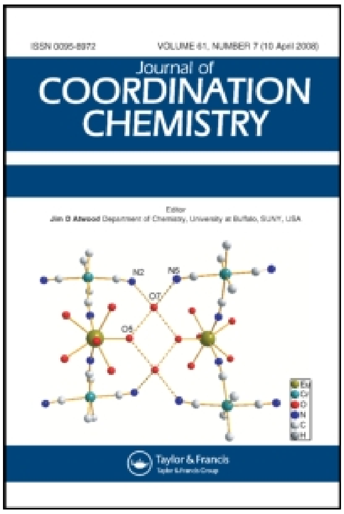

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Synthesis, characterization and the thermodynamic studies of some unsymmetrical tetradentate Schiff-base ligands and their Ni(II) and Cu(II) complexes

Mozaffar Asadi[a]; Zahra Asadi[a]
[a] Chemistry Department, College of Sciences, Shiraz University, Shiraz, I.R. Iran

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Synthesis, characterization and the thermodynamic studies of some unsymmetrical tetradentate Schiff-base ligands and their Ni(II) and Cu(II) complexes

MOZAFFAR ASADI* and ZAHRA ASADI

Chemistry Department, College of Sciences, Shiraz University,
Shiraz 71454, I.R. Iran

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Some new unsymmetrical tetradentate Schiff-base ligands, (N-salicylidene-N′-pyrrolidene)-1,2-ethylenediamine(H_2salpyren) (H_2L^1), (H_2Mesalpyren) (H_2L^2), (H_2phsalpyren) (H_2L^3), (N-salicylidene-N′-pyrrolidene)-1,3-propylenediamine (H_2salpyrpd) (H_2L^4), (H_2Mesalpyrpd) (H_2L^5), (H_2phsalpyrpd) (H_2L^6) and their Ni(II) and Cu(II) complexes were synthesized and characterized by elemental analyses, IR, UV-Vis, ^{1}H NMR and mass spectra and magnetic moments. Possible structures of these complexes have been proposed. The thermodynamic formation constants of the complexes were determined spectrophotometrically at constant ionic strength 0.1 M ($NaClO_4$), at 25°C in methanol.

Keywords: Copper complex; Formation constant; Nickel complex; Thermodynamics; Unsymmetrical Schiff-base

1. Introduction

Symmetric tetradentate Schiff-base complexes have been used extensively as macrocycle models [1], while unsymmetric complexes are very important in biological systems as well as in industrial catalysis and also interesting from the theoretical point of view. This has been stimulated partly by awareness that in many metalloproteins the metals are contained in non-symmetrical environments. Transition metals occur in metalloenzymes [2–7] bound to a macrocycle such as a heme ring or to donor atoms of peptide chains usually in a distorted environment, as in hemerytrin [4] (Fe_2) or hemocyanin [6] (Cu_2). Modification of the properties of the complexes derived from the ligands having asymmetrically derived mixed donor sets are also of interest [8]. Studies of some metal complexes with unsymmetrical Schiff bases have been reported [9–19].

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*Corresponding author. Tel.: +98 711 228 4822. Fax: +98 711 228 6008. Email: asadi@susc.ac.ir

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As a possible route to the synthesis of unsymmetrical Schiff bases the two step process has been considered according to the following equations [20]:

$$R_1R_2C = O + H_2N - (CH_2)_n - NH_2 \rightarrow R_1R_2C = N - (CH_2)_n - NH_2 \tag{1}$$

$$R_1R_2C = N - (CH_2)_n - NH_2 + O = CR_3R_4 \rightarrow R_1R_2C = N - (CH_2)_n - N = CR_3R_4 \tag{2}$$

Ligands of singly condensed carbonyl compounds with diamines are referred to as "half-units" (equation 1).

This article reports the preparation and characterization of six unsymmetrical Schiff-base ligands and their complexes with Cu(II) and Ni(II). The thermodynamic formation constant K_f and the free energy ΔG° at 25°C for the complexes are determined spectrophotometrically.

2. Experimental

2.1. *Reagents*

All chemicals were used as obtained from Merck, Fluka or Aldrich. Anal. grade solvent from Merck was used without further purification. The amines and salicylaldehyde were distilled before use.

