



Synthesis and characterization of new Azo-Chalcone ligand and its divalent transition metal ion complexes

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Abstract : A new Azo-Chalcone ligand (SACAN) was synthesized via the reaction of the daiznoium salt of pre-synthesized chalcone amine (SAC) with the coupling component 2-naphthol.

Both of the amino chalcone (SAC) the new azo dye (SACAN) were identified with the analytical techniques (elementary analysis, FTIR and Mass Spectroscopy for (SACAN)),for certaintyof these compounds were prepared. A UV-Visible study was performed for the new ligand and their aqueous complexes for three divalent transition metal ion (Co,Ni and Cu), via determination the optimal concentration and λ_{max} , for use in the preparation of solid complexes after knowing the suitable mole ratios.

The solid complexes were prepared and diagnosed with the previous techniques, indeed the complementary techniques to suggest the complexes geometry were working out such (electrical molar conductivity, magnetic susceptibility and electronic spectroscopy), these will enhance in the suggestion of :

All complexes have non-electrolytic properties

Cobalt and Copper complexes have the octahedral geometry, while Nickel has the square planar geometry.

Introduction

Chalcones an α,β -unsaturated carbonyl compounds, play an important role in the synthesis of manyhetrocyclic compounds such(benzothiazepines, pyrazolines, pyrimidines, flavones, isoxazolines, etc)¹, in addition to there biological activity that enhanced when chalcone have functional group as methoxy, glucoside, hydroxyl and halogens²and it can be asource of many drugs³.

Azo compound on the side, regard an important and vital compounds in the industry of color and pigments⁴, food colorant, pesticides⁵, lubricating oil improvers⁶and in the medical and pharmaceuticals such in HIV inhibetor of the viral replication⁷,and recently in the LCD color filter⁸CD-DVD production.

In addition to the utilization of azo compounds in the analytical chemistry fields⁹, due to their abilities to coordinate with different ions and detected them in trace amounts due to their sensing to these trace amounts of ions, using different techniques , such PAR for detection of ($Ba^{2+},Cr^{2+},Al^{3+},Mn^{2+},pb^{2+},Fe^{3+},Co^{2+},Zn^{2+},Ni^{2+}$ and Cu^{2+})¹⁰, the selective electrode¹¹ (NPHSA) syntheized from the reaction of the azo compound 5-(4-nitrophenyl azo) salicyldehyde with 6-amino hexane,while the ligand can made (PCV) membrane for Mn^{2+} .

Due to the scarcity of specialized literature and the importance of the subject under study, it led us to enter into the midst of the subject and prepare a new azo-chalcone ligand and its complexes.

Instrumentation & procedure

All chemicals that used in this work were of analytical reagent grade from (Fluka, BDH and Sigma), with a high grade of purification.

- Mass Spectra was taken with Shimadzu GCMS-QP2010 Ultra (semi chemical ionization) with 5-20eV ionization energy, Metal analysis was performed by Shimadzu 6800AA (Flame Atomic Absorption Spectrophotometer. Elemental analysis (C.H.N) of compounds was carried out by (Micro Analytical unit, 1108 CHN Elemental analyzer).

- ^1H NMR spectroscopy (Bruker-300MHz) using DMSO as a solvent

- UV-Visible study and electronic spectra were recorded on a Shimadzu (UV-Visible 1650) spectrophotometer using a quartz cell. FTIR Spectra were recorded by Shimadzu FTIR8400 test scan series using the KBr disc in the wave number range ($4000\text{-}400\text{cm}^{-1}$), magnetic susceptibility measurement was determined by Faraday's method using Magnetic Susceptibility Balance Model – M.S.B Auto. The molar conductivity was measured at room temperature in two solvents (ethanol and dimethyl formamide) in $1 \times 10^{-3}\text{M}$ ligand concentration using (Info lab terminal). Melting points were determined using Satrates digital SPM30.

2.1 Synthesis of the chalcone amine ¹²

Chalcone amine (*E*)-1-(4-aminophenyl)-3-(2-hydroxyphenyl)prop-2-en-1-one (SAC) was prepared via reaction of (p-aminoacetophenone, 0.01 mole, 1.35 gm) and (salicylaldehyde, 0.01 mole, 1.22 gm = 1.06 ml) in absolute ethanol (30 ml), then stirring and cooling at 5C° , within 30 min. Dropping of (3M KOH) solution to the reaction component with stirring till the thickening, then stirring continued for 24 hrs. Decant this thickened solution in iced bath and neutralized with dil. HCl, the yellow precipitate appears, filter and wash with deionized water several times to remove the trace of acid and salt formed, then air drying the precipitate, recrystallize the product with hot ethanol.

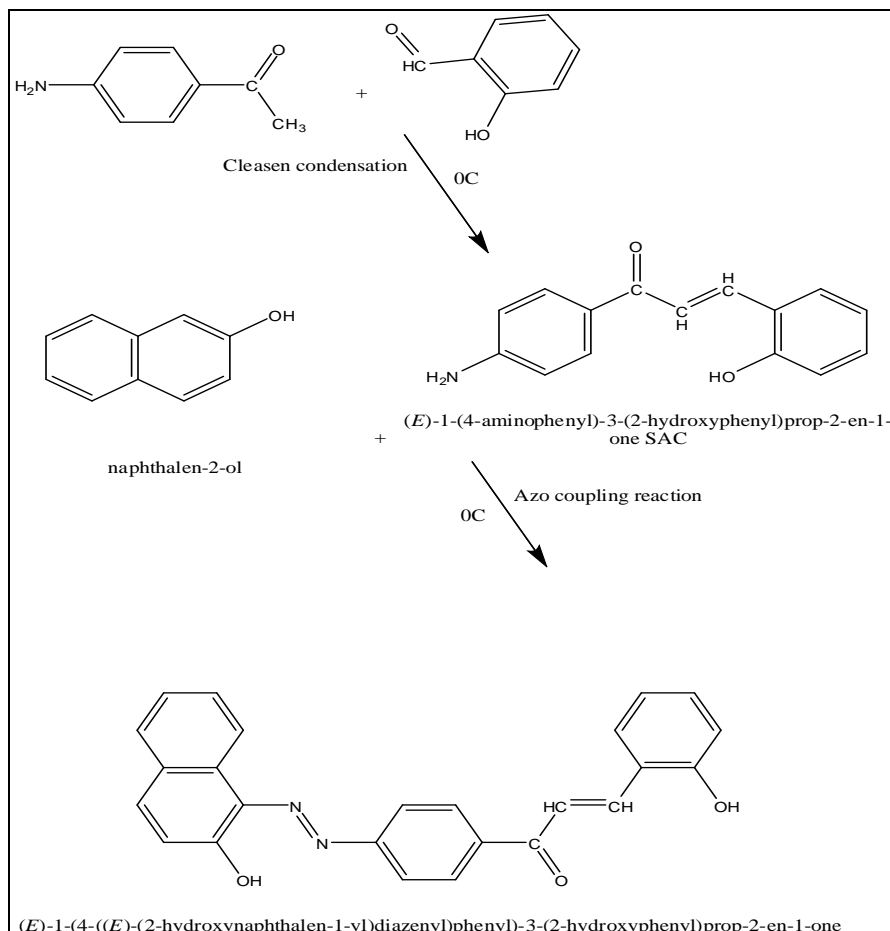
2.2 Synthesis of the Azo-Chalcone (SACAN):

Azo-chalcone (SACAN) was prepared according to Shibata method¹³, the ligand ((*E*)-1-(4-((*E*)-(2-hydroxynaphthalen-1-yl)diazenyl)phenyl)-3-(2-hydroxyphenyl)prop-2-en-1-one SACAN) was synthesized by preparation of diazonium salt of the chalcone amine (SAC) by dissolving (5 mmole, 1.195 gm) of this amine in an acidic mixture (8 ml conc. HCl + 15 ml D.W) and cooling in 0C° water bath, then (5 mmole, 0.35 gm NaNO_2 in 10 ml D.W) solution was added carefully to the amine with stirring at the same temperature, within 15 min the diazonium salt was formed. The coupling component (2-naphthol) was prepared by dissolving (5 mmole, 0.72 gm) in alkaline alcoholic solution (2M NaOH). Then transferred in the ice cold bath, the diazonium salt was added dropwise to the coupling component with stirring at 0C° , a red-orange color was formed, complete the process until the end of diazonium solution, then neutralization of the pH value to complete the precipitation of the azo compound, the precipitate was filtered washed many times to remove the salt traces then drying and recrystallized with a hot ethanolic solution. A deep orange powder was collected. The preparation stepwise was outlined in scheme 1 and the physical properties in the table 1.

