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Synthesis, Characterization and Spectroscopic Studies of A Novel 2-[(E)-[(2,4-dichlorophenyl)imino]methyl]phenol Schiff Base and Its Metal Complexes

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Abstract: A novel Schiff base 2-{(E)-[(2,4-dichlorophenyl)imino]methyl}phenol (L_B) was synthesized from the condensation reaction of 2,4-dichloroaniline with salicyladehyde in [1:1] ratio in the presence of glacial acetic acid as catalyst. Complexation reaction of this Schiff base with copper (II), cobalt (II) as nitrate salts and with Rhodium (III) as chloride salt to produce three coordinate metal complexes, with a Schiff base: Metal ion ratio of 2:1. These compounds have been characterized by a variety of physico-chemical and spectroscopic techniques. The ligand and its metal complexes were expected to show an interesting bioactivity and cytotoxicity.

Keywords: salicyladehyde , aniline, Schiff base.

Introduction

Schiff bases, which also known as azomethines because they have R-C=N-R$^-$ group, has been widely synthesized due to their important roles in biological systems. They are facing an increasing interest because of their various applications, like biological properties [1-6]. Schiff bases were used as ligands in coordination chemistry due to their donation and chelating abilities [7-11]. Ligands and their metal complexes have a wide applications in industry, especially in analytical reagents [12], dying [13-14] and catalysis [15-17]. In this research, we synthesized one Schiff base (L_B) derived of 2,4-dichloroaniline with salicyladehyde and complication reaction of this Schiff base with copper (II), cobalt (II) as nitrate salts and with Rhodium (III) as chloride salt to produce three coordinate metal complexes. Characterization to the prepared compounds has been done to them by using different spectroscopic and analytical techniques.

Materials and Methods

Materials

Chemicals that have been used in this research are: salicylaldehyde (BDH), 2,4-dichloroaniline (BDH), Cupper(II) nitrate trihydrate (BDH), Cobalt (II)nitrate hexahydrate (fluka), Rhodium(III) trichloride hydrate (BDH). All chemicals were of analytical grade and were used as supplied without any further purification. sulphoxide (DMSO) (99% BDH), absolute ethanol (99.99%, BDH), dimethyl Diethyl ether (fluka), diethylether (fluka), glacial acetic acid (BDH).

Physical Measurements

Melting points were carried out using Gallen kamp M.F.B 600.01. The infrared spectra of the prepared compounds were recoded using FT-IR-8300-Shimadzu**,** in the wave length range of (4000-400) cm^{-1}. The metals content of the complexes were measured using atomic absorption technique by Perkin-Elmer-5000. The electronic spectra of the prepared compounds were obtained using (UV-Vis-160A) Shimadzu Spectrophotometer, of wave-length (200-1100 nm) all prepared compounds were dissolved in (DMSO) at (10^{-3} M). Carbon, hydrogen, nitrogen and sulfur analyses were carried out using a Leco CHNS-932 analyzer. The molar conductivity measurements were carried out using Wissenschaftlich-Technisch Werk-statten 8120 Weilheim I.O.B, Drucker-Printer. The magnetic susceptibility values were obtained at room temperature using (Magnetic Susceptibility Balance), of Johnson mattey catalytic system division. The metals content of the complexes were measured using atomic absorption technique by Perkin-Elmer-5000.

