



Synthesis of Ethyl-8-Quinolyl Phosphate (C₂H₅O)(C₉H₆NO)(OH)P=O and preparation of its Cobalt complex

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Abstract Ethyl -8- Quinolyl Phosphate (C₂H₅O)(C₉H₆NO)(OH)P=O was synthesized via reacting Ethanol C₂H₅OH, Phosphorous trichloride POCl₃ with 8-hydroxyquinoline C₉H₆NOH, in order to investigate it to form complex with Cobalt (II), which lead to the Cobalt (II) extraction reaction, afterword the physical constants of the prepared ligand and complex were determined. The structure was confirmed by using FT/IR spectroscopy, UV-VIS spectroscopy, ¹H NMR and ³¹P NMR spectroscopy and elemental analysis. The given results have been compared with reference studies.

Keywords Cobalt (II), Phosphoric compounds, Trans metal, 8-hydroxyquinoline, Complexes

Introduction

Cobalt and its compounds possess a range of diverse applications in many fields especially in medicine and industry, due to its unique properties such as high melting point and the preservation of durability and magnetic properties at high temperatures [1]. Cobalt forms tetrahedral complexes, and because of the small energy difference between its tetrahedral and octahedral complexes in many cases, the two forms can be found together in the same solution [2]. Phosphorous organic chemistry is based on the presence of highly stable functional groups containing a phosphorous-oxygen-carbon bond. The organic derivatives of phosphorous acid contain the functional groups (P = O) and (P = S) which are easy to form and resist chemical changes and can support the metal ions [3]. Cobalt and phosphorous organic compounds are widely used in many applications:

- In medicine: One of the most important uses of cobalt is its use by living organisms in the form of vitamin B12, which helps in the synthesis of hemoglobin in the blood. This vitamin deficiency leads to anemia and mental retardation [4]. Radioactive cobalt-60 isotope is used for food sterilization, radiology applications and cancer treatment [5]. Cobalt complexes have been widely used in recent years in applications of biological systems such as antimicrobial and antibacterial agents [6]. Cobalt complexes are used in the study of DNA and cellular toxicity studies [7].
- In industry: The most important industrial use for it is the manufacture of distinctive alloys of different resistance, as its alloys have demonstrated high resistance to corrosion and oxidation at high temperatures. Therefore, they are used in the manufacture of machinery and are mainly used in the manufacture of highly effective cutting tools [1], and many Cobalt salts have wide commercial applications. Cobalt oxide is used in glass which can give it a pink color if it is wet, or blue, if it is dry. Cobalt compounds are used as catalysts in many industrial processes [5].



- In agricultural applications: phosphate esters are considered as the main compounds in the manufacturing of pesticides. Since their discovery and until now a large number of pesticides have been manufactured using phosphate esters and dispensing with each other due to its high toxicity towards humans and other mammals, and work is still ongoing to obtain relatively safe pesticides towards humans [8].
- In pharmacological applications: phosphorus acid derivatives play a major role in biological systems, where phosphate esters form the stable backbone of nucleic acids. Therefore, they are used in the treatment of dementia, bilharset and muscle weakness in humans and in the treatment of head lice, as they are used in veterinary medicines to treat external parasites with animals such as scabies and ticks, and some of their compounds are used to treat horse wounds and treat skin diseases for cats and dogs [7,8, 9].
- In chemical applications: they are used in the manufacture of nerve gas and flame retardants, as they are used in separating some elements from their solutions such as separating the element Rutherfordium. Phosphate esters are added to detergents as surfactants and detergents as well [10, 11, 12].

Numerous applications of phosphorous organic compounds are due to their high stability, especially with oxygen. Oxygen can easily be replaced with sulfur, thus obtaining a very large group of compounds [12]. The stability of the complexes formed between phosphorous organic reagents and mineral ions depends on several factors:

- Including those related to phosphorous organic reagents such as the number and nature of electron-donor atoms and their spatial arrangement, the composition of the organic reagent and the base strength of the detector [13].
- Some of them are related to the metallic ion, such as the electronic structure of the outer layer of the ion, its radius and the polarizing strength of the organic detector related to the density of charge of the metallic ion [13].

