

**Synthesis and Characterization of N-salicylidene-β-alanine (KHL)
and its caffeine complexes $[M(LH)(Caf)_2H_2O]_n$;
 $M = Cd^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}$; Caf=caffeine**

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Abstract

In this work it was possible to synthesize and characterize the ligand of N-salicylidene-β-alanine (KHL). A series of metal caffeine complexes involving a tridentate (NO₂)-donor Schiff base and two monodentate N9 caffeine and water coordination with the composition $[M(LH)(Caf)_2H_2O]_n$; $M = Cd^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}$; Caf= caffeine have been prepared and characterized by FT-IR, ¹H, ¹³C NMR, DEPT, UV-Visible and Molar Conductance.

Keywords: N-salicylidene-β-alanine, caffeine complexes, $Cd^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}$ ¹H, ¹³C NMR, FT-IR, UV-Visible, Molar conductance.

Introduction

Schiff bases derived from aminoacides and aromatic aldehydes have a wide variety of applications in many fields, e.g. biological, inorganic and analytical chemistry [1-5]. Application of many new analytical devices requires the presence of organic reagents as essential compounds of the measuring system. They are used, e.g. in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection of enhance selectivity and sensitivity [6]. Moreover, Amino acid Schiff bases are avowed intermediates in studying amino acid transformations in enzymatic [7] and non- enzymatic [7] reactions with pyridoxal participation. [7]

The Schiff base complex is a kind of important compound due to some special functions. Various Schiff base complexes have been synthesized and studied with their biological or antitumor activity [8–11]. Salicylalanine is often used to synthesize Schiff base complexes because of its special structure [12–13]. As for the extent of the studies of the Schiff base complexes derived from salicylaldehyde and amino acids, first extensive observations were performed when the vitamin B6-like activities were described. 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 [14].Caffeine is

also used as a decongestant, increase in energy, weight loss, analgesic, appetite suppressant and diuretic [15].

There are many reports on the synthesis and properties of metal complexes with α -amino acid derived Schiff bases [16-21]; but, fewer studies are reported on complexes with Schiff bases of β -amino acids, such as β -alanine [22-24]. On the basis of stated facts, we have decided to prepare and characterize Schiff base caffeine complexes with a bidentate (N,O) Schiff base ligand (See Scheme 1) and a monodentate N9 caffeine (See Scheme 2), forming the coordination units of a general formula $[M(LH)(Caf)2H_2O]_n$ (where $M = Cu^{2+}, Zn^{2+}, Ni^{2+}$ and Caf= caffeine).

Material and methods

All chemicals were obtained from commercial sources and were used without purifications: ($NiCl_2 \cdot 6H_2O$ BDH; $CdCl_2 \cdot 1/2H_2O$ Panreac; $CuCl_2 \cdot 6H_2O$ BDH; KOH BDH, $ZnCl_2 \cdot 2H_2O$ BDH), β alanine 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 $4000-400\text{ cm}^{-1}$ 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 $25^\circ C$. 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 $25^\circ C$ in DMSO using Hach HQ430d flexi.

Preparation of the Schiff base (KHL)

The Schiff base ligand, KHL, was prepared by the following reaction: to a mixture of β -alanine (0.01 mole, 0.89 g) and potassium hydroxide (0.01 mole, 0.56 g) dissolved in 15 mL of ethanol, the solution of salicylaldehyde (0.01 mole, 1.22 g) in 10 mL of ethanol was added with stirring. The resulting yellow solution was stirred at $78^\circ C$ for 2 h. Then, the yellow crystalline product of KHL was formed by slow evaporation of the solvent. The crude product was filtered off and washed several times with ethanol.

General procedure for preparation of complexes

$[M(LH)(Caf)_2H_2O]_n$ ($M = Cd, Zn, Ni, Cu$; Caf=caffeine)

The N-salicylidene- β -alanine caffeine complexes with $Cd(II)$, $Zn(II)$, $Ni(II)$, $Cu(II)$ were prepared by adding a solution of the metal salt $ZnCl_2$ (0,001 mole, 0.14 g), $CdCl_2$ (0,001 mole, 0,22g), $NiCl_2$ (0,001 mole, 0,23g) or $CuCl_2$ (0,001 mole, 0,17g) to a solution of N-salicylidene- β -alanine (KHL) (0,002 mole, 0.39 g) dissolved in 10 mL of methanol and (0,002 mole, 0.38 g) of the caffeine. The reaction mixture is heated under stirring at $78^\circ C$ for 4h. Then, the resulting products were filtered and washed several times with methanol.

