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Preparation and identification of new Azo (methyl-xanthine) ligands and their transition metal complexes.

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Abstract : Two of new azo methyl-xanthine ligands were prepared, via the reaction of the diazonium salt of amino antipyrine with the coupling components (caffeine and theophylline) in a 5% basic media in 0°C . The legends were identified with many techniques to ensure the formation of these compounds such (FTIR spectroscopy, elementary analysis and mass spectroscopy).

Three of divalent transition metal ion complexes (Co, Ni and Cu) for each ligand prepared, after the fixation of the preparation demands (optimal concentration, optimal pH and M:L ratio), these were resulted from the an extensive UV-Visible study of the aqueous solutions of these complexes. Two methods were used for M: L ratio determination (the mole ratio & continuous variation methods), all these indicated the (1:2, M:L) ratios for all complexes.

The solid complexes were prepared and identified with the previous techniques (except mass spectroscopy). Indeed there are many complimentary techniques were used for the determination of the solid complexes geometry as (electrical molar conductivity, magnetic susceptibility).

All complexes have the ionic properties with the presence of chloride ion out of the coordination core.

Magnetic susceptibility data agreed with the present of (three odd electrons for cobalt complexes, two odd electron for nickel complexes & odd electron for copper complexes) for the two prepared ligands.

One pot data indicate the octahedral geometry for all complexes, and the prepared ligands behaves as bidentate ligand via the imidazole nitrogen and the far azo nitrogen atom.

Keywords : methyl xanthine - Azo, Azo compounds, caffeine, theophylline, transition metal complexes.

Introduction:-

Drugs can characterize and analyzed by using many analytical techniques (Spectrophotometric, FTIR, NMR, MS and others)¹, the colorimetric method regarded as one the famed one², while the formation of azo dye was one of them³ when the drug component have a degree of nucleophilicity that can react readily with the diazonium salt to form a suitable color azo compound, that can characterize colorimetry owning specific λ_{max} in the visible region of the UV-visible spectrum.

Methyl-xanthines (Caffeine and theophylline) are in the family of alkaloid methyl-xanthins, can be normally found in cola nuts, coffee bean, tea leaves and other kind of plants⁴ they were used as stimulators especially caffeine the most frequently psychoactive substance in the world⁵.

Methyl-xanthine (especially theophylline) can determine by spectrophotometry⁶, titrimetry⁷, complexometry⁸, colorimetry⁹, phosphorimetry¹⁰ and chromatography¹¹. While an azo coupling reaction with (sulfanilic acid) act as classic method for determination (pauly reaction)¹². Indeed, many azo-theophylline was synthesized from coupling with salt of diazonium of different aniline derivatives^{13,14,15}.

Caffeine in the other hand, measured mostly by chromatography method (HPLC)¹⁶, and scarce literature, which focused on the determination of caffeine using the azo reaction¹⁷.

The utilizing of these azo-methylxanthine in the field of analytical chemistry, via complexation of these chelates with ions of the metals.

Through our expansion in search of the literature, we did not find only a few research^{18,19}, it is believed that the reason for this is attributed to the lack of researchers in this area, while we did not find any inorganic chemistry study and was limited to the analytical side only.

So it was our vision to engage in the midst of thread and worked to prepared and identified of two azo-methyl xanthine ligands (TAAP & CAAP) and their transition metal element complexes.

Experimental

All chemicals used in this work were of analytical reagent grade from (Fluke, BDH and Sigma).

- (C.H.N) % for the ligand and its complexes determined by (Micro Analytical unit, 1108 CHN Elemental analyzer).
- Melting points with (Stuarts SPM300).
- UV-Visible spectroscopic data by (Shimadzu 1650 PC).
- Mass spectra was done by (Shimadzu GCMS QP2010 ultra) with ionization energy (5-20 eV).
- IR Data by using (Shimadzu 8400S FTIR test scan series).
- Molar electrical conductivity measured by (Info lab terminal).
- Balance magnetic Susceptibility Model MSB-MKI.

Procedures

Azo compound preparation

Azo -methylxanthine ligands were prepared, via preparation of diazonium salt of p-amino antipyrine (0.01 mole, 2.03 gm) dissolved in a cold acidic media (10 ml conc. HCl + 10 ml D.W), then transfer the component to a crushed ice bath, then a solution of NaNO₂ (0.01 mole, 0.7 gm) in 10 ml D.W was added carefully and dropwise to the antipyrine solution at 0°C then it left for 15 min. to complete the diazotization.

The coupling component of methylxanthin (theophylline 0.01 mole, 1.8 gm & caffeine 0.01 mole, 1.94 gm) were dissolved in 5% aqueous basic solution (KOH for theophylline¹³, NaOH + Na₂CO₃ (modified procedure) for caffeine), then transfer the container to the iced bath, after the diazotization period was complete, the diazonium solution was dropped on the methylxanthin solutions with stirring at 0°C, the brown colour was observed within operation and the pH value was adjusted to a neutral value, hence the azo dye was formed as fine powder, then they filtered and washed with DDW to remove the trace of salt formed and dried with 80°C oven, then recrystallized with hot ethanol, and the yields were calculated for each dye.

