

# Synthesis and Characterization of Salicylaldazine ( $H_2L$ ) and its mixed Ligand complexes $[ML(H_2O)]$ , $[M(LH)_2(caf)_n]$ ; $M= Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}$ ; $n=1,2$ ; Caf= caffeine

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Received 24<sup>th</sup> September 2014, revised 2<sup>nd</sup> October 2014, accepted 15<sup>th</sup> October 2014

## Abstract.

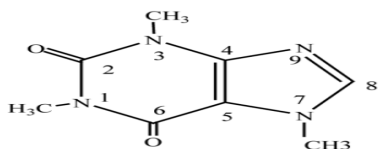
The ligand salicylaldazine ( $H_2L$ ) was prepared by condensation of salicylaldehyde and hydrazine in (2/1) molar ratio. The synthesized ligand was investigated using different physical techniques such as infrared, Raman spectroscopy,  $^1H$ ,  $^{13}C$  NMR and UV-Visible. Transition metal complexes  $[ML(H_2O)]$ ;  $M= Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}$  and the mixed ligand complexes  $[M(LH)_2(caf)_n]$ ;  $M= Zn^{2+}, Cd^{2+}$  for  $n=1$  and  $M= Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}$  for  $n=2$  derived from the ligand have been widely studied. The infrared, Raman and UV-Visible data of the metal complexes show that the ligand is coordinated to the metal ions in a tridentate manner, with NOO donor sites of the azine. It is also found that the geometrical structures of these complexes are tetrahedral. Based on the obtained infrared, Raman, NMR spectroscopy, UV-Visible and literature indications, the ligand is coordinated to the metal in bidentate manner through NO donor sites of the azine and with N9 imidazol of the caffeine. Thus, the mixed ligand complexes  $[M(LH)_2(caf)_n]$  exhibit a distorted pentahedral geometry for  $n=1$ ;  $M=Zn^{2+}, Cd^{2+}$  and a distorted octahedral geometry for  $n=2$ ;  $M= Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}$ .

**Keywords:** Salicylaldazine, caffeine, complexes, FT-IR, Raman,  $^1H$ ,  $^{13}C$  NMR, UV-Visible, molar conductance.

## Introduction

Azines,  $R_1R_2C=N-N=CR_1R_2$ , have achieved great significance in organic synthesis<sup>1-3</sup>. Many studies have shown that azines are good synthones for obtaining heterocyclic compounds such as pyrazols, purines and pyrimidines<sup>4</sup>. These compounds can be utilized for some useful synthetic transformations<sup>5</sup> and they constitute an important class of compounds with unexpected biological activities<sup>6</sup>. Azines are obtained of condensation between the hydrazine and two carbonyl compounds. Azines, and aromatic azines, are receiving increasing attention for their biological, chemical and physical properties<sup>7-10</sup>.

Salicylaldazine (scheme-1) and other ligands essentially containing a (C=N) group have been popularly called Schiff bases, which are versatile multidentate ligands capable of bonding from several alternate sites resulting in the formation of metal complexes having suitable properties for theoretical studies and practical applications<sup>11</sup>. They constitute an interesting class of chelating agents capable of coordinating with one or more metal ions giving mononuclear as well as polynuclear metal complexes.



**Scheme-1**  
Structure of the caffeine

Caffeine (1, 3,7-trimethylxanthine) (scheme-1) is one of purine alkaloids and it belongs to xanthine chemical groups and it plays an important role in pharmacological properties<sup>15</sup>. Caffeine probably is the most popular drug in the world<sup>16</sup>, which includes antagonistic effect on adenosine receptors, inhibition of phosphodiesterase and stimulation of muscle contraction<sup>17,18</sup>.

In this paper, we have been undertaken in order to get information on the structure of the salicylaldazine ( $H_2L$ ), metal and caffeine complexes  $[ML(H_2O)]$  and  $[M(LH)_2(caf)_n]$ ;  $n=1,2$ ) using FT-IR, Raman,  $^1H$ ,  $^{13}C$  NMR, UV-Visible and molar conductance.

## 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; MnCl<sub>2</sub>, 2H<sub>2</sub>O BDH; CoCl<sub>2</sub>, 6H<sub>2</sub>O BDH; FeCl<sub>2</sub>, 4H<sub>2</sub>O BDH), hydrazine Sigma Aldrich, salicylaldehyde SAFC, Ethanol and DMSO Sigma Aldrich.

Infrared spectra were recorded as KBr pellets on a Shimadzu 460 spectrophotometer in the range of 4000–400 cm<sup>-1</sup> at 298 K. Raman spectra were recorded with Vertex 70, while the electronic spectra (UV-Vis) were obtained on a Shimadzu UV-1800 Spectrophotometer. The  $^1H$ ,  $^{13}C$  NMR spectra of the

ligand was recorded with a Bruker AVANCE 300 at 25°C. All chemical shifts  $^1\text{H}$  and  $^{13}\text{C}$  are given in ppm using tetramethylsilane (TMS) as internal reference and DMSO as solvent. Conductivity measurements were performed at 25°C in acetonitrile using Hach HQ430d flexi.

**Synthesis of the salicyldazine ( $\text{H}_2\text{L}$ ):** The salicyldazine ligand ( $\text{H}_2\text{L}$ ) was prepared by adding a ethanol (15 ml) solution of salicylaldehyde (0.02 mol, 2.44g) to hydrazine (0.01mol, 0,5 g). The mixture was refluxed for two hours. The yellow powder-like product was collected by filtration and washed several times with ethanol. (Yield (%) = 88)

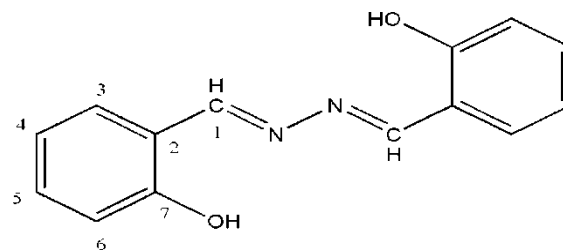
**Synthesis of the metal complexes  $[\text{ML}(\text{H}_2\text{O})]$ ;  $\text{M} = \text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ :** Complexes of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  were synthesized using a general procedure : The salicyldazine ligand ( $\text{H}_2\text{L}$ ) was prepared in the presence of a metal ion in the reaction mixture. (0.001 mol, 0.24g) of salicyldazine ligand ( $\text{H}_2\text{L}$ ) with (0,002 mol, 1.12g) of hydroxyl potassium (KOH) were dissolved in the 10 ml of ethanol and 0.001 mol of a metal (chloride) salt ( $\text{MnCl}_2$  (0.2 g),  $\text{FeCl}_2$  (0.13 g),  $\text{CoCl}_2$  (0.24 g),  $\text{NiCl}_2$  (0.24 g),  $\text{CuCl}_2$  (0.17 g),  $\text{ZnCl}_2$  (0.14 g) and  $\text{CdCl}_2$  (0.23 g)) was added to the resulting solution, which was shaken and/or heated until all of it dissolved. This mixture was refluxed for about two hours. The resulting colored precipitate was then filtered off and washed several times with ethanol.

**Synthesis of the mixed ligand complexes  $[\text{M}(\text{LH})_2(\text{caf})_n]$ ;  $\text{M} = \text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  ;  $n=1,2$ ;  $\text{caf} = \text{caffeine}$ :** Complexes of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  with caffeine were prepared by adding (0,001 mol) of a metal (chloride) salt ( $\text{MnCl}_2$  (0.2 g),  $\text{FeCl}_2$  (0.13 g),  $\text{CoCl}_2$  (0.24 g),  $\text{NiCl}_2$  (0.24 g),  $\text{CuCl}_2$  (0.17 g)) to (0,002 mol, 0.48 g) of the salicyldazine ligand ( $\text{H}_2\text{L}$ ) with (0,002 mol, 1.12g) of hydroxyl potassium (KOH) in ethanol and (0,002 mol, 0.39 g) of the caffeine in ethanol dropwise with stirring for 2h. In the same way, the caffeine complexes of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  were synthesized by adding (0,001 mol) of a metal (chloride) salt  $\text{ZnCl}_2$  (0.14 g) and  $\text{CdCl}_2$  (0.23 g) to (0,002 mol, 0.48 g) of the salicyldazine ligand ( $\text{H}_2\text{L}$ ) with (0,002 mol, 1.12g) of hydroxyl potassium (KOH) in ethanol and (0,001 mol, 0.20 g) of the caffeine in ethanol drop wise with stirring for 2h.