Preparation of 2-{(E)-[(2,4-dichlorophenyl)imino]methyl}phenol [L_B] ligand:-

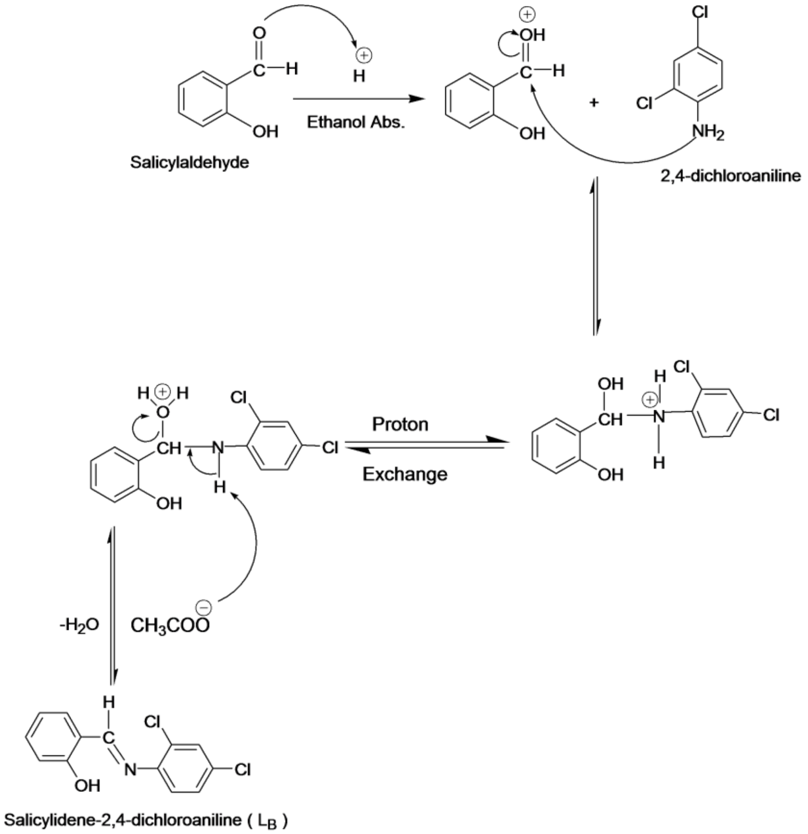
A mixture of (10 mmol) of salicylaldehyde with (10 mmol) of 2,4-dichloroaniline was dissolved in (25 mL) of absolute ethanol. Then, to this mixture, few drops of glacial acetic acid were added as catalyst, the resulting mixture was refluxed for two hours. The resulting precipitate was filtered, washed with diethyl ether and recrystallized. Then the product was dried under vacuum oven at 40°C for two days. Pale green Schiff base collected with melting point 75 ºC and yield (77%).

Preparation of the Metal Complexes of [L_B]:-

A Solution of (0.94 mmol) Copper nitrate trihydrate, Cobalt nitrate hexahydrate, Rhodium chloride monohydrate dissolved in (10 mL) of absolute ethanol was added to (1.88 mmol) of [L_B] dissolved in (15 mL) of absolute ethanol. The mixture was refluxed with stirring for three hours, the resulting precipitate was filtered and washed with diethyl ether and recrystallized from hot ethanol then dried under vacuum at 40°C for two days. Yields: *ca.* 74-80%.

Results and Discussion

The new Schiff base, 2-{(E)-[(2,4-dichlorophenyl)imino]methyl}phenol [L_B] ligand has been prepared and characterized successfully. Three metal complexes were also synthesized by reacting metal ions salts Cu(II), Co(II), and Rh(III) with the new ligand.
Scheme 1 shows the synthesis route for the novel Schiff base.



Scheme 1. Synthesis of L_B ligand.

All the physical measurements of the synthesized ligand (L_B), the metal complexes and the expected formula of the synthesized complexes are shown in Table (1). The data are very near to the expected formula to all the prepared compounds.

Table 1. Physical properties of the synthesized compounds.

Compound	Colour	Yield %	Melting point (°C) ± 1 °C	% Found(calculated)				
				%C	**%H**	**%N**	**%O**	**%M**
L_B $C_{13}H_9Cl_2NO$	Pale green	77	75	56.34 (58.67)	3.63 (3.41)	5.15 (5.26)	6.62 (6.01)	-
L_BCu(II) $[Cu(L_B)_2(H_2O)_2]$	Brown	74	191	52.69 (49.58)	3.78 (3.20)	4.18 (4.45)	10.85 (10.16)	10.85 (10.09)
L_BCo(II) $[Co(L_B)_2(H_2O)_2].3H_2O$	Yellowish green	80	151	49.01 (45.97)	4.23 (3.86)	4.97 (4.12)	17.11 (16.49)	9.45 (8.68)
L_BRh(III) $[Rh_2(L_B)_4(Cl_2)]$ $4H_2O$	Red	76	211	47.48 (44.32)	3.19 (2.86)	4.27 (3.98)	9.62 (9.08)	14.03 (14.60)

