

Synthesis and Characterization of Co²⁺ Complexes with Hydroxynaphthohydrazone and Investigation of different anions on their behavior

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Abstract: In this research, we have reported the results of synthesis of bi and tridentate hydrazine Schiff base ligands derived from 3-hydroxy-2-naphthohydrazone and pyridine-2-carbaldehyde and their complexes with Co²⁺ cation in the presence of different anions including nitrate, acetate, carbonate, thiocyanate, azide and perchlorate. After the separation of compounds in solid state, we used different spectroscopic methods including IR and Uv/Vis for determining characteristics of our compounds. For the prediction of the structure of complexes, besides IR, we determined the conductivity of solutions of complexes. Cyclic Voltammetry and CV, were used for investigating electrochemical behaviors of compounds.

Key words: Different anions, hydroxynaphthohydrazone, cobalt transition metal.

I. Introduction

Part of the Chemistry that deals with complex compounds of transition metals is called Coordination Chemistry. Today, researchers synthesize new complexes, many of them are scientifically interesting and some of them also have significant economic importance. In recent years, regarding to the importance of the synthesis of Schiff base complexes, many theoretical studies and scientific research have been done on such complex. The Schiff base are compounds that derived from condensation reaction of first amine with acarbonyl compound. Functional group is the main characteristic of Schiff bases (R'-N = C-R) which is called Azomethyn or imine and it has a double bond between carbon and nitrogen. [1, 2] Schiff base ligands in terms of electron donor atoms are divided into two categories: monodentate and polydentate. Another type of classification of these compounds takes place based on the type and number of coordinate atoms. The simplest role of each of the ligands is that they can coordinate to a metal through unshared pair of electrons; these ligands are called monodentate ligands. Depending on the number and type of donor atoms on the Schiff bases, they are divided to, bidentate, tridentate, tetradentate, and etc. The complexes that are synthesized by this ligands are known as the chelating complexes.

Ligands that bind to a metal by two donor atoms of electrons, are called bidentate ligands, and those coordinate to a metal by three donor atoms of electrons are known as 4, 5, and 6 dentate, respectively. Asymmetrically Schiff base ligands are divided into two categories: symmetric and asymmetric. The symmetric are ones that have same electron groups on both sides of the molecule, otherwise they are called asymmetric. The Schiff bases have an important role in the improvement of Coordination Chemistry, because these compounds often readily create stable complexes with some of the transition metals. [3] These compounds have many applications in the production of anti-cancer drugs, catalysts, corrosion inhibitors and other agents of antibacterial compounds. It passes more than a century since the discovery of the first Schiff base, and during this time, several Schiff base complexes with transition metal and with different sustainability were prepared and studied. Schiff bases exhibit good catalytic properties and hence these compounds are extremely important. [4] It seems that the similarity in chemical activities of Schiff Bases especially in the case of asymmetric chemical structure of the ligands is related to the manner of coordination with central atom and by making changes in the structure of ligand some complexes can be produced that are used for specific purposes. [5]

Hydrazones are an important group in the family of Schiff base compounds and they belong to the large class of Azomethynes, and their general formula is "RR'C = NR R" [24,25]. The presence of two nitrogen atoms attached to them distinguished from Imines, Oxy imines, oximes and other Schiff base ligands. Depending on the nature of substituents attached to the hydrazine unit, the Hydrazone ligands can be act as, bidentate, tridentate or tetradentate. [19] Hydrazone ligands that synthesized from condensation of aliphatic and aromatic hydrazide acids with 2-hydroxy carbonyl aromatic groups, are one of the important nitrogen and oxygen donor ligands bunch in which usually due to the short length of N-N bonds, they serve as tetradentate. [15,16] These ligands act as chelating ligands and they are coordinated by the Imine nitrogen and Amide oxygen and phenolic. [8] Several studies showed that, the Azometine group with an un-bonded electron pair in sp² hybrid orbital or in p orbitals on nitrogen, has a considerable biological importance [11,

20]. Various methods of Hydrazone ligand coordination due to density of pyridine 2-carboxyaldehyde and benzo-hydrazone are shown in Figure (1).

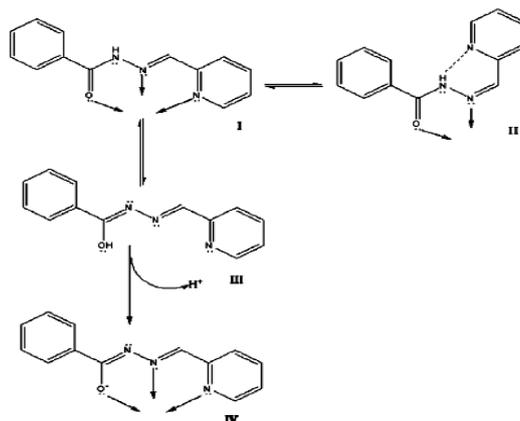


Figure (1). Various methods of coordination of Hydrazone tetradentate ligand

II. Methodology

2.1 Devices and equipment

The ligands and complex of IR spectrum after purification and preparation of KBr tablets were taken by using a Mastson1000 and Bruker in the area of 400 cm^{-1} 4000. UV-Vis spectra were recorded by using a photometer of S2100 Diode Array spector device and quartz cell. Melting point of ligands and complexes were measured by using the 9100 Electrothermal device. Responses of voltammetry reactions were surveyed by using voltammetry Analyzer metrohmb and were equipped with computers AA 7577 models. Three platinum electrode systems were used as the auxiliary electrode. Reference electrode, was the saturated Ag / AgCl hydrate electrode. Also, conductivity of ligands and complexes were measured by using the Conductor Meter 4320 JENWAY. Furthermore, balloons cc 50, magnet, thermometer, refrigerant, glass funnel, beaker, filter paper, digital scale model Cp124, and also Heater- stirrer were used.