Azo complex preparation

Methyl xanthine azo complexes were prepared with the same procedure, after the fixation of optimal conditions (pH and concentration), indeed to the suitable mole ratio for solid complex preparation (M:L, 1:2), that a 0.01 mole of each ligands (0.79 gm of TAAP and 0.818 gm of CAAP) were dissolved in 75 ml hot absolute ethanol and transferred to the 250 ml round bottom flask, then a 0.005 mole of metal chloride salts of (Cobalt, Nickel and Copper) dissolved in their optimal pH value of ammonium acetate buffer solutions, the salt solution was dropped slowly on the ligand solution with stirring and heating at 70°C, and the reaction complete within one hour, with the monitoring by TLC technique then the reaction mixture reduced to the half, and with the assistance of iced bath, the colored fine crystal of the complex appeared, filtered and washed with

few amount of hot ethanol : water mixture to remove unreacted compound , dried at 80C° oven then the yield calculated.

Table 1. Some Physical properties and Elementary analysis for the ligands and their 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)
CAAP	408.41	brown	144-146	88%	55.93 (55.88)	4.98 (4.94)	27.45 (27.44)	----- ----
[Co(CAAP) ₂ (H ₂ O)Cl]	964.68	Black brown	163-165	80%	47.38 (47.31)	4.42 (4.39)	23.28 (23.23)	6.16 (6.11)
[Ni(CAAP) ₂ (H ₂ O)Cl]	964.44	Deep maron	173-175	83%	47.33 (47.32)	4.43 (4.39)	23.27 (23.24)	6.15 (6.09)
[Cu(CAAP) ₂ (H ₂ O)Cl]	969.30	Brisk	151-153	79%	47.11 (47.09)	4.40 (4.37)	23.18 (23.12)	6.59 (6.56)
TAAP	394.39	Brown reddish	149-151	86%	54.88 (54.82)	4.61 (4.60)	28.48 (28.41)	----- ----
[Co(TAAP) ₂ (H ₂ O)Cl]	936.63	Honey	210-212	82%	46.22 (46.16)	4.11 (4.09)	23.99 (23.93)	6.33 (6.29)
[Ni(TAAP) ₂ (H ₂ O)Cl]	936.39	Maroon	213-215	81%	46.20 (46.18)	4.13 (4.09)	23.98 (23.93)	6.35 (6.27)
[Cu(TAAP) ₂ (H ₂ O)Cl]	941.24	Deep brisk	170-172	81%	45.98 (45.94)	4.10 (4.07)	23.88 (23.81)	6.80 (6.75)

CAAP= C₁₉H₂₀N₈O₃ , TAAP= C₁₈H₁₈N₈O₃

CAAT = Caffiene azo antipyrine

TAAP= Theophylline azo antipyrine

Results and discussion

Azo compound preparation methods vary depending on their components (coupling and amine) and their condition is not the same²⁰.

Methyl xanthines can be regarded as coupling components, due to they owned a degree of nucleophilicity at C8 position, it can developed in a basic media.

In this article they used 5% KOH solution for theophylline, while a mixed 5% basic (NaOH +Na₂CO₃) solution was used for caffeine, to avoid dissociation and enhanced the nucleophilicity.

Two of methyl xanthine azo ligands were prepared, via coupling the diazonium salt of 4-amino antipyrin with (theophylline and caffeine) in 5% basic solution at 0 C° as in the following reaction.

