

## ORIGINAL ARTICLE

# Synthesis and Characterization of Mixed Ligand Complexes [M(L)(caf)](H<sub>2</sub>O) M=Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>; H<sub>2</sub>L=azo, caf=caffeine

M. Bouhdada<sup>1</sup>, M.EL.Amane\*<sup>1</sup>, M. Hadad<sup>2</sup>

1 Team Metallation, molecular complexes and Applications Laboratory Molecular Chemistry and Natural substances Moulay Ismail University, Faculty of Science, BP11201 Zitoune Meknes, Morocco

2 Team archiometric spectrometry and physical chemistry of materials (lasmar, URAC11)

Moulay Ismail University, Faculty of Science, BP11201 Zitoune Meknes Morocco

\*Corresponding author: lelamane@gmail.com

### ABSTRACT

(Sodium 2,2'- hydroxyl -1,1'- Azonaphthalene-4-sulfonic-) azo ligand (H<sub>2</sub>L) and its Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> complexes have been synthesized and characterized by Infrared, <sup>1</sup>H, <sup>13</sup>C NMR, UV-Visible, EPR, molar ratio method and molar conductance. These results are in agreement for the formula [M (L)(caf)](H<sub>2</sub>O); M= Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup>. Correlation of all spectroscopic data suggest that (H<sub>2</sub>L) ligand acts as dianionic tridentate ligand with NOO sites coordinating to the metal ions via deprotonated naphtholic-O and nitrogen azo (N=N) with monodentate caffeine coordinating to the metal ions via the N9 imidazol group. All complexes have mononuclear structure and tetrahedral geometry have been proposed.

**Keywords:** Azo, caffeine, Complexes, FT-IR, <sup>1</sup>H, <sup>13</sup>C NMR, UV-Visible, EPR, molar ratio, molar conductance.

Received 01.04.2016 Accepted 05.06.2016

© 2016 AELS, INDIA

### INTRODUCTION

Nitrogen donor ligand such as caffeine (1,3,7-trimethylxantine) is one of the main alkaloid formed in various kinds of foods and drinks that we consumed in daily life. It is naturally found in leaves, see do of fruits of 63 plant species [1]. The most common sources of caffeine are coffee, coca beans, cola must and tea leaves [2]. The caffeine mostly coordinated through it's N-donor atom or went through O-donor atom, with is a rarity. The metal complexes are monomeric, dimeric, several correlations are stabilized and discussed for coordination of caffeine and derivatives.

The azo are the most important class of synthetic dyes representing (60-80 %) of all organic colorants they are used widely in substrates such as textile fibers [3], leather, plastic [4], papers, hair, mineral oils, waxes, food stuffs and cosmetics [5]. Many other in industrial applications, such as the manufacturing of dyes, cosmetic [6], medicine [7] and rubble, release wastes into streams, with concentrations as high as 10 g l<sup>-1</sup>.

Because of their threat to the environment [9], different methods have been developed to provide a rapid and sensitive means to detect these compounds.

Azo dyes present in textile wastewater require removal due their negative environmental and health effects current method in the removal of azo dye either require the absorption, advance oxidation processes photo catalysis or Fenton's reagents etc. [10]

The azo ligand have the general structure R-N=N-R', where R and R' are alkyl, aryl, or heterocyclic group. Most of them are prepared by the condensation of azo compounds with hydroxyl aldehydes or ketones, several bidentate azo in which the phenolic or naphtholic OH group and azo nitrogen are present in such a way that they form six membered rings with metal ions [11]. A series of naphtholic azo dyes are extremely important in variety of industries for variety of technical purposes.

Azo ligand have been investigated by many workers as chelating agent and metallochromic indicators [8] their metal chelate and complexes have been widely used in various fields and technologies [12].

Azo compounds are known for their medicinal importance and are well recognized for their use as antineoplastics, antidiabetics, antiseptics, antibacterial, antitumors [13]. Metal complexes of reactivity important ligand are sometimes more effective than the free ligand transition metal ions Ag, Au, Fe, Co, Ni, Cu, and Zn have show more promising in analytical chemistry and biologically activity etc [14].

Studying the coordination nature of caffeine, azo ligand and determining the binding site to metal ions is perhaps a key to understand the physical and chemical properties. The azo ligand and caffeine are used widely in different areas, but any study related to the mixed ligand complexes of azo and caffeine was not found in the literature.

## MATERIAL AND METHODS

All chemicals were obtained from commercial sources and were used without purifications: (NiCl<sub>2</sub>, 6H<sub>2</sub>O BDH; ZnCl<sub>2</sub>, 2H<sub>2</sub>O BDH; CdCl<sub>2</sub>, 1/2H<sub>2</sub>O Panreac; CuCl<sub>2</sub>, 6H<sub>2</sub>O BDH, (Sodium 2,2'-hydroxyl -1,1'-Azonaphthalene-4-sulfonic-) azo ligand (H<sub>2</sub>L) and anhydrous caffeine was purchased from Riedel-Haen A.G, Ethanol and DMSO Sigma Aldrich, double distilled water was used.