2.2 Chemical materials

All of the materials used in this research including 3-hydroxy-2- Naphtoichdrazide acid (98%), Ethanol (98%), Sodium pherchlorate (99%), potassium thiocyanate (98%), Sodium acetate (99%), Sodium nitrate (99%), cobalt nitrate (97%), Sodium azide (99%), and pyridine 2 carbaldehyd (98%) are made by Merck Company. Also 3-hydroxy-2- Nephtodrazid ($C_{17}H_{13}N_3O_2$) ligand have been achieved in the lab by using solution of 3-hydroxy-2- Nephtodrazid in ethanol and mixed to pyridine 2 carbaldehyde reflexes and deposition was gained in lab. Schiff base synthesis reaction of this ligand is shown in (Figure.2).

To prepare the cobalt II complex with potassium thiocyanate ($C_{18}H_{13}N_2O_2SCo$), in the laboratory, first some amount of hydrazone ligand solved in 25 ml of ethanol and then shed on their surface some, cobalt salts. And then somepotassium thiocyanate was added and the resulted mixture was refluxed for 4 hours on magnetic stirrer, then let the product to dry just after cooling and washing with methanol, so the complex was prepared.

So the rest of the complexes such as cobalt complexes with sodium nitrate ($C_{18}H_{13}N_4O_5Co$), sodium acetate ($C_{20}H_{16}N_3O_4Co$), sodium azide ($C_{18}H_{13}N_6O_2Co$) and sodium pherchlorate ($C_{18}H_{13}N_3O_6ClCo$), were obtained by the above method and were prepared in the laboratory environment. Each of the complex synthesis reaction is shown in Figure (3).