Table 2: ^{13}C NMR spectral data of N-salicylidene- β -alanine

Carbone	1	2	3	5	6	7	8	9	10	11
δ (ppm)	174.04	39.81	56.06	162.95	117.55	165.35	117.91	131.95	118.88	132.65

Table 1 Physical data of ligand (KHL)

Compound	colour	M.P.(°C)	Yield (%)	Formula	Molar Mass (g/mol)
N-salicylidene- β -alanine (KHL)	Yellow	180	83	$\text{C}_{10}\text{H}_{10}\text{O}_3\text{K}$	211,19

Table 3 Physical characterization, analytical and Molar Conductance data of the caffeine complexes $[\text{M}(\text{LH})(\text{Caf})_2\text{H}_2\text{O}]_n$.

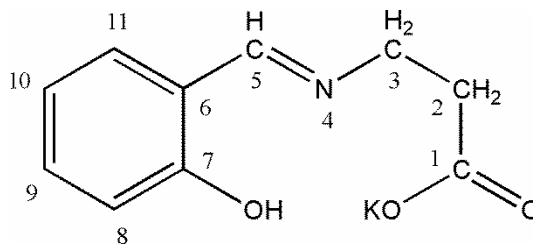
Complexes	Colour	M.P. (°C)	Yield (%)	Λ ($\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	(%found) %cal	
					M*	Caffeine*
$[\text{Zn}(\text{LH})\text{Caf}_2\text{H}_2\text{O}]_n$	Half White	>260	70	28.65	-	(59.74) 59.78
$[\text{Cd}(\text{LH})\text{Caf}_2\text{H}_2\text{O}]_n$	Half White	>260	66	33.12	-	(57.88) 58.17
$[\text{Ni}(\text{LH})\text{Caf}_2\text{H}_2\text{O}]_n$	Light Green	>260	63	33.54	(27,02) 28,22	(58.69) 59.96
$[\text{Cu}(\text{LH})\text{Caf}_2\text{H}_2\text{O}]_n$	Dark Green	>260	58	32.01	(21.47) 22.16	(59.39) 59.87

*The caffeine and metals in the complexes are quantitatively determined with UV-Visible spectroscopy.

Results and discussion

Characterization of the Schiff base ligand (KHL)

The proposed structure of the N-salicylidene- β -alanine is shown in Scheme 1:



Scheme 1: Schematic representation of the N-salicylidene - β -alanine (KHL)

The structure of prepared ligand (KHL) was elucidated from its spectroscopic properties and by comparing with the literature wherever possible.