2.2. *Analytical instruments*

All of the scanning UV-Vis spectra were recorded on a Jasco V-530 spectrophotometer. FT-IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer in $CDCl_3$ solvent using TMS as an internal standard at 250 MHz. Mass spectra (+ion) were obtained with a QP 1000 mass spectrophotometer. The effective magnetic moment was measured using a Gouy balance.

2.3. *Preparation of ligands*

The unsymmetrical Schiff bases were obtained by condensation of the half units and the appropriate aldehyde; half units were synthesized by mono condensation of the appropriate diamines, aldehyde or ketones. The scheme for preparations is shown in figure 1.

2.3.1. The synthesis of half-units. To the vigorously stirred and cool dilute solution of the diamine (i.e. ethylenediamine and propylenediamine) (20 mmol) in anhydrous ethanol (100 mL) was added dropwise a cooled solution of salicylaldehyde or 2-hydroxyacetophenone or 2-hydroxybenzophenone (15 mmol) in anhydrous ethanol (80 mL). After the addition was complete, the mixture was stirred for 15–30 min and then refluxed for 15–45 min. The resulting solution was evaporated in vacuum to remove the solvent and the excess diamine and was used for the next step without further purification.

2.3.2. The synthesis of tetradentate ligands. To the stirred solution of the precursor (half units HL^x ($x = 1$–6)) (10 mmol) in anhydrous ethanol (60 mL) was added a solution of pyrrol-2-carbaldehyde (10 mmol) in anhydrous ethanol (20–30 mL) and the solution refluxed for 3–8 h. The mixture was concentrated by evaporating the solvent and a yellow solid precipitated. The product was filtered and washed with ethanol and then recrystallized from ethanol 96%.

2.4. *The synthesis of four-coordinate complexes*

The various complexes of Ni(II) (red) and Cu(II) (green) (figure 2) were prepared by addition of 10 mmol of appropriate metal acetate, dissolved in 20–30 mL methanol, into

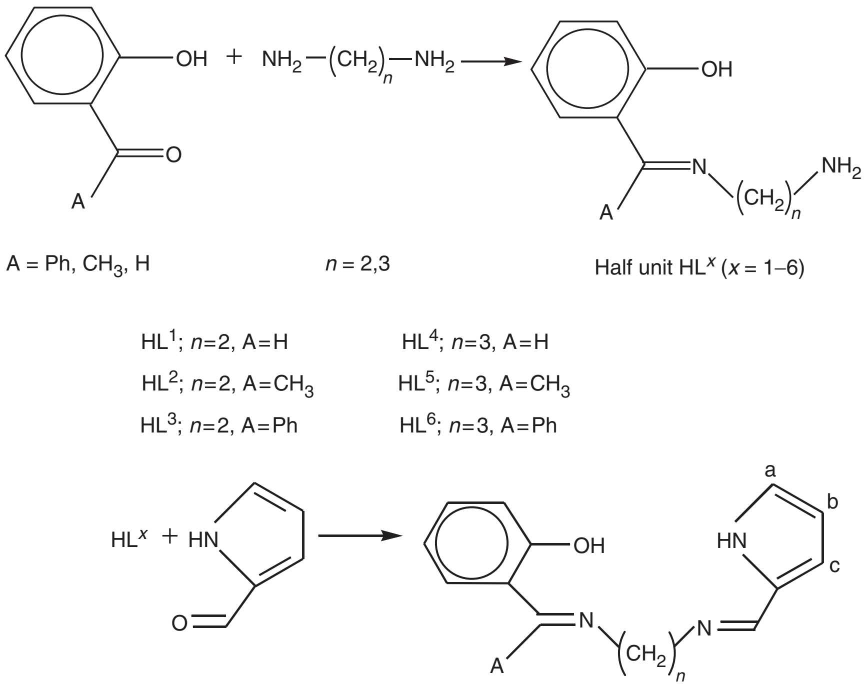

Figure 1. General structure of the precursors (half units) and the tetradentate ligands.