2.3 Synthesis of the complexes

All the divalent transition metal element (Co, Ni and Cu) complexes were prepared with the same procedure, that:

In 100 ml rounded bottom flask 10 mmole of (SACAN) dissolved in 40 ml absolute ethanol and refluxed with 5 mmole of metal chloride (that dissolved in the minimum amount of absolute ethanol); they refluxed for 1 hr. with the addition of few mls. of 10% KOH (for phenol protonation) With stirring, then the solvent reduced to the quarter in hot water bath, then the hot solution, transferred to crushed ice bath, the colored precipitate was developed, then collected, dried and re-crystallized with hot ethanol.



Scheme 1 preparation of the (SACAN) Ligand

Table1. Some physical properties and Elementary analysis of SACAN and Its Complexes

| Compounds | M.Wt g/mol | Color | m.p C° | Yield | Elementary analysis | | | |
|---|---------------|--------------------|-----------------|-------|--------------------------|---------------------------|--------------------------|--------------------------|
| | | | | | C% found (calculated) | H % found (calculated) | N% found (Calculated) | M% found (calculated) |
| SAC C ₁₅ H ₁₃ NO ₂ | 239.09 | Yellow | 116 - 118 | 77% | 75.30 (75.39) | 5.48 (5.50) | 5.85 (5.90) | ----- |
| SACAN C ₂₅ H ₁₈ N ₂ O ₃ | 394.42 | Reddish- orange | 115 - 117 | 70% | 76.13 (76.22) | 4.60 (4.62) | 7.10 (7.18) | ----- |
| [Co(SACAN) ₂ (H ₂ O) ₂] [CoC ₅₀ H ₃₈ N ₄ O ₈] | 881.79 | Brawn | 134 - 136 | 77% | 68.10 (68.22) | 4.34 (4.39) | 6.35 (6.40) | 6.68 (6.77) |
| [Ni (SACAN) Cl H ₂ O] [NiC ₂₅ H ₁₉ N ₂ O ₄ Cl] | 504.04 | Deep brawn | 220 - 222 | 82% | 59.39 (59.47) | 3.79 (3.83) | 5.54 (5.58) | 11.61 (11.71) |
| [Cu(SACAN) ₂ (H ₂ O) ₂] [Cu C ₅₀ H ₃₈ N ₄ O ₈] | 885.20 | Red- brown | 198 - 200 | 69% | 67.75 (68.15) | 4.32 (4.38) | 6.32 (6.41) | 7.17 (7.22) |

Results

A new azo- chalcone (SACAN) was synthesized via the preparation of the amino chalcone first (SAC) , then coupling of the diazonium salt of this amine with 2-naphthol. The product was fine (reddish-orange)

powder, insoluble in water but soluble in most organic solvents (ethanol, methanol, chloroform, dichloromethane, DMF and DMSO).

FTIR Spectra

The FTIR Spectra is a valuable technique used for functional group's determination¹⁴ with their assessments of which ether these groups attached to form complexes or not in the inorganic chemistry field.

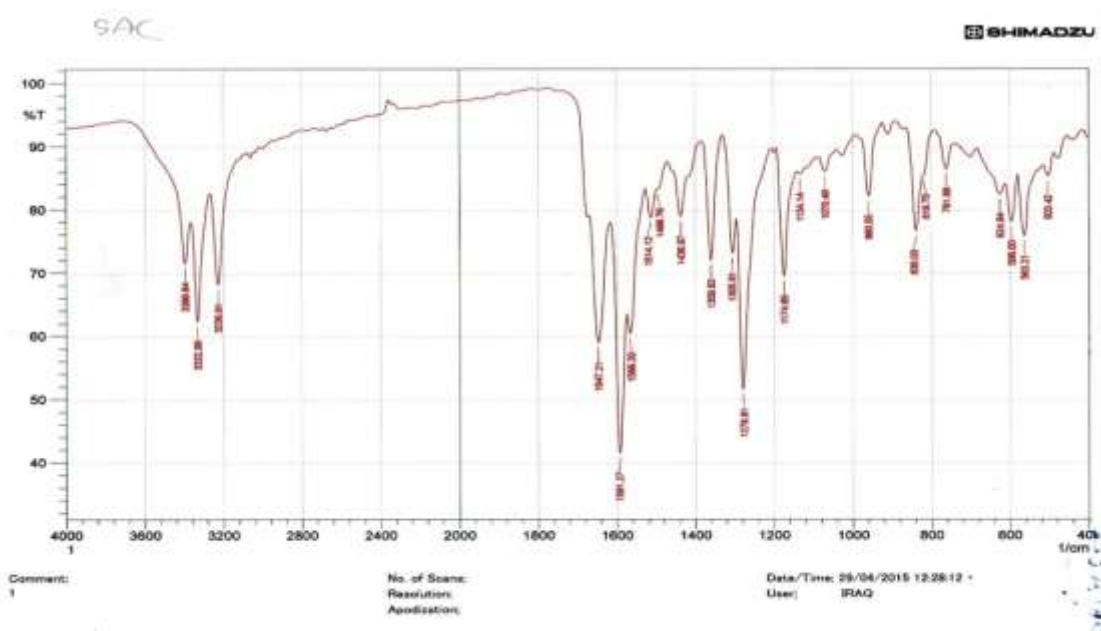
In this work a new azo- chalcone was synthesized by two steps:

Firstly the amino chalcone (SAC) was synthesized by the Cleasien – Schmidt condensation of the p-amino acetophenone with salicylaldehyde in 10% alkaline alcoholic media to form the amino chalcone (SAC), the TLC (petroleum: ethyl acetate 4:1) with $R_f = 0.28$ indicate the completion of the reaction.

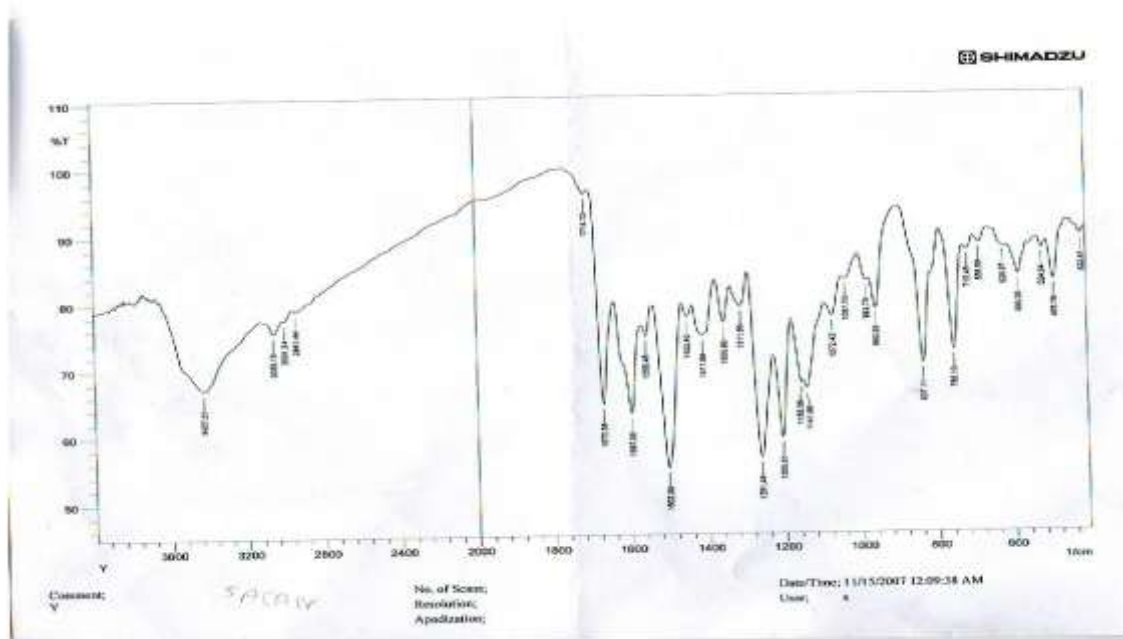
The certainty of the chalcone preparation can be enhanced with the FTIR spectral data that the appearance of the functional group of the compound in their regions gives us confidence to the formation; the main bands were :

-The hydroxyl group of the salicylaldehyde gives str. band at 3396 cm^{-1} , while the primary amine gives two adjacent str. bands at 3332 cm^{-1} & 3226 cm^{-1} respectively.

