Synthesis, Characterizationand Spectroscopic Studies of 2-{(*E*)-Hydroxyphenyl)imino]methyl}Phenol Schiff Base with Some Metal Complexes

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Abstract

A Schiff base ligand 2-{(*E*)-[2-hydroxyphenyl)imino]methyl}phenol [L_F] was prepared by condensation of salicylaldehyde with 2-aminophenol. The [L_F] ligand was characterized by using melting point measurement, F.T.IR and UV-Vis spectroscopy. New series of transition metal complexes of Cu (II), Co (II) and Rh (III) ions were synthesized with this Schiff base. The complexes were characterized by using FTIR, UV-Vis spectroscopy, metal analysis spectrophotometer, conductivity and magnetic susceptibility measurements. The metal coordinated with Schiff base through nitrogen azomethine and phenolic hydroxyl oxygen atoms of the ligand. Magnetic susceptibility data coupled with electronic spectra and suggest a square planar geometry for the Cu(II) complex and octahedral structure for the Co(II) and Rh(III) complexes.

Keywords**:** Salicyladehyde, Schiff base.

Introduction

In recent years, great attentions have been paid to the construction using flexible N-donor bridging ligands. Transition metal complexes of Schiff bases are extensively studied due to synthetic flexibility, selectivity and sensitivity toward a variety of metal atoms [1]. The use of ligands in generation of metal complex relatively spars, they found useful in catalysis, in medicine as antibiotics and anti-inflammatory agent [2,3]. In particular salicylal dimines are useful for the synthesis of transition metal complexes. Schiff base ligands and their metal complexes have been extensively studied over past few decades. Some Schiff bases are used as ion-selective electrode [4]. Some complexes containing nitrogen and oxygen donor atoms in the complexes are effective as stereo specific catalysts for oxidation, reduction, hydrolysis, biological activity and other transformations of organic and inorganic chemistry [5,6].

Materials and Methods

Materials

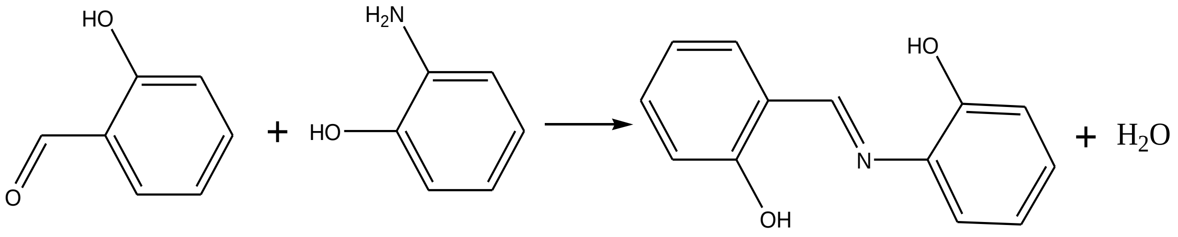
Chemicals used in this research are:salicylaldehyde (BDH), 2-aminophenol (BDH), Cupper (II) nitrate trihydrate (BDH), Cobalt (II) nitrate hexahydrate (Fluka), Rhodium (III) trichloride hydrate (BDH). All chemicals were of analytical grade and used as supplied without any further purification. sulphoxide (DMSO) (99% BDH), absolute ethanol (99.99%, BDH), diethyl ether (Fluka), dimethylether (Fluka), glacial acetic acid (BDH).

Physical Measurements

Melting points were carried out using Gallenkamp M.F.B 600.01. The infrared spectra of the prepared compounds were recorded using FT-IR-8300-Shimadzu**,** in the wave length range of (4000-400) cm^{-1}. The metal content of the complexes was measured using Perkin-Elmer-5000 atomic absorption. 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). 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.

Preparation of 2-{(E)-[2-hydroxyphenyl) imino] methyl} Phenol ligand

The ligand was prepared by modification of a literature method [7]. The complex, 2-{(E)-[2-hydroxyphenyl) imino]methyl}phenol was prepared by reacting an equimolar mixture of salicylaldehyde (10 mmol) and 2-aminophenol (10 mmol) in absolute ethanol (30 ml). A few drops of glacial acetic acid were then added as catalyst. The resulting mixture was heated under reflux for 48 h. The obtained precipitate was isolated by filtration, washed with diethyl ether, recrystallized, and then dried under vacuum at 40 ºC for 2 days. The yield was 65.72 %. (Scheme 1) shows the synthesis equation.



Salicylaldehyde 2-aminophenol (*E*)-2-(2-hydroxybenzylideneamino)phenol (L_F)

Scheme (1): Synthesis equation of the 2-{(E)-[2-hydroxyphenyl)imino]methyl}phenol.

