Synthesis, Characterization, and Potential Applications of Novel Schiff Base Metal(II) Complexes Derived from 3-Hydroxy-2-Naphthoic Hydrazide and 3-Acetyl-2-Hydroxy-6-Methyl-4H-Pyran-4-One

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Abstract

Schiff base metal complexes presents a broad range of opportunities in the industry and pharmaceuticals alike. Here, we present the synthesis and characterization of novel Schiff base metal complexes. The Synthesis of metal(II) complexes of (*E*)-3-hydroxy-*N'*-(1-(6-methyl-2,4-dioxo-3,4-dihydro-2*H*-pyran-3-yl)ethylidene)-2-naphthohydrazide was conducted through a two-pot synthesis method. The mechanism of reaction of the ligand involved the nucleophilic attack of the primary amine (3-hydroxy-2-naphthoic hydrazide) on one of the carbonyl carbon atoms of 3-acetyl-2-hydroxy-6-methyl-4H-pyran-4-one in an alcohol medium to give the ligand. The reaction of the ligand with metal chlorides of Co(II) and Ni(II) afforded two metal complexes. The mass spectrometry and the color and melting point of the sample was analyzed, the Mass Spectra, Percentage Metal and Elemental properties were analyzed as well H^1 NMR, C^{13}NMR to confirm the formation of the novel Schiff base metal complexes. While the color and elemental properties gave a satisfactory result, the ligand spectrum gave a molecular ion of 353.087. The M^+ ions of 482.0478 and 483.0428 was obtained from the spectra of the complexes respectively. The protons of the methyl groups were seen as singlet peaks at 2.66 and 2.16 ppm. Aromatic C-H of the naphthene ring gave peaks within the range 8.49-7.34 ppm in the spectrum of the ligand. The ^{13}C NMR spectrum of the ligand was used to corroborate inferences drawn from the proton NMR spectrum. The carbon atoms of the carbonyl groups were seen at 181.51 and 168.53, 162.68 ppm. The carbon atom of the azomethine group presented a peak at 162.84 ppm which is indicative of the formation of the Schiff base ligand. The carbon atoms of the naphthene ring were observed at

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105.98-129.29 ppm. Carbon atoms of the methyl groups were assigned to the peaks at 17.16 and 19.77ppm confirming the formation of the metal complex. While other characterization attempts proved a successful synthesis of the target Schiff metal complexes, it is recommended for application in the industry and pharmaceuticals.

Keywords: Schiff base, Complex, Transition metal, hydrazine, naphthene

1.0 Background information

Coordination compound(s)[1] is a catalogue of compounds consisting of ligand(s) bonded to the central metal ion through coordinate covalent bond[2]. The element in the ligand that is directly bonded to central metal ion is known as the donor atom. A donor atom usually possesses a lone pair of electron with which it can bond to the central metal atom via coordinate covalent bonding. Quite a good number of coordination compounds have been synthesized and reported in literature. In recent times, complexes were Schiff base ligands are used are becoming prevalent[3, 4].

A Schiff is a heterocylcilc ligand that consists of an azomethine (C=N) group in its molecular structure. It was named after Hugo Schiff after his publication on Schiff bases obtained from the condensation reaction of salicylaldehyde with various primary amines [5]. The ligand is reported to chelate the central metal ion through the nitrogen of the azomethine group which acts as its donor atom. A large number of Schiff bases and their metal complexes have been reported in literature [3, 6, 7]. This is due to the numerous industrial and biological applications of this group of compounds. They have been reported to be useful as dyes, corrosion inhibitors and catalyst in a number of organic reactions. They have also been reported to possess antiviral [8], antifungal[7], anticancer[9] [10], antibacterial [10] [11] activities.

Cobalt(II) and nickel(II) complexes of various Schiff base have been reported to exhibit an array of geometry ranging from octahedral, tetrahedral and square planar. Their geometries are determined through spectroscopic techniques and magnetic measurements [6]. Metal complexes of Schiff bases derived from 3-hydroxy-2-naphthoic hydrazide and various aldehydes or ketones have been reported. They have been established as possessing antimicrobial and corrosion inhibition properties [12]. However, the synthesis of a Schiff base obtained from the condensation reaction of 3-hydroxy-2-naphthoic hydrazide with dehydroacetic acid has not been reported.

2.0 Review on Cobalt (II) Schiff base complexes

Cobalt complexes exhibit variety of geometries such as octahedral, tetrahedral and square planar. The type of geometry adopted by a cobalt complex can be ascertained by the values of the magnetic moment. Cobalt(II) complex in an octahedral field should have spin-only magnetic moment value of 3.88B.M but experimental values are within the range of 4.70-5.20BM. The values of the magnetic moment for cobalt complexes are affected by large orbital contribution due to three-fold orbital degeneracy of ^4T_1g ground state. Cobalt(II) complex in a tetrahedral field will have magnetic moment within the range of 4.20-4.60BM, that of square planar geometry will have magnetic moment within 1.72-2.72BM [13]. Cobalt (II) complex of a variety of ligands have been reported by[14].