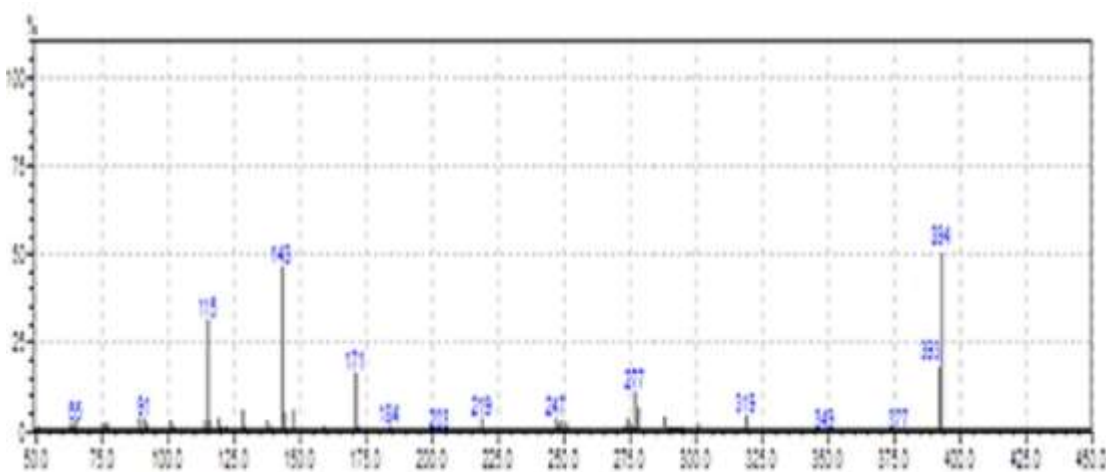
-The appearance of the chalcone bands clearly at (1647 cm^{-1} & 1514 cm^{-1}) related to the carbonyl and methylene groups¹⁵, as shown :-



While SACAN was synthesized from the above amino chalcone with the coupling component (2-naphthol), we can see within its FTIR chart the disappearance of the amine group and development of the azo group in 1452 cm^{-1} region, in addition to broad band in 3427 cm^{-1} region related to the (naphthol & salicylaldehyde) hydroxyl groups, these can be observed with the following figure.




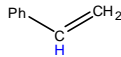
Mass spectroscopy act as a documented technique for the identification of the particles and molecules, via its sorts the ions based on their mass (weight), one of the mass spectrum importance's for the determination the masses of the particles and of molecules, and to elucidate the chemical structure of the molecules¹⁶, instudy, the mass spectra showed us the demand ligand mass (m/z) that equivalent to the molecular mass of (SACAN) at **394** and its fragmentation products , that totally indicate the formula of our compound , this can be observed in the following fig:

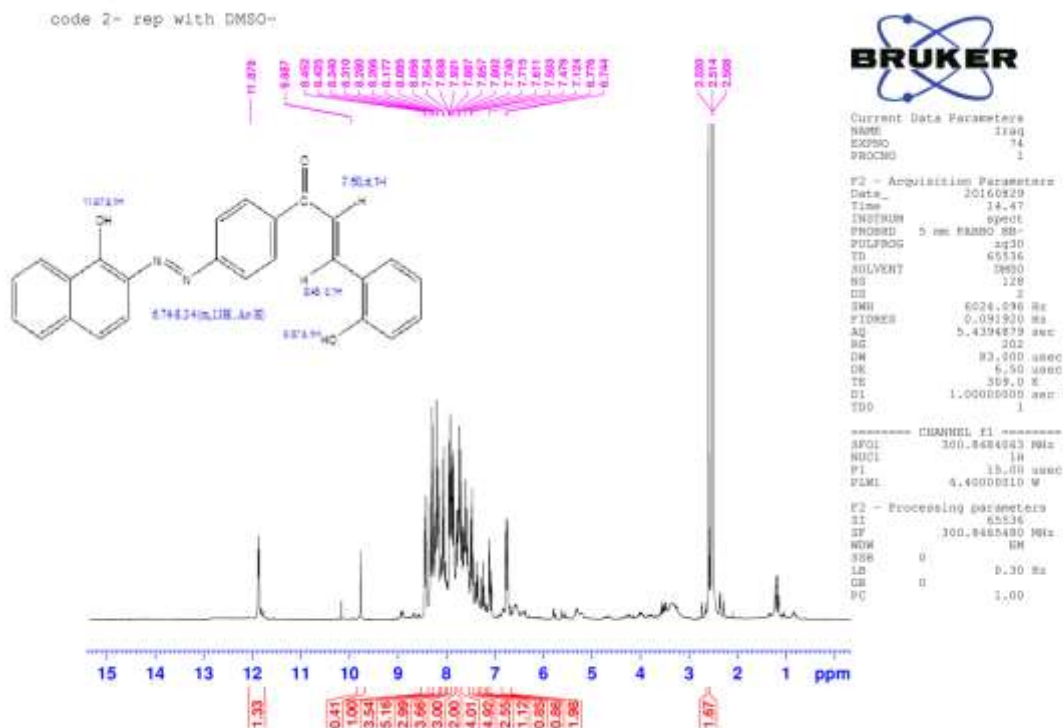
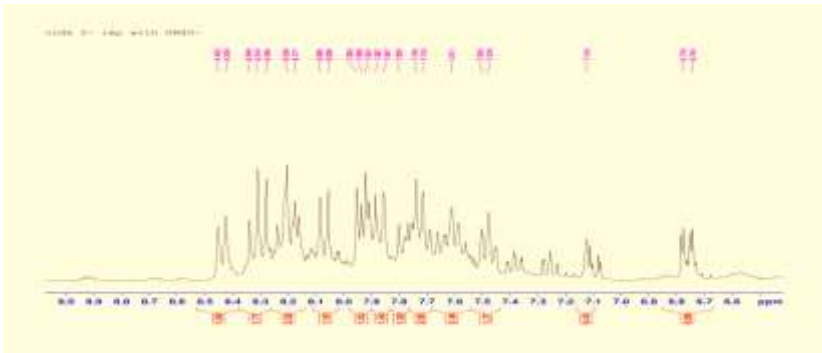


These fragmentation route illustrated in the appendixes.