Study Methods

POCl₃ phosphoryl trichloride was taken and an appropriate amount of ethanol in a ratio of (1: 1) was added, where the ethyl dichlorophosphate is formed and the resultant was stirred well for a period of not less than an hour. An amount of 8-hydroxyquinoline was added to the resulting mixture in the ratio (1: 1) dissolved in pyridine, then the pyridine was eliminated. Then the result was hydrolyzed with sodium hydroxide in a ratio of (1: 1) with continuous stirring in presence of an excess amount of pyridine at 0°C. The pyridine is disposed of using a rotary evaporator and the resulting compound was checked with 8-quinolyl phosphate, then a quantity of cobalt chloride (II) was added as aqueous solution to the ethyl 8-quinolyl phosphate dissolved in chloroform. The product was formed in the organic phase that separates and evaporates chloroform until the resulting complex compound remains.

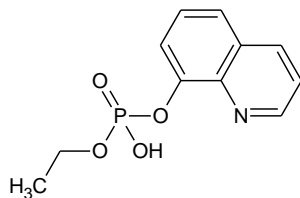
The compounds resulting from the previous reactions are confirmed by using the UV-VIS and FT/IR spectrum apparatus and ¹H NMR and ³¹P NMR spectroscopy and elemental analysis.

Research Aims

The importance of the research emerges from the importance of cobalt metal and its complexes and their various applications in industrial as well as medical areas. In addition to the importance of phosphorous acid esters and their ability to extract dissolved transitional minerals through complexity reactions, and also the importance of the prepared complex in its potential for chemical mediation [2]. It also contains the organic derivative used for quinoline in its structure, and derivatives containing quinoline have proven useful in treating many diseases (such as cancer, tuberculosis, diabetes, malaria, and convulsions) [13].

- The research aims to prepare the phosphorous derivative ethyl 8-quinolyl phosphate (C₂H₅O)(C₉H₆NO)(OH)PO and study some of its physical and chemical properties.





- The study of the complexicity properties for synthesized phosphoric acid ester: Ethyl 8-quinoline phosphate with Cobalt (II) and the study of the resultant complex structure.

Experimental Work

Material

- Single-neck flask, reflux, magnet stirring bar, beakers, flasks, separating funnel, Buchner funnel, filter funnel, different glass joints, filter paper, test tubes, capillary tubes, air pump, heater, Magnetic mixture.
- UV-visible spectroscopy: (UV-Visible Spectrophotometer-T60)
- Infrared Spectroscopy type: IR (FT / IR-4200 (Fourier Transform Infrared Spectrometer (JAS.CO))
- Electro thermal Engineering Ltd Serial No. 4995 melting point
- Heidolph-Laborata 4000-efficient rotary evaporator
- ¹H NMR type: BrukerBiospin GmbH 400.13MHz
- ³¹P NMR type: BrukerBiospin GmbH 200.15MHz
- Elemental analysis a Leco CHNS-932 apparatus

Results and Discussion

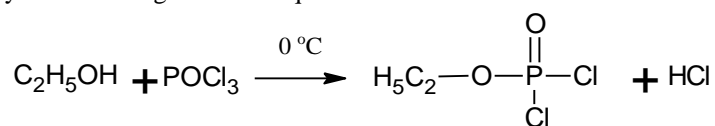
Synthesis of Ethyl-8-quinolyl phosphorous acid: (C₂H₅O)(C₉H₆NO)(OH)PO

Preparation of Ethyl dichlorophosphate (C₂H₅O)P(O)Cl₂

A quantity of (20 ml) of phosphoryl trichloride (POCl₃) equivalent to (0.13 mol) was taken and placed in a flask (500 ml) and an amount of (6 ml) of ethanol equivalent to (0.13 mol) was added, so that ethanol was added dropwise using dropping funnel, and the reaction was at temperature (0°) C using an ice bath with continuous stirring as the flask was settled on a magnetic mixture and the mixture stirred for an hour and a half. At the end of the reaction a viscous liquid of dichlorophosphate was produced.

