Synthesis and Characterization of N-salicylidèneglycinate (KHL) And caffeine complexes with Cd (II),Cu(II),Ni(II), Zn (II)

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Abstract

A two series of metal complexes $[M(LH)_2(H_2O)_2]$ and $[M(LH)_2(caf)_2]$ M=Cu(II),Ni(II),Cd(II),Zn(II),caf= caffeine, KHL=N-salicylidèneglycinate, have been synthesized and characterized by metal analysis, molar conductivity ,infrared, electronic and EPR spectral measurements N-salicylidèneglycinate (KHL) were obtained by condensation of salicylaldehyde, glycine and KOH. The stoichiometries reaction between the metal(II) ion and (KHL) ligand in molar ratio of M:LH(1,2) resulted in the formation of the metal complexes of type $[M(LH)_2(H_2O)_2]$ or molar ratio of M:LH:Caf (1,2,2) of type $[M(LH)_2(caf)_2]$ (where M=Cu(II),Ni(II),Cd(II),Zn(II),caf= caffeine. The ligand LH acts in a chelate manner (NO) donor and coordination of water or caffeine by N9 coordination through metal ion.

Keywords: caffeine, N-salicylidèneglycinate, complexes, molar conductivity.

Introduction

Schiff base ligand and transition metal complexes with Schiff bases have expanded enormously and Embraced wide and diversified subject comprising west areas of chemical, physical, and biological [1] etc. Many studies have been done on transition metal complexes of Schiff base due to the fact that Schiff bases offer opportunities for inducing substrate chirality [2], tuning metal centered electron factor, enhancing the solubility and stability of either homogeneous or heterogeneous catalysts [3] as well stabilizing Schiff bases ligand are able to coordinate many different metals and stabilize then in various oxidation states [4].

Amino acids constitute the building blocks of proteins [5] and are chemical species indispensable for performing a huge number of biological functions as exemplified by the role of enzyme [6] Considerable interest have been developed in transition metal complexes with amino acids Schiff base ligand as structural models. The complexes $[M(salgly)_2(OH)_2]$,$[M(salgly)_2(caf)_2]$,caffeine have been synthesized and characterized by analysis of metal, caffeine, molar conductivity infrared, UV-visible and EPR spectroscopy.

Experimental

All the chemicals were obtained from commercial sources and were used without purifications: KOH,$Nicl_2$ H_2O BDH, $Cdcl_2$ $1/2H_2O$ Panreoc, $Cucl_2$ $2H_2O$ LOBA chemie, $Zncl_22H_2O$ LOBA chemie, glycine norma pur analytical reagent 100°/◦,Salicylaldehyde >=98°/◦ SAFC , Ethanol Fischer, acetone Fischer , Caffeine Riedl-deHaen.A.G.

Preparation of the N-salicylidèneglycinate Ligand (KHL)

N-salicylidèneglycinate ligand (KHL) formed from salicylaldehyde and glycine was prepared by adding (1,04ml, 10^{-2} mole) Salicylaldehyde in 10 ml anhydrous ethanol to the some volume of ethanolic, glycine (0,75ml, 10^{-2} mole) with potassium hydroxide (1,12g,10^{-2} mole). The mixture was refluxed for three hours. The yellow formed precipitate was filtered, washed several times with ethanol, ether, the yield of the reaction was 76°/◦.

Preparation of [M(LH)2(OH2)2](1,2,3,4) M=Cu(II)(1),Ni(II)(2) Cd(II)(3),Zn(II)(4).

The Complexes $[M(LH)_2(H_2O)_2]$(1,2,3,4) were prepared using general method for example complexes of Cu cl_2 $6H_2O$ (II) with N-salicylidèneglycinate (KLH) were synthesized by mixing 10 ml ethanol of 0,43g,(2mmole) ligand (KLH) with ethanolic Solution of(0,17g (1mmole),($Cucl_2$,6H2O).The mixture was refluxed three hours. The precipitates were filtered and wasted several times with acetone and Ethanol the yield of the reaction was 63°/◦.

Preparation of [M(LH)2(caf)2](5,6,7,8) (M = Cu(II)(5) ,Ni(II)(6) ,Cd(II)(7) ,Zn(II)(8) caf=caffeine).

Complexes of $[M(LH)_2$ $(caf)_2]$ were prepared using a general procedure. The complexes $[M(LH)_2$ $(caf)_2]$ was prepared by $[M(LH)_2(OH_2)_2]$by caffeine in the reaction mixture or by mixing ethanolic solution (15ml). The N-salicylidèneglycinate ligand (KHL) and caffeine (2mmole) with an ethanolic solution (10ml) of 1 mmole of (MCl_2, xH_2O) salts. The precipitates were filtered, and washed with acetone and ethanol. The analytical data of complexes $[M(LH)_2$ $(caf)_2]$(5,6,7,8) M=Cu(II)(5),Ni(II)(6),Cd(II)(7),Zn(II)(8) is summarized.

