

## COMPLEXES OF 2-HYDROXY- 4-DIMETHOXYPHENYL-6-BENZYLOXY PHENYLPYRIMIDINE WITH SOME METAL IONS

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### Abstract

New complexes of the ligand 2-hydroxy-4-dimethoxyphenyl-6-benzyloxy phenylpyrimidine with metal ions Cr (III), Fe (III), Co (II), Ni (II) and Cu (II) were prepared in alcoholic medium.

The prepared complexes were characterized by magnetic susceptibility, molar conductance, FTIR, Uv-Vis. The data showed that these complexes have the composition of  $[ML_2]$ .

### Introduction

Schiff bases play an important role in inorganic chemistry, as they easily form stable complexes with most transition metal ions [1]. Schiff bases rapidly decompose in aqueous media of acidic metals, but very stable in aqueous solutions of basic metals. Kuhn [2] prepared Schiff bases, derived from ketones and primary amines through preparation of silver iodide complexes. Schiff base and its complexes have a variety of applications in biological, clinical and pharmacological areas [3, 4]. Increasing physiological importance of oxygen donor organic compounds [5] and active role played by coordination certain metal ions to them [6] have interested us in synthesizing and studying structural aspects of metal complexes with some oxygen and nitrogen donor ligands [7]. The wide range of application of the ligand and its metal complexes aroused our interest to prepare a new series of some metal complexes.