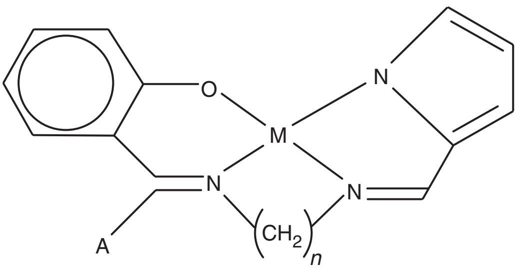

Figure 2. Suggested structure of the complexes (M = Ni(II), Cu(II); A = H, CH_3, Ph; $n = 2, 3$).

a hot solution of 10 mmol of Schiff-base ligand in 10–20 mL methanol (1 : 1 mol ratio). For Cu(II) complexes the reaction was carried out under nitrogen. The mixture was stirred for 1–2 h at room temperature and the complex precipitated. It was filtered and washed with methanol and then recrystallized from methanol and dried in vacuum at 70°C.

3. Results and discussion

Syntheses of the Schiff-base ligands H_2L^x ($x = 1$–6), shown in figure 1, may be represented by equation 3.

$$M(OAc)_2 \cdot nH_2O + H_2L^x \rightarrow ML^x + 2HOAc + (n-2)\,H_2O \quad (x = 1-6) \tag{3}$$

The elemental analyses and the physical constants of the prepared ligands and their complexes are shown in table 1.

3.1. *IR spectra*

The spectral data, table 2, of the complexed Schiff base show some changes compared with the non-coordinated Schiff base. The vibration around 3000–3200 cm^{-1} is due to (O–H) stretching which is affected by the intramolecular hydrogen bond to the azomethine group (O–H $\cdots$ N=C). These bands disappeared through complexation with the metal [21].

The weak bands, 2800–3100 cm^{-1}, are related to (C–H) vibrations. The vibrations of the azomethine groups (C=N) of the free ligands are observed at 1550–1650 cm^{-1}.

Table 1. Analytical and physical data of the ligands and their complexes.

						Anal. Found (Calcd)%		
Compounds	Empirical formula	Formula weight	Yields (%)	Color	m.p. (°C)	C	H	N
H_2L^1	$C_{14}H_{15}N_3O$	241.27	65	Yellow	104	69.71(69.70)	6.58(6.26)	17.58(17.42)
H_2L^2	$C_{15}H_{17}N_3O$	255.30	65	Yellow	140	70.42(70.57)	6.75(6.70)	16.85(16.46)
H_2L^3	$C_{20}H_{19}N_3O$	317.35	85	Yellow	155	75.84(75.70)	6.10(6.03)	13.53(13.23)
H_2L^4	$C_{15}H_{17}N_3O$	255.30	80	Yellow	70	70.48(70.57)	6.78(6.70)	16.58(16.46)
H_2L^5	$C_{16}H_{19}N_3O$	269.31	75	Yellow	80	71.66(71.35)	7.20(7.10)	15.81(15.60)
H_2L^6	$C_{21}H_{21}N_3O$	331.25	89	Yellow	100	76.23(76.11)	6.41(6.38)	12.65(12.68)
NiL^1	$C_{14}H_{13}N_3NiO$	297.95	62	Red	>250	56.58(56.43)	4.36(4.37)	14.21(14.10)
NiL^2	$C_{15}H_{15}N_3NiO$	311.98	65	Red	>250	57.84(57.75)	4.86(4.84)	13.54(13.47)
NiL^3	$C_{20}H_{17}N_3NiO$	374.03	65	Red	>250	64.35(64.22)	4.44(4.58)	11.87(11.23)
NiL^4	$C_{15}H_{15}N_3NiO$	311.98	75	Red	>250	57.51(57.75)	4.85(4.84)	13.57(13.47)
NiL^5	$C_{16}H_{17}N_3NiO$	325.01	70	Red	>250	59.23(59.13)	5.27(5.26)	12.87(12.93)
NiL^6	$C_{21}H_{19}N_3NiO$	388.06	70	Red	>250	65.12(64.99)	4.88(4.93)	10.61(10.83)
CuL^1	$C_{14}H_{13}CuN_3O$	302.78	56	Green	>250	55.67(55.53)	4.37(4.32)	14.08(13.87)
CuL^2	$C_{15}H_{15}CuN_3O$	316.81	50	Green	>250	56.97(56.87)	4.81(4.77)	13.33(13.26)
CuL^3	$C_{20}H_{17}CuN_3O$	378.88	55	Green	>250	63.58(63.40)	4.44(4.52)	11.35(11.09)
CuL^4	$C_{15}H_{15}CuN_3O$	316.81	48	Green	>250	56.55(56.87)	4.69(4.77)	13.33(13.26)
CuL^5	$C_{16}H_{17}CuN_3O$	330.84	45	Green	>250	58.22(58.08)	5.21(5.17)	12.64(12.70)
CuL^6	$C_{21}H_{19}CuN_3O$	392.90	45	Green	>250	64.36(64.20)	4.89(4.87)	10.55(10.69)

In the complexes, these bands shift to lower frequencies, indicating that the nitrogen of the azomethine group coordinates to the metal [22, 23]. Coordination of azomethine nitrogen is confirmed by presence of a new band at 470–580 cm^{-1} region assignable to υ(M–N) for the complexes [24, 25].