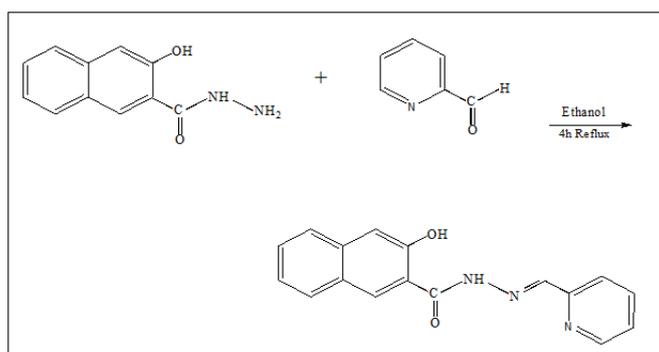


Figure 2. Schiff base ligand synthesis reaction

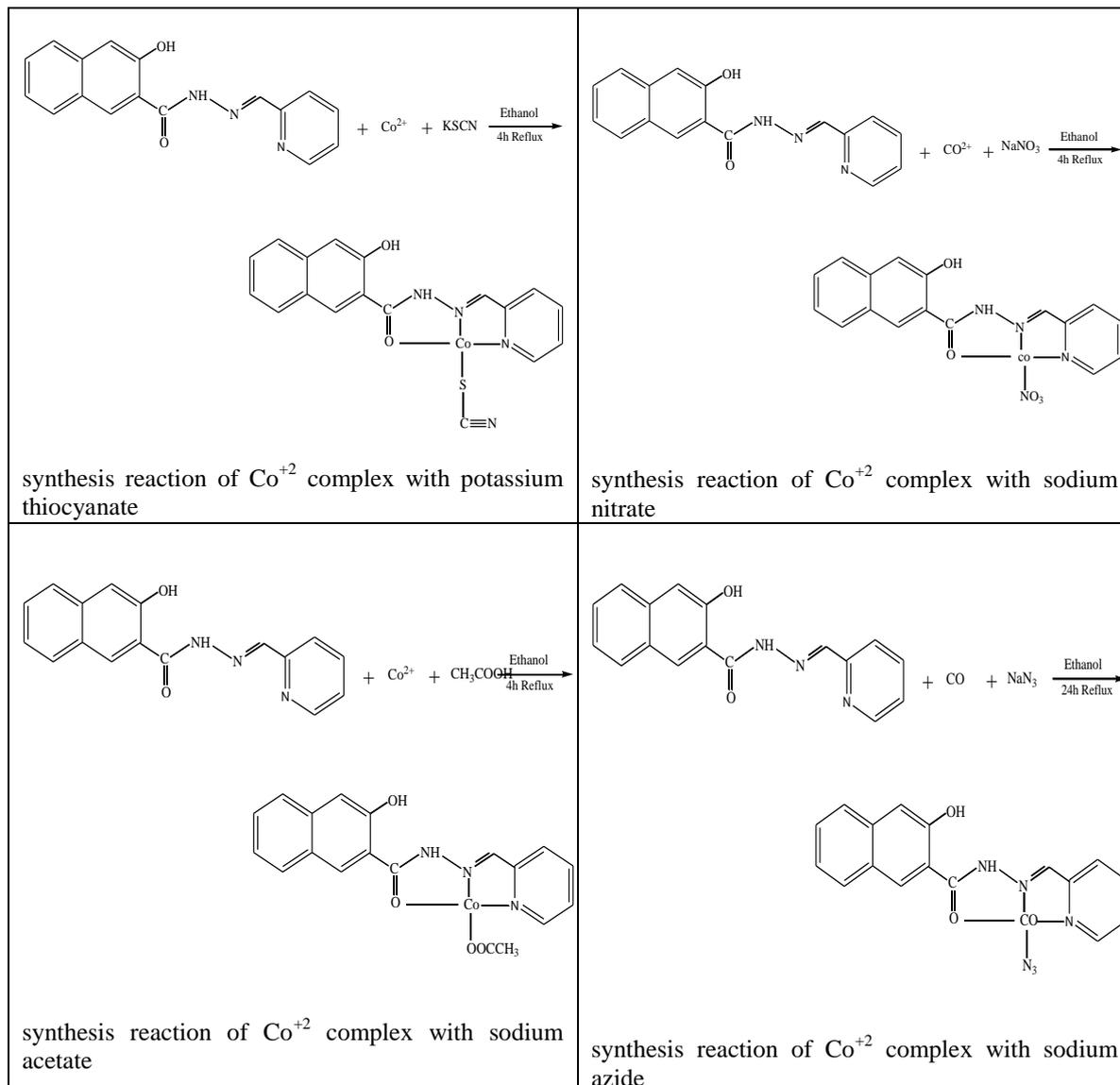


Figure (3). Each of the complex synthesis reaction

III. Results and discussion

3.1 Investigation of infrared spectrum FT-IR

In this work we first examined the synthesized ligand in the laboratory by using of infrared spectroscopy, then the complex which was made from this ligand was tested in the same way. Infrared spectroscopy puts at our disposal required information about changes in ligand due to Coordination. In FT-IR spectra, the most important signals of the synthesized ligands, related to stretching of bonds $\text{C}=\text{O}$ and $\text{C}=\text{N}$ and in the case of the complexes the most signals are related to stretching of bonds $\text{H}-\text{N}$, $\text{C}-\text{O}$, and $\text{C}=\text{N}$. Existence of the shift in the absorption band of the $\text{C}=\text{N}$ bond in the complex compared with free ligand can be due to complex formation.

3.1.1 Characteristics of hydrazone ligand FT-IR spectrum

Absorption band was appeared in the region 3240.25, can be related to the phenolic OH stretching vibration, and strong absorption band in the region of 1649.2, is related to the Imine group $\text{C}=\text{N}$ stretching vibration. Also an absorption band that appeared in the area 1210.72, is related to $\text{C}-\text{O}$ groups of phenolic.

3.1.2 FT-IR spectrum characteristics of Cobalt II complex with potassium thiocyanate

By comparing the FT-IR spectra in Potassium thiocyanate Cobalt II complex and ligand, it becomes clear that stretching vibration absorption band of $\text{C}=\text{N}$ bond in Imine group has increased to wave number of 1632.32, and the absorption band of $\text{C}-\text{O}$ phenolic has increased to wave number of 1212.27, and vibration

absorption band of phenolic OH was decreased to 3339.61. So the data showed that the Coordination was performed with the central metal. Also, wave number of 2090.94 is dependent to thiocyanate ions.

3.1.3 FT-IR spectrum characteristics of Cobalt II complex with sodium nitrate

By comparing the FT-IR spectra of sodium nitrate Cobalt II complex and ligand, it becomes clear that stretching vibration absorption band of C = N bond in Imine group has increased to wave number of 1795.05, and the absorption band of C-O phenolic has increased to wave number of 1368.34, and vibration absorption band of H-N was decreased to 3031.99, and according to the data, the Coordination was performed.

3.1.4 FT-IR spectrum characteristics of Cobalt II complex with sodium azide

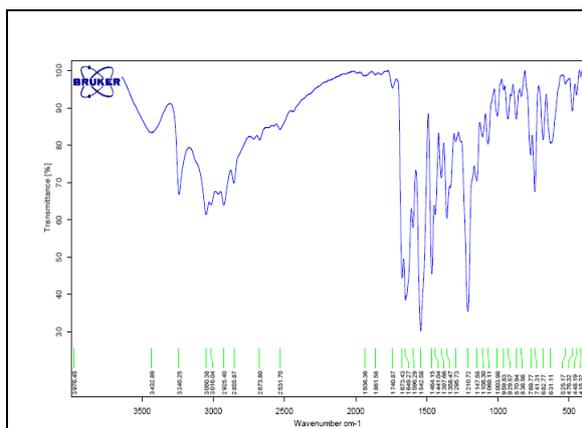
By comparing the FT-IR spectra of sodium azide Cobalt II complex and ligand, it becomes clear that stretching vibration absorption band of C = N bond in Imine group has increased to wave number of 1639.32, and the absorption band of C-O phenolic has increased to wave number of 1244.60, and vibration absorption band of H-N was decreased to 3010.61, so data showed that, the Coordination was performed.

