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Mixed ligand Complexes of Cobalt (II) and Nickel (II) with 2-{(E)-[(3-hydroxyphenyl)imino]methyl}phenol and Imidazole compounds

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Abstract

The bi-dentate Schiff base 2-{(E)-[(3-hydroxyphenyl)imino]methyl}phenol derived from the reaction between salicylaldehyde and 3-aminophenol was synthesised ligand. Mixed complexes of (HPIMP) Co(II) and Ni(II) with imidazole (IMD) were synthesised and characterized by spectral analysis (UV-Visible and IR techniques), molar conductivity, atomic absorptionand magnetic susceptibility. The composition of cobalt (II) complex was confirmed to be $Co(HPIMP)_2(IMD)_2$, while the nickel(II) forma complex with the structure of $Ni(HPIMP)(IMD)_2$. Special attention was given to the influence of the ligand basicity and the hydrogen bonding on the coordination course. The tautomeric structure of HPIMP was also discussed in terms of its impact on coordination. The coordination surrounding the metal ion seems to emergeas two different structures, the octahedral form in case of cobalt (II) and square planar in case of nickel (II).

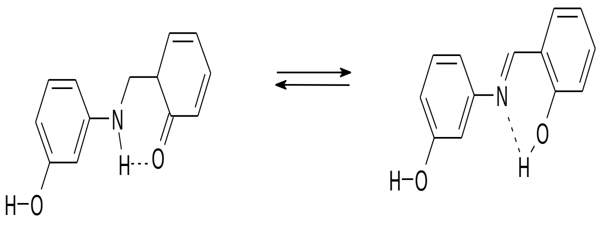
Keywords: Schiff base, ligand basicity, photochromism, thermochromism, hydrogen bonding.

Introduction

Schiff bases are of the main significant compounds in organic chemistry and have a broad utilizationin biological systems, polymers and as ligands in the area of coordination chemistry especially in transition metal coordination chemistry [1,2]. Their metal complexes demonstrate attraction chemical, optical, electrical, thermal, and catalytic properties and have been well illustrated since the late 1920's; nevertheless their relativelylow stability confinestheir usage [3]. Schiff base ligand with two phenolic oxygen atoms and azomethine seems to behave as a dibasic bidentate or tridentate with (ONO) properties depending on the situation of the phenolic groups in the molecule structure [4].

Some Schiff bases of salicylaldehyde or salicylaldehyde derivatives exhibit photochromism and / or thermochromism phenomena in the solid state; these phenomena are actually related to the proton transfer, which results in enol and ketotauromerism [5-7].

Intra-hydrogen bonding is expected to contribute into the physical and chemical phases of the ligand (HPIMP); in addition to inter-hydrogen bonding between discrete molecules, as the free hydroxyl groups would involved in such hydrogen bonding [8]. Intra-hydrogen bonding forms a compact six membered ring between the acidic hydrogen atom of the ortho-hydroxyl andthe nearby nitrogen atom. This type of hydrogen bonding is not, actually, expected to preclude the coordination, as in general the hydrogen bond is small in energy. On the other hand and as a result of delocalization developing from the intra-molecular interaction, mentioned above, it would actually formulate the structure to be in almost planar shape [9]. (HPIMP) molecule might give arise to photochromismas a result of intra-molecular bonding where proton transfer could alter the π structure system [10].The Schiff bases compounds can be classified by their photochromic, thermochromic characteristics [3,10] and movement of proton through intra-hydrogen bonding between the hydroxyl group and nitrogen atom allows two possible tautomerism [either N - H…..O (keto form) or N…..H - O (enol form) (See Scheme (1)) [11,12].



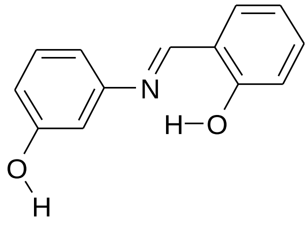
Keto-form Enol- form

Scheme (1).

It has been found in similar compounds that the enol form would dominant over the keto form [13]. Other possible intra-hydrogen bonding might be established between the methen hydrogen and the oxygen atom of the ortho hydroxyl. Methine hydrogen with sp^2 hybridization is expected to be slightly acidic; the degree of acidity is actually increased due to the attachment of the carbon atom to the phenol ring from one side and to the double bond from the other side; where more electron movement towards the nitrogen atom occurs. So, it is more acidic than the other hydrogen in the benzene rings, and it could be compared with the hydrogen of the hydroxyl group. The coordination, of course, would enhance this property and making this hydrogen even more acidic; but it is not expected that the coordination is strong enough to cause the release of this hydrogen as a proton [14]. Imidazole and imidazole derivatives have a vital role in biological effect [15] and also can be used as intermediates in drug industry [16].