Table 2. IR bands of the ligands and complexes (cm^{-1}).

Compounds	$\upsilon_{\text{O–H}}$	$\upsilon_{\text{C–H}}$	$\upsilon_{\text{C=N}}$	$\upsilon_{\text{C=C}}$	$\upsilon_{\text{C–O}}$	$\upsilon_{\text{N–M}}$	$\upsilon_{\text{O–M}}$
H_2L^1	3180	3062 2923 2852	1639 1600	1570 1500	1120		
H_2L^2	3170	3053 2935 2871	1616 1610	1575 1523	1151		
H_2L^3	3168	3062 2947 2864	1639 1604	1560 1490	1134		
H_2L^4	3122	3051 2947 2840	1645 1606	1505 1495	1122		
H_2L^5	3051	2900 2837	1639 1612	1541 1417	1110		
H_2L^6	3051	2935 2829	1639 1600	1585 1507	1147		
NiL^1		3000 2923 2829	1622	1537	1089	495	410
NiL^2		3000 2912 2890	1598 1581	1533 1519	1032	510	450
NiL^3		3050 2912 2886	1571 1558	1525 1444	1033	515	469
NiL^4		3000 2900 2850	1620 1589	1510 1473	1033	487	412
NiL^5		3000 2923 2850	1620 1581	1527 1442	1026	532	483
NiL^6		3010 2900 2840	1600 1571	1527 1436	1022	516	442
CuL^1		3000 2923 2853	1627	1545 1448	1053	550	448
CuL^2		2990 2923 2840	1598	1535 1431	1024	538	433
CuL^3		3000 2932 2838	1620 1596	1537 1448	989	571	434
CuL^4		3000 2908 2854	1589 1620	1530 1442	1026	522	465
CuL^5		3010 2923 2854	1589	1534 1434	1026	511	473
CuL^6		3000 2889	1585	1518 1436	1035	547	435

The stronger bands between 1400–1600 cm^{-1} are due to the skeletal stretching vibrations of the benzene rings [26].

In the ligands, the bands at 1000–1200 cm^{-1} range can be assigned to phenolic (C–O) group vibrations [22]. In the metal complexes, these bands are displaced to lower frequencies, indicating chelation of oxygen to the metal. The new bands in 400–500 cm^{-1} region in the spectra of the complexes are assignable to υ(M–O) [27].

3.2. ^{1}H NMR spectra

In the ^{1}H NMR spectra of the ligands, the hydroxy proton is at 14–16 ppm. The absence of this proton in the complexes shows that the Schiff bases are coordinated (tables 3 and 4). The pyrrol ring proton signals resolve into three groups in the range $\delta = 6.2$–7.4 ppm as a triplet and doublet that are related to the protons in positions b and (a, c) (figure 1). The signal about 6.7 ppm is overlapped with the aromatic phenyl protons and not clear.

Table 3. ^{1}H NMR spectral data of the Schiff bases (δ, ppm) in $CDCl_3$.

Compounds	O–H	H–C=N	Ar–H	Pyrrol-H	–CH$_2$–	CH$_3$
H_2L^1	13.2	8.33	6.8–7.2	6.21 H^b	3.77	
		8.04		6.45 H^a	3.89	
				6.5 H^c		
H_2L^2	15.9	8.04	6.79–7.54	6.22 H^b	3.73	2.38
				6.44 H^a	3.98	
				6.50 H^c		
H_2L^3	15.18	8.05	6.74–7.49	6.22 H^b	3.62	
				6.62 H^a	3.77	
				6.70 H^c		
H_2L^4	13.84	8.28	6.47–7.2	6.23 H^b	2.01	
		8.38		6.47 H^a	3.5–3.7	
				6.71 H^c		
H_2L^5	16.46	8.07	6.69–7.49	6.21 H^b	2.11	2.37
				6.45 H^a	3.71	
				6.70 H^c		
H_2L^6	15.51	8.05	7.17–7.49	6.55 H^b	3.66	
				6.70 H^a	3.45	
				7.40 H^c	1.98	

Table 4. ^{1}H NMR spectral data of the nickel complexes (δ, ppm) in $CDCl_3$.