3.1.5 FT-IR spectrum characteristics of Cobalt II complex with sodium acetate

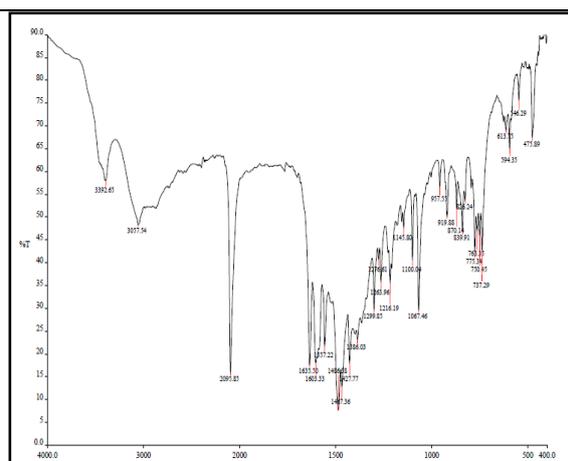
By comparing the FT-IR spectra of sodium azide Cobalt II complex and ligand, it becomes clear that stretching vibration absorption band of C = N bond in Imine group has increased to wave number of 1645.05, and the absorption band of C-O phenolic has increased to wave number of 1222.34, and vibration absorption band of H-N was decreased to 3031.99, so data showed that, the Coordination was performed.

3.1.6 FT-IR spectrum characteristics of Cobalt II complex with sodium perchlorate

By comparing the FT-IR spectra of sodium azide Cobalt II complex and ligand, it becomes clear that stretching vibration absorption band of C = N bond in Imine group has increased to wave number of 1645.05, and the absorption band of C-O phenolic has increased to wave number of 1222.89, and vibration absorption



1. FT-IR spectrum of hydrazone ligand



2. FT-IR spectrum of Cobalt II complex with potassium thiocyanate

band of H-N was decreased to 3031.99, so data showed that, the Coordination was performed.

