programs in the field of coordination chemistry, we report here a microwave-assisted convenient and economic method for the synthesis and characterization of new Mannich bases **1** and **2**, formed by 3-component condensation in good yield when compared with the classical method. The proposed structures of the synthesized Mannich bases (**1** and **2**) are given in Scheme 1.

It is well known from the literature that these types of ligands have the ability to form metal complexes via the N and O atoms. We also report metal complexes of **1** and **2** with Ni(II) (**3** and **5**) and Cu(II) (**4** and **6**). The proposed structures of the synthesized complexes **3–6** are shown in Scheme 2.

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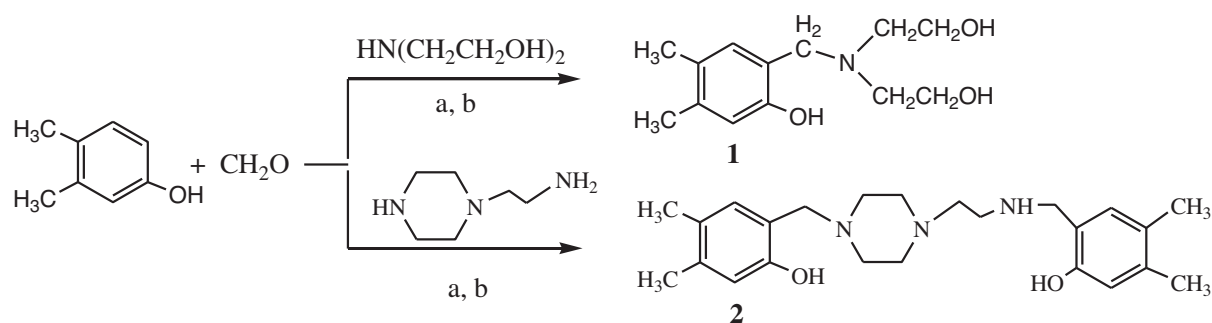
Scheme 1. Conditions of Mannich reaction for **1**: a) ethanol, 30–40 °C, 12 h, 59%; b) solvent-free, MW (200 W), 50 min, 85%; and for **2**: a) ethanol, 30–40 °C, 60 min, 68%; b) solvent-free, MW (200 W), 35 min, 89%.

$$M = Ni(II) \, (\mathbf{5}), \, n = 2$$
$$M = Cu(II) \, (\mathbf{6}), \, n = 0$$
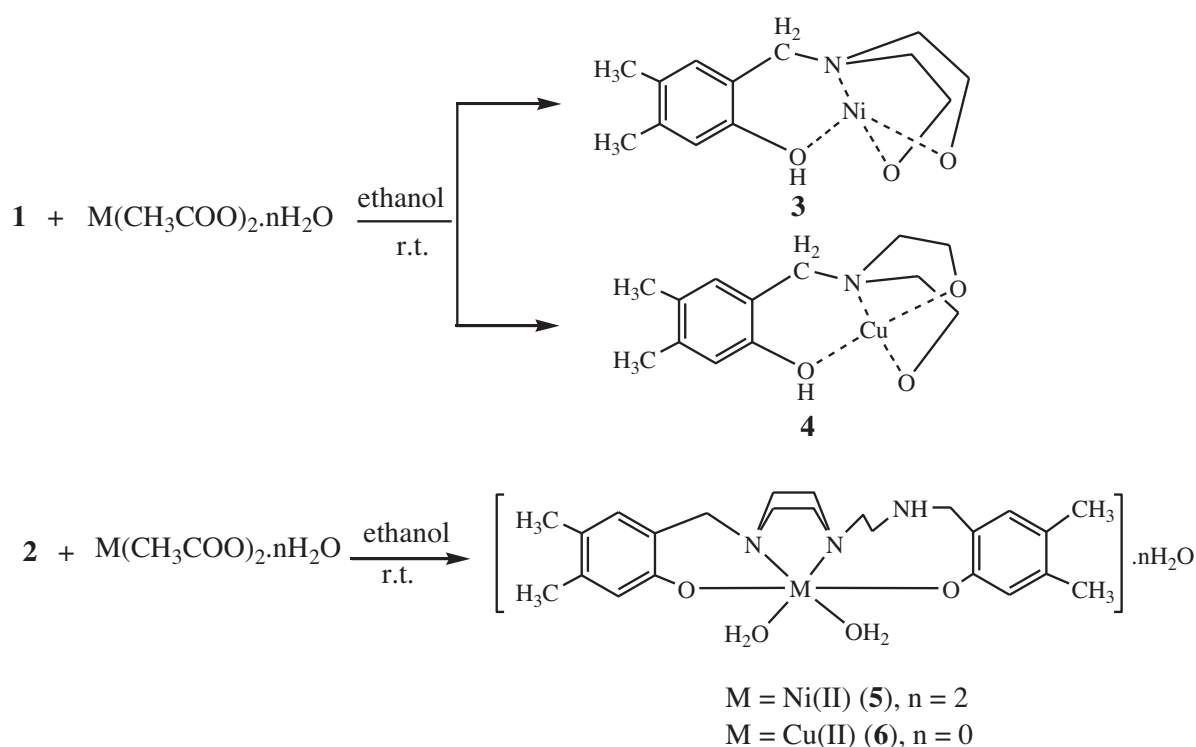
Scheme 2. The proposed structure of complexes **3**–**6**.