Infrared spectra was recorded as KBr pellets on a JASCO FT-IR 4100 spectrophotometer in the range of 4000-400 cm<sup>-1</sup> at 298 K. While the UV-Visible spectra were obtained on a Shimadzu UV-1800 Spectrophotometer. The <sup>1</sup>H, <sup>13</sup>C NMR spectra of the ligand was recorded with a Bruker AVANCE 300 at 25°C. All chemical shifts <sup>1</sup>H and <sup>13</sup>C are given in ppm using tetramethylsilane (TMS) as internal reference and DMSO as solvent. The EPR spectrum was recorded on a conventional X band Bruker ER 200D spectrometer operating at 9.5 GHz et l'electroaimant de livre un champ allant jusqu'a 800 Gauss. Molar ratios and Conductivity measurements were performed at 25°C in DMSO using Shimadzu UV-1800 Spectrophotometer and Hach HQ430d flexi.

### Synthesis of the mixed ligand complexes [M(L)(caf)] (H<sub>2</sub>O) ; M= Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>; Caf=caffeine

Complexes of Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> with caffeine were prepared by adding (0.001mol) of a metal CuCl<sub>2</sub>, 6H<sub>2</sub>O (0.17g), ZnCl<sub>2</sub> (0.14g), CdCl<sub>2</sub>, 1/2H<sub>2</sub>O (0.23g), NiCl<sub>2</sub>, 6H<sub>2</sub>O (0.24g), to (0.41 g, 0.001mol) of the azo ligand (H<sub>2</sub>L) with (0.11g, 2 10<sup>-3</sup>mol) of hydroxyl potassium (KOH) in ethanol and (0.19 g, 0.001mol) of the caffeine in ethanol. After completion of the reaction, the precipitated was removed by filtration, washed with ethanol and dried over in a vacuum desiccators.

## RESULTS AND DISCUSSIONS

### Synthesis and Characterization infrared spectroscopy and UV-Visible of azo ligand (H<sub>2</sub>L)

The infrared spectra of azo ligand display a strong broad band at (3500-3400) cm<sup>-1</sup> corresponding to the ν OH of the naphthol[13-15] and crystalline water molecules figure (1). The two medium bands within the (2925-2852) cm<sup>-1</sup> range are assigned to the ν (OH...N)[15-16].

The high value ν(OH) indicates that this hydroxyl groups is involved in an intramolecular hydrogen bonding with the azo (N=N) group. In addition azo (H<sub>2</sub>L) can exist as hydroxyl azo or keto hydrazone tautomers and cis-trans isomers[15]. The band at 1615 cm<sup>-1</sup> belong to stretching vibration ν(C=N), which is in enol form and weak band at 3140 cm<sup>-1</sup> is due to the NH hydrazone form[14]. The bands at (1595-1513) cm<sup>-1</sup> corresponds to the ν (C=C) stretching vibrations of aromatic ring. The bands at 1506 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> are attributed to the ν (N=N) group in cis and trans isomers respectively[15-16]. The bands at 1506 cm<sup>-1</sup> of (N=N) group vibration in spectra of cis isomer is very strong, where as there is a weak band at 1400 cm<sup>-1</sup> of trans isomer[15]. The infrared spectra of the ligand exhibit two bands around (1303-1288) cm<sup>-1</sup> range corresponding to naphtholic bending OH hydroxyl [16-20]. The high value indicates that OH groups is involved in an intramolecular and intermolecular hydrogen bonding with the N=N group in solid state [16-20].

Moreover, the azo ligand (H<sub>2</sub>L) spectrum display the characteristic vibration of S=O associated with the stretching vibration of SO<sub>3</sub> group at 1186 cm<sup>-1</sup> and 1066 cm<sup>-1</sup> correlate to ν<sub>as</sub> SO<sub>3</sub> asymmetrical stretching and ν<sub>s</sub> SO<sub>3</sub> symmetrical stretching respectively [17-20].

In addition the two weak band within the (3056-2966) cm<sup>-1</sup> range are assigned to the ν CH vibrations of two naphtholic rings[18].

The UV-Visible spectrum of the free azo ligand (H<sub>2</sub>L) showed five absorption bands in the (225-567)nm region table(3). The strong absorption at 225nm was assigned to the naphtholic rings. The three broad and medium bands at 475nm, 537 nm, 576 nm was assigned to the azo π→π\* transition in the cis and trans isomers. The band at 335 nm are due to n→π\* transition; figure(5). [14].

### Synthesis and Characterization of the complexes [M(L)(caf)](H<sub>2</sub>O) ; M= Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> caf=caffeine

Three complexes have also been prepared by reacting then ligand H<sub>2</sub>L with metal ions Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup>. The preparation has been conducted in potassium hydroxide of stoichiometry metal / ligand / KOH (1/1/2). UV-visible spectra of these complexes solutions have been studied for a range of concentration (10<sup>-4</sup>-10<sup>-5</sup>)M which obey Lambert-Beers law. The formula of complexes are deduced according to molar ratio method which were obtained from the spectroscopic studies of the complexes solutions. The ratios of metal /ligand obtained are (1 /1) for all complexes.

