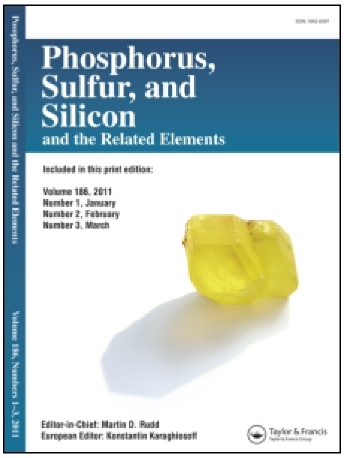

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Mozaffar Asadi[a]; Sheida Esmaielzadeh[a]; Khosro Mohammadi[b]
[a] Chemistry Department, College of Sciences, Shiraz University, Shiraz, I. R. Iran [b] Chemistry Department, Faculty of Sciences, Persian Gulf University, Bushehr, I. R. Iran

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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-chlorophenyl)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, $K_f$, 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, $\Delta G^\circ$, 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

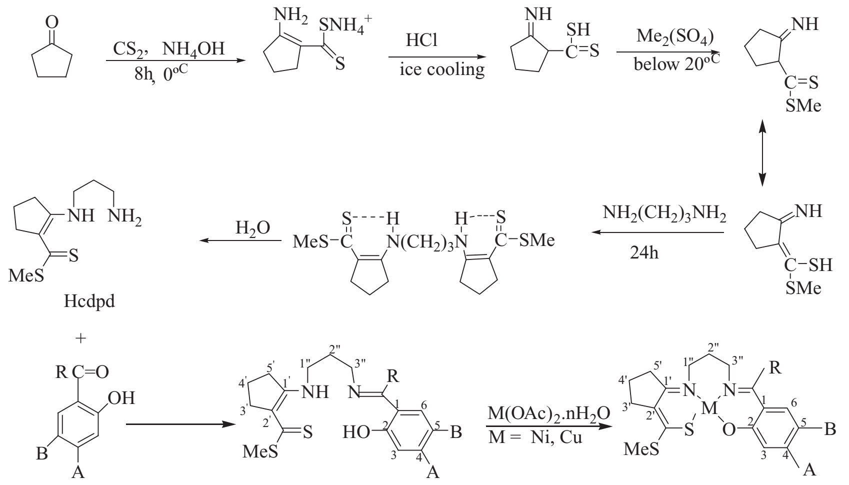
Synthesis of the Schiff base complexes may be represented by Equation (1):

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

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 $\pi$–$\pi^*$ transition, and a relatively intense band in 395–398 nm region, which is due to n–$\pi^*$ 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 | $H_2$cdPhsalpd |
| $H_2L^2$ | $C_{18}H_{24}N_2O_2S_2$ | H | OMe | H | $H_2$cd4OMesalpd |
| $H_2L^3$ | $C_{18}H_{24}N_2O_2S_2$ | H | H | OMe | $H_2$cd5OMesalpd |
| $H_2L^4$ | $C_{17}H_{22}N_2O_2S_2$ | H | OH | H | $H_2$cd4OHsalpd |
| $H_2L^5$ | $C_{17}H_{21}N_2ClOS_2$ | H | H | Cl | $H_2$cd5Clsalpd |
| $H_2L^6$ | $C_{17}H_{21}N_2BrOS_2$ | H | H | Br | $H_2$cd5Brsalpd |
| $H_2L^7$ | $C_{17}H_{21}N_3O_3S_2$ | H | H | $NO_2$ | $H_2$cd5$NO_2$salpd |
| $H_2L^8$ | $C_{17}H_{21}N_2O_4S_3Na$ | H | H | $SO_3Na$ | $H_2$cd5$SO_3$Nasalpd |

**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 $\pi$–$\pi^*$ 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 $H_2$cd5Brsalpd. 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 $H_2$cd5Brsalpd solution showed the absorption bands at 313 and 395 nm. As the $Cu^{2+}$ ion solution was added, the signal of $H_2$cd5Brsalpd 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 ($\delta$) 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 $\nu$(C—O) stretching band is observed at 1230–1296 $cm^{-1}$.[35] Strong bands at 1440–1490 $cm^{-1}$ have been previously assigned to $\nu$(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 $\nu(C{-}S)_+\nu(C{-}N)$.[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 $\nu$(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 $\nu$(S−O) and $\nu$(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, $\Delta G^\circ$, 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 $\pi$-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 $H_2$cd5$NO_2$salpd and $H_2$cd5$SO_3$Nasalpd 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 $H_2$cd3OMesalpd,[11] $H_2$cd4OMesalpd ($H_2L^2$), and $H_2$cd5OMesalpd ($H_2L^3$) 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 $H_2$cd3OMesalpd, 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 $H_2$cdPhsalpd, $H_2$cdMesalpd,[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 > cd5$SO_3$Nasalpd > cd5$NO_2$salpd
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 [$H_2$cdRABsalpd], 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 $H_2$cd5Brsalpd 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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