Table 4. Infrared data of the ligand and its caffeine complexes

$[M(LH)(caf)_2H_2O]_n$ ($M=Ni^{2+}$, Cd^{2+} , Zn^{2+} , Cu^{2+}) in KBr

	Caffeine [34]	Ligand (KHL)	$[ZnLH(Caf)_2H_2O]_n$	$[CdLH(Caf)_2H_2O]_n$	$[NiL(Caf)_2H_2O]_n$	$[CuL(Caf)_2H_2O]_n$
$\nu OH/H_2O$		3503vs	3420L	3468L	3400s, 3236L	3434L
νCH	3114m	3100w, 3066w, 3036w	3111w	3099w, 3005w	3031w	3122w
$\nu CH_3 / \nu CH_2$	2954w	2933m, 2865w	2977w, 2922w, 2867w	2931w	2970w, 2909w, 2862w	2956w, 2919w, 2862w
$\nu C=O$ caf	1702vs		1698s	1700vs	1698s	1700s
$\nu C=O / \nu C=N$ caf	1662s		1652s	1654s	1659w	1650s
$\nu C=N+\delta H_2O$		1630vs	1635s	1640s	1635s	1641s
$\nu C=C$ caf/ $\nu C=Car$	1600m	1570vs	1586vs	1584s	1585s	1589s
$\nu aCO_2 + -\delta HCN + \nu ring$ imidazole+ $\nu ring$ pyrimidine	1551w	1531s	1543m	1538s	1538s	1538s
$\delta CH_2/\delta CH_3$ + $\nu C-N$	1487m, 1466m, 1405m, 1431m	1464s, 1447m, 1420s, , 1337m	1461m 1443m, 1416m, , 1341w	1458m, 1436m, 1350m	1461s, 1441s, 1412s, 1335m	1460m, 1440m, 1347w
νsCO_2^-		1397s	1385m	1380m	1380m	1378m
$\nu ring(imidazole) +$ $\nu ring(pyrimidine)$	1327w		1322m	1320m	1320s	1322m
δOH		1310m	1300w	1291m	1297s	1271w
$\delta C-Oph+$ $\delta(CH) + \rho r(CH_3)$	1190m	1190m	1193m 1240m	1186m 1240m	1188m 1241m	1195m 1242m
δCH In plane def		1151m, 1134m, 1104m, 1050w, 1009w	1150w, 1128w, 1092w, 1042w, 1029w	1150m, 1124m, 1075w, 1027m	1150m, 1124m, 1087w, 1040w, 1028w, 1007w	1145m, 1123w, 1108w, 1089w, 1063w, 1021m
$\nu(N-CH_3) +$ $\delta ring(imidazole)$	974s		970w	973m	970m	970w
$\rho r(CH_3) +$ $\nu(N-CH_3) + \delta(C-O)$	861m		869w	857w	866m	850w
CH Out-of-plane def	754m	965w, 930w, 918m, 895m, 872w, 789m, 748m, 727m, 624m, 642m	928w, 910w, 881w, 869w, 847w, 788w, 755m, , 678m, 642w	911w ,881w, 779w, 758w, 747m, 672w, 657w, 636w	924w, 906w, 879m, 844m, 825w, 786m, 755s, , 641w	916w, 885w, 825w, 789w, 774w, 752w, 671w, 656w, 625w
$\gamma ring(pyrimidine) +$ $\gamma ring(imidazole)$	746s		744m	740m	740m	742w
ρCH_2		692w	696w	694w	696m	696w
$\gamma ring(imidazole)$	610vs		610w	608m	609m	607w
CH ring def		588w, 548w, 510m	577w, 516w	578w, 554w, 509w	570w, 511m	560w, 507w
CH Out-of-plane ring def	485w, 466w, 427w	481w, 468m, 443m, 414m	475w, 453w	494w, 476m, 424w,	494w, 474w, 460w, 447m,	493w, 473w, 460w, 444w, 432w, 412w,
$\nu M-O$			533w	535w	534m	536w
$\nu M-N$			410w	409w	406m	408w

Table 5 : U.V-Visible data of the caffeine and the Schiff base caffeine complexes in DMSO

Compound	λ_{max} (nm)	Assignment
CA	275	$\pi \rightarrow \pi^*$
	316	$n \rightarrow \pi^*$
	365	$n \rightarrow \pi^*$
KHL	216	$\pi \rightarrow \pi^*$
	243	$\pi \rightarrow \pi^*$
	274	$\pi \rightarrow \pi^*$
	321	$n \rightarrow \pi^*$
	390	$n \rightarrow \pi^*$
[Cu(LH)(Caf) ₂ H ₂ O] _n	205	CT
	232	CT
	267	CT
	353	$M \rightarrow L$
	543	${}^2a_{1g}(D) \rightarrow {}^2b_{1g}(D)$
	740	${}^2e_{2g}(D) \rightarrow {}^2b_{1g}(D)$
[Zn(LH)(Caf) ₂ H ₂ O] _n	206	CT
	268	$M \rightarrow L$
	351	shift with hypochromic effect
[Cd(LH)(Caf) ₂ H ₂ O] _n	210	CT
	266	$M \rightarrow L$
	379	Shift with hypochromic effect
[Ni(LH)(Caf) ₂ H ₂ O] _n	224	CT
	272	CT
	356	$M \rightarrow L$
	401	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P) (v_3)$
	597	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) (v_2)$
	947	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) (v_1)$

¹H NMR spectroscopy

The ¹H NMR spectrum of the N-salicylidene-β-alanine in DMSO (Figure 1) exhibits multesignals within the δ (6.74–7.36) ppm range, attributed to aromatic protons. The singlet observed at δ 8.84 ppm corresponds to protons CH=N. The triplet observed at δ 2.20 ppm and δ 3.70 ppm corresponds to CH₂ proton of methylene group. Furthermore, the singlet obtained at δ 4.81 ppm due to the proton of the phenolic OH-group [25]. We note that the singlet observed at δ 2.48 ppm corresponds to protons of methylene of DMSO.