Synthesis of Co(II), Cu(II) and Rh(III) complexes

These complexes were prepared using a general procedure [8, 9] in which a solution of each of (0.34g, 1.408 mmole) copper nitrate trihydrate added to (0.30 g, 1.408 mmole) of [L_F], (0.204g, 0.704 mmole) of cobalt nitrate hexahydrateadded to (0.30 g, 1.408 mmole) of [L_F] and (0.213 g, 0.938 mmole) of rhodium chloride monohydrate dissolved in (15 ml) absolute ethanol were added to (0.40 g, 1.877 mmole) of [L_F] dissolved in (20 ml) of absolute ethanol. The mixtures were refluxed with stirring for three hours, the resulting precipitates were filtered and washed with diethyl ether and recrystallized from hot ethanol then dried under vacuum at 40ºC for two days. Table (1) shows the physical properties of the ligand and metal complexes.

Table (1)
Some physical properties of the new compounds.

Symbol	*Colour*	*M.P (ºC)*	*Yield (%)*	*Metal (%)* *% Found (Cal.)*	*Molecular formula*
L_F	**Deep Red**	**153-155**	**65.72**	**-**	**$C_{13}H_{11}NO_2$**
L_F Cu(II)	**Green**	**233-235**	**73.45**	**15.00 (13.90)**	**$[Cu(L_F)(ONO_2)(H_2O)].NO_3$**
L_F Co(II)	**Deep Brown**	**228-230**	**78.27**	**5.50 (7.91)**	**$[Co(L_F)_2(H_2O)_2].9H_2O$**
L_F Rh(III)	**Black**	**250 Dec.**	**69.74**	**13.00 (13.67)**	**$[Rh(L_F)_2(Cl)(H_2O)].6H_2O$**

Dec. = Decompose

Results and Discussion

The complexes are soluble in polar organic solvents, such as DMSO, DMF, and MeOH, but insoluble in nonpolar organic solvents, such as benzene and CCl_4.

Infra-Red spectra

The formation of ligand is confirmed by the absence of stretching vibration due to amino ν(NH_2) moiety of 2-aminophenol and instead, a strong new band appeared at (1629 cm^{-1}) corresponding to the azomethine ν(C=N) group. IR spectrum of the ligand, L_F shows a sharps bands centered at (3305 cm^{-1}) and (3375 cm^{-1}) assigned to phenolic (OH) group [10-12].

A strong band at (1274 cm^{-1}) assigned to the frequency of the phenolic (C-O) bond [13]. The IR spectrum showed multiple bands at (3045 cm^{-1}) which is due to ν (C–H) (arom.), while the band at (1539 cm^{-1})is attribute to ν(C=C) (arom.) [14]. Table (2) shows the main and significant bands of IR spectra of the ligand and the metal complexes.

Table (2)
The significant bands of FTIR spectra of [L_F] and its metal complexes.

Symbol	*ν (O-H)*	*ν (C=N)*	*Phenolic ν (C-O)*	*ν (C=C) arom.*	*ν (C-H) arom.*	*ν (M-N)*	*ν (M-O)*
L_F	**3305 3375**	**1629**	**1274**	**1539**	**3045**	**_**	**_**
L_FCu(II)	**3055 -**	**1600**	**1369**	**1531**	**3008**	**538**	**447**
L_FCo(II)	**3006 -**	**1602**	**1307**	**1531**	**3053**	**538**	**422**
L_FRh(II	**3191 -**	**1604**	**1330**	**1500**	**3064**	**534**	**447**

The IR spectra of all complexes showed that the ligand L_F behaves as a bidentate with two coordinating sites (O&N). This behavior was proved by the shift of ν(C=N) signals to lower frequencies (1600, 1602 and 1604) cm^{-1} for L_FCu(II), L_FCo(II) and L_FRh(II) complexes respectively indicating the coordination through of azomethine-nitrogen [15]. And The bands around (3305,3375) cm^{-1} due to phenolic OH, which were observed in ligand, one of them was disappears in complexes, This indicates the ligand co-ordinate to the metal ion through one oxygen of OH group via deprotonation and the other band was changes to (3055,3006 and 3191)cm^{-1} for L_FCu(II), L_FCo(II) and L_FRh(II) complexes respectively improved there is no coordination through other oxygen of phenolic group [15,16]

The ν (C-O) frequency were changed from (1274 cm^{-1}) to (1369, 1307 and 1330) cm^{-1} for L_FCu(II), L_FCo(II) and L_FRh(II) complexes respectively) this blue shift indicates the coordination through oxygen of phenolic group [15-17].