It was immediately noticed when the first drop of ethanol was added the release of the reaction-generated HCl gas which was confirmed by a glass rod moistened with ammonium solution. Where white fumes of ammonium chloride were formed.

The resulting mixture was stirred continuously for 48 hours until the dissolved HCl gas completely released. The reaction was expressed by the following chemical equation:



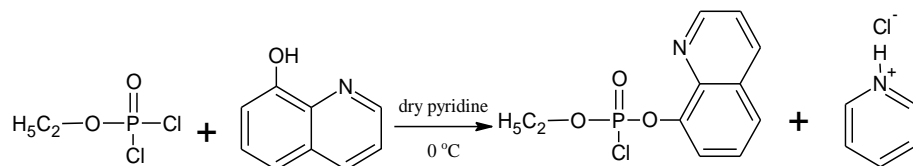
Synthesis of Ethyl-8-quinolyl chlorophosphate: (C₂H₅O)(C₉H₆NO)P(O)Cl

A quantity of (5.3 gr) of 8-hydroxyquinoline (equivalent to 0.03 mol) was taken and dissolved in an excess amount of pyridine (15 ml) and then added to (6 gr) of Ethyl dichlorophosphate (0.03 mol) via dropping funnel and slowly to 500 ml flask with continuous stirring using a magnetic mixture at 0°C, where the flask was placed in an ice bath.

It was immediately observed that a white precipitate was formed from pyridinium chloride C₅H₅N⁺HCl⁻ and the color of the solution changed to light yellow. The resulting mixture was filtered to remove the confirmed sediment by dissolving it in water, chloroform and ethanol.



The remaining pyridine was removed using a rotary evaporator at 63 °C, then the product was washed with water and then with benzene to get rid of the pyridine residues and unreacted 8-hydroxyquinoline and the boiling point of the resulting liquid Ethyl -8-quinolyl chlorophosphate was determined at 112 °C. The reaction obtained is expressed by the following chemical equation:

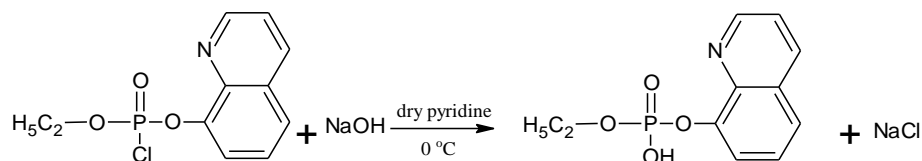


Synthesis of Ethyl-8-quinolyl phosphate: $(C_2H_5O)(C_9H_6NO)(OH)P=O$

A quantity of (5 gr) of Ethyl-8-quinylchlorophosphate (equivalent to 0.018 mol) was taken and dissolved in an excess amount of pyridine (15 ml) and an amount of (0.75 gr) of sodium hydroxide equivalent to (0.018 mol) was added with continuous stirring at 0 °C. Stirring continued for about 60 minutes, then a white precipitate of sodium chloride was formed and the color of the solution changed to yellow.

The resultant from the previous reaction was filtered to separate NaCl which was confirmed by taking an amount of it and dissolving it in water and then adding silver nitrate to it, and a white precipitate was formed that melts when adding ammonium solution to it.