**Conductance measurement:** The physico-chemical characteristics of the synthesized complexes are given in the table (1). The complexes are soluble in DMF and DMSO. The observed molar conductances of the complexes in DMSO for  $10^{-4}$  M solutions at room temperature are consistent with the non-electrolytic nature of the complexes.

Complexes	M.P. (°C)	Yield (%)	$\Lambda(\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1})$
[Cu(L)(caf)](H <sub>2</sub> O)	>280	40	5,16
[Ni(L)(caf)](H <sub>2</sub> O)	>280	35	4,92
[Cd(L)(caf)](H <sub>2</sub> O)	>280	33	4,50
[Zn(L)(caf)](H <sub>2</sub> O)	>280	30	3,58

**Table(1)** : Physico-chemical data of the complexes[M (L)(caf)] (H<sub>2</sub>O)

**Infrared spectroscopy of metal complexes [M(L)(caf) ] (H<sub>2</sub>O) ;M= Cu<sup>2+</sup>, Ni<sup>2+</sup>,Cd<sup>2+</sup> and Zn<sup>2+</sup> caf =caffeine; L= azo ligand.**

In the infrared spectrum of the complexes was observed between (3500-3450) $\text{cm}^{-1}$ . Bands were attributed to the stretching  $\nu(\text{OH})$  water hydration, figure(2). The hydrated water were eliminated from the complexes at relatively low temperature. The main infrared characteristic stretching frequencies of the ligands and its complexes [M(L) (caf)] (H<sub>2</sub>O) ; M= Cu<sup>2+</sup> Ni<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup>, caf= caffeine, L=Azo, along with their proposed assignments are given in table (2) The determination of the coordinating atoms is made on the basis of the comparison of the infrared of the two free ligands and its complexes.

The infrared spectra of free ligand (H<sub>2</sub>L), free caffeine and its complexes are given in figure(1). The two carbonyl group in the the azo caffeine complexes exhibit a strong absorption band in the (1698-1695)  $\text{cm}^{-1}$  range due to  $\nu(\text{CO})$  asymmetric. Another strong band in the (1652-1650)  $\text{cm}^{-1}$  range belong to  $\nu(\text{CO})$  symmetric and  $\nu(\text{C}=\text{N})$  is shifted to lower frequencies[18], compared with the free caffeine.

The bands at the 1615 $\text{cm}^{-1}$  and 1600  $\text{cm}^{-1}$  in the free azo ligand are due to  $\nu(\text{C}=\text{C})_{\text{caf}}$  and  $\nu(\text{C}=\text{C})_{\text{naph}}$ . In the infrared spectra for Cu(II), Ni(II), Cd(II) and Zn(II) complexes figure(2), the bands have been found in the range 1590  $\text{cm}^{-1}$  shifted to lower frequencies by (10-26)  $\text{cm}^{-1}$

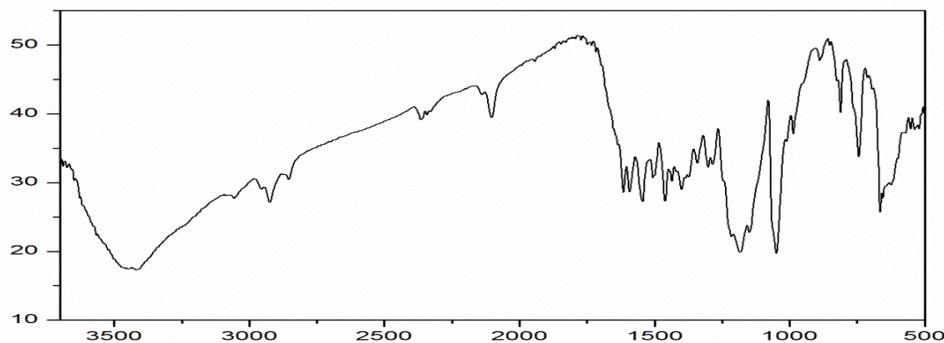
The bands at the 1558  $\text{cm}^{-1}$ , 1545  $\text{cm}^{-1}$  and 1513  $\text{cm}^{-1}$  in the free azo, caffeine ligands are due to  $(\nu(\text{C}=\text{C})_{\text{naph}} + \delta(\text{HCN}) + \nu(\text{imid}) + \nu(\text{pyri}))$ [12]. The bands have been found in the range 1540  $\text{cm}^{-1}$ , indicating coordination of the caffeine through the azomethine nitrogen atom (N9). The azo ligand (H<sub>2</sub>L) spectrum showed a band at 1506  $\text{cm}^{-1}$  due to  $\nu(\text{N}=\text{N})_{\text{cis}}$  in the spectra of the complexes show this band stretching about (1480-1490) $\text{cm}^{-1}$  shifted to lower frequencies by (16-26)  $\text{cm}^{-1}$ , which indicate the coordination of the ligand through the nitrogen atom of the azo group[14]. In the infrared Spectrum of the free azo ligand (H<sub>2</sub>L), the two naphtholic stretching  $\nu(\text{OH})$  and bending  $\delta(\text{OH})$  is observed at 3450  $\text{cm}^{-1}$ , 3400  $\text{cm}^{-1}$  and 1303  $\text{cm}^{-1}$ , 1288  $\text{cm}^{-1}$ . These bands of  $\nu(\text{OH})$ ,  $\delta(\text{OH})$  naphthol were absent indicates the coordination through the oxygen of naphthol group[14-18].