H¹ NMR spectroscopy

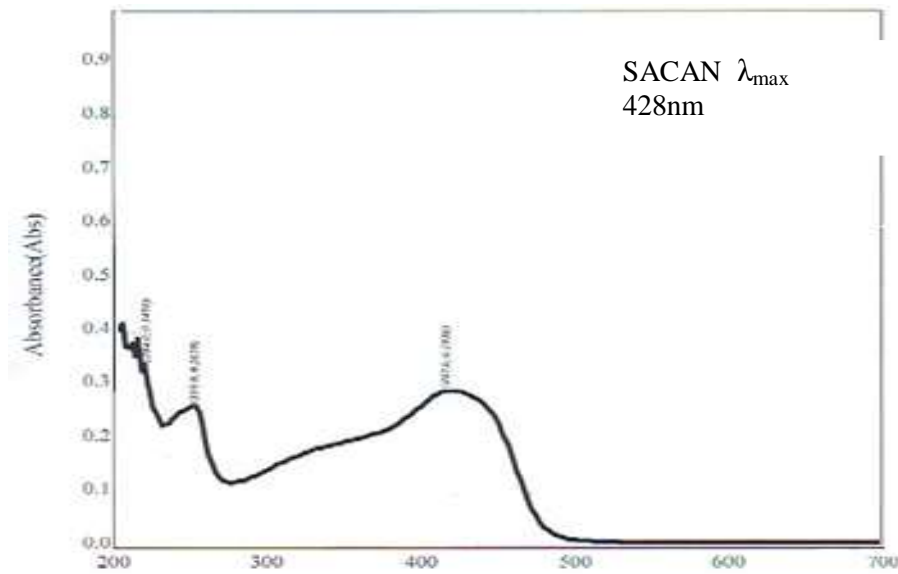
The most favored technique used in the organic compounds study, that give the information about the magnetically distinct hydrogen atoms as well as obtain information regarding the nature of the immediate environment of each type¹⁴, that compounds could easily investigated with a high precision , for this study the ligand (SACAN) investigated with 300MHz (Burker H NMR), giving :- (6.74-8.34,m,13H, Ar-H), (7.5, d,1H,

, (8.45,d,1H, ) , (9.88,s,1H, sal-OH) this agreed with literature¹⁷ and (11.87,s,1H, naphthol-OH) the down field shift of this proton,s may thought that the hydrogen bonding with the azo nitrogen atom occurred¹⁸, the NMR data clarified in the following figure;

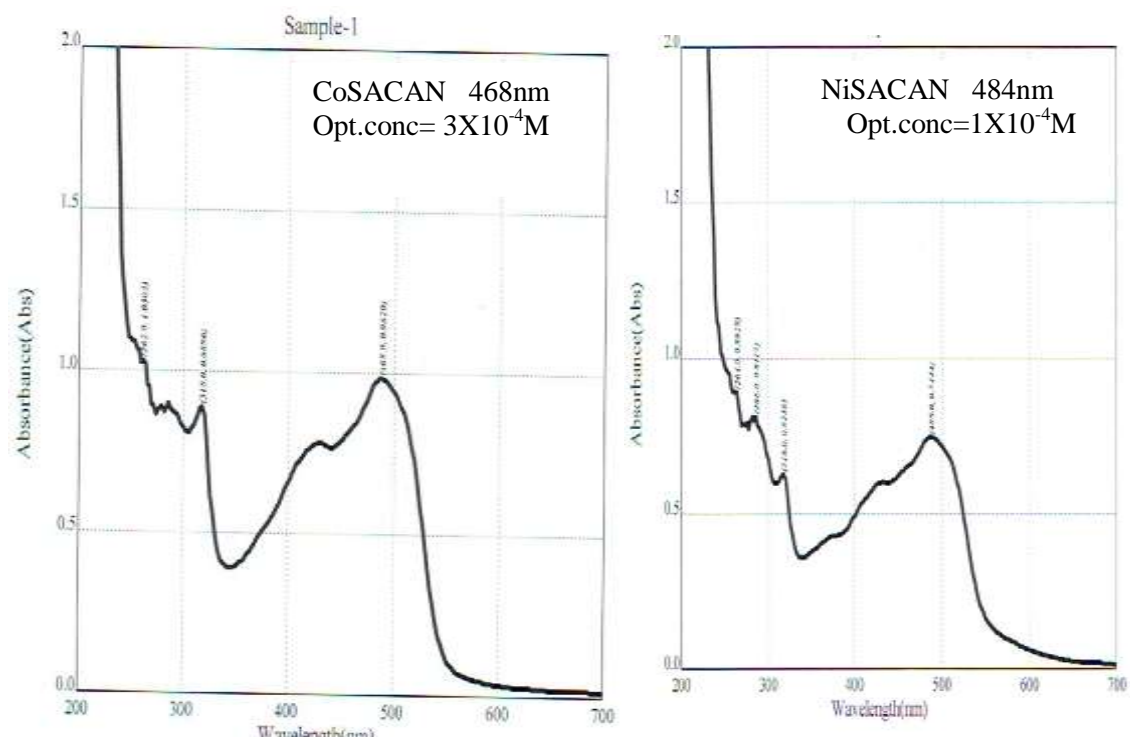


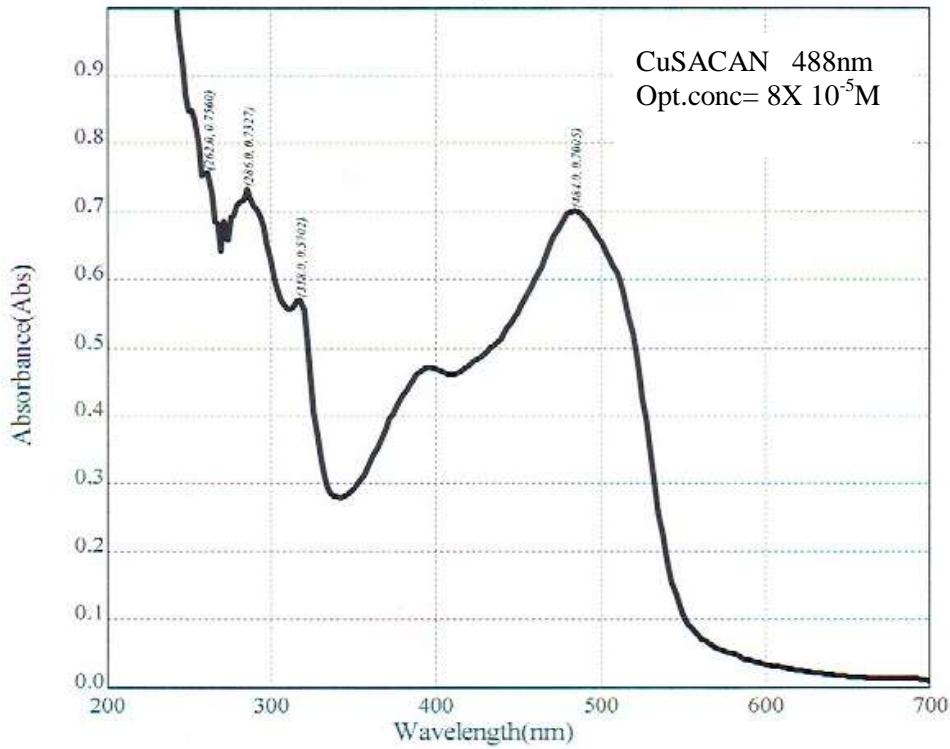
Uv-visible study

Uv-visible study for the prepared ligand (SACAN) and their metallic complex solutions was done within their optimal conditions that obey the beer-lambert law ,the ligand give two observable absorption band , one at (428)nm the λ_{max} of the ligand and the other (312) nm due the transition ($\pi \longrightarrow \pi^*$) of the conjugated system. As shown below:

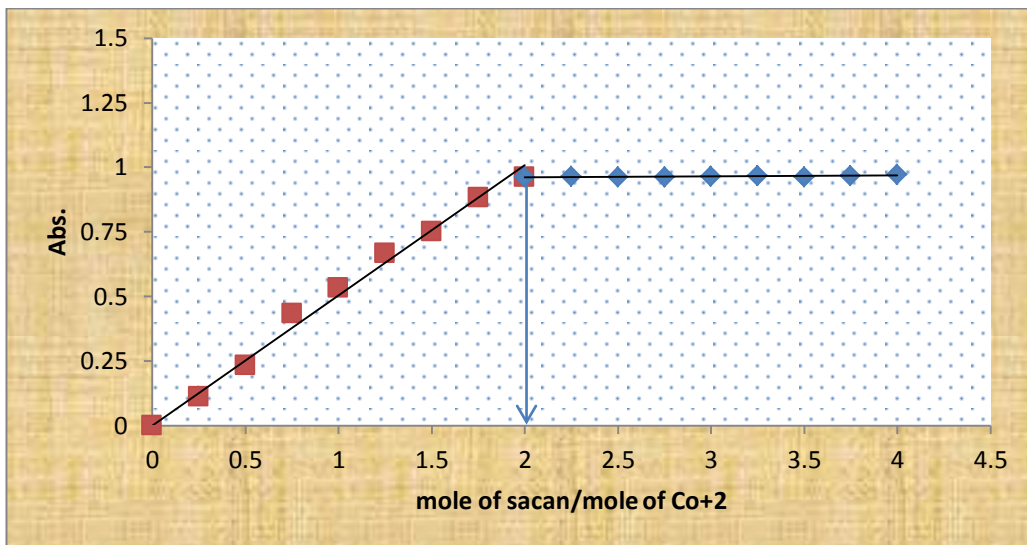


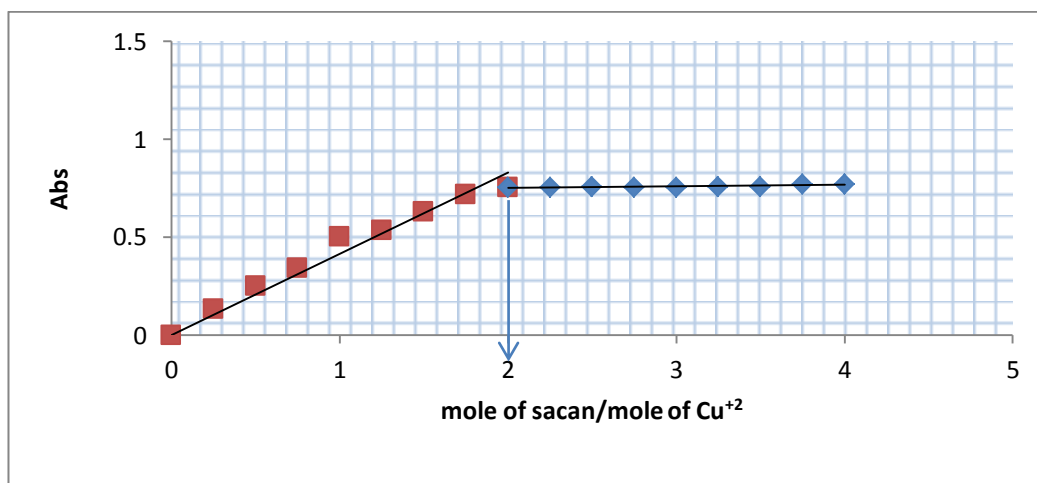
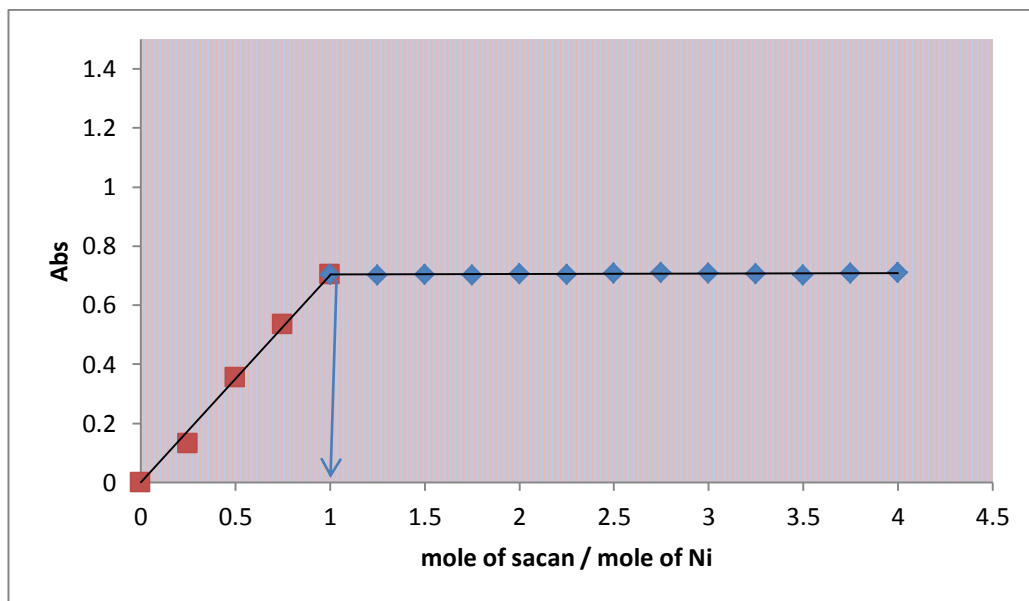
While when the aqueous solutions of the transition metal salt divalent ions (Co, Ni and Cu) was mixed with ethanolic ligand solution, the λ_{max} was shifted toward higher wavelength (red shift), this may be due to the coordination¹⁹ between the lone pairs of the ligand to the vacant orbitals in the metals, in addition to the variation of the ligand color to a vivid color, the Beer's law compliance takes place within ($5 \times 10^{-5} - 5 \times 10^{-4} M$), they can observe it on the figure below :



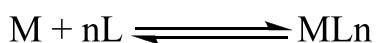


The UV-visible data can be utilized in the complex components determination, by using the mole ratio method (a suitable for the soluble complex determination)²⁰, from the obtained data, we observe that the mole ratio of the cobalt and copper complexes were (M:L, 1:2), while the Nickel complex has the (M:L, 1:1). These are shown in the following figures.





The stability constants of these complexes can calculate from the relations:



$$\alpha \quad (n\alpha c) \quad (1-\alpha)c$$

$$\beta = \frac{[ML_n]}{[M][L]^n} \quad \text{When } \beta = \text{formation constant}$$

$$\beta = \frac{1-\alpha}{\alpha^2 c^2} \quad \text{When } n=1, \text{ but when } n=2, \text{ hence} \quad \beta = \frac{1-\alpha}{4\alpha^3 c^2}$$

And the β value can determine when α (dissociation constant) are known

$$\alpha = \frac{A_m - A_s}{A_m}$$

Table2. SACAN Complexes Stability

| Metal ion Complex | A_m | A_s | α | β | $\text{Log}\beta$ |
|--|-------|-------|----------|-----------------------|-------------------|
| [Co(SACAN) ₂ (H ₂ O) ₂] | 0.972 | 0.961 | 0.0113 | 1.86×10^{12} | 12.27 |
| [Ni (SACAN) ClH ₂ O] | 0.711 | 0.705 | 0.0084 | 1.40×10^8 | 8.14 |
| [Cu (SACAN) ₂ (H ₂ O) ₂] | 0.775 | 0.755 | 0.0091 | 4.31×10^{12} | 12.63 |

The results agreed with Irving-William²¹, that the copper complex owning the highest stabilities, with some exception of the nickel complex²².

Solid complexes were prepared after learning the appropriate mole ratio and optimal conditions. Many techniques was used to investigate the formation of these complexes, beginning from TLC within reaction, then the elementary analysis (CHN & flame atomic absorption) as mentioned in (table 1).

FTIR data illustrated the action of complexes formation, via the variation in the site and shape of the functional groups, such the disappearance of the naphtholic hydroxyl group (N=N also group), due the coordination between the ligand electronic pairs and ionvacant orbits.²³

Indeed, the appearance of the (M-O) band of the coordination water molecule²⁴. Spectra can show in the appendixes.

Electrical molar conductivity & magnetic susceptibility

Ionic characteristic of the complexes could be deduced with their conductivity measurement, that the conductivity proportional with the ionic species in the solution²⁵, and varies according to solvent type, the non-electrolytic property can deduce when the conductivities have small values or when reaches zero. As we have shown in (SACAN) complexes, mentioned in the table.