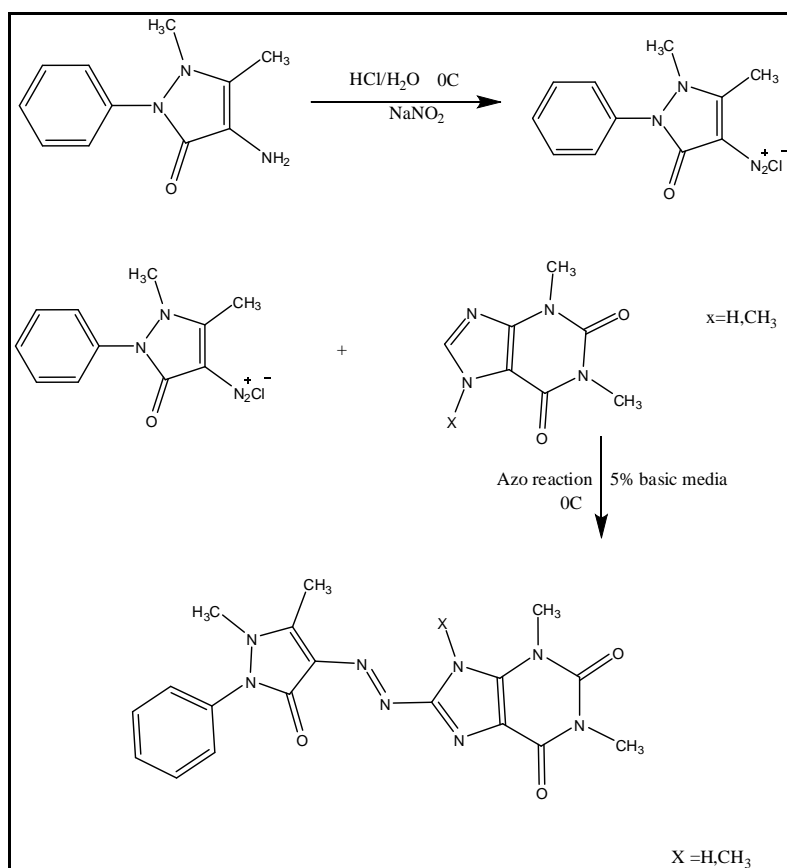
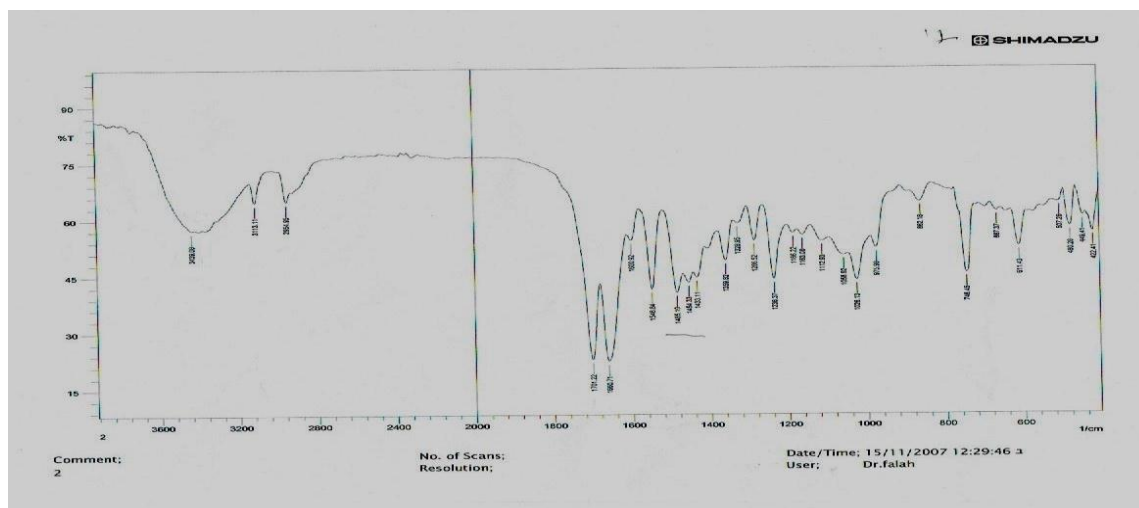


Fig.1 Schematic reaction of (TAAP & CAAP) preparation

These ligands were brown fine powder, insoluble in water, but soluble in most organic solvents (ethanol, methanol, acetone, DMF, DMSO, acetonitrile, chloroform and dichloromethane).

FTIR technique can be utilized for organic compound identification²¹, it can show the functional groups of the chemicals, the main functional groups of azo compounds can be observed in the IR spectra, in this work there are some groups developed for (CAAP & TAAP) as (N-H imid str. 3438cm^{-1} & 3487cm^{-1}) for the two ligands respectively.

Imidazole azomethine gives a strong band in the region (1600 & 1597) cm^{-1} , while the azo dye group (N=N) is observed within (1454 & 1452) cm^{-1} , xanthine carbonyl system was clearly shown at (1660 - 1701) cm^{-1} , these can be seen in Figure 2.



