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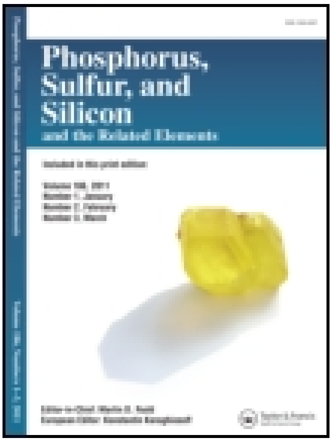

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Nickel (II) and Copper (II) Complexes Derived from NNOS Donor Unsymmetrical Tetradentate Schiff Base Ligands: Synthesis, Characterization, and Thermodynamic Studies

Mozaffar Asadi [a], Sheida Esmaielzadeh [a] & Khosro Mohammadi [b]
[a] Chemistry Department, College of Sciences, Shiraz University, Shiraz, I. R. Iran
[b] Chemistry Department, Faculty of Sciences, Persian Gulf University, Bushehr, I. R. Iran

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NICKEL (II) AND COPPER (II) COMPLEXES DERIVED FROM NNOS DONOR UNSYMMETRICAL TETRADENTATE SCHIFF BASE LIGANDS: SYNTHESIS, CHARACTERIZATION, AND THERMODYNAMIC STUDIES

Mozaffar Asadi,[1] Sheida Esmaielzadeh,[1]
and Khosro Mohammadi[2]
[1]Chemistry Department, College of Sciences, Shiraz University, Shiraz, I. R. Iran
[2]Chemistry Department, Faculty of Sciences, Persian Gulf University,
Bushehr, I. R. Iran

A set of eight unsymmetrical tetradentate Schiff bases (cdPhsalpd = Methyl-2-{[3-(2-hydroxyphenyl)phenylidynenitrilo]propyl}amino-1-cyclopentenedithiocarboxylate; cd3-, 4-, 5-OMesalpd = Methyl-2-{[3-(2-hydroxy 3-, 4-, 5-methoxyphenyl)methylidynenitrilo]propyl} amino-1-cyclopentenedithiocarboxylate; cd5Clsalen = Methyl-2-{[3-(2-hydroxy-5-chloro phenyl)methylidynenitrilo]propyl}amino-1-cyclopentenedithiocarboxylate; cd5Brsalen = Methyl-2-{[3-(2-hydroxy-5-bromophenyl)methylidynenitrilo]propyl}amino- 1-cyclopentenedithiocarboxylate; cd5NO$_2$salen = Methyl-2-{[3-(2-hydroxy-5-nitrophenyl)methylidynenitrilo]propyl}amino-1-cyclopentenedithiocarboxylate; and cd5SO$_3$Na = Methyl-2-{[3-(2-hydroxy-5-sodiumsulfitephenyl)methylidynenitrilo]propyl} amino-1-cyclopentenedithiocarboxylate, have been obtained by condensation of methyl-2-(3-aminopropylamino) cyclopentenedithiocarboxylate (Hcdpd) with some substituted salicylaldehydes, 2-hydroxy acetophenone, and 2-hydroxy benzophenone, which present a NNOS coordination spheres. Also, the metal complexes (M = Cu, Ni) of these ligands were prepared and characterized by elemental analysis, IR, ^{1}H NMR, UV-Vis, and mass spectrometry.

The formation constants and the thermodynamic free energies were measured using UV-Vis spectrophotometry titration for 1:1 complex formation at constant ionic strength 0.1 M (NaClO$_4$) at 25°C in DMF. The trend of the complex formation of the nickel and copper complexes is as follows: [M(cdMesalpd)] > [(Mcdsalpd)] > [M(cdPhsalpd)] and [M(cd5OMesalpd)] > [M(cd3OMesalpd)] > [M(cd4OMesalpd)] and [M(cd5OMesalpd)] > [M(cdsalpd)] > [M(cd5Brsalpd)] > [M(cd5Clsalpd)] > [M(cd5SO$_3$Nasalpd)] > [M(cd5NO$_2$salpd)]. Our results revealed the thermodynamic formation constant, $\mathbf{K}_f$, and the free energy values for Cu(II) complexes are higher than the Ni(II) complexes.