The new bands appeared in the spectra of metal complexes at (560-540)  $\text{cm}^{-1}$  and (440-435)  $\text{cm}^{-1}$  attributed to the stretching  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$  respectively[18].

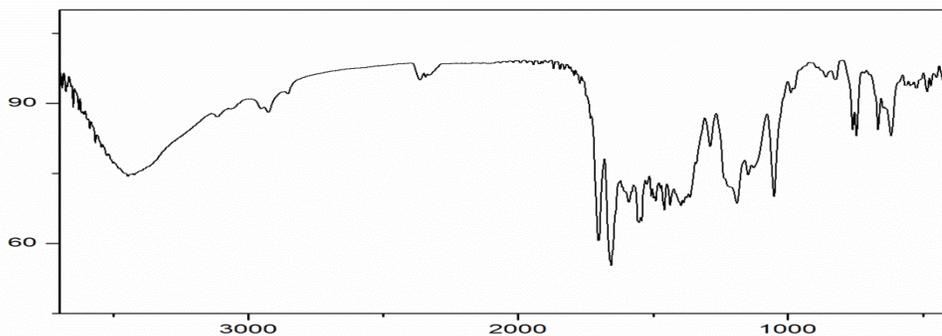
Azo H <sub>2</sub> L	Caffeine	[Ni(L)(caf)] (H <sub>2</sub> O)	[Cu(L)(caf)] (H <sub>2</sub> O)	[[Cd(L)(caf)] (H <sub>2</sub> O)]	[Zn(L)(caf)] (H <sub>2</sub> O)	Attribution
3450 vs 3400 vs 3140	-	3450L	3450L	3480L	3450L	$\nu(\text{OH})$
3056w	3114m	3110m	3100m	3100m	3090m	$\nu(\text{CH})_{\text{naph}}$
2966w	2955w	2950m	2960m	2950m	2950m	$\nu(\text{CH}_3)_{\text{caf}} + \nu(\text{CH})_{\text{naph}}$
2925m 2852m	-	2925s- 2850s	2920s 2851s	2920s 2852s	2927s 2850s	$\nu(\text{OH} \dots \text{N})$
-	1702vs	1698vs	1700vs	1695vs	1698vs	$\nu(\text{C}=\text{O})_{\text{caf}}$
-	1662s	1652vs	1650vs	1650vs	1650vs	$\nu(\text{C}=\text{O})$
1615m 1600m	1600m	1590s	1590m	1590s	1590s	$\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C})_{\text{naph}}$
1545m 1513m	1558s	1540s	1540s	1540s	1540s	$\delta(\text{HCN}) + \nu(\text{imid}) + \nu(\text{pyri}) + \nu(\text{C}=\text{C})_{\text{naph}}$
1506vs	1487m	1480s	1480m	1480s	1490s	$\nu(\text{N}=\text{N})_{\text{cis}} + \delta(\text{CH}_3) + \delta(\text{HNC})$
1466s	1456m	1455s	1450m	1450s	1451s	$\delta(\text{CH}_3) + \delta(\text{HCN})$

						+ $\nu(\text{C-C}) + \delta(\text{CH})$
1435s	1431m	1430s	1420m	1430s	1435s	$\delta(\text{CH}_3) + \nu(\text{C=C})$ naph + $\gamma(\text{CH}_3)$ + $\delta(\text{CH})$ naph
1400w	1405m	1400m	1398m	1400m	1400m	$\nu(\text{N=N})$ trans+ $\delta(\text{CH}_3) + \nu(\text{C=C})$ naph + $\delta(\text{CH})$ naph
1378	-	1380s	1380s	1380s	1370s	$\delta(\text{HCN}) + \delta(\text{CH})$
1366	1360s	1360m	1360m	1355m	1358m	$\delta(\text{HCN}) + \nu(\text{imid}) + \delta(\text{CH}_3)$ $\delta(\text{CH})$
1303m 1288m	-	1280w	1280w	1280m	1280m	$\nu(\text{C-O}) + \nu(\text{pyri})$
1248s 1228m	1241vs 1213vw 1190m	1240m 1180m	1238m 1182m	1238m 1183m	1240m 1180m	$\nu(\text{C-H})$ naph + $\nu(\text{C-O}) + \delta(\text{CH})$ caf + $\nu(\text{CH}_3)$
1186vs	-	1180m	1182m	1183m	1180m	$\nu(\text{SO}_3)$
1160s 1066vs	1026s	1140w 1050m	1140w 1050m	1140m 1050m	1140w 1050m	$\nu(\text{SO}_3) + \nu(\text{CH}_3)$ + $\nu(\text{CH})$
980m	974s	975vw	976vw	980w	980w	$\nu(\text{N-CH}_3) + \delta(\text{imid})$ + $\nu(\text{CH}_3)$
884w	861m	860vw	860vw	860w	865vw	$\nu(\text{C-SO}_3) + \nu(\text{CH}_3) + \delta(\text{C=O})$
815m 744m	746vs	835vw 760w-740w	825vw 760w-740m	830w-760w 742m	830vw 760w-740m	$\gamma(\text{pyri}) + \gamma(\text{imid}) + \delta(\text{CH})$
663s- 651m	-	660w	660w	660w	660w	$\rho(\text{SO}_3\text{Na}), \delta(\text{CH})$
621s- 572m	610vw	610w	610w	610w	610w	$\gamma(\text{imid}) + \delta(\text{CH})$
550w- 530w	-	560vw	560vw	560vw	540vw	$\nu(\text{M-N})$
465w	482w	480vw	480vw	480w	480vw	$\tau(\text{caffeine}) + \delta(\text{CH})$
427vw	-	440vw	440vw	435vw	440vw	$\nu(\text{M-O})$