The remaining pyridine was removed using a rotary evaporator at 63 °C until an oily compound of dark yellow viscosity remained in the flask. The product was washed with water and then toluene to get rid of the unreacted pyridine and sodium hydroxide and its boiling point was determined at 148 °C. The reaction is expressed by the following chemical equation:



Complex Preparation

A quantity of (2 gr) of ethyl-8-quinolyl phosphorous acid (equivalent to 0.0079 mol) was taken and dissolved in the amount of chloroform (10 ml) and an amount of (0.95 gr) of cobalt chloride $CoCl_2 \cdot 6H_2O$ equivalent (0.0039 mol) dissolved in 25ml of distilled water was added. It was noted that the color of the organic phase changed from yellow to brown and the color of the aqueous phase disappeared, then the contents were transferred to a separating funnel.

The organic phase was separated and the entire amount of chloroform was evaporated, so a brown complex remained $Co[(C_2H_5O)(C_9H_6NO)(O)P=O]_2$. The complex was purified using diethyl ether in a quantity of it, the solution was filtered and the filtrate was heated until the entire amount of solvent was evaporated.

Melting point of the resulting complex was determined (227 °C).

The resulting complex can be dissolved in toluene - carbon tetrachloride - ethanol - acetone.

Spectroscopic study of the Ethyl-8-quinolyl phosphate and its complex with cobalt using UV-Visible spectroscopy:

Figures 1 and 2 show the peaks of the visible spectrum associated with Ethyl -8-quinolyl phosphate in ethanol and for the (Ethyl -8-quinolyl phosphato) complex Cobalt (II).

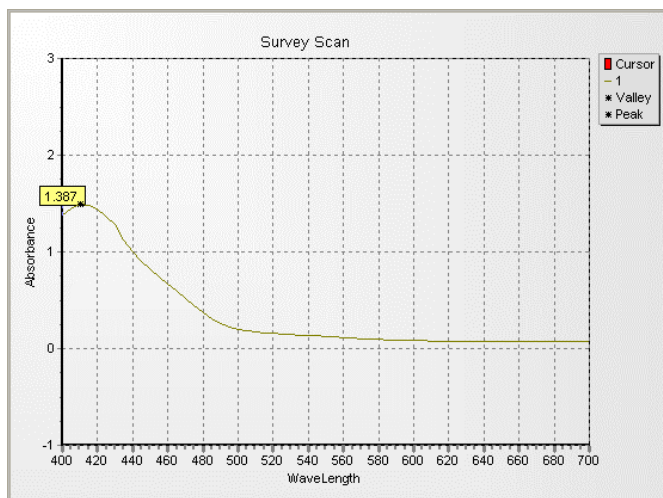


Figure 1: The visible spectrum peaks associated with ethyl-8-quinolyl phosphate in ethanol

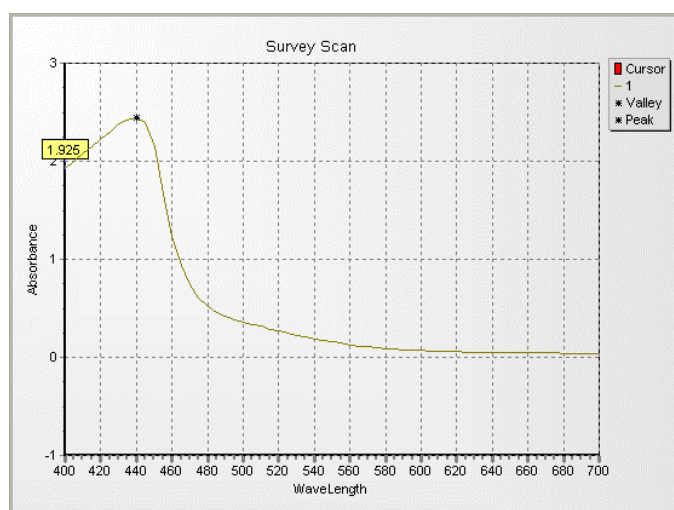


Figure 2: Peaks of the visible spectrum of the complex

In comparison between the previous two figures, it was noticed that the maximum absorbance of the Ethyl -8-quinolyl phosphate was obtained at the maximum wavelength $\lambda_{\max} = 440$ nm, whereas that of the complex was at the maximum wavelength $\lambda_{\max} = 410$ nm.

