# Preperation and Characterization of 1, 3-Bis (methylsalicylate5-yl diazo) Benzene and Its Complexes with Some of First Period Transition Metals

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## Abstract

In this study azo dye was prepared by the reaction of m-phenylendidiazonium chloride with methyl salicylate, the resultant compound was used as a ligand for complex formation with $Fe^{+2}$, $Cu^{+2}$, $Zn^{+2}$, $Ni^{+2}$ and $Co^{+2}$ ions. The prepared ligand was characterized by $^{H1}$NMR, UV-Vis., And FTIR spectroscopy, CHN analysis, in addition the complexes were characterized by TGA, UV-Vis., FTIR and conductivity methods. The results indicate that the ligand chelated through phenoxy and carboxyl groups as a O4 quadra dentate ligand, the Co complex complet its hexagon coordination by bonding with chlorine and the complex wouid be electrolytic in opposite with rest complexes.

**Key words**: Azo compounds, 3d metal complexes, transition metal complexes, Azo ligands

# Introduction

Organic reagents have wide spread and miscellaneous applications due to its stability and high speed of reaction with different metal ions [1], in addition many of them have a high selectivity and sensitivity which draw a considerable attention. Azo compounds are one of the mostly important types of organic reagents because azo bond can act as coordination center usually [2,3] but not always[4], at the same time azo group is considered as a strong chromophoric center in these compounds [5]. This character makes the azo compounds play a major rule in qualitative and quantitative chemical analysis of metal ions [6], in addition to their use as indicators, in industrial field azo compound used from long time as drugs and dyes, at present they have a wide application in printing, electronic photography, color formers, liquid crystal display, laser technology, data storage, optical actuators, photorefractive media, fiber dye, food and cosmetics industry [7]. This study aims to prepare a ligand from Methylsalicylate with m-phenelendiamine by diazo coupling and then attach the prepared ligand with ionic metals Co and Ni.

# Experemental

## Materials

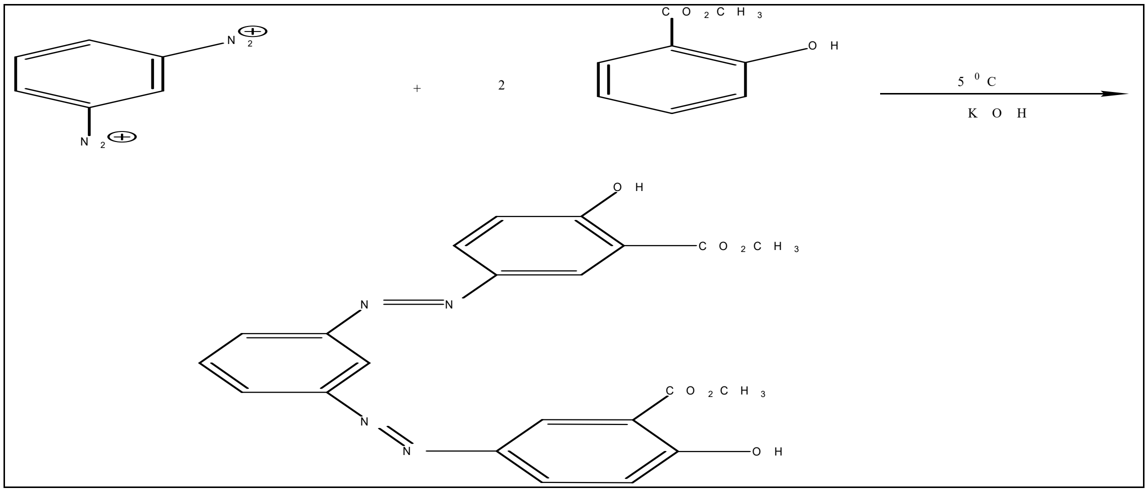
All chemicals used in this study were analytical grade and used without further purification. $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $FeSO_4.7H_2O$, $ZnSO_4$ and $CuSO_4.5H_2O$ m-phenelyendiamine hydrochloride, NaNO2, HCl, Methylsalicylate, Methanol, Ethanol, DMSO, $H_2SO_4$ and KOH