Supplemental materials are available for this article. Go to the publisher's online edition of **Phosphorus, Sulfur, and Silicon and the Related Elements** ***to view the free supplemental file.***

Keywords Coordination; metal complexes; Schiff base ligand; thermodynamic; unsymmetrical

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Address correspondence to Mozaffar Asadi, Chemistry Department, College of Sciences, Shiraz University, Shiraz 71454, I. R. Iran. E-mail: asadi@susc.ac.ir, mozaffarasadi@yahoo.com

INTRODUCTION

Schiff base ligands are of significant interest not only for their pharmacological properties as antibacterial, anticancer, and antifungal agents,[1,2] but also for their capacity for chemical recognition of anions and metals of biochemical and environmental importance.[3–5] Schiff base complexes containing different central metal atoms have been studied in great detail for their various crystallographic features, enzymatic reactions, steric effects, structure-redox relationships, mesogenic characteristics, catalysis, magnetic properties, and their important role in the understanding of the coordination chemistry of transition metal ions.[6]

Symmetric tetradentate Schiff base complexes have been used extensively as macrocycle models,[7] while unsymmetric complexes are very important in biological systems and in industrial catalysis.[8,9] One of the most important classes of unsymmetric complexes mixed nitrogen–sulfur donor ligands with metal ions by bonding through sulfur and azomethine nitrogen of ligands. Tetradentate ligands with N_2OS[10,11] and N_2S_2[12] coordination spheres were prepared. In recent years, complexes containing sulfur donors have received considerable attention due to the identification of a sulfur-rich coordination environment in biological centers.[13] When the ligands are complexed with metal ions, their biological activities are increased.[14] The first reports of the active site structure of type I blue copper (II) containing protein were published in 1983.[15,16] There has been great interest in designing highly distorted MN_2S_2 systems that may serve as spectral models of the active sites of the metalloenzymes.[17,18] Nickel has been discovered of the active site of several other classes of enzymes, including hydrogenases,[19–22] methyl co-enzyme reductases,[23] and CO dehydrogenases.[24]

In this article, we report the synthesis and characterization of some unsymmetrical Schiff base ligands and their Ni(II) and Cu(II) complexes (see Scheme 1). The compounds were characterized by elemental analysis, IR, NMR, mass, and UV-Vis techniques. We have also measured the thermodynamic formation constant, K_f, and the free energy, ΔG°, at 25°C in DMF solvent for the complexes. By comparing the spectral and the thermodynamic properties of Ni(II) and Cu(II) Schiff base complexes, we aimed to investigate the effects of different electronic and steric behaviors.

RESULTS AND DISCUSSION

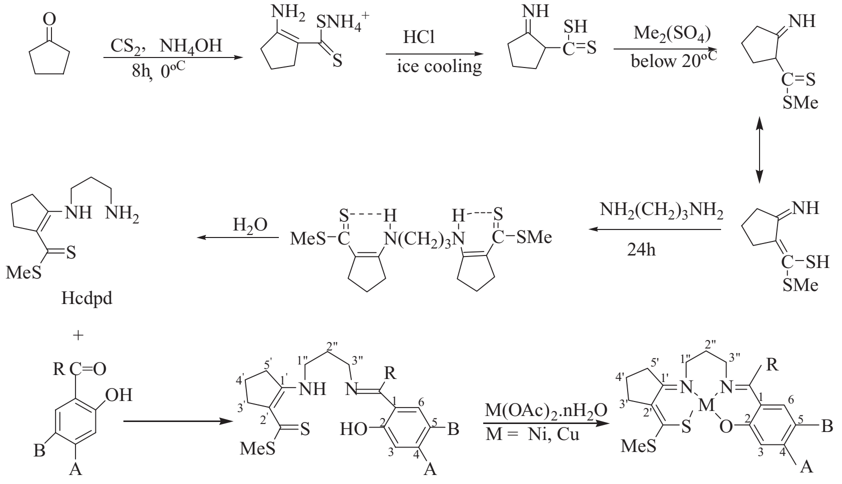
Synthesis of the Schiff base complexes may be represented by Equation (1):

$$M(OAc)_2 \cdot nH_2O + H_2L^X \rightarrow ML^X + 2HOAc + (n\text{-}2)H_2O (X = 1 - 8) \qquad (1)$$

The analytical data of the ligands and their complexes together with physical properties are summarized in Table I. All the ligands and their complexes gave satisfactory elemental analysis.

