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Synthesis And Characterization of N-Salicylidene γ- butyric acid (KHL) And its Caffeine Complexes $[M(LH)(Caf)_2H_2O]n$

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ABSTRACT

In this article, the N-salicylidene γ -butyric acid (KHL) was synthesized by the reaction of salicylaldehyde and γ -aminobutyric acid. The Schiff base ligand (KHL) was obtained and characterized by Infrared, ^{1}H, ^{13}C NMR and UV-Visible. Four mixed ligand complexes of general formula $[M(LH)(Caf)_2H_2O]_n$ where LH=N-salicylidene γ -butyric acid, Caf=Caffeine, M= Zn(II), Cd(II), Ni(II) and Cu(II) have been prepared and characterized using spectroscopic techniques- IR, UV-Visible and EPR. The ligands (KHL, Caf) and their corresponding complexes were screened for their antimicrobial activities.

Keywords: N-salicylidene γ -butyric acid, caffeine, Schiff base, mixed ligand complexes, infrared, NMR, UV-Visible, EPR and antimicrobial activity.

INTRODUCTION

There is continuous interest in the investigation of salicylidene-aminoacidato Schiff bases obtained by condensation between aldehydes and amino acids. They are able to coordinate many different metals such as rare-earths and transition metals, and to stabilize them in various oxidation states [1].

Salicylidene-aminoacidato Schiff bases complexes are used as non-enzymatic models for the metal-pyridoxal (Vitamin B6) amino acid Schiff base systems which are key intermediates in many metabolic reactions of amino acids catalyzed by enzymes which require pyridoxal as a cofactor (transamination, decarboxylation, and elimination, racemization, etc.) [2]. Many other roles for pyridoxal phosphate and its Schiff base complexes have been suggested [3] which would indicate that studies of Schiff base complexes composed of amino acids and salicylaldehyde derivatives may provide useful information to elucidate some of these roles. The coordination of a metal ion to N pyridoxylideneamino acid Schiff bases stabilizes the azomethine linkage, under conditions that would otherwise promote bond cleavage [4]. In addition, complexes of amino acid Schiff bases are considered to constitute new kinds of potential antibacterial and anticancer reagents [5–7]. Therefore, synthesis and characterization of non-enzymatic models for the metal-pyridoxal amino acid Schiff base systems [8], and the design of new N salicylidene aminoalkanoato complexes with antimicrobial [9], anti-inflammatory [10], antipyretic activities [11] together with a superoxide dismutase-like activity [12] have been the driving force for the study of new N-salicylidene amino acidato Schiff base complexes [13].

There are many interesting studies on the salicylidene-aminoacidato Schiff bases and their complexes, Al-Shaheen J. and al. [14] synthezised four Schiff bases from vanillin and amino acids (glycine, L-serine, L-tyrosine and L-phenylalanine). Their complexes with Fe(III) have a tetracoordinated tetrahedral configuration through the atoms NOOO, or tridentate NOO. Schiff base ligands derived from o-phthalaldehyde and aminoacids viz., glycine, L-alanine, L-phenylalanine were synthesized by M. A. Neelakantan and al. [15]. Also, a Schiff base ligand derived from leucine and 5-bromosalicyaldehyde was synthesized by Easwaramoorthi D. and al. [16]. The Schiff base and its complexes of Cu(II), Co(II) and Ni(II) were characterized by different spectral techniques. Recently we have studied salicylidene-aminoacidato Schiff bases derived from glycine and β-alanine [17-19].

Caffeine (3,7-dihydro-1, 3,7-trimethyl-1H-purine-2,6-dione or 1, 3,7-trimethylxanthine) is a well-known compound that occurs in nature in coffee, tea, cola nuts, mate' leaves, guarana paste, and other related natural products. It is also obtained as a byproduct in the manufacture of caffeine-free [20]. Caffeine is also used as a decongestant, increase in energy, weight loss, analgesic, appetite suppressant and diuretic [21]. The metal complexes of caffeine have been widely studied [22-25]. These complexes play a dominant role in many biochemical internations [22].

In this paper, we prepare and characterize Schiff base caffeine complexes with a tridentate (NO_2) Schiff base ligand and a monodentate N9 caffeine (Figure 1), forming the coordination units of a general formula $[M(LH)(Caf)_2H_2O]_n$, where M = Cu^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+} and Caf= caffeine.