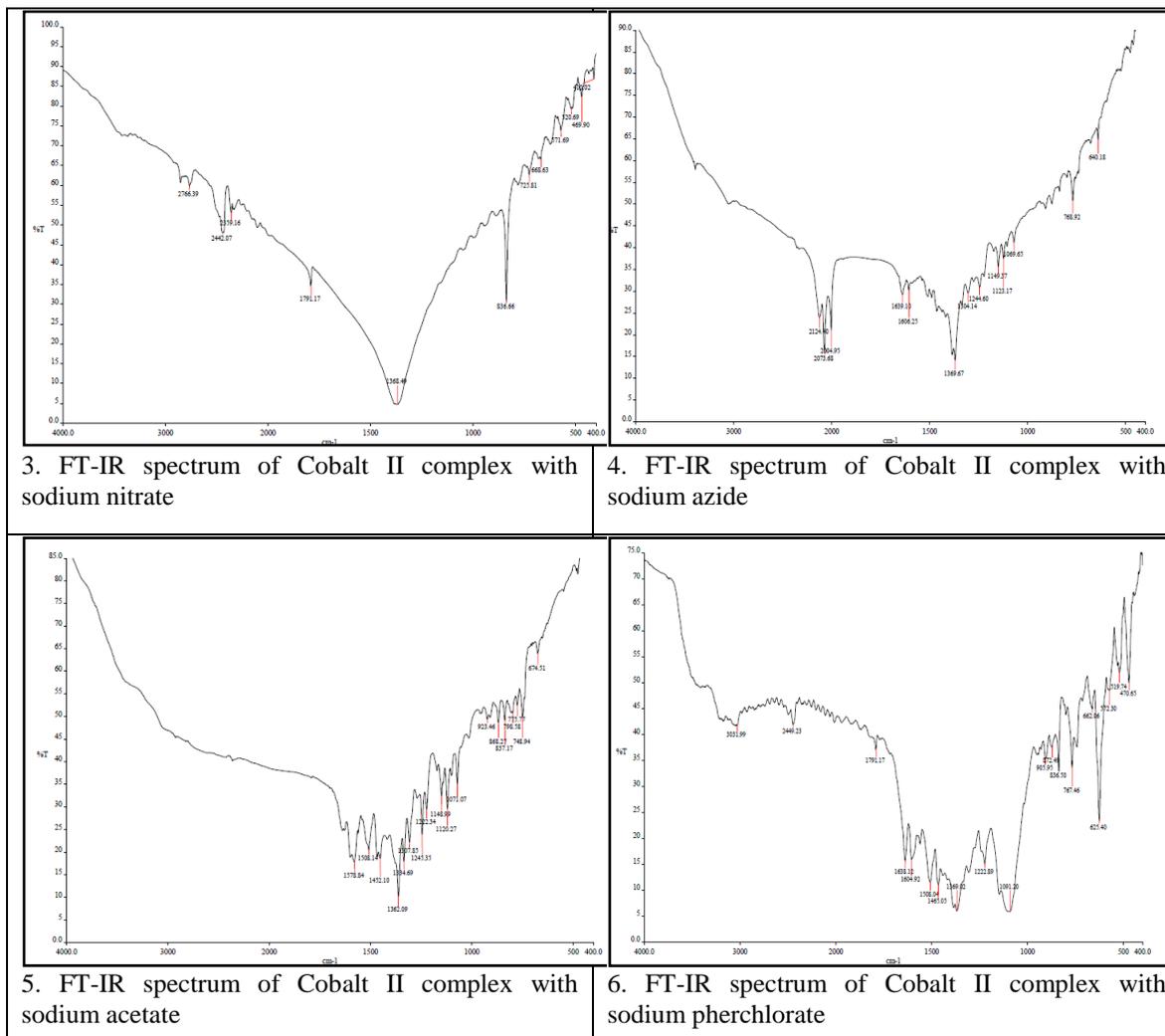


Figure4. FT-IR spectrum of hydrazone ligand and Co^{+2} complex with potassium thiocyanate, sodium nitrate, sodium azide, sodium acetate and sodium perchlorate respectively

3.2 Investigation of the synthesized compounds UV- Vis spectrum

3.2.1 UV- Vis spectrum of Hydrazone ligand

In the case of Hydrazone ligand, transfers in the area around 200-250nm can be seen, which mainly is related to the transfer of electrons $\pi \rightarrow \pi^*$ in phenyl rings, and in area around 300 -350 mainly is due to $\pi \rightarrow \pi^*$ electron transfer in Imine banding system. But the transition of $n \rightarrow \pi^*$ is observed in the area around 400-350 nm, which corresponds to the un-bonded electrons of nitrogen atoms on Azomethyn

3.2.2. UV- Vis spectrum of Co^{+2} complex with potassium thiocyanate

In the absorption spectra of Co^{+2} complex with potassium thiocyanate, the bands in the range of 200 - 250 nm can be seen that was related to $\pi \rightarrow \pi^*$ transition of phenyl rings in ligands. An absorption bands is visible in the range of 300- 350 nm, which is related to the transition of $\pi \rightarrow \pi^*$ of $C = N$ bond, even though this peak is long, but it is shorter than peak of phenyl ring. And a short and broad peak can be observed in the range of 350-420 that is related to $n \rightarrow \pi^*$ transitions. Also, corresponding $d \rightarrow d$ transitions can be observed in upper than 700 nm.

3.2.3 UV- Vis spectrum of Co^{+2} complex with sodium nitrate

In the absorption spectra of Co^{+2} complex with sodium nitrate, the bands in the range of 200 - 250 nm can be seen that was related to $\pi \rightarrow \pi^*$ transition of phenyl rings in ligands. An absorption band is visible in the range of 300- 350 nm, which is related to the transition $\pi \rightarrow \pi^*$ of $C = N$ bond, even though this peak is long but it is shorter than peak of phenyl ring. And a short and broad peak can be observed in the range of 350-420 that is related to $n \rightarrow \pi^*$ transitions. Also, corresponding $d \rightarrow d$ transitions can be observed in upper than 700 nm.

3.2.4 UV- Vis spectrum of Co^{+2} complex with sodium azide

In the absorption spectra of Co^{+2} complex with sodium azide, the bands in the range 200 - 250 nm can be seen that was related to $\pi \rightarrow \pi^*$ transition of phenyl rings in ligands. An absorption band is visible in the range of 300- 350 nm, which is related to the transition $\pi \rightarrow \pi^*$ of C = N bond, even though this peak is long but it is shorter than peak of phenyl ring. And a short and broad peak can be observed in the range of 350-420 that is related to $n \rightarrow \pi^*$ transitions. Also, corresponding $d \rightarrow d$ transitions can be observed in upper than 700 nm.