Spectral Characterization

Electronic absorption spectra. The electronic spectra of the Schiff base ligands in the DMF solvent show a low intensity band in the 295–314 nm region, which is assigned to π–π^* transition, and a relatively intense band in 395–398 nm region, which is due to n–π^* excitation.[25,26] Electronic spectra of M(cdRABsalpd) were recorded in the interval 300–700 nm in DMF solvent at room temperature. Spectra of Ni(II) and Cu(II) complexes are very



No.	Empirical formula	R	A	B	Abbreviation of compounds
H_2L^1	$C_{23}H_{26}N_2OS_2$	Ph	H	H	H_2cdPhsalpd
H_2L^2	$C_{18}H_{24}N_2O_2S_2$	H	OMe	H	H_2cd4OMesalpd
H_2L^3	$C_{18}H_{24}N_2O_2S_2$	H	H	OMe	H_2cd5OMesalpd
H_2L^4	$C_{17}H_{22}N_2O_2S_2$	H	OH	H	H_2cd4OHsalpd
H_2L^5	$C_{17}H_{21}N_2ClOS_2$	H	H	Cl	H_2cd5Clsalpd
H_2L^6	$C_{17}H_{21}N_2BrOS_2$	H	H	Br	H_2cd5Brsalpd
H_2L^7	$C_{17}H_{21}N_3O_3S_2$	H	H	NO_2	H_2cd5NO_2salpd
H_2L^8	$C_{17}H_{21}N_2O_4S_3Na$	H	H	SO_3Na	H_2cd5SO_3Nasalpd

Scheme 1

similar, where two or three intense bands in the region 320–448 nm are observed (see Table S1, available online in the Supplemental Materials). In Ni(II) complexes, the observed bands in the region 430–450 nm are probably due to S–M and O–M, LMCT transitions, and occur at energies similar to those found for the corresponding symmetric metal complexes [M(salen)][27] and [M(cd$_2$en)].[12] The low energy band is typical of d–d transitions in square planar nickel (II) complexes with mixed coordination spheres containing nitrogen and sulfur atoms, suggesting that all the nickel (II) complexes studied remain approximately square planar, even in strong donor solvents.[28] This is in accordance with the ^{1}H NMR spectra obtained in $CDCl_3$, DMSO-d_6, which show that the Ni(II) complexes are diamagnetic in this solvent[29] (see the Supplementary Materials). The d–d bands are not observed due to the low concentration ($\sim 10^{-4}$ M) of the complexes solution. These bands should be low in intensity in the region of 600–700 nm.[30]

The electronic spectra of unsymmetrical Schiff base copper (II) complexes have a band in the region of 320–336 nm attributed to the π–π^* transition. The broad, slightly intense, and poorly resolved bands between 390–398 nm may be assigned to O(phenolat)↔Cu^{II} LMCT or MLCT.[31] The d–d bands were not observed in these complexes similar to Ni(II) complexes.