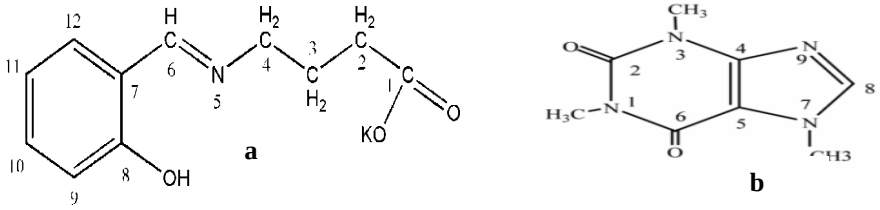

Figure 1: Proposed structure of the **a.** N-salicylidene γ -butyric acid, **b.** structure of the caffeine.

MATERIALS AND METHODS

All chemicals were obtained from commercial sources and were used without purifications: ($NiCl_2$, $6H_2O$ BDH; $CdCl_2$,$1/2H_2O$ Panreac; $CuCl_2$, $6H_2O$ BDH; KOH BDH, $ZnCl_2$, $2H_2O$ BDH), γ -aminobutyric acid FLUKA, salicylaldehyde SAFC, Ethanol and DMSO Sigma Aldrich, Caffeine Riedel-De Haen AG. Infrared spectra were recorded as KBr pellets on a Shimadzu 460 spectrophotometer in the range of 4000–400 cm^{-1} at 298 K. while the electronic spectra (UV–Vis) were obtained on a Shimadzu UV-1800 Spectrophotometer. The ^1H, ^{13}C NMR spectra of the ligand were recorded with a Bruker AVANCE 300 at 25°C. All chemical shifts ^1H and ^{13}C are given in ppm using tetramethylsilane (TMS) as internal reference and DMSO as solvent. Conductivity measurements were performed at 25°C in DMSO using Hach HQ430d flexi. EPR spectra were recorded on Bruker ER 200D spectrometer.

Preparation of the Schiff base (KHL): To a solution of γ -aminobutyric acid (10 mmol, 0.24g) in Ethanol (10 mL) containing KOH (10 mmol, 0.56g), salicylaldehyde (10 mmol, 1.22g) was added. The above solution was magnetically stirred at 78°C for 2 h. The volume of yellow solution was reduced by slow evaporation of the solvent. Then, the crystalline product so formed were filtered off and washed several times with ethanol.

Preparation of complexes $[M(LH)(Caf)_2H_2O]n$ (M=Cd(II), Zn(II), Ni(II), Cu(II); Caf=caffeine):

The complexes of Cu(II), Ni(II), Cd(II) and Zn(II) were prepared by the following procedure: a solution of the metal salt $ZnCl_2$, $2H_2O$ (1 mmol, 0.14 g), $CdCl_2$, $1/2H_2O$ (1 mmol, 0.23g), $NiCl_2$, $6H_2O$ (1 mmol, 0.24 g) or $CuCl_2$, $6H_2O$ (1 mmol, 0.17g) was added to an ethanolic solution (25 mL) of N-salicylidene γ -

butyric acid (3 mmol, 0.49g) with potassium hydroxide (2 mmol, 1.12g) and (2 mmol, 0.38 g) of the caffeine. The reaction mixture was stirred at 78 °C for 4h. The resultant solid product was filtered, washed with ethanol and dried.

RESULTS AND DISCUSSION

Characterization of the ligand (KHL)