## Instruments

C.H.N (Shimadzu )elemental analyser, $^{H1}$NMR (Bruker 400MHz the solvent deuterized DMSO). FTIR spectra with KBr disc in the range (400-4000) $cm^{-1}$ (Shimadzu FTIR-8400S). Electronic spectra were recorded on (Shimadzu UV-Vis. 160A) spectrophotometer. Conductivty were measured for 0.0001M of complexes in ethanol at $25^0C$ using (Philips PW-Digital Conductometer). Thermal analysis was done by DSC-TGA (Linseis).

## Synthesis of the Ligand

The Ligand was synthesized by dissolving (2 g) of m-phenylenediamine hydrochloride in a mixture of (2 ml) $H_2SO_4$, 10 ml Ethanol, 10 ml of distilled water, the mixture was cooled to $5^0C$. 10ml of cooled 10% aqueous solution of $NaNO_2$ was added dropwise with stirring in order to obtain the diazonium salt solution. After 30 minute the diazonium solution was slowly added to a cooled solution of a mixture of (3 g) methylsalicylate and (1.2 g) of KOH to obtain the Ligand, the dark colored mixture containing the solid precipitate was filtered off, washed then re-crystallized with 70% ethanol. The reaction scheme is:



## Preparation of metal complexes

The complexes was prepared by the addition of (10 ml)aqueous solution of the metal salt its concentration 1 M to 0.01 mmole of the Ligand dissolved in 20 ml 50% methanolic aqueous solution. The darck precipitate was settled over night then recrysallized from 70% ethanol.

# Results and Discussion

## $^{H1}$NMR

Figure(18) indicates $^{H1}$NMR spectra of the Ligand contain a singlet band at 2.4 ppm belong to the methyl protons, a multiplet band between (6-9ppm) belongs to the Aromatic protons, finally a singlet band at (10.512 ppm) belongs to the phenolic protons.

## Electric conductivity

The measured electric conductivity for the complexes in DMSO solvent, the results indicates that the Co complex is charged complex while the other complexes were neutral complexes.

## Thermal analysis

The TGA thermograms of, figures(1,2,3,4 and 5) Co, Fe, Zn and Cu complexes showing two conversion regions while in Ni complex they were three . The first one is represented by losing of hydration water molecules in all complexes [8]. The second conversion region is the most characteristic and it represents the decomposition point of the complex, at this stage all the complexes lose their organic part leaving the metal (II) oxide, in Co complex case this its producing oxide was combined with KCl while in Ni complex this stage produces $NiCO_3$ which is further decomposed at the third conversion to NiO [9,10].

$$\underset{19mg}{Ni(C_{22}H_{16}N_4O_6).6H_2O}\xrightarrow{\substack{\Delta\\-6H_2O\\249.8^0C}}\underset{15.5762mg}{Ni(C_{22}H_{16}N_4O_6)}\xrightarrow{\substack{\Delta\\-organic\,frag.\\344.3^0C}}\underset{3.767mg}{NiCO_3}\xrightarrow{\substack{\Delta\\-CO_2\\381.1^0C}}\underset{2.37mg}{NiO}$$

$$\underset{17.7mg}{Fe(C_{22}H_{16}N_4O_6).H_2O}\xrightarrow{\substack{\Delta\\-H_2O\\\sim195^0C}}\underset{17.0702mg}{Fe(C_{22}H_{16}N_4O_6)}\xrightarrow{\substack{\Delta\\-organic\,frag.\\361^0C}}\underset{2.1192mg}{FeO}$$

$$\underset{18mg}{Zn(C_{22}H_{16}N_4O_6).H_2O}\xrightarrow{\substack{\Delta\\-H_2O\\\sim200^0C}}\underset{17.3714mg}{Zn(C_{22}H_{16}N_4O_6)}\xrightarrow{\substack{\Delta\\-organic\,frag.\\361^0C}}\underset{2.9956mg}{ZnO}$$