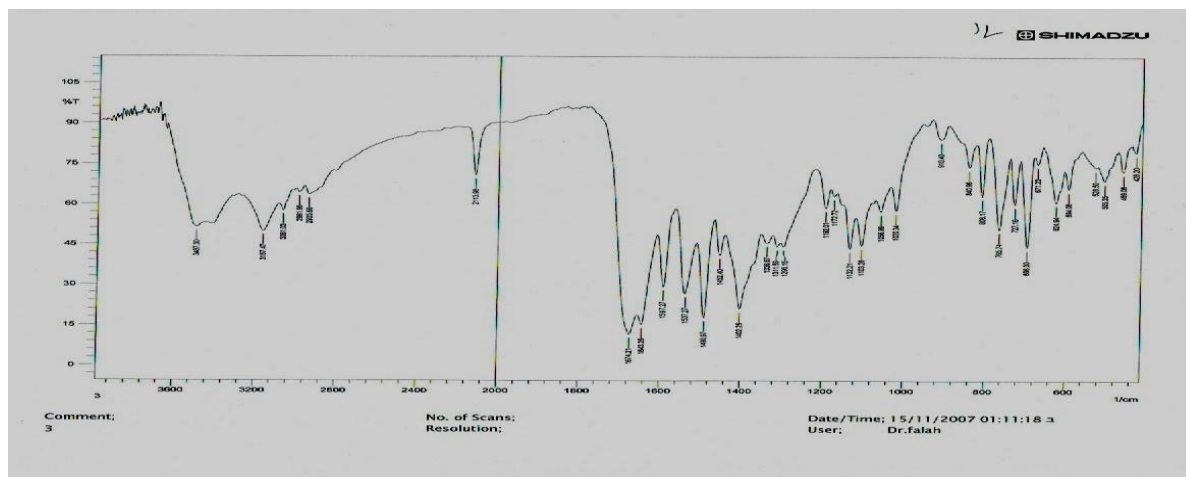


Fig.2 FTIR Spectra for (CAAP) & (TAAP)

Another analytical technique was used for identification, **Mass spectroscopy**, they can able to sort ions based on their mass (weight), one of the mass spectrum usage to determine the masses of the particles and of molecules, and to elucidate the chemical structure of the molecules²².

Mass fragmentation of the ligands (TAAP & CAAP), detected the M and (M+1) clearly, that the molecular mass of these ligands obtained from their spectras , as aresults the (m/z)that equavelant to the mass of CAAP , was equal to (408), while TAAP (m/z)equal to (394), the spectras can shown in fig.3

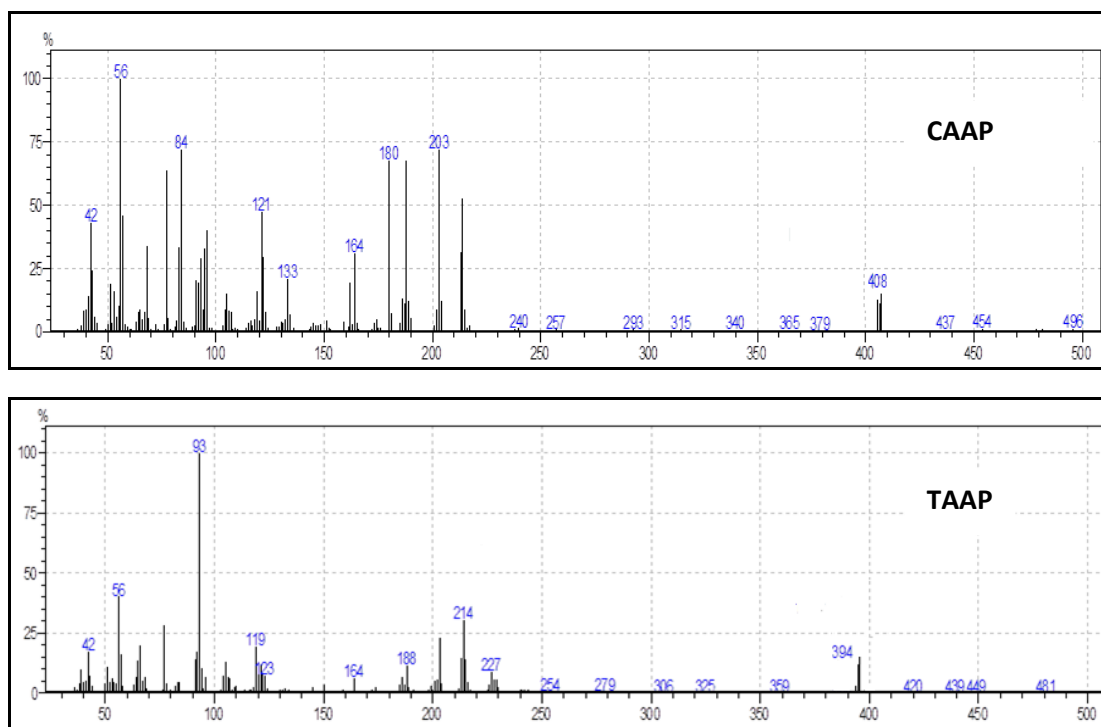


Fig.3 Mass spectra of (CAAP & TAAP)

Optimal condition determination

Organic ligands can act as chelating agent, due to their owing of donating atomsthat used for ions coordinating and they can determine them colorimetry using UV-Visible technique, that the colored mixtures have specific (λ_{max}) under condition (conc.&pH), that obey the lambert – beers low.