Infrared spectroscopy: The characteristic IR bands of the ligand (KHL) are given in Table 1. The IR spectrum (Figure 2) show the broad and moderate band at 3444 cm^{-1} due to OH vibration of the phenolic group [26]. The weak bands at (2836-3102) cm^{-1} are assigned to the aromatic and aliphatic C–H stretch. The strong band around 1617 cm^{-1} is related to υ(C=N) [26]. Also the symmetric and antisymmetric stretching of the carboxylate group $–COO^-$ are at 1363 cm^{-1} and 1526 cm^{-1} respectively [27]. The bands appearing at 1595 cm^{-1} and in the (1341-1462) cm^{-1} range can be attributed to υ(C=C) and δCH_2/ δCH_3+ ν(C-N) respectively. The band at 1295 cm^{-1} due to bending mode of the phenolic group δ(OH). Bands in the (1022-1194) cm^{-1} range due to δ (CH) in plane deformation. The medium and/or weak band observed in the (618-903) cm^{-1} range can be attributed to δ(CH) out-of-plane deformation. The bands in the (510-550) cm^{-1} range are assigned to δ(CH) in plane ring deformation and the bands in the(424-470) cm^{-1} range is attributed to δ(CH) out plane ring deformation. From the literature, the infrared spectral data of the free caffeine (Table 1) [28] shows weak and sharp band at 3114 cm^{-1} which belongs to ν(C-H) aromatic. Another weak band belongs to ν(C-H) aliphatic was found at 2954 cm^{-1}. The strong band at 1702 cm^{-1} was attributed to ν(C=O), strong band at 1662 cm^{-1} was attributed to ν(C=O) and ν (-N=C). The ν(C=C) was noticed at 1546 cm^{-1} with shoulder at 1600 cm^{-1}. The (δHCN +υring imid + υring pyrimi) stretching and deformation heterocyclic imidazol and pyrimidine fragment were noticed at 1551 cm^{-1} and 1327 cm^{-1} respectively.

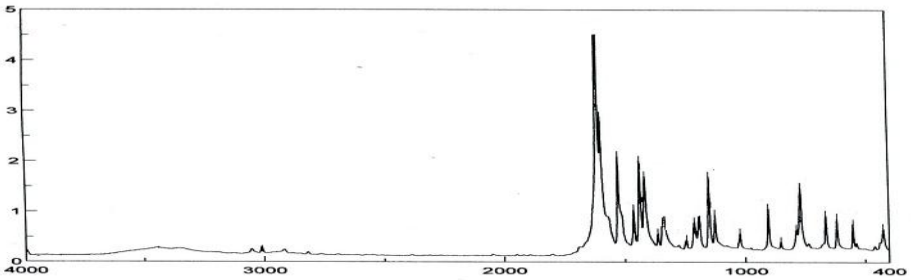

Figure 2: Infrared spectrum of the N-salicylidene γ -butyric acid (KHL) in KBr

^{1}H NMR spectroscopy : The ^{1}H NMR spectrum of Schiff base ligand (KHL) in D_2O, Figure 3, exhibits singlet signals at 8.24 ppm and 4.67 ppm, attributed to CH=N and OH protons respectively [29,30]. The multi signals within the (6.54-7.48) ppm range are assigned to the aromatic protons of benzene ring. A quintuplet at 1.9 ppm, attribued to ($-CH_2-C\underline{H}_2-CH_2$) group. The two triplets at 2.19 and 3.58 ppm are assigned to ($-C\underline{H}_2-CH_2-C\underline{H}_2$) groups.

Table 2: ^{13}C NMR spectral data of the N-salicylidene γ-butyric acid (KHL)

Carbone	1	2	3	4	6	7	8	9	10	11	12
δ (ppm)	181,84	34,28	26,15	50,94	167,71	115,37	174,74	115,08	137,65	121,94	134,61