The FT-IR Spectra of [L_B] and The Metal Complexes:-

The F.T.IR spectrum of [L_B] shows a broad band appearing at (3456 cm^{-1}) has been assigned to stretching vibration of the hydrogen bonded of (OH) group in the ligand [L_B]. A broad band was observed at (665 cm^{-1}) assigned to the hydrogen bonded out-of the plane of (O-H) bending vibration (18, 19). The medium to strong intensity bands appear at (1280 cm^{-1}) which assigned to the phenolic (C-O) (18, 20) stretching mode which was changed from (1280cm^{-1}) to (1325cm^{-1}) after complexation with central metal ion(21, 22) this indicates displacement the metal ion by the hydrogen-phenol (23). The (1554 cm^{-1}) band is due to the presence of (C=C) of aromatic system (24). The two strong band at (788 and 819) cm^{-1} *are* due to the ortho and para substitution respectively (25). The ν(C-H) of the aromatic moiety appeared in (2758 cm^{-1}) (26, 22).

The band at (1614 cm^{-1}) is due to (-C=N-) azomethine group stretching which shifted to lower value *ca.,*1604 in the metal complexes(27, 28) due to metal-ligand coordination (23, 29).

The new bands which have been observed around (530, 524, and 570) cm^{-1} were attributed to ν (Cu-N), ν (Co-N), and ν (Rh-N) respectively (30), while the bands at (455, 450 and 447) cm-1 attribute to (Cu-O), ν (Co-O) and ν (Rh-O) respectively (31, 32).

The strong sharp band at (829 cm^{-1} and 729 cm^{-1}) indicates the presence of H_2O molecules ν (Cu-H_2O and Co-H_2O) in the coordination of [L_BCu(II) and L_BCo(II)] complexes respectively (31). The spectrum of Rh(III) complex shows a broad band which appeared at (3422 cm^{-1}) refer to the presence of water molecules out of the coordination sphere in the structure of [L_BRh(III)] complex. (32) Table 2 shows the necessary bands of the new ligand and the metal complexes.

Table 2. The most significant IR bands of [L_B] and its metal complexes in (cm^{-1}).

Compound	ν (O-H)	ν(C=N)	Phenolic (C-O)	ν(C=C) Aromatic	ν(C-H) Aromatic	Ortho sub. C-Cl	Para sub. C-Cl	ν(M-N)	ν(M-O)
L_B	3454	1614	1280	1554	2758	748	819	-	-
L_BCu(II)	-	1604	1325	1579	3012	754	829	530	455
L_BCo(II)	-	1604	1325	1531	2877	750	850	524	450
L_BRh(III)	-	1604	1330	1521	2923	756	827	570	447

Table 3. Magnetic moments, Conductivity and Suggested Structures for Complexes in (10^{-3} M) DMSO solvent.

Complex	Magnetic moment μeff. (B.M.)	Conductivity μS.cm^{-1}	λ $_{max}$ (log ε) (nm)	Suggested structure
L_B	-	-	405(2.8), 327(3.7), 272(3.2)	-
L_BCu(II)	1.83	15.3	657(0.01)	Octahedral
L_BCo(II)	4.85	13.4	671(0.01), 388(0.3)	Octahedral
L_BRh(III)	Diamagnetic	18.2	721(0.003), 464(0.6), 337(0.2)	Octahedral

Study of the Magnetic Susceptibility and Conductivity Measurements

The conductivity to all the complexes was measured; all the complexes are not ionic as shown in Table 3. The value of ($\mu_{eff.}$) that have been measured for all the metal complex it was found (1.83 B.M, 4.85 BM) for Cu(II) and Co(II) complexes respectively,(33, 34). The Rhodium (III) complex is diamagnetic which refer to strong field. These values are in the range of mononuclear octahedral geometry for all the metal complexes (34) .