This difference in maximum wavelength values is explained by the occurrence of a reaction during the process of adding cobalt chloride to the phosphorous derivative and the formation of a cobalt complex with the ligand. The resulting compounds are fixed towards acids and water, as new supporting bonds are formed between the nitrogen with the cobalt.

Reference No. [14] was adopted to compare spectra.

Spectroscopic study of the manufactured ethyl-8-quinolyl phosphate and its cobalt complex using the infrared spectroscopy:

Figures 3 and 4 show the infrared spectrum of the compound for the Ethyl -8-quinolyl phosphate binding and for its complex with cobalt (II):



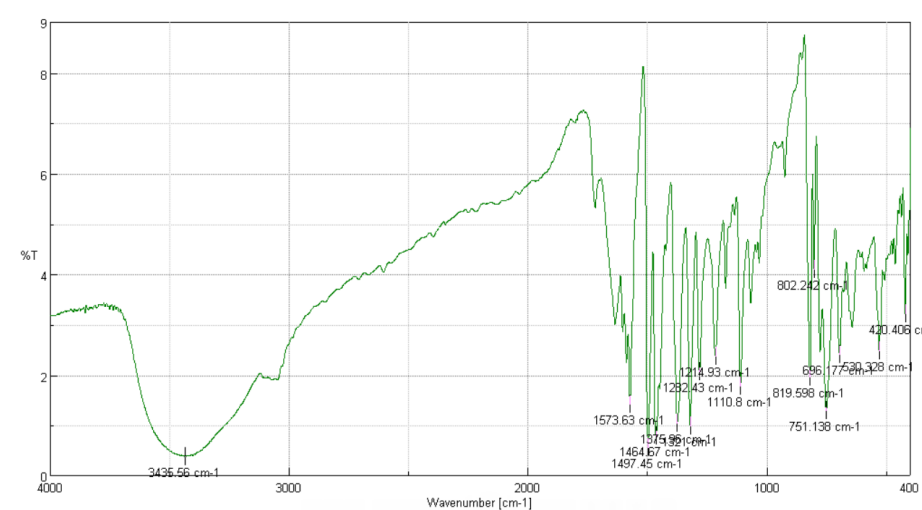


Figure 3: IR spectrum of Ethyl -8-quinolyl phosphate

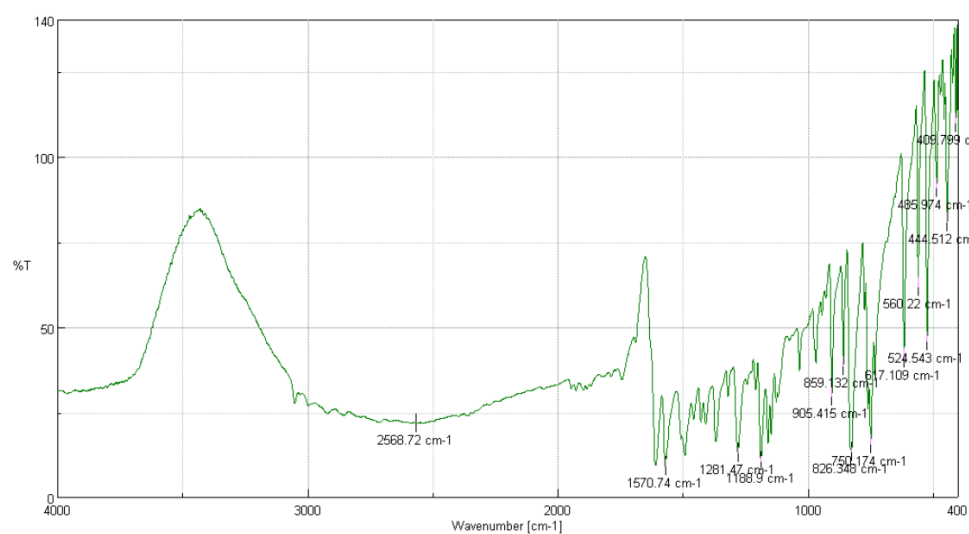


Figure 4: IR spectrum of complex

Table 1: A comparison of the two spectra in Figures 3 and 4

Compound	O-H	C-H	P-O	P=O	Co-O
Ethyl-8-quinolyl phosphate	3435	3040	802	1215	-
complex	-	3050	859	1281	485

Reference [15] was used to compare spectra.