All caffeine complexes were formed and settled down on standing. They were filtered and washed with ethanol.

## Results and discussion

**Characterization of the Salicyldazine ligand ( $\text{H}_2\text{L}$ ):** The proposed structure of salicyldazine ( $\text{H}_2\text{L}$ ) is shown in scheme-2. This structure was confirmed by X-ray diffraction in our previous study<sup>19</sup>. Then, the salicyldazine ( $\text{H}_2\text{L}$ ) crystallizes in the monoclinic space group  $\text{P}2_1/\text{n}$  and it has unit cell dimensions:  $a = 8,3988$  (6)  $b = 6,2980$  (4)  $c = 11,6697$  (8)  $\alpha = \gamma = 90^\circ$   $\beta = 107,054^\circ$



Scheme-2  
Molecular structure of salicyldazine ( $\text{H}_2\text{L}$ )

This crystallographic data are in agreement with the conformation (E, E). In other study published recently<sup>11</sup>, we carried out a theoretical study of N, N'-di (ortho-substituted benzyl) hydrazine with  $\text{R} = \text{H}$ ,  $\text{Me}$ ,  $\text{OH}$  and  $\text{OMe}$  with Theory Density Functional (DFT) using the hybrid method B3LYP with the basis 6-31G (d) and the semi-empirical method ZINDO. The Gaussian 03 program has been used to predict structural geometries of of N, N'-di (ortho-substituted benzyl) hydrazine in gas phase.

**$^1\text{H}$  NMR spectra:**  $^1\text{H}$  NMR spectrum of the Salicyldazine ( $\text{H}_2\text{L}$ ) (figure-1) was recorded in DMSO. The spectrum exhibits a multiplet at  $\delta$  (6.94-7.70) ppm for the hydrogens of the aromatic rings. The azomethine hydrogen ( $-\text{CH}=\text{N}-$ ) leads to a singlet of integration intensity equivalent to one hydrogen at  $\delta 8.99$  ppm. Furthermore, the spectrum exhibit a signal due to the hydrogen bonded hydroxyl group at  $\delta 11.07$  ppm. We note that the singlet observed at  $\delta 2.48$  ppm corresponds to protons of methyl of DMSO.

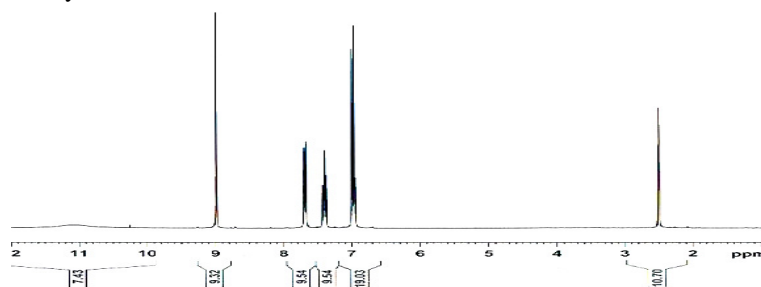
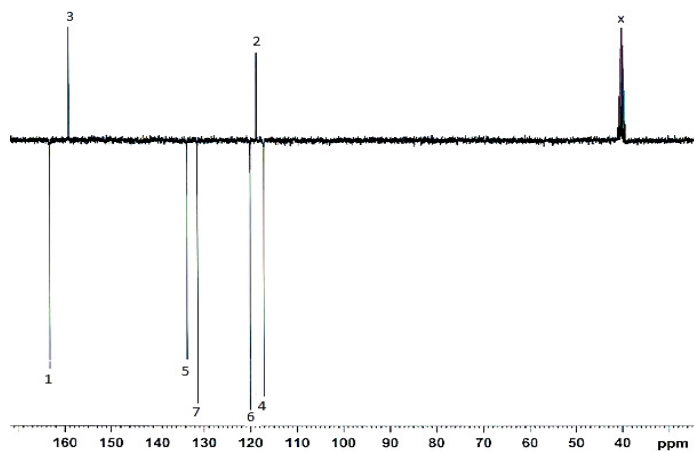


Figure-1  
 $^1\text{H}$  NMR spectrum of Salicyldazine ( $\text{H}_2\text{L}$ ) in DMSO

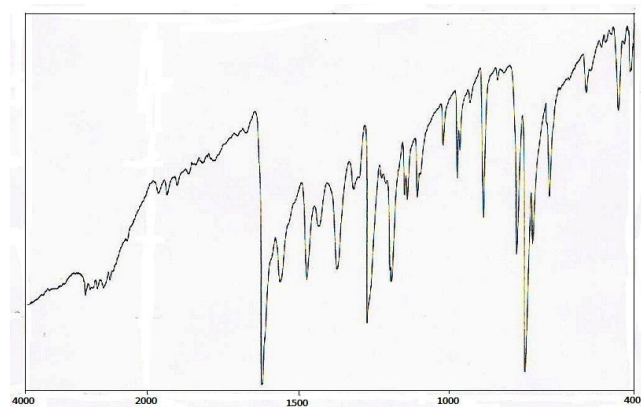
**$^{13}\text{C}$  NMR spectra:** More detailed information about the structure of ligand was provided by  $^{13}\text{C}$  NMR spectral data. A summary of the  $^{13}\text{C}$  NMR chemical shifts for the ligand is given in table-1.  $^{13}\text{C}$  NMR spectrum (figure-2) exhibits the azomethine  $\text{C}=\text{N}$  carbon (C1) at  $\delta 163.23$  ppm. The aromatic carbon atoms (C2, C3, C4, C5, C6 and C7) are observed at  $\delta 118.69$  ppm,  $\delta 159.14$  ppm,  $\delta 117.01$  ppm,  $\delta 133.64$  ppm,  $\delta 120.04$  ppm and  $\delta 131.36$  ppm, respectively. We note that the (Cx) at  $\delta 40.25$  ppm is attributed to methyl carbon of DMSO.



**Figure-2**  
 $^{13}\text{C}$  NMR spectrum of salicylaldazine ( $\text{H}_2\text{L}$ ) in DMSO

**Infrared and Raman spectroscopy:** Salicylaldazine ligand ( $\text{H}_2\text{L}$ ) was previously found to have a  $\text{C}_{2h}$  symmetry from an X-ray diffraction<sup>19,20</sup> and IR, Raman spectroscopy in the solid state and in solution<sup>13,14</sup>. Its vibrations can thus be distributed as  $\Gamma_{\text{vib}}=35\text{A}_g+34\text{B}_u+17\text{A}_u+16\text{B}_g$ .

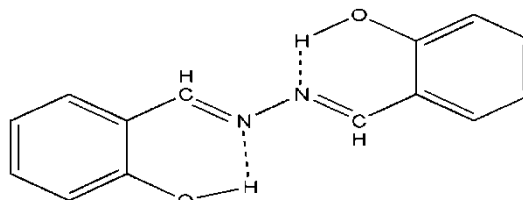
Selected infrared and Raman absorption of the salicylaldazine ( $\text{H}_2\text{L}$ ) are shown in table-2. The infrared and Raman spectra of salicylaldazine ( $\text{H}_2\text{L}$ ) are given in figure-3 and figure-4 respectively.