**Table(2):** Infrared data of the free azo ligand ( $\text{H}_2\text{L}$ ), caffeine, and its metal complexes  $[\text{M}(\text{L})(\text{caf})](\text{H}_2\text{O})$ ;  $\text{M} = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ ; caf=caffeine; in KBr.



**Figure(1):** Infrared spectrum of the azo ligand ( $\text{H}_2\text{L}$ ) in KBr

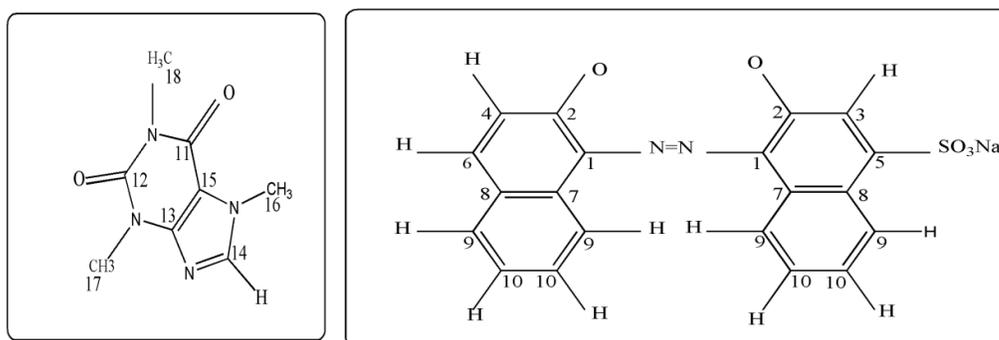


**Figure(2):** Infrared spectrum of the complex  $[\text{Cd}(\text{L})(\text{caf})](\text{H}_2\text{O})$  in KBr

$^{13}\text{C}, ^1\text{H-NMR}$  spectroscopy

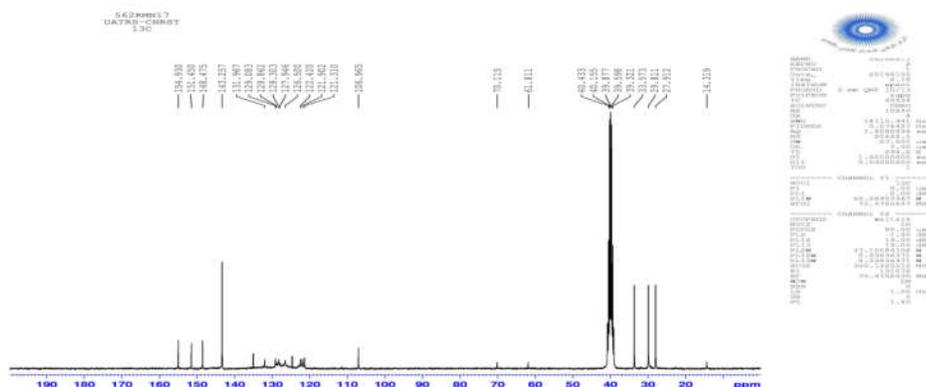
The  $^1\text{H}$  NMR spectral data of the  $[\text{Zn}(\text{L})(\text{caf})](\text{H}_2\text{O})$  complex in DMSO were analyzed in comparison of the spectrum of the free azo ( $\text{L}_2\text{H}$ ) and the free caffeine ligand. The disappearance of the signal due to naphthalic (OH) proton in the Zn(II) complex referring to its involvement in coordination with the metal ion after deprotonation. The coordination of the azo nitrogen is inferred by the down field shifting of the two -CH-N proton signal from  $\delta$  (8,21- 8,41) ppm is the free ligand to  $\delta$  (8,65 - 8,62) ppm in the complex. The aromatic proton were observed as a multiplet at  $\delta$  (7,66 -7,167) ppm range characteristic for the two naphthyl rings [14-19]. In addition the signal CH imidazol at  $\delta$ (7,952) ppm is indicative of coordinated caffeine by N9 nitrogen atom. The  $^1\text{H}$  NMR spectrum showed three signals at 3,815ppm, 3,340ppm, 3,148ppm corresponding the protons methyl groups, these signals at down field for the free caffeine [18-21].