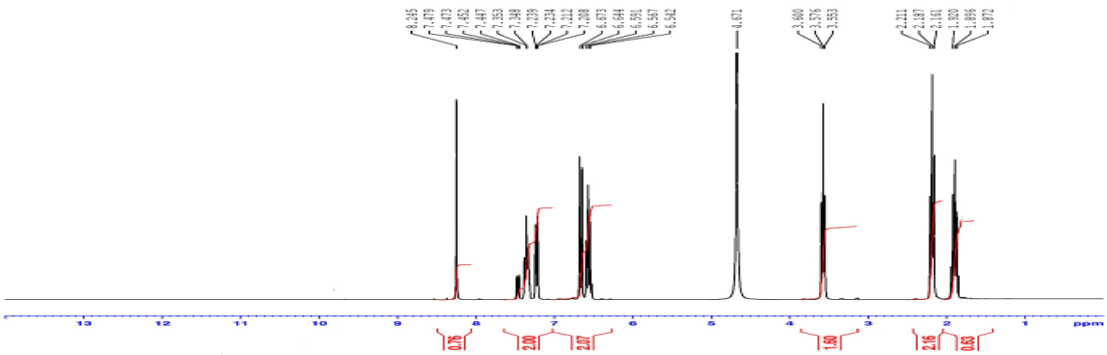

Figure 3: ^{1}H NMR spectrum of N-salicylidene γ-butyric acid (KHL) in D_2O

^{13}C NMR and DEPT spectroscopy: The ^{13}C NMR data of the N-salicylidene γ -butyric acid (KHL) are collected in (Table 2). The ^{13}C NMR spectrum of N-salicylidene γ -butyric acid (Figure 4) in D_2O exhibits the azomethine C=N carbon C(6) and the carboxylate carbon C(1), at 167.71 and 181.84 ppm, respectively [31]. The methylenes carbons C(2) C(3) and C(4) appear at 34.28, 26.15 and 50.94 ppm, respectively, which were confirmed by using the DEPT-135 method (Figure 5). The chemical shifts of aromatic carbons C(6), C(7), C(8), C(9), C(10) and C(11) appear in the (115–181) ppm range.

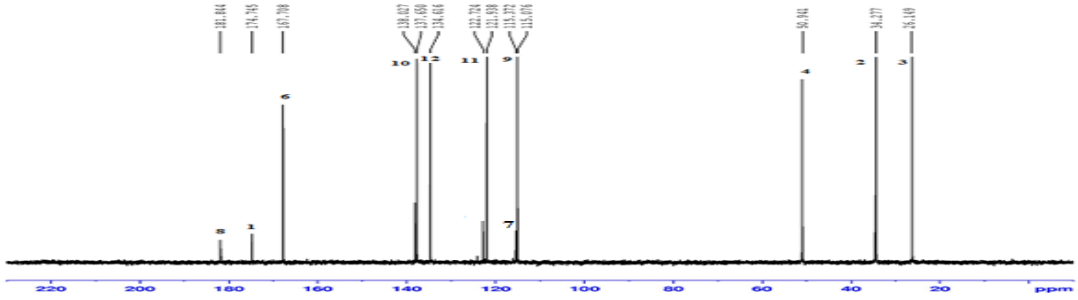

Figure 4: ^{13}C NMR spectrum of the N-salicylidene γ -butyric acid (KHL) in D_2O

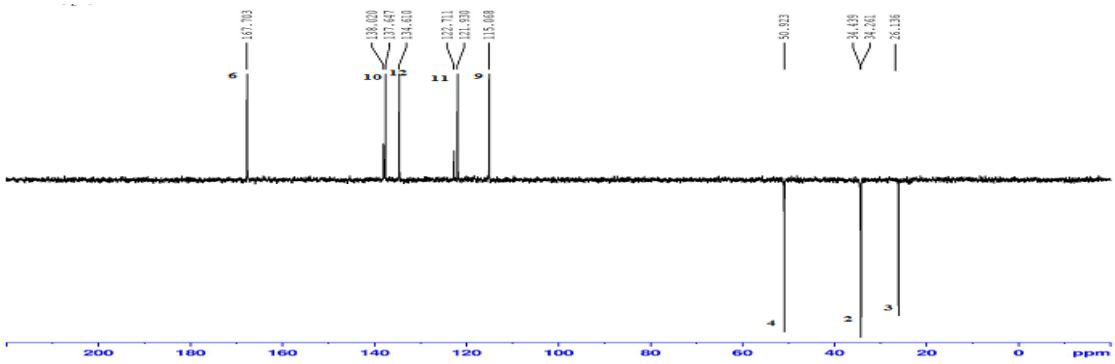

Figure 5: ^{13}C{1H} DEPT-135 spectrum of the N-salicylidene γ-butyric acid (KHL) in D_2O

UV-Visible : The UV-Visible spectrum of the N-salicylidene γ-butyric acid in DMSO (Figure 6) show three bands at 210, 256, 274 nm and two bands at 326, 394 nm, which are due to π→π*(phenyl ring) and n→π* of C=N or C=O linkages or both of them, respectively [26].