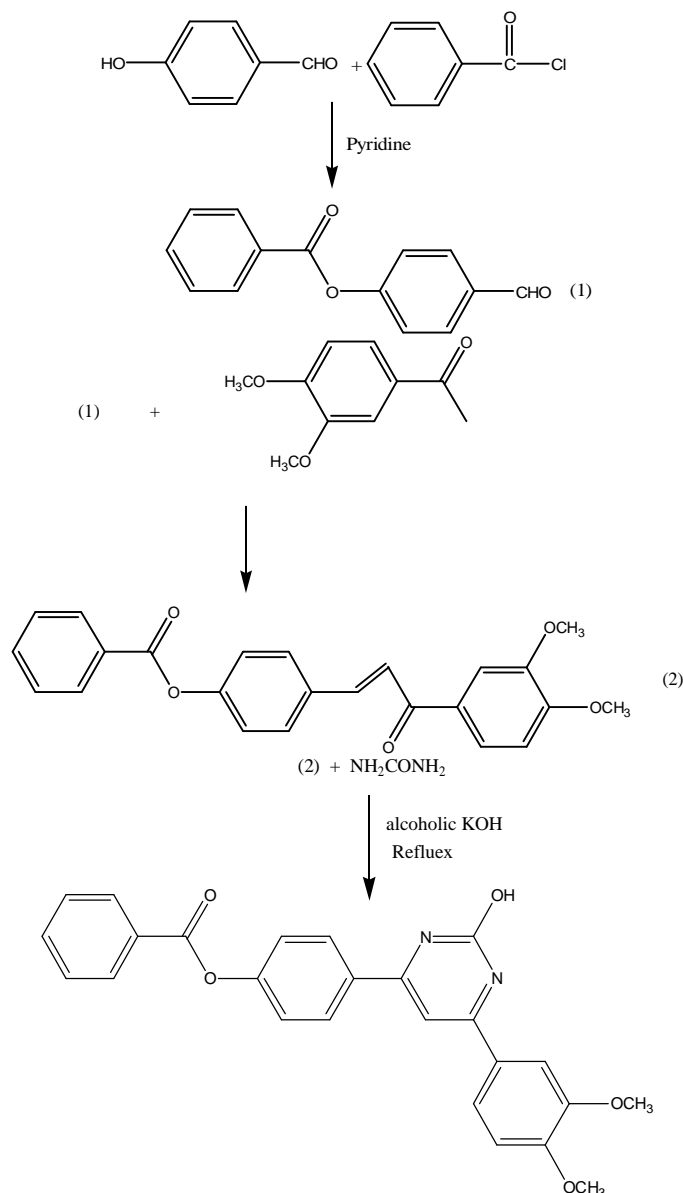
### Experimental

All chemicals used were of reagent grade (supplied by either Merck or fluka company) and used as supplied. Elemental C, H, N and O analysis were carried out on a fison EA1108 analyzer, the FTIR spectra in the range (4000-200  $\text{cm}^{-1}$ ) were recorded as cesium iodide disc on FTIR 8300 Shimadzu, Spectrophotometer. The Uv-Visible Spectra were measured in DMF using Shimadzu Uv- Vis 160 Ultraviolet Spectrophotometer in the range (200-1000) nm. Magnetic susceptibility measurements for complexes were obtained at room temperature using (magnetic susceptibility balance) Jhonson Maltery catalytic system division. Atomic absorption measurements of the

prepared complexes were obtained using shimadzu 860 cc-flame.

### Synthesis of Schiff Base (L)

*p*-Hydroxy benzaldehyde (1.22 g, 0.01 M) in 5 ml of pyridine was stirred with benzoyl chloride (2 ml, 0.01 M) for 7hrs. (Fig.(1)). The yellow solid (I) formed was filtered and recrystallized from ethanol. Compound (I) (2.26 g, 0.01 M) in 20ml of ethanol was refluxed with 3,4 dimethoxyaceto phenone (1.8 g, 0.01 M) to which (40% NaOH) was added 5ml with constant stirring for (7-8) hrs, and acidified with dil. HCl the solid obtained was washed with cold water, filtered and recrystallized from ethanol compound [2]. A mixture of compound [2] (3.68 gm, 0.01 M) and urea (1.8 gm, 0.03 M) in alcoholic KOH was refluxed for (8) hrs, after adding anhydrous potassium carbonate (10 gm). The potassium carbonate was filtered off from the reaction mixture and the solvent was evaporated. The white solid product was filtered and recrystallized from ethanol Fig. (1).



**Fig. (1) : Preparation of 2- hydroxyl -4-dimethoxy phenyl-6-benzyloxy phenyl pyrimidine.**

### Synthesis Of Complexes

The complexes were prepared by the addition of an aqueous solution of the metal salts ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) to an alkaline solution of (L). After stirring for (3) hrs.

Crystalline of different colored precipitates are formed at room temperature, the resulting solid was filtered off washed with distilled water recrystallized from ethanol and dried at  $50^\circ\text{C}$ . Physical properties of these complexes are listed in Table (1).

**Table (1)**  
**Physical data for preparation ligand and their complexes.**

| Symbol | Color      | Suggested molecular                                       | Dec. point | Found (calcd)% |            |             |              |              |
|--------|------------|---|------------|----------------|------------|-------------|--------------|--------------|
|        |            |   |            | C              | H          | N           | O            | M            |
| L      | White      | $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_3$          | 221        | 64 (64.61)     | 6.50(6.10) | 10.7(10.76) | 18.39(18.46) | –            |
| CuL    | Green      | $\text{Cu}(\text{L})_2$                                   | 241        | 57.27(57.38)   | 5.49(5.46) | 9.43(9.56)  | 16.27(16.39) | 10.83(10.84) |
| NiL    | Pale Green | $\text{Ni}(\text{L})_2$                                   | 253        | 57.34(57.87)   | 5.68(5.85) | 9.75(9.64)  | 16.79(16.53) | 10.15(10.09) |
| CoL    | blue       | $\text{Co}(\text{L})_2$                                   | 290        | 57.99(57.84)   | 5.47(5.50) | 9.78 (9.64) | 16.48(16.52) | 10.06(10.13) |
| CrL    | Gray       | $\text{Cr}(\text{L})_2\text{Cl} \cdot \text{H}_2\text{O}$ | 215        | 53.23(53.53)   | 5.21(5.10) | 8.87(8.92)  | 10.28(10.20) | 8.18(8.26)   |
| FeL    | Brown      | $\text{Fe}(\text{L})_2\text{Cl} \cdot \text{H}_2\text{O}$ | 187        | 53.27(53.39)   | 5.10(5.08) | 8.79(8.89)  | 10.08(10.17) | 8.83(8.87)   |