¹³C NMR and DEPT spectroscopy

¹³C NMR spectrum of N-salicylidene-β-alanine is shown in Figure 2. The ¹³C NMR spectral data of N-salicylidene-β-alanine are given in (Table 2). The spectrum exhibit the azomethine C=N carbon C(5) and the carboxylate carbon C(1), at 162.95 and 174.07 ppm, respectively. The two methylenes carbons C(2)

and C(3) appear at 39.81 and 56.06 ppm, respectively. Those were confirmed by using the DEPT-135 method (Figure 3). The chemical shifts of aromatic carbons C(6), C(7), C(8), C(9), C(10) and C(11) appear in the 117–165 ppm range.

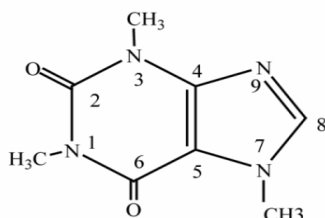
Infrared spectroscopy

The most important infrared spectral bands that provide conclusive structural evidence of the N-salicylidene-β-alanine are given in Table 3. The Infrared spectrum of the Schiff base ligand is shown in Figure 4. The spectrum showed the broad and moderate band at 3486 cm^{-1} due to –OH vibration of the phenolic –OH group [25]. Moreover, the medium–weak bands at (3100 , 3066 and 3036 cm^{-1}) and (2933 and 2865 cm^{-1}) are assigned to the aromatic and aliphatic C–H stretch, respectively. The strong band around 1630 cm^{-1} can be attributed to $\nu(\text{C}=\text{N})$ [26].

The characteristic absorption bands from the symmetric and antisymmetric stretching vibration of the COO^- group in the carboxylate are about at $\nu_s=1400\text{ cm}^{-1}$ and at $\nu_{as}=1530\text{--}1610\text{ cm}^{-1}$ [27]. So, the bands at 1397 cm^{-1} and at 1531 cm^{-1} can be assigned to the symmetric and antisymmetric stretching vibration of the COO^- group, respectively.

The band appearing in the $1337\text{--}1464\text{ cm}^{-1}$ can be connected to $\delta\text{CH}_2/\delta\text{CH}_3+\nu(\text{C-N})$. The band at 1310 cm^{-1} due to bending mode of the phenolic –OH group (δOH). In addition, The band of phenolic $\nu(\text{C}_{\text{ph}}\text{-O})$ vibration in 1190 cm^{-1} was identified [25]. Bands in the $1009\text{--}1151\text{ cm}^{-1}$ range due to $\delta(\text{CH})$ in plane deformation. The medium and/or weak band observed in the $965\text{--}642\text{ cm}^{-1}$ range can be attributed to $\delta(\text{CH})$ out-of-plane deformation. The bands in the $510\text{--}588\text{ cm}^{-1}$ range are assigned to $\delta(\text{CH})$ in plane ring deformation and the bands in the $414\text{--}481\text{ cm}^{-1}$ range is attributed to $\delta(\text{CH})$ out plane ring deformation.

From the literature, the infrared spectral data of the free caffeine (Table 3) [28] shows weak and sharp band at 3114 cm^{-1} which belongs to $\nu(\text{C-H})$ aromatic. Another weak band belongs to $\nu(\text{C-H})$ aliphatic was found at 2954 cm^{-1} . The strong band at 1702 cm^{-1} was attributed to $\nu(\text{C=O})$, strong band at 1662 cm^{-1} was attributed to $\nu(\text{C=O})$ and $\nu(-\text{N}=\text{C})$. The $\nu(\text{C}=\text{C})$ was noticed at 1546 cm^{-1} with shoulder at 1600 cm^{-1} . The ($\delta\text{HCN} + \text{vring imid} + \text{vring pyrimi}$) stretching and deformation heterocyclic imidazol and pyrimidine fragment were noticed at 1551 cm^{-1} and 1327 cm^{-1} respectively.