$$\underset{20.5mg}{Cu(C_{22}H_{16}N_4O_6).H_2O}\xrightarrow{\substack{\Delta\\-H_2O\\\sim180^0C}}\underset{19.7814mg}{Cu(C_{22}H_{16}N_4O_6)}\xrightarrow{\substack{\Delta\\-organic\,frag.\\322^0C}}\underset{3.1549mg}{CuO}$$

$$\underset{4mg}{K_2[Co(C_{22}H_{16}N_4O_6)Cl_2].H_2O}\xrightarrow{\substack{\Delta\\-H_2O\\224^0C}}\underset{3.9010mg}{K_2[Co(C_{22}H_{16}N_4O_6)Cl_2]}\xrightarrow{\substack{\Delta\\-organic\,frag.\\<690^0C}}\underset{1.3994mg}{CoO+2KCl}$$

## FTIR spectra:

Figure (6) shows the FTIR spectrum for the ligand that display a broad band at 3381 cm$^{-1}$ belongs to the stretching vibration of phenolic OH group. This band is merged with weak aromatic and aliphaic C-H stretching bands at 3067 and 2953 cm$^{-1}$ respectively. A strong band at 1674 cm$^{-1}$ is due to stretching vibration of C=O bond. The low value that took place as a result of the resonance with aromatic ring which decreases its bond order and hence its force constant [11]. In addition, the stretching vibration of N=N bond appears at 1612 cm$^{-1}$. The C-O vibration frequency displays two values, the first one at 1215 cm$^{-1}$ belongs to phenolic group, and the second one is part of carboxyl group. Finally, there is a very important absorption band at 847 cm$^{-1}$ belongs to out of the plane bending vibration of C-H aromatic group which is characteristic to the para substituted aromatic compounds [12]. The existence of this group is a good indicator to explain that: the azo group takes the para position relative to phenolic OH group and does not take the ortho position. Figures (7, 8, 9, 10 and 11) show the FTIR spectra of the complexes. In complexes there is an existence of weak broad band above 3300 cm$^{-1}$ assigned to stretching vibration of OH groups in hydration water molecules [13]. There is a great alteration in the C=O absorption band in all complexes. This suggests that the carbonyl group plays a major rule in the coordination with the metal ion. The stretching vibration of azo group is red shifted to lower frequency. This happens due to the change of the resonance state in the aromatic ring that which caused by the alteration in its electronic density through the formation of the complex. The C-O bands is also affected by coordination we believe the later band that belongs to phenolic C-O, bond has lost its H atom and coordinated with metal ion to form the complex. As a result of this coordination, we observed the appearance of a new band below 520 cm$^{-1}$ assigned to M-O bond.

## Electronic spectra

The electronic spectra of compounds in DMSO solvent are shown in Figures (12, 13, 14, 15, 16 and 17). The ligand shows strong absorption bands at 310, 364 and 457nm with molar absorbance $5*10^3$, $5.6*10^3$, and $4.8*10^3$ mole.cm$^{-2}$ respectively. The UV-vis. Spectrum indicates that the 364nm band belongs to $\pi \rightarrow \pi^*$ transition of –N=N- azo chromophoric group[14]. While the 310nm band belongs to $\pi \rightarrow \pi^*$transition of phenolic group[5], finally the shoulder band at 457nm is due to $n \rightarrow \pi^*$transition of the same group[5]. The excited state in the $\pi \rightarrow \pi^*$transition of azo group plays a major rule in the conformational transformations in the ligand, because it acts to ease the rotation N=N bond. This process is observed in the cis-trans transformations of the azo compounds. In the electronic spectra of the complexes, we have observed that the $\pi \rightarrow \pi^*$transition of azo group is not greatly affected by coordination which supported the assumption that the azo group did not act as a coordination center with metals. On the other hand there is a considerable alteration of the bands that belong to phenolic group which considered as evidence that the phenolic group is one of the coordination centers that chelated with metal ion. In addition we observed the increase of the intensity of band of azo group, this may relate to the fact that the quantum probabilistic transition of this bond is stabilized after complex formation. Indeed the formation of complex through the contribution of the phenoloic and the carbonyl groups upon complexation through the chelating with metal ions require fold of the two salicylic parts that close to each other in the ligand which are accomplished by twisting of the –N=N- bond. The transition state of this bond may help to satisfy this condition. The above discussion is proceeding for all complexes as well. Finally, the high values of the molar absorbance of the ligand chromophores act to cover the d-d transitions in the metal ions of the complexes [15].