The study of ¹H NMR spectroscopy

Figures 5 and 6 show the NMR spectrum of the Ethyl -8-quinolyl phosphate ligand and for its complex with cobalt:

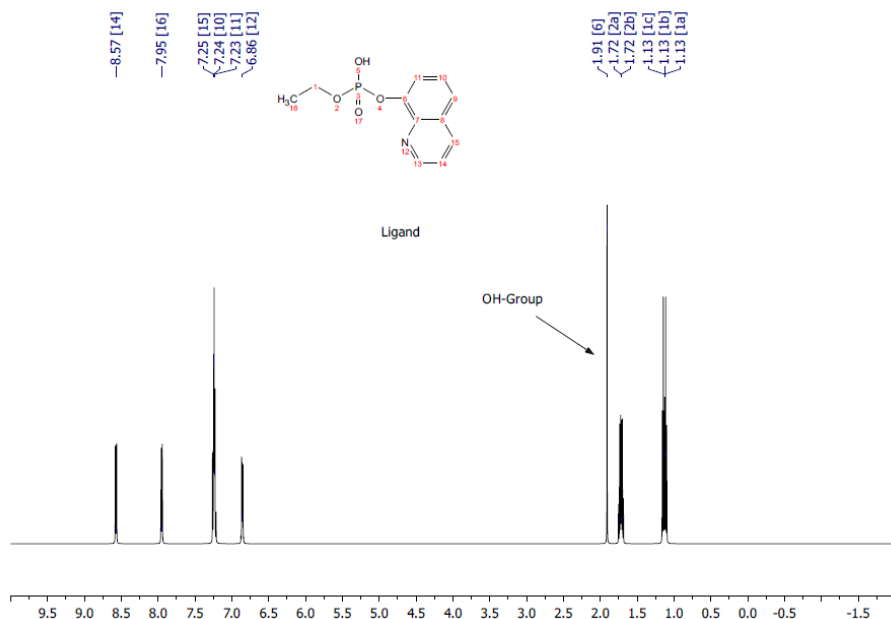


Figure 5: ¹H-NMR spectrum of Ethyl -8-quinoyl phosphate

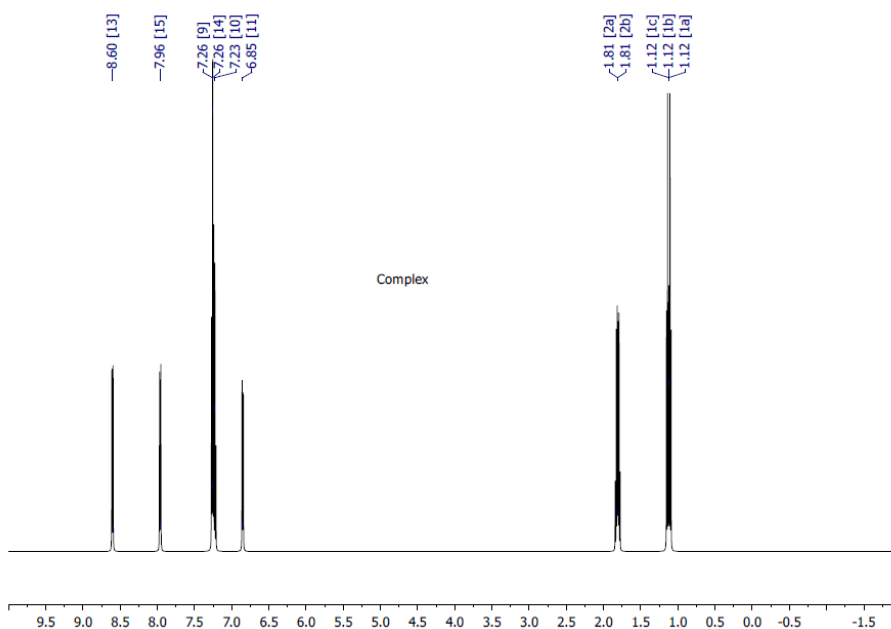


Figure 6: ¹H-NMR spectrum of complex

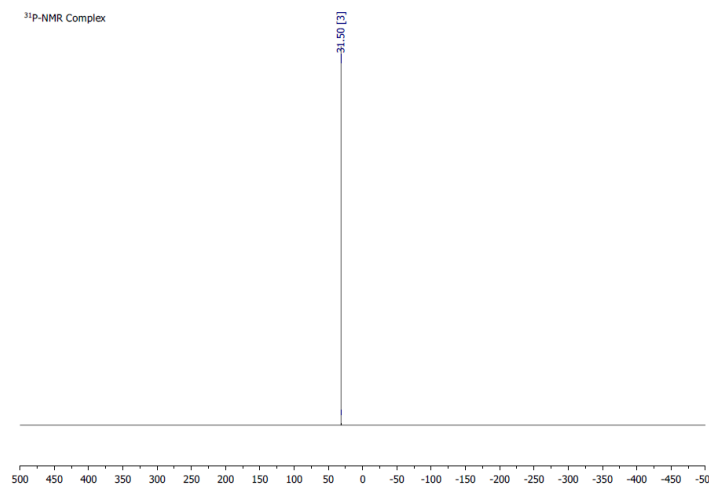
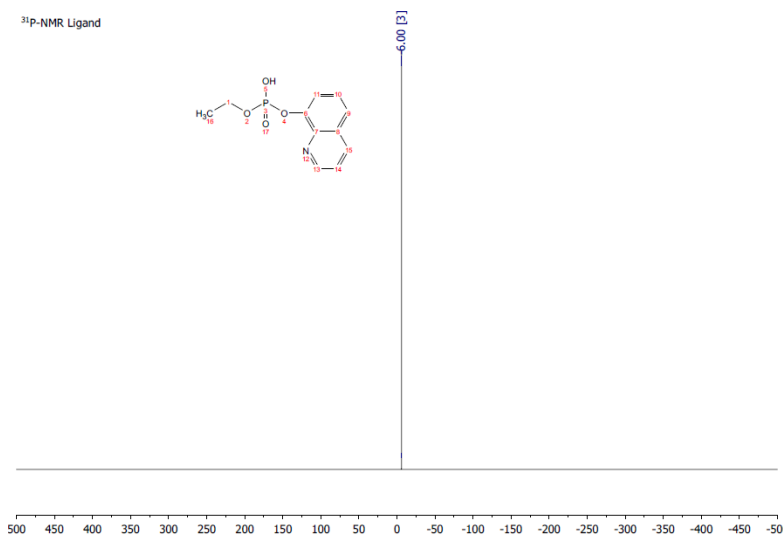
A peak of the hydroxyl group (-OH) is observed in Figure 5 at 2.13 ppm and disappeared in Figure 6 of the complex.

the formation of a new bond between oxygen from the ligand and cobalt is deduced. Reference No. 16 was used for spectra comparison.

Spectra study ³¹P NMR

Figures 7 and 8 show the ³¹P-NMR spectrum of the Ethyl -8-quinoyl phosphate ligand and its complex with cobalt:





In comparison between the previous two figures, a peak of the phosphorous atom is observed in the ligand spectrum at (-6) and its shift to (31.5) in the complex spectrum. By this it is deduced the occurrence of an interaction between ligand and added cobalt chloride.