Scheme 2. Structure of the caffeine

UV-Visible

The UV-Visible spectrum of Schiff base under study is shown in Figure 5.

The lower wavelengths bands have a range of values between 215-274 nm. They are assigned to $\pi \rightarrow \pi^*$ (phenyl ring). The longer wavelengths bands have a range of values between 321-391 nm and are assigned to $n \rightarrow \pi^*$ of C=N or C=O linkages or both of them.

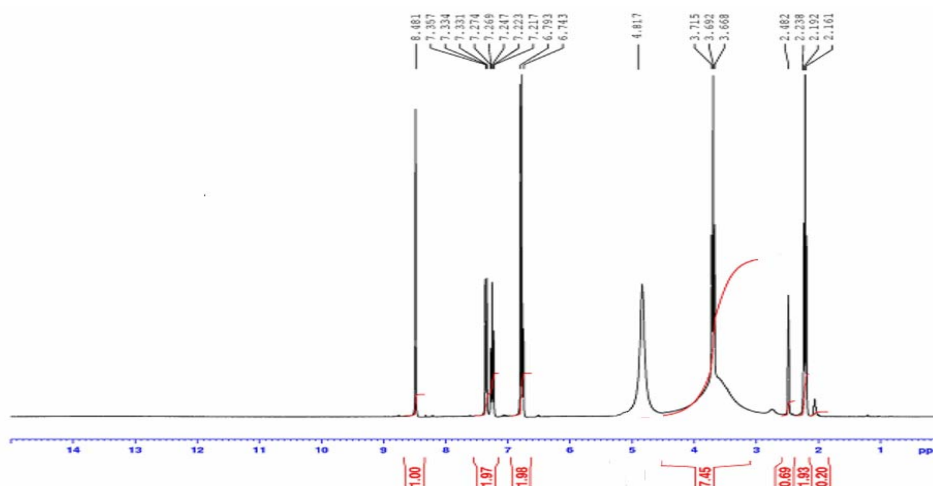


Figure 1: ^1H NMR spectrum of N-salicylidene- β -alanine in DMSO

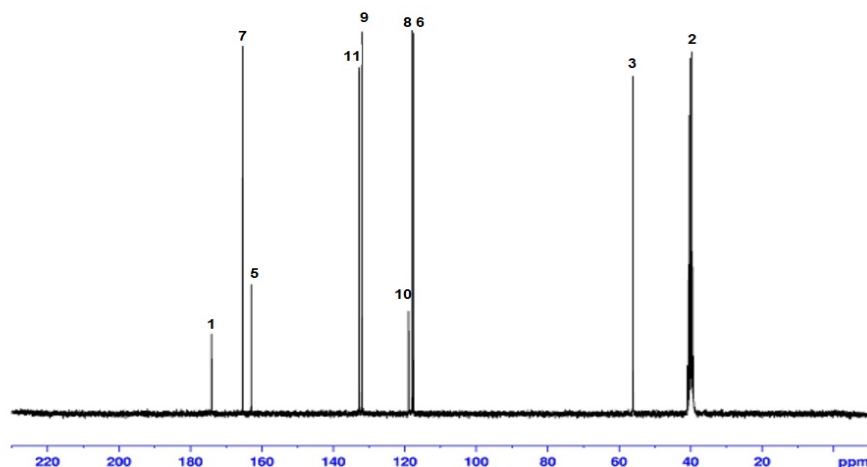


Figure 2: ^{13}C NMR spectrum of N-salicylidene- β -alanine in DMSO

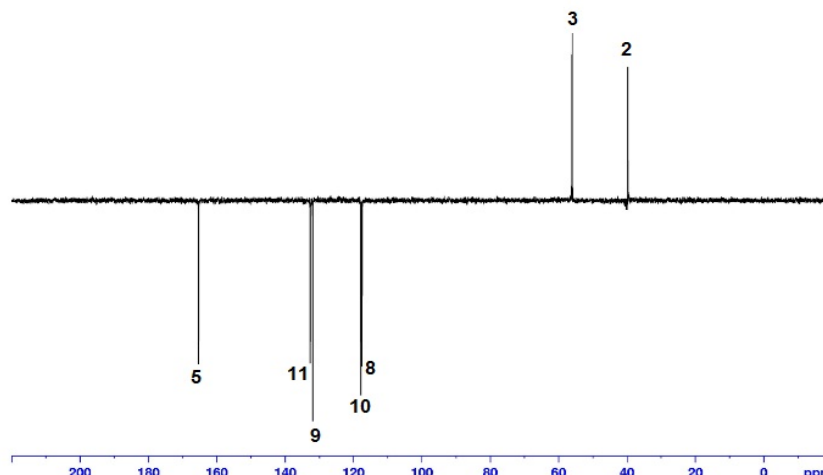


Figure 3: ^{13}C (1H) DEPT-135 spectrum of N-salicylidene- β -alanine in DMSO

Synthesis and characterization of the caffeine complexes

$[\text{M}(\text{LH})(\text{Caf})_2\text{H}_2\text{O}]_n$ ($\text{M}=\text{Cd}^{2+}$, Zn^{2+} , Ni^{2+} , Cu^{2+})

The caffeine complexes are stable with high melting point ($>260^\circ\text{C}$). All the complexes are insoluble in most organic solvents. This behavior could be attributed to the nature of the complexes; the caffeine complexes are soluble in DMF and DMSO solvents.

Molar conductance

The molar conductance of the Schiff base caffeine complexes were measured using 10^{-4} M DMSO solvent at room temperature.

The conductivity values of the complexes are in the range (28.65- 33.54) $\text{Ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$. These lower values of molar conductivities indicates the non-electrolyte behavior of the Schiff base caffeine complexes of Zn(II), Cd(II), Ni(II) and Cu(II).

Infrared spectroscopy

