

Preparation, Characterization and Photo Study of Di (Meta-Hydroxyl Acetone Phenome) Ethylene Di Amine Cobalt (II) Complexes in Organic Solvents

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Abstract

Preparation of Schiff base tetra dentate ligand (bis (m-hydroxy aceto phenone) ethylene di amine). Cobalt (II) complex was prepared with (H) Ligand. Both Ligand and it`s complex were characterized by using FTIR, Uv-visible, Molar conductivity, Kinetic study for the photo chemical study was achieved for the prepared complex by using different polar organic solvent (Di methyl sulfoxide, Chloroform, carbon tetra chloride) by using source of mono wave length ($\lambda = 365\text{nm}$) at 25°C). Order of photo reaction were calculated which showed that reaction was from the first order at the same time the K_d of photo reaction was computed by follow up spectral changes through photo radiation process. K_d value increased by increasing of solvent polarity.

Key word: ethylene di amine, organic solvent, wave length, first order.

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تحضير وتشخيص ودراسة ضوئية للمعقد الثنائي (ميتا – هيدروكسيل اسيتو فينون) اثلين ثنائي امين الكوبلت الثنائي في مذيبات عضوية

الاء عيسى سلطان

قسم الكيمياء – كلية العلوم – جامعة ديالى

الخلاصة

تم تحضير معقد قاعدة شف رباعية السن (ثنائي (ميتا – هيدروكسيل اسيتوفينون) اثلين ثنائي امين) الكوبلت الثنائي. تم تشخيص الليكاند و المعقد باستخدام التقنيات التالية (Uv-visible- F.T.I.R- التوصيلية المولارية). تم دراسة حركية الكيمياء الضوئية للمعقد المحضر في مذيبات عضوية مختلفة القطبية وهي (ثنائي مثل سلفوكسايد – الكلوروفورم – رابع كلوريد الكربون وباستخدام ضوء احادي الطول الموجي (365) وبدرجة مئوية $25C^{\circ}$ حيث وجد ان مرتبة التفاعل الضوئي هي من المرتبة الاولى . كما تم حساب ثابت السرعة للتجزئة الضوئية (K_D) بواسطة متابعة التغيرات الطيفية خلال عملية التشيع الضوئي كما تم التوصل الى ان قيمة (K_d) تزداد بزيادة قطبية المذيب.

الكلمات المفتاحية: اثلين ثنائي امين ، مذيبات عضوية ، الطول الموجي ، المرتبة الاولى .

Introduction

Schiff base have the ability to metal coordinated complexes because of the nature of functional group (Azomethene) (C=N) which can involve by the electron pair of Nitrogen atom. Coordination bond will be formed by using Nitrogen pair electron⁽¹⁾. As well as some kinds of Schiff base have another donor groups like Oxygen⁽²⁾ or Sulfur⁽³⁾, So it can behave like bi dentate ligand , tri dentate, tetra dentate or polydentate which have homogeneous or heterogeneous donor atoms⁽⁴⁾. (N, N`-bis(β - Salicylalimino ethyl)-2,6-pyridine di carboxylic acid) was derived from salicylaldehyde and acetyl acetone with Di aliphatic and aromatic amines⁽⁵⁾. Complexes of transition metal ($Cu^{+2}, Co^{+2}, Mn^{+2}, Pd^{+2}$) with (N,N`-bis(β - Salicylalimino ethyl)-2,6-pyridine di carboxylic acid) ligand were prepared⁽⁶⁾. This ligand and its metal complexes were characterized by using FTIR, HNMR and Mass spectroscopy⁽⁷⁾. Schiff base complexes with transition metal were used as antibacterial and antifungal⁽⁸⁾.

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Schiff base complex with transition metal (Ni^{+2}) was used as dyes ⁽⁹⁾. As well as some Vanadium – Schiff base quartet and quintet complexes were used to oxidize Sulfur to Sulfoxide ⁽¹⁰⁾ which play a prominent role at Pharmaceutical Industry ⁽¹¹⁾.

Methods and Material

Preparation of Schiff base:

Schiff base was prepared by dissolved (0.01mole) of Ethylene di amine (0.6gm) at (10ml) in Carbon tetrachloride and this solution was mixed with another solution consisted from (0.02mole, 0.27gm) of m-hydroxy aceto phenome) which dissolved in (10ml) of Carbon tetra Chloride . The final solution was refluxed for 2 hours. Then the solution was cooled, filtered, dried and recrystallized ⁽¹²⁾.