Compounds	H–C=N	Ar, Pyrrol-H	–CH$_2$–	CH$_3$
NiL^1	7.51		3.31	
	7.37	6.1–7.26	3.81	
NiL^2	7.40	6.08–7.40	3.38	2.22
			3.85	
NiL^3	7.44	6.29–7.43	2.82	
NiL^4	7.67			
	7.56	6.10–7.26	1.80–3.39	
NiL^5	7.44	6.06–7.43	2.03–3.35	2.36
NiL^6	7.47	6.11–7.45	1.67–3.18	

The ^{1}H NMR spectra of the Schiff bases provide compelling evidence of the presence of either one or two azomethine proton groups at ~8.0 ppm. Due to the different chemical environments two signals are recorded for the azomethine protons in the H_2salpyren (H_2L^1) and H_2salpyrpd (H_2L^4) (see table 3 and figure 1).

The ethyl and propyl protons, about 3 ppm, and the CH_3 protons, about 2.3 ppm, shift upon complexation with Ni(II) (see table 3).

3.3. *Electronic spectra*

The electronic spectra (table 5) of the free ligand have a band in the region of 396–417 nm attributable to the n–π* transition and at 280–300 nm assigned to the π–π* transition [28, 29]. The bands at wavelength about 404 nm in the nickel complexes can be assigned to charge transfer transitions involving the metal-ligand bonds [28, 30, 31]. The d–d bands were not observed due to the low concentration (~10^{-4} M) of the solution. These bands should be low in intensity in the region of 500–600 nm [28]. A typical change of the electronic spectra is shown in figure 5.

3.4. *Mass spectra*

The mass spectra of all compounds show intense molecular ion peaks M^+ (see table 6). A typical mass spectra of H_2Mesalpyrpd (MW = 269.3) is shown in figure 3.

Table 5. Electronic spectral data of the Schiff bases and their complexes (nm) in $CHCl_3$.

Compounds	π–π* (nm)	n–π* (nm)	Charge transfer transition (nm)
H_2L^1	290	417	
H_2L^2	294	396	
H_2L^3	292	417	
H_2L^4	289	414	
H_2L^5	289	398	
H_2L^6	288	413	
NiL^1	318	364	404(sh)
NiL^2	318	368	404(sh)
NiL^3	318	340	402(sh)
NiL^4	318	368	398(sh)
NiL^5	320	364	404(sh)
NiL^6	322	368	404(sh)
CuL^1	264	368	–[a]
CuL^2	264	366	–[a]
CuL^3	266	372	–[a]
CuL^4	270	360	–[a]
CuL^5	268	356	–[a]
CuL^6	268	354	–[a]

sh: shoulder.
[a] Not found.

Table 6. Mass spectral data of the Schiff bases and their complexes.

Compounds	*m*/*e*
H_2L^1	241, 214, 148, 120, 107, 93, 80, 62, 51
H_2L^2	255, 161, 148, 138, 107, 80
H_2L^3	317, 223, 198, 178, 120, 91
H_2L^4	255, 178, 148, 134, 121, 108, 94, 80, 57, 44
H_2L^5	269, 162, 148, 134, 121, 107, 91, 80
H_2L^6	331, 237, 224, 210, 194, 178, 161, 152, 134, 121, 107, 91, 80
NiL^1	297, 164, 137, 85
NiL^2	311, 270, 164, 137, 97, 57.
NiL^3	378, 268, 256, 224, 196, 139, 92
NiL^4	311, 284, 180, 164, 137, 107, 85, 58
NiL^5	325, 284, 178, 164, 137, 91, 58
NiL^6	387, 254, 224, 210, 164, 127, 91, 80, 44
CuL^1	302, 256, 224, 197, 169, 148, 107, 91
CuL^2	316, 256, 185, 149, 129, 109, 69
CuL^3	378, 368, 359, 313, 254, 243, 210, 183, 167, 152, 107, 92, 83, 71, 57
CuL^4	316, 169, 132, 106, 80, 63
CuL^5	330, 224, 195, 169, 148, 107, 80, 63
CuL^6	392, 286, 210, 169, 152, 134, 107, 91, 63

