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Synthesis and Characterization of Some Cobalt(II), Copper(II), and Nickel(II) Complexes with New Schiff Bases from the Reaction of p-Aminoazobenzene with Salicylaldehyde

Esin Peker^a & Selahattin Serin^b

^a Department of Chemistry, Faculty of Science and Arts, Kahramanmaraş Sütçü İmam University, Kahramanmaraş, Turkey

^b Department of Chemistry, Faculty of Science and Arts, Çukurova University, 01133, Balcalı, Adana, Turkey

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Synthesis and Characterization of Some Cobalt(II), Copper(II), and Nickel(II) Complexes with New Schiff Bases from the Reaction of *p*-Aminoazobenzene with Salicylaldehyde

Esin Peker¹ and Selahattin Serin^{2,*}

¹Department of Chemistry, Faculty of Science and Arts, Kahramanmaraş Sütçü İmam University, Kahramanmaraş, Turkey
²Department of Chemistry, Faculty of Science and Arts, Çukurova University, Balcalı, Adana, Turkey

ABSTRACT

Two new Schiff bases have been synthesized by the reaction of *p*-aminoazobenzene with salicylaldehyde ($L^{1}H$) and the oxidative polycondensation product of $L^{1}H$ ($L^{2}H_{2}$). The complexes of cobalt(II), copper(II), and nickel(II) with $L^{1}H$ and $L^{2}H_{2}$ have been prepared. The ligands and their complexes have been characterized by elemental analyses, IR spectra, electronic absorption spectra, mass spectra, ¹H and ¹³C NMR spectra, and magnetic susceptibility measurements. The thermal properties of all complexes have been

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^{*}Correspondence: Selahattin Serin, Department of Chemistry, Faculty of Science and Arts, Çukurova University, 01133 Balcalı, Adana, Turkey; E-mail: serin@cu.edu.tr.

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studied by TG and DTA. The analytical data show that the metal to ligand ratio in the $L^{1}H$ complexes is 1 : 2, but in the $L^{2}H_{2}$ complexes it is 1 : 1.

Key Words: p-Aminoazobenzene; Schiff bases; Salicylaldehyde; Hydroquinones.

INTRODUCTION

Apart from their purely chemical interest, azo-azomethine dyes are being increasingly used in the textile, leather, and plastic industries.^[1] Regarding the industrial importance of metallized azo dyes relative to their structures, they can be classified into two main types: those in which the azo group participates in the coordination to the metal ion with formation of the chelate ring and those in which it is not.^[2]

Schiff bases derived from the salicylaldehydes are known as polydentate ligands, coordinating in deprotonated or neutral forms.^[3] Schiff base complexes containing different central metal atoms such as Cu, Ni, Co, and Pd 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. In some Schiff base metal chelates, it has been shown that minor changes in the structure of the ligands containing hard/soft donor atoms, e.g., nitrogen, sulfur and/or oxygen markedly affected the activity of these compounds.^[4,5]

It is known that phenol, naphthols, hydroquinone, and aldehydes enter into an oxidative polycondensation reaction and form polyconjugated compounds. The oligophenols and their derivatives have been used in various fields, because of their electron structure properties.^[6]

In the present paper, the synthesis and characterization of two new Schiff bases (Fig. 1) and their Co(II), Cu(II), and Ni(II) metal complexes (Fig. 2) are reported.

EXPERIMENTAL

Materials

The metal salts $Co(OAc)_2 \cdot 4H_2O$, $Cu(OAc)_2 \cdot H_2O$, and $Ni(OAc)_2 \cdot 4H_2O$, *p*-aminoazobenzene and salicylaldehyde were obtained from Fluka. Solvents were analytical grade and purified by standard procedures.

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Figure 1. Structures of Schiff base ligands.