Materials and Methods

Synthesis of 2-{(E)-[(3-hydroxyphenyl) imino]methyl}phenol (HPIMP) ligand: All chemicals used as of reagent grade and have been used without further purification. (HPIMP) was synthesized by the literature method [1]. A solution of salicyilaldehyde was preparedby dissolving 0.015 mol in 30 ml. of ethanol; then the other solution was prepared by dissolving 0.015 mole of 3-amino phenol dissolved in 30 ml. of ethanol. The two solutions were mixed together to produce a solution with an orange color. The mixture was heated then refluxed for one hour with stirring; after that the mixture was transferred into a beaker and evaporated to half of its volume and left for four days. The orange precipitate formed was filtered off, andre-crystallized from ethanol. Imidazole used was of reagent grade.



Scheme (2) 2-{(E)-[(3-hydroxyphenyl)imino]methyl}phenol.

Synthesis of Co(II) ((HPIMP))$_2$(IMD)$_2$: A solution of Co(II)Chloride (0.278g, 0.001mol) in ethanol (10 ml) was added to a solution of (HPIMP) (0.426g ,0.002mol) in ethanol (5 ml), it has been noticed that the solution turned to a deep green color. Afterward the synthesis process was completed by the addition of Imidazole solution which has prepared by dissolving (0.136g, 0.002 mol of imidazole into (5 ml) of ethanol. The pH of the solution was raised up to 7 by using 10 % ammonia solution. The solution was refluxed for 45 minutes and left to cool down, then left to evaporate for one day. The evaporation left a precipitate which was then re-crystallized from ethanol. Synthesis of Ni(II)((HPIMP))(IMD)$_2$: A solution of Ni(II)Chloride (0.237g, 0.001mol) in ethanol (15 ml) was added to a solution of(HPIMP)(0.002mol) in ethanol (5 ml), slight change in color of solution was noticed. Afterward the synthesis process was completedby the addition of Imidazole solution which was prepared by dissolving 0.002 mol of imidazole into (5 ml) of ethanol. The pH of the solution was raised up to 7 by using 10 % ammonia solution. The solution was then refluxed for a period of one hour; no change in color was noticed here eitherand no precipitate was observed. The solution left to cool down, and then left to evaporate for four days. The evaporation left a precipitate which was then re-crystallized from ethanol.

IR spectra were recorded on shimadzy(FT-IR-8400) spectrophotometer. UV-Visible spectra were taken on Shimadzu (Cary 100) spectrophotometer. Atomic absorption measurements were taken by (Phoneix-986). Magnetic Susceptibility measurements were obtained at 250C on the solid state applying Faraday‘s method using Balance Magnetic Susceptibility model (MSB-MKI).

Table (1)
The physical data and absorption of 2-{(E)-[(3-hydroxyphenyl) imino]methyl}phenol, imidazole and its complexes.

Compound	Color	M.P C^0	Yield %	M%	
				Cal.	Found
HPIMP	Orange	89-91	75	-	-
Imidazole	Light yellow	112-114	60	-	-
Co(II) ((HPIMP))$_2$(IMD)$_2$	Dark green	208-210d*	80	9.51	9.94
Ni(II)((HPIMP))(IMD)$_2$	Brown	223-225 d*	65	13.85	14.08

Results and Discussion

In this study the complexes of Co(HPIMP)$_2$(IMD)$_2$ and Ni(HPIMP)(IMD)$_2$ were synthesized. The formation of mono-complex Ni (HPIMP)$_1$ from the reaction between the Ni(II) ion and the (HPIMP) ligand revealed the extent strength of the coordination ability of this ligand. So, despite that the ratio of metal to ligand used was 1:2, no trace for bis-complex was detected; this unveils the weakness of this compound (HPIMP) as a ligand towards the metal ion. This can be explained in terms of the possible decrease of the basic properties of the nitrogen atom in the molecule, which affects the coordination power of this ligand. In other words, the availability of the pair of electrons on the nitrogen atom would be disturbed by the substituted phenol group that has the influence to withdraw electron density, causing electron deficiency which in turn affects the coordination property of nitrogen atom towards metal ion. The hydroxyl group in the ortho position, which will contribute in the coordination course, is expected to be more acidic than in case of phenol; this contributes to a decrease inthe basicity of the ligand in general. The precipitation of the Ni(HPIMP)$_1$ complex occurs as a result of the neutralization in a basic medium; where the other acidic hydrogen in the hydroxyl group (in meta position) will be neutralized under the experimental conditions. Bearing in mind, that upon coordination of the ligand with the metal ion, the acidity of the hydroxyl group increases via the electron withdrawal towards the metal ion; in other words the coordination enhances the dissociation of acidic hydrogen [17].