**Figure-3**  
Infrared spectrum of salicylaldazine ( $\text{H}_2\text{L}$ ) in KBr

In the study of hydrogen bonding for a salicylaldazine ( $\text{H}_2\text{L}$ ), it was possible to confirm that the salicylaldazine ( $\text{H}_2\text{L}$ ) form several kinds of hydrogen bonded species, such as  $-\text{OH}\dots\text{O}$  intermolecular hydrogen bonding,  $-\text{OH}\dots\text{O}$  intermolecular hydrogen bonding and  $-\text{H}\dots\text{N}$  intermolecular bonding<sup>21</sup>. Then, in the infrared spectrum of the salicylaldazine ( $\text{H}_2\text{L}$ ), the bond centered at  $3445\text{ cm}^{-1}$  shows the existence of  $-\text{OH}\dots\text{O}$  intermolecular hydrogen bonding, and the broad band between  $2941\text{ cm}^{-1}$  and  $2606\text{ cm}^{-1}$  might be designated for  $-\text{OH}\dots\text{O}$  intermolecular hydrogen bonding and  $-\text{OH}\dots\text{N}$  intermolecular

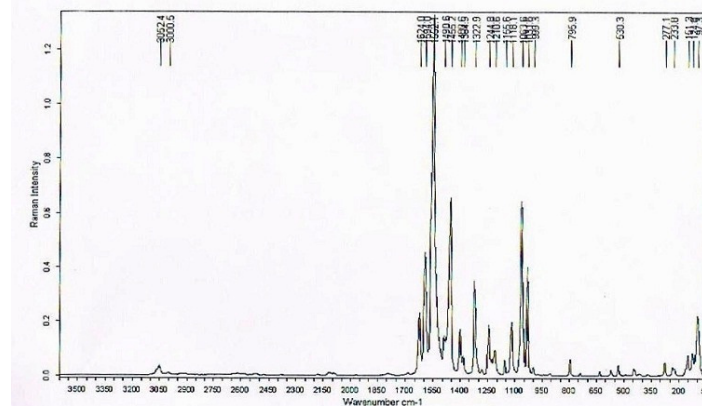
hydrogen bonding. It is well established that the Schiff bases having o-hydroxy group either on aldehyde or aniline residue can form intermolecular hydrogen bonding with azomethine nitrogen (scheme-3)<sup>22</sup>. This has direct impact on the  $\nu(\text{OH})$  vibrations and the band due to  $\nu(\text{OH})$  shifts to the lower frequency with broadening of the band and decrease in the intensity. The extent of shift depends on the strength of hydrogen bonding<sup>23</sup>.



**Scheme-3**  
Tautomerism in the salicylaldazine ( $\text{H}_2\text{L}$ )

The IR spectrum of the salicylaldazine ( $\text{H}_2\text{L}$ ) shows also a weak band at  $3019\text{ cm}^{-1}$ , assigned to  $\nu(\text{CH}, \text{Ar-H})$ . The  $\nu_s(\text{C}=\text{N})$  are only observed in the Raman spectrum<sup>13</sup>, whereas  $\nu_a(\text{C}=\text{N})$  are observed in the Infrared spectrum<sup>13</sup>. The very strong band at  $1622\text{ cm}^{-1}$  in infrared spectrum of salicylaldazine and at  $1594\text{ cm}^{-1}$  in Raman spectrum of salicylaldazine due to asymmetric and symmetric azomethine ( $\text{C}=\text{N}$ ) linkage respectively. The bands at  $1567\text{ cm}^{-1}$  and  $1479\text{ cm}^{-1}$  are attributed to  $\nu(\text{C}=\text{C})$ .

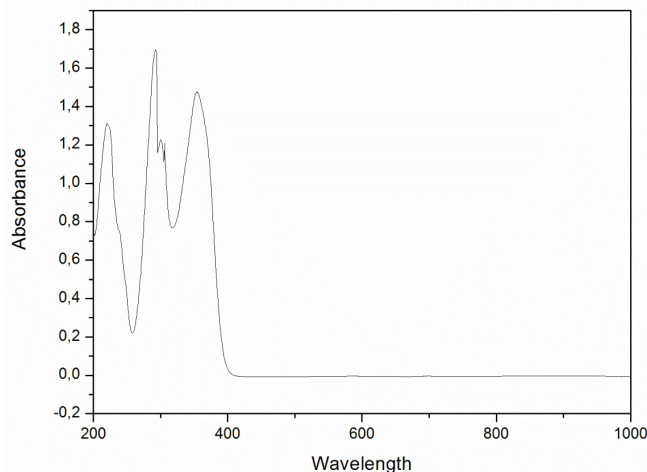
The band appearing in the  $(1443-1300)\text{ cm}^{-1}$  can be connected to  $\delta\text{CH} + \nu(\text{C-N})$ . Two interesting bands observed at  $1328\text{ cm}^{-1}$  and  $1280\text{ cm}^{-1}$  represent the vibrations modes  $\nu(\text{C-O})_{\text{ph}}$  and  $\nu(\text{OH})$  respectively. In the Raman spectrum of the salicylaldazine ( $\text{H}_2\text{L}$ ) (figure-4), the vibration  $\nu(\text{N-N})$  was located at  $1063\text{ cm}^{-1}$  which is absent in the IR spectrum. This result is comparable to those found for others arylazines<sup>24</sup>.



**Figure-4**  
Spectre Raman de salicylaldazine ( $\text{H}_2\text{L}$ )

Bands in the  $(1162-1038)\text{ cm}^{-1}$  range due to  $\delta(\text{CH})$  in plane deformation. The medium and/or weak band observed in the  $(990-739)\text{ cm}^{-1}$  range can be attributed to  $\delta(\text{CH})$  out-of-plane deformation. Bands in the  $(687-624)\text{ cm}^{-1}$  is assigned to  $\delta(\text{CH})$  in plane ring deformation and the bands in the  $(569-416)\text{ cm}^{-1}$  range is attributed to  $\delta(\text{CH})$  out plane ring deformation.

**UV/Visible spectra:** The UV and visible data of salicyldiazine ( $H_2L$ ) is summarized in table-3. The spectrum of salicyldiazine ( $H_2L$ ) in acetonitrile (figure-5) exhibits two intense bands at 221 nm and 292 nm which are attributed to  $\pi \rightarrow \pi^*$  (phenyl ring). Other important band at 354 nm is assigned to  $n \rightarrow \pi^*$  of azomethine group ( $C=N$ ).

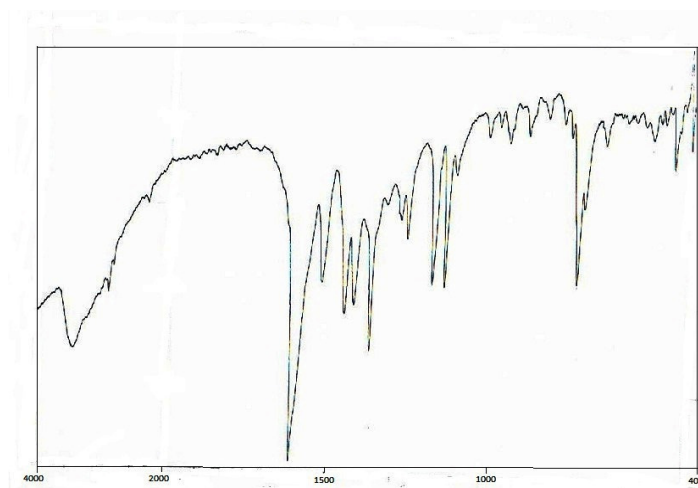


**Figure-5**  
**Electronic spectrum of salicyldiazine ( $H_2L$ )**

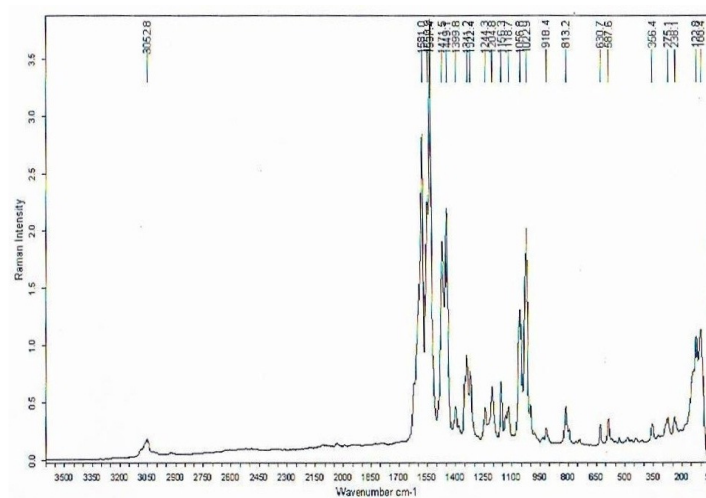
**Characterization of the mixed ligand complexes  $[ML(H_2O)]$  and  $[M(LH)_2(caf)_n]$ ;  $M= Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}$ ;  $n=1, 2$ ;  $caf=$  caffeine:** After establishing the chemical composition, the complexes were studied by physical and chemical techniques for elucidating their coordination number, bonding sites and stereochemistry. The chemical and physical methods employed for structural investigation of the complexes in the present work are: FT-IR, Raman,  $^1H$  NMR, electronic spectra and molar conductance.