Physical Measurements

Elemental analyses (C, H, N) were performed using a Carlo Erba 1106 elemental analyzer. Infrared spectra were obtained using KBr discs (4000–400 cm⁻¹) on a Shimadzu 8300 FTIR spectrophotometer. The electronic spectra in the 200–900 nm range were obtained using THF, EtOH, CHCl₃, *n*-hexane, *n*-heptane, and toluene on a Shimadzu UV-160 A spectrophotometer. ¹H and ¹³C NMR spectra were taken on a Varian XL-200 NMR instrument. TMS was used as internal standard and deuterated DMSO as solvent. Magnetic measurements were carried out by the Gouy method using Hg[Co(SCN)₄] as calibrant. Mass spectra of the ligands were recorded on a VG Zab Spec. GC-MS spectrometer with fast atom bombardment. Thermal analyses were performed on Shimadzu DTA 50 and TG 50 H models using 10 mg samples. The DTA and TG curves were obtained at a heating rate of 10 °C min⁻¹ in dry N₂ atmosphere in the 25–750 °C range.

Synthesis of *N*-(*p*-Phenylazobenzene)salicylaldeimine (L¹H)

p-Aminoazobenzene (1.97 g, 10 mmol) dissolved in EtOH (10 mL) was carefully added with stirring to a solution of salicylaldehyde (1.22 g, 10 mmol) in EtOH (10 mL). The resulting mixture was allowed to stir magnetically under reflux for 2–3 hr. After cooling the resulting precipitate was filtered, washed with cold EtOH, recrystallized from EtOH, and dried in a vacuum dessicator. Yield: 2.53 g (84 %), M.p.: 160 °C, M.w.: 301 g mol⁻¹.

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 $(ML^2)_n$ M = Cu(II), Co(II) and Ni(II); n = 10

Synthesis of *m,m*'-di[*N*-(*p*-Phenylazobenzene)]salicylaldeimine (L²H₂)

The ligand $L^{1}H$ (1 g, 3 mmol) was dissolved in EtOH (40 mL). Then 5 mL of a solution of KOH (0.19 g, 3 mmol) was added with stirring to the solution of L¹H. Subsequently 0.83 mL of an aqueous solution of NaOCl (30%, 0.83 g, 11.10 mmol)^[7] was added to the mixture and the solution was allowed to stir



Figure 2. Proposed structures of the complexes.



magnetically for 5 hr. The resulting solution was neutralized with HCl. After neutralization, the precipitated solid was filtered, washed with water, recrystallized from n-heptane, and dried in a vacuum dessicator.

Synthesis of the Metal Complexes

Cobalt(II) Complex of $L^{1}H$

A solution of $Co(OAc)_2 \cdot 4H_2O(0.125 \text{ g}, 0.5 \text{ mmol})$ in MeOH (20 mL) was added to a solution of the ligand L¹H (0.301 g, 1 mmol) in absolute EtOH (40 mL). The mixture was refluxed for 2–4 hr at 80 °C. The precipitated compound was filtered, washed with cold EtOH, and dried *in vacuo* over P₄O₁₀.

Cobalt(II) Complex of L²H₂

A solution of $Co(OAc)_2 \cdot 4H_2O(0.125 \text{ g}, 0.5 \text{ mmol})$ in MeOH (20 mL) was added to a solution of the ligand L^2H_2 (0.300 g, 0.5 mmol) in absolute EtOH (40 mL). The mixture was refluxed for 2–4 hr at 80 °C. The precipitated compound was filtered, washed with cold EtOH, and dried *in vacuo* over P_4O_{10} .

Copper(II) Complex of L¹H

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A solution of $Cu(OAc)_2 \cdot H_2O(0.100 \text{ g}, 0.5 \text{ mmol})$ in MeOH (20 mL) was added to a solution of the ligand L¹H (0.301 g, 1 mmol) in absolute EtOH (40 mL). The mixture was stirred at 80 °C. The precipitated complex was filtered, washed with cold EtOH, and dried *in vacuo* over P₄O₁₀.

