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Some New Unsymmetrical Diimino Tetradentate Schiff Base Derived from 3,4-Diaminobenzophenone: Synthesis, Characterization and the Formation Constant of Ni(II) and Cu(II) Complexes

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Some new unsymmetrical diimino tetradentate Schiff bases derived from 3,4-diaminobenzophenone, (N-salicyliden-N'-5-OMe.salycyliden)-3,4-diaminobenzophenone (H_2sal-5-OMe.sal.dabp) (H_2L^1), (H_2sal-5-Br.sal.dabp) (H_2L^2), (H_2sal-5-Cl.sal.dabp) (H_2L^3) and (H_2sal-5-NO_2.sal.dabp) (H_2L^4) and their Ni(II) and Cu(II) complexes were synthesized and characterized by elemental analysis, IR, ^{1}H NMR, UV-Vis spectra and mass spectra. The thermodynamic formation constants of the complexes were determined spectrophotometrically at constant ionic strength (0.1 M $NaClO_4$) at 25 ºC in DMF and their free energies of formation were calculated at 25 ºC.

Keywords: Formation constant, Free energy, Metal complex, Thermodynamic, Unsymmetrical Schiff base

INTRODUCTION

Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility, and diverse range of applications [1,2]. The interest in the design, synthesis and characterization of the transition metal complexes of unsymmetrical Schiff base ligands has come from the realization that coordinated ligands around central metal ions in natural systems are unsymmetrical [3]. Recently, this class of compounds has also attracted much attention in the field of optoelectronic technologies for their large nonlinear responses [4]. In the area of the bioinorganic chemistry, interest in the Schiff base complexes with transition and inner-transition metals has centered on the role of such complexes in providing synthetic interesting models for the metal-containing sites in metallo-proteins and enzymes [5-7]. They appear to be of importance for a broad range of transition metal catalyzed reactions including lactide polymerization [8,9], epoxidation of olefins [10] and hydroxylation [11]. Several reviews have been published on metal Schiff bases especially on metal Salen Schiff base complexes [12,13]. Unsymmetrical Schiff base ligands have clearly offered many advantages over their symmetrical counterparts in the elucidation of the composition and the geometry of the metal ion binding sites in the metallo-proteins and the enzymes, and the selectivity of the natural systems with synthetic materials [14].

The aminooxidase enzyme requires such a coenzyme besides copper(II) ions for catalytic activity. Urease, the first enzyme crystallized to be shown to possess nickel ions [15], is an important enzyme in both agriculture and medicine, which rapidly catalyzes the hydrolysis of urea to form ammonia and carbamic acid [16]. Recently Cu(II) and Ni(II) Schiff base complexes have been investigated as inhibitor against urease and xanthine oxidase (XO) [17].

In continuation of our work on unsymmetrical Schiff bases

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[18-20], in this work a new half unit and some new unsymmetrical tetradentate Schiff base ligands and their Ni(II) and Cu(II) complexes were synthesized and characterized by elemental analysis, IR, ^{1}H NMR, UV-Vis spectra, mass spectra and magnetic moments. The thermodynamic formation constants (K_f) of the complexes were determined spectrophotometrically and their free energies ΔG° were calculated at 25 ˚C.

EXPERIMENTAL

Materials

All chemicals were obtained from Merck, Fluka and Aldrich. Anal. Grade DMF solvent from Merk was used without further purification. The salicylaldehyde was distilled before use.