In the  $^{13}\text{C}$  NMR spectra figure (4), the ten carbons C1,C2, C3,C4, C5,C6, C7,C8, C9 and C10 for the twenty carbons of the two naphthyl rings partially in equivalent figure (3), are observed respectively at  $\delta$  131,96 ppm,  $\delta$  143,25 ppm,  $\delta$  121,31 ppm,  $\delta$  121,90 ppm,  $\delta$  129,08 ppm,  $\delta$  128,30 ppm,  $\delta$  122,42 ppm,  $\delta$  128,86 ppm,  $\delta$  126,50 ppm and  $\delta$  127,94 ppm [19]. and five signals at  $\delta$  154,93 ppm,  $\delta$  151,45 ppm,  $\delta$  148,475 ppm,  $\delta$  143,250ppm,  $\delta$  106,965ppm, attributed for (C11, C12, C13, C14 and C15). In addition three signals  $\delta$  33,57 ppm,  $\delta$  29,811 ppm and  $\delta$  27,912 ppm we attributed carbon methyl  $\text{C}_{16}\text{H}_3$ ,  $\text{C}_{17}\text{H}_3$ ,  $\text{C}_{18}\text{H}_3$  groups respectively [12-15]. We note that the Carbone around  $\delta$  40.25 ppm attributed to methyl carbon of DMSO.



**Figure (3):** Molecular structure of caffeine and azo ligand ( $\text{H}_2\text{L}$ )

$^1\text{H}$   $^{13}\text{C}$  NMR spectra of the Zn(II) complex indicate that azo ligand and the caffeine coordinate to metal ion through the two hydroxyl group and the nitrogen N9 imidazol group.

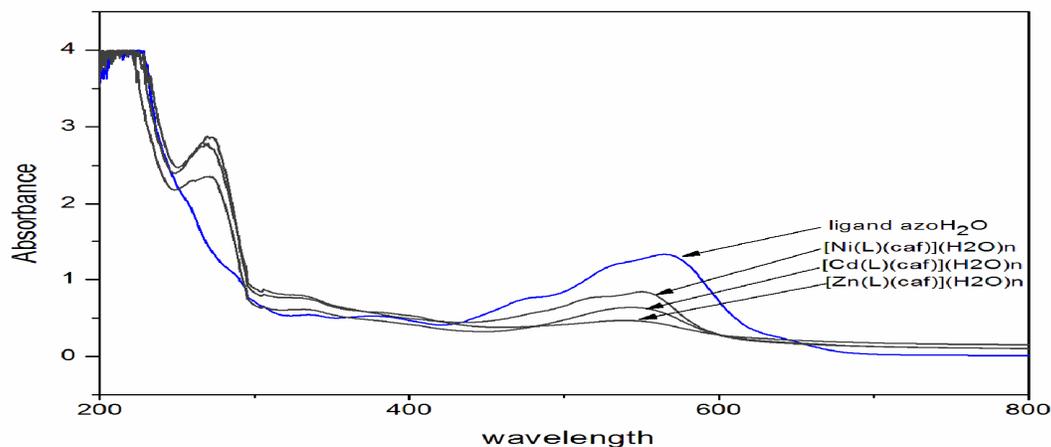


**Figure 4:**  $^{13}\text{C}$  NMR spectrum of complex  $[\text{Zn L caf}](\text{H}_2\text{O})$  in DMSO

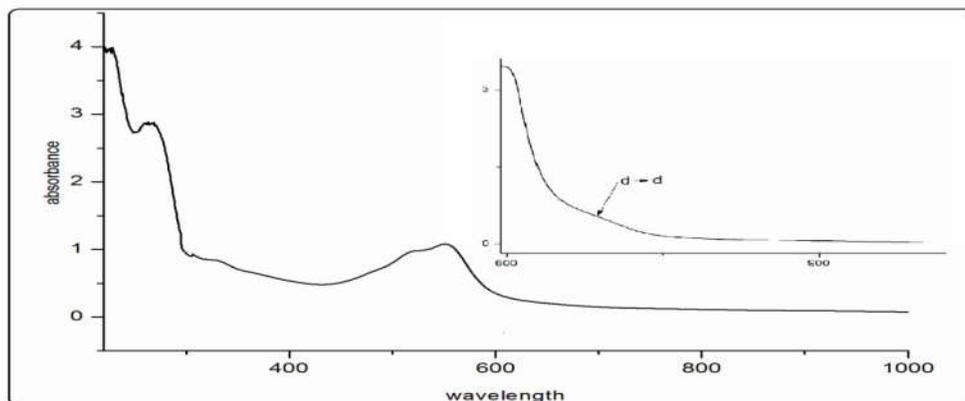
### UV-Visible spectroscopy

The UV-Visible spectra of the mixed ligand complexes were recorded in their solutions in DMSO in the (1000-200) nm range figure (5). The spectra of the free ligand (the azo  $\text{H}_2\text{L}$  and the caffeine) showed five and three bands, suggesting the presence of  $\pi-\pi^*$  and  $n-\pi^*$  transitions [14-21-22]. The electronic spectra of the  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  display two strong bands, in the (216-220) nm range and the (265-267) nm range. Table (3). The two bands are due to  $\pi-\pi^*$  transitions for the azo and the caffeine were shifted to lower wave length compared to free ligands. In addition we showed two medium bands at (520-516) nm and (553-540) nm range assigned to charge transfer (CT) transition from the metal to ligand [14]. However, a shift to lower wave length can be considered as being due to coordinate the metal ions

through the oxygen and the azo nitrogen. The electronic spectra of the Cu(II), Ni(II) complexes exhibits bands at 665 nm and 705 nm respectively assignable to the d-d transition indicating tetrahedral geometry[19].