The synthesis and characterization of a series of Co(II) Schiff base complexes which were obtained by the reaction of $Co(CH_3COO)_2•H_2O$ and the Schiff bases; *1-{3-[(3-Hydroxypropylimino)methyl]-4-hydroxyphenylazo}-4-nitrobenzenato)I* (HL1), *1-{3-[(3-Hydroxypropylimino)methyl]-4-hydroxyphenylazo}-2-chloro-4-nitrobenzenato* (HL2) *and 1-{3-[(3-Hydroxypropylimino)methyl]-4-hydroxyphenylazo}-4-chloro-3-nitrobenzenato* (HL3) [15]. The elemental and spectroscopic analysis supported the formation of the complexes. The IR-Spectra of the complexes indicating the various functional groups are; 1,641 (C=N), 1,479 (N=N), 1,344 (C-O, phenolic), 414 (Co-N), 584 (Co-O) cm^{-1} for Cobalt complex of *1-{3-[(3-Hydroxypropylimino)methyl]-4-hydroxyphenylazo}-2-chloro-4-nitrobenzenato,* 1,635(C=N), 1,479 (N=N), 1,336 (C-O, phenolic), 408 (Co-N), 576 (Co-O) cm^{-1} for the cobalt complex of *1-{3-[(3-ydroxypropylimino)methyl]-4-hydroxyphenylazo}-4-nitrobenzenato; and* 1,602 (C=N), 1,475 (N=N), 1,330 (C-O, phenolic), 443 (Co-N), 592 (Co-O) cm^{-1} for cobalt of *(1-{3-[(3-Hydroxypropylimino)methyl]-4-hydroxyphenylazo}-4-chloro-3-nitrobenzenato.* More so, the prominent bands of the Uv-Vis spectra were observed at 256($\pi \rightarrow \pi^*$), 278 ($n \rightarrow \pi^*$), 489 and 605 nm (d-d); 257($\pi \rightarrow \pi^*$), 270 ($n \rightarrow \pi^*$), 508 and 622 nm (d-d); 259($\pi \rightarrow \pi^*$), 285 ($n \rightarrow \pi^*$), 438 and 528 nm (d-d) for cobalt complexes of HL1, HL2 and HL3 respectively.

Similarly, the synthesis and characterization of Co(II) complex obtained from the reaction of Schiff base 3*E*)-3-[(2-{(*E*)-[1-(2,4-dihydroxyphenyl)ethylidene]amino}ethyl)imino]-1-phenylbutan-1-one have been reported [16]. The analytical result suggests an octahedral geometry for the Co(II) complex. The IR Spectrum of the ligands showed a band at 3479 cm^{-1} due to stretching vibration of the phenolic hydroxyl group. The absorptions at 3076 (Ar-CH), 2981(Aliphatic CH), 1605 (C=N), 1543 and 1470(C=C), 1288 and 1241(C-O) cm^{-1}. In the spectrum of the cobalt complex the broad band at 3479 cm^{-1} was absent which is an indication of the deprotonation of the phenolic group and coordination of the oxygen atom to the central metal ion. Also, there was a decrease in wavenumber for the bands initially observed within 1601-1584cm^{-1} due to the participation of nitrogen atom of the azomethine in coordination to the central metal ion. The Uv spectrum of the ligand gave bands at 329, 339 and 378nm were assigned to π-π*, π-π* and n-π* transitions respectively. These bands were observed at 318 (π-π*), 357(π-π*), 377 (n-π*) in the UV of the cobalt complex. This visible spectrum of the complex gave bands at 406, 609 and 682 nm which were assigned to ^4T_1g (F) → ^4T_1g (P), ^4T_1g (F) → ^4A_2g (F) and ^4T_1g (F) → ^4T_2g (F) transitions respectively, confirming the formation of the metal complex. The cobalt complex adopted a square planar geometry [16].

The synthesis and characterization of Co(II) Schiff base complex derived from the reaction of [(4-oxo-4*H*-chromen-3-yl) methylene] benzohydrazide and $CoCl_2$ has been recorded [17]. The ligand was tridentate, coordinating to the central metal ion through nitrogen atom of azomethine group, oxygen atom of keto group of *γ*-pyrone ring and oxygen atom of hydrazoic group of benzoyl hydrazine. The result of the spectral studies all supported the formation of the complex. From the molar conductance experiment, the conductance values that fell in the range of 102-148 $\Omega^{-1}cm^2mol^{-1}$ indicates that the complex is a 2:1 electrolyte. More so, IR spectrum gave bands at 1679 cm^{-1}, characteristic of the stretching vibration of (C=O) which shifted to lower region by 33-53 cm^{-1} compared to the value obtained from the spectrum of the ligand. The band at 1617 cm^{-1} due to the stretching vibration of the azomethine (C=N) group also shifted to lower region by 27–45 cm^{-1} compaed to the value obtained from the spectrum of the ligand, indicating the formation of the complex. A magnetic moment of 4.95B.M was obtained which is characteristic of an octahedral Co(II) complex since it fell within 4.6-5.2 BM that is the expected range for the geometry.