**Conductance measurement:** All complexes prepared in this work showed conductivity values ranged between (6.55-5.08)  $Ohm^{-1}.mol^{-1}.cm^2$ , in DMSO at room temperature, these values indicating that no conductivity species exist. The conductivity measurements data are listed in table-4.

**Infrared and Raman spectroscopy of the metal complexes  $[ML(H_2O)]$ ;  $M= Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}$ :** The infrared spectra of the metal complexes  $[ML(H_2O)]$ ;  $M= Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}$  and  $Fe^{2+}$  are compared with that of the salicyldiazine ( $H_2L$ ) to determine the changes that might have taken place during the complexation. The infrared and Raman spectral data of the metal complexes  $[ML(H_2O)]$ ;  $M= Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}$  and  $Fe^{2+}$  are given in table-2. The infrared and Raman spectra of  $[ZnL(H_2O)]$  are given in figure-6 and figure-7, respectively.



**Figure-6**  
**Infrared spectrum of the  $Zn^{2+}$  complex  $[ZnL(H_2O)]$  in KBr**



**Figure-7**  
**Raman spectrum of the  $Zn^{2+}$  complex  $[ZnL(H_2O)]$**

The infrared band assignments of all metal complexes exhibit broad bands in the (3341-3409)  $cm^{-1}$  range indicating the presence of coordinated water molecule<sup>25</sup>. For the salicyldiazine ( $H_2L$ ), the broad bands in the (2900–2600)  $cm^{-1}$  range are assigned to the OH group vibration (ortho position) associated intramolecularly with the nitrogen atom of the  $CH=N$  group<sup>25</sup>. These bands disappear in the metal complexes  $[ML(H_2O)]$ ;  $M= Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}$  and  $Fe^{2+}$  as a result of proton substitution by cation coordination to oxygen.

On coordination with  $Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}$  and  $Fe^{2+}$ , the  $\nu(C=N)$  band of salicyldiazine ( $H_2L$ ) is observed to shift towards the lower frequency region ((1610-1593)  $cm^{-1}$ , which suggests that the metal-ligand  $\pi$  electron interaction in the newly formed chelate rings changes the vibrational frequency of the  $C=N$  group.

In the Raman spectra, the  $\nu_s(C=N)$  was located at 1594  $cm^{-1}$  for

the salicyldazine ( $H_2L$ ). This band was shifted to the (1592-1547)  $cm^{-1}$  range for the metal complexes  $[ML(H_2O)]$ ;  $M= Zn^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ . In the infrared spectra, the  $\nu(C=N)$  wasn't appeared.

In the region (1587-1458)  $cm^{-1}$ , two or three bands are observed in the case of  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$  and  $Fe^{2+}$  complexes, which may be assigned to the  $C=C$  stretching vibration of the phenyl groups. The observed phenyl ring bands shift towards the low frequency region in all the metal complexes.

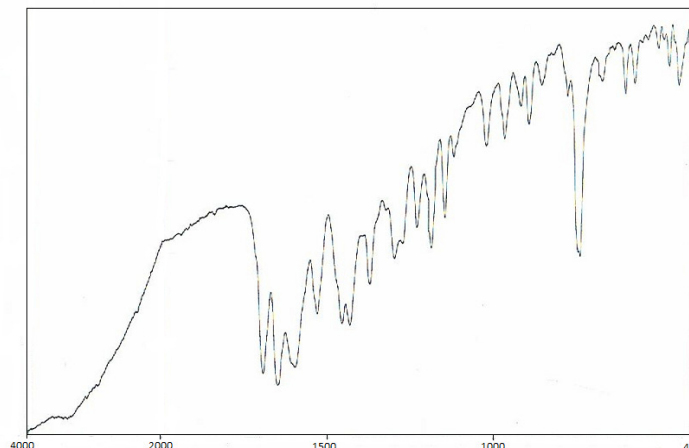
The bending vibration  $\delta CH$  and stretching vibration  $\nu(C-N)$  are located in the (1438-1300)  $cm^{-1}$  range. These vibrations are shift to lower frequencies confirming the coordination of the salicyldazine ( $H_2L$ ) through the azomethine nitrogen atom.

The next important absorption band in the salicyldazine ( $H_2L$ ) is found at 1328  $cm^{-1}$  and it is attributed to the  $\nu(C-O)$  stretching vibration<sup>26</sup>. In the metal complexes of  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$  and  $Co^{2+}$ , this band disappears from this position and appears at a higher frequency region (1375-1330)  $cm^{-1}$ . This shift to higher frequency is expected due to the main tenure of ring currents arising from electron delocalization in the chelating. The band at 1280  $cm^{-1}$  assigned to  $\delta OH$  of salicyldazine ( $H_2L$ ) is disappeared for the metal complexes.

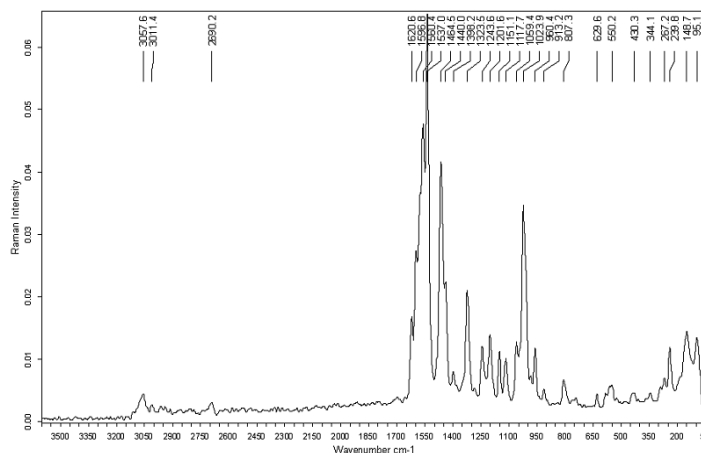
The stretching vibration  $\nu(N-N)$  in the Raman spectra of the metal complexes  $[ML(H_2O)]$ ;  $M= Zn^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$  was shifted to (1060-1045)  $cm^{-1}$ , respectively by (3-18)  $cm^{-1}$ . Moreover, this negative shift in  $\nu(N-N)$  vibration on complexation can be added as a further support to the coordination of the azomethine nitrogen atom to the metal ion.

Such coordination is further substantiated by the appearance of new bands in the complexes characteristic of  $\nu(M-N)$  and  $\nu(M-O)$  in the (596-576)  $cm^{-1}$  and (456-432)  $cm^{-1}$  regions, respectively<sup>27-28</sup>.

**Infrared and Raman spectroscopy of the mixed ligand complexes  $[M(LH)_2(caf)_n]$ ;  $M= Zn^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ;  $n=1,2$ ;  $caf=$  caffeine:** Comparison of infrared and Raman spectra of salicyldazine ligand ( $H_2L$ ) and free caffeine with that of their complexes  $[M(LH)_2(caf)_n]$ ;  $M= Zn^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$  and  $Fe^{2+}$ ;  $n=1,2$  have been adopted to determine the coordinating atoms of the salicyldazine ligand ( $H_2L$ ) and the free caffeine to metal ions. The infrared and Raman spectra of the caffeine complexes  $[Cd(LH)_2caf]$  are shown in figure-8 and figure-9 respectively. The assignments of the seven studied caffeine complexes  $[M(LH)_2(caf)_n]$ ;  $M= Zn^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$  and  $Fe^{2+}$ ;  $n=1,2$  are reported in table-5. From the literature<sup>29,30</sup>, the infrared and Raman spectral data of the free caffeine are given in the table 5. Then, the infrared spectra of the caffeine complexes  $[M(LH)_2(caf)_n]$ ;  $M= Zn^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ;  $n=1,2$  exhibit the vibration  $\nu(OH)$  stretching in the (3452-3450)  $cm^{-1}$  range.