Table I Analytical and physical data of the unsymmetrical Schiff bases complexes

No.	Formula weight	Yield (%)	Mp (°C)	Anal. Found (Calc.)(%)			
				C	H	N	S
H_2L^1	410.59	61	182	67.04	6.74	7.03	15.40
				(67.28)	(6.38)	(6.82)	(15.62)
H_2L^2	364.52	73	117	59.34	6.87	8.04	17.28
				(59.31)	(6.64)	(7.69)	(17.59)
H_2L^3	364.52	80	126	58.96	6.83	7.89	17.45
				(59.31)	(6.64)	(7.69)	(17.59)
H_2L^4	350.49	77	197	58.04	6.60	7.68	18.40
				(58.26)	(6.33)	(7.99)	(18.29)
H_2L^5	368.93	70	112	55.12	5.43	7.61	17.18
				(55.34)	(5.74)	(7.59)	(17.38)
H_2L^6	413.39	70	120	49.12	5.40	6.53	15.78
				(49.39)	(5.12)	(6.78)	(15.51)
H_2L^7	379.49	92	128	53.64	5.89	11.32	16.58
				(53.81)	(5.58)	(11.07)	(16.90)
H_2L^8	436.53	54	238	46.51	5.11	6.71	21.98
				(46.77)	(4.85)	(6.42)	(22.03)
NiL^3	421.20	80	204	51.15	5.55	6.72	15.34
				(51.33)	(5.26)	(6.65)	(15.22)
NiL^4	407.17	74	248	50.04	5.27	6.75	15.78
				(50.15)	(4.95)	(6.88)	(15.75)
NiL^5	425.62	67	240	47.61	4.67	6.32	14.90
				(47.97)	(4.50)	(6.58)	(15.06)
NiL^6	470.07	68	233	43.15	4.25	6.05	13.75
				(43.44)	(4.07)	(5.96)	(13.64)
NiL^7	436.17	95	226	46.83	4.47	9.70	14.45
				(46.81)	(4.39)	(9.63)	(14.70)
NiL^8	493.21	51	265	41.68	4.24	5.47	19.63
				(41.40)	(3.88)	(5.68)	(19.50)
CuL^1	472.12	61	216	58.85	5.32	5.78	13.68
				(58.51)	(5.12)	(5.93)	(13.58)
CuL^2	426.05	74	219	50.68	5.04	6.77	14.83
				(50.74)	(5.20)	(6.58)	(15.05)
CuL^3	426.05	83	208	51.04	5.29	6.83	14.77
				(50.74)	(5.20)	(6.58)	(15.05)
CuL^4	421.03	74	221	49.64	4.67	7.05	15.32
				(49.56)	(4.89)	(6.80)	(15.56)
CuL^5	439.40	71	217	47.79	4.21	6.22	14.65
				(47.43)	(4.45)	(6.51)	(14.90)
CuL^6	474.92	68	205	43.24	4.11	5.68	13.24
				(42.99)	(4.03)	(5.90)	(13.50)
CuL^7	441.02	92	214	46.57	4.12	9.77	14.32
				(46.30)	(4.34)	(9.53)	(14.54)
CuL^8	498.06	52	265	41.04	4.18	5.35	19.40
				(41.00)	(3.84)	(5.62)	(19.31)

Analysis of the results shows that the positions of the LMCT bands are not very sensitive to different substitutions on salicylaldehyde and imine band, and may not be directly related to the electron donor/acceptor ability of the substituents.[32]

Figure S1 (Supplemental Materials) shows the electronic spectral change observed in DMF solution when Cu^{2+} ion was added to Schiff base ligand H_2cd5Brsalpd. In the absence

Table II ^{1}H NMR data of the unsymmetrical Schiff bases and their Ni(II) complexes (in ppm)

No.	OH proton	NH or SH proton	Imine proton	Phenyl proton	1,3-Diaminopropan proton	SCH_3	Substituted (X,Y)
H_2L^{1a}	15.40	12.03	—	7.15–7.52	2.07, 3.41, 3.50	2.55	—
H_2L^{2a}	13.70	12.44	8.28	6.39–7.11	2.03, 3.44, 3.71	2.60	3.81
H_2L^{3a}	12.86	12.38	8.34	6.75–6.87	2.17, 3.69, 3.82	2.55	3.86
H_2L^{4a}	13.63	12.25	8.36	6.15–7.15	1.87, 3.44, 3.54	2.49	—
H_2L^{5a}	13.20	12.45	8.35	6.88–7.23	2.05, 3.44, 3.76	2.60	—
H_2L^{6a}	13.21	12.45	8.35	6.84–7.34	2.06, 3.44, 3.76	2.58	—
H_2L^{7a}	14.46	12.46	8.47	6.98–8.25	2.10, 3.47, 3.83	2.57	—
H_2L^{8b}	13.50	12.26	8.59	6.78–7.65	1.94, 3.30, 3.65	2.46	—
NiL^{1a}	—	—	—	6.33–7.67	1.81, 3.44, 3.56	2.69	—
NiL^{2a}	—	—	7.44	6.10–6.90	1.83, 3.49, 3.63	2.67	3.70
NiL^{3a}	—	—	7.64	6.50–6.81	1.77, 3.60, 3.67	2.67	3.70
NiL^{4a}	—	—	7.45	6.06–6.92	1.80, 3.48, 3.60	2.67	—
NiL^{5a}	—	—	7.53	6.68–7.01	1.85, 3.60, 3.65	2.67	—
NiL^{6a}	—	—	7.52	6.63–7.26	1.84, 3.62, 3.70	2.66	—
NiL^{7a}	—	—	8.11	6.70–7.94	1.82, 3.62, 3.75	2.68	—
NiL^{8b}	—	—	8.26	6.33–7.40	1.78, 3.52, 3.59	2.46	—