Copper(II) Complex of L^2H_2

A solution of $Cu(OAc)_2 \cdot H_2O(0.100 \text{ g}, 0.5 \text{ mmol})$ in MeOH (20 mL) was added to a solution of the ligand L^2H_2 (0.300 g, 0.5 mmol) in absolute EtOH (40 mL). The mixture was stirred at 80 °C. The precipitated complex was filtered, washed with cold EtOH, and dried *in vacuo* over P₄O₁₀.

Nickel(II) Complex of L¹H

A solution of $Ni(OAc)_2 \cdot 4H_2O(0.124 \text{ g}, 0.5 \text{ mmol})$ in MeOH (20 mL) was added to a solution of the ligand $L^1H(0.301 \text{ g}, 1 \text{ mmol})$ in absolute EtOH

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(40 mL). The mixture was stirred at 80 °C. The precipitated complex was filtered, washed with cold EtOH and dried *in vacuo* over P_4O_{10} .

Nickel(II) Complex of L^2H_2

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A solution of Ni(OAc)₂ · $4H_2O(0.124 \text{ g}, 0.5 \text{ mmol})$ in MeOH (20 mL) was added to a solution of the ligand L^2H_2 (0.300 g, 0.5 mmol) in absolute EtOH (40 mL). The mixture was stirred at 80 °C. The precipitated complex was filtered, washed with cold EtOH, and dried *in vacuo* over P₄O₁₀.

RESULTS AND DISCUSSION

In this study, L^1H , L^2H_2 and their Cu(II), Co(II), and Ni(II) metal complexes were synthesized and characterized. The complexes were synthesized by the general equations shown below.

$$M(OAc)_2 \cdot xH_2O + 2L^1H \longrightarrow [M(L^1)_2] + 2AcOH + xH_2O$$
$$M(OAc)_2 \cdot xH_2O + 2L^2H_2 \longrightarrow \frac{1}{n}[M(L^2)]_n + 2AcOH + xH_2O$$

The physical data and elemental analysis data of the ligands and their complexes are given in Table 1. These data show that the metal to ligand ratio in the L¹H complexes is 1:2, but in the L²H₂ complexes it is 1:1 and, consequently, the general formula of the Schiff base complexes are $M(L^1)_2$ and $(ML^2)_n$. The Schiff base ligands *N*-(*p*-phenylazobenzene)salicylaldeimine (L^1H) and *m*,*m'*-di[*N*-(*p*-phenylazobenzene)] salicylaldeimine (L^2H_2) were synthesized in high yields in EtOH. The ligands are stable at room temperature and soluble in common organic solvents such as EtOH, CHCl₃, and MeOH. The ¹H NMR and thin-layer chromotography results show only one isomer for *m*,*m'*-di[*N*-(*p*-phenylazobenzene)]salicylaldimine (L^2H_2) . The complexes are also stable at room temperature and soluble in *n*-hexane, *n*-heptane, benzene, toluene, *etc*.

Infrared Spectra

The infrared spectral data of the ligands and their complexes are given in Table 2. In the ligand spectra, both ligands exhibit bands at 3420 and 3055 cm^{-1} that are assignable to $\nu(\text{OH})$ and $\nu(\text{Ar-CH})$.^[8,9] But in the complexes, the band at 3420 cm^{-1} is absent. The ligands exhibit bands at 1566 and 1591 cm^{-1} , which are assigned to the vibration of the N=N group.^[1]