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### Table (1): FTIR band values

| Compound | $\nu\ H_2O$ $cm^{-1}$ | $\nu N = N$ $cm^{-1}$ | $\nu C = O$ $cm^{-1}$ | $\nu C - O$ $cm^{-1}$ | $\nu M - O$ $cm^{-1}$ | $\nu OH\ phenolic$ $cm^{-1}$ |
|---|---|---|---|---|---|---|
| L | ------ | 1612 | 1674 | 1213 | -------- | 3381 |
| Ni-comp. | 3345 | 1595 | 1668 | 1231 | 484 | ------ |
| Co-comp. | 3354 | 1601 | 1630 | 1234 | 446 | ------ |
| Cu-comp. | 3300 | 1599 | 1682 | 1200 | 513 | ------ |
| Fe-comp. | 3300 | 1599 | 1682 | 1209 | 490 | ------ |
| Zn-comp. | 3381 | 1606 | 1666 | 1192 | 513 | ------ |

### Table (2): Elemental analysis of the Ligand

| Element % | C | H | N |
|---|---|---|---|
| Practical | 59.855 | 4.234 | 17.603 |
| Theoretical | 60.830 | 4.148 | 17.603 |

### Table (3):UV-Vis. Band values

| Compound | $\lambda\ azo$ $\pi - \pi^*$ (nm) | ε*$10^{-3}$ L.$mol^{-1}$.$cm^{-1}$ | $\lambda\ phenolic$ $\pi - \pi^*$ (nm) | ε*$10^{-3}$ L.$mol^{-1}$.$cm^{-1}$ | $\lambda\ phenoli$ $n - \pi^*$ (nm) | ε*$10^{-3}$ L.$mol^{-1}$.$cm^{-1}$ |
|---|---|---|---|---|---|---|
| L | 364 | 5.6 | 310 | 5 | 457 | 4.8 |
| Ni-comp. | 364 | 6.1 | ----- | ----- | 461 | 5 |
| Co-comp. | 366 | 5.3 | ----- | ----- | 466 | 4.9 |
| Cu-comp. | 365 | 4.5 | ----- | ----- | 465 | 4.2 |
| Fe-comp. | 370 | 5.1 | ----- | ----- | 465 | 4.9 |
| Zn-comp. | 370 | 5 | ----- | ----- | 469 | 4.9 |

### Table (4) :Physical properties of the Ligand and its complexes

| Compound | M.wt/ g.$mol^{-1}$ | Colour | Yeild% | m.p./$^0$C (dec.) | $\Lambda_M$/ $ohm^{-1}$.$cm^2$.$mol^{-1}$ |
|---|---|---|---|---|---|
| Ligand | 434 | Reddish brown | 62 | 235 | ----- |
| $NiL.6H_2O$ | 598.7 | Dark brown | 86 | 337.7 | 1.207 |
| $K_2[CoLCl_2].H_2O$ | 599 | Dark brown | 88 | 224.8 | 32.1 |
| $FeL.\ H_2O$ | 505.85 | Dark brown | 85 | 360.9 | 1.33 |
| $CuL.\ H_2O$ | 513.5 | Dark brown | 84 | 321.7 | 1.32 |
| $ZnL.\ H_2O$ | 515.4 | Dark brown | 88 | 423.6 | 1.02 |

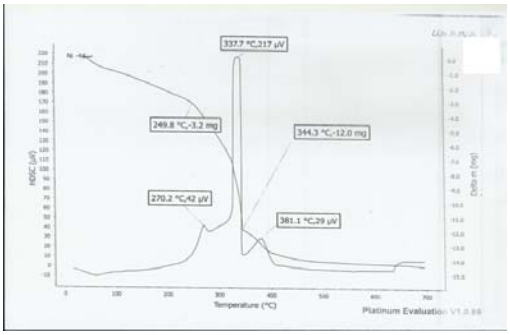


Figure (1): Thermogram of the Ni complex.