The assignment of the important bands was made and recorded in Table 4. In order to give conclusive idea about the structure for the coordination of the Schiff base ligand and the caffeine to the central metal ions (Zn^{2+} , Cd^{2+} , Ni^{2+} and Cu^{2+}), the main infrared bands were compared with those of the free ligand (KHL) and the free caffeine. The Infrared spectrum of the $[\text{Zn}(\text{LH})\text{caf}_2\text{H}_2\text{O}]_n$ and $[\text{Ni}(\text{LH})\text{caf}_2\text{H}_2\text{O}]_n$ is given in Figure 6-1 and Figure 6-2.

The infrared band assignments of all metal complexes exhibit broad bands in the range of 3500 to 3400 cm^{-1} indicating the presence of coordinated water molecules [29] and the phenolic OH-group. In addition, the presence of water coordination is confirmed by isotopic exchange for $[\text{Ni}(\text{LH})\text{caf}_2\text{H}_2\text{O}]_n$ (Figure 6-3). In this way, we note the disappearance of the band at 3400 cm^{-1} corresponding to $\nu(\text{OH})$ of water

coordination with the reappearance of a new band at 1550 cm^{-1} attributed to $\delta(\text{OD})$. The isotopic ratios $\nu(\text{OH})/\delta(\text{OD})$ have values of 1.05 [30].

The bands in $(3099\text{--}3122)\text{ cm}^{-1}$ and in $(2862\text{--}2977)\text{ cm}^{-1}$ ranges which are attributed to νCHar and $\nu\text{CH}_3/\nu\text{CH}_2$ respectively.

The free caffeine contains two carbonyl group vibrations in the meta position. The very strong bands observed are considered to be due to $\nu(\text{CO})$ symmetric and asymmetric $\nu(\text{CO},\text{CN})$ stretching vibrations in caffeine [31]. Then, the carbonyl group in the caffeine complexes exhibit a strong absorption bands about at 1700 cm^{-1} due to $\nu(\text{CO})$ symmetric. The bands in the $1652\text{--}1658\text{ cm}^{-1}$ range belong to $\nu(\text{CO})$ asymmetric and $\nu(\text{C}=\text{N})$ are shifted to lower frequencies by $(4\text{--}10)\text{ cm}^{-1}$, compared with the free caffeine, indicating coordination of the caffeine through the azomethine nitrogen atom (N_9).