Results and Discussion

FTIR spectroscopy of the free ligand N-salicylidèneglycinate (KHL)

Infrared Spectra provide valuable information regarding the nature of the functional groups, structure of the mixed ligand and the mode of coordination of it to the metal ion in the complexes. The N-salicylidèneglycinate ligand (KHL) was synthesized by condensation of salicylaldehyde, and glycine. The infrared spectrum for free ligand (KHL) was obtained from FTIR in KBr in the range (4000- 400) cm^{-1} figure (1).The infrared spectrum of the ligand (KHL) show vibrations bands with the frequencies 3340 cm^{-1} attributed υ(OH), and 3058 cm^{-1} attributed υ(CH),The stretching vibration υ(C=N) observed at 1641 cm^{-1}[16],and υ(C=C) observed at 1611 cm^{-1}, the stretching frequency observed at 1520cm^{-1} attributed (νC-C/νC-N), The bands at 1390 cm^{-1} and at 1611 cm^{-1} can be assigned to the symmetric and antisymmetric stretching vibration of the $-COO^{-}$ group, respectively[7,13]. The band at 1315 cm^{-1} due to bending mode of the phenolic –OH group (δOH)[16].And the strong band around 1194 cm^{-1} attributed υ(C-O), and the band 1222 cm^{-1}, 1115 cm^{-1} ,1054 cm^{-1} attributed (δ ArCH) in plane deformation, 936 cm^{-1},900,741 cm^{-1} attributed (δ ArCH) out plane deformation, and 506 cm^{-1} ,527 cm^{-1} attributed (δ Ar CH) in plane ring deformation and 487 cm^{-1},410 cm^{-1} attributed (δ Ar CH) out plane ring deformation were observed for ligand respectively Table (1)[7-8].

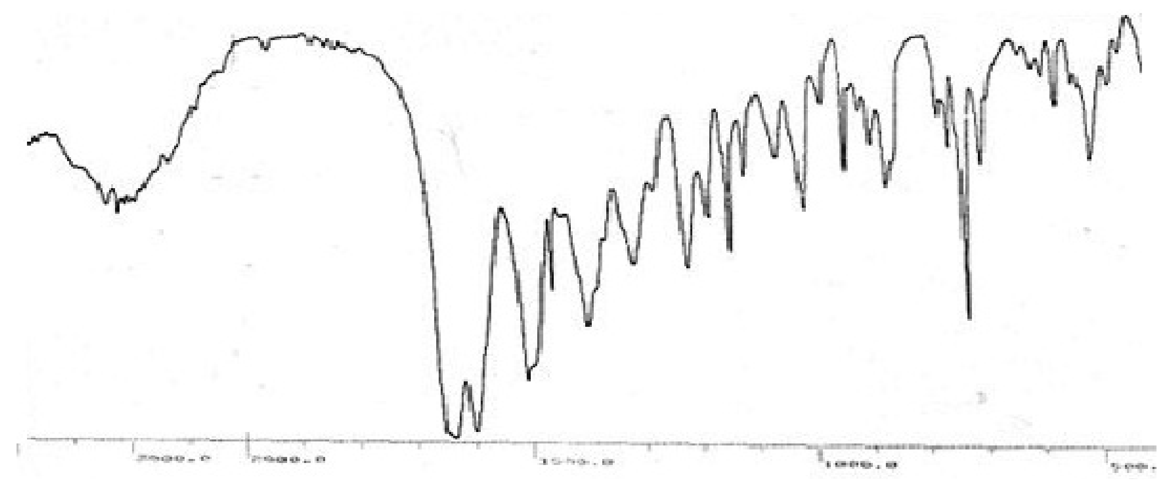

Figure 1. Infrared spectra of the ligand N-salicylidèneglycinate (KHL) in KBr

Table 1. Infrared spectra data of the ligand N-salicylidèneglycinate free (KHL) in KBr

Ligand (KHL)	Attribution
3340w	ν OH
3058 m	ν CH
2807w ,2615w	ν CH_2
1641 s	ν C=N
1611vs	$\nu C=C/\nu_a CO_2^-$
1520s	νCC/νCN
1460m	δCH_2
1390vs	$\nu_s CO_2^-$
1315 s	δOH
1194 vs	νC-O
1222,1115 ,1054m	δ (Ar CH) In plane def
936, 900m ,741 vs	δ (Ar CH) out plane def
506 , 527s	δ (Ar CH) In plane ring def
487,410w	δ (Ar CH) out plane ring def

S: strong m: medium w: weak vs: very strong vw: very weak

FTIR spectroscopy for complexes [M (LH)2 (OH2)2](1, 2,3,4), M=Cu (II)(1), Ni(II)(2),Cd(II)(3),Zn(II)(4).

The infrared spectrum of ligand N-salicylidèneglycinate complexes was recorded within the (4000-400) cm^{-1} range (figure 2), and compared with that of the four complexes [M(LH)$_2$(OH$_2$)$_2$] M=Cu(II)(1),Ni(II)(2])Cd(II)(3),Zn(II)(4)Table (2).