2. Experimental section

2.1. General methods and materials

All reagents $(Ni(CH_3COO)_2 \cdot 4H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, 3,4-dimethylphenol, formaldehyde) were of the highest grade, commercially available, and used without further purification. Elemental analyses for C, H, and N were performed on a Leco CHNS-932 instrument. IR spectra were recorded on a Bruker Optics vertex 70 FT-IR spectrometer using attenuated total reflectance techniques. Thermal analyses were performed on the SII Exstar 6000 TG/DTA 6300 model using a platinum crucible with 10 mg of sample. Measurements were taken in the static air, within a 30–700 °C temperature range. The UV-Vis spectra were carried out with a Shimadzu UV-2550 spectrometer in the range of 200–900 nm. Magnetic susceptibility measurements at room

temperature were taken using a Sherwood Scientific Magway MSB MK1 model magnetic balance by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. A domestic microwave oven manufactured by BEKO was used for the microwave-assisted reactions at the highest power (1200 W) and a 2450-MHz operating frequency.

2.2. General procedure for syntheses of ligands (1 and 2)

Upon mixing of 3,4-dimethylphenol (0.2 mol), amine (0.1 mol), and formaldehyde (0.2 mol), the following reaction conditions were employed:

a. Reaction mixture was stirred in ethanol at 30–40 °C for 12 h and 1 h for compounds **1** and **2**, respectively.

b. Reaction mixture was irradiated by microwave at 200 MW without solvent for 50 and 35 min for compounds **1** and **2**, respectively.

2.2.1. Synthesis of 2,2'-(2-hydroxy-4,5-dimethylbenzylazanediyl)diethanol (1)

The reaction mixture obtained from both methods was cooled to room temperature and the oily residue was washed with toluene and dried in air to give pale yellow oil of **1** with 59% (a) and 85% yield (b).

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.48 (br s, 1H, H-7), 6.65 (s, 1H, H-2), 6.39 (s, 1H, H-5), 4.40 (br, 2H, H-13, H-13'), 3.56 (s, 2H, H-10), 3.35 (t, 4H, H-12, H-12', $^3J_{H11,11'-H12,12'} = 5.18$ Hz), 2.46 (t, 4H, H-11, H-11', $J_{H11,11'-H12,12'} = 5.18$ Hz), 2.00 (s, 3H, H-8), 1.98 (s, 3H, H-9); ^{13}C NMR (400 MHz, DMSO-d_6): δ 149.1 (C-6), 135.7 (C-4), 129.8 (C-2), 125.5 (C-3), 121.3 (C-1), 116.6 (C-5), 59.8 (C-12, C-12'), 57.1 (C-11, C-11'), 51.2 (C-10), 18.2 (C-8, C-9). IR ν_{max} (cm^{-1}): 3500–3200 (O-H), 3020 (Ar-H), 2987, 2891 (C-H), 1578, 1456, 1443 (Ar C=C), 1119 (C-O); UV-Vis [λ (nm), ε_{max} (L mol^{-1} cm^{-1})]: 273 (22180) (π-π*), 324 (810) (n-π*). Anal. Calc. for $C_{13}H_{21}NO_3$: C, 65.25; H, 8.84; N, 5.85%, found: C, 65.18; H, 8.86; N, 5.79%.