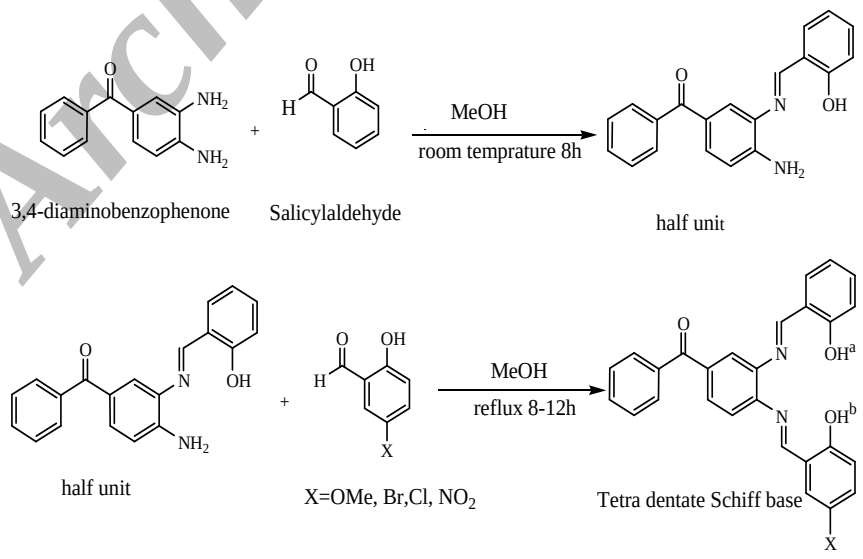
Analytical Instruments

All of the scanning UV-Vis spectra were recorded by Shimadzu Perkin Elmer Lambda 2- UV-Vis spectrophotometer. The NMR spectra were recorded by Bruker Avance DPX 250 MHz spectrometer. IR spectra were recorded by Perkin Elmer Infrared spectrophotometer. Elemental microanalysis (C.H.N.), were done by Thermo Finningan Flash EA-1112 elemental analysis apparatus. Mass spectra were recorded by a Perkin-Elmer R MU-6E instrument. The effective magnetic moments were measured using a Gouy balance and the melting points were measured in capillary tubes by using BUCHI 535 melting point.

Preparation of the Ligands

The unsymmetrical Schiff bases were synthesized by condensation of the half unit and the appropriate aldehydes or ketones. The half units were synthesized by mono condensation of the appropriate diamines with aldehydes or ketones. Overall scheme for the preparation is shown in Scheme 1. H_2L^x ligands (x = 1-4) and their complexes were prepared by literature method [21].

Synthesis of the half unit. To the vigorously stirred solution of the diamine (10 mmol) in anhydrous methanol (25 ml), was added dropwisely a solution of the salicylaldehyde (12 mmol) in anhydrous methanol (20 ml). After addition was completed, the mixture was stirred for 8 h at room temperature. During this time a yellow precipitate was formed. The reaction mixture was stirred for an additional hour and then filtered. The yellow crystals were washed three times with methanol and then recrystallized from methanol. Then the resulting yellow compound was dried in vacuum at 50 °C.



Scheme 1. Overall synthesis path for the preparation of the half unit and the tetradentate Schiff bases. H_2L^1: X = OMe, H_2L^2: X = Br, H_2L^3: X = Cl, H_2L^4, X = NO_2.

Synthesis of the tetradentate unsymmetrical ligands. To the stirred solution of the precursor (half unit (10 mmol)) in hot methanol (25 ml), a solution of 15 mmol in 10 ml anhydrous methanol of each of 5-methoxysalicylaldehyde, 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde and 5-nitro-salicylaldehyd was added and the solution was refluxed for 8-12 h. During this time a colored solid was precipitated. The product was filtered and washed three times with methanol and recrystallized from 1:1 methanol/chloroform mixture and dried in vacuum at 50 °C. Yields ranged from 60 to 85% based on the diamine used in the stochiometric molar ratio (see Table 1).

Synthesis of the Four Coordinated Ni(II) and Cu(II) Complexes. The various complexes of Ni(II) (red) and Cu(II) (brown) were prepared under ambient condition. To a solution of H_2L^x (1.5 mmol) in a mixed solvent (for H_2L^x, x = 1,2,3, $CHCl_3$ 20 ml/MeOH 15 ml and x = 4; DMF 20 ml/MeOH 15 ml) a solution of the appropriate metal acetate tetrahydrate (1.5 mmol), dissolved in 10 ml methanol was added. The mixture was stirred for 2-3 h at room temperature, the precipitate was filtered and washed with methanol and dried in vacuum at 70 °C (Fig. 1).

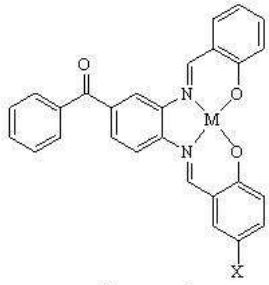


Fig. 1. Structural representation of the Schiff base complexes.

RESULTS AND DISCUSSION

The unsymmetrical ligands were prepared by the reaction of the half unit with the desired aldehydes. The yellow or the orange crystalline products were isolated in excellent yields. The elemental analysis and some physical properties for the ligands and their complexes are listed in Table 1.