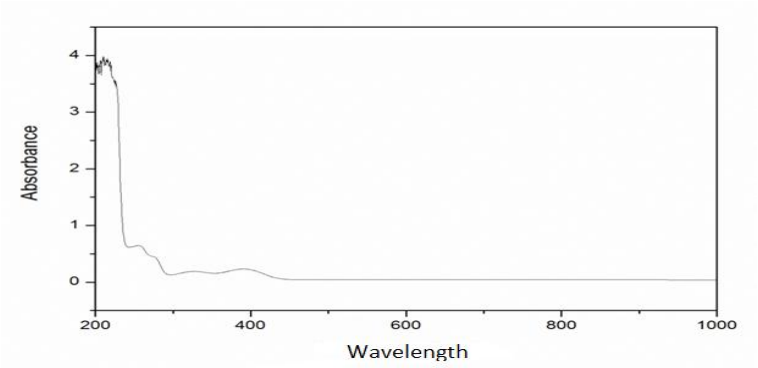

Figure 6: Electronic spectrum of the N-salicylidene γ-butyric acid in DMSO

Synthesis and characterization of the caffeine complexes $[M(LH)(Caf)_2H_2O]_n$ (M=Cd(II), Zn(II), Ni(II), Cu(II)) : The formation of caffeine complexes $[M(LH)(Caf)_2H_2O]_n$ (M= M=Cd(II), Zn(II), Ni(II), Cu(II)) in EtOH is presented in the following reaction :

$$KHL + 2caf + MCl_2, xH_2O \longrightarrow [M(LH)(Caf)_2H_2O]n$$
$$(M=Cd(II), Zn(II), Ni(II), Cu(II))$$

All the caffeine complexes are stable. The complexes are insoluble in common organic solvents but soluble in DMF and DMSO. The analytical data (Table 3) for the complexes show that, one metal of Cd(II), Ni(II), Cu(II) and Zn(II) to one Schiff base ligand and two caffeine. The molar conductance values are too low to account for any dissociation of the complexes in DMSO, indicating the non electrolytic nature of the complexes in DMSO [32,33] (Table 3).

Table 3: Physical characterization, analytical and Molar Conductance data of the caffeine complexes $M(LH)(Caf)_2H_2O]_n$

Complex	Colour	M.P. (°C)	Yield (%)	Λ (Ohm^{-1} cm^2 mol^{-1})	%cal (%found*)	
					M	Caf
$[Zn(LH)(caf)_2H_2O]_n$	Half White	>260	68	24.56	-	54.16 (51.96)
$[Cd(LH)(caf)_2H_2O]_n$	Half White	>260	62	28.24	-	50.82 (48.62)
$[Ni(LH)(caf)_2H_2O]_n$	Light Green	>260	73	28.92	8.26 (7.64)	54.67 (57.64)
$[Cu(LH)(caf)_2H_2O]_n$	Dark Green	>260	66	26.15	8.88 (9.77)	54.29 (56.47)

Infrared spectroscopy: In order to study the bonding mode of ligand (KHL) and caffeine to metal in the complexes, IR spectrum of free ligands (KHL and caf) was compared with the complexes. The IR spectral data are given in Table 1. The IR spectrum of a representative system of Zn(II) complex is shown in Figure 7. The infrared band assignments of all caffeine complexes exhibit broad bands in the range of 3400 to 3500 cm^{-1} indicating the presence of coordinated water molecules [34] and the phenolic OH-group. The weak bands in (3002-3116) cm^{-1} and (2844-2972) cm^{-1} ranges which are attributed to υCHar and $\upsilon CH_3/\upsilon CH_2$ respectively. The free caffeine contains two carbonyl group vibrations in the meta position. The very strong bands observed are considered to be due to υ(CO) symmetric and asymmetric υ(CO,CN) stretching vibrations in caffeine [35]. Then, the carbonyl group in the caffeine complexes exhibit a strong absorption bands about at 1700 cm^{-1} due to υ(CO) symmetric. The bands in the (1645-1652) cm^{-1} range belong to υ(CO) asymmetric and υ(C=N)caf are shifted to lower frequencies by (10-17) cm^{-1}, compared with the free caffeine, indicating coordination of the caffeine through the azomethine nitrogen atom (N9). Others bands in the (1535-1543) cm^{-1} range are assigned to *ν*as(COO^-)+(δHCN+ υring imid +υring pyrimi) which are showed overlap of two bands : The first band at 1550 cm^{-1}, assigned to (δHCN+ υring