2.2.2. Synthesis of 2-((2-(4-(2-hydroxy-4,5-dimethylbenzyl)piperazin-1-yl)ethylamino)methyl)-4,5-dimethylphenol (2)

The residue obtained from both methods was washed and recrystallized from ethanol to give white crystals of **2** with 68% (a) and 89% yield (b).

Mp 131–133 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.17 (s, 2H, H-15), 9.45 (s, 2H, H-7, H-23), 6.63 (s, 2H, H-2, H-18), 6.37 (s, 2H, H-5, H-21), 4.15 (s, 2H, H-16), 3.77 (s, 2H, H-10), 3.33 (t, 2H, $^3J_{H11,11'-H12,12'} = 5.01$ Hz, H-11, H-11'), 3.12 (t, 2H, $^3J_{H11,11'-H12,12'} = 5.01$ Hz, H-12, H-12'), 2.80 (t, 2H, $^3J_{H13-H14} = 4.98$ Hz, H-14), 2.62 (t, 2H, $^3J_{H13-H14} = 4.98$ Hz, H-13), 2.29 (s, 6H, H-9, H-25), 2.18 (s, 6H, H-8, H-24); ^{13}C NMR (400 MHz, DMSO-d_6): δ 154.6 (C-6), 151.2 (C-22), 130.0 (C-4, C-20), 127.5 (C-2), 125.3 (C-18), 117.2 (C-3), 116.5 (C-19), 112.9 (C-1, C-17), 110.3 (C-5), 109.9 (C-21), 56.1 (C-10), 52.9 (C-11, C-11'), 52.0 (C-12, C-12'), 49.3 (C-13), 48.0 (C-14, C-16), 19.0 (C-9, C-25), 18.2 (C-8, C-24); IR ν_{max} (cm^{-1}): 3500–3200 (O-H), 3020 (Ar-H) 2998, 2896 (C-H), 1615, 1543, 1500 (Ar C=C), 1268 (C-N), 1259 (C-O); UV-Vis [λ (nm), ε_{max} (L mol^{-1} cm^{-1})]: 288 (24,190) (π-π*), 332 (800) (n-π*). Anal. Calc. for $C_{24}H_{35}N_3O_2$: C, 72.51; H, 8.87; N, 10.57%, found: C, 73.08; H, 8.41; N, 10.26%.

2.3. The general experimental procedure for complexes (3–6)

A solution of $M(CH_3COO)_2 \cdot nH_2O$ (M = Ni and Cu) (2.04×10^{-3} mol) in ethanol (5 mL) was added dropwise to the solution of ligand (2.04×10^{-3} mol) in ethanol (30 mL) with stirring at room temperature. The pH of the reaction mixture was adjusted by addition of 0.1 M aqueous NaOH solution in the range of 6.0 to 7.0. After addition of base, the solid complex formed, and then it was filtered, washed with water, and dried in air.

2.3.1. 2,2'-(2-Hydroxy-4,5-dimethylbenzylazanediyl)diethanolatonickel(II) (3)

Green solid with 76% yield. IR ν_{max} (cm^{-1}): 3400–3200 (O-H), 3012 (Ar-H), 2973, 2898 (C-H), 1613, 1543, 1498, 1458 (Ar C=C), 1100 (C-O), 569 (Ni-O), 435 (Ni-N); UV-Vis [λ (nm), ε_{max} (L mol^{-1} cm^{-1})]: 248 (15500), 300 (13400), 382 (5410) (π-π*), 523 (235), 613 (175) (d-d). Anal. Calc. for $C_{13}H_{19}NiNO_3$: C, 52.75; H, 6.47; N, 4.73%, found: C, 52.46; H, 6.38; N, 4.86%.