IR Spectra

IR spectral data of the compounds and their relative assignments are shown in Table 2. The infrared spectrum of

Table 1. Analytical and Some Physical Data of the Ligands and Their Complexes

Compounds	Empirical formula	Formula weight	Yield (%)	Color	m.p (°C)	Anal. Found (Calcd.)%		
						C	H	*N*
Half unit	$C_{20}H_{16}N_2O_2$	316.36	80	Yellow	134	76.13(75.93)	5.14(5.10)	8.87(8.85)
H_2L^1	$C_{28}H_{22}N_2O_4$	456.9	75	Orange	216	74.23(74.13)	4.80(5.03)	6.44(6.13)
H_2L^2	$C_{27}H_{19}N_2O_3Br$	4.99.36	65	Yellow	192	64.85(64.94)	3.61(3.83)	5.89(5.61)
H_2L^3	$C_{27}H_{19}N_2O_3Cl$	468.42	75	Yellow	215	69.19(69.23)	3.96(4.14)	5.98(5.98)
H_2L^4	$C_{27}H_{19}N_3O_5$	465.46	85	Yellow	>250	69.75(69.67)	3.95(4.11)	9.25(9.03)
NiL^1	$C_{28}H_{20}N_2NiO_4$	507.18	65	Red	>250	66.56(66.31)	3.71(3.97)	5.52(5.52)
NiL^2	$C_{27}H_{17}N_2BrNiO_3$	577.66	60	Red	>250	56.38(56.14)	3.07(3.38)	4.98(4.85)
NiL^3	$C_{27}H_{17}N_2ClNi_3$	533.21	65	Red	>250	60.59(60.82)	3.37(3.67)	5.15(5.25)
NiL^4	$C_{27}H_{19}N_3$ Ni O_5	543.77	76	Red	>250	63.58(63.37)	3.75(3.82)	8.35(8.21)
CuL^1	$C_{28}H_{20}CuN_2O_4$	522.8	60	Brown	>250	64.31(64.32)	4.02(4.09)	5.49(5.36)
CuL^2	$C_{27}H_{17}BrlCuN_2O_3$	587.02	45	Brown	>250	55.48(55.25)	3.17(3.42)	5.07(4.77)
CuL^3	$C_{27}H_{17}$ ClCu N_2O_3	542.56	55	Brown	>250	59.58(59.77)	3.85(3.7)	5.07(5.16)
CuL^4	$C_{27}H_{19}$ Cu N_3O_5	521.2	65	Brown	>250	62.17(62.23)	3.91(3.85)	8.36(8.06)

Table 2. IR Bands of the Ligands and the Complexes (cm^{-1})

Compounds	ν_{NH2}	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C=C}$	ν_{O-H}	ν_{N-M}	ν_{O-M}
Half unit	3344,3468	1647	1609,1577	1508,1488	-	-	-
H_2L^1	-	1647	1616,1585	1513,1465	3375	-	-
H_2L^2	-	1639	1616,1589	1473,1446	3436	-	-
H_2L^3	-	1643	1616,1589	1474,1446	3436	-	-
H_2L^4	-	1620	1620,1578	1523,1481	3413	-	-
NiL^1	-	1635	1608,1577	1519,1465	-	536	451
NiL^2	-	1654	1608,1577	1512,1446	-	540	451
NiL^3	-	1653	1612,1582	1512,1456	-	544	450
NiL^4	-	1653	1604,1582	1542,1504	-	563	455
CuL^1	-	1647	1612,1573	1515,1462	-	545	440
CuL^2	-	1643	1608,1577	1504,1454	-	551	460
CuL^3	-	1668	1608,1577	1508,1450	-	552	461
CuL^4	-	1662	1608,1582	1542,1495	-	543	454

the new half unit shows two bands in the range 3470-3350 cm^{-1}. These two bands are assigned to the primary amine stretchings. The lack of a band due to the free OH stretching vibration in the spectrum of the half unit, is consistent with the findings of Kovacic [22]. An intense sharp band around 1616 cm^{-1} in the spectrum of the half unit and H_2L^x x = 1-4 are assigned to the azomethine (C=N) vibrations**.** In the complexes, these bands were shifted to lower frequencies, indicating that the nitrogen of the azomethine group has coordinated to the metal [23,24]. IR absorption bands in the 1620-1670 cm^{-1} region in the half unit, the tetradentate ligands and the complexes can be attributed to the C=O stretching vibrations. The weak absorption bands in the 2800-3200 cm^{-1} region are related to (C-H) vibrations. The strong bands between 1400-1600 cm^{-1} are due to the skeleton stretching vibrations of the benzene rings [25]. Assignment of the proposed coordination sites is further supported by the appearance of bands at 480-580 cm^{-1} and 400-500 cm^{-1} which could be attributed to ν_{N-M} and ν_{O-M}, respectively.