Also, the synthesis and characterization of five cobalt complexes by reacting $CoCl_2.H_2O$ with the following Schiff base ligands N'-(4-Hydroxy-3-methoxyphenyl)methylidene]formic hydrazide (L-1), N'-[-(4-hydroxy-3-methoxyphenyl)methylidene]-3'-hydroxynaphthalene-2'-carbohydrazide

(L-2) N'-[-(5-methylfuran-2-yl)methylidene]-3'-hydroxynaphthalene-2'-carbohydrazide (L-3), N'-[-1''-(4-fluorophenyl)ethylidene]-3'-hydroxynaphthalene-2'-carbohydrazide (L-4) and N'-[(-1'-(4-chlorophenyl)ethylidene]formic hydrazide (L-5) have reported [18]. The molar conductance values of the complexes were in the range of 31-116 $\Omega^{-1}cm^{2}mol^{-1}$, which is an indication of their electrolytic nature. More so, from the results of IR spectra, showed that the ligands were bidentate and coordinated through the carbonyl oxygen and the azomethine nitrogen. In addition, bands within the range of 540-533 cm^{-1} and 420-440 cm^{-1} due to M-O and M-N respectively were observed, comfirming the coordination of the donor atoms to the metal ion. Also a decrease in the band at 1607 cm^{-1} which was assigned to azomethine C=N vibration in the spectrum of the ligands was found increased by 20Cm^{-1} or more in the spectra of the complexes indicating participation of the azomethine nitrogen in coordination.

Kavitha and Lakshmi[19] have also reported the synthesis and characterization of Co(II) Schiff base metal complex obtained from the reaction of the ligand 3-(2-(1-(2,4-dihydroxyPhenyl)ethylidene)hydrazinyl)-2H-benzo[b][1,4]oxazin-2-one (obtained from the reaction of 3-hydrazino-1,4-benzoxazin-2-one and 2,4-dihydroxyacetophenone), and $CoCl_2$. The result of the IR Spectra, showed broad peak at 3430 cm^{-1} due to the stretching vibration of (OH) (phenolic) A sharp peak at 3268 cm^{-1} was assigned to the stretching vibration of N-H moiety. The strong bands at 1603 and 1567 cm^{-1} were attributed to vibration bands of C=O and azomethine groups. The decrease of the band assigned to the zomethine group compared th the value obtained in the spectrum of the ligand were due to participation of the nitrogen atom of the imine group in coordination. The Uv-Vis spectrum gave bands at 37,735 cm^{-1} and 33,670 cm^{-1} due to π-π^* and n– π^* transition respectively of the ligand. These bands were seen at 31,948 and 31,645 cm^{-1} in the spectrum of the complex. The magnetic moments of Co(II) was found to be 5.27B.M which indicates that the complex conformed to an octahedral geometry.

2.1 Review on Nickel (II) Schiff base complexes

Nickel in a +2 oxidation state has a d^8 electronic configuration and can adopt different geometries. However the assignment of a geometry to Ni(II) complexes can easily be done by the use of their magnetic moment values[20]. Magnetic moments within the range of 2.9-3.3 BM are assigned to Ni(II) complexes of octahedral geometry while magnetic moments within 3.2-4.2 BM are characteristic of Ni(II) complexes of tetrahedral geometry. Ni(II) complexes of Square planar geometry are diamagnetic with magnetic moment below 1BM.

Kavitha *et al.* [19] reported the synthesis and characterization of the Ni(II) Schiff base complex of the ligand 3-(2-(1-(2,4-DihydroxyPhenyl)ethylidene)hydrazinyl)-2H-benzo[b][1,4]oxazin-2-one. The result of the IR spectrum gave a broad band at 3543 cm^{-1} due to stretching vibration of the phenolic OH group. The sharp band at 3268 cm^{-1} was assigned to stretching vibration of NH group. The vibration band for phenolic C–O of ligand was observed at 1171 cm^{-1}. The strong band at 1603 cm^{-1} was attributed to the lactone carbonyl group. A broad band with a shoulder at 1567 cm^{-1} was attributed to azomethine group. The m(N–N) bending vibration is noticed at 1058 cm^{-1}. A small band noticed at 3038 cm^{-1} was ascribed to CH group of the aromatic ring while the asymmetric CH stretching of the aliphatic group is observed at 2924.

However, in the IR of the ligand, the C=O was observed at a lower wavenumber of 1167 cm^{-1} due to the participation of the oxygen in the coordination. The decrease of the band from 1567cm^{-1} (spectrum of the complex) to 1536cm^{-1} (in the spectrum of the ligand) is an indication that the free and azomethine nitrogen has been used in coordination. The extra bands 487 cm^{-1} and 416 cm^{-1} which is due to the coordination of the free and azomethine nitrogen further supports the formation of the complex.