2.3.2. 2,2'-(2-Hydroxy-4,5-dimethylbenzylazanediyl)diethanolatocopper(II) (4)

Dark green solid with 65% yield. IR ν_{max} (cm^{-1}): 3400–3200 (O-H), 3010 (Ar-H), 2987, 2849 (C-H), 1612, 1551, 1494, 1455 (Ar C=C), 1095 (C-O), 599 (Cu-O), 496 (Cu-N); UV-Vis [λ (nm), ε_{max} (L mol^{-1} cm^{-1})]: 271 (14060), 288 (32490), 295 (33690), 389 (2970) (π-π*), 696 (550) (d-d). Anal. Calc. for $C_{13}H_{19}CuNO_3$: C, 51.90; H, 6.37; N, 4.66%, found: C, 51.26; H, 6.34; N, 5.03%.

2.3.3. Diaqua-2-((2-(4-(4,5-dimethyl-2-oxidobenzyl)piperazin-1-yl)ethylamino)methyl)-4,5-dimethylphenolatonickel(II)dihydrate (5)

Light green solid with 78% yield. IR ν_{max} (cm^{-1}): 3500–3300 (O-H), 3144 (N-H), 3006 (Ar-H), 2987, 2876 (C-H), 1613, 1468 (Ar C=C), 1274 (C-N), 1261 (C-O), 575 (Ni-O), 410 (Ni-N); UV-Vis [λ (nm), ε_{max} (L mol^{-1} cm^{-1})]: 233 (2140), 241 (2450), 262 (2330), 289 (32990) (π-π*), 495 (100) (d-d). Anal. Calc. for $C_{24}H_{41}NiN_3O_6$: C, 54.77; H, 7.85; N, 7.98%, found: C, 54.15; H, 7.12; N, 8.45; Ni%.

2.3.4. Diaqua-2-((2-(4-(4,5-dimethyl-2-oxidobenzyl)piperazin-1-yl)ethylamino)methyl)-4,5-dimethylphenolatocopper(II) (6)

Brown solid with 72% yield. IR ν_{max} (cm^{-1}): 3550–3300 (O-H), 3142 (N-H), 3008 (Ar-H), 2987, 2876 (C-H), 1612, 1511, 1467, (Ar C=C), 1274 (C-N), 1262 (C-O), 558 (Ni-O), 479 (Ni-N); UV-Vis [λ (nm), ε_{max} (L mol^{-1} cm^{-1})]: 227 (10280), 233 (10880), 249 (10850), 257 (11610), 288 (40390), 364 (10710) (π-π*), 815 (200) (d-d). Anal. Calc. for $C_{24}H_{37}CuN_3O_4$: C, 58.22; H, 7.53; N, 8.49%, found: C, 57.88; H, 7.04; N, 7.77%.

3. Results and discussion

3.1. ^{1}H NMR and ^{13}C NMR spectra of 1 and 2

The ^{1}H and ^{13}C NMR spectra of compounds **1** and **2** were obtained in DMSO-d$_6$ at room temperature using TMS as the internal standard; ^{1}H and ^{13}C NMR assignments are listed in Tables 1 and 2, respectively. The ^{1}H NMR spectrum of **1** exhibits a broad singlet at 7.48 ppm due to proton H-7 with 1 H intensity. Aromatic protons (H-2 and H-5) with 1 H intensity for each are observed at 6.65 and 6.39 ppm. A singlet for protons H-13 and H-13' with 2 H intensity is obtained at 4.40 ppm. The singlet signal with 2 H intensity at 3.56 ppm is assigned to H-10 protons indicating accomplishment of an aminomethylation reaction. The 2 sets of triplets are observed with 4 H intensity for each at 3.35 ppm ($^3J_{H11,11'-H12,12'} = 5.18$ Hz) for protons H-12 and H-12'

and 2.46 ppm ($^3J_{H11,11'-H12,12'}$ = 5.18 Hz) for protons H-11 and H-11', respectively. The 2 singlets with 3 H intensity for each corresponding to methyl protons (H-8 and H-9) are found at 2.00 and 1.98 ppm, respectively. The ^{1}H NMR spectrum of **2** exhibits a singlet at 11.17 ppm due to proton H-15 with 1 H intensity and a broad singlet at 9.45 due to H-7 and H-23 with 2 H intensity. Aromatic protons (H-2, H-18 and H-5, H-21) with 2 H intensity for each are observed at 6.63 and 6.37 ppm. Two singlets for protons H-16 and H-10 with 2 H intensity for each are obtained at 4.15 and 3.77 ppm, respectively, confirming the Mannich aminomethylation reaction. The 2 sets of triplets are observed with 4 H intensity for each at 3.33 ppm ($^3J_{H11,11'-H12,12'}$ =5.01 Hz) for protons H-11 and H-11' and 3.12 ppm ($^3J_{H11,11'-H12,12'}$ = 5.01 Hz) for protons H-12 and H-12', respectively. The protons H-14 (2.80 ppm) and H-13 (2.62 ppm) couple to each other to give triplets with coupling constant $^3J_{H13,14}$ = 4.98 Hz. The 2 singlets with 6 H intensity for each correspond to methyl protons (H-9, H-25 and H-8, H-24) found at 2.29 and 2.18 ppm, respectively.