**Figure-8**  
Infrared spectrum of the  $Cd^{2+}$  caffeine complex  
 $[Cd(LH)_2caf]$  in KBr



**Figure-9**  
Raman spectrum of the  $Cd^{2+}$  caffeine complex  $[Cd(LH)_2caf]$

The medium/weak bands in (3113-3002)  $cm^{-1}$  range are attributed to  $\nu CHar$ . The carbonyl group in the caffeine complexes exhibit a strong absorption band about 1700  $cm^{-1}$  due to  $\nu(CO)$  symmetric. Another strong band in the (1656-1646)  $cm^{-1}$  range belong to  $\nu(CO)$  asymmetric and  $\nu(C=N)$  is shifted to lower frequencies by (6-16)  $cm^{-1}$ , compared with the free caffeine, indicating coordination of the caffeine through the azomethine nitrogen atom ( $N9$ )<sup>31</sup>. The next strong band at 1622  $cm^{-1}$  attributed to  $\nu(C=N)$  symmetric of the salicyldazine ( $H_2L$ ) shifted towards a lower frequency by (12-24)  $cm^{-1}$ . The  $\nu(C=N)$  asymmetric of the salicyldazine ( $H_2L$ ) is appeared only in the Raman spectra and shifted to (1589-1551)  $cm^{-1}$  region by (5-43)  $cm^{-1}$  on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation.

In addition, the band at 1551  $cm^{-1}$  is assigned to ( $\delta HCN+$  vring imid +vring pyrimi) which is shifted to lower frequencies by (13-31)  $cm^{-1}$  compared with the free caffeine. Then, we may

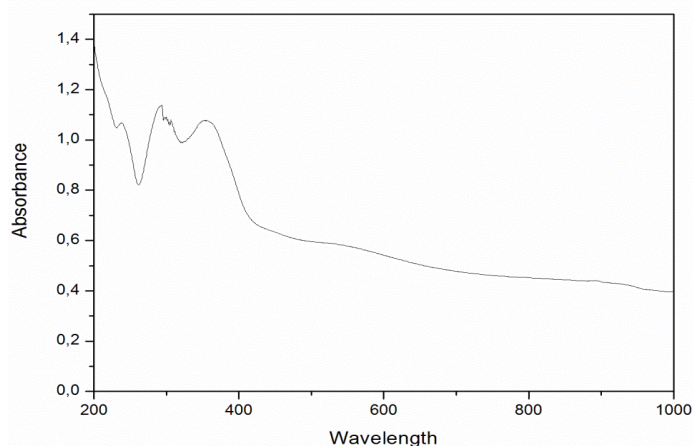
confirm that imidazol fragment of the caffeine is coordinated with metal ions through the nitrogen atom N9<sup>32</sup>. The band of salicylaldazine (H<sub>2</sub>L) at 1328 cm<sup>-1</sup> which involves the  $\nu(\text{C-Oph})$  stretching as the major coordinate shifts to (1356-1335) cm<sup>-1</sup> region for all caffeine complexes<sup>26</sup>. This shift to higher frequency is expected due to the main tenure of ring currents arising from electron delocalization in the chelate ring. Indeed, other vibration  $\delta(\text{OH})$  is appeared at 1275 cm<sup>-1</sup> in all caffeine complexes which confirm that one of two hydroxyls group isn't coordinated with metal ions.

The Raman spectra of the caffeine complexes show the stretching vibration  $\nu(\text{N-N})$  in (1061-1054) cm<sup>-1</sup> which is shifted to lower frequencies by (2-9) cm<sup>-1</sup> and isn't appeared in the Infrared spectra. New bands are attributed to  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$  vibrations, respectively. The appearance of these new bands vibrations in (590-575) and in (450-425) cm<sup>-1</sup> ranges respectively supports the involvement of nitrogen and oxygen atoms in complexation with metal ions under investigation<sup>33,34</sup>.

**<sup>1</sup>H NMR spectra of the mixed ligand complexes [M(LH)<sub>2</sub>caf]; M=Zn<sup>2+</sup> and Cd<sup>2+</sup>:** The <sup>1</sup>H NMR spectra of the caffeine complexes [M(LH)<sub>2</sub>caf] M= Zn<sup>2+</sup> and Cd<sup>2+</sup> were recorded in dimethylsulfoxide (DMSO). The <sup>1</sup>H NMR spectra of these complexes show the following signals: Phenyl as multiplet at  $\delta(6.79-7.64)$  ppm. The signal attributed to proton of CH=N- is shifted to  $\delta 8.93$  ppm and  $\delta 8.92$  ppm for Zn<sup>2+</sup> and Cd<sup>2+</sup> caffeine complexes, respectively, indicating the coordination of azomethine to Zn<sup>2+</sup> and Cd<sup>2+</sup>. In other hand, the <sup>1</sup>H NMR spectrum of the free caffeine has shown proton signals at  $\delta 3.30, \delta 3.54, \delta 3.90$  and  $\delta 7.76$  ppm corresponding to the three methyl groups N1-CH<sub>3</sub>, N3-CH<sub>3</sub>, N7-CH<sub>3</sub> and C8-H respectively<sup>35</sup>. In the case of Zn<sup>2+</sup> and Cd<sup>2+</sup> caffeine complexes, the signals of N1-CH<sub>3</sub>, N3-CH<sub>3</sub> and N7-CH<sub>3</sub> are shifted to  $\delta 3.20, \delta 3.40$  and  $\delta 3.86$  ppm. The signal due to the C8-H was shifted to  $\delta 7.92$  and  $\delta 7.94$  on the Zn<sup>2+</sup> and Cd<sup>2+</sup> complexation, respectively. The downfield shift was attributed to the involvement of N9 in complexation.

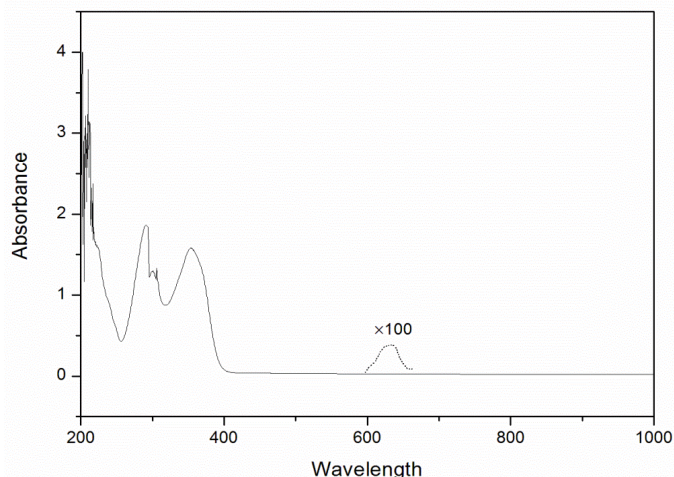
**UV/Visible spectra:** Information concerning the geometry of the complexes was obtained from the electronic spectra. Upon the electronic spectrum of the salicylaldazine (H<sub>2</sub>L), the two essential absorption bands were observed at 354 nm and at (221 and 292) nm, assigned to the transitions  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$ , respectively (figure-5). These transitions were existed also in the spectra of the complexes, but they shifted to different lower intensities, confirming the coordination of the salicylaldazine (H<sub>2</sub>L) to the metal ions. In UV-Visible spectra, the weak band should be at 400-300 nm is due to charge-transfer (CT) band in the complexes [ML(H<sub>2</sub>O)] and [M(LH)<sub>2</sub>(caf)<sub>n</sub>]; M= Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup> and Fe<sup>2+</sup>; n=1,2 which is absence in the salicylaldazine (H<sub>2</sub>L). However, the weak broad band at 1000-400 nm is due to different d-d transitions of the metal ions as mentioned. The electronic spectral data for all complexes are given in table-3.