Table (2)

The absorption bands of the infra-red spectra for (L) and its complexes, in  $\text{cm}^{-1}$ .

| No. | Symbol | $\nu(\text{O-H})$ | $\nu(\text{C=N})$ | $\nu(\text{C-O})$ | $\nu(\text{M-N})$ | $\nu(\text{M-O})$ | $\nu(\text{M-Cl})$ |
|-----|--------|-------------------|-------------------|-------------------|-------------------|-------------------|--------------------|
| 1   | L      | 3500(S)           | 1620(S)           | 1025              | –                 | –                 | –                  |
| 2   | CrL    | –                 | 1605              | 1021              | 431(S)            | 490               | 325                |
| 3   | NiL    | –                 | 1606              | 1017              | 433(S)            | 405               | –                  |
| 4   | FeL    | –                 | 1606              | 1016              | 437(S)            | 428               | 380                |
| 5   | CoL    | –                 | 1607              | 1012              | 432(S)            | 446               | –                  |
| 6   | CuL    | –                 | 1608              | 1014              | 362(S)            | 440               | –                  |

Table (3)

The electronic spectra data for ligand and its complexes in DMF and their suggested structure.

| No. | Symbol | Absorption Bands (nm) | Assigned transitions                    | Suggested Structure |
|-----|--------|-----------------------|---|---------------------|
| 1   | L      | 260                   | $\pi \rightarrow \pi^*$                 |                     |
|     |        | 285                   | $n \rightarrow \pi^*$                   |                     |
| 2   | CuL    | 250                   | $\pi \rightarrow \pi^*$                 | Square Planar       |
|     |        | 271                   | $n \rightarrow \pi^*$                   |                     |
|     |        | 305                   | Charge transfer                         |                     |
|     |        | 660                   | $B_{1g} \rightarrow {}^2B_{2g}$         |                     |
| 3   | CoL    | 225                   | $\pi \rightarrow \pi^*$                 | Tetrahedral         |
|     |        | 243                   | $n \rightarrow \pi^*$                   |                     |
|     |        | 299                   | Charge transfer                         |                     |
|     |        | 590                   | ${}^4A_2 \rightarrow {}^4T_{1(P)}$      |                     |
|     |        | 655                   | ${}^4A_2 \rightarrow {}^4T_{1(P)}$      |                     |
| 4   | NiL    | 254                   | $\pi \rightarrow \pi^*$                 | Tetrahedral         |
|     |        | 285                   | $n \rightarrow \pi^*$                   |                     |
|     |        | 308                   | Charge transfer                         |                     |
|     |        | 654                   | ${}^3T_{1(f)} \rightarrow {}^3A_{2(f)}$ |                     |
|     |        | 725                   | ${}^3T_{1(f)} \rightarrow {}^3T_{1(f)}$ |                     |
| 5   | CrL    | 241                   | $\pi \rightarrow \pi^*$                 | Octahedral          |
|     |        | 264                   | $n \rightarrow \pi^*$                   |                     |
|     |        | 305                   | Charge transfer                         |                     |
|     |        | 475                   | ${}^4A_{2g} \rightarrow {}^4T_{1(P)}$   |                     |
|     |        | 595                   | ${}^4A_{2g} \rightarrow {}^4T_{1(f)}$   |                     |
|     |        | 690                   | ${}^4A_{2g} \rightarrow {}^4T_{2g}$     |                     |
| 6   | FeL    | 225                   | $\pi \rightarrow \pi^*$                 | Octahedral          |
|     |        | 290                   | $n \rightarrow \pi^*$                   |                     |
|     |        | 304                   | Charge transfer                         |                     |
|     |        | 503                   | ${}^6A_{1g} \rightarrow {}^4T_{1g(G)}$  |                     |

### Result and Discussion

Table (1) shows the physical data for the ligand and the prepared complexes, which contain the CHNO analysis were obtained

using flame atomic absorption technique. The calculated values were in a good agreement with the experimental values.