Table 1. ^{1}H and ^{13}C NMR chemical shifts (ppm) with coupling constants (Hz) and assignments for compound **1**.

^{1}H NMR data		^{13}C NMR data	
H-7	7.48	C-6	149.1
H-2	6.65	C-4	135.7
H-5	6.39	C-2	129.8
H-13, H-13'	4.40	C-3	125.5
H-10	3.56	C-1	121.3
H-12, H-12'($^3J_{H11,11'-H12,12'}$ = 5.18 Hz)	3.35	C-5	116.6
H-11, H-11'($^3J_{H11,11'-H12,12'}$ = 5.18 Hz)	2.46	C-12, C-12'	59.8
H-8	2.00	C-11, C-11'	57.1
H-9	1.98	C-10	51.2
		C-8, C-9	18.2

The ^{13}C NMR spectra of **1** and **2** are in good agreement with the expected signals. The ^{13}C NMR spectrum of **1** exhibits 10 resonances. Six peaks in the range between 149.1 and 116.6 ppm are assigned to aromatic carbon atoms. Two peaks are observed in the aliphatic region for C-12 and C-12' (59.8 ppm) and C-11 and C-11' (57.1 ppm), respectively. The other 2 peaks are observed at 51.2 ppm for carbon C-10 and at 18.2 ppm for carbons C-8 and C-9. The ^{13}C NMR spectrum of **2** displays 10 resonances in the aromatic region in the range of 154.6–109.9 ppm. The peaks are observed in the aliphatic region for C-10 (56.1 ppm) and for piperazine ring carbon atoms (C-11, C-11' and C-12, C-12') observed at 52.9 and 52.0 ppm, respectively. Two signals are observed at 49.3 and 48.0 ppm for C-13 and C-14, C-16, respectively. The methyl carbons with 2 C intensity for each are obtained at 19.0 ppm for C-9, C-25 and 18.2 ppm for C-8, C-24.

3.2. FT-IR measurements

The coordination modes and sites of ligands **1** and **2** to the metal(II) ions were investigated by comparing the IR spectra of **1** and **2** with their complexes (**3** and **5** for Ni(II), **4** and **6** for Cu(II)) (Table 3). The IR spectra of **1** and **2** show a broad band in the region of 3500–3200 cm^{-1}, which is assigned to ν(O-H) vibration,[22] and

Table 2. ^{1}H and ^{13}C NMR chemical shifts (ppm) with coupling constants (Hz) and assignments for compound **2**.

^{1}H NMR data		^{13}C NMR data	
H-15 (s, 1H)	11.17	C-6	154.6
H-7, H-23 (s, 2H)	9.45	C-22	151.2
H-2, H-18 (s, 2H)	6.63	C-4, C-20	130.0
H-5, H-21 (s, 2H)	6.37	C-2	127.5
H-16 (s, 2H)	4.15	C-18	125.3
H-10 (s, 2H)	3.77	C-3	117.2
H-11, H-11'(t, 2H, $^3J_{H11,11'-H12,12'} = 5.01$ Hz)	3.33	C-19	116.5
H-12, H-12'(t, 2H, $^3J_{H11,11'-H12,12'} = 5.01$ Hz)	3.12	C-1, C-17	112.9
H-14 (t, 2H, $^3J_{H13-H14} = 4.98$ Hz)	2.80	C-5	110.3
H-13(t, 2H, $^3J_{H13-H14} = 4.98$ Hz)	2.62	C-21	109.9
H-9, H-25 (s, 6H)	2.29	C-10	56.1
H-8, H-24 (s, 6H)	2.18	C-11, C-11'	52.9
		C-12, C-12'	52.0
		C-13	49.3
		C-14, C-16	48.0
		C-9, C-25	19.0
		C-8, C-24	18.2

Table 3. IR spectral data (cm^{-1}) of free ligands (**1** and **2**) and complexes **3**–**6**.

