SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL STUDIES OF Co(II), Ni(II) AND Cu(II) COMPLEXES CONTAINING TRIPHENYLPHOSPHINE AND SCHIFF BASE LIGAND BASED ON SALICYLALDEHYDE

G. Gokulnath¹, R. Manikandan², P. Anitha³, and C. Umarani¹, ✉

¹Department of Chemistry, Government Arts College (Autonomous),
Salem-636007, Tamilnadu, India

²Department of Chemistry, Loyola College of Arts and Science, Mettala, Rasipuram,
Namakkal-636202, Tamil Nadu, India

³Department of Chemistry, Government College of Engineering,
Salem-636011, Tamil Nadu, India

✉Corresponding Author: jpchem20@gmail.com

ABSTRACT

Schiff base ligand (HL) derived from the condensation of salicylaldehyde with 4-amino benzoic acid and its metal(II) complexes containing triphenylphosphine of the type $[MCl(PPh_3)(L)]$ ($M = Ni, Co$ or Cu ; $L =$ bidentate Schiff base ligand) were synthesized. The synthesized compounds were characterized by techniques of analytical and spectroscopic (FT-IR, electronic, ESI-Mass, 1H , ^{13}C NMR, and ^{31}P NMR). The antibacterial activities of the ligand and metal complexes were studied against Gram-positive bacteria and Gram-negative bacteria using the agar well diffusion method.

Keywords: Salicylaldehyde, Schiff Base, Metal Complexes, Spectroscopic Investigation, Antibacterial Activity

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INTRODUCTION

Metal complexes of the Schiff bases have attracted great interest because of their extensive applications, including antimicrobial,¹ anticancer,² antitumor,³ antioxidant,⁴ anti-inflammatory,⁵ antiviral⁶ and herbicidal⁷ activities, in addition to catalytic⁸, thermal⁹ and electrochemical¹⁰ properties. Recently, Schiff bases metal complexes derived from salicylaldehyde derivatives have received generous attention.¹¹⁻¹³ These compounds make use of phenolic O and imine N donor atoms which lead to typically stable bidentate coordinated complexes.^{14,15} Schiff base metal complexes containing neutral and anionic molecules as addition ligands are of recent attention in view of their solid-state structures and mainly, the complex structure consisting of triphenylphosphine derivatives are of particular magnitude due to their probable beneficial catalyst and biological activities.¹⁶⁻¹⁸ The present paper deals with the synthesis and characterization of Schiff base, 4-((2-hydroxybenzylidene)amino)benzoic acid ligand (HL) and their Co(II), Ni(II) and Cu(II) complexes containing triphenylphosphine ligand. These synthesized complexes were characterized by various physicochemical techniques. The antibacterial activities of the ligand and metal(II) complexes were examined.

EXPERIMENTAL

Materials and Physical Measurements

The solvents and chemicals used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures.¹⁹ The precursors $[MCl_2(PPh_3)_2]$ ($M = Co, Ni$ and Cu) were prepared by the literature procedure.²⁰ Elemental analyses of C, H and N were measured using a Vario EL III elemental analyzer. FT-IR spectra of the compounds were recorded on a Nicolet Avatar model spectrometer from 4000 to 400 cm^{-1} using KBr pellets. Electronic spectra were carried out on Shimadzu UV-1650 PC spectrophotometer in 800-200 nm range using methanol as the solvent. 1H NMR and ^{13}C NMR spectra were obtained in Jeol GSX - 400 instruments using TMS as the internal standard. ^{31}P NMR

spectrum was recorded in Joel GSX - 400 instruments using *o*-phosphoric acid as a reference. The electron spin resonance spectrum (ESR) of the powder sample was recorded with a JEOL JES-FA200 instrument in X-band frequencies at room temperature using 2,2'-diphenyl-1-picrylhydrazyl radical (DPPH[•]) as an internal standard at SAIF-IIT, Madras. The ESI-Mass spectra were performed on LC-MS Q-ToF Micro Analyzer (Shimadzu) at SAIF-Panjab University, Chandigarh. Melting points were measured on a Technico micro heating table and are uncorrected.

Synthesis of 4-((2-hydroxybenzylidene)amino)benzoic acid ligand (HL)

A solution of 4-amino benzoic acid (0.27 g, 2 mmol) in 10 mL of ethanol was added to a solution of 2-hydroxy benzaldehyde (0.25 g, 2 mmol) in 10 mL of warm ethanol and the resulting solution was refluxed for 4 h. Yellow solid was obtained after cooling at room temperature. The product was filtered off, washed with cold ethanol and dried under *vacuum*.

Synthesis of Metal(II) Complexes

A warm ethanolic solution (10 mL) of 4-(2-hydroxybenzylideneamino) benzoic acid (HL) (0.5 mmol) was added to metal precursors (0.5 mmol) in ethanol (10 mL). The resulting mixture was refluxed for 5 hours. A crystalline powder was obtained on slow evaporation. They were filtered off, washed with ethanol and dried under *vacuum*.