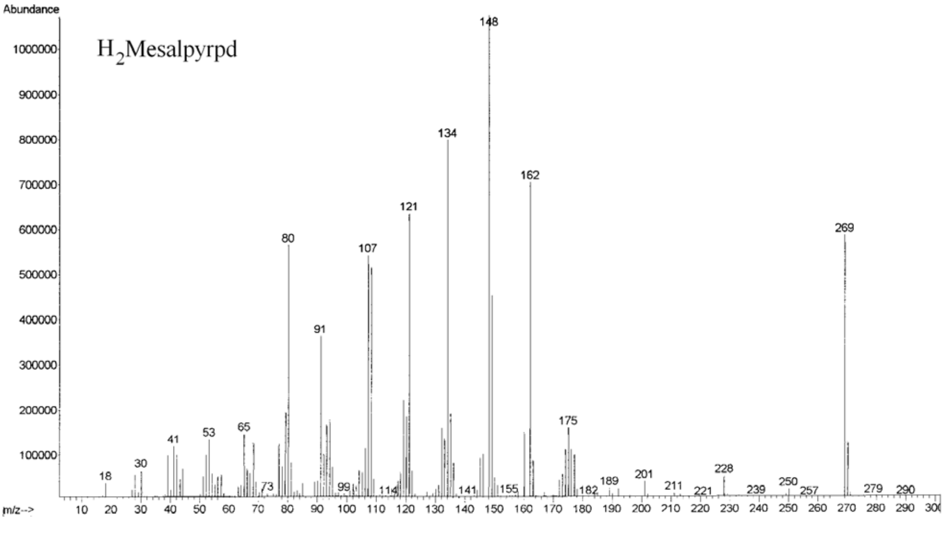

Figure 3. Mass spectra of H_2Mesalpyrpd.

3.5. *Magnetic moment*

The effective magnetic moments of Cu(II) complexes are listed in table 7.

3.6. *Thermodynamic studies of complex formation for unsymmetrical Schiff bases with Ni^{2+} and Cu^{2+} in methanol*

Formation constants have been determined by UV-Vis absorption spectroscopy through titration of the ligands with various concentrations of the metal ions at

Table 7. The effective magnetic moments of the copper complexes.

Compounds	μ_{eff} (B.M.)
CuL^1	1.34
CuL^2	1.25
CuL^3	1.21
CuL^4	1.17
CuL^5	1.22
CuL^6	1.37

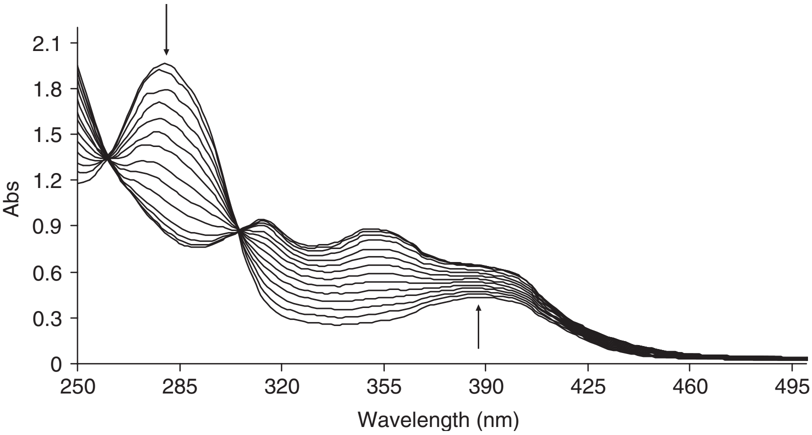

Figure 4. The variation of the electronic spectra of H_2Mesalpyrpd titrated with various concentrations of $Ni^{(II)}$ acetate at 25°C in $I = 0.1$ M ($NaClO_4$) and in MeOH.

constant ionic strength (0.1 M $NaClO_4$) and at 25°C. The interaction of $NaClO_4$ with the ligands in methanol was negligible.