Ejidike and Ajibade [16]have reported the synthesis and characterization of Ni(II)Schiff base metal complexes of the ligand 3*E*)-3-[(2-{(*E*)-[1-(2,4-Dihydroxyphenyl) ethylidene]amino}ethyl)imino]-1-phenylbutan-1-one. Form the electronic spectrum, the bands bands at 329, 339 and 378 nm are due to intraligand π-π* and n-π* transitions indicating the formation of the ligand and the shift from 374–380 nm observed are due to coordination to the central metal ion. Furthermore, it was also found that the Ni(II) complex exhibited two absorption bands at 433and 568 nm which are assignable to two spin allowed transitions, $^{1}A_{1}g \rightarrow {}^{1}A_{2}g$, $^{1}A_{1}g \rightarrow {}^{1}B_{1}g$ characteristic of a square planar nickel complex. The IR spectrum, gave bands at 3479 cm^{-1} that was attributed to the phenolic hydroxyl group, while the absorptions at 3076, 2981, 1605, 1543, 1288 and 1241 cm^{-1} were ascribed to Ѵ(Ar-CH), (Aliphatic-CH), Ѵ(C=N), Ѵ(C=C), Ѵ(C-O) respectively. However, the shift by 48–61 cm^{-1} lower in the spectrum of the ligand for phenolic Ѵ(C-O) and the azomethine band confirms the participation of the azomethine and the enolic axygen in coordination. The complex was found to be nonelectrolyte given the value of the conductance measure at 4.31$\Omega^{-1}Cm^{2}mol^{-1}$.

Various mixed ligand Ni(II) complex obtained from the reaction of $NiCl_2 \cdot 6H_2O$, 3-benzyl-1H-4-[(2-methoxybenzylidine) amino]-1, 2, 4-triazole-5-thione (MBT) and 3-bezyl-1H-4-[(4-chlorobenzylidine)amino]-1, 2, 4-triazole-5-thione (CBT) have been recorded [21].

The synthesis and characterization of four Ni(II) Schiff base complexes with the formula $[Ni(L)(H_2O)]$, where L = N-(dehydroacetic acid)-thiosemicarbazide (H2dha-tsc), N-(dehydroacetic acid)-4-methyl-3-thiosemicarbazide (H2dha-mtsc), N-(dehydroacetic acid)-4-phenyl-3-thiosemicarbazide(H2dha-ptsc), or N-(dehydroacetic acid)-4-phenylsemicarbazide (H2dha-psc) have been reported. The coordinating properties and stereochemistry of these complexes have been deduced from elemental analysis, infrared and electronic spectral studies, molar conductance, magnetic measurements, mass spectrometry, thermogravimetric analysis, ^{1}H NMR and ^{13}C NMR studies, and cyclic voltammetry. The results of the analysis led to the proposition of the geometry of the complex to be square planar [10].

2.2 Industrial application of Schiff bases and their metal complexes

Schiff bases and their metal complexes have recently garnered considerable attention in the scientific community due to their diverse industrial applications. These versatile compounds, formed by the condensation of primary amino compounds with aldehydes or ketones, exhibit a wide range of properties that render them valuable in various sectors[23, 24].

In the chemical industry, Schiff base complexes have demonstrated remarkable catalytic activity in a multitude of reactions, including oxidation, hydrogenation, epoxidation, and cyclopropanation[25]. They are particularly effective in the catalytic oxidation of organic compounds and polymers, with recent research focusing on metal-catalyzed oxidation processes[26]. Moreover, these complexes have been employed as fine chemistry catalysts, with ruthenium complexes exhibiting particular efficacy in alkene metathesis and associated reactions[25].

Additionally, Schiff base metal complexes have shown promise in the field of materials science. They can be incorporated into discrete molecules, oligomers, or polymers to generate new functional materials with enhanced mechanical, thermal, and optoelectronic properties. This has resulted in their utilisation in energy-related applications, including organic light-emitting diodes, dye-sensitized solar cells, and prospective conductive thermoelectric materials[27].

The industrial applications of Schiff bases and their metal complexes are diverse and continue to expand. From catalysis to materials science, these compounds offer unique properties that make them valuable in various sectors. As research in this field progresses, it is likely that new and innovative applications will emerge, further underscoring the importance of Schiff bases and their metal complexes in industry.

2.3. Biological application of Schiff bases and their metal complexes

Schiff bases and their metal complexes have been reported to possess various biological potentials such as antibacterial, antifungal, anticancer, anti-inflammatory, antioxidant properties etc[2].
For example, the Schiff bases, 3-{2-[l-(6-Chloro-2-oxo-2//-chromen-3-yl)ethylidene]hydrazinyl} quinoxalin-2(l//)-one and 3-[2-(propan-2-ylidene)hydrazinyl]quinoxalin-2(l//)-one have been reported for their antimicrobial properties[28]. Similarly, the Schiff base, 5-methyl-4-oxo-3-phenyl-thiazolidin-2-ylidene)-hydrazide have been reported to possess antimicrobial potentials. Edrees *et al.*(2010) synthesized a series of 2-[A-aryl-2-oxo-2-(4-chlorophenyl) ethanehydrazonoyl]-6-methyl-4(3//)-pyrimidinones and screened their antimicrobial potential against *S. aureus* (SA), *P.aeruginosa* (PA), *B. subtilis* (BS), and *E. coli* (EC), *Aspergillus fumigatus.* The ligand exhibited good antimicrobial properties [29].
Schiff bases and their metal complexes have recently attracted considerable attention in the scientific community due to their diverse biological applications. These compounds, formed by the condensation of primary amines with carbonyl compounds, exhibit a wide range of activities, including antimicrobial, antifungal, antitumor, and cytotoxic properties[30]. The biological activity of Schiff bases is frequently augmented when coordinated with metal ions, rendering their metal complexes especially intriguing for medicinal chemistry applications[31,32].