In the UV-Visible study the ligands (CAAP & TAAP) λ_{max} were determined, spectrophotometry as shown;

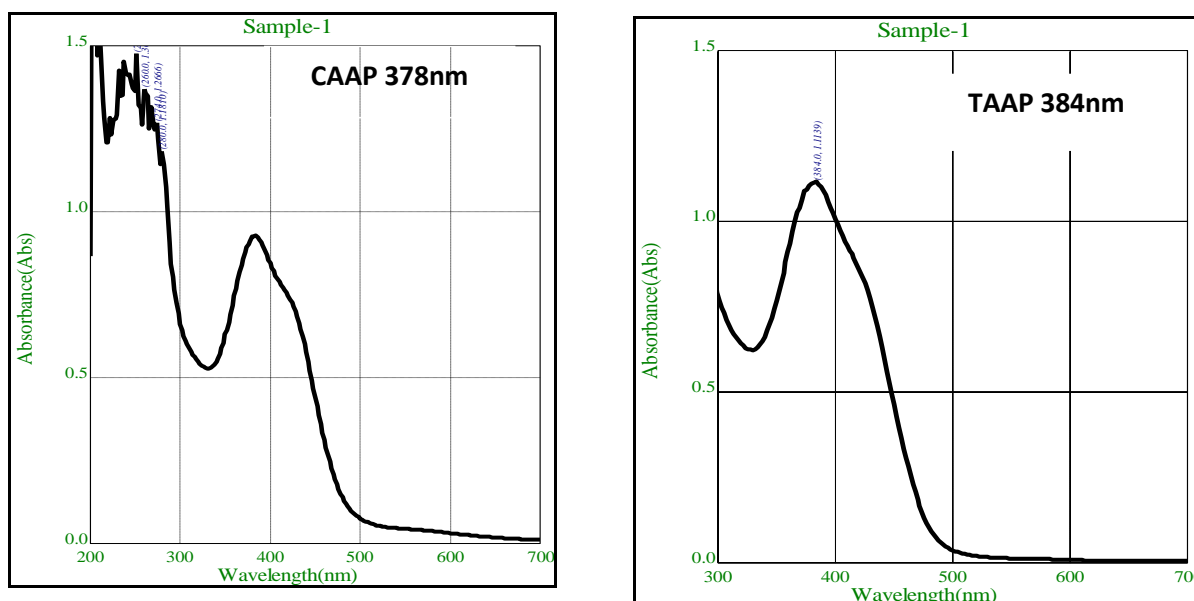


Fig.4 UV-Visible spectra of the prepared ligands.

Optimal conditions must be obtain, for solid complexes preparation, an extensive study done in this work that the limit of concentration given (10^{-6} - 10^{-3})M and the pH range (5-11) using the ammonium acetate as a buffer, in the study three divalent transition metal ions (Co^{2+} , Ni^{2+} and Cu^{2+}) were used, the vivid color of the mixture which differ from the ligands color, and the red shifting of the spectra believed because of the coordination.

In the results, the optimal concentration that obey (Lambert-Beer) law within (10^{-5})M, and the optimal pH values (7-9.5).

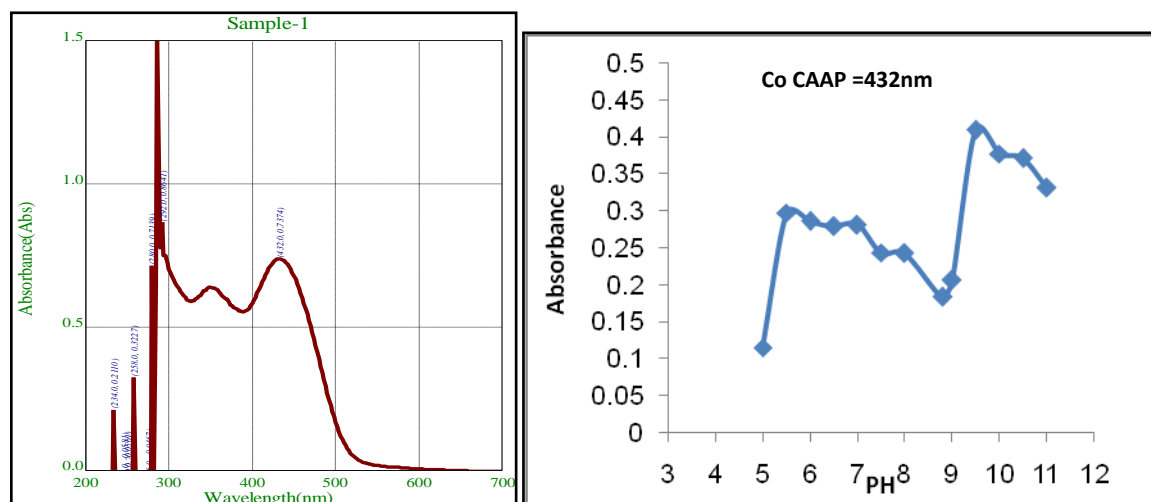


Fig. 5 optimal condition for the cobalt –CAAP at 8×10^{-5} M

Metal :ligand ratio

was used to deduce the possible structural formula of the prepared complexes, under their optimal conditions and maximum wavelengths, two ways were adopted in this work (mole ratio and continuous variation method)²³ used to obtain the M:L value, all results indicated that the M:L values were (1:2) for all complexes in the two methods used, as in the following:

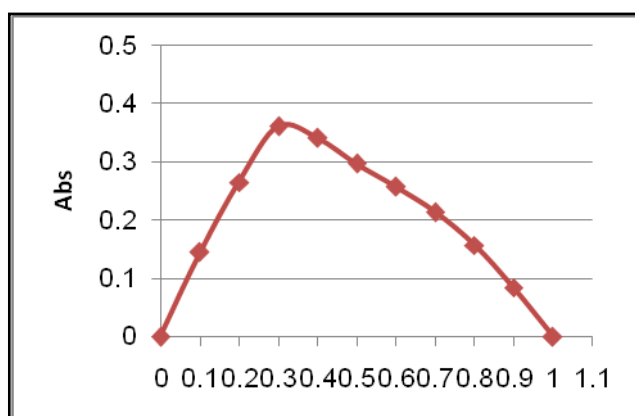
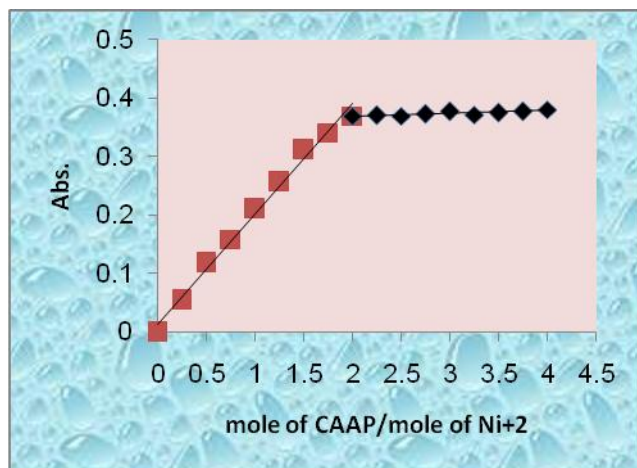


Fig.6 M:L ratio of the Nickel CAAP complex.

Stability constant calculation

Stability constant for the complexes in their solutions can determine with spectroscopic method²⁴, especially if colored complexes have taking the advantages of the absorbances values of the (ligand-metal ion)mixtures at optimal condition and (λ_{max}), in mole ratio method, by using the relation

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

where A_s = the absorbance at the mole ratio, A_m = the absorbance with a ligand component increment. α =

dissociation constant. $\beta = \frac{1 - \alpha}{4\alpha^3 c^2}$, for (1:2) ratio, β = stability constant and c = the concentration of the two components (ligand & metal ion) in the study.

Data was observed in table.2, the stability constants of the studied complexes was agreed the Irving-Williams arrangements²⁵ that the copper complexes more stable than others, with some deviation in nickel complexes.²⁶

Optimal condition can illustrate in table.2

Table .2 Optimal condition data for (TAAP&CAAP)

Ligand (5×10^{-5})M Conc.	Metal ion	λ_{\max} nm	Optimal Conc. $\times 10^{-5}$	Optimal pH	$\epsilon \times 10^3$ L / mol.cm	β L ² /mol ²	log β
TAAP $\lambda_{\max} = 384\text{nm}$ $\epsilon = 12 \times 10^3$ L /mol.cm	Co(II)	426	8	9	4.2	2.29×10^{12}	12.3
	Ni(II)	444	7	9	4.18	1.11×10^{12}	12.04
	Cu(II)	450	6	7	4.5	3.32×10^{12}	12.52
CAAP $\lambda_{\max} = 378\text{nm}$ $\epsilon = 9 \times 10^3$ L /mol.cm	Co(II)	432	8	9.5	5.1	2.65×10^{12}	12.42
	Ni(II)	430	7	9	5.2	2.07×10^{12}	12.31
	Cu(II)	428	7	8.5	4.4	4.32×10^{12}	12.63

Solid complexes were prepared depending on the optimal condition needed, the complexes synthetic were confirmed via TLC, elementary analysis and FTIR technique, an increment in (hydrogen atom) in elementary analysis may attributed to the presence of an aqua molecule within complexes, this will be confirmed with FTIR results, later.

FTIR data emphasized the complex formation²⁷ via the alteration of the shape and site of two means bands, due to the coordination with the azo-methylxanthin ligands, by shifting of the azomethane and azo group towards lower frequencies, included the appearance of metal-nitrogen band²⁸, while a broadening in most complexes due to the appearance of an aqua molecule, that has a hydroxyl group interfered with (imidazole N-H) band, and appeared clearly in the others. And its oxygen atom can coordinate to the metal ions²⁸.