imid +υring pyrimi) in the free caffeine and shifted to higher frequencies by (6-14) cm^{-1} in the complexes. Then, we may confirm that imidazol fragment of the caffeine is coordinated with metal ions through the nitrogen atom N9 [36]. The second band at 1526 cm^{-1}, attributed to the asymmetric carboxyl stretching *v*as(COO^-) in the ligand (KHL) and shifted to higher frequencies by (9-17) cm^{-1} in the complexes. Moreover, the symmetric carboxyl stretching *v*s (COO^-) is shifted to higher frequency in the (1387–1400) cm^{-1} range, indicating the linkage between the metal ion and carboxylato oxygen atom [30,37]. The difference between *v*as(COO^-) and *v*s(COO^-) for the Cd(II), Ni(II), Cu(II) and Zn(II) caffeine complexes in the present study are, respectively 140, 155, 151 and 140 cm^{-1}. This value compares favorably with that of (120–160) cm^{-1}, characteristic for the bidentate coordination of the carboxylato group [30,38]. Thus, in all the complexes, the carboxylato group is bidentate bridging. Furthermore, these results are compared with those found in the caffeine complexes with β-alanine [17] which the difference between *v*as(COO^-) and *v*s(COO^-) is in the (150-158) cm^{-1} range.

In the Schiff base ligand, the strong band observed at 1617 cm^{-1} can be assigned to the *v*(C=N) azomethine stretching vibration. On complexation, this band was shifted to higher frequency in the (1622–1635) cm^{-1} range indicating the coordination of the azomethine nitrogen atom to the central metal ion [26]. The new bands υ(M-N) observed in the (534-583) cm^{-1} range for all synthesized caffeine complexes indicated the formation of metal nitrogen linkage [36]. Also the bands υ(M-O) observed in the (410-432) cm^{-1} range for complexes indicated the formation of metal to oxygen linkage [34].

Table 1: Characteristic IR frequencies in (cm^{-1}) of the N-salicylidene γ-butyric acid (KHL), caffeine and their caffeine complexes

Compound	ν(OH)/H_2O	ν(C=N)caf	ν(C=N)	νas(CO_2^-)	νs(CO_2^-)	ν(M-N)	ν(M-O)
KHL	3444(b)	-	1617 (vs)	1526 (s)	1363 (m)	-	-
Caf	-	1662 (s)	-	-	-	-	-
$[Zn(LH)(caf)_2H_2O]_n$	3416(b)	1652 (s)	1628 (s)	1535 (m)	1395 (m)	580 (w)	415 (w)
$[Cd(LH)(caf)_2H_2O]_n$	3450(b)	1652 (s)	1623 (vs)	1540 (vs)	1400 (s)	583 (w)	410 (w)
$[Ni(LH)(caf)_2H_2O]_n$	3420(b)	1650 (vs)	1635 (vs)	1542 (vs)	1387 (m)	534 (m)	432 (w)
$[Cu(LH)(caf)_2H_2O]_n$	3402(b)	1645 (s)	1622 (s)	1543 (s)	1392 (m)	583 (w)	421 (w)

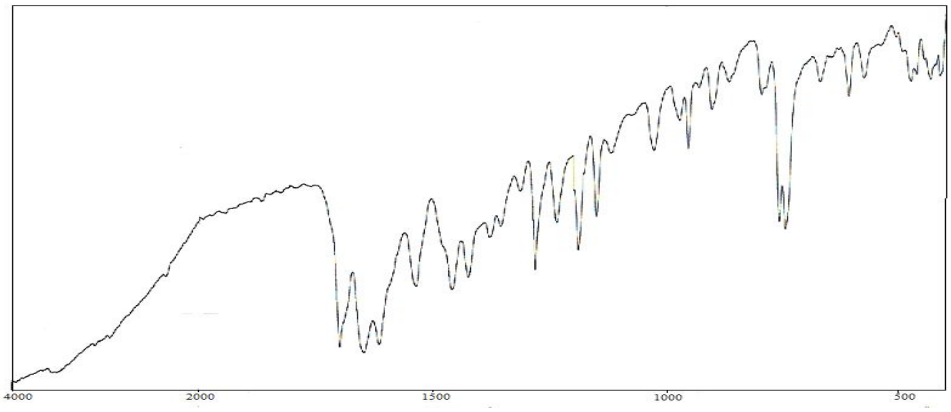

Figure 7: Infrared spectrum of $[Zn(LH)(caf)_2H_2O]_n$ in KBr

Electronic spectra : The electronic spectrum of the Schiff base ligand shows a broad band at 394 nm, which is assigned to n–π* transition of the C=N chromophore. On complexation, this band was shifted to lower wavelength region, suggesting the coordination of azomethine nitrogen with the metal ion. Ni(II) caffeine complex shows two absorption bands in the visible region at 424 nm and 895 nm, which is due to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transitions [39]. This indicates octahedral geometry for the complex. The electronic spectrum of the Cu(II) caffeine complex shows two absorption bands at 687 nm