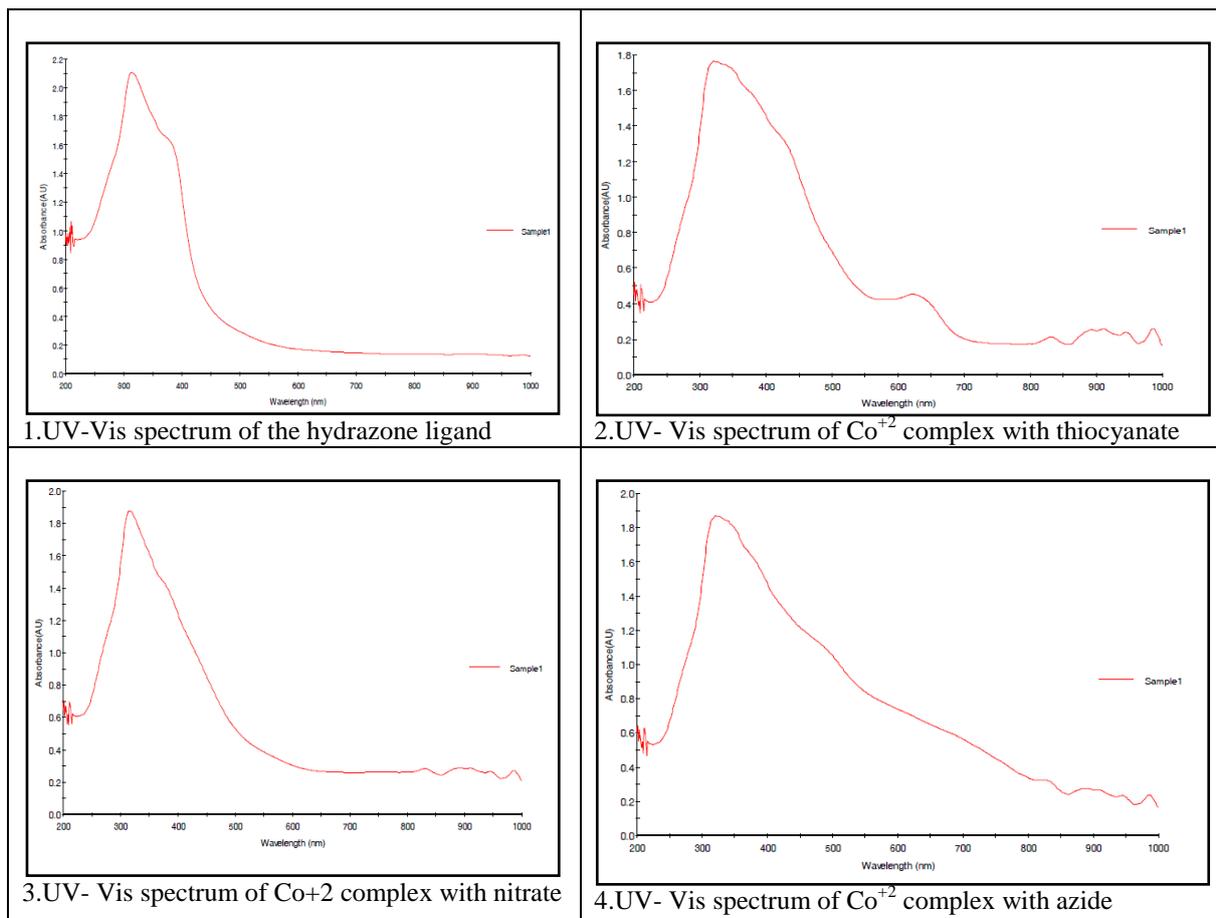
3.2.5 UV- Vis spectrum of Co^{+2} complex with sodium acetate

In the absorption spectra of Co^{+2} complex with sodium acetate, the bands in the range 200 - 250 nm can be seen that was related to $\pi \rightarrow \pi^*$ transition of phenyl rings in ligands. An absorption band is visible in the range of 300- 350 nm, which is related to the transition $\pi \rightarrow \pi^*$ of C = N bond, even though this peak is long but it is shorter than peak of phenyl ring. And a short and broad peak can be observed in the range of 350-420 that is related to $n \rightarrow \pi^*$ transitions. Also, corresponding $d \rightarrow d$ transitions can be observed in upper than 700 nm.

3.2.6 UV- Vis spectrum of Co^{+2} complex with sodium perchlorate

In the absorption spectra of Co^{+2} complex with sodium perchlorate, the bands in the range 200 - 250 nm can be seen that was related to $\pi \rightarrow \pi^*$ transition of phenyl rings in ligands. An absorption band is visible in the range of 300- 350 nm, which is related to the transition $\pi \rightarrow \pi^*$ of C = N bond, even though this peak is long but it is shorter than peak of phenyl ring. And a short and broad peak can be observed in the range of 350-420 that is related to $n \rightarrow \pi^*$ transitions. Also, corresponding $d \rightarrow d$ transitions can be observed in upper than 700 nm.

UV-Vis spectrum of the hydrazone ligand and each of corresponding ligand complexes of Co^{2+} , with potassium thiocyanate, sodium nitrate, sodium azide, sodium acetate and sodium perchlorate is shown in Figure (5) respectively.