^{1}H NMR Spectra

^{1}HNMR spectrum of the half unit shows a single hydroxy proton signal at 12.1 ppm but the tetradentate Schiff base ligands of N_2O_2 donor sets show two signals in this region. The half unit NH_2 protons show a singlet at 6.1 ppm. The absence of these protons in the tetradentate ligands show that the unsymmetrical ligands are formed. The half unit, the ligands and the nickel complexes show the aromatic protons as multiplet in the range 6.9-8.2 ppm. The O-H protons of the phenolic groups for the tetradentate ligands have signals in the range 12.4-13.4 ppm. The absence of these protons in the nickel complexes shows that the Schiff bases are coordinated. In H_2L^4 the phenolic hydrogen signals are broad probably due to inter hydrogen bonding between phenolic hydrogens and the oxygen of the NO_2 group. It's confirmed by high melting point of H_2L^4 (Table 1). The azomethine protons appear at 8.9-9.2 ppm (Table 3).

Electronic Spectra

The electronic spectra of the free ligands (H_2L^{1-3}) show a weak band, as a shoulder in the region of 440-480 nm which is assigned to n→π* transition involving molecular orbitals of the C=N chromophore and the benzene ring [26-29]. This type of transition for H_2L^4 is a sharp peak with λ_{max} 428 nm. The band in the range of 330-350 nm for H_2L^{1-3} is assigned to π→π* type transition, which involves molecular orbitals essentially localized on the C=N group and the benzene ring thus the transition involves the azomethine group. This type of

Table 3. ^{1}H NMR Spectral Data of the Schiff Base and Complexes (δ, ppm) in d^6 DMSO

Compounds	O-H[a]	O-H[b]	NH_2	H-C=N	Ar-H	CH_3
Half unit	12.1	-	6.1	8.8	6.8-7.7	-
H_2L^1	12.8	12.5	-	8.9	6.8-7.8	3. 8
H_2L^2	12.5	12.8	-	9.0	6.9-7.8	-
H_2L^3	12.5	12.8	-	9.0	6.9-7.8	-
H_2L^4	12.7(broad)	13.5(broad)	-	9.1	7.1-8.2	-
NiL^1	-	-	-	8.9	6.9-7.7	3.7
NiL^2	-	-	-	8.9	6.9-7.7	-
NiL^3	-	-	-	9.1	6.9-7.7	-
NiL^4	-	-	-	9.0	6.5-8.5	-

Table 4. Electronic Spectral Data of the Schiff Bases and Their Complexes (nm) in DMF

Compound	π→π* (C=N) (nm)	n→π* (nm)	π→π* (metal-ligand transition) (nm)
H_2L^1	340	465 (sh)	-
H_2L^2	340	465 (sh)	-
H_2L^3	338	465 (sh)	-
H_2L^4	370	428	-
NiL^1	380	-	486
NiL^2	378	-	484
NiL^3	380	-	490
NiL^4	375	-	430
CuL^1	314	-	434
CuL^2	308	-	434
CuL^3	306	-	434
CuL^4	370	-	425

transition in H_2L^4 is a sharp peak with λ_{max} 370 nm. These differences in shape and position of the bands in H_2L^4 are probably due to the presence of the NO_2 chromophore in the ligand.