The formation constants, K_f, in all the reactions were determined by spectrophotometric titration of a fixed concentration of the ligands (1.56×10^{-4} M) with various concentrations of the metal acetate (1.0×10^{-5}–1.0×10^{-4} M) at 25°C. In a typical titration 3 mL of the ligand solution was transferred into the thermostated cell compartment of the UV-visible instrument, which was kept at constant temperature (±0.1°C) by circulating water, and was titrated by the metal ion solution. The titration was performed by adding aliquots of the metal ion with a Hamilton µL syringe to the ligand. Light-absorption measurements in the UV-Vis region were made with a Jasco-V-530-UV/vis spectrophotometer equipped with a Lauda-ecoline-RE thermostat. The absorption measurements were carried out at various wavelengths where the difference in absorption was the maximum after equilibrium. The formed product shows different absorption from the free ligand, while the metal ion solution shows no absorption at those wavelengths. As an example, the variation of the electronic spectra for H_2Mesalpyrpd, titrated with various concentrations of Ni(II) acetate at 25°C in MeOH is shown in figure 4. The same procedure was followed for all systems. The electronic spectra of the complexes formed were the same as the electronic spectra of the separately synthesized complexes (figure 5).

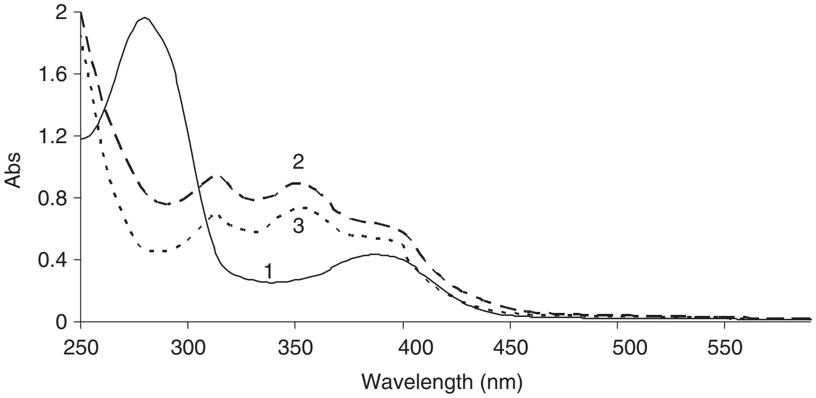

Figure 5. The electronic spectra of the ligand (H_2Mesalpyrpd) (1) in MeOH, the end point of the titration of the ligand with $Ni^{(II)}$ (acetate) in MeOH (2), and separately synthesized Ni(Mesalpyrpd) (3) in MeOH.

Table 8. The formation constants, $\log K_f$, for the complexes of the unsymmetrical ligands with the metal ions at 25°C, in MeOH and at $I = 0.1$ M ($NaClO_4$).

	Ni^{2+}		Cu^{2+}	
Ligand cation	$\log K_f$	ΔG° ($kJ\,mol^{-1}$)	$\log K_f$	ΔG° ($kJ\,mol^{-1}$)
H_2L^1	4.48(0.60)	−25.56(1.48)	...	...
H_2L^2	4.60(0.62)	−26.24(1.53)	5.87(0.23)	−33.49(0.57)
H_2L^3	4.60(0.21)	−26.24(0.52)	5.99(0.97)	−34.17(2.40)
H_2L^4	4.60(0.57)	−26.24(1.41)	4.60(0.34)	−26.24(0.84)
H_2L^5	4.60(0.18)	−26.24(0.44)	4.96(0.95)	−28.29(2.35)
H_2L^6	4.60(0.39)	−26.24(0.96)	4.60(0.61)	−26.24(1.51)

The numbers in parentheses are the standard deviations.

The complex formation constants, K_f, were calculated using the SQUAD computer program [32], designed to calculate the best values for the formation constants of the proposed equation model (equation 3) by employing a non-linear, least-squares approach. Also the free energy change ΔG° of the formed complexes were calculated from $\Delta G^\circ = -RT \ln K_f$ at 25°C (see table 8). That Cu(II) has more tendency to bind with the ligands than Ni(II) may be attributed to its higher positive charge distribution and the ligand deformation geometry.

4. Conclusion

The synthesis and characterization of six new unsymmetrical Schiff bases and their complexes with Ni(II) and Cu(II) were performed. The thermodynamic formation constant, K_f, and the free energy of formation for the above mentioned complexes were determined spectrophotometrically at 25°C. The K_f values for Cu(II) complexes are higher than the Ni(II) complexes.

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