As with the (HPIMP), ligand coordination occurs through the oxygen atom of hydroxyl and the nitrogen atom, where they bonded through covalent and coordinated bonds respectively, and six membered ring is formed. It is expected that bonding of (HPMIP) with metal ion set the complex into planarity structure, as in case of similar ligands [18]. In the next step for the mixed complex formation the addition of imidazole molecules will take place, two molecules of imidazole find their way towardsthe complexed ion to form the final complex.

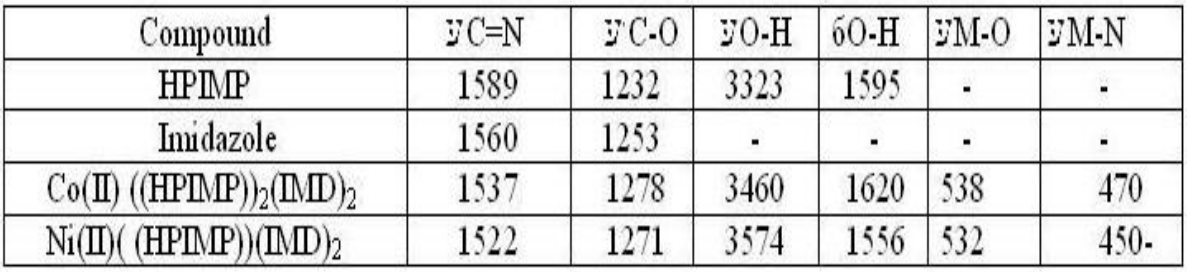
The infrared spectrum of the (HPIMP) ligand showed the absorption band at 1589Cm^{-1} which was assigned to (C=N). It seems that this absorption is less than that expected as the normal assignment for the (C=N) is 1615 to 1700 cm^{-1}[19]. Shifting to the above value can be attributed to the intra-hydrogen bonding [20], which influences the double bond and eventually showed the extent of the strength of the intra-hydrogen bonding in this molecule. Hydrogen bonding leads at the extreme state to convert the keto-form of this molecule into enol-form [11]. In other words, hydrogen bonding is enhancing the keto isomer of the ligand and also reflects the acidity of the ortho hydroxyl group. The Band observed at 1232 cm^{-1} is due to (C-O) phenolic, in the mean time the usual absorbance of this group is 1200 cm^{-1} [12] so the shifting towards higher frequency is a consequence of the weaken O-H bond which leads to increase electron flow toward benzene ring causing enhance in the C-O bond.

The band at 3323 cm^{-1} assigned for the ortho O-H, reflects the effectiveness of the hydrogen bonding to shift the absorbance to this value, because the normal absorption band for free O-H in phenols is in the range of 3610-3520 cm^{-1}[21], which is in agreement with similar compounds [17].

Other frequencies appeared at 538 cm^{-1} and 470 cm^{-1} in the case of the Co(II) complex, and other sets of frequencies appeared in the case of the Ni(II) complex at 532 cm^{-1} and 450 cm^{-1}.

The first value in each complex indicates the formation of an M-O bond, while the second value indicates the formation of an M-N bond [22-23].

Table (2)
FT-IR (υ cm-1) spectral data of 2-{(E)-[(3-hydroxyphenyl) imino]methyl}phenol, imidazole and its complexes.



Compound	$\bar{\upsilon}$C=N	$\bar{\upsilon}$C-O	$\bar{\upsilon}$O-H	δO-H	$\bar{\upsilon}$M-O	$\bar{\upsilon}$M-N
HPIMP	1589	1232	3323	1595	-	-
Imidazole	1560	1253	-	-	-	-
Co(II) ((HPIMP))$_2$(IMD)$_2$	1537	1278	3460	1620	538	470
Ni(II)((HPIMP))(IMD)$_2$	1522	1271	3574	1556	532	450-

The cobalt (II) complex Co(HPIMP)$_2$(IMD)$_2$ showed several electronic spectra; some of them related to the ligand only, while others related to the metal ion. These spectra may be characterized as follows: absorption at wavelength 215 nm and 234 nm are assigned to the $\pi \rightarrow \pi^*$ transitions in the aromatic rings within the two ligands.