[a] Solvent is $CDCl_3$.
[b] Solvent is DMSO-d_6.

of a Cu^{2+} ion the yellow H_2cd5Brsalpd solution showed the absorption bands at 313 and 395 nm. As the Cu^{2+} ion solution was added, the signal of H_2cd5Brsalpd decreased, and those of the new complex [Cu(cd5Brsalpd)] at 287, 336, and 390 increased in intensity with the isobestic points at 305, 322, 373, 424 nm. The last spectrum of the titration was similar to the spectrum of [Cu(cd5Brsalpd)] complex that has been synthesized and characterized separately by different methods.

^{1}H NMR spectra. The spectra of the complexes were recorded in $CDCl_3$ and DMSO-d_6 solution at 250 MHz, and chemical shifts are in units of ppm relative to TMS as internal standard on the delta (δ) scale. The ^{1}H NMR spectra of the Schiff base ligands and their complexes was collected in Table II. Five distinct peaks at 2.46–2.69 ppm, 6.06–8.25 ppm, 7.52–8.59 ppm, 12.03–12.46 ppm, and 13.20–15.40 ppm are assigned to SCH_3, phenyl, azomethine, amine or thio, and hydroxyl protons, respectively. The hydroxyl proton and amine or thio (NH or SH) proton disappears in the complexes, indicating that the OH and NH or SH groups have been deprotonated and bonded to metal ions.[12] Comparing the ^{1}H NMR spectra of the free ligands and complexes shows that the azomethine and aromatic protons resonance of the ligands are shifted to upfield in the Ni complexes.[33] A singlet signal at $\delta = 3.81, 3.86$ ppm is assigned to those Schiff bases and their complexes that have an OCH_3 group. The signals due to OCH_3 are also affirmed by an up-field change in chemical shift for Ni(II) complexes.

IR spectra. Important IR bands of the ligands and complexes with their assignment are presented in Table III. The absorption band around 1600 cm^{-1} is assigned to an azomethine group,[34] and the phenolic ν(C—O) stretching band is observed at 1230–1296 cm^{-1}.[35] Strong bands at 1440–1490 cm^{-1} have been previously assigned to ν(C=C) phenyl ring stretching vibrations.[36] Some of their sulfur addition products assigned the bands in the range 700–800 cm^{-1} to C—S, and the bands between 1100–1185 cm^{-1} are probably due to the coupling ν(C—S)$_+\nu$(C—N).[37–39] Upon complexation, the positions of these bands are

Table III Infrared data of the unsymmetrical Schiff bases and their complexes (in cm^{-1})

Compounds	(C=S)	(C−S + C−N)	Phenolic (C−O)	(C=C)	(C=N)	Substituted (A,B)
H_2L^1	756	1134	1280	1481	1604	
H_2L^2	790	1140	1272	1488	1635	
H_2L^3	779	1153	1269	1481	1639	
H_2L^4	786	1164	1234	1458	1643	3296
H_2L^5	761	1130	1269	1479	1635	
H_2L^6	763	1181	1280	1481	1635	
H_2L^7	740	1105	1296	1442	1651	1353, 1550
H_2L^8	732	1118	1272	1481	1635	650, 1200
NiL^1	748	1134	1280	1442	1602	
NiL^2	786	1126	1268	1458	1614	
NiL^3	748	1153	1215	1461	1623	
NiL^4	784	1134	1234	1450	1620	3233
NiL^5	723	1120	1268	1450	1627	
NiL^6	732	1172	1280	1458	1620	
NiL^7	736	1103	1291	1442	1627	1356, 1550
NiL^8	720	1110	1244	1458	1620	650, 1200
CuL^1	748	1134	1270	1442	1596	
CuL^2	786	1118	1271	1450	1625	
CuL^3	767	1149	1261	1442	1631	
CuL^4	784	1134	1226	1450	1630	3217
CuL^5	717	1120	1264	1456	1635	
CuL^6	725	1180	1275	1458	1627	
CuL^7	726	1103	1294	1442	1635	1351, 1548
CuL^8	732	1110	1265	1465	1627	650, 1190