FTIR data presented in table.3

Table.3 FTIR data for (CAAP &TAAP) and their complexes in cm^{-1}

Compound	imdN-H	Aq.(OH)	Imd(C=N)	N=N	M-O ^w (H ₂ O)	M-N
CAAP	3439	----	1600	1454	-----	-----
CoCAAP	3440	Int.	1591	1435	914	462
NiCAAP	3434	Int.	1591	1429	910	437
CuCAAP	3432	Int.	1591	1446	900	435
TAAP	3487	----	1597	1452	-----	-----
CoTAAP	3485	3429	1593	1435	916	457
NiTAAP	3488	3408	1591	1442	881	432
CuTAAP	3484	3414	1589	1444	875	439

FTIR Spectra of the copper complexes are shown as :

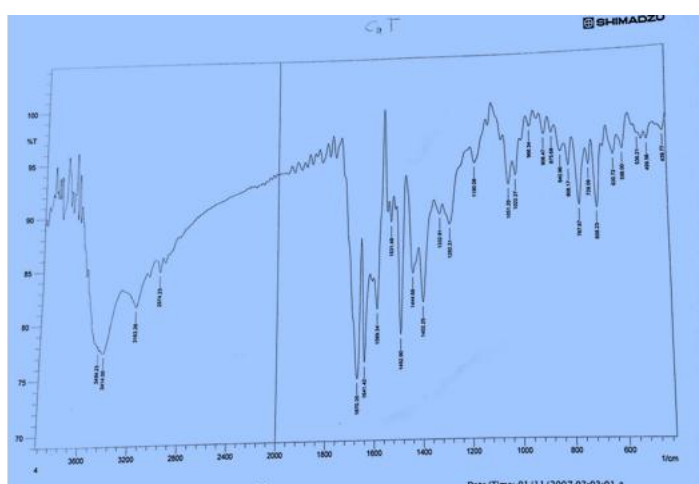
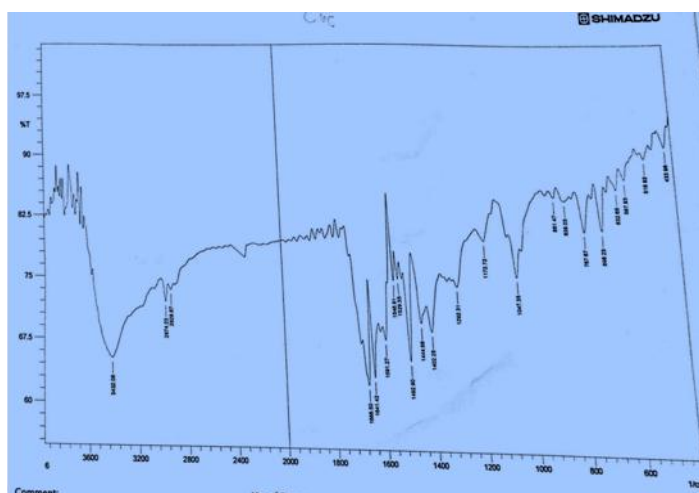


Fig.7 Copper complexes FTIR Spectra

Electrical Molar conductivity

Ionic formula of the complexes could be known by conductivity measurement, that the electrical conductivity proportional to the charged species in the solution²⁴, reach zero value in non-ionic complexes.

The present work , three solvents was used for solvation of the complexes at room temp and 10^{-3} M concentration, all measurements confirmed that all complexes were ionic by the ratio (1:1), this means the presence of free chloride ion in the solutions, the electrical molar conductivity data shown in the following table :

Table .4Electrical molar conductivity at 25C° and 1×10^{-3} M conc.

A_m (S.mol ⁻¹ .cm ⁻²)			Complex
(DMF)	(DMSO)	(EtOH)	
35.1	42.5	42.1	[Co(TAAP) ₂ (H ₂ O)Cl] Cl
39.0	26.5	34.8	[Ni(TAAP) ₂ (H ₂ O)Cl] Cl
52.0	34.5	36.6	[Cu(TAAP) ₂ (H ₂ O)Cl] Cl
42.3	48.6	37.4	[Co(CAAP) ₂ (H ₂ O)Cl] Cl
87.0	60.7	45.3	[Ni(CAAP) ₂ (H ₂ O)Cl] Cl
75.0	52.2	41.7	[Cu(CAAP) ₂ (H ₂ O)Cl] Cl

Magnetic susceptibility data

Magnetic susceptibility data act as a complementary tool for the complexes geometry suggestion (especially for TME's)²⁹, via the study influence of the partially filled outer orbital, magnetic data supplied us with the electronic contribution and the metal oxidation state, that the number of odd electron(s) for the metal play a role which either complex in the high - spin state or low³⁰.

-The Cobalt complexes have a (4.18 & 4.33 B.M) values for (Co-CAAP and Co-TAAP) complexes respectively and this agreed with the abundance of three odd electrons of octahedral cobalt complexes³¹

While the Nickel complexed gives a (3.08 & 3.11) B. M for (CAAP and TAAP) complexes respectively , this will agreed with octahedral nickel complexes that have two odd electrons³⁰.