Absorption at 261 nm is assigned to the $n \rightarrow \pi^*$ transition from the n (non-bonding electrons) available on the pyridine nitrogen in imidazole and the phenolic oxygen in (HPIMP). The absorption at 346 nm is related to the charge transfer, which occurred between the two ligands and the metal ion within the complex. The d → d transitions which were confined to the d orbital of the metal ion are exhibited in three spectra; the first one did not show up due to its low energy and it will be calculated theoretically through the d^7 system of Tanabe–Sugano diagram [24]. The second absorption occurs at 630 nm, and this is equivalent to the absorption band of 15873 cm^{-1}; and the third absorption occurs at 594 nm which is again equivalent to band of 16835 cm^{-1}.

All the above absorptions are related to the following transitions:

$\upsilon_1 = {}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ … (8403 cm^{-1})
$\upsilon_2 = {}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$.(15873 cm^{-1})
$\upsilon_3 = {}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$.(16835 cm^{-1})

Value of (υ_1) has been calculated from (Tanabe –Sugano) diagrams [19]; where value of B (Racah parameter) needs to be obtained first, which was 500 cm^{-1}, and then using the following relationship ($15B = \upsilon_3 + \upsilon_2 - 3\upsilon_1$) to determine the value of υ_1.
υ_1 8403 (Cal), = 750 . B = 971 , $\beta = 0.77$
15 $\bar{B}$ = 11250. Dq / $\bar{B}$ =0.94, 10Dq B = 7050 and found to be 8403 cm^{-1} which is equivalent to the wavelength of 1190 nm; which is not in the visible area anymore. $\Delta_\circ$ determined similarly and was found to be 900 cm^{-1}.

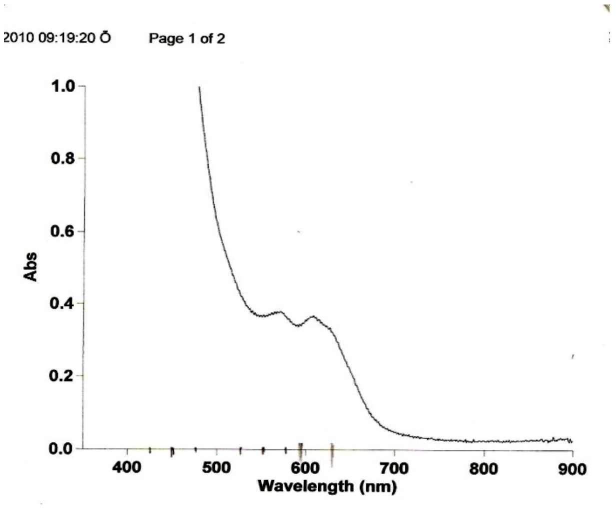


Fig.(1) Electronic Spectrum of Co-Complex.

With regard to the atomic spectra of the nickel complex; it showed similar absorption, with minor differences, to that of the cobalt complex in the case of the absorption related to the ligands and charge transfer absorption. But in case of d → d transition there is a difference between cobalt and nickel; as the nickel exhibitedonly one absorption peak at wavelength of 508 nm which is equivalent to the value of 19685 cm^{-1}. This is due to the following transfer, which is within the visible region.

$\upsilon = {}^1A_{1g} \rightarrow {}^1B_{1g}$……..(19685 cm^{-1})

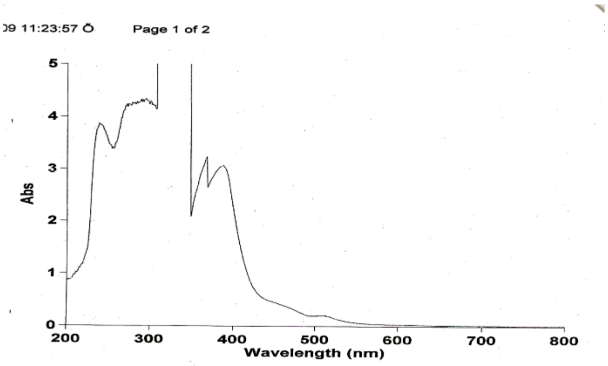


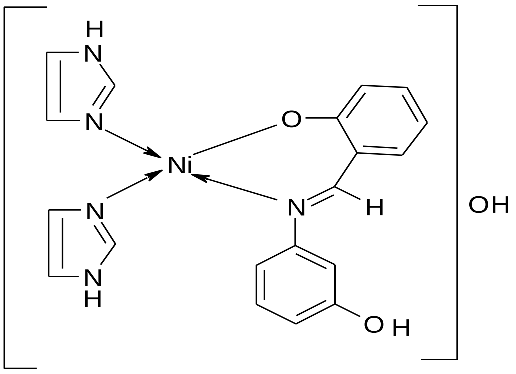
Fig.(2) Electronic Spectrum of Ni–Complex.