Magnetic susceptibility enhanced the data with the determination of the electronic configuration of the metals and their oxidation state and the spin state of the complexes via odd electrons deducing that led to suggest the complex geometry.²⁶

-the cobalt complex owned (4.22BM), this agreed with the presence of three odd electrons of the octahedral cobalt complexes.²⁷

Due to the diamagnetic property of the nickel complex, its complex have a zero value with square planar complexes.²⁸

While copper complex has (1.81BM), for one odd electron in the octahedral complexes.²⁶ As in table.3

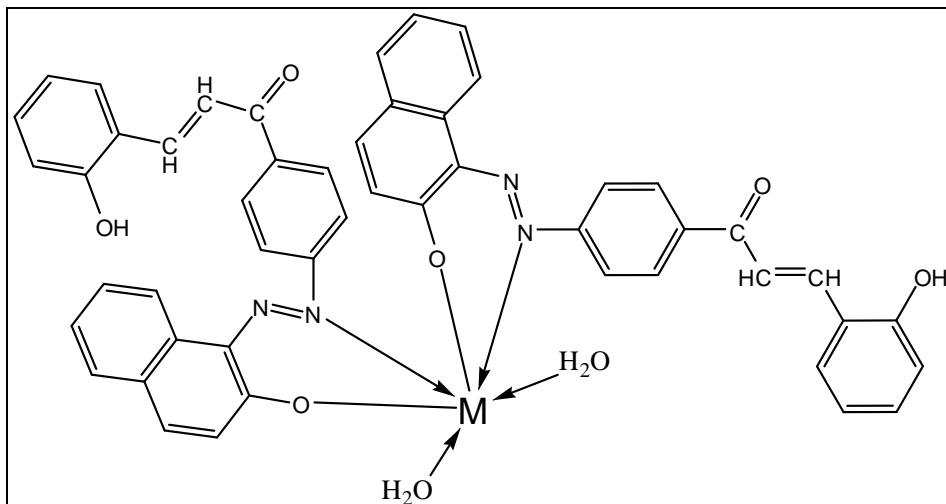
Table.3 conductivity and magnetic data for SACAN complexes

| Complex | Λ_m (S.mol ⁻¹ .cm ²) molar conductivity | | Magnetic susceptibility |
|--|--|---------|-------------------------|
| | DMF | Ethanol | |
| [Co(SACAN) ₂ (H ₂ O) ₂] | 18 | 22 | 4.22 |
| [Ni (SACAN) ClH ₂ O] | 12 | 21 | 0 Dia |
| [Cu (SACAN) ₂ (H ₂ O) ₂] | 20 | 15 | 1.81 |

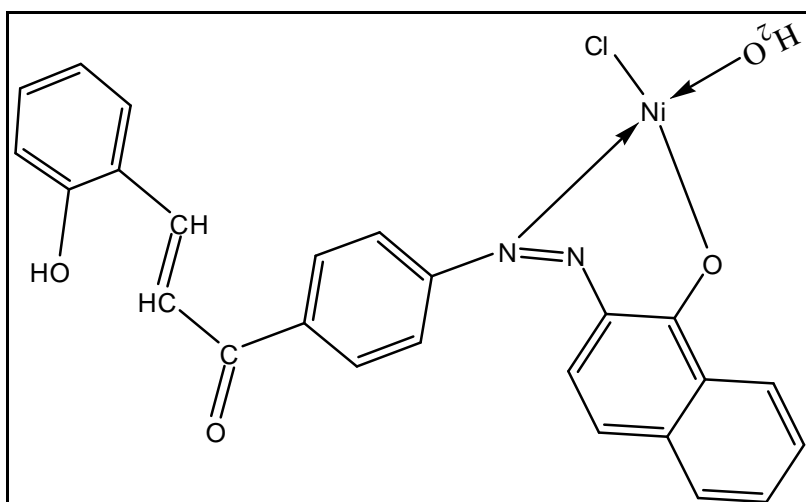
due the difficulties in the electronic spectra determination (especially d-d transition), because it was forbidden firstly, and very weak to detected, they was excluded in this study.

From the data results in this study, they can conclude that the ligand SACAN behave as bidentate ligand that chelated from the nitrogen azo atom and naphthol oxygen atom to form two type of complexes with the metallic ions, as below :-

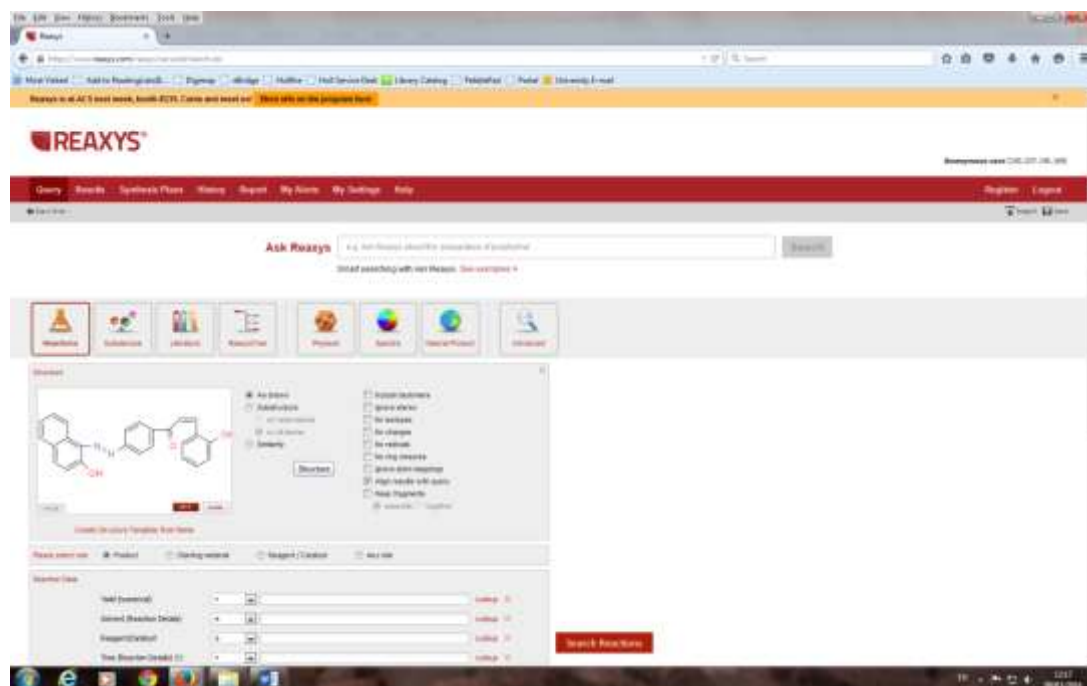
An octahedral complexes with Cobalt and Copper, with the present of two aqua molecule within coordination (that proved with CHN and FTIR data), with a non-electrolyte property and the mole ratio (1:2 M:L).

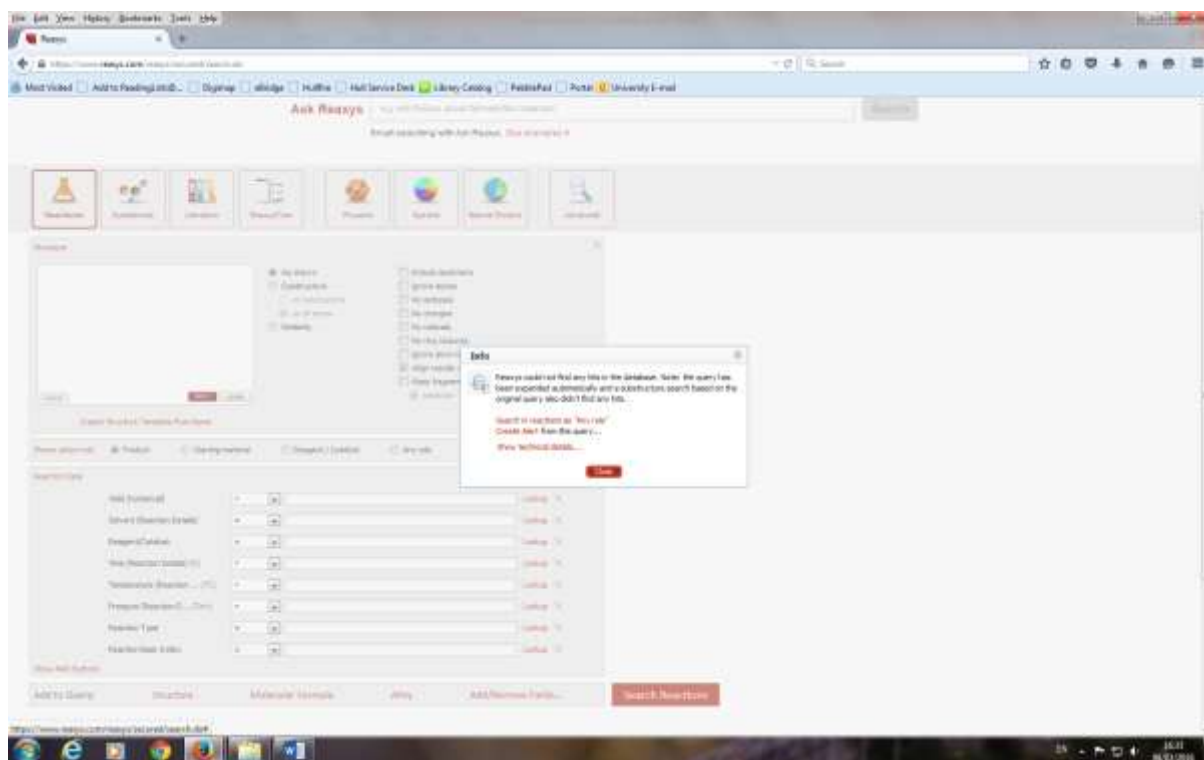


While the Nickel complex owned the square planer geometry ,with the presence of an aqua molecule and the mole ratio (1:1 M:L).