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	Table]	I. Some ar	nalytical data and pl	hysical pro	perties of lig	ands and complex	es.	
				1		Calc	culated (found,	(2)
Compound	Empirical formulas	Formula weight	Color	M.p. (°C)	Yield (g, %)	С	Н	N
L ¹ H	$C_{19}H_{15}N_3O$	301	Orange	160	2.53 (84)	75.75 (75.25)	4.98 (4.36)	13.95 (13.84)
$Co(L^1)_2$	$C_{38}H_{28}CoN_6O$	658.9	Brown	260	2.77 (84)	69.20 (68.92)	4.25 (4.00)	12.75 (12.23)
$Cu(L^1)_2$	C ₃₈ H ₂₈ CuN ₆ O	663.5	Dark brown	245	2.59 (78)	68.73 (68.41)	4.22 (4.03)	12.66 (12.16)
$Ni(L^1)_2$	C ₃₈ H ₂₈ NiN ₆ O ₂	658.7	Orange	>250	2.67 (81)	69.24 (68.85)	4.25 (3.99)	12.75 (12.25)
$L^{2}H_{2}$	$C_{38}H_{28}N_6O_2$	600	Dark orange	149	1.56 (78)	75.75 (75.28)	4.98 (4.86)	14.00 (14.39)
$(CoL^2)_n$	$C_{38}H_{26}C_0N_6O$	6,810	Reddish brown	225	5.21 (79)	69.21 (69.01)	3.95 (3.90)	12.66 (12.46)
$(CuL^2)_n$	C ₃₈ H ₂₆ CuN ₆ O	6,728	Brown	249	5.11 (77)	68.73 (68.52)	3.92 (3.85)	12.66 (12.35)
$(NiL^2)_n$	$C_{38}H_{26}NiN_6O_2$	6,798	Reddish brown	250	5.27 (80)	69.24 (68.92)	3.95 (3.89)	12.75 (12.37)





Compound	ν(OH)	$\nu(ArC-H)$	ν(CH=N)	$\nu(N=N)$	v(M-O)	v(M-N)
$L^{1}H$	3,425 m	3,055 m	1,614 s	1,591 s	_	
$Co(L^1)_2$	·	3,058 m	1,604 s	1,573 s	422 w	596 m
$Cu(L^1)_2$	_	3,037 m	1,608 s	1,587 m	418 w	599 m
$Ni(L^1)_2$	_	3,057 m	1,612 s	1,562 s	445 m	563 m
L^2H_2	3,425 m	3,055 m	1,614 s	1,591 s		
$(CoL^2)_n$	_	3,058 m	1,616 s	1,560 m	418 m	607 m
$(CuL^2)_n$	_	3,060 m	1,606 m	1,579 s	420 w	594 m
$(NiL^2)_n$	—	3,058 m	1,618 s	1,558 m	420 w	611 m

Table 2. IR spectral data of the ligands and their complexes (cm⁻¹, KBr).^a

^as, strong; m, medium; w, weak.

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The band at 1614 cm^{-1} is due to the vibration of the azomethine group in both ligands. This band in the complexes is shifted towards lower frequencies as a result of coordination of the azomethine nitrogen atom to the metal ion.^[10] In the complexes, new weak bands in the 611–520 and 445–418 cm⁻¹ range may be attributed to $\nu(M-N)$ and $\nu(M-O)$ stretching.^[2,11]

Electronic Spectra

The electronic absorption spectral data^[12,13] for the ligands are given in Table 3 and for the complexes in Table 4. In order to investigate the ketoamine-enolimine tautomeric forms of the Schiff base ligands, the electronic spectra are recorded in EtOH, CHCl₃, toluene, *n*-hexane, and *n*-heptane. As seen in Table 3, the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of L¹H in non-polar solvents such as toluene, *n*-hexane, and *n*-heptane were observed at 373, 348, and 335 nm, respectively. The same transitions in polar solvents such as CHCl₃ and EtOH, are observed in the 462–432 and 369–348 nm ranges. These data show that, L¹H prefers the tautomeric ketoamine form in non-polar solvents and the tautomeric enolimine form in non-polar solvents (Fig. 3).