The Magneticmoment value for Co^{+2} complex was (5.4) BM which indicate a higher orbital contribution but in case of Ni^{+2} complex it‘s appear diamagnetic. Molar conductivity measurement for both cobalt and nickel complexes were taken in 0.001solution in DMF; and it was found that the solution for cobalt complex contained no ions. But the solution for nickel complex contained ions. The value of conductivity of solution for nickel complex equal (60.6 $us.cm^{-1}$).

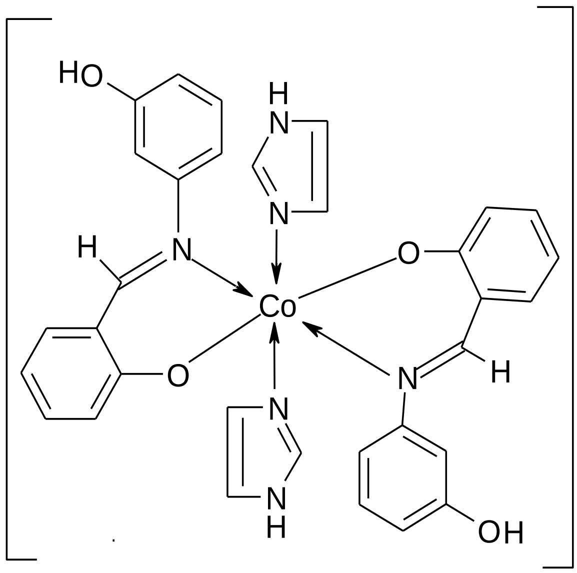
Table (3)
Electronic transitions, magnetic moments and molar conductivities of the prepared compounds.

Compound	Absorption λ_{max}(nm)	Transition	μ (BM)	molar conductivities ohm^{-1} cm^2 $mole^{-1}$	Proposed geometry
HPIMP	215 261	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	-	-	-
Imidazole	234 264	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	-	-	-
$Co(II)((HPIMP))_2(IMD)_2$	645 630 594	${}^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ ${}^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ ${}^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$	5.82	20	Octahedral
$Ni(II)((HPIMP))(IMD)_2$	508	${}^1A_{1g}\rightarrow{}^1B_{1g}$	0.0	60.6	Square planar

From the all above data taken for the whole complexes, it can be confirmed thatthe cobalt complex has an octahedral structure with the formula of $Co(HPIMP)_2(IMD)_2$, while the nickel complex is adapting a square planar shape with the formula of $Ni(HPIMP)(IMD)_2OH$ (See Scheme (3 ,4)).



Scheme (3) $Ni(HPIMP)(IMD)_2OH$.



Scheme (4) $Co(HPIMP)_2(IMD)_2$.

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الخلاصة

في هذا البحث تم تحضير الليكاند 2-{(E)-[(3-hydroxyphenyl)imino]methyl}phenol(HPIMP) ثنائي السن بشكل قاعدة شف مشتقة من تفاعل السلسلديهايد مع 3− امينو فينول. تم تحضير معقدات جديدة لعنصري الكوبلت (II) والنيكل(II) مع الليكاند اعلاه بصيغة اولية وبنسبة مولية 2:1 فلز:ليكاند وباستخدام الايثانول المطلق كمذيب ومن ثم تم اضافة ليكاند الايميدازول وبنسبة مولية 2:2:1 فلز: ليكاند ليكاند وباستخدام نفس المذيب تم عزل المعقدات المحضرة ودراستها باعتماد الطرق الطيفية (UV-Visible و IR) والامتصاص الذري اللهبي (atomic absorption) والتوصيلية الكهربائية المولارية والحساسية المغناطيسية فقد اظهرت اطياف الاشعة المرئية وفوق البنفسجية ان الشكل الهندسي للمعقد $Co(HPIMP)_2(IMD)_2$ ثماني الوجوه والشكل الهندسي للمعقد $Ni(HPIMP)(IMD)_2$ مربع مستوي كما تم التطرق بالبحث على تأثير قاعدية الليكاند والاصرة الهيدروجينية على قابلية الليكاند على التناسق كما بينت نتائج قياسات التوصيلية الكهربائية لمعقد الكوبلت المحضر طبيعة غير الكتروليتية بينما لمعقد النيكل طبيعة الكتروليتية.