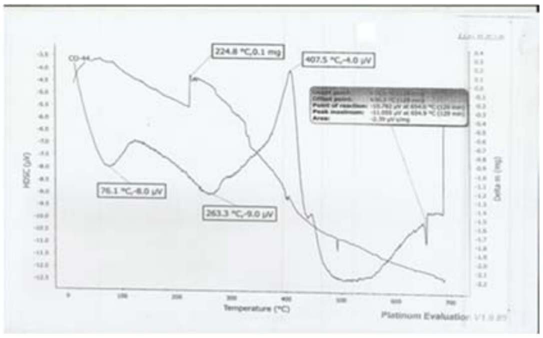


Figure (2): Thermogram of the Co complex.

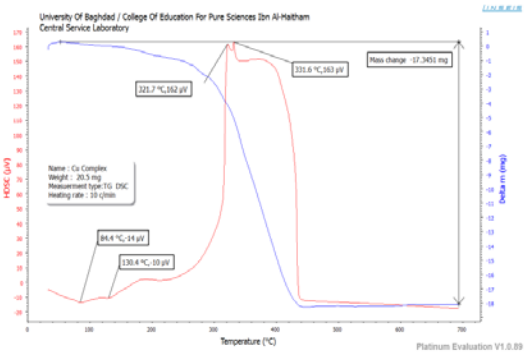


Figure (3): Thermogram of the Cu complex.

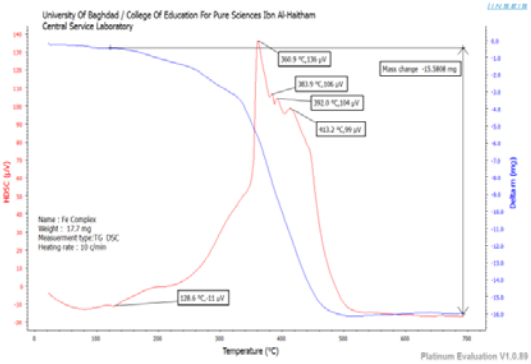


Figure :(4) Thermogram of the Fe co complex

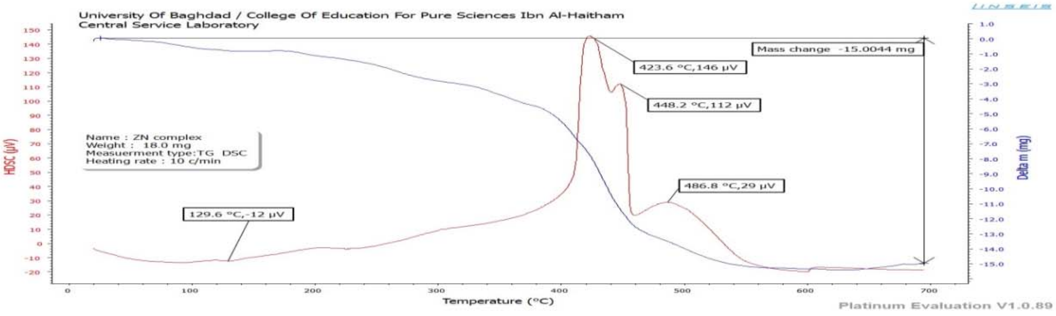
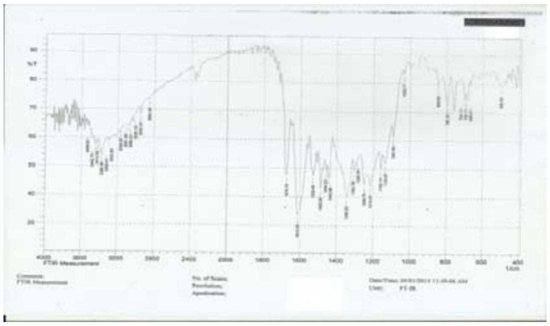


Figure (5) :Thermogram of the Zn complex.