Preparation of complex:

Complex was prepared by dissolving (0.041gm, 0.01mole) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in (10ml) of ethanol. Then the mixture was added with stirring to another solution which composed from (0,03gm, 0.01mole) of dissolved ligand in (10ml) of ethanol. Dark green solution was conformed. The mixture was refluxed for 4hrs. After refluxing, the solution was cooled, filtered and dried the precipitate which was stored at dark and dry place ⁽¹³⁾.

Result and discussion:

1: Infrared spectra study:

1-1: Infrared spectra of prepared ligand study:

Infrared spectra of prepared ligand showed strong band referred to bending vibration of azomethine ($\text{C}=\text{N}$) at (1594cm^{-1}) ⁽¹⁴⁾. Absorption spectra of prepared ligand showed strong band at (1293cm^{-1}) referred to bending frequency for phenolic hydroxyl group ⁽¹⁵⁾ and another absorption band appeared at (1209.9cm^{-1}) which returned to vibration bending of ($\text{C}-\text{O}$) phenolic bond⁽¹⁶⁾. As well as absorption band appeared at (1511.7cm^{-1}) referred to ($\text{C}=\text{C}$) aromatic bond ⁽¹⁷⁾, Figure (1) showed the FTIR spectra of ligand.

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1-2: Infrared spectra of prepared complex study:

When the infrared spectra of complex showed red shifting with (12cm^{-1}) of main band which referred to azomethine group ($\text{C}=\text{N}$). This illustrates that Cobalt (II) ion coordinated with ligand through Nitrogen group⁽¹⁸⁾. At the same time a red shifting of phenolic group ($\text{C}-\text{O}$) of ligand with (20cm^{-1}) which referred to coordinated of this group with Cobalt (II) ion⁽¹⁸⁾. A new absorption peak of prepared complex appeared at (458cm^{-1}) referred to bending vibration of bond ($\text{Co}\rightarrow\text{N}$) which indicated to Nitrogen coordination with Cobalt (II). As shown at figure (1)

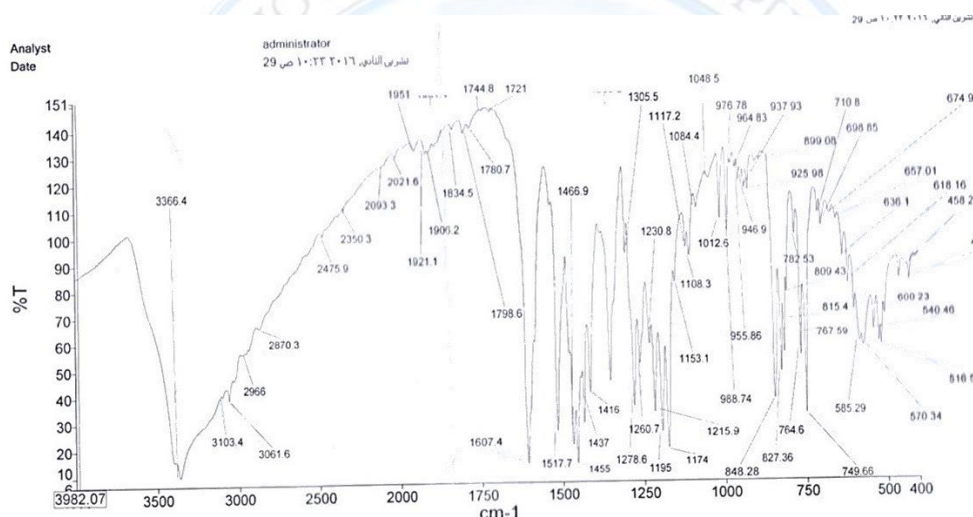


Fig. (1): FT-IR spectrum of complex Co(II)

2: Electronic spectra study:

2-1: Electronic spectra of ligand:

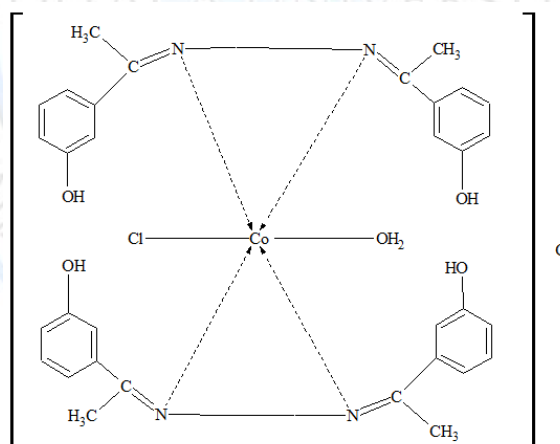
Electronic spectra study of prepared ligand was achieved by using ethanol as solvent with (10^{-3}M) concentration, as shown at fig. (2). the electronic spectrum of ligand showed three main peaks. The first one appeared at (265nm) referred to ($\pi\rightarrow\pi^*$) electronic spectrum of phenyl group for Schiff base⁽²⁰⁾. While the second one indicated at (322nm) which attributed to ($\pi\rightarrow\pi^*$) of azomethine group ($\text{C}=\text{N}$). At the same time the third band appeared at (352nm) which referred to electronic spectra ($n\rightarrow\pi^*$) of azomethine⁽²⁰⁾.

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2-2: Electronic spectra of prepared complex:

The absorption of electronic spectra of prepared can be attributed to two groups of peaks ⁽²¹⁾. First group back to the ligand basically which appeared as three bands where the first one appear at (256nm) referred to electronic spectra ($\pi \rightarrow \pi^*$) of phenyl group of ligand. As for the second band appeared at (304nm) which referred to electronic spectra ($\pi \rightarrow \pi^*$) of azomethine group (C=N). When the third band occurred at (365nm) which referred to electronic spectra ($n \rightarrow \pi^*$) for (C=N). The second group consisted of the transition which happened between the Cobalt atom and the ligand which is named charge transfer spectra ⁽²²⁾. As Cobalt ion at low oxidation for this charge transfer from Cobalt ion to ligand which appeared (456nm) ($M \rightarrow L$)⁽²²⁾ and d-d transition bands of Co(II) complexes displayed in the region 400-650nm. These transitions referred to the electronic spectra: ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) \nu_1$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) \nu_2$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) \nu_3$ respectively. This assigned that Co(II) complex was octahedral configuration^(23,24).



Complex structure

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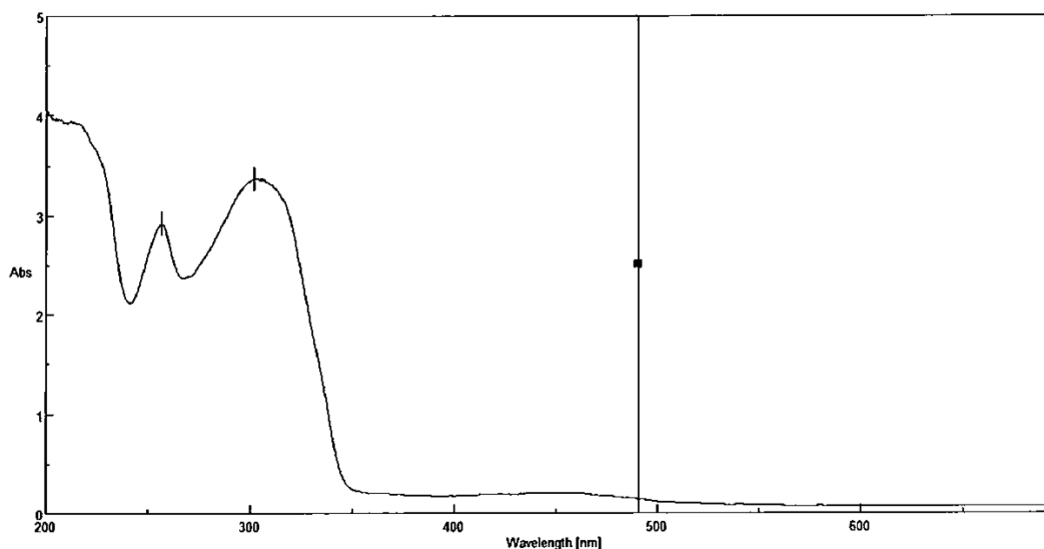


Fig.(2):Uv spectrum of Prepared complex(Co^{II})

3: Kinetic study of prepared complex:

After radiation of complex by using Uv-visible spectroscopy at different organic solvent with different polarity (DMSO, Chloroform, Carbon tetrachloride). The complex suffered from photolysis process which can be followed through the change of complex color at radiation process for different time (A_t). For calculation the rate constant of photolysis process (K_d) of prepared complex. A solution of metal complex was exposure to photo radiation for a long time to determine the final concentration (A_∞). After radiation for different time, (A_t) was found for (t) min. . Then the value $\ln (A_\infty - A_t)$ was calculated. A straight line relationship between $\ln (A_\infty - A_t)$ at Y and t at X axis and the value of ($-K_d$) was computed from the slope that referred to first order reaction of photolysis reaction. As shown at table (1) the photolysis constant reaction showed different value differs according to solvent polarity. The constant degradation value increased when the polarity of solvent increased according to the following sequence. Fig. (3) Referred to Uv spectrum of complex after radiation.