It is noteworthy that the biological spectrum of Schiff base metal complexes extends beyond antimicrobial and anticancer properties. Recent studies have demonstrated the potential of Schiff base metal complexes to exert antioxidant effects, inhibit enzymes, and even facilitate photodynamic therapy for the treatment of tumors with reduced side effects[31, 33]. The versatility of these compounds is further exemplified by their applications in the food and dye industries, agrochemicals, polymers, and as catalysts in various chemical processes[25, 30].

The recent literature underscores the increasing significance of Schiff bases and their metal complexes in biological applications. The capacity to modify their characteristics through ligand design and metal selection presents a significant opportunity for the development of novel therapeutic agents. As research in this field continues to evolve, it is reasonable to anticipate the emergence of additional innovative applications of these versatile compounds in addressing a range of biological challenges[31-33].

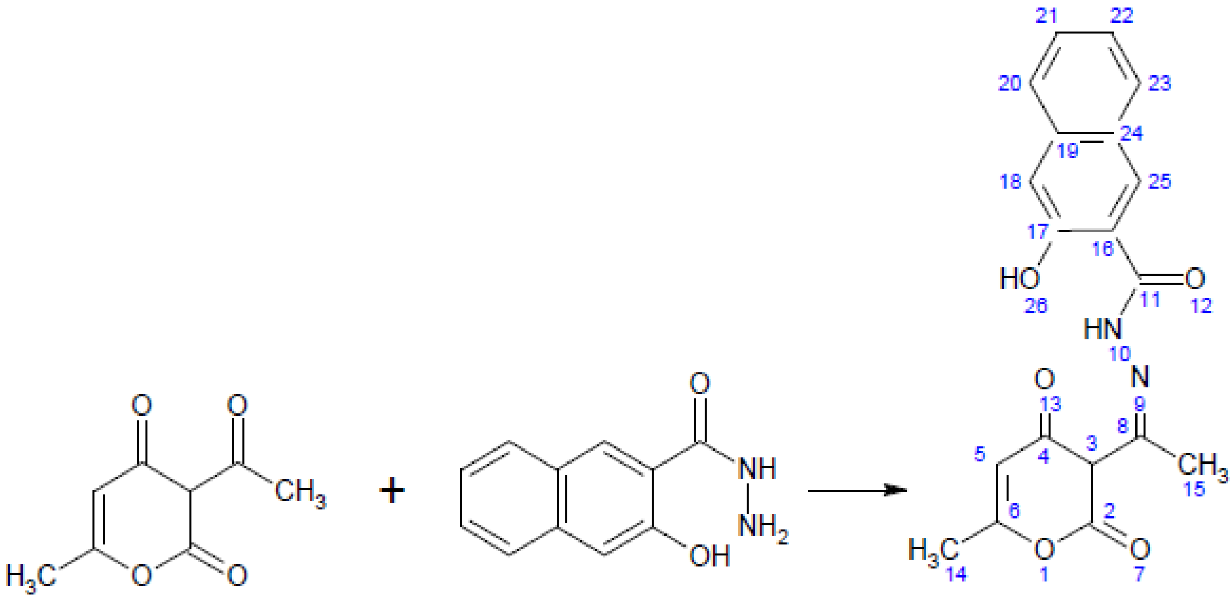
3.0 Synthesis and Characterization Techniques

High-purity reagents were used in the synthesis of the Schiff base and metal complexes, including 3-acetyl-2-hydroxy-6-methyl-4H-pyran-4-one, 3-hydroxy-2-naphthoic hydrazide, acetic acid, acetone, $NiCl_2$, and $CoCl_2$. The Schiff base was synthesized by adding a methanol solution of 3-acetyl-2-hydroxy-6-methyl-4H-pyran-4-one to an equimolar solution of 3-hydroxy-2-naphthoic hydrazide, followed by the addition of glacial acetic acid and refluxing for 4 hours. The resulting precipitate was filtered, recrystallized from hot methanol, and stored under vacuum over silica gel. Nickel and cobalt complexes of the Schiff base were prepared by reacting the ligand with the corresponding metal salts in methanol, buffered with triethylamine, and refluxed for 4 hours. The green and brown precipitates of the nickel and cobalt complexes, respectively, were filtered, washed with cold methanol, recrystallized, and dried under vacuum.

The synthesized compounds were characterized by several techniques to confirm their structure and properties. Melting points were determined using an Electrothermal Temp-Mel apparatus, while elemental analysis (CHNS) was carried out using a Vario EL Cube analyzer. Infrared spectra were recorded using a Perkin-Elmer FT-IR Spectrum BX spectrophotometer, and UV-Visible spectra were obtained with a Perkin-Elmer λ20 spectrophotometer. The Schiff base was further analyzed by ^1H NMR spectroscopy on a Bruker Advance III 600 MHz spectrometer, and magnetic susceptibility measurements were taken using a Sherwood Susceptibility Balance. Electrolytic conductivities were measured in DMSO using a Hanna conductivity meter, and mass spectra were acquired using a Waters Micromass Q-TOF II spectrometer with electrospray ionization. All products were stored under vacuum in a desiccator to maintain their stability.