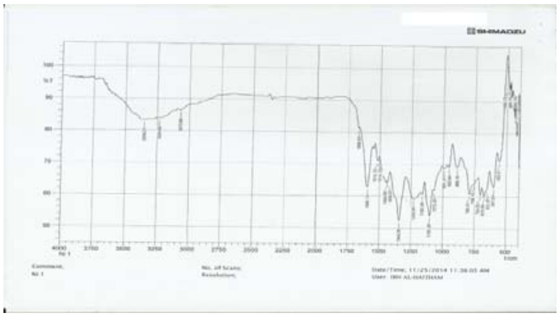
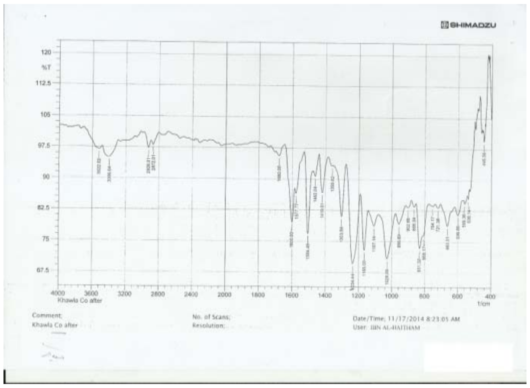


**Figure (6): FTIR spectrum of the ligand.**

**Figure (7): FTIR spectrum of the Ni complex .**



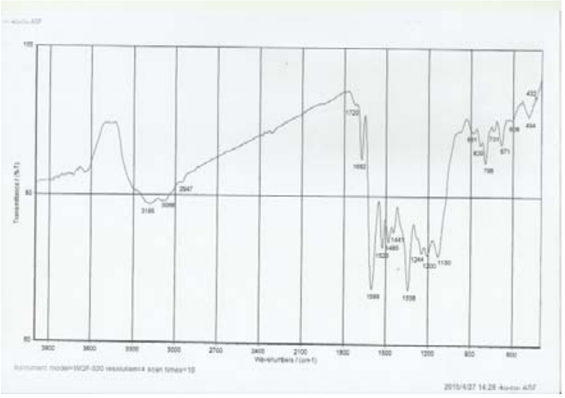
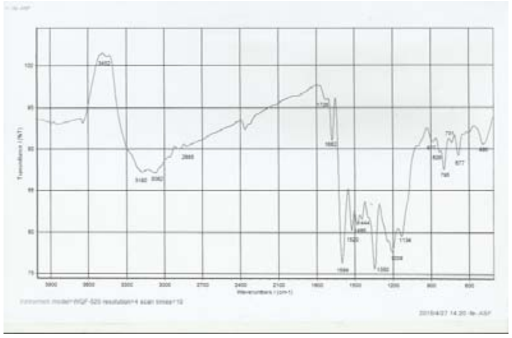


**Figure (8): FTIR spectrum of the Co complex**

**Figure (9): FTIR spectrum of the Cu complex**



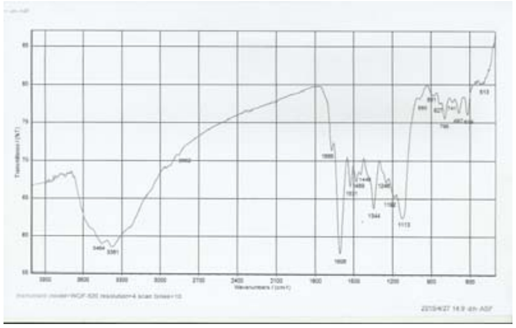
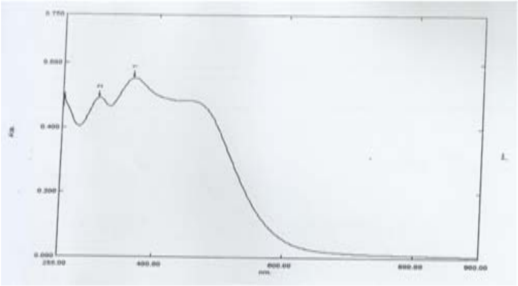