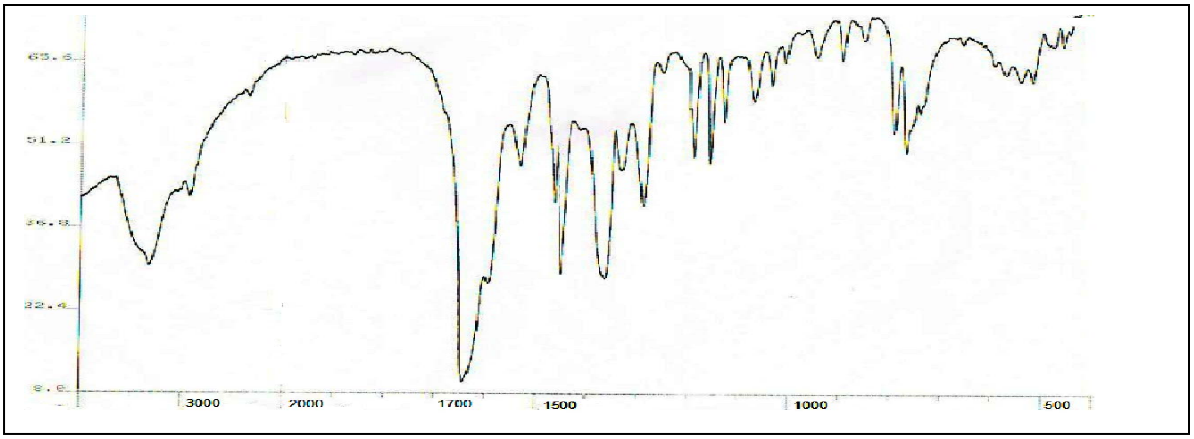

Figure 2 Infrared spectra of complex [Cd (LH)$_2$(OH$_2$)$_2$] in KBr.

Table 2. Infrared spectra of Metal- N-salicylidèneglycinate complexes [M (LH)$_2$ (OH$_2$)$_2$]in KBr M=Cu(II)(1),Ni(II)(2) Cd(II)(3),Zn(II)(4).

	1	2	3	4
Assignment	[Cu(LH)$_2$(OH$_2$)$_2$]	[Ni (LH)$_2$(OH$_2$)$_2$]	[Cd (LH)$_2$(OH$_2$)$_2$]	[Zn (LH)$_2$(OH$_2$)$_2$]
νOH (OH$_2$+OH)	3400 L	3360 L	3400L	3300L
ν CH	3011m	3021m	2950 m	3000 m
ν C=N	1631vs	16 36vs	1635 vs	1633 vs
νC=C /ν$_a$CO$_2^-$	1600s	1589s	1598 s	1600 s
νCC/νCN	1539m	1529s	1535 s	1530 s
δCH$_2$	1457s	1459vs	1460 vs	1460 s
ν$_s$CO$_2^-$	1350s	1384s	1380 s	1360 s
δOH	1308 s	1305s	1310 s	1305 s
νC-O	1191m	1185s	1190 m	1190 s
In plane def CH$_{ar}$	1149m,1130m 1088w,1038m	1150s,1130s 1068m,1038m	1130 m,1080s 1040m,1020m	1160 m,1130 s 1075 m 1040m
CH aromatiques W,ρ(OH$_2$)	935w,904w 864w,750s	945m,853w 792m,761m	950w, 900 w 860 m, 770w	950w, 900m 860w,760 w
ρCH$_2$	670w	669m	665m	660w
δ C=O	608m	587m	600m	605m
νM-N	577m	562m	560m	570m
def CH ar	526m	522m	540 m,520w	540m, 530w
νM-O	455w	461w	460w	460w

S: strong m:medium w: weak vs: very strong vw: very weak

The broad band is the (3500-3400) cm^{-1} region in all complexes attributed to the presence of water coordinated molecules [9] and υ (OH) phenolic associated the presence of water coordination. FTIR investigation of [Cd $(LH)_2(OH_2)_2$] complex by HOD isotopic exchange proved to be a very sensitive method for determining OH group coordination [20] The OH stretching ν(OH)H2O is observed at 3450 cm-1. However, in the range of ν(OH)HOD vibrations of HOD molecules, one band appears at about 2925 cm−1.The isotopic ratios υ(OH)/δ(OD) have values of 1.18.

The phenolic group which may be attributed ArCH to υ(OH) vibration of coordinated water and phenolic group associated the appearance of bands around (1313-1305)cm-1 and(864-853)cm-1 due to bending δ(OH) phenolic group and wagging, rocking modes of coordinated water molecules. The (10-14) cm-1 shift in intense band appearing in the range (1636-1631)cm-1 [11]for all the complexes has indicated the involvement of nitrogen atom of azomethine group and bending δ(OH) water coordination for metal . For as the coordination of the carboxylate ion is concerned the information is drawn from the position and difference of stretching νas and νsCOO- frequencies occurring at about (1600-1590) cm-1, (1360-1385)cm-1 respectively in the spectrum of the complexes. This data is compared with glycine and metal glycine complexes (1,2,3,4).The frequency difference Δν>200 cm-1 between asymmetric and symmetric stretching vibration attributes at monodentate coordination of the carbonyl group of the glycine with the metal ions. The new stretching vibration observed in the lower frequencies the frequencies, noticed at about (577,560) cm-1 and (455,461) cm-1 respectively attributed for M-N and M-O band[10-11]. The infrared results show that the metal is coordinated through nitrogen atoms azomethine and oxygen atoms carboxyl- ate of the glycine besides water molecules.

FTIR spectroscopy for caffeine N-salicylidèneglycinate complexes

[M(LH)2(caf)2](5,6 ,7,8), M=Cu(II)(5), Ni(II)(6), Cd (II)(7) , Zn (II)(8),caf =caffeine

FTIR spectra and vibrationnal frequencies assignment the corresponding vibrations are observed in infrared spectra table (3). It may be noted that the spectra of the complexes obtained [M(LH)2(caf)2], M= Cu(II),Zn(II) ,Cd(II), Ni(II) are similar in the range (4000-400) cm-1 (figure3.1, figure3.2 ,figure3.3 and figure3.4). The broad band noticed at 3350 cm-1 is confirmed by thermal analysis and attributed of stretching υ(OH) hydratation water. The infrared spectra show characteristic weak bands at (3100 cm-1 and 2950cm-1 shifted to lower frequencies by (5-14) cm-1 compared with caffeine free.