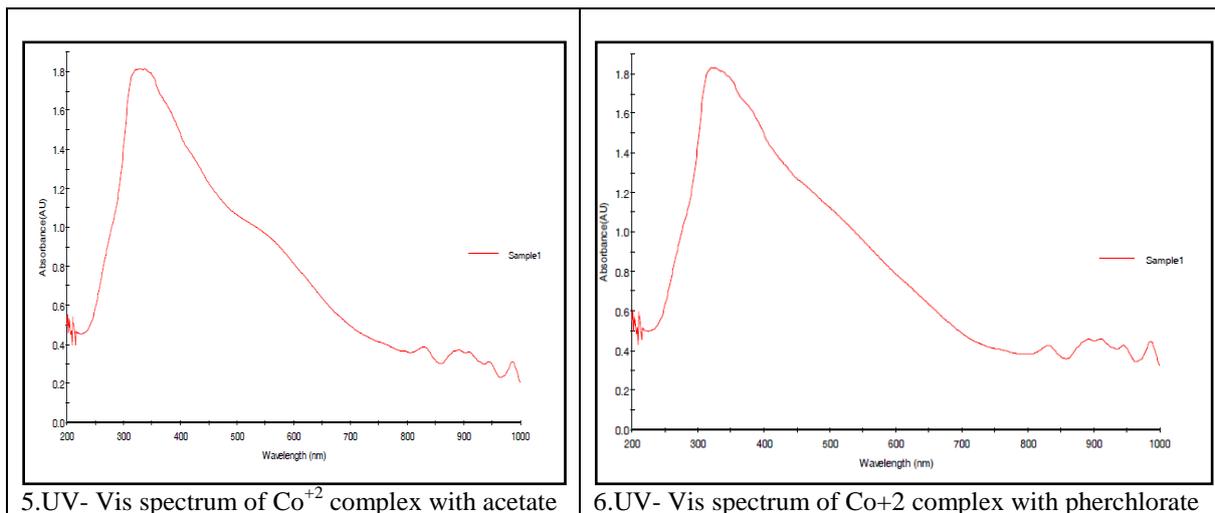


Figure 5. UV-Vis spectrum of the hydrazone ligand and each of corresponding ligand complexes of Co^{2+} , with potassium thiocyanate, sodium nitrate, sodium azide, sodium acetate and sodium perchlorate, respectively.

3.3 Investigation of electrical conductivity

Electrolytic conductivity is the conduction that takes place by migration of ions. Any material that has ions in the liquid state or in a solution state is considered as electrolyte. Strong electrolytes are materials that have high solubility and can separated to ions completely. Weak electrolyte solutions are containing few ions in comparison with strong electrolyte solutions. Non-electrolyte solutions don't have ion and are not able to pass electric current.

The electrical conductivity in solution is done by ions and the affecting factors of electrical conductivity in the solution are as follow:

1. Type of particles: solved particles must be as ions
2. The number of particles: when the number of electrical conductivity is greater, the number of particles will be greater.
3. Particles gender: the electrical conductivity will be greater, when the mobility of ions in the solution is greater.

The disadvantage of direct conductivity meter method is that the presence of trace impurities will change the results. Indirect method, (drawing conductivity changes vs the concentration, with knowing of all species conduct other than the target species) was identified in these cases. The results of the conductivity investigation in synthesized complexes in this study, represents that, the complexes are electrolyte and ionic solutions.

3.3.1 The evaluation of conductivity results in complex and ligand

Electrical conductivity of the ligand and complex solution which has 10^{-4}M concentration was measured. The results of the conductivity for complexes and ligands have been recorded in table (1), the data show that the ligand is non-electrolytes and nonionic, also these data show that complexes are electrolytes and ionic.

Table (1). Results of conductivity meter of ligand and complex at a concentration of 10^{-4}M

Compound	electrical conductivity	Solvent	Temperature
hydrazone ligand	4.36 μs	ethanol	18.4
Co^{2+} complex with potassium thiocyanate	225 μs	ethanol	19.2
Co^{2+} complex with sodium nitrate	170 μs	ethanol	18.1
Co^{2+} complex with sodium azide	728 μs	ethanol	18.3
Co^{2+} complex with sodium acetate	348 μs	ethanol	18.3
Co^{2+} complex with sodium perchlorate	727 μs	ethanol	18.1

3.4 Cyclic voltammetry of ligand and complexes

Cyclic voltammetry experiments were performed by using a Metrohm device. The conventional three-electrode system was used that includes a glassy carbon electrode with an area of 3.14mm^2 as the working electrode and a platinum wire were used as the auxiliary electrode, The reference electrode was saturated Ag / AgCl that was separated from the bulk solution by the bridge of solvent and electrode holder. Before each test, the working electrode by means of alumina powder was acted as a solvent and is washed with distilled water; from sodium perchlorate was used as the electrolyte and from the DMF was used as a solvent. Before each

experiment, the nitrogen gas was passed within solution for 3 minutes, because in testing and measurement it prevents from oxygen disturbance. All of the experiments were performed at room temperature. In all of these cases, to record the streaming basic first 1.40 grams of sodium perchlorate dissolved in the DMF solvent 50 cc, and then its cyclic voltammogram was measured. For measuring the cyclic voltammogram of synthesized complex, the required amount of this complex dissolved in DMF solvent 50 cc, and tests carried out in the presence of sodium perchlorate.

3.4.1 Investigation of ligand and complex cyclic voltammetry

As shown in Figure (6a) it can be observed that, the ligand has an anodic and cathodic wave, and system behavior is irreversible. Important factors that extracted from a voltammogram, are including, system ΔE_p , i_{pa}/i_{pc} . The results of voltammetry for ligands solution and the corresponding complexes are summarized

in Table 2. The cyclic voltammogram of all Co^{+2} complexes that have been studied in this work are shown by ΔE_p , which is equal to 0.3 volts, and $i_{pa}/i_{pc} = 0.0001$, as a result the system behavior is irreversible. Cyclic

voltammetry chart of ligands and complexes are shown in Figure (6).