**Figure (10): FTIR spectrum of the Fe complex**

**Figure (11):FTIR spectrum of the Fe complex.**



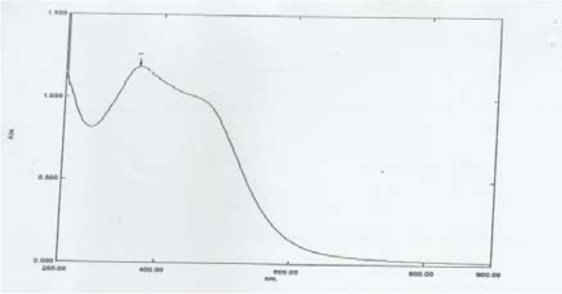
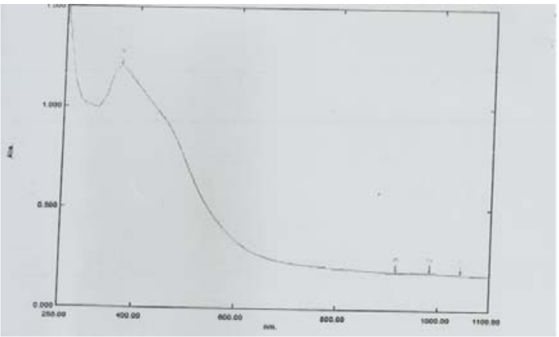


Figure (12): electronic spectrum of the ligand.

Figure (13): electronic spectrum of the Ni complex



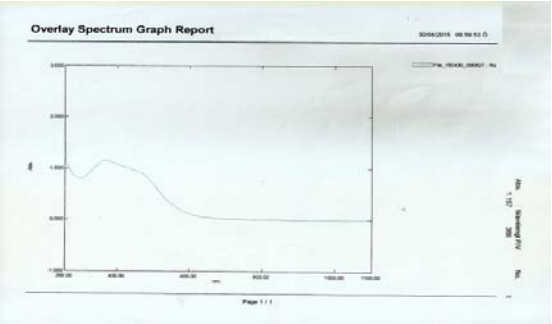
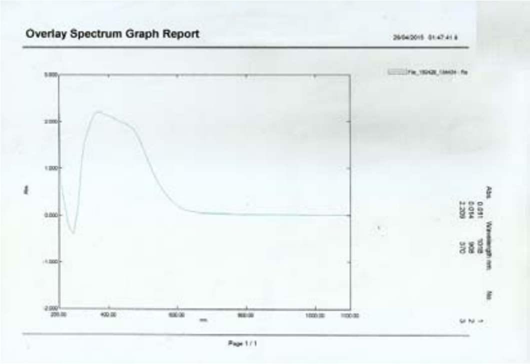


Figure (14): UV-Vis. of the Co complex.

Figure (15): UV-Vis. of the Cu complex.



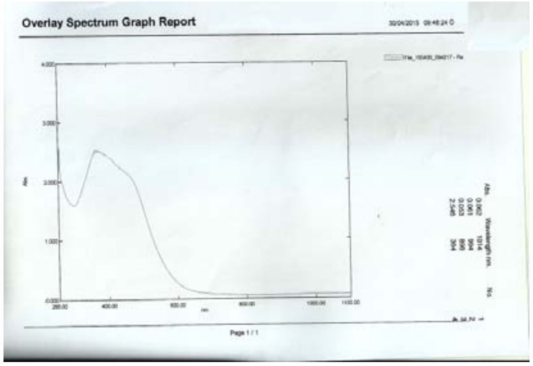


Figure (16) :UV-Vis. of the Fe complex.

Figure (17): UV-Vis. of the Zn complex.