**UV/Visible spectra of the metal complexes [ML(H<sub>2</sub>O)]:** The electronic spectrum of Fe<sup>2+</sup> complex [FeL(H<sub>2</sub>O)] is given in figure-10. The spectrum of the Co<sup>2+</sup> complex [CoL(H<sub>2</sub>O)] shows an absorption band at 448 nm, attributed to <sup>4</sup>A<sub>2</sub>(F) → <sup>4</sup>T<sub>1</sub>(F) transition. Another bands appeared at 892 and 928 nm were assigned to <sup>4</sup>A<sub>2</sub>(F) → <sup>4</sup>T<sub>2</sub>(F). These values are accepted for Co<sup>2+</sup> tetrahedral complexes<sup>34</sup>. The Mn<sup>2+</sup> complex [MnL(H<sub>2</sub>O)] show two absorption bands at 386 cm<sup>-1</sup> and 494 cm<sup>-1</sup> assigned to <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>A<sub>1g</sub> and <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub> transition respectively, suggest the tetrahedral geometry of Mn<sup>2+</sup><sup>36</sup>. The spectrum of the Ni<sup>2+</sup> complex [NiL(H<sub>2</sub>O)] shows two absorption bands at 496 nm and 931 nm, attributed to the electronic transitions <sup>3</sup>T<sub>1</sub>(F) → <sup>3</sup>A<sub>2</sub>(F), <sup>3</sup>T<sub>1</sub>(F) → <sup>3</sup>T<sub>1</sub>(P) and <sup>3</sup>T<sub>1</sub>(F) → <sup>3</sup>T<sub>2</sub>(F) respectively. These transitions are characteristic for tetrahedral complexes of Ni<sup>2+</sup><sup>34</sup>. The green complex of Cu<sup>2+</sup> [CuL(H<sub>2</sub>O)] exhibited an absorption band in the visible region at 402 nm which belong to electronic transition <sup>2</sup>T<sub>2</sub> → <sup>2</sup>E<sup>37</sup>. The electronic spectrum of the Fe<sup>2+</sup> complex [FeL(H<sub>2</sub>O)] consisted of a pair of low intensity bands at 550 and 905 cm<sup>-1</sup>, arising from <sup>5</sup>E → <sup>5</sup>T<sub>2</sub> transitions, suggest the tetrahedral environment of Fe<sup>2+</sup><sup>37</sup>. The electronic configurations of Zn<sup>2+</sup> and Cd<sup>2+</sup> complexes were (d<sup>10</sup>) which confirms the absence of any (d-d) transitions. The absorption bands in their spectra were suffered blue shift with Hypo or Hyper chromic effect<sup>34,38</sup>.



**Figure-10**  
**Electronic spectrum of the Fe<sup>2+</sup> complex [FeL(H<sub>2</sub>O)] in acetonitrile**

**UV/Visible spectra of the mixed ligand complexes [M(LH)<sub>2</sub>(caf)<sub>n</sub>]; M= Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>; n=1,2; caf= caffeine:** The electronic spectrum of Cu<sup>2+</sup> caffeine complex [Cu(LH)<sub>2</sub>(caf)<sub>2</sub>] is given in figure-11. The electronic spectrum of the Mn<sup>2+</sup> caffeine complex shows two bands at 356 nm and 450 nm assigned to <sup>6</sup>A<sub>1</sub> → <sup>4</sup>T<sub>1g</sub> (4G) and <sup>6</sup>A<sub>1</sub> → <sup>4</sup>T<sub>1g</sub> (4Eg), respectively, for a Mn<sup>2+</sup> ion in an distorted octahedral field<sup>39</sup>. The electronic spectrum of the Fe<sup>2+</sup> caffeine complex shows absorption band at 535 nm assignable to the <sup>5</sup>T<sub>2g</sub> → <sup>5</sup>E<sub>g</sub> transition consistent with an octahedral geometry for Fe<sup>2+</sup> caffeine complex<sup>40</sup>. The electronic spectrum of octahedral Cu<sup>2+</sup> caffeine complex has three types of transitions observed at 634 nm due to <sup>2</sup>E<sub>g</sub>(D) → <sup>2</sup>T<sub>2g</sub>(D).



**Figure-11**  
**Electronic spectrum of the Cu<sup>2+</sup> caffeine complex [Cu(LH)<sub>2</sub>(caf)<sub>2</sub>] in acetonitrile**

The electronic spectrum of the Co<sup>2+</sup> caffeine complex shows two d-d bands at 286, 436 and 781 nm assignable to <sup>4</sup>T<sub>1g</sub>(F) →

<sup>4</sup>T<sub>2g</sub>(F) , <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>A<sub>2g</sub>(F) and <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P) transitions respectively, in an octahedral geometry<sup>41</sup>. The electronic spectrum of the Ni<sup>2+</sup> caffeine complex shows three d-d bands at 396 and 985 assignable to <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F) and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F) respectively, in octahedral geometry<sup>42</sup>. The Zn<sup>2+</sup> and Cd<sup>2+</sup> caffeine complexes are found diamagnetic as expected from their electronic configurations and may have pentahedral geometry<sup>43</sup>.

### Conclusion

From the previous analysis we can conclude that the metal complexes and the mixed ligand complexes were found to have the general formulae [ML(H<sub>2</sub>O)] and [M(LH)<sub>2</sub>(caf)<sub>n</sub>] n=1,2, respectively. All complexes were synthesized and characterized by molar conductance, infrared, Raman, UV-Visible and <sup>1</sup>H NMR spectra. Based on the obtained experimental data and literature indications, structural formulae to these complexes were assigned.

**Table-1**  
**<sup>13</sup>C NMR spectral data of the Salicyldazine (H<sub>2</sub>L)**

Carbone	1	2	3	4	5	6	7
δ (ppm)	163.23	118.69	159.14	117.01	133.64	120.04	131.36

**Table-2**

**Infrared and Raman data of the salicyldazine (H<sub>2</sub>L) and its metal complexes [ML(H<sub>2</sub>O)]; (M= Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>) Values in ( ) are the Raman data of the metal complexes**

	Salicyldazine (H <sub>2</sub> L)	CdL(H <sub>2</sub> O)	ZnL(H <sub>2</sub> O)	FeL(H <sub>2</sub> O)	CuL(H <sub>2</sub> O)	NiL(H <sub>2</sub> O)	CoL(H <sub>2</sub> O)	MnL(H <sub>2</sub> O)
<b>νOH/H<sub>2</sub>O</b>	3445 m,br	3409 m,br	3341 m,br	3380 m,br	3391 m,br	3385 m,br	3345 m,br	3345 m,br
<b>ν CHar</b>	3019 m (3000m)	3002w (3016)	3055w (3052w)	3053w (3040w)	3075w, 3010w (3005w)	3040w (3038w)	3012w (3050w)	3025w (3034w)
<b>OH...N</b>	2941w,2709w, 2606w	-	-	-	-	-	-	-
<b>νaC=N, δH<sub>2</sub>O</b>	1622vs (1624s)	1610vs (1605s)	1610vs (1581s)	1593vs (1609s)	1606vs (1605m)	1600vs (1606vs)	1600vs (1621m)	1606vs (1607s)
<b>νsC=N</b>	(1594s)	(1580s)	(1550s)	(1580s)	(1588m)	(1547vs)	(1592s)	(1586s)
<b>νC=C (ring)</b>	1567s, 1479s (1552vs, 1490w, 1455s)	1535s, 1462s (1542vs, 1473s,1443s)	1530s, 1458m (1537vs, 1471s, 1449s)	1569s, 1528s 1478w,1458m (1550vs, 1466s, 1449s)	1587s, 1525s, 1458m (1550m, 1480m, 1450m)	1528s, 1460vs, (1547vs, 1470m, 1451m)	1571s, 1519s, 1458m (1550vs, 1454s)	1572s, 1520s, 1492w, 1457m (1534vs, 1472m, 1455m)
<b>δCH + νC-N</b>	1443m, 1382m, 1300m (1430w,1384w)	1425s,1397w, 1379w 1300s (1400w)	1431m,1380m 1300m (1400w)	1426m,1305m (1410m, 1348w, 1318m)	1438s,1316m (1410w, 1341w, 1316m)	1434s, 1300m (1400w)	1434s, 1372m 1310m (1320m)	1433s, 1372m, 1312m (1442m, 1411m,