shifted by ca. 2–25 cm^{-1} to lower frequency. This indicates that coordination takes place through the azomethine nitrogen and sulfur of the ν(C=S) group and oxygen atom of the phenolic group.[33,39] Two sharp peaks at around 1300 cm^{-1} and 1550 cm $^{-1}$ are typical of nitro group in H_2L^7, NiL^7, and CuL^7 and two absorption bands in 650 and 1200 cm^{-1} are assigned to ν(S−O) and ν(S=O) stretching in H_2L^8, NiL^8, and CuL^8, which undergo minor changes in their complexes. It may therefore be that the NO_2 and SO_3 groups are not coordinated to the metal ions.[40]

Mass spectra. The mass spectra of the ligands show intense molecular ion peaks m/z $[M]^+$. The mass spectra of some compounds, also a show prominent peak corresponding to m/z $[M+1]^+$ (see Table S2 in the Supplemental Materials).

The Formation Constants and the Thermodynamic Free Energy Calculations

Formation constants have been determined by UV-vis absorption spectroscopy through titration of the ligands with various concentrations of the metal ions at constant ionic strength 0.1 M ($NaClO_4$) at 25°C. The complex formation constants, K_f, were calculated using the SQUAD computer program,[41] designed to calculate the best values for the formation constants of proposed equation model [Equation (1)] by employing a nonlinear, least-squares approach.

Also the free energy change, ΔG°, of the formed complexes was determined by $\Delta G^\circ = -RT \ln K_f$, where K_f is the complex formation constant, R is the gas constant, and T is the temperature in Kelvin. The formation constants and the free energy data are collected in Table S3 (Supplementary Materials). The results show that Cu(II) has a greater tendency to bind with the ligands than Ni(II), which may be attributed to its higher positive charge distribution and the ligand deformation geometry.

The electronic effect of para substituted Schiff base ligands. In this part of the work, we studied the electronic effect of *para* substitutional groups bonded to Schiff base ligands complexed to Ni(II) and Cu(II) ions. The formation constants and the thermodynamic parameter are collected in Table S4 (Supplemental Materials). On the basis of the thermodynamic results, the trend of the interaction between the unsymmetrical ligands and Cu(II) and Ni (II) ions is as follows:

$$\text{cd5OMesalp} > \text{cdsalpd} > \text{cd5Brsalpd} > \text{cd5Clsalpd} > \text{cd5SO}_3\text{Nasalpd} > \text{cd5NO}_2\text{salpd}$$

In the *para* substituted Schiff base ligands, the formation constants varies as can be expected from the electronic effects of the substituents at position 5. Thus, the formation constants decrease according to the sequence OMe > H > Br > Cl > SO_3 > NO_2, i.e., in order of an increase in both electron-withdrawing and π-acceptor qualities of the substituents and the donor ability of the ligand groups (mainly the phenoxy groups). Similar results have been reported previously for electrochemical properties of the analogous Cu(II), Ni(II), and Co(III) systems.[42–44] The acceptor functional groups make the Schiff base a poor donor ligand and decrease the formation constants, while the donor groups increase the formation constants because they leads to increased donor ability of Schiff base ligands; therefore the ligands have NO_2 and SO_3 group, and H_2cd5NO_2salpd and H_2cd5SO_3Nasalpd have the smallest formation constant, while the ligands that have OMe groups have the highest formation constant because OMe is a donating group.[45] Therefore, in the stabilization of the tetra-coordinated complex, the donation power of the Schiff base is important, and hence their formation constants, K_f, with donors are higher.