Assign.	1	2	3	4	5	6
ν(O-H)	3500–3200 (br)	3500–3200 (br)	3400–3200 (br)	3400–3200 (br)	3500–3300 (br)	3550–3300 (br)
ν(N-H)					3144(w)	3142(w)
ν(C-H)$_{ar.}$	3020(w)	3020(w)	3012(w)	3010(w)	3006(w)	3008(w)
ν(C-H)$_{aliph.}$	2987(w) 2891(w)	2998(w), 2896 (w)	2973(w) 2898(w)	2987(w) 2849(w)	2987(w), 2876(w)	2987(w), 2876(w)
ν(C=C)	1578(s) 1456(s) 1443(s)	1615(s), 1543(s), 1500(s)	1613(s) 1543(s) 1498(s) 1458(s)	1612(s) 1551(s) 1494(s) 1455(s)	1468(s) 1613(s),	1612(s), 1511(s), 1467(s)
ν(C-N)		1268(s)			1274(s)	1274(s)
ν(C-O)	1119(s)	1259(s)	1100(s)	1095(s)	1261(s)	1262(s)
ν(M-O)			569(s)	599(s)	575(s)	558(s)
ν(M-N)			435(s)	496(s)	410(s)	479(s)

w: weak, br: broad, m: medium, s: strong

the bands due to ν(C–H) and ν(C=C) in regions 2998–2891 and 1615–1443 cm^{-1}, respectively.

The IR spectra of the metal complexes (**3** and **4**) of **1** show the broad bands in the region of 3400–3200 cm^{-1} consistent with the coordinated ν(O-H) mode. The ν(C=C) stretching vibrations appeared in the

Table 4. Optical properties of free ligands (**1** and **2**) and complexes **3**–**6** in DMSO.

	λ_{max} (nm) (ε (L mol^{-1} cm^{-1}))					
	1	**2**	**3**	**4**	**5**	**6**
	273(22,180)	288(24,190)	248(15,500)	271(14,060)	233(2140)	227(10,280)
	324(810)	332(800)	300(13,400)	288(32,490)	241(2450)	233(10,880)
DMSO			382(5410)	295(33,690)	262(2330)	249(10,850)
			523(235)	389(2970)	289(32,990)	257(11,610)
			613(175)	696(550)	495(100)	288(40,390)
						364(10,710)
						815(200)

region of 1613–1458 cm^{-1} for **3** and 1612–1455 cm^{-1} for **4**. The shifts in ν(C-O) of the phenolic O-H group, from 1119 cm^{-1} in the free ligand to 1100 and 1095 cm^{-1} in complexes **3** and **4**, respectively, indicate the participation of the O-H group in complex formation.[23] Both complexes exhibit bands at 569 and 599 cm^{-1}, which are assignable to ν (M–O), and the bands at 435 and 496 cm^{-1} due to ν(M–N) modes. The ν(M–O) stretching vibration usually occurs in the higher frequency region and is usually sharper and stronger than ν(M–N). These observations are in accordance with the structure of the Ni(II) (**3**) and Cu(II) (**4**) complexes with **1**, in which the central metal ions acquire a coordination number of 4.[22]

As seen from Table 3, the IR spectra of complexes **5** and **6** are similar to each other, indicating the similar structures for the complexes. There are some significant differences between the complexes (**5** and **6**) and the free ligand (**2**) upon chelation, as expected. The broad bands in the region of 3500–3300 cm^{-1} for **5** and 3550-3300 cm^{-1} for **6** are due to the ν(O-H) vibrations.[22] The only proton of the -NH$_2$ group of the 2-(piperazin-1-yl)ethanamine takes part in the Mannich aminomethylation reaction. IR spectra of complexes **5** and **6** exhibit a band at 3144 and 3142 cm^{-1}, respectively, indicating the uncoordinated N-H group. Complexation takes place for 2 N atoms of the piperazine ring and the O atom of the deprotonated phenolic O-H group. In comparison with ligand **2** (1268 cm^{-1}), the ν(C–N) absorption is shifted to higher frequency in complexes **5** and **6** (1274 cm^{-1}), showing the coordination of piperazine nitrogens to the metal(II) ions.[23] The band at 1259 cm^{-1} is assigned to ν(C–O) of the phenolic O-H group.[24] The participation of the deprotonated O-H group is confirmed by the shift of ν(C–O) towards higher frequency in the spectra of coordination complexes **5** (1261 cm^{-1}) and **6** (1262 cm^{-1}) due to the formation of metal–oxygen bonds.[25] These have been further confirmed by the bands at 575 and 410 cm^{-1} for Ni(II) (**5**) and at 558 and 479 cm^{-1} for Cu(II) (**6**), which may be assigned to the ν(M-O) and ν(M-N) stretching vibrations of the coordinated O and N atoms of the free ligand (**2**), respectively.[26]