								1329m)
<b>vC-Oph</b>	1328s (1322m)	1330m (1332m)	1336m (1340w)	1373m (1377w)	1374m (1365w)	1375m (1344m)	1353m (1368m)	1350m (1369m)
<b>δOH</b>	1280vs	-	-	-	-	-	-	-
<b>vC-HPH</b>	1238w, 1203s (1244m, 1210w)	1247m (1252w, 1206m)	1252w (1244w, 1204w)	1240w, 1200m (1240w)	1242w (1244m)	1250m (1237w)	1255w, 1201m (1243m, 1208m)	1251w, 1200m (1291w, 1255m, 1208w)
<b>δCH (ring) In plane bend</b>	1162m, 1152m, 1118m, 1038m (1155w, 1118m, 1031m)	1190s, 1152s, 1123m, 1038m (1154m, 1125w, 1088w, 1012s)	1192m, 1155m, 1126w, 1029w (1156w, 1118w, 1022m)	1147m, 1122m, 1029m (1146w, 1117w, 1017m)	1195s, 1148s, 1130m, 1017w (1150w, 1120w, 1015w)	1194m, 1151m, 1124m, 1031m (1196w, 1152w, 1028m)	1154m, 1130w, 1003m (1153w, 1029m)	1151m, 1126m (1155w, 1120m, 1090w)
<b>vN-N</b>	(1063s)	(1045w)	(1056m)	(1057m)	(1055m)	(1058m)	(1060m)	(1056m)
<b>δCH (ring) Out-of- plane bend</b>	990m, 981m, 949w, 901m, 859w, 839w, 790m, 760vs, 739m (999m, 795w)	981w, 956m, 932m, 905m, 834w 855m, 800s, 760s, 734s (963m, 943w, 918w, 815w, 766w)	997w, 966w, 907w, 847w, 800w, 774w, 746m, 732w (918w, 813w)	997w, 981w, 938w, 900w, 857w, 832w 800w, 779m, 749m (960w, 946w, 920w, 815w, 796m)	958m, 902m, 852m, 835w 800w, 750m, 737m (985w, 950w, 915w, 815w, 788w)	982w, 971w, 920w, 900m, 852m, 830w 781w, 748m (985w, 960w, 945w, 815w, 766w)	969w,940 w 908m 867w,856 w 832w 803w,760 m711w (794w)	997m,963w, 932w,902w, 848w, 832w 796w,755m, 700w (995w,960w 910w,850w8 22w, 788w)
<b>δCH In plane ring def</b>	687m, 655w, 624w (655vw)	670m, 615w (634w)	670m, 623w, 604w (630w)	685w, 622m (644w)	660w, 644w, 620w (641w, 614w)	675m, 657w, 621w (655w, 610w)	665w, 638w, 617w	656w,629w 611w (650w, 605w)
<b>vM-N</b>	-	596m (593w)	593w (587w)	585m (588w)	576m (586w)	583m (580w)	578w (580w)	577w (585w)
<b>δCH Out-of- plane ring def</b>	569m, 555w, 520w, 491w, 478w, 460w, 440m, 416w (550vw, 530w, 450vw, 420vw)	542w, 465m, 411w (554w)	550w, 524w, 487w, 470w, 406m (540w)	555w, 537w, 490w, 478w, 460w, 410w (550w)	538w, 411w (550w, 420w)	555w, 534w, 492w, 460w, 407m (555w,)	545w,479 w467w,41 5w (529w)	535w,472w4 60w, 406w (558w,546w 455w,422w)
<b>δCCN</b>	510w	494m	500w	507w (503w)	498w (500w)	506m (506w)	513w	504w (505w)
<b>vM-O</b>	-	434w (428w)	456m (445w)	432w (450w)	451w (449)	443m (445w)	455w (443w)	444w (440w)



**Table-3**  
**U.V-Visible data of the salicylaldazine (H<sub>2</sub>L), the caffeine, the metal complexes and the mixed ligand complexes in acetonitrile**

Compound	$\lambda_{max}$ (nm)	Assignment
caf	275	$\pi \rightarrow \pi^*$
	316	$n \rightarrow \pi^*$
	365	$n \rightarrow \pi^*$
H <sub>2</sub> L	221	$\pi \rightarrow \pi^*$
	292	$\pi \rightarrow \pi^*$
	354	$n \rightarrow \pi^*$
[FeL(H <sub>2</sub> O)]	202, 238	CT
	357	M → L
	550	$^5E \rightarrow ^5E_g$
	905	
[CoL(H <sub>2</sub> O)]	204, 282	CT
	357	M → L
	448	$^4A_2(F) \rightarrow ^4T_1(F)$
	892, 928	$^4A_2(F) \rightarrow ^4T_2(F)$
[MnL(H <sub>2</sub> O)]	204, 234, 292	CT
	349	M → L
	365	$^6A_{1g} \rightarrow ^4T_{1g}$
	403	$^6A_{1g} \rightarrow ^4T_{2g}$
[NiL(H <sub>2</sub> O)]	204, 275	CT
	357	M → L
	496	$^3T_1(F) \rightarrow ^3A_2(F)$
	931	$^3T_1(F) \rightarrow ^3T_1(P)$ $^3T_1(F) \rightarrow ^3T_2(F)$
[CuL(H <sub>2</sub> O)]	204, 282	CT
	350	M → L
	402	$^2T_2 \rightarrow ^2E$
[CdL(H <sub>2</sub> O)]	214, 286	CT
	400	Red Shift with hypochromic effect
[ZnL(H <sub>2</sub> O)]	214, 282	CT
	389	Red Shift with hypochromic effect
[Fe(LH) <sub>2</sub> (caf) <sub>2</sub> ]	204, 276	CT
	356	M → L
	535	$^5T_{2g} \rightarrow ^5E_g$
[Co(LH) <sub>2</sub> (caf) <sub>2</sub> ]	206, 262	CT
	286	$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$
	436	$^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$
	781	$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$
[Mn(LH) <sub>2</sub> (caf) <sub>2</sub> ]	202, 289	CT
	356	$^6A_{1g} \rightarrow ^4T_{1g}(4G)$
	450	$^6A_{1g} \rightarrow ^4T_{1g}(4Eg)$
[Cu(LH) <sub>2</sub> (caf) <sub>2</sub> ]	204, 272	CT
	634	$^2E_g(D) \rightarrow ^2T_{2g}(D)$
[Ni(LH) <sub>2</sub> (caf) <sub>2</sub> ]	202, 286	CT
	396	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$
	985	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$
[Cd(LH) <sub>2</sub> (caf)]	205, 289	CT
	364	Red Shift with hypochromic effect
[Zn(LH) <sub>2</sub> (caf)]	202, 292	CT
	359	Red Shift with hypochromic effect

Table-4

Physical characterization and Molar Conductance data of the complexes  $[ML(H_2O)]$  and  $[M(LH)_2(caf)_n]$ ;  $M= Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}$ ;  $n=1,2$ ;  $caf=$  caffeine

Complexes	Colour	M.P. (°C)	Yield (%)	$\Lambda$ (Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
$[ZnL(H_2O)]$	Yellow	>260	82	5.34
$[CdL(H_2O)]$	Yellow	>260	76	5.76
$[NiL(H_2O)]$	Light Green	250	72	5.87
$[CuL(H_2O)]$	Dark Green	>260	68	5.90
$[CoL(H_2O)]$	Light Brown	>260	78	5.92
$[MnL(H_2O)]$	Dark Orange	>260	75	5.46
$[FeL(H_2O)]$	Black	>260	70	6.55
$[Zn(LH)_2caf]$	Yellow	>260	77	5.08
$[Cd(LH)_2caf]$	Yellow	>260	83	5.14
$[Ni(LH)_2(caf)_2]$	Light Green	>260	78	5.28
$[Cu(LH)_2(caf)_2]$	Dark Green	>260	76	5.44
$[Co(LH)_2(caf)_2]$	Light Brown	>260	84	5.48
$[Mn(LH)_2(caf)_2]$	Dark Orange	>260	78	5.11
$[Fe(LH)_2(caf)_2]$	Black	>260	72	5.50

Table-5

Infrared and Raman data of the salicylaldazine ( $H_2L$ ), caffeine and their complexes  $[M(LH)_2(caf)_n]$ ;  $M= Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}$ ;  $n=1,2$ ;  $caf=$  caffeine