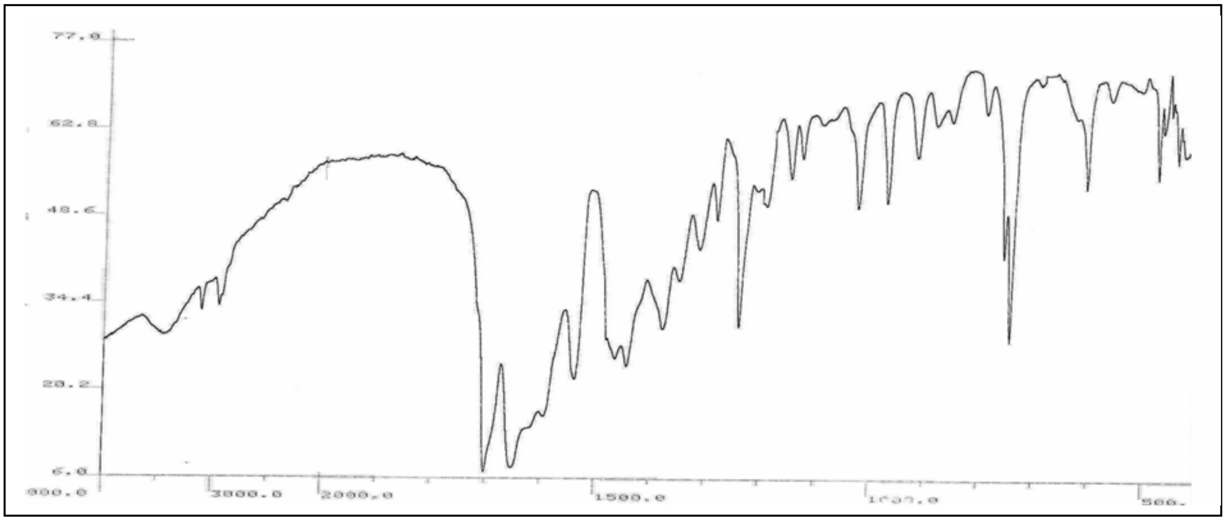

Figure 3.1 Infrared spectra of complexes [Cu(LH)$_2$ (caf)$_2$] (5) in KBr.