The strong sharp band at (831,837 and 852) cm^{-1} indicates the presence of H_2O molecules ν (M-H_2O) in the coordination of L_FCu(II), L_FCo(II) and L_FRh(II) complexes respectively [18].

The simultaneous appearance of new bands in the (534-538) cm^{-1} and (422-447)cm^{-1} are due to (M-N) and (M-O) respectively suggesting the coordination of the metal ions with the ligand via nitrogen and oxygen [19].

For the L_FCu(II) metal complex, three bands were absorbed at (1377, 1298 and 921) cm^{-1} refer to coordination of nitrate group (NO_3^-) to the metal atoms[16,20].

For L_FCo(II) and L_FRh(II) abroad band which appeared at (3450 and 3359) cm^{-1} respectively refer to the presence of water molecules out of the coordination sphere in the structure of complex[18].

UV-Vis, Magnetic Susceptibility and Molar Conductivity Analysis

The molar conductivities of the complexes in DMSO at (10^{-3} M) are in the range 15–20 Ω^{-1} cm^2 mol^{-1} indicating their non-electrolytic nature, with the exception of the Cu(II) complex, which is

1:1 electrolyte [21, 22].

The magnetic susceptibility measurements, Table (3) showed that only Rh(III) complex has diamagnetic nature, while Cu(II) and Co(II) complexes are paramagnetic. A square planar geometry is expected for the Cu(II) complex while the Co(II) and Rh(III) complexes are expected to have octahedral [23].

The electronic spectrum of the Schiff base exhibits The aromatic band at 245 nm is attributed to benzene π–π^* transition while the bands at (303 and 375) nm are ascribed to the n–π^* transitions of the non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base [24,25].

The Cu (II) complex displays a broad band centered at 821 nm assigned to the $^2B_{1g}\rightarrow {}^2E_g$ transition due to Jahn-teller effect which removes the degeneracy of the d-orbital and the resulting distorted square planar geometry [26,27]. The magnetic moment value at room temperature of this complex is (1.17 B.M) indicated the formation of square planar geometry [28].

The electronic spectrum of the Co(II) compound exhibits two bands at (654 and 442) nm arise from the $^4T_{1g}$ (F) → ^4A_2g (F) and ^4T_1g (F) → ^4T_1g (P) transition respectively These transitions correspond to octahedral geometry, which is also supported by the magnetic moment value (4.93 BM) [24].

The Rh (III)] complex Show tow absorption band at 438 nm, a second band at 396 nm which assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$, and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, These transitions refer to low spin crystal-field and octahedral geometry for this complex [29].

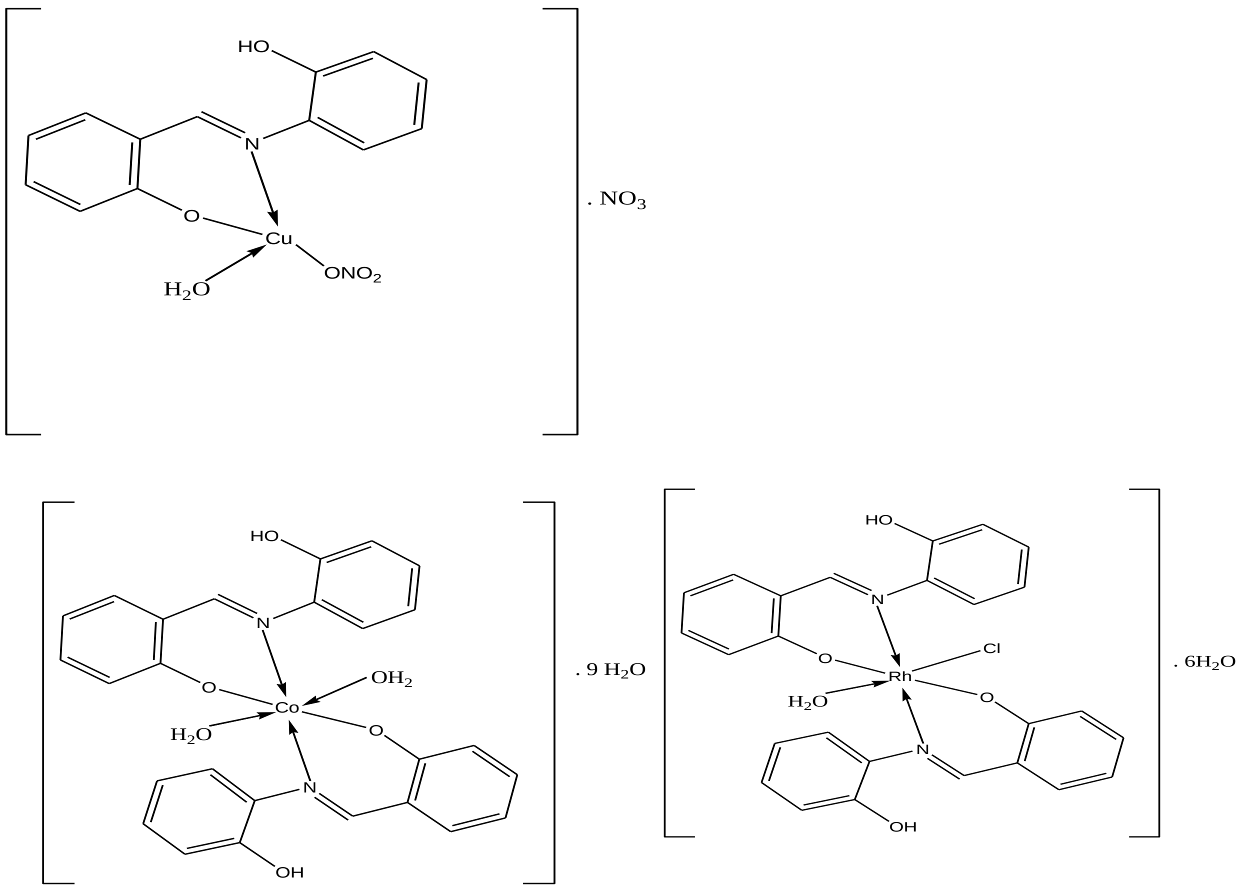
Table (3) shows the Magnetic moment, molar conductance and electronic spectral data of the ligand and the complexes.