The effect of the position of substituents. In continuation of our studies on formation constants of complexes, we have studied here the effect of the position of substituents on the phenyl ring of Schiff base on the formation constant of the complexes of H_2cd3OMesalpd,[11] H_2cd4OMesalpd (H_2L^2), and H_2cd5OMesalpd (H_2L^3) with Cu(II) and Ni(II) ions. The results show the following trend of complex formation of a given cation towards the Schiff bases:

$$\text{cd5OMesalpd} > \text{cd3OMesalpd} > \text{cd4OMesalpd}$$

In the case of H_2L^3, the methoxy group situated in the *para* position to the phenolic oxygen donor atoms of N_2OS backbone can release the electron directly and stabilize the tetra-coordinate complex, so the formation constant is larger than that for *meta* position in the H_2L^2, and H_2cd3OMesalpd, which has the steric effect (see Table S4).[43]

The electronic effect of the equatorial Schiff base ligands. The substitutional effects on the imine bond were studied by determining the formation constants for [M(cdPhsalpd)] and [M(cdMesalpd)] where M = Ni, Cu. The results show the following trend in the complexes formation between ligand Schiff bases H_2cdPhsalpd, H_2cdMesalpd,[11] with Ni(II) and Cu(II) ions (Table S5): M(cdMesalpd) > M(cdsalpd) > M(cdPhsalpd).

These values for electron-releasing methyl Schiff bases were more than those for electron-withdrawing phenyl Schiff bases.[46] The phenyl group makes the Schiff base a poor donor ligand (and a good acceptor ligand) and decreases the formation constants, while the methyl group is a donating group and increases the formation constant.

CONCLUSION

1. The formation constants, K_f, and the free energy values for Cu(II) complexes are higher than the Ni(II) complexes, which may be attributed to its higher positive charge distribution and the ligand deformation geometry.
2. The trend of the complex formation of the *para* substitutional groups bonded to Schiff base ligands complexed to Ni(II) and Cu(II) ion decreases as follows: cd5OMesalpd > cdsalpd > cd5Brsalpd > cd5Clsalpd > cd5SO_3Nasalpd > cd5NO_2salpd
3. The formation constants for M[(cd3-, 4-, 5-OMesalpd)] complexes has the following trend: cd5OMesalpd > cd3OMesalpd > cd4OMesalpd
4. The trend of the complex formation of the substitutional on imine bond Schiff base ligands complexed to Ni(II) and Cu(II) ion decreases as follow: cdMesalpd > cdsalpd > cdPhsalpd
5. In the series [H_2cdRABsalpd], it seems that the combination of strain, strength of the ligand field, the electronic effect, the geometry of the ligand, the electron configuration, and the ionic radii of the metal can affect the complex formation constants.

EXPERIMENTAL

Synthesis of Schiff Base Ligands

Methyl-2-(3-aminopropylamino)cyclopentenedithiocarboxylate (Hcdpd) was prepared by published methods.[11,47,48] The ligands were prepared by addition of the equimolar amount of the appropriate salicylaldehyde derivatives to a methanolic solution of Hcdpd. The yellow products were recrystallized from methanol/chloroform 1:1 (v:v) (see Scheme 1).

Synthesis of the Complexes

A novel series of mononuclear tetradentate complexes M(cdRABsalpd), (M = Ni, Cu) were synthesized as follows: To a solution of the appropriate ligand (1 mmol) in 10 mL of chloroform/methanol 2:1 (v:v), a solution of metal acetate (1 mmol) in 10 mL of methanol was added. The solution was stirred for 15 min and then allowed to stand at room temperature for 24 h. After filtering, the brown and the green powders were recrystallized from acetonitrile/methanol 1:1 (v:v) (see Scheme 1).

Thermodynamic Studies

The formation constant measurements were carried out by spectrophotometric titration at constant ionic strength 0.1 M ($NaClO_4$) at 2 5°C (± 0.1°C). In a typical measurement, 2.5 mL solution of ligands (10^{-5} M) in a DMF was titrated with various concentrations of the metal acetate (10^{-5}–10^{-4} M) in DMF. UV-vis spectra were recorded in the range

290–700 nm about 5 min after each addition. The formed product shows different absorption from the free ligand, while the metal ion solution shows no absorption at those wavelengths. For example, the variation of the electronic spectra for H_2cd5Brsalpd titrated with various concentration of Cu(II) acetate at 25°C in DMF is shown in Figures S1 and S2. The same is valid for other systems.

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