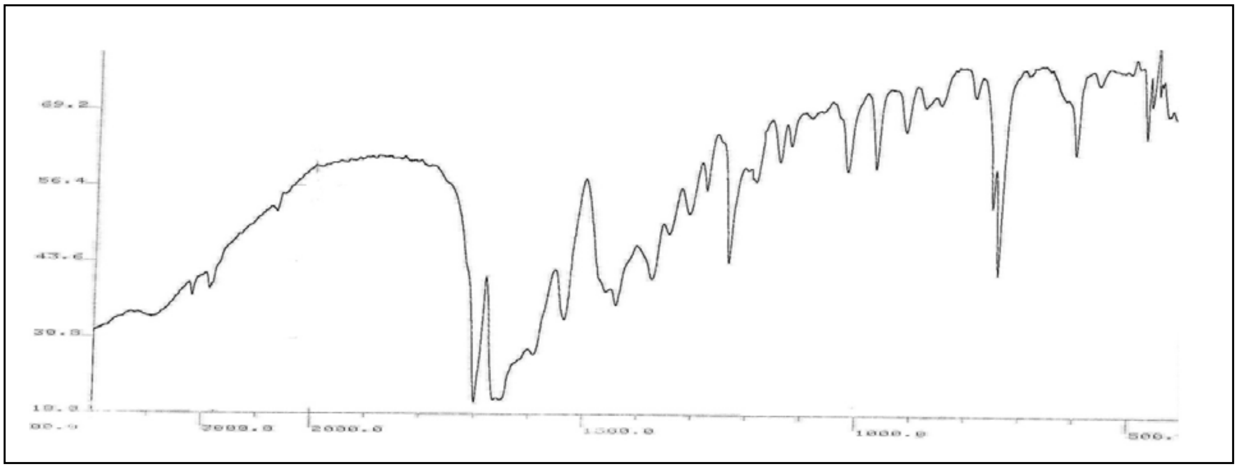

Figure 3.2. Infrared spectra of complexes [Ni(LH)$_2$ (caf)$_2$] (6) in KBr

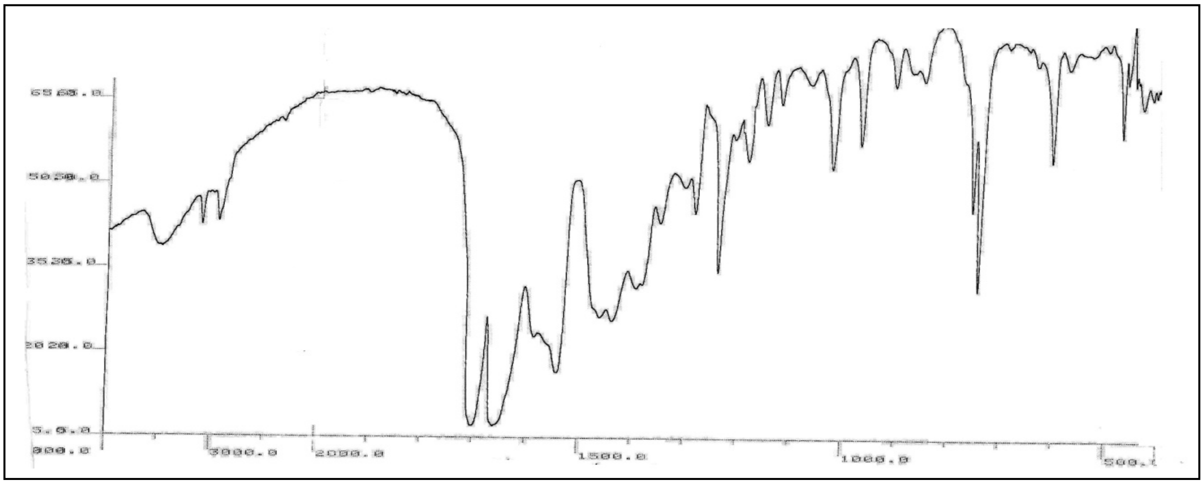

Figure 3.3. Infrared spectra of complexes [Cd(LH)$_2$ (caf)$_2$] (7) in KBr

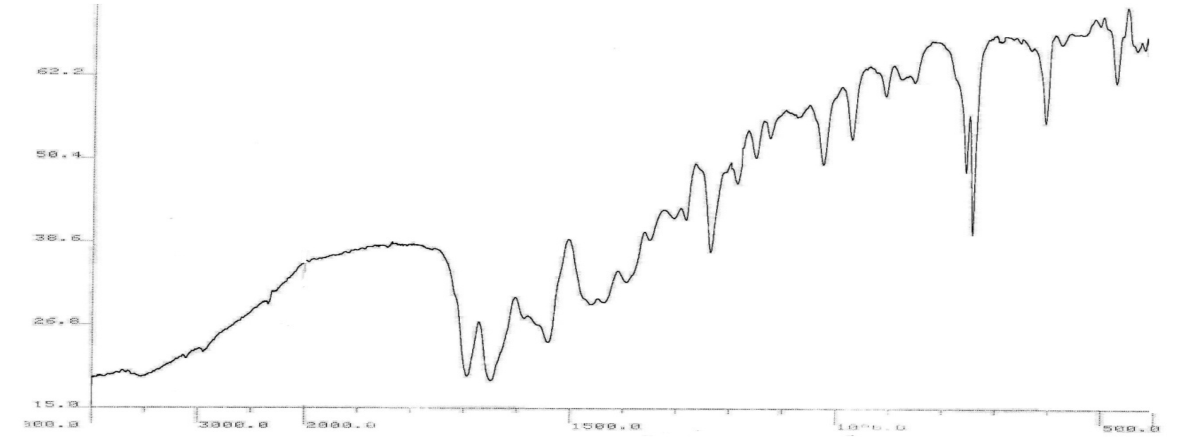

Figure 3.4. Infrared spectra of complexes [Zn(LH)$_2$ (caf)$_2$] (8) in KBr

TABLE 3.INFRARED SPECTRA OF N- SALICYLIDÈNEGLYCINATE -M-CAFFEINE COMPLEXES [M(LH)2(CAF)$_2$] IN KBR
M=CU(II)(5),NI(II)(6),CD(II)(7),ZN(II)(8) , CAF =CAFFEINE .

Assignment	Free ligand	**5**	**6**	**7**	**8**
	Caffeine	[Cu (LH)$_2$ (caf)$_2$]	[Ni (LH)$_2$ (caf)$_2$]	[Cd(LH)$_2$ (caf)$_2$]	[Zn(LH)$_2$ (caf)$_2$]
νHO		3450 L	3400,3350 L	3450,3330 L	3450 L
ν CHar	3114m	3100 w	3100w	3100w	3100w
ν CH3+ν CH2	2955w	2950 vw	2948w, 2850vw	2950w	2950w, 2900vw
ν C=O caf	1702vs	1698 s	1697vs	1692vs	1695vs
ν C=O ν C=N	1662s	1650s 1625 vs	1648vs	1650vs	1655vs 1627vs
νC=Ccaf/νC=Car /νaCO2-	1600m	1600 e	1590vs	1590s	1600vs
δHCN + νring imidazole+ νring pyrimidine + νCC/νCN	1551 s	1540 s	1540 s	1540 s	1540 vs
δCH3+ δCH2 νC-N	1487m,1466m 1431m 1405m	1474 s ,1420e 1400 s	1472vs, 1444s 1400m	1480s, 1442m, 1390m	1470 vs, 1440vs 1400 vs
νsCO2-		1350 s	1360m	1350m	1360m

*ν*ring(imidazole) + *ν*ring(pyrimidine)+ δOH	1327w	1310 m	1323m	1320w	1325m
δ CH caf+δ C-Oph	1241vs	1240 m	1240vs	1240s	1240s
δ(CH) + νC-O	1213m 1190m	1200 w	1185s	1190m	1195s
δCH In Plane def		1158w ,1130m 1080m	1155w, 1122m 1080w	1150w, 1120w 1070w	1160s, 1130m 1080m
*ρ*r(CH3) + *ρ*r(CH)	1026s	1022m	1025s	1025s	1025s
ν(N-CH3) + *δ*ring(imidazole)	974s	990 w,970 m	970 m	974w	975m
*ρ*r(CH3) + *ν*(N-CH3) + *δ*(C O)	860m	850m	860m	860w	865m
CH Out-of-plane def		940w,922w 900w	940w,920w 790w, 760m	925vw,900w 790vw, 760s	955m,930m 900m
*γ*ring(pyrimidine) + *γ*ring(imidazo)	746vs	740vs	740vs	745vs	750vs
*Δ*ring (imidazole) δ COO-	610m	610 s	610 s	610m	610s
CH ring def		570w, 525w	545w, 510w	520w	560m, 530m
Tcaffeine	481m,450 m, 420w	478m	476w	480w	480m
νM-N		440w	440w	440w	442w
νM-O		420w	420w	420w	423m