The interaction of enolimine with a hydrogen bond-forming solvent (EtOH) would presumably reduce the O–H bond strength and facilitate proton transfer to the nitrogen center.^[14]

For L^2H_2 the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in all solvents were observed at 371–366 and 348 nm. These data show that L^2H_2 prefers the tautomeric enolimine form in both polar and non-polar solvents. The spectra of all complexes (Fig. 2, Table 4) contain absorption bands in the 813, 812, 706, and 569 nm ranges, which may be assigned to the d-d transition of metal ions.^[15]

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	Tab	le 3. Electronic spectra	al data of ligands in differ	ent solvents.	
Compound	EtOH $\lambda_{\max}^{a}(\varepsilon)^{b}$	$ ext{CHCl}_{3} \lambda_{ ext{max}}^{ ext{a}}(arepsilon)$	<i>n</i> -Hexane $\lambda_{\max}(\varepsilon)$	<i>n</i> -Heptane $\lambda_{\max}(\varepsilon)$	Toluene $\lambda_{\max}(\varepsilon)$
H ₁ H	462 (2,100), 367 (35,000), 348 (32,000)	462 (1,808), 369 (29,404), 348 (25,865)	368 (30,980), 349 (29,204)	368 (16,826) 348 (15,228)	373 (17,467), 349 (15,511), 335 (10,304)
$L^{2}H_{2}$	371 (11,889), 352 (10,778), 349 (11,137)	369 (22,606), 350 (20,082), 337 (16,246)	366 (4,557), 341 (3,757)	366 (2,097), 348 (1,911)	371 (2,024), 348 (1,854)
$^{\mathrm{aIn\ nm.}}$ $^{\mathrm{bIn\ mm.}}$					



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Table 4. UV-VIS and magnetic moment data of the complexes in THF.

Compound	$\lambda_{\max}{}^{a}\left(arepsilon ight)^{b}$	μ_{eff} (BM)
$Co(L^1)_2$	630 (4,647), 448 (9,294), 361 (97,764), 303 (52,706), 274 (6,411)	4.99
$Cu(L^1)_2$	603 (1,360), 490 (1,560), 361 (30,680), 349 (31,700), 265 (10,350)	1.65
$Ni(L^1)_2$	539 (185), 490 (1,259), 375 (57,741), 283 (12,519)	Diamagnetic
$(CoL^2)_n$	812 (118), 422 (9,529), 358 (77,706), 346 (92,706)	5.57
$(CuL^2)_n$	706 (40), 394 (23,740), 360 (35,900), 267 (5,660)	2.21
$(NiL^2)_n$	813 (4), 385 (7,133), 346 (6,358), 275 (262)	2.98

^aIn nm.

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 b In M⁻¹, cm⁻¹.

¹H and ¹³C NMR Spectra

In order to better understand the structure of the ligands, ¹H and ¹³C NMR spectral data in DMSO- d_6 as solvent are given in Table 5 and exhibit all expected signals. The ¹H NMR spectra of the ligands exhibit singlet signals in the 10.7–12.7 and 8.9–8.1 ppm ranges, which are attributed to the OH group and azomethine group protons, respectively.^[16] In the spectra of the Ni(II) complexes, the singlets which are attributed to the OH groups, are absent and the signals in the 8.9 and 8.1 ppm ranges, which are attributed to the azomethine group protons appear downfield at 8.7 and 9.3 ppm, indicating coordination of the ligands to the metal ion via the azomethine nitrogen. In L¹H, multiplets at 6.5–7.9 ppm that may be assigned to aromatic ring protons.^[17]

In L^2H_2 there is a singlet for Ha–Ha' protons in the 6.0 ppm and a doublet for Hb–Hb' and Hc–Hc' protons in the 6.64–6.74 ppm.^[18] In the L^2H_2 , multiplets at 6.0–7.9 ppm that may be assigned to aromatic ring protons.^[17] These signals and thin-layer chromotography results show only one isomer for L^2H_2 , with the coupling point being para to the hydroxyl group (Fig. 4).

The ¹³C NMR spectra of the ligands exhibit singlet signals at 163.30 ppm, which can be assigned to the azomethine group carbon atoms.^[12] In the spectra of the Ni(II) complexes, this signal shifted downfield to the 170.2 ppm range. The signals due to the carbon atoms of aromatic ring are observed in the 117–133 ppm range.^[19]



Figure 3. Ketoamine-enolimine tautomeric forms of Schiff base ligand (L¹H).