The novelty of the ligand SACAN was insured with REAXYS.com

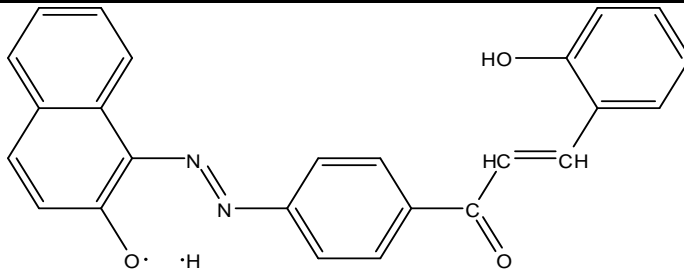




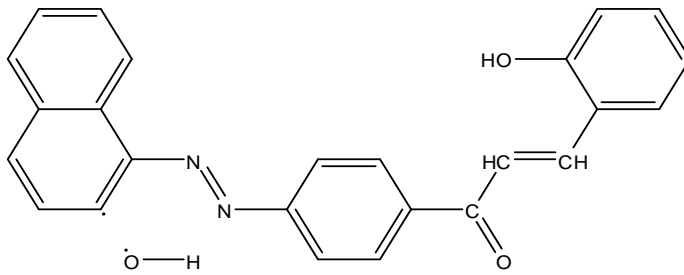
Appendixes

1. The ligand (SACAN) fragmentation route .
2. FTIR Spectra of Cobalt complex.
3. FTIR Spectra of Nickel complex.
4. FTIR Spectra of Copper complex.

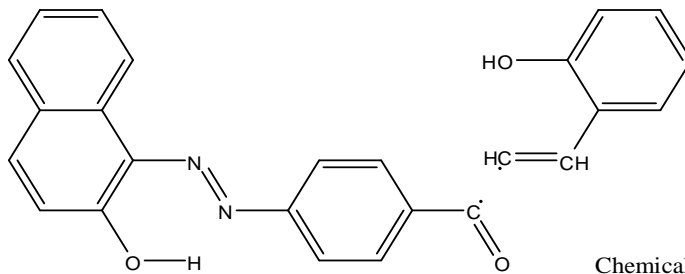
1.Many fragments appears within the (SACAN) Mass spectra, this includes;



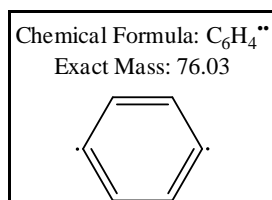
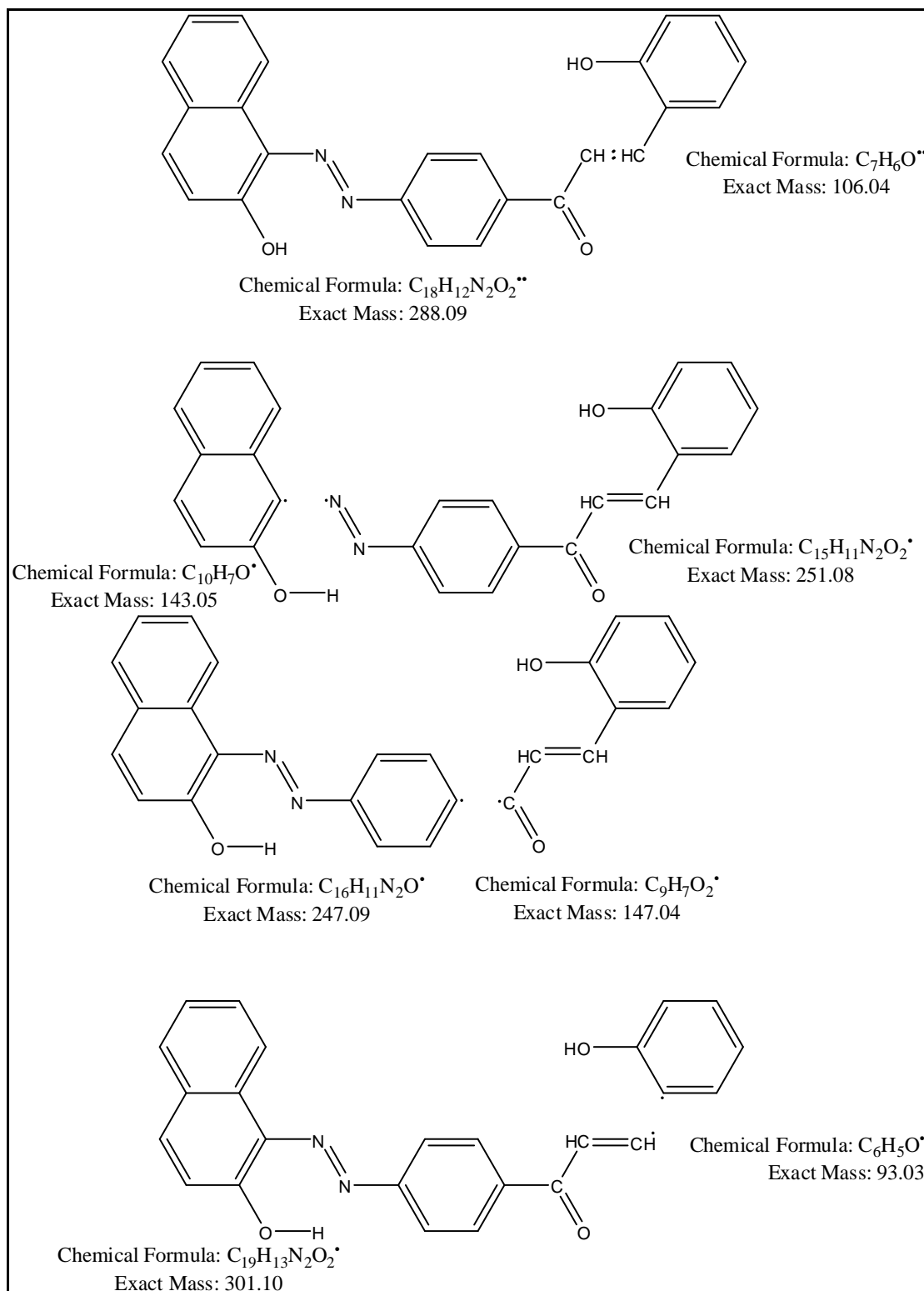
Chemical Formula: H^{\bullet} Chemical Formula: $C_{25}H_{17}N_2O_3^{\bullet}$
 Exact Mass: 1.01 Exact Mass: 393.12