Antibacterial Activity

The antibacterial activity of the ligand and its metal(II) complexes was determined by using the agar well diffusion method.²¹ The compounds were studied for the inhibitory effect on the growth of different bacteria such as *Staphylococcus aureus*, *Bacillus sphaericus*, *Pseudomonas aeruginosa* and *Escherichia coli*. The concentration of the ligand and its metal(II) complexes is 0.6 – 1.5 µg/mL in DMSO for antibacterial studies. Each test bacterial was swabbed on sterile Muller-Hinton agar plates using a sterile cotton swab followed by punching wells of 6 mm diameter with the help of a sterile cork borer. The plates were incubated at 37 °C overnight. After 24 h, the antibacterial activities were expressed in terms of the diameter of the zone of inhibition (in mm) of each bacterial species by different samples.

RESULTS AND DISCUSSION

The reaction of salicylaldehyde with 4-amino benzoic acid in ethanol yielded the ligand (HL). The synthesis of the metal(II) complexes was achieved by reacting one equivalent ethanolic solution of ligand (HL) with one equivalent metal precursor [MCl₂(PPh₃)₂] (M = Co, Ni and Cu) in ethanol (Scheme-1). The elemental analysis and physicochemical data of the ligand and their complexes are provided in Table-1.

Scheme-1: Synthetic Route of Ligand and Complexes

IR spectra

The IR spectrum of the free ligand shows a strong vibration at 3506 cm⁻¹ due to the hydroxyl group. This band vanished in the spectra of the new complexes suggesting that the ligand underwent deprotonation prior to coordination to metal ion.²² In addition, a band appeared in the region 1282 cm⁻¹ due to the phenolic C–O group of the free ligand being shifted to 1230-1264 cm⁻¹ in the IR spectra of the complexes indicating the coordination through a phenolic oxygen atom.²² A medium sharp band at 1680 cm⁻¹ due to the azomethine C=N stretching frequency of the free ligand was shifted to a lower frequency in the spectra of the complexes 1651-1676 cm⁻¹, indicating that the other coordination is through azomethine N

atom.²³ Both free ligand and the new complexes show the broad band around in the region of 3213-3315 cm^{-1} can be assigned to COOH group and this observation suggests that the non-participation of COOH group in bonding. On the other hand, the bands present in the 599-688 and 470-475 cm^{-1} ranges may be taken as an indication of the coordination between the metal ions with oxygen and nitrogen atoms, respectively. The bands due to triphenylphosphine were also present in the predictable region.²³ The IR spectral data are given in Table-2.

Tables-1: Elemental Analysis and ESI Mass Spectral Data of Ligand and Metal(II) Complexes

Compound	Colour	m.p. (°C)	Elemental Analysis Data Calculated (Found) (%)			ESI Mass (m/z) Calculated/Found
			C	H	N	
HL	Yellow	156	69.70(69.35)	4.19(4.66)	5.81(5.61)	-
[CoCl(PPh ₃)(L)]	Green	210	64.39(64.23)	4.22(4.67)	2.35(2.62)	596.91/597.10
[NiCl(PPh ₃)(L)]	Brown	197	64.42(63.72)	4.22(3.92)	2.25(2.56)	596.67/596.07
[CuCl(PPh ₃)(L)]	Yellow	205	63.90(63.52)	4.19(3.92)	2.33(2.83)	601.52/601.01

Table-2: IR Absorption Frequencies (cm^{-1}) and Electronic Spectral Data (nm) of Ligand and Metal(II) Complexes

Compound	$\nu(\text{COOH})$	$\nu(\text{OH})$	$\nu(\text{CN})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	λ_{max} (nm)
HL	3213	3506	1680	-	-	250, 310
[CoCl(PPh ₃)(L)]	3315	-	1651	688	472	255, 280, 340, 482
[NiCl(PPh ₃)(L)]	3278	-	1651	688	475	248, 305, 370, 430
[CuCl(PPh ₃)(L)]	3313	-	1676	599	470	253, 307, 387, 417

Electronic Spectra

The electronic spectrum of the free ligand exhibit bands at 250 and 310 nm corresponding to the $n \rightarrow \pi^*$ transition of the azomethine and $\pi \rightarrow \pi^*$ transitions of the aromatic ring, respectively. The absorption bands observed for all the complexes in the regions of 248-307 and 340-387 nm are attributed to the intra ligand transitions within the coordinated ligand moiety and ligand-to metal charge transfer (LMCT) transitions.²⁴ The band that appeared in this region 417-482 nm has been assigned to d-d transition.²⁵ The electronic spectral data are given in Table-2.