Table 2. The results of voltammetry of ligands and complexes solutions

Compound	$E_{p,a}$	$I_{p,c}$	$E_{p,c}$	$I_{p,a}$
hydrazone ligand	1.000	0.00057	-0.5	-0.00008
Co^{+2} complex with potassium thiocyanate	0.6	0.00056	-0.5	-0.0001
Co^{+2} complex with sodium nitrate	0.6	0.00056	-0.5	-0.0001
Co^{+2} complex with sodium azide	0.6	0.00056	-0.5	-0.0001
Co^{+2} complex with sodium acetate	0.6	0.00056	-0.5	-0.0001
Co^{+2} complex with sodium perchlorate	0.6	0.00056	-0.5	-0.0001

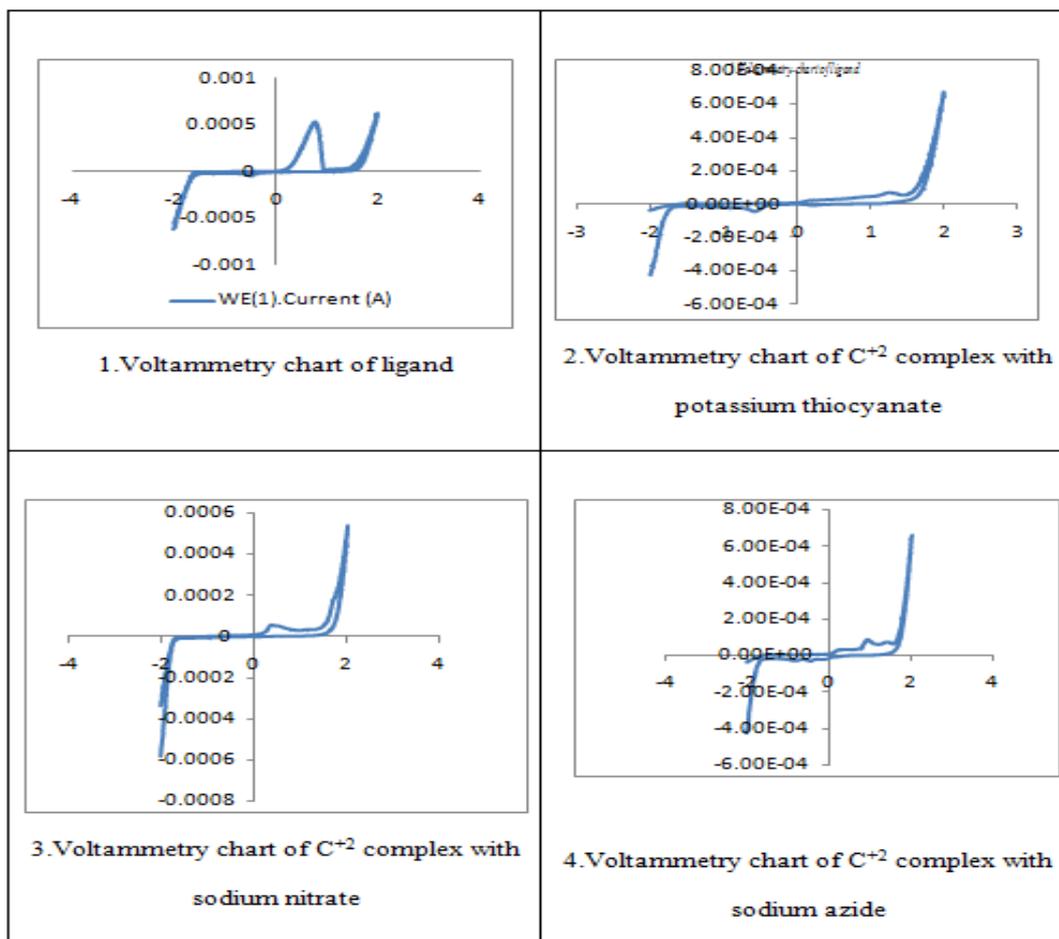


Figure 6. Voltammetry chart of ligand and Co^{+2} complex with potassium thiocyanate, sodium nitrate, sodium azide, sodium acetate and sodium perchlorate respectively.

IV. Conclusion

Because of the importance of Coordination Chemistry, the Schiff base complexes and their application in catalytic reactions and biological studies have attracted the attention of many researchers, and many complexes have been synthesized, identified and evaluated. According to the fact that the hydrazone Schiff base ligands have medical properties, in this study, hydrazone Schiff base ligand complexes were used for synthesis of cobalt complexes with potassium thiocyanate, sodium nitrate, sodium azide, sodium acetate and sodium perchlorate. Then their structure was studied by the means of UV-Vis and IR spectra, and electrochemical behavior of complexes has been investigated by conductivity meter and cyclic voltammetry. By comparing the ligand and complex IR spectra it will be determined that, the absorption bands bond C = N and C-O was increased and absorption band of H-N was decreased. Comparing the ligand and complex's electronic spectrum it becomes clear that, the peak of the areas in the ranges of 230, 330 and 360 respectively in ligand has been displaced with other areas in complex. The electrochemical behavior of complexes checked out by cyclic voltammetry in solutions of di-methyl formaldehyde and perchlorate-sodium electrolyte. In which, those complexes have an irreversible redox process.

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