All of these characteristic features of the IR studies suggest the proposed structures of the coordination compounds (**3**–**6**) as shown in Scheme 2.

3.3. UV/Vis spectra and magnetic susceptibility

The electronic spectra of compounds **1** and **2** and their complexes (**3** and **5** for Ni(II), **4** and **6** for Cu(II)) were recorded in DMSO solution with 1×10^{-3} M concentration at room temperature (Table 4). The electronic spectra of the ligands show absorptions at 273 and 324 nm for **1** and at 288 and 332 nm for **2** due to π-π* and n-π* transitions, respectively.

The Ni(II) complex (**3**) of **1** exhibits absorptions at 248, 300, and 382 nm that were assigned to π-π*, and the absorptions at 523 and 613 nm were assigned to d-d transitions of a 4-coordinate tetrahedral geometry.[27]

Table 5. Thermogravimetric analysis of complexes **3**–**6**.

Complex	Decomposition temperature (°C)	DTG$_{max}$ (°C)	Weight loss		Eliminated special	Solid residue* (%)
			found	calculated		
3	30–345	256 and 316	35.30	35.19	C_8H_8	
	345–450	376	40.20	39.55	$C_5H_{10}NO_2$	
	-	-	19.20	19.83		Ni
4	35–342	223	32.30	32.01	C_6H_8O	
	342–550	477	41.70	41.68	$C_7H_{11}NO$	
	-	-	20.76	21.12	-	Cu
5	30–284	79, 144, and 221	13.30	13.68	$4\ H_2O$	
	284–456	290 and 305	40.00	39.58	$C_{16}H_{16}$	
	456–1000	504	35.50	35.57	$C_8H_{17}N_3O_2$	
	-	-	11.20	11.15	-	Ni
6	30–177	68 and 166	8.00	7.27	$2\ H_2O$	
	177–477	202, 328, and 467	35.40	35.23	$C_{13}H_{18}$	
	477–600	482 and 500	43.82	44.67	$C_{11}H_{15}N_3O_2$	
	-	-	12.78	12.83	-	Cu

*Calculated from the MO residue

Characteristic $\pi - \pi^*$ transitions are observed in the spectrum of the Cu(II) complex (**4**) of **1** at 271, 288, 295, and 389 nm.[28] The electronic spectrum of **4** also exhibits a broad band at 696 nm attributable to d-d transitions, which strongly favor square-planar geometry around the Cu(II) ion.[26,29]

The Ni(II) complex (**5**) exhibits absorptions at 233, 241, 262, and 289 nm assigned to π-π^* transitions and a broad absorption band at 495 nm due to d-d transitions.

Characteristic $\pi - \pi^*$ transitions are observed in the spectrum of **6** at 227, 233, 249, 257, 288, and 364 nm.[30,31] The electronic spectrum of **6** also exhibits a broad band at 815 nm attributable to d-d transitions, which strongly distorted the octahedral geometry around the Cu(II) ion.[32]

The magnetic susceptibility results of transition metal complexes give an indication of the geometry of the ligands around the central metal ion. The magnetic moment of the Ni(II) complex (**3**) is 3.37 B.M., which is in good agreement with a d^8 system in a tetrahedral environment.[33] The measured magnetic moment value for **4** is 1.86 B.M., which is consistent with the expected spin-only magnetic moment of d^9 Cu(II) systems. Thus, in view of the formulation of the complexes and their magnetic moments, it seems quite reasonable to propose a tetrahedral environment around the Ni(II) (**3**) and square-planar geometry around the Cu(II) (**4**) centers.