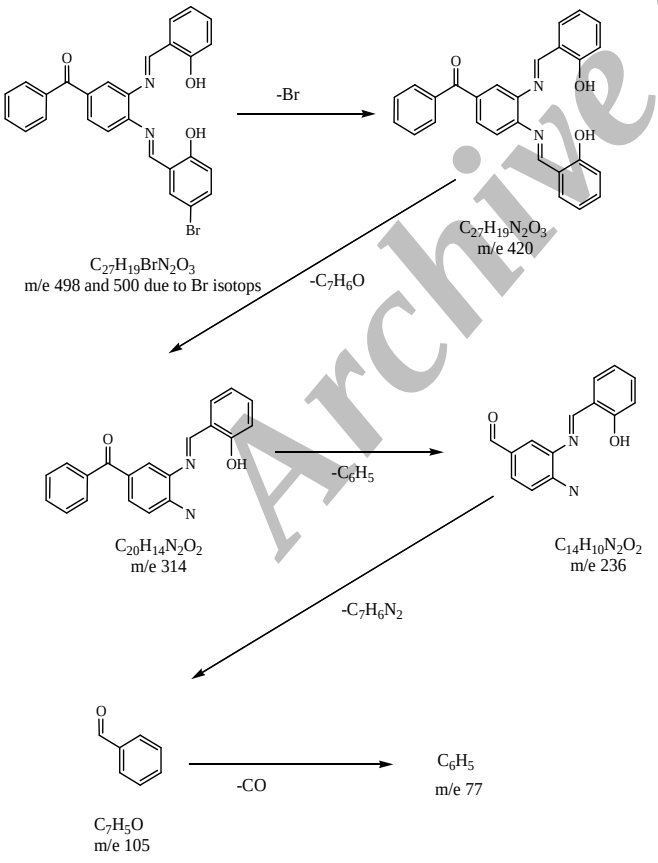
Differences are observed in the visible spectra of the metal complexes when compared with that of the corresponding free ligand. The formation of the metal-nitrogen bond stabilizes the electron pair on the nitrogen atom *i.e.* the energy of its nonbonding orbital is lowered and the transition occurs at a lower wavelength or this band is obscured by the strong band which can be assigned to π→π* type transitions involving the metal-ligand bands [30-32]. The d-d bands even at high concentration of the complexes were obscured by an intense band of the charge transfer (MLCT).

Mass Spectra

The mass spectra of all ligands and complexes show an intense molecular ion peak m/z $[M]^+$. The mass spectra of some compounds also show a prominent peak corresponding to m/z $[M+1]^+$, $[M-2]^+$ or $[M-1]^+$ due to isotopic effect (Table 5). The pathway fragmentation pattern of the mass spectrum of the H_2L^2 ligand is depicted in Scheme 2. The spectrum shows

Table 5. Mass Spectral Data of Schiff Bases and Their Complexes

Compounds	m/z	Assignments
Half unit	316	$[M]^+$
H_2L^1	450	$[M]^+$
H_2L^2	498, 500	$[M-1]^+$, $[M+1]^+$
H_2L^3	454	$[M]^+$
H_2L^4	465	$[M]^+$
NiL^1	507	$[M+1]^+$
NiL^2	554,556	$[M]^+$, [$[M-2]^+$
NiL^3	510,512	$[M]^+$, $[M-2]^+$
NiL^4	522	$[M]^+$
CuL^1	511	$[M]^+$
CuL^2	559, 561	$[M]^+$, $[M-2]^+$
CuL^3	515,517	$[M-1]^+$,$[M+1]^+$
CuL^4	526	$[M]^+$



Scheme 2. Fragmentation pattern for ligand H_2L^2

two isotopic peaks at m/z 498 $[M-1]^+$ and 500 $[M+1]^+$ with almost the same intensity due to bromide isotopes (^{79}Br and ^{81}Br).

Thermodynamic Studies of the Complex Formation for the Tetradentate Schiff Bases with Cu^{2+} and Ni^{2+} in Dimethylformamide (DMF)

The formation constants, K_f, have been determined by UV-Vis absorption spectroscopy through titration of fixed concentration of the ligands (5×10^{-5} M) with various concentration of the metal ions (1.25×10^{-3}-5×10^{-3} M) as metal acetate tetrahydrate at constant ionic strength (0.1 M $NaClO_4$) and at 25 ºC. The interaction of $NaClO_4$ with the ligands in dimethylformamide was negligible.

In a typical titration 2.5 ml of the ligand solution was transferred into the thermostated cell compartment of the UV-Vis instrument, which was kept at constant temperature (±0.1 ºC) 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. 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 spectrum for H_2L^3 titrated with various concentrations of Ni(II) acetate tetrahydrate at 25 ºC in DMF is shown in Fig. 2. The same procedure was followed for all other systems. The electronic spectra of the complexes formed were the same as the electronic spectra of the separately synthesized complexes (Fig. 3).

The complex formation constants, K_f, were calculated using the SQUAD computer program [33], designed to calculate the best values for the formation constants by employing a non-linear, least-squares approach. Also the free energy change ΔG^o of the formed complexes were calculated from $\Delta G^o = -RTlnK_f$ at 25 ºC (Table 6).