Study of the Electronic Spectra

The Electronic spectra measurements of the ligand and the metal complexes are shown in Table 3, the data was collected in (UV-Vis) region in DMSO solvent at (10^{-3}M).

The Schiff base have been generally exhibit in three main bands, the first absorption band appeared at 272 nm which can be attributed to ($\pi \rightarrow \pi^*$) transition for the aromatic system while the second absorption band attribute to ($\pi \rightarrow \pi^*$) transition of imines group, which appeared at 327 nm (35). These bands were not significantly affected by chelating.

The third absorption band appeared at 405 nm assigned to ($n \rightarrow \pi^*$) transition (36).Which was shifted to a longer wavelength (red shift) upon formation of the complexes. This shift may be attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff base to the metal ion (N:→M) (37).

The electronic spectra of Cu(II) compounds show single broad absorption band in the region 657 nm (38). The brown color [L_B Cu(II)] which suggest a strong field complex and show a broad band(38, 39) at 657 nm this band refer to distort octahedral geometry (Jahn-Teller distortion) (38, 40) which can be assigned to $^2Eg \rightarrow {}^2T_2g$ transitions.

The Co(II) complex which shows two bands, one at 671 nm and 388 nm which was assigned to the transition [ν_2 ^4T_1g (F) → ^4A_2g (F)] and [$\nu_3$$^4T_1g$(F) → ^4T_1g(P)], respectively. The electronic spectra of brown of [L_B Rh(III)] complex, shows three absorption band at 464 nm, 337 nm which can be assigned to [ν_1 $^1A_{1g} \rightarrow {}^1T_{1g}$, and ν_2 $^1A_{1g} \rightarrow {}^1T_{2g}$] transitions, while the third weak absorption band appear at (721 nm) which can be assigned to transitions [$^1A_{1g} \rightarrow {}^3T_{1g}$]. These transitions agreed well with low spin and octahedral geometry for this complex (38, 41).

The expected structures of the new metal complexes are shown in the Figure 1.

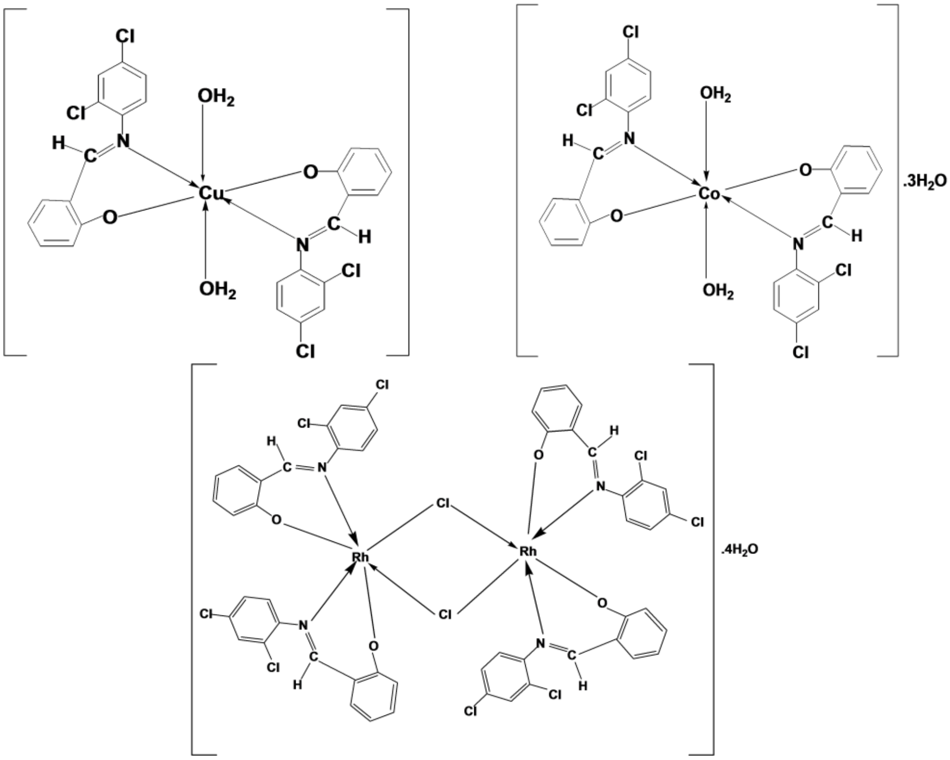


Figure 1. Expected structures of Cu(II), Co(II), and Rh(III) complexes.