**Figure(5)** : UV-Visible spectra of azo ligand (H<sub>2</sub>L) and its metal complexes [M(L)(caf)] (H<sub>2</sub>O) caf= caffeine, M = Ni<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> in DMSO



**Figure (6):** UV-Visible spectra of complex[Cu L caf](H<sub>2</sub>O) in DMSO

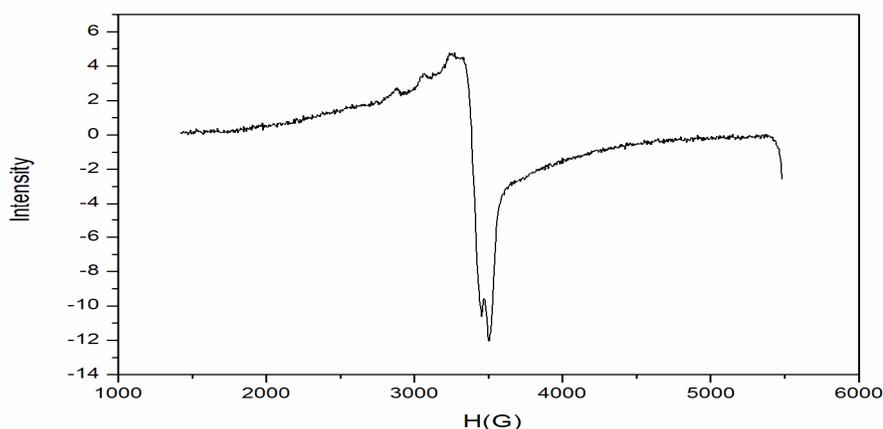
Compound	$\lambda_{max}$ (nm)	Assignment
caffeine	275	$\pi \rightarrow \pi^*$
	316	$n \rightarrow \pi^*$
	365	$n \rightarrow \pi^*$
Azo (H <sub>2</sub> L)	225	$\pi \rightarrow \pi^*$
	335	$n \rightarrow \pi^*$
	475	$\pi \rightarrow \pi^*$
	537	$\pi \rightarrow \pi^*$
[Cu(L)(caf)] (H <sub>2</sub> O)	567	$\pi \rightarrow \pi^*$
	220	$\pi \rightarrow \pi^*$
	265	$\pi \rightarrow \pi^*$
	331	$n \rightarrow \pi^*$
	520	CT
[Ni(L)(caf)](H <sub>2</sub> O)	553	CT
	665	d-d
	216	$\pi \rightarrow \pi^*$
	267	$\pi \rightarrow \pi^*$
	330	$n \rightarrow \pi^*$
[Ni(L)(caf)](H <sub>2</sub> O)	516	CT
	552	CT
	705	d-d

[Cd (L)(caf)] (H <sub>2</sub> O)	218	$\pi \rightarrow \pi^*$
	266	$\pi \rightarrow \pi^*$
	334	$n \rightarrow \pi^*$
	545	CT
[Zn(L) (caf)] (H <sub>2</sub> O)	220	$\pi \rightarrow \pi^*$
	266	$\pi \rightarrow \pi^*$
	332	$n \rightarrow \pi^*$
	540	CT

**Table(3)** : UV-Visible data of the caffeine, the Azo ligand (H<sub>2</sub>L) and there complexes [M (L)(caf)] (H<sub>2</sub>O) in DMSO.

#### EPR spectra of the complex [Cu (L) (caf)] (H<sub>2</sub>O) in solid state

The solid state EPR spectrum of [Cu (L) (caf)] (H<sub>2</sub>O) complex is displayed at room temperature on X band at frequency 9.7 GHz under the magnetic field strength 3400 G. EPR spectra of the complex [Cu (L) (caf)] (H<sub>2</sub>O) in the solid state is shown in Figure(7). This species shows  $g_{\parallel} = 2.2829$  and  $g_{\perp} = 2.0572$ . [23]. The higher g value for the investigated complex, when compared to that of free electron revealing an appreciable covalence of metal ligand bonding characteristic of tetrahedral stereochemistry.



**Figure 7** : EPR spectrum of [Cu(L) (caf)] (H<sub>2</sub>O) ,caf= caffeine.in solid state

#### CONCLUSION

In this article, the azo ligand (H<sub>2</sub>L) complexes with caffeine of Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> were synthesized and characterized the analytical data and the spectroscopic studies suggested that the complexes had the general formula [M(L)(caf)] (H<sub>2</sub>O) , caf= caffeine, L=Azo. Basis on the infrared, UV-Visible, <sup>1</sup>H <sup>13</sup>C NMR and EPR spectral data of ligand LH<sub>2</sub>, was coordinated to the metal ion through the nitrogen azo , two naphtholic oxygen atoms and N9 nitrogen caffeine . Azo ligand probably forms a tetrahedral complexes with M= Cu<sup>2+</sup> ,Ni<sup>2+</sup>,Cd<sup>2+</sup> and Zn<sup>2+</sup>.