The metal effect. Cu(II) has more tendency to bind with the ligands than Ni(II) this may be attributed to its higher positive charge distribution and the ligand deformation geometry due to the d^9 configuration and the presence of an odd electron in the d_{x2-y2} orbital [20] while Ni(II) in their complexes is diamagnetic and therefore the expected geometry is square planar [14].

The electronic effect of the *para* substituted Schiff's base ligands. In the para substituted Schiff base ligands, the formation constant varies as can be expected according to the electronic effect of the substituents in position 5. Thus, the formation constants decrease according to the sequence OMe > Br > Cl > NO_2 in a trend of an increase in both electron-withdrawing and π-acceptor qualities of the substituents and the donor ability of the ligand groups. The withdrawing functional group makes the Schiff base a poor donor ligand and decreases the formation constants while the electron donor group increases the formation constants. Therefore the ligand having NO_2 group (H_2L^4) has the smallest formation constant while the ligand with OMe (H_2L^1) group has the highest (Ttable 6).

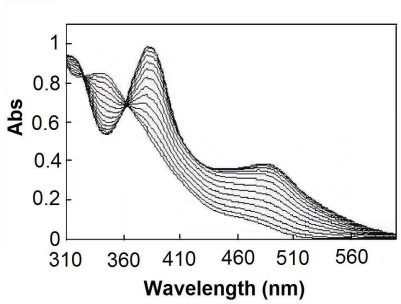


Fig. 2. The variation of the electronic spectrum of H_2L^3 titrated with various concentration of Ni(II) acetate tetrahydrate at 25 °C in I = 0.1 M ($NaClO_4$) and in DMF.

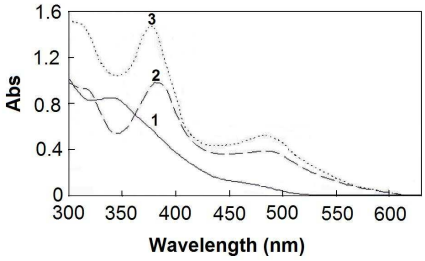


Fig. 3. The electronic spectrum of the ligand (H_2L^3) in DMF (1), the end point of the titration of the ligand with Ni(II) acetate tetrahydrate in DMF (2) and the separately synthesized NiL^3 in DMF (3).

Table 6. The Formation Constant, $logK_f$, for the Complexes of the Unsymmetrical Ligands with the Metal ions at 25 °C, in DMF and at I = 0.1 M ($NaClO_4$)

	Ni^{2+}		Cu^{2+}	
Ligand	$logK_f$	$\Delta G°$ (kJ mol^1)	$logK_f$	$\Delta G°$ (kJ mol^1)
H_2L^1	5.53(0.15)	31.55(0.37)	5.97(0.15)	34.06(0.37)
H_2L^2	4.97(0.06)	28.35(0.15)	5.31(0.11)	30.29(0.27)
H_2L^3	4.65(0.13)	26.53(0.32)	5.08(0.09)	28.98(0.22)
H_2L^4	3.97(0.14)	22.65(0.35)	4.23(0.11)	24.13(0.27)

The numbers in parentheses are the standard deviations.

CONCLUSIONS

In the first part of this work the synthesis of a set of unsymmetrical Schiff bases derived from salicylaldehyde derivatives and hindered aromatic diamine(3,4-diaminobenzo-phenone) with N_2O_2 moieties has been reported. In this type of Schiff bases the catalytic polymerization is an important process, to stabilize the Ni(II) cationic intermediates. The thermodynamic results in the second part of this work confirm our recent work on Fe(III) Schiff base complexes in a way that the electron withdrawing substituents reduce the K_f of the Ni(II) and Cu(II) complexes. By considering the synthesis and the thermodynamic studies, the following conclusions have been drawn:

i) To prepare a new precursor (half unit) a very simple method has been suggested. This half unit is stable and can be used for the synthesis of a large number of unsymmetrical Schiff bases.

ii) The, K_f, and the free energy change values for Cu(II) complexes are higher than Ni(II) complexes.

iii) The formation constant for a given metal decreases according to the electronic effect of the substituents at position 5, which follow the sequence of the ligands: $H_2L^1 > H_2L^2 > H_2L^3 > H_2L^4$.

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