S: strong m:medium w: weak vs: very strong vw: very weak

The carbonyl group in caffeine and their complexes [M(LH)2(caf)2], M= Cu(II),Zn(II),Cd(II), Ni(II) exhibits a strong absorption bands due the υ(CO),stretching vibration and is observed in the region (1698-1648)cm-1 .Caffeine free contain two carbonyl vibration in the meta position. The strong bands observed are considered to be due to υ(CO) symmetric and asymmetric υ (CO)+(C=N)caf [12]. The infrared spectrum of the complexes is characterized by significant shift (10cm-1) for asymmetric υ (CO)+(C=N) the to lower frequencies. The shift frequencies are observed for vibration (δHCN+ υring imid +υring pyrimi) of 10cm-1were attributed for authors [10-12], by coordination on the nitrogen N9 atom of caffeine ligand.

The bands noticed at 1625cm-1 and 1627 cm-1 for copper and zinc complexes is shifted to lower frequencies by 10 cm-1 corresponding of azomethine group coordinated for metal atom. As for as the coordination of the carboxylate ion is concerned the information is draw from the position and difference of stretching υasymmetric and υsymmetric COO- frequencies occurring about (1600-1590) cm-1 ,(1360-1350) cm-1 and Δ= (υas-υs)= 240 cm-1 respectively in the spectrum of the complexes, are behaving in monodentate carboxylate ligand [13-17].The bands noticed in the range (1325-1310) cm-1 and (1195-1185) cm-1 in the complexes table (3) assigned respectively to bending δ(ph Ar-O) and stretching υC-O, phenolic group. The news band in the range (570-545) cm-1 and 440cm-1 may be assigned for the stretching υ M-O (azomethine+caffeine) and υ M-O (carboxylate) respectively[18] table (3). It this case, the ligands are behaving in bidendate chelate coordination by N nitrogen atoms (azomethine) and oxygen atoms carboxyl-to glycine for metal ions besides caffeine coordinated by N9 nitrogen atom.

EPR Spectra

The EPR spectra of the [Cu (LH)2 (caf)2] complex measured in the solid state gave a single, very broad line with g = 2.086 . The value of g = 2.086 observed for [Cu (LH)2 (caf)2] at room temperature are normal for typical mononuclear copper complexes.

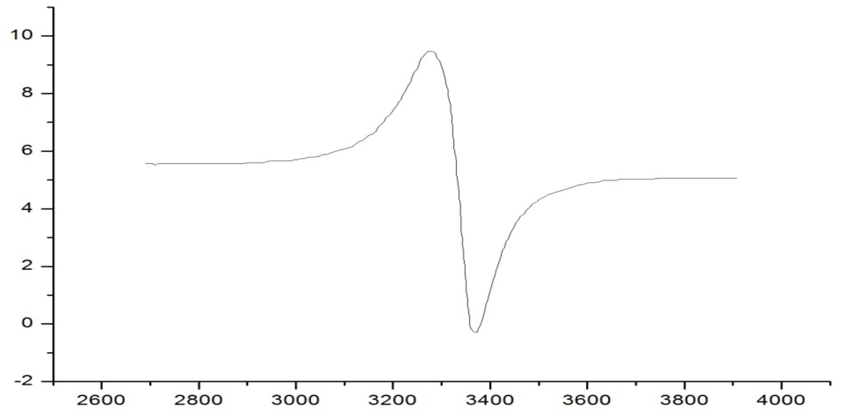

Figure 4EPR of complexes [Cu(LH)2 (caf)$_2$] (8) ,caf= caffeine.

Molar conductivity

The molar conductivity of the Schiff base caffeine complexes were measured using 10-4M DMSO solvent at room temperature. The conductivity values of the complexes are in the range (3,89 - 9,68) Ohm-1 cm2 mol-1. These lower values of molar conductivities indicates the non-electrolyte behavior of the Schiff base caffeine complexes of Cu(II), Ni(II), Cd(II) and Zn (II).

UV-visible spectra for ligand LH and their complexes [M(LH)2(caf)2](5,6,7,8) M=Cu(II)(5),Ni(II)(6),Cd(II)(7),Zn(II)(8) ,KHL =N- salicylidèneglycinate, caf=caffeine.

The electronic spectra data of free ligands in the UV-visible region were studied in DMSO solvent shows strong absorption band of salicylidèneglycine at 218 nm and 274 nm is attributed to π→π* transition another bands at 319 nm, 386 nm respectively which is assigned to n→π* transition (figure5.1, figure5.2 ,figure5.3 and figure5.4).The caffeine spectra shows three absorption bands at 275 nm is attributed to π→π* transition, another bands at 316nm, 365nm respectively which is assigned to n→π* transition[14-15]. The spectrum of the complexes [M(LH)2 (caf)2](5,6,7,8) M=Cu(II)(5),Ni(II)(6),Cd(II)(7),Zn(II)(8).

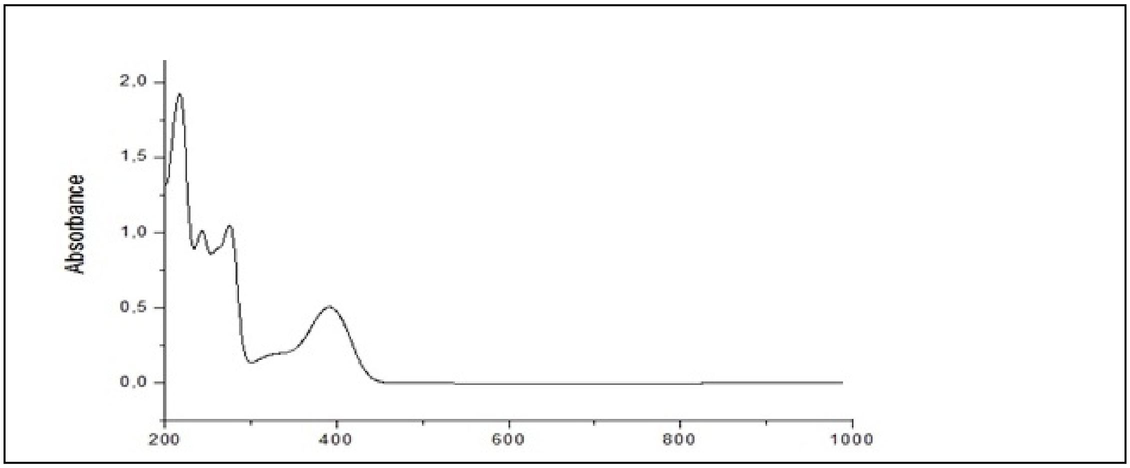

Figure 5.1.UV-visible spectra for ligand N-salicylidèneglycinate (KHL)

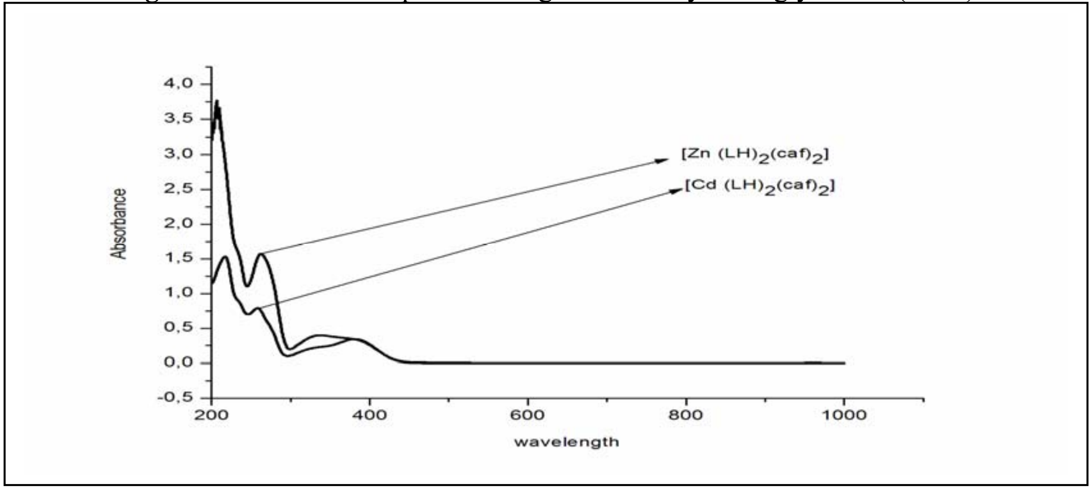

Figure 5.2. Electronic spectrum of their complex $[Zn(LH)_2(caf)_2]$ and $[Cd\ (LH)_2(caf)_2]$ in DMSO , caf=caffeine.

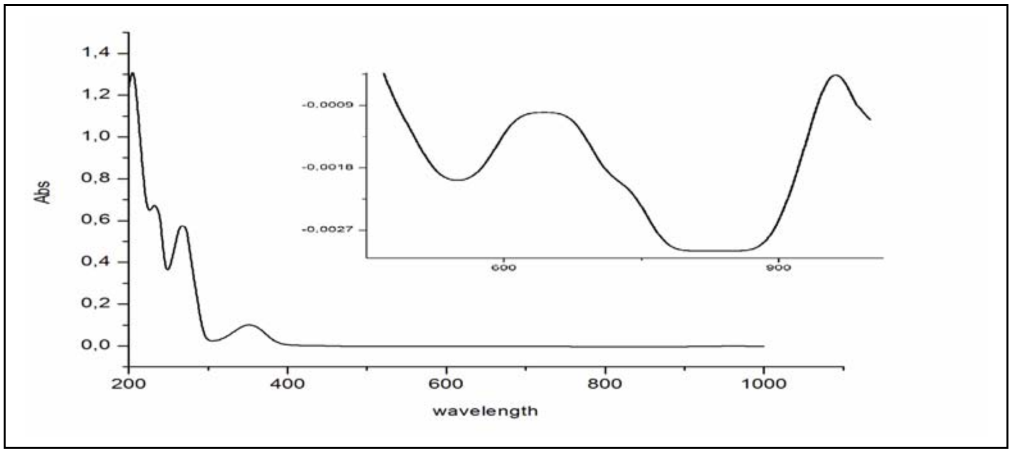

Figure 5.3. Electronic spectrum of the complex [Ni $(LH)_2(caf)_2$] in DMSO, caf=caffeine.

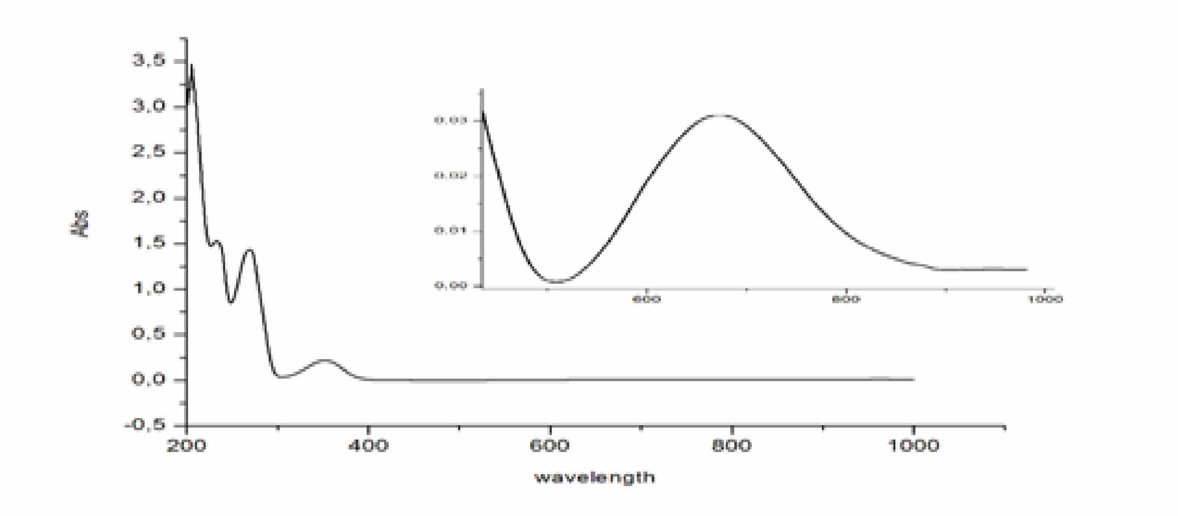

Figure 5.4. Electronic spectrum of the complex [Cu $(LH)_2(caf)_2$] in DMSO , caf=caffeine.

The electronic spectrum of Ni(II) complex exhibited absorption bands at 660 nm and 952 nm which are attributed to the electronic transition 3A2g(F) →3T1g(F) (υ2) and 3A2g(F) →3T1g(F) (υ1) [19]. The spectrum of Cu(II) complex shows that its bands in the visible region is attributed to the electronic transitions of 2a1g(D) →2b1g(D) at 680 nm[19]. Finally, the electronic configuration of Zn (II) and Cd(II) complexes were d10 which confirm the absence of any (d-d) transitions, but the absorption bands in their spectra suffered red shift with hypochromic effect [19]. The prepared complexes were found to be solids insoluble in water and polar solvents but they were soluble in some polar organic solvents like DMF, DMSO table (4).

Table 4 Electronic data for free ligands (KHL) and their complexes [M$(LH)_2(caf)_2$] in *DMSO (5,6,7,8) M=Cu(II)(5),Ni(II)(6),Cd(II)(7),Zn(II)(8),caf=caffeine. (*DMSO = Dimethylsulphoxide)

	λ_{max}(nm)	**Absorbance**	**Transitions**
Caffeine	275	0.49	$\pi \rightarrow \pi^*$
	316	0.006	$n \rightarrow \pi^*$
	365	0.014	$n \rightarrow \pi^*$
N-salicylidèneglycine	218	1,79	$\pi \rightarrow \pi^*$
	274	0,81	$\pi \rightarrow \pi^*$
	319	0,18	$n \rightarrow \pi^*$
	386	0,47	$n \rightarrow \pi^*$
[Cu $(LH)_2(caf)_2$]	205	3,27	Transfer de charge
	233	1,46	Transfer de charge
	269	1,35	Transfer de charge
	350	0,16	M ⟶ L
	680	0,03	$^2a_{1g}(D) \rightarrow {}^2b_{1g}(D)$
[Ni $(LH)_2(caf)_2$]	211	3,88	Transfer de charge
	233	3,34	Transfer de charge
	269	2,76	Transfer de charge
	356	0,44	M ⟶ L
	660	-0,0008	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)\ (\upsilon_2)$
	952	-0,0005	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)\ (\upsilon_1)$
[Cd $(LH)_2(caf)_2$]	220	1,48	Transfer de charge
	258	0,75	M ⟶ L
	378	0,32	shift with hypochromic effect
[Zn $(LH)_2(caf)_2$]	209	3 ,65	Transfer de charge
	261	1,47	M ⟶ L
	364	0,30	shift with hypochromic effect

Conclusions

In this study two series of complexes [M (LH)2 (H2O)2] and [M (LH)2 (caf)2] the formulation were in accordance with the data of analysis molar conductivity, IR,UV-visible and EPR spectra. The low molar conductivity valeurs of the complexes indicate them to be non-electrolytes. The spectroscopic data indicates that the eight complexes are all containing a bidentate N-salicylidèneglycinate with azomethine nitrogen and carboxyl oxygen as two donor atoms and coordination of two water or two caffeine to metal ion. The UV-visible and EPR spectral data suggest the octahedral geometry for the [M(LH)2 (H2O)2] and [M(LH)2 (caf)2] complexes.

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