#### REFERENCES

1. R.R. McCusker, B.A. Goldberger, E.J. Cone, J. Anal. Toxicol, 27(7), (2003), 520-522.
2. S.K. Srivastava, V.B. Singh, Spectrochimica Acta Part A: Mol. Biomol. Spec. 115 , (2013), 45-50.
3. B.kinkan,R.Gup,Turk.J.chem 32,(2008),9-17.
4. American Association of Textile chemists and colourists. Technical manual, Research Triangle Park,North Carolina , RJ chudgar,J.Oakes,Dyes azo, Kirk-Ohmer Encycl.Chem.Tech 116, (2003), 199-208.
5. H.Zollinger, Color chemistry, Syntheses Properties Application of organic dyes and pigments ,Third revised Ed, Wiley-VCH(2012).
6. Y.Zhi.Gang, Z.Chun-Xia,Z.Dc-Feng, H.S.Freeman Part 2,Azo acid dyes.pigm 81, (2009),137-143.
7. H.G Garg,C.Praksh,J.Med.chem, 15, (2012),435-436.
8. E.Machevsky, R.Olsina,C.Marone,Talanta,32, (1985),54-56.
9. A.deliman, R.O.A.P,Baso et al Mutation Research. Genetic. Toxicology and Environmental Mutagen sis 626,(1-2),(2007),53-63.
10. A.Agnedach, S.Brasillon Applied catalysis B. Envi 57(1),55-62,
11. V.Augugliaro ,C.Baiocchi, Chemosphere ,49(10), (2002), 1223-1230 .

12. N.Daneshar, D Salari ital J.Photo chem. Photobio, A, chemistry 157(1) 111-116
13. K.M. Rathod,N.S.Thakre, Chem.Sci.Trans 2(1),(2013),25-28.
14. M. Asniza, A.M. Issam,H.P.S. Abdul khalil,Sains Malaysiana,40(7),(2011),765-770.
15. R. Aravindhan,T. Sreelatha, P.T. Perumal, A. Gnanamani, Complex .Metals, 1, ( 2014), 69-79, and reference,P.R. Dandawate, A.C. Vyas, S.B. Padhye, M.W. Singh, J.B Baruah. Mini Rev Med Chem., 10, 436 (2010),M.J.A. Martínez, P. Bermejo Benito. Stud. Nat. Prod. Chem., 30, 303 (2005),
16. M.D. Siegelin, T. Gaiser, Y. Siegelin. Neurochem. Int., 55, 423 (2009),P.T. Deshmukh, V.B. Gupta. J. Asian Nat. Prod. Res., 15, 158 (2013),
17. R. Joshi, J.P. Kamat, T. Mukherjee. Chem. Biol. Interact., 167, 125 (2007).
18. M. Tunçel, Asian .J. Chem,26(7),(2014), 2161-2165,
19. O.O.Ajani ,O.E.Akinremi,A.O.Ajani,A.Edobor-Osoh,W.U.Anake,Phys.Rev.Int.3(1), (2013),28-41.
20. S .Pysarevska, L.Dubenska, I.Spanik,J.Kovalyshyn,S.Tvorynsk,J.chem.(2013)
21. M.N.Al.Jibouri Eur.chem.Bull,3(5),(2014),447-451.
22. L.ABD.Alredha,R.Al-Rubaie.R.J.Mhessn,E.J.Chem,9(1),(2012),465-470.
23. M. El Amane ,Y. Kennouche ,H. M. El M, Res. J. Chem. Sci , 4(10),(2014) 72-84.
24. D. Çanakcia, O .Y.Saribiyikb , S.Serinc,Int.J.Sci,Res ,Innov, Tech ,(1) (2) (2014).
25. Lukas Gala, Michael Lawson 1, Klaudia Jomova , Lubomir Zelenicky , Molecules , 19, (2014). 980-991
26. L .Szabo, K. Herman, N.Leopold, C. Buzumurg,V.Chis,Spectrochimica Acta , (2011) 226-231.
27. S .S.Marwaha,J.Kaur,G.S.Sodhi, 2(1),(1995).
28. T.Atomssa, A.V. Gholap, African J. of Pure and Applied Chemistry , 5(1),(2011), 1-8.
29. N.Raman , S.Ravichandran ,C. Thangaraja, J. Chem. Sci , Vol. 4(116),(2004),215-219.

**CITE THIS ARTICLE**

M. Bouhdada, M.EL.Amane, M. Hadad. Synthesis and Characterization of Mixed Ligand Complexes [M(L)(caf)](H<sub>2</sub>O) M=Cu<sup>2+</sup>,Zn<sup>2+</sup>,Cd<sup>2+</sup>,Ni<sup>2+</sup>;H<sub>2</sub>L=azo,caf=caffeine. Res. J. Chem. Env. Sci. Vol 4 [4] August 2016. 21-28