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$CCl_4 < CHCl_3 < DMSO$

| Comp. | DMSO | CHCl ₃ | CCl ₄ |
|-------|------|-------------------|------------------|
| A | 3.22 | 2.94 | 2.26 |

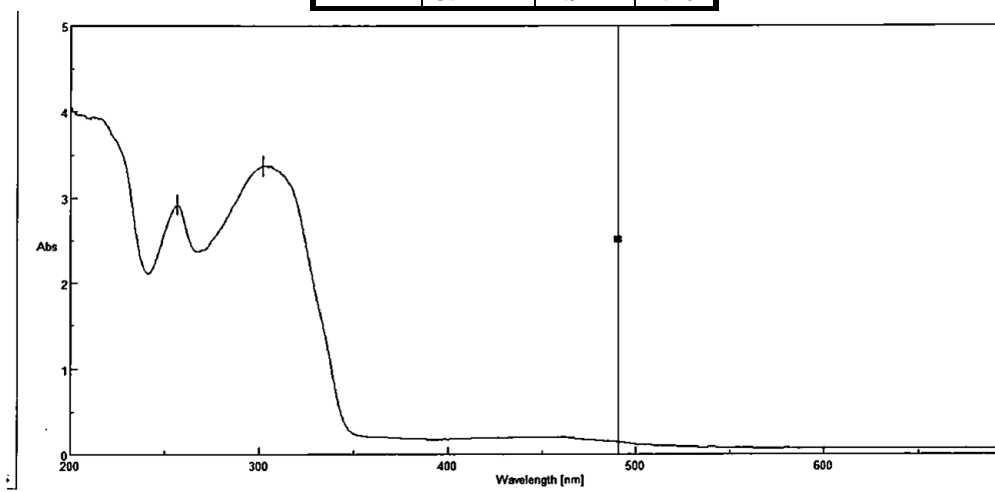
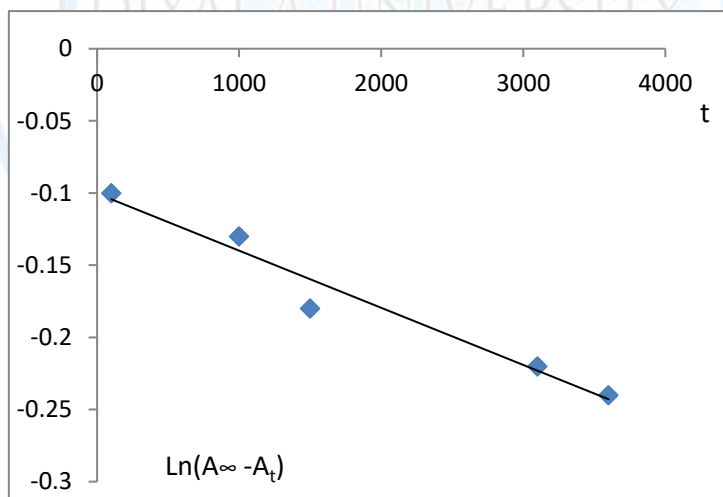


Fig.(3) Uv spectrum of Co^{II} complex after radiation.



| Ln (A _∞ -A _t) | T (sec) |
|--------------------------------------|---------|
| -0.1 | 100 |
| -0.13 | 1000 |
| -0.18 | 1500 |
| -0.22 | 3100 |
| -0.24 | 3600 |

Figure (4): Showed the relationship between t and Ln (A_∞ -A_t)

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Determination the stability constants and magnetic moment of Co (II) complex:

The molar conductivity with different concentration was indicated of Cobalt (II) complex which was dissolved in ethanol. The conductance measurements only can elucidate whether group in solution are ionic or it coordinated to the transition metal ion⁽²⁵⁾. The plotting values of (Λ_m) against the square root of different complex concentration according to Kohlraush's equation⁽²⁶⁻²⁸⁾:

$$\Lambda_m = \Lambda_\infty - K_c (C)^{1/2}$$

Where Λ_∞ = infinite dilution

C = Concentration

K_c = Constant

Fig. (4) showed a shape line for electrolyte for Cobalt (II) complex a result of the coordination between negative Chloride ion and the positive coordination sphere (complex, Cation ion) which could refer as well that the dissolvent may substituted the negative Chloride ions (Cl^-) in coordination with Cobalt metal ion⁽²⁹⁻³⁰⁾. The result which was indicated agreed with expected once help in having a good idea about the chemical structure formula and the geometry shape of the prepared complex^(31, 32). The data of (Λ_m) which indicated at different concentrations expounded the increasing (Λ_m) value with the dilution because of increasing number of moving ions in solution and this characterized by Kohlraush's equations. More benefit matter for weak electrolytes was determined of dissociation constant (K_d) for prepared complex and can be revealed by using cruze rearrangement, which derived from Ostwald eq. of dilution^(34,35):

$$\Lambda_m C = K_d \Lambda_0 \left(\frac{1}{\Lambda_m} - K_d \Lambda_0 \right)^2$$

Where Λ_0 = Molar conductivity at infinite dilution.

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The plotting between $\Lambda_m(C)$ at X-axis against $(1/\Lambda_m)$ at Y-axis achieved a straight line of slope to $K_d \Lambda_o^2$ while the intercept of line this line at X-axis will obtain $(1/\Lambda_o)$. So the K_d value can be calculated⁽³⁶⁾ as shown in fig.(4).

From all obtained previous data the formation constant (K_f) of Cobalte complex can be indicated according to eq.^(37,38):

$$K_f = 1/K_d$$

Table (2, 3): Measurement of K_f and K_d for the complex:

| | | | | |
|---|-----------------------|----------------------|-----------------------|------------------------|
| Conc. | 1.17×10^{-3} | 0.5×10^{-3} | 0.71×10^{-3} | 0.035×10^{-3} |
| Co complex Λ_m ($\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) | 38.5 | 62.5 | 100 | 196.1 |

| Comp. | $1/\Lambda_o$ | $K_d \cdot \Lambda_o$ | K_d | K_f |
|------------|---------------|-----------------------|----------------------|-------------------|
| Co complex | 0.003 | -0.005 | 1.5×10^{-5} | 0.6×10^5 |

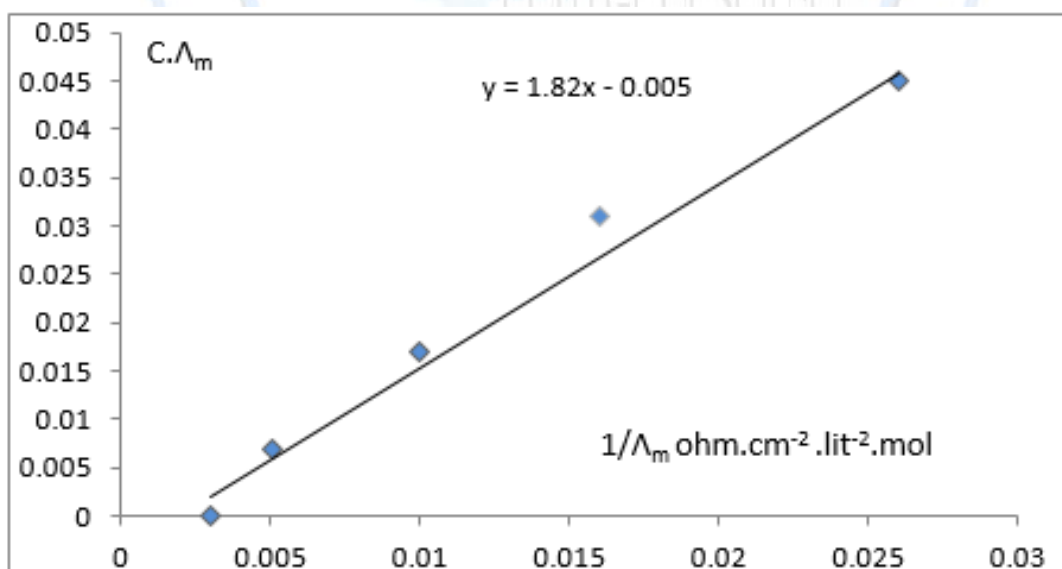


Fig.(4): relation between $\Lambda_m(C)$ and $1/\Lambda_m$ for prepared complex

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