NMR Spectra

The ^1H NMR and ^{13}C NMR spectral data of ligand and Ni(II) complex are provided in Table-3. The singlet observed at δ 12.95 ppm in the ligand due to phenolic OH proton has disappeared in the ^1H NMR spectrum of Ni(II) complex. This revealed the coordination of ligand to Ni(II) through phenolic oxygen atoms.²⁶ The ligand and their nickel complex show a sharp singlet at δ 12.72 and 12.55 ppm, respectively, which is due to COOH group. A singlet obtained at δ 8.03 in the spectra of the free ligand assigned to the azomethine proton undergoes a shift to δ 8.85 ppm in the metal complex, indicating the coordination of the azomethine nitrogen atom to the metal. The signals corresponding to the protons of the aromatic moieties of the ligand and their complex were obtained as multiplets in the range δ 6.37 - 8.01 ppm. The ^{13}C NMR spectra of ligand and nickel complex showed a sharp peak at δ 182.64 and 191.62 ppm, which has been attributed to COOH carbon. The phenolic carbon (C-O) and azomethine (CH=N) carbon have exhibited peaks at δ 165.29 - 167.26 ppm and δ 160.76 - 160.62 ppm regions, respectively. In addition, all the aromatic carbon atoms exhibited their corresponding peaks in the region δ 113.30-152.64 ppm as expected. ^{31}P NMR spectrum of the nickel complex was recorded to confirm the presence of the triphenylphosphine group in the complex. A sharp singlet was observed at δ 27.80 ppm due to the presence of triphenylphosphine ligand in the complex.

ESR Spectra

The solid-state EPR spectra at X-band frequencies for copper(II) complex were recorded at room temperature (Fig.-1). The ESR spectrum of Cu(II) complex exhibited anisotropic signal with $g_{\parallel} = 2.20$ and $g_{\perp} = 2.10$ and $g_{\text{aver.}} = 1/3(g_{\perp} + 2 g_{\parallel}) = 2.13$. The trend in the observed “g” values $g_{\parallel} > g_{\perp} > g_e$

(2.0023) suggested that the unpaired electron lies predominantly in the dx^2-y^2 orbital, which is in agreement with the electronic absorption spectroscopic assignments. In square planar complexes, the unpaired electron occupies the dx^2-y^2 orbital with $^2B_{1g}$ ground state resulting in $g_{\parallel} > g_{\perp}$.

Fig.-1: ESR Spectrum of Cu(II) Complex

Table-3: ^1H NMR and ^{13}C NMR of Ligand and Ni(II) Complex

Compound	^1H NMR (ppm)	^{13}C NMR (ppm)
HL	12.95 (-OH), 12.72 (COOH), 8.03 (CH=N), 6.98-8.01 (Aromatic H)	182.64 (COOH), 165.29 (phenolic C-O), 160.76 (CH=N), 117.16-152.64 (Aromatic C).
[NiCl(PPh ₃)(L)]	12.55 (COOH), 8.85 (CH=N), 6.37-7.87 (Aromatic H)	191.62 (COOH), 167.26 (phenolic C-O), 160.62 (CH=N), 113.30-136.71 (Aromatic C).

Mass Spectra

ESI-mass spectral analyses of the new complexes were recorded in order to confirm the molecular mass of the complexes (Fig.-2). The m/z (m stands for mass and z stands for the charge number of ions) values of the molecular ion peaks for the complexes [CoCl(PPh₃)L], [NiCl(PPh₃)L] and [CuCl(PPh₃)L] were obtained at 597.10, 596.07, and 601.01 $[M]^+$ respectively. The calculated molecular masses corresponding to these complexes are 596.91, 596.67 and 601.52. The obtained m/z values of the complexes are in good agreement with the calculated molecular masses of complexes.

Antibacterial Activity Study

The antibacterial activities of ligand and metal(II) complexes were studied against the Gram positive bacteria (*Staphylococcus aureus* and *Bacillus sphaericus*) and Gram negative bacteria (*Pseudomonas aeruginosa* and *Escherichia coli*). The result of the antibacterial activities of ligand and metal complexes are given in Table-4. From the report, it is evident that the Co(II), Ni(II) and Cu(II) complexes are most active than the ligand. The higher activity of the complexes, as compared to the free ligand, can be understood in terms of the chelation theory. This theory explains that a decrease in the polarizability of the metal could develop the lipophilicity of the complexes.²⁷

Table-4: Antibacterial Activities Data of Free Ligand and Metal(II) Complexes

Compound	Zone of Inhibition in (mm)															
	<i>S. aureus</i>				<i>P. aeruginosa</i>				<i>E. coli</i>				<i>B. sphaericus</i>			
	0.6	0.9	1.2	1.5	0.6	0.9	1.2	1.5	0.6	0.9	1.2	1.5	0.6	0.9	1.2	1.5
HL	8	8	8	8	8	10	12	14	10	13	15	17	10	12	14	16
[CoCl(PPh ₃)L]	13	15	17	19	18	20	22	24	13	15	17	17	11	13	15	17
[NiCl(PPh ₃)L]	10	13	16	19	14	18	20	24	12	14	16	18	13	16	18	20
[CuCl(PPh ₃)L]	16	18	20	22	13	15	17	17	12	14	16	18	16	18	20	22

Fig.-2: ESI Mass Spectrum of Cu(II) Complex

CONCLUSION

Some metal(II) complexes containing triphenyl phosphine and Schiff base ligand were synthesized and characterized. The basis of analytical data and spectral studies revealed the square planar geometry proposed for Ni(II), Co(II) and Cu(II) complexes. The metal complexes exhibit more diverse antibacterial activity than ligand due to the reduction of the polarity of the metal ion.

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