**Infrared Spectra:**

The IR spectra provide valuable informations regarding the nature of functional groups attached to the metal atoms. The FTIR spectra of the ligand, showed a characteristic stretching absorption bands at 3500 and 1620  $\text{cm}^{-1}$  respectively, Table (2) which assigned to  $\nu$  OH and  $\nu$ C=N group [8]. On complexation these bands were shifted to a lower frequency region [9]. This shift is probably due to the complexation of the metal to the ligand through nitrogen and oxygen of the ligand, the disappearance of the hydrogen from hydroxyle group on complexation indicate the complexation is through the oxygen atom. The spectrum of the ligand shows two different-C=N bands in the region ( $1620 \text{ cm}^{-1}$ )one is shifted to lower frequencies in the spectra of the complexes ( $1605\text{-}1608 \text{ cm}^{-1}$ ) indicting the involvement of C=N nitrogen in coordination to metal ion [10]. The second nitrogen atom is not involved in the complexation due to steric factor. Assignments to the proposed coordination sites in further are supported by the appearance of medium bands at  $431\text{-}362 \text{ cm}^{-1}$  which could be attributed to  $\nu$ (M-N) respectively [11]. In addition the appearance bands at  $490\text{-}440 \text{ cm}^{-1}$  which could be attributed to  $\nu$  (M-O) [12].

**Ultraviolet-Visible Spectroscopy:**

The ultraviolet visible electronic spectrum of 2-hydroxy-4-dimethoxy phenyl-6-benzyloxy phenyl pyrimidine (L) in DMF solvent is showed bands at the wavelengths

(260, 285 nm) this transition may be attributed to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  respectively.

The electronic spectrum of 2-hydroxy-4-dimethoxy phenyl-6-benzyloxy phenyl pyrimidine expected to give, different absorptions for the free ligand and complexes. These bands were shifted to different wavelength than the corresponding bands in the ligand as shown in Table (3).

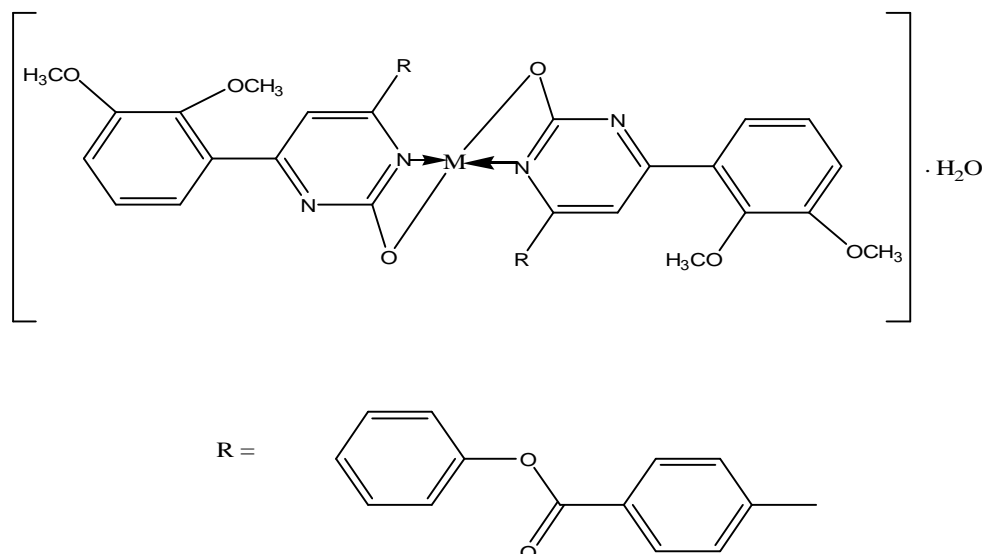
**Magnetic Susceptibility and Conductivity Measurements:**

The experimental magnetic moment for each metal complex is listed in Table (4). The magnetic moment for Ni(II) and Co(II) complexes are approximately 2.99 B.M and 3.24 B.M which refer to high spin tetrahedral structure, while the value for Cu(II) is approximately 0.83 led to the suggested square planar structure [13] which in a good agreement with the data of electronic transition. The magnetic moment of the Cr(III) complex is found to be 3.80 B.M which is in a good agreement with other octahedral Cr(III) complexes. The value of the measured magnetic moment for Fe (III) is 4.10 B.M in accordance with the presumption of high spin  $d^5$  ferric ion in octahedral geometry. Molar conductivity measurements in DMF solvent at  $25^\circ\text{C}$  showed that the complexes were non-electrolyte [14].