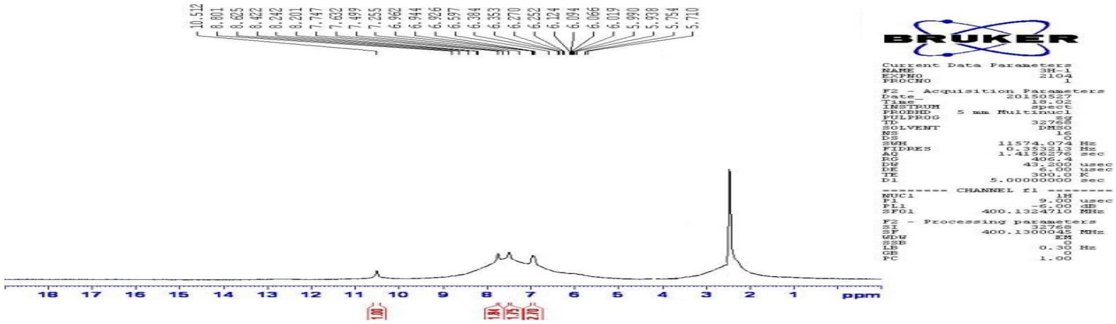


**Figure (18): $^{H1}$NMR spectrum of the Ligand.**

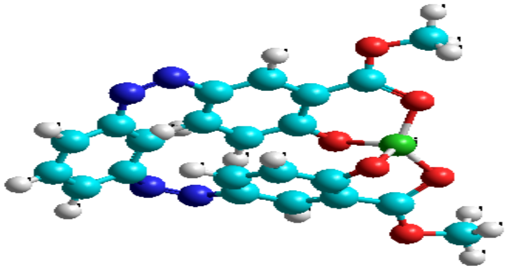


**Figure (19): The general structure of Ni, Cu, Fe and Zn complexes.**

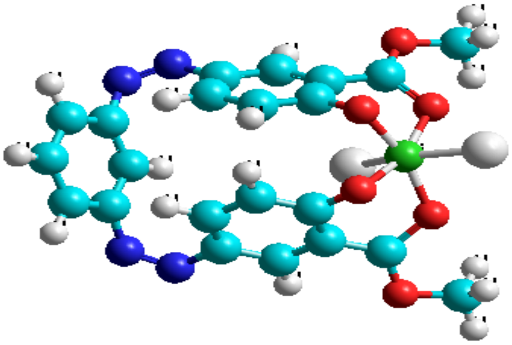


**Figure (20) :The general structure of Co complex.**

# تحضير و تشخيص 1,3-Bis (methylsalicylate5-yl diazo)benzene مع معقداته لبعض عناصر الدورة الانتقالية الاولى

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**استلم في: 22/اذار/2015 ، قبل في: 30/حزيران/2015**

## الخلاصة

تم تحضير صبغة ازو من تفاعل m-phenylendidiazonium chloride مع methyl salicylate. في هذه الدراسة استعمل المركب المحضر كليكند لتكوين معقدات تناسقية مع ايونات $Fe^{+2}$, $Cu^{+2}$, $Zn^{+2}$, $Ni^{+2}$, $Co^{+2}$ اذ تم تشخيص الليكند المحضر مع معقداته بمطيافيتي $^{H1}$NMR و FTIR و UV-vis. وتحليل العناصر CHN فضلا عن ان المعقدات المحضرة شخصت ايضا بقياس TGA FTIR و UV-vis. و التوصيلية اذ بينت النتائج ان الليكند يرتبط مغ الايونات من خلال مجاميع الفينوكسي و الكاربونيل و بذلك يكون ليكند رباعي السن من نوع O4. كما انه في معقد الكوبلت فانه يتم اكمال التناسق السداسي من خلال الارتباط بالكلور وبذلك يكون هذا المعقد الكتروليتي بخلاف المعقدات الاخرى.

**الكلمات المفتاحية:** مركبات الازو, معقدات عناصر 3d, معقدات العناصر الانتقالية, ليكندات الازو.