Copper susceptibility values were (1.87 & 1.83) B.M for copper complexes of the two ligands (CAAP and TAAP); this was tuned with the odd electron octahedral copper complexes as in literature³².

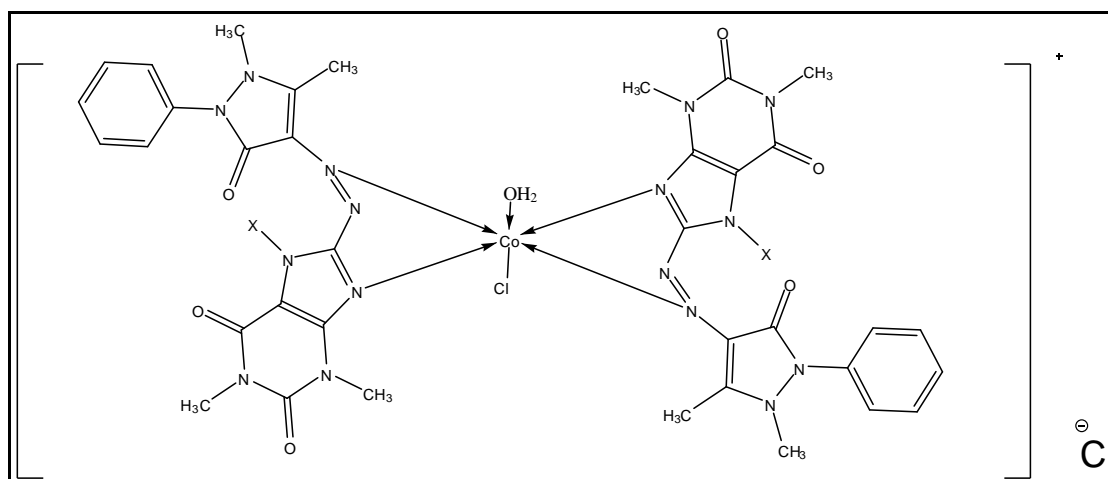
Electronic spectra of the complexes was not studied in this work, due to the weakness of the d-d transitions (forbidden), and there are interfered with the CT band of the complexes.

Suggested complexes geometry

Work results indicated that the azo methylxanthin ligands (TAAP&CAAP) complexes have

- the octahedral geometry
- the ligands chelated from the imidazole nitrogen atom and the far azo nitrogen atom.
- the complexes was ionic
- the present of aqua molecule within coordination sphere .

An example of these complexes geometry , as shown in the following cobalt complexes.



Where x = H for (CoTAAP), x=CH₃ for (CoCAAP).

Figure.8 Cobalt complexes geometry

Conclusions:-

Form the work results , we coulded :-

1. Methyl xanthin (theophylline and caffeine) can measure spectrophotometrically via azo reaction, in addition to the chromatographic methods.
2. They can form an organic ligands via coupling with different amines, in a feasible procedure .

3. These ligands can utilize in the field of analytical chemistry, due to their sensitivity to a low ionic concentration, and formation of vivid colored solution can detect colorimetry .
4. Azo methylxanthin can formed a stable complexes with metallic ions, espically TME, have different geometries according to their conditions and results.
5. They believe that the ligands and their complexes have to some extent, biological activity against microbial .

The novelty of the ligands was developed in (REAXYS), that they were new ligands as :

The screenshot shows the Reaxys search interface. At the top, there is a search bar with the text "Ask Reaxys" and a search button. Below the search bar, there are several navigation icons: Reactions, Substances, MedChemistry, Literature, ReaxysTree, Physical, Spectra, Natural Product, and Advanced. The main area displays a chemical structure of a ligand, which is a substituted benzothiazine derivative. To the right of the structure, there are several checkboxes for search options, including "Include tautomers", "Ignore stereo", "No isotopes", "No charges", "No radicals", "No ring closures", "Ignore atom mappings", "Align results with query", and "Keep fragments". Below the structure, there is a "Please select role" section with radio buttons for "Product", "Starting material", "Reagent / Catalyst", and "Any role". At the bottom, there is a "Reaction Data" section with dropdown menus for "Yield (numerical)", "Solvent (Reaction Details)", and "Reagent/Catalyst", each with a "Lookup" button. A "Search Reactions" button is located at the bottom right.

The screenshot shows an "Info" dialog box with the following text: "Reaxys could not find any hits in the database. Note: the query has been expanded automatically and a substructure search based on the original query also didn't find any hits." Below this text, there are three links: "Search in reactions as 'Any role'", "Create Alert from this query...", and "Show technical details...". A "Close" button is located at the bottom right of the dialog box.

This screenshot is identical to the one above, showing the Reaxys search interface with the same search bar, navigation icons, chemical structure, search options, and "Search Reactions" button.

This screenshot is identical to the one above, showing the "Info" dialog box with the same text and links.

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