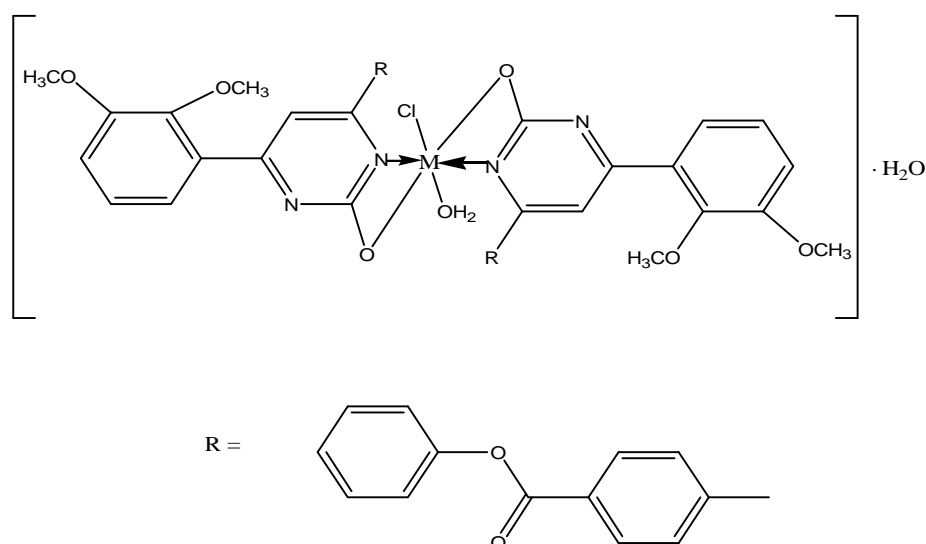
**Table (4)**  
**Conductivity measurement and Magnetic moment in DMF solvent.**

| No. | Symbol | Conductivity $\mu\text{s cm}^{-1}$ | $\mu_{\text{eff}}(\text{BM})$ |
|-----|--------|------------------------------------|-------------------------------|
| 1   | L      | 12                                 | –                             |
| 2   | CuL    | 17                                 | 0.83                          |
| 3   | CoL    | 19                                 | 2.99                          |
| 4   | NiL    | 20                                 | 3.24                          |
| 5   | CrL    | 18                                 | 3.80                          |
| 6   | FeL    | 20                                 | 4.10                          |

On the basis of the preceding discussion, the structure of the complexes may be suggested as follows:



**Fig. (2) :** The proposed structure of the complexes,  $M=Cu(II)$ ,  $Ni(II)$ , and  $Co(II)$ .



**Fig. (3) :** The proposed structure of the complexes  $M=Cr(III)$  and  $Fe(III)$ .

### References

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(CHN) والتحليل الطيفي تحت الحمراء والمرئي فوق البنفسجية وتقنيات اخرى. اقترحت الصيغ الكيميائية والاشكال الهندسية للمعقدات على ضوء النتائج التي تم الحصول عليها.

#### الخلاصة

حضرت الليكاند [ 2 - هيدروكسيل 4 - ثنائي ميثوكسي فينل 6 - بنزولوكسي فينل بيرامبين ] (L). شخصت عن طريق تحليل العناصر الدقيقة (CHN) والتحليل الطيفي تحت الحمراء. الفلزات المنتقاة كانت Cu(II) و Ni(II) و Co(II) و Fe(III) و Cr(III) تم تفاعلها مع الليكاند الجديد (L) لتحضير معقدات جديدة. شخصت هذه المعقدات عن طريق تحليل العناصر الدقيقة