Table (3)
Magnetic, Conductivity and Electronic data for the Ligand and the Metal Complexes in (10^{-3} M).

Complex	*Magnetic moment μeff. (B.M.)*	*Conductivity μS.cm^{-1}*	*λ max (log ε) (nm)*	*transition*	*Suggested structure*
L_F	**-**	**-**	**375(3.4), 303(3.6), 245(3.5)**	**n→π* n→π* π→π*(aromatic)**	**-**
L_FCu(II)	**1.17**	**33**	**821(0.3)**	**$^2B_1g\rightarrow {}^2Eg$**	**Square planer**
L_FCo(II)	**4.93**	**15**	**654(0.47), 442 (2.9)**	**$^4T_{1g}$ (F) → ^4A_2g (F) ^4T_1g (F) → ^4T_1g (P)**	**Octahedral**
L_FRh(III)	**Diamagnetic**	**19**	**438 (2.8) 396(3.1)**	**$^1A_{1g} \rightarrow {}^1T_{1g}$ $^1A_{1g} \rightarrow {}^1T_{2g}$**	**Octahedral**

Conclusions

In this paper reported the preparation, isolation, and characterization of a new bidentate Schiff base derived from 2-{(*E*)-[2-Hydroxyphenyl)imino] methyl}Phenol the Schiff base ligand coordinates through the nitrogen of the azomethine group and the oxygen of the phenol ring, forming a stable chelate structure. Based on the above observations of FTIR, electronic spectral data, magnetic, conductance measurements and high melting points, proposed the octahedral structure to Co(II), Rh(III) and square planar geometry for Cu(II) complexes. The expected structures of the metal complexes are shown in Scheme (2).



Scheme (2): Structures of the synthesis complexes.

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الخلاصة

قاعدة شف الليكاند2-{(اي)[2-هايدروكسي فنيل) أمينو] مثيل }فينول (L_F) حضرت من تكثيفِ السلسلديهاد مع ثاني امينو فينول. تم تشخيص الليكاند باستعمال مقياس درجة الأنصهار، والأجهزة الطيفية، الأشعة تحت الحمراء والأشعة فوق البنفسجية-المرئية. السلسلة الجديدة من معقدات العناصر الأنتقالية للنحاس الثنائي والكوبلت الثنائي والروديوم الثلاثي حضرت مع هذة قاعدة شف. تم تشخيص المعقدات باستعمال الأجهزة الطيفية، الأشعة تحت الحمراء والأشعة فوق البنفسجية-المرئية وجهاز المطياف الذري، التوصيلية الكهربائية وقياس الحساسية المغناطيسية. المعدن تناسق مع قاعدة شف من خلال ذرات النتروجين للازموثين وأوكسجين الهيدروكسيل للفينول من الليكاند. إقترنتْ بياناتُ الحساسية المغناطيسية مع الأطياف الألكترونية وأُقترح شكل هندسي مربع مستوي لمعقد النحاس الثنائي وتركيب ثماني السطوح للكوبلت الثنائي والروديوم الثلاثي.