	Salicylaldazine ( $H_2L$ )	Caffeine e <sup>29, 30</sup>	$Cd(LH)_2(caf)$	$Zn(LH)_2(caf)$	$Fe(LH)_2(caf)_2$	$Cu(LH)_2(caf)_2$	$Ni(LH)_2(caf)_2$	$Co(LH)_2(caf)_2$	$Mn(LH)_2(caf)_2$
<b>vOH</b>	3445 m,br	-	3450 m,br	3450 m,br	3452 m,br	3452 m,br	3450 m,br	3450 m,br	3452 m,br
<b>vChar</b>	3019 m (3000m)	3114m	3103w, 3045w, 3004w (3057w, 3011w)	3110w, 3040w, 3003w (3033w, 3006m)	3112w, 3053w, 3004w (3022w)	3113w, 3042w, 3002w (3070w, 3050w)	3100w, 3002w (3050w, 3015w)	3110w, 3040w, 3005w (3045w, 3011w)	3102w, 3050w, 3002w (3090m, 3055w)
<b>vCH<sub>3</sub>caf</b>	-	2954w (2963w, 2957w)	2950w (2962w, 2944w)	2950w (2946w)	2984w, 2961w (2936w)	2953w (2955w)	2950w (2933m)	2982w, 2954w (2953w)	2946w (2953w)
<b>OH...N</b>	2941w, 2709w, 2606w	-	-	-	-	-	-	-	-
<b>vsC=O</b>	-	1702vs (1700s)	1698vs (1700w)	1696vs (1695m)	1695s (1704m)	1697vs (1700w)	1700vs (1697m)	1694s (1692m)	1697s (1697m)
<b>vaC=O /vC=Ncaf</b>	-	1662s (1656s)	1650vs (1650m)	1654vs (1647s)	1648s (1652m)	1656vs (1650m)	1646s (1653)	1647s (1654m)	1653vs (1648m)
<b>vsC=N/ vC=Ccaf</b>	1622vs (1624s)	1600m (1600m)	1610vs, 1580e (1620m, 1596m)	1610vs, 1575e (1617m)	1598s, 1573e (1594s)	1606vs, 1555e (1613s)	1600vs (1601s)	1598s, 1570m (1604s)	1593vs, 1575e (1619m)
<b>vaC=N</b>	(1594s)	-	(1560s)	(1589s)	(1551vs)	(1581s)	(1578m)	(1585m)	(1586s)
<b>vC=C(ring)+ <math>\delta</math>HCN + vring imidazole+ vring pyrimidine</b>	1567s, 1479s (1552vs, 1490w, 1455s)	1551w (1550w)	1535m, 1458m (1537vs, 1464s)	1536m, 1457w (1548vs, 1493w, 1454s)	1538m, 1458m (1454s)	1534m, 1461m (1551s, 1452s)	1530m, 1458s (1533s, 1495m, 1470m)	1520s, 1458s (1531s, 1491m, 1443s)	1532m, 1468m (1548s, 1477m, 1450w)
<b><math>\delta</math>CH<sub>3</sub> +</b>	1443m,	1487m,	1424m	1433m,	1434m,	1442s,	1436vs, 13	1438s, 137	1435m,

<b>vC-N</b>	1382m, 1300m (1430w,1 384w)	1466m 1431m, (1470w, 1466w, 1403w)	(1440m, 1398w)	1300m (1402w, 1377m)	1378w, 1300m (1402m, 1378w)	1380w (1398w,)	77w, 1300w (1403m, 1375w)	4w, 1300w (1410m)	1375m, 1351w, 1303m (1403m,13 75m)
<b>vring (imidazole) + vring (pyrimidine)</b>	-	1327w (1331w)	1318m (1325m)	1320m (1323m)	1321e (1320s)	1318m (1320m)	1316m (1323w)	1318m (1326m)	1325w (1323m)
<b>δC-Oph</b>	1328s (1322m)	-	1356m (1325)	1354m (1330m)	1352m (1345s)	1343m (1350w)	1338m (1350w)	1340m (1353m)	1335m (1350m)
<b>δOH</b>	1280vs	-	1280m (1243w)	1275m (1250m)	1275m (1252w)	1280m (1243w)	1275w (1250w)	1275w (1258m)	1275w (1252w)
<b>vC-HPh+ δCH caf</b>	1238w, 1203s (1244m, 1210w)	1241vs (1251m, 1241m, 1215m)	1238m (1201w)	1240m (1203m)	1240m (1202w)	1240m (1208w)	1240m (1212m)	1240m (1219m)	1238m (1212w,12 31s)
<b>δ(CH) + vC- O</b>	-	1190m (1189m)	1186m (1150m)	1182m (1152m)	1198m (1152w)	1198m (1147m)	1190m (1150m)	1196m (1151m)	1198m (1153m)
<b>δCH(ring) In plane bend</b>	1162m,1 152m 1118m, 1038m (1155w, 1118m, 1031m)	(1131m, 1080w, 1020w)	1118w, 1025m (1151w, 1117w, 1023w)	1132w 1030m (1154m, 1102w)	1124w, 1050w, 1022m (1153w, 1118w, 1027m)	1128w, 1050w, 1030w (1152w, 1115w)	1123m, 1025m (1152w, 1121w)	1122w, 1043w, 1022w (1153m 1114m)	1131m, 1050w, 1025m (1145s, 1115s)
<b>vN-N</b>	(1063s)	-	(1059s)	(1061s)	(1056m)	(1060m)	(1057w)	(1054m)	(1058m)
<b>v(N-CH3) + δring (imidazole)</b>	-	974s (975m)	975m (960w)	975m (974m)	974m (950w)	974m	970m (974w)	970w (975m)	976m (972w)
<b>δCH (ring) Out-of-plane bend + v(N- CH3)</b>	990m, 981m, 949w, 901m, 859w, 839w, 790m, 760vs, 739m (999m, 795w)	861m, 754m (925w, 850w)	955m, 935w, 901m, 856w, 817w, 796w, 784m, 760s (913w, 807w)	933w, 905w, 897w, 880w, 856w, 817w, 796w, 780w (992w, 876s, 848m, 801w)	923w, 903w, 877w, 856w, 830w, 794w, 780w, 758w (903w, 844w, 800w)	937m, 903m, 895w, 862m, 837w, 781m (795w)	921m, 895m, 855w, 781w, 760m (924w, 892w, 825w)	923w, 909w, 863w, 835w, 810w, 797w, 758m (931m, 873w, 850m, 802m)	924m, 858w, 826w, 792w, 758m (900m, 872w, 841w, 815s)
<b>γring (pyrimidine) + γring (imidazole)</b>	-	746s (745w, 700w)	744s (750w, 702w)	756s (753m, 707m)	742m (740w)	748s (748w, 702w)	742s (750w, 708w)	743s (742m, 702w)	742m (757m, 704w)
<b>δCH In plane ring def</b>	687m, 655w, 624w (655vw)	-	670m, 644w (629w)	670w, 643w (655w)	680w, 661w, 644w, 631w (665w, 624w)	698w, 678w, 643w (680w, 645w)	680w, 641w (686w, 656w)	695w, 682w, 660w, 641w, 631w (647w)	678m, 643w (644m, 620s)
<b>γring</b>	-	610vs(6)	605m	608m(61)	608w	608w	606w	607w	606w

(imidazole)		13w)		2w)					
vM-N	-	-	578m(575w)	580w(562w)	576w(568w)	590w(588w)	578w(585w)	575w(579w)	577w(583w)
$\delta$ CH Out-of-plane ring def + $\delta$ ring pyrimidine	569m, 555w, 520w, 491w, 478w, 460w, 440m, 416w (550vw, 530w, 450vw, 420vw)	485w, 466w, 427w (444w)	543w, 495w, 476m, 466m, 458w, 442w, 417m (550w, 445w)	558w, 533w, 478w, 462w, 451w, 420w, 418w (551m, 480w, 447m, 413w)	561w, 541w, 498w, 478w, 464w, 450w, 415w (555w, 502w)	562w, 542w, 494w, 478w, 463w, 454w, 438w, 417w (556w, 534w, 443w)	540w, 493w, 478w, 462w, 440w, 410w (554w, 471w)	540w, 493w, 478w, 462w, 440w, 410w (550w, 524w, 475w)	540w, 495e, 477w, 466w, 458w, 440w, 416w (555w, 517m, 489m)
$\delta$ CCN	510w	-	506w (508w)	508w	505w	506w	505w	506w	508w
vM-O	-	-	438w (430w)	436w (432w)	437w (436w)	422w (418w)	438w (444w)	450w (432w)	425w(431w)

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