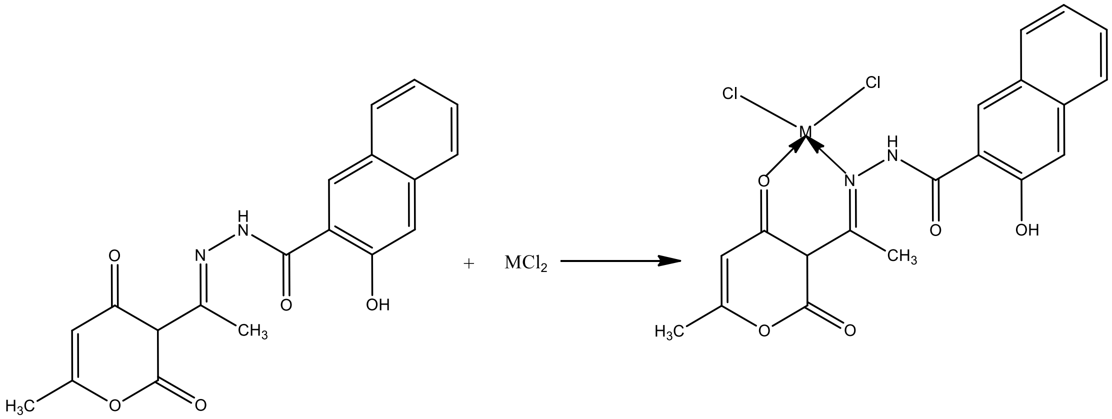
4.0 General information.

The mechanism of reaction of the ligand involved the nucleophilic attack of the primary amine (3-hydroxy-2-naphthoic hydrazide) on one of the carbonyl carbon atoms of 3-acetyl-2-hydroxy-6-methyl-4H-pyran-4-one in an alcohol medium to give the ligand as shown in **scheme 1**.



Scheme 1: Synthesis of metal(II) complexes of (*E*)-3-hydroxy-*N'*-(1-(6-methyl-2,4-dioxo-3,4-dihydro-2*H*-pyran-3-yl)ethylidene)-2-naphthohydrazide

The reaction of the ligand with metal chlorides of Co(II) and Ni(II) afforded two metal complexes (**Scheme 2**). The compounds were characterized by NMR, mass, FT-IR and Uv-vis spectroscopies, elemental analysis, magnetic susceptibility and molar conductance measurements.



Where M = Ni(II), Co(II) and Cu(II)

Scheme 2: Synthesis of metal(II) complexes of (*E*)-3-hydroxy-*N'*-(1-(6-methyl-2,4-dioxo-3,4-dihydro-2*H*-pyran-3-yl)ethylidene)-2-naphthohydrazide.

4.1 Colour and Melting Point/ Decomposition temperature of the compounds

The Schiff bases and its metal complexes gave various types of colours as shown in **Table** 1. The colour of the ligand can be ascribed to the presence of chromophores that absorb light in the visible region of electromagnetic spectrum. The colours of the metal (II) complexes could be attributed to d-d transitions of electrons within the metal molecular orbitals when an electron absorb light in the visible region of the electromagnetic spectrum.

The results of the melting point determination of the compounds were presented in **Table 1**. The melting point of the ligand is lower compared to its metal complexes. The increase in the melting point of the complexes when compared to the ligands was due to coordination of the ligands to the various metal ions.

Table 1: Analytical data of the Schiff base and its metal complexes

							Anal (Cal)			
Compound Formula	**Formula Weight**	**Colour**	**Melting Point [34]**	**B.M**	**$\wedge_m$**	**% Yield**	**%C**	**%H**	**%N**	**%metal Theo (Exp)**

HL	352.34	Yellow	149-151	-	-	75	64.78	4.58	7.95	-
$C_{19}H_{16}O_5N_2$							(64.77)	(4.58)	(7.95)	
[CoLCl_2]	482.27	Brown	200-202	0.14	11.56	80	47.36	3.36	5.83	26.92
$CoC_{19}H_{16}O_5N_2Cl_2$							(47.32)	(3.34)	(5.81)	(26.94)
[NiLCl_2]	481.85	Green	256-258	4.7	14.01	60	47.40	3.36	5.78	26.90
$NiC_{19}H_{16}O_5N_2Cl_2$							(47.36)	(3.35)	(5.76)	(26.93)

B.M = Bohr magneton; ^_m = conductivity measurement ($\Omega^{-1}cm^2mol^{-1}$); L = deprotonated HL

4.2 Mass Spectra, Percentage Metal and Elemental analyses

The mass spectra of the ligand and its metal complexes are presented in **Figure 2a-2c**. The molecular ions were in agreement with the proposed molecular formula of the compounds. The ligand spectrum gave a molecular ion of 353.0871 which is in agreement with a calculated value of 352.341. The M^+ ions of 482.0478 and 483.0428 obtained from the spectra of the complexes corresponded to the calculated values of 482.034 and 482.271 for nickel and cobalt complexes respectively. Furthermore, the results of the elemental analysis and percentage metal determination presented in **table 1** supported the proposed elemental composition of the compounds as their calculated and experimental values were close juxtaposition.