In addition, the band due to $\nu(\text{C}=\text{N})+\delta\text{H}_2\text{O}$ stretching (1630 cm^{-1} in KHL spectrum) underwent a positive shift ($5\text{--}11\text{ cm}^{-1}$) on complexation, suggesting that azomethine group is involved in coordination [32-33].

Others bands in the $(1538\text{--}1543)\text{ cm}^{-1}$ range are assigned to $(\nu\text{as}(\text{COO}^-)+\delta\text{HCN}+\text{vring imid}+\text{vring pyrimi})$ which are shifted to higher frequencies by $(7\text{--}12)\text{ cm}^{-1}$ compared with free caffeine. Then, we may confirm that imidazol fragment of the caffeine is coordinated with metal ions through the nitrogen atom N_9 [34].

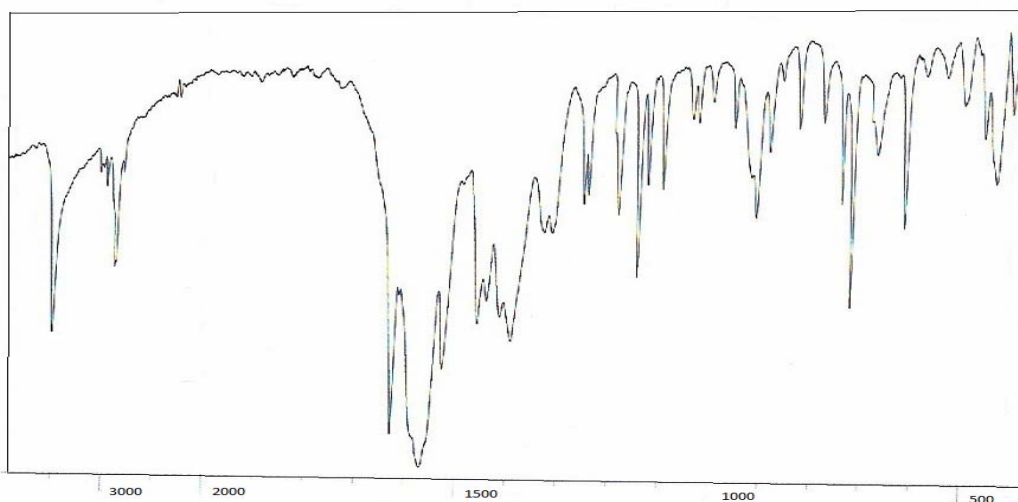


Figure 4 : Infrared spectrum of the N-salicylidene- β -alanine (KHL) in KBr

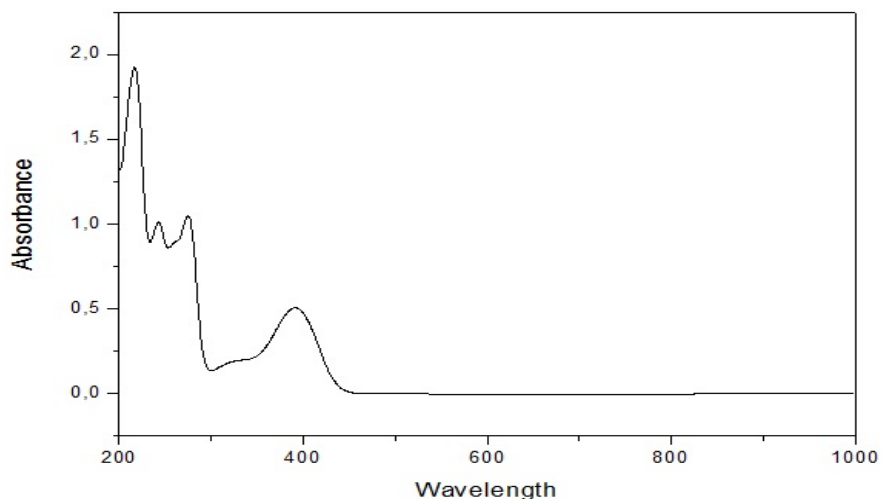


Figure 5. Electronic spectrum of the N-salicylidene-β-alanine(KHL)