Table 5. The 1 H NMR (13 C NMR) spectral data^a of the ligands and their nickel complexes.

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Compound	OH group (δ, ppm)	CH=N group (δ,ppm)	Ar−H (δ, ppm)	Ha–Ha′	Hb-Hb', Hc-Hc'
$L^{1}H$	10.7 (s)	8.9 (s)	6.5-7.9 (m)	_	_
		(163.3)	(117–133)		
L^2H_2	12.7 (s)	8.1 (s)	6.0-7.6 (m)	6.0 (s)	6.64-6.74 (d)
		(163.3)	(117-133)		
$Ni(L^1)_2$		8.7 (s)	6.7-8.1 (m)		_
		(170.2)	(118-133)		
$(NiL^2)_n$		9.3 (s)	6.2-7.9 (m)	6.0 (s)	6.65-6.73 (d)
		(170.2)	(118–133)		

^as, singlet; m, multiplet.

Mass Spectra

In the mass spectrum of the ligand $L^{1}H$, the peak observed at m/z 301 may be assigned to the molecular ion M^{+} and the peak at m/z 302 is due to the $[M + 1]^{+1}$ ion. The most intense peak at m/z 289 corresponds to



Figure 4. The synthesis reaction of L^2H_2 .



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 $[C_6H_4-N=N-C_6H_4-N=CH-C_5H_4OH]^+$, which results from loss of one carbon atom from the parent ligand. The other important peaks at m/z 273 and m/z 154 correspond to $[C_6H_4-N=N-C_6H_4-N=CH-C_5H_5]^+$ and $[C_6H_4-N=CH-C_5H_5]^+$ resulting from loss of one oxygen and the $[C_6H_4-N=N]^+$ fragment.

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The dimer ligand L^2H_2 has been synthesized by the oxidative condensation reaction of L^1H . The molecular weight distribution of L^2H_2 has been determined by HPLC. Mn (the number of average molar mass) and the Mw (the weight of average molar mass) values for L^2H_2 were determined by HPLC^[20] to be 600. As expected the results found for Mn and Mw, were the same. The polydispersity (Mw/Mn) value for L^2H_2 is 1. This data shows that L^2H_2 contains only dimer units.^[21] The elemental analyses are in agreement with this molecular weight.

The molecular weight distribution of L^2H_2 metal complexes has been determined by HPLC. Mn (the number of average molar mass) and the Mw (the weight of average molar mass) values for L^2H_2 metal complexes were analyzed by HPLC and determined to be 6589–6810 (CoL²)_n, 6635–6728 (CuL²)_n, and 6590–6798 (NiL²)_n. The polydispersity (Mw/Mn) values are 1.033 for (CoL²)_n, 1.014 for (CuL²)_n, and 1.031 for (NiL²)_n. These data show that the L^2H_2 metal complexes are oligomers.

Magnetic Measurements

Magnetic moment data of the complexes are given in Table 4. The copper(II) complexes exhibit 1.65-2.21 B.M. values suggesting that copper(II) ion has square-planar geometry.^[21] The values of 4.99 and 5.52 B.M. observed for Co(L¹)₂ and (CoL²)_n reveal tetrahedral geometry around the Co(II) ion. The nickel(II) complex of L¹H is diamagnetic and has square-planar geometry around the metal center. The magnetic moment of the nickel(II) complex of L²H₂ is 2.98 B.M., which is consistent with a tetrahedral structure.^[5]

Thermal Studies

Thermal degradation of the complexes proceeded in two steps. The first step represents the primary decomposition of the complexes in the 225-300 °C range. The second step within the 600-675 °C range represents the final decomposition of the complexes to the metal oxides. The thermal studies of complexes show that there are no water molecules in the complexes.^[5]

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