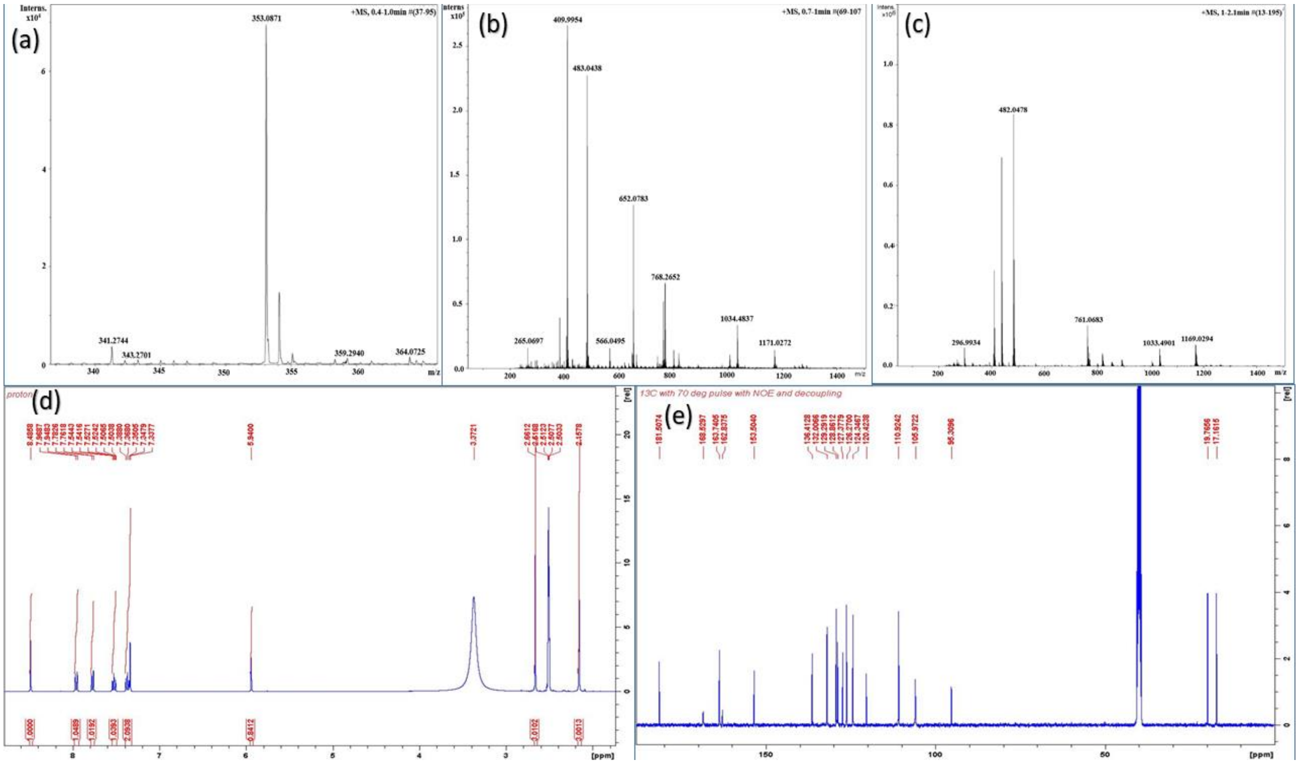


Figure 2: a) Mass Spectrum of the synthesized ligand b) Mass Spectrum of Ni(II)complex. c) Mass Spectrum of Co(II) complex d) ^{1}H NMR of the ligand e) ^{13}C NMR of the ligand

4.3. NMR spectra results of the ligands

The ^{1}H NMR and ^{13}C NMR spectra of the ligand are presented in **Figure 2d and 2e**. The ^{1}H NMR spectrum of the ligand showed a singlet peak at 5.94ppm, which was ascribed to proton of the secondary amine group in the ligand. The protons of the methyl groups were seen as singlet peaks at 2.66 and 2.16 ppm. Aromatic C-H of the naphthene ring gave peaks within the range 8.49-7.34 ppm in the spectrum of the ligand. The ^{13}C NMR spectrum of the ligand was used to corroborate inferences drawn from the proton NMR spectrum. The carbon atoms of the carbonyl groups were seen at 181.51 and 168.53, 162.68 ppm. The carbon atom of the azomethine group presented a peak at 162.84 ppm which is indicative of the formation of the Schiff base ligand. The carbon atoms of the naphthene ring were observed at 105.98-129.29 ppm. Carbon atoms of the methyl groups were assigned to the peaks at 17.16 and 19.77ppm.