Reference No. [16] was used for spectra comparison.

Elemental analysis:

Table 2: Elemental Analysis of Ethyl -8-Quinolyl Phosphate:

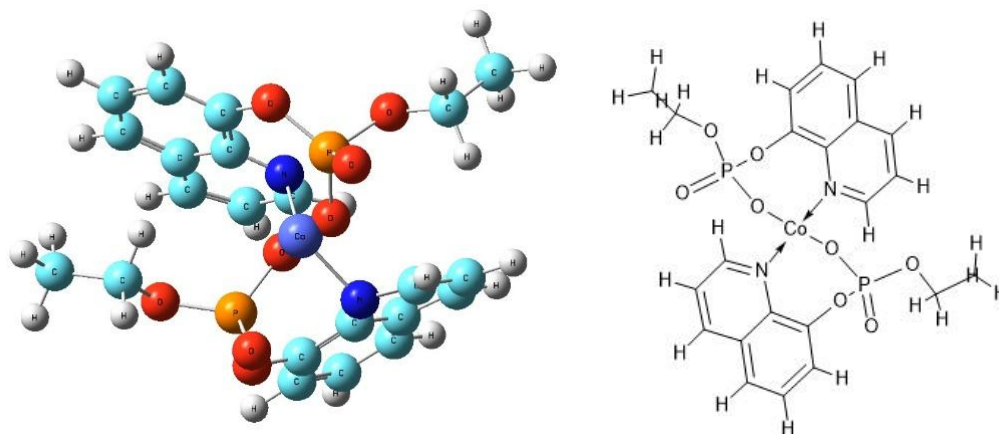
Atom	Theoretical %	Result %
C	52.18	51.57
H	4.78	4.86
N	5.53	5.28
O	25.58	25.83
P	12.23	12.21
%	100	99.75

Table 3: Elemental Analysis of the Complex complex

Atom	Theoretical %	Result %
C	46.91	46.87
H	3.94	3.61
N	4.97	4.76
O	22.72	22.34
P	11.00	10.93
Co	10.46	10.38
%	100	98.89

It is concluded from the previous tables that the experimental results of the elemental analysis for ligand and complex coincide with their theoretical proportions.

By studying UV-VIS, FT/IR, ^1H NMR, ^{31}P NMR and elemental analysis it was deduced that the complex bis(ethyl 8-quinolyl phosphato) cobalt(II) was formed. The form of the complex can be written after its improvement using the MM2 (half-test) theory as follows:



Dipole/Dipole: -39.1956, Total Energy: 311.4204 kcal/mol, Calculation by MM2

Conclusion

Spectroscopic studies indicate that the synthesized compound is ethyl 8-quinolyl phosphate from its primary compounds. This compound is characterized by its stability towards extended acids and towards a high temperature of 150°C . It is inferred through spectroscopic studies that the complex formed is bis(ethyl-8-quinolyl phosphato) cobalt (II), produced through the reaction between ethyl 8-quinolyl phosphate ligand and cobalt chloride (II) at a ratio of (2:1). The study of the ligand and its complex with Cobalt (II) by UV-VIS indicate a λ_{max} shift from 410nm to 440nm due to the electronic redistribution of the complex formed as a result of the supporting bonds.

The study of the ligand and its cobalt complex by IR spectroscopy shows the formation of the complex by forming bonds between the oxygen present in the ligand with cobalt (II) in addition to the supporting bonds of nitrogen in the ligand with cobalt (II). The study of the ligand and its cobalt complex by ^1H NMR shows the disappearance of the peak of the O-H bond in the complex spectrum that was present in the ligand spectrum indicating the occurrence of a reaction.

The study of the ligand and its cobalt complex by ^{31}P NMR indicates the shift of the peak from (-6) in the ligand spectrum to (31.5) in the complex spectrum due to electronic density changes around the phosphorus atom.

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