The Ni(II) (**5**) and Cu(II) (**6**) complexes of **2** are paramagnetic and their magnetic susceptibilities are 3.62 and 1.91 B.M., which indicates 2 and 1 unpaired electrons for Ni(II) (**5**) and Cu(II) (**6**), respectively. The magnetic moments of the complexes at room temperature lie in the range of 3.53–4.26 B.M. for mononuclear octahedral Ni(II)[34] and 1.83–1.96 B.M. for mononuclear octahedral Cu(II) centers.[35,36]

3.4. Thermal analyses of complexes $3-6$

The data for the TG-DTG and DTA curves of compounds **3**, **4**, **5**, and **6** are listed in Table 5. The thermal decomposition studies of complexes **3** and **4** show no appreciable change at about 200 °C when heated due to the absence of coordinated or uncoordinated H_2O molecules in **3** and **4**.

For compound **3**, the first stage, an endothermic peak (DTG$_{max}$ = 256, 316 °C) between 30 and 345 °C,

corresponds to the loss of the C_8H_8 group (found 35.30, calc. 35.19%). The endothermic second stage (DTGmax = 376 °C), between 345 and 450 °C, corresponds to the loss of the $C_5H_{10}NO_2$ group of the ligand (found 40.20, calc. 39.55%). The amount of Ni was calculated from the final decomposition product Ni (found 19.20%, calc. 19.83%).

For compound **4**, the first stage, an endothermic peak (DTG$_{max}$ = 223 °C) between 35 and 342 °C, corresponds to the loss of the C_6H_8O group from the ligand (found 32.30, calc. 32.01%). The endothermic second stage (DTG$_{max}$ = 477 °C), between 342 and 550 °C, is consistent with the loss of $C_7H_{11}NO$ from ligand residue in compound **4** (found 41.70, calc. 41.68%). The amount of Cu was calculated from the final decomposition product Cu (found 20.76%, calc. 21.12%).

The Ni(II) complex (**5**) was thermally decomposed in 4 steps. The first step (DTG$_{max}$ = 79, 144, 221 °C) within the temperature range of 30–280 °C may be attributed to the liberation of coordinated and uncoordinated water molecules (found 13.30, calc. 13.68%). The second step (DTG$_{max}$ = 290, 305 °C) occurred within the temperature range of 284–456 °C with an estimated mass loss of 40.00% (calc. 39.58%), which is accounted for by the removal of the $C_{16}H_{16}$ group. The third step (DTG$_{max}$ = 504 °C) occurred within the temperature range of 456–1000 °C, corresponding to the loss of the $C_8H_{17}N_3O_2$ group of the ligand (found 35.50, calc. 35.57%). The amount of Ni was calculated from the final decomposition product Ni (found 11.20%, calc. 11.15%).

For compound **6**, the first decomposition step (DTG$_{max}$ = 68, 166 °C) represents the loss of coordinated water molecules within the temperature range of 30–177 °C (found 8.00, calc. 7.27%). The endothermic second stage (DTG$_{max}$ = 202, 328, 467 °C), between 177 and 477 °C, is consistent with the loss of the $C_{13}H_{18}$ group from the ligand residue in compound **6** (found 35.40%, calc. 35.23%). The third step (DTG$_{max}$ = 482, 500 °C) within the temperature range of 477–600 °C corresponds to the loss of the $C_{11}H_{15}N_3O_2$ group of the ligand (found 43.82, calc. 44.67%). The amount of Cu was calculated from the final decomposition product Cu (found 12.78%, calc. 12.83%).

4. Conclusions

We have synthesized 2 new Mannich bases (**1** and **2**) with a very simple, efficient, and practical method under microwave irradiation in the absence of solvent, which gives high yield. We have also synthesized new Ni(II) complexes **3** and **5** of **1**, and Cu(II) complexes **4** and **6** of **2**. The elemental and other spectral studies confirm the bonding of Mannich base **1** to Ni(II) (**3**) in tetrahedral and Cu(II) (**4**) in square-planar geometry and the bonding of **2** to Ni(II) (**5**) and Cu(II) (**6**) in octahedral geometry.

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