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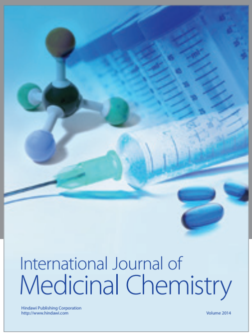
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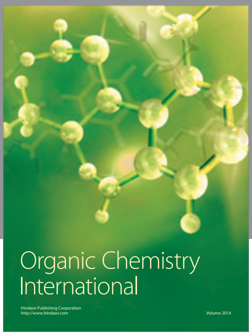
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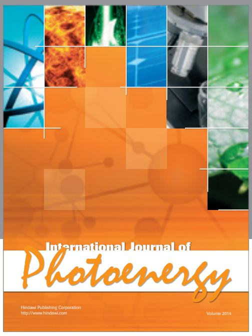
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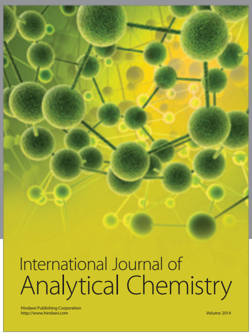
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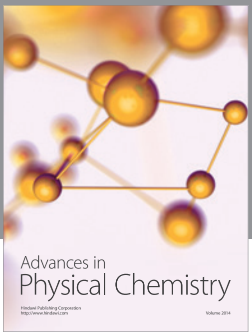
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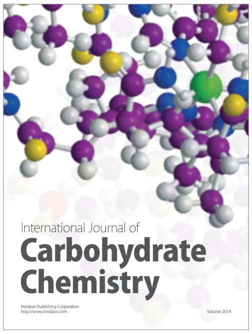
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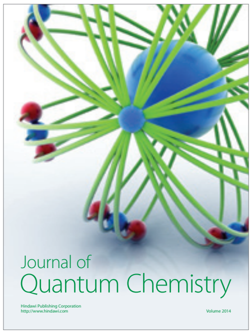
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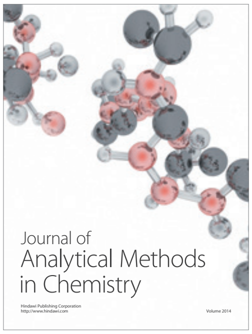
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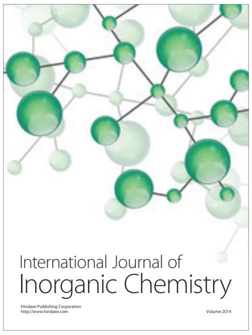
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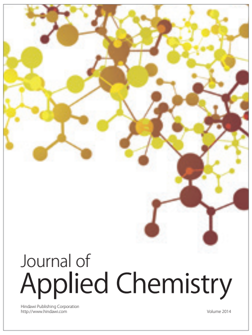
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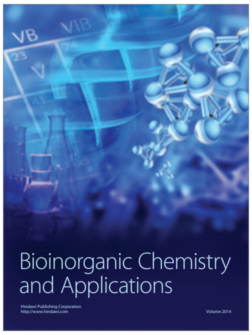
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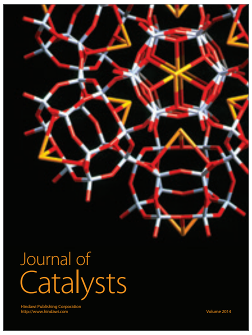
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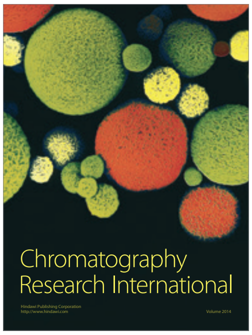
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