and 891 nm, which is due to the $^2a_{1g}(D) \rightarrow ^2b_{1g}(D)$ and $^2e_{2g}(D) \rightarrow ^2b_{1g}(D)$ [39], indicating octahedral geometry. Finally, the electronic configuration of Zn(II) and Cd(II) caffeine complexes were d^{10} which confirm the absence of any (d-d) transitions, but the absorption bands in their spectra suffered red shift with hypochromic effect [40]. These absorptions were fully assigned in Table 4 and the electronic spectrum of $[Cu(LH)(caf)_2H_2O]_n$ is shown in Figure 8.

Table 5 : U.V-Visible data of the caffeine, the N-salicylidene γ-butyric acid (KHL) and their caffeine complexes in DMSO

Compound	λmax (nm)	Assignment
Caf	275 316 365	π→π* n→π* n→π*
KHL	212 256 274 326 394	π→π* π→π* π→π* n→π* n→π*
$[Zn(LH)(caf)_2H_2O]_n$	214 270 389	π→π* M→L n→π*
$[Cd(LH)(caf)_2H_2O]_n$	212 272 390	π→π* M →L n→π*
$[Ni(LH)(caf)_2H_2O]_n$	220 271 378 424 895	π→π* π→π* M→L $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ (υ_3) $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ (υ_1)
$[Cu(LH)(caf)_2H_2O]_n$	214 227 267 354 687 891	π→π* π→π* π→π* M→L $^2a_{1g}(D) \rightarrow ^2b_{1g}(D)$ $^2e_{2g}(D) \rightarrow ^2b_{1g}(D)$

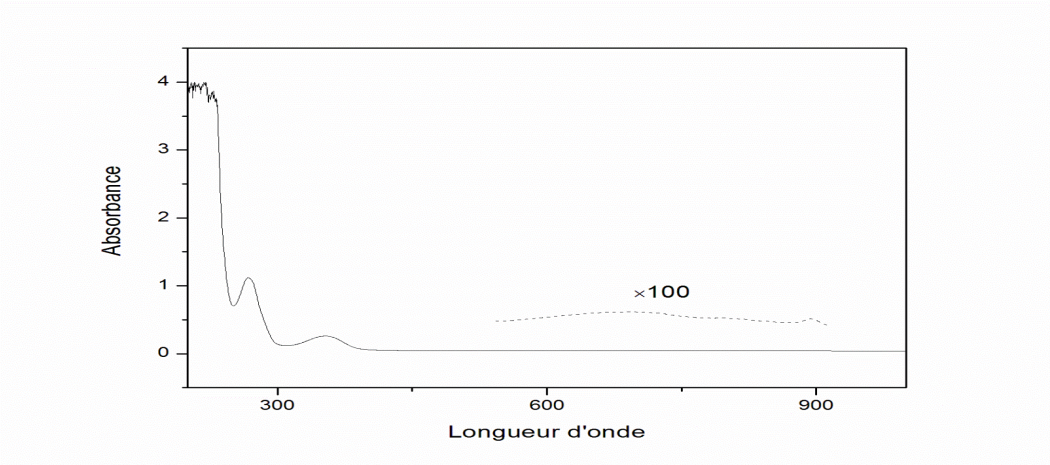

Figure 8: Electronic spectrum of $[Cu(LH)(Caf)_2H_2O]_n$ in DMSO

EPR spectroscopy: The EPR spectrum of Cu(II) complex provides information about hyperfine and super hyperfine structures which are important in studying the metal ion environment, i.e. the geometry, nature

of the ligation sites from the Schiff bases to the metal and the degree of covalency of the metal ligand bonds. The solid state ESR spectrum of $[Cu(LH)(Caf)_2H_2O]_n$ complex is displayed at room temperature on X-band at frequency 9.3 GHz under the magnetic field strength 4000 G. The analysis of spectrum (Figure 9) gives g|| value of 2.061 and g⊥ value of 2.143. The trend $g\perp > g\| > g_e = 2.0023$ observed for the complex indicate that the unpaired electron is localized in the dz^2 orbital of the Cu(II) ion and is characteristic of the axial symmetry [41]. The parameter 'G' is calculated by using the expression, i.e.,$G = g\| - 2/g\perp - 2$. The G value of 2,397 indicates negligible exchange interaction between metal centres in solid complex consistent with Hathaway approach [42-45].