4.4. Infrared Spectra of the Ligands and their metal complexes

The FT-IR spectra gave characteristic peaks that can be used to give credence to the formation of the compounds and fathom the coordination modes of the ligands. The IR spectra of the compounds are presented in the appendices. The band at 3472 cm^{-1} in the spectrum of the ligand was attributed to the stretching vibration of the O-H group. The band was seen within 3411-3414 cm^{-1} in the spectra of the complexes indicating the non-participation of the OH group in coordination. Bands at 1713 and 1672 cm^{-1} were ascribed to the stretching vibrations of carbonyl groups in the ligand. However, the bands were seen within at a lower wavenumber presumably due to the participation of one of the carbonyl oxygen in coordination. In addition, the stretching vibration of the azomethine group at 1628 cm^{-1} was observed at a higher wavenumber in the spectra of the metal complexes, 1630-1638 cm^{-1} presumably due to the participation of the nitrogen atom of one of the imine group to the metal ion. Additional vibration peaks were observed in the spectra of the complexes within the range 400-499 cm^{-1} and 500-599 cm^{-1} due to M-O and M-N vibrations. These bands were due to the coordination of nitrogen atom of the azomethine group and one of the carbonyl oxygen to the metal ions of the complexes. These peaks were absent in the spectra of the ligands. However, some bending vibration peaks were observed in the spectra of the compounds around 400-600 cm^{-1}. The assignment of the peaks was in accordance with other reported studies[6].

4.5 Electronic Spectra, magnetic moment and conductance measurements of the Schiff base and its metal(II) Complexes

The results of the electronic spectra and magnetic susceptibility measurement were used to assign various geometries to the complexes. The data obtained from the electronic spectra was presented in Table 2 while the results obtained for the magnetic moment and conductance measurements were presented in **Table 1**. The ligands exhibited electronic absorption bands due to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions ascribed to the presence of aromatic ring and electronegative atoms in the ligand, mostly from C=C and C=N respectively. The bands at 229 and 247, and 344 nm in the ultraviolet spectrum of the ligand was assigned to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions respectively. These bands were seen at lower or higher wavelengths in the spectra of the metal complexes because of electronic changes due to coordination of the ligand to the metal ions[4]. The visible region of the electronic spectrum of the nickel complex gave a band at 414 nm due to $^1Ag \rightarrow {}^1Eg$ transition which is characteristic of a square planar geometry[13]. The assignment of this geometry was supported by the magnetic moment value of 0.14BM since a moment less than 1BM is expected for nickel complex in a square planar environment[4]. The visible spectrum of the cobalt complex gave a band at 405 nm due to $^4A_2 \rightarrow ^4T_1(F)$ transitions (**Table 2)**, which is characteristic of a tetrahedral geometry. The assignment of this geometry was supported by a magnetic moment value of 4.35BM. The μeff of Co(II) complexes are expected to be higher than spin-only value for tetrahedral complexes due to orbital contributions and could be within the range 4.20-4.60 B.M[6].

The molar conductance results of the complexes in DMSO showed that the complexes are non-electrolytes. According to standard Geary reference, 23-45 Ω^{-1} cm^2 mol^{-1} is the expected range for 1:1 electrolytes, while below that range represents non electrolytes [35]. The molar conductance of the metal complexes in DMSO were 14.01 and 11.56 Ω^{-1} cm^2 $mol^{-1}$for Ni(II)) and Co(II) complexes respectively.

Table 2: Electronic spectra data of the Schiff base and its metal complexes

Compounds	**Wave length (nm)**	**Interpretation**	**Geometry**
HL^3	229	$\pi \rightarrow \pi^*$	
	247	$\pi \rightarrow \pi^*$	
	344	$n \rightarrow \pi^*$	

$[NiL(Cl)_2]$	245	$\pi\rightarrow\pi^*$	Square Planar
	391	$n\rightarrow\pi^*$	
	414	$^4A_2\rightarrow{}^4T_1(F)$	
$[CoL(Cl)_2]$	229	$\pi\rightarrow\pi^*$	Tetrahedral
	378	$\pi\rightarrow\pi^*$	
	404	$^1Ag \rightarrow {}^1Eg$	

5.0 SUMMARY

The Schiff base, (*E*)-3-hydroxy-*N’*-(1-(6-methyl-2,4-dioxo-3,4-dihydro-2*H*-pyran-3-yl)ethylidene)-2-naphthohydrazide [22] was synthesized by the condensation reaction of 3-acetyl-2-hydroxy-6-methyl-4H-pyran-4-one (dehydroacetic acid) and 3-hydroxy-2-naphthoic hydrazide in a 1:1 stoichiometric ratio. Two metal complexes were obtained by the reaction of the Schiff base with anhydrous nickel(II)chloride and cobalt(II) chloride hexahydrate salts. The compounds (Schiff base and its nickel and cobalt complexes) were characterized by spectroscopic techniques, elemental, magnetic and molar conductivity analysis. The spectroscopic data gave credence to the formation of the compounds. The ligand acts as a bidentate ligand chelating the metal ions using oxygen atom of one of the carbonyl group and nitrogen atom of the azomethine group. The cobalt complex adopted tetrahedral geometry while the nickel complex adopted square planar geometry as obtained from their magnetic moment values. The metal complexes are non-electrolytes in dimethylsulfoxide (DMSO) with values less than 23 $\Omega^{-1}cm^{2}mol^{-1}$.

5.1 Suggestions and Conclusion

I suggest that x-ray crystal structures of the compounds should be developed using different solvent mixtures. I also suggest that the biological properties of the compounds should be studied.

The synthesis of the compounds has been achieved as shown by the results obtained from the various characterization techniques.

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