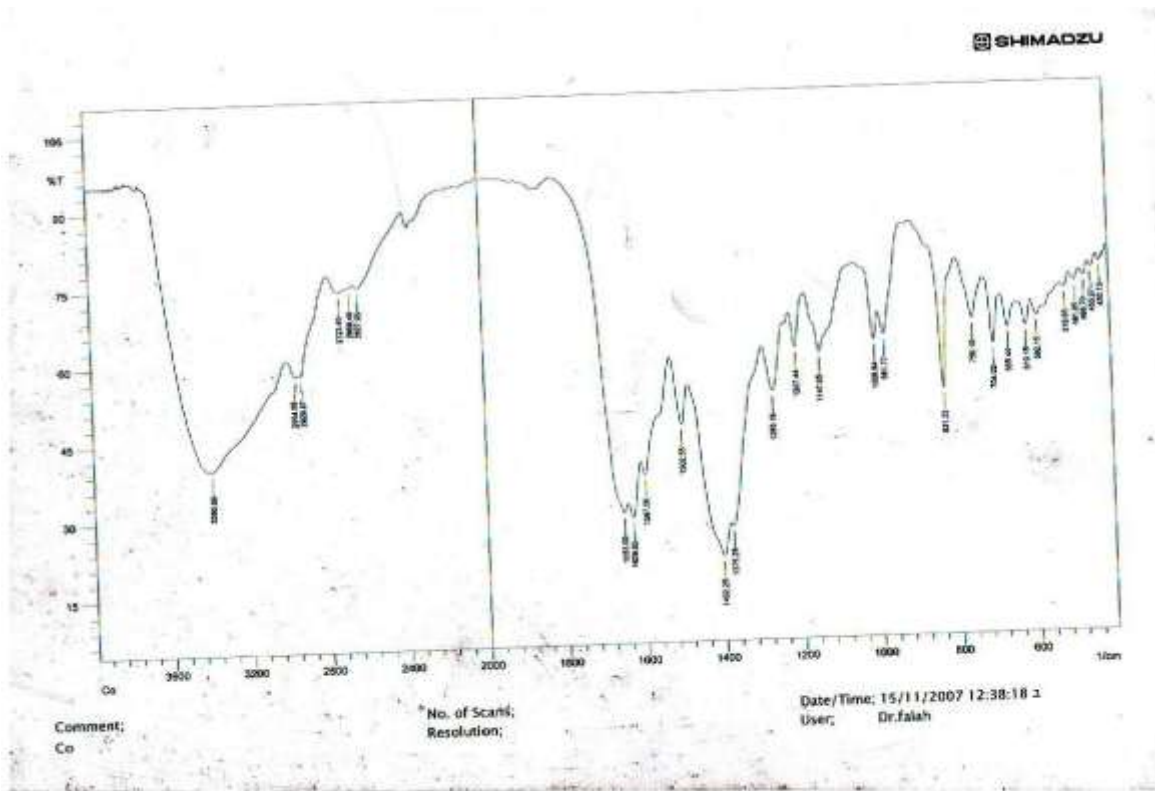
Chemical Formula: HO^{\bullet} Chemical Formula: $C_{25}H_{17}N_2O_2^{\bullet}$
 Exact Mass: 17.00 Exact Mass: 377.13



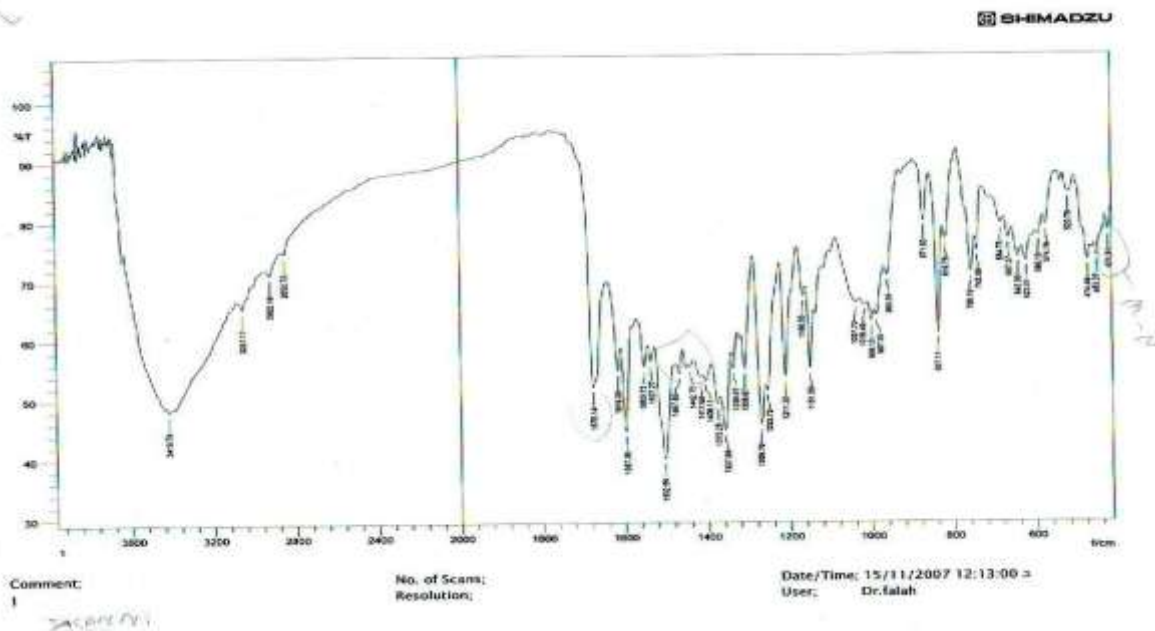
Chemical Formula: $C_{17}H_{11}N_2O_2^{\bullet}$ Chemical Formula: $C_8H_7O^{\bullet}$
 Exact Mass: 275.08 Exact Mass: 119.05



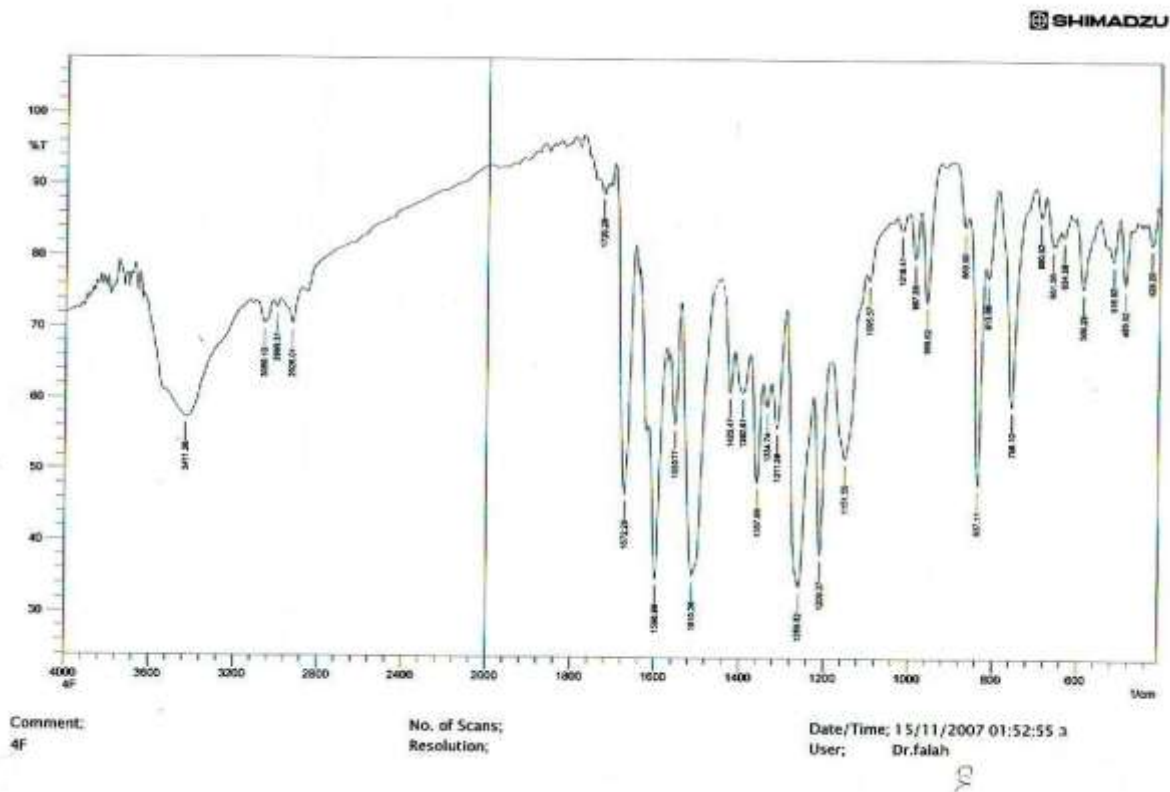
2.Cobalt complex



3.Ni complex



4. Copper complex



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