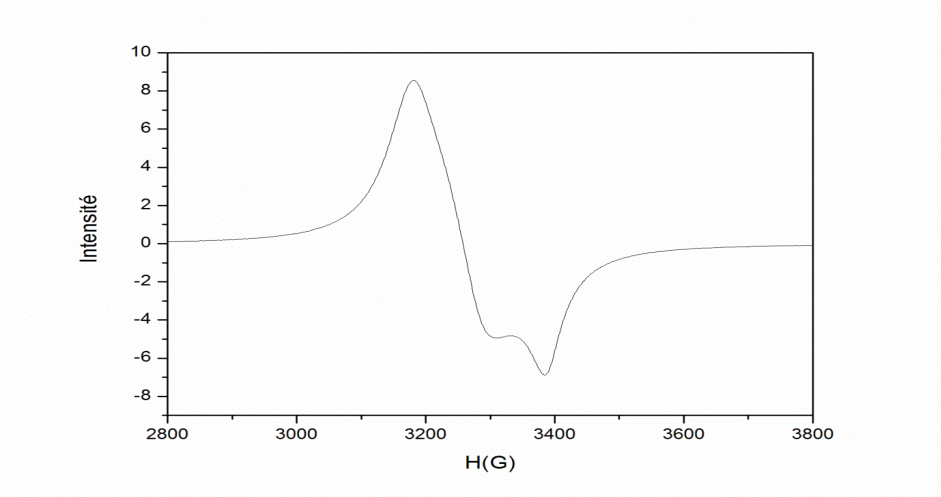

Figure 9: EPR spectrum of $[Cu(LH)(Caf)_2H_2O]_n$ at room temperature on X band

APPLICATIONS

Antimicrobial activity : Antibacterial and antifungal activities of the ligands (KHL, Caf) and their complexes were studied against *Escherichia coli*, *Staphyloccoccus aureus*, *Streptococcus pneumoniae*, *Stenotrophomonas maltophilia* and *Candida albicans* at 20 mg/ml^{-1} concentration by single disc method [46]. Against all the organism, the ligands (KHL and Caf) did not exhibit any remarkable activity whereas all the complexes showed moderate activities.(Table 6). The Ni(II) complex exhibit inhibition towards all the studied microorganisms. Howerver, Zn(II), Cd(II) and Cu(II) complexes have no activity towards some microogranisms. It is suggested that the compounds having antimicrobial activity may act either by killing the microbe or by inhibiting multiplication of the microbe by blocking their active sites [46, 47].

Table 6: Antimicrobial screening results of tested compounds at 20 $mg.mL^{-1}$

Compound	Bacteria				Fungi
	E. coli	***Staph. aureus***	***Strep. pneumoniae***	***Steno. maltophilia***	***C. albicans***
Caf	7 mm	-	-	8 mm	8 mm
KHL,	-	-	-	-	-
$[Zn(LH)(caf)_2H_2O]_n$	-	-	-	8 mm	-
$[Cd(LH)(caf)_2H_2O]_n$	8 mm	-	18 mm	-	-
$[Ni(LH)(caf)_2H_2O]_n$	9 mm	11 mm	7 mm	8 mm	20 mm
$[Cu(LH)(caf)_2H_2O]_n$	-	8 mm	-	8 mm	-

CONCLUSIONS

We reported the synthesis and characterization of a N-salicylidene γ-butyric acid (KHL) and a series of four caffeine complexes. The synthesized ligand (KHL) bind the metal ions in a tridentate manner (NO_2) with two caffeine and a coordinated water molecule. Spectral data (IR, UV-Vis and EPR) suggest octahedral geometry for all caffeine complexes. Further, these complexes were screened for antimicrobial activity and results suggest that the most of caffeine complexes have higher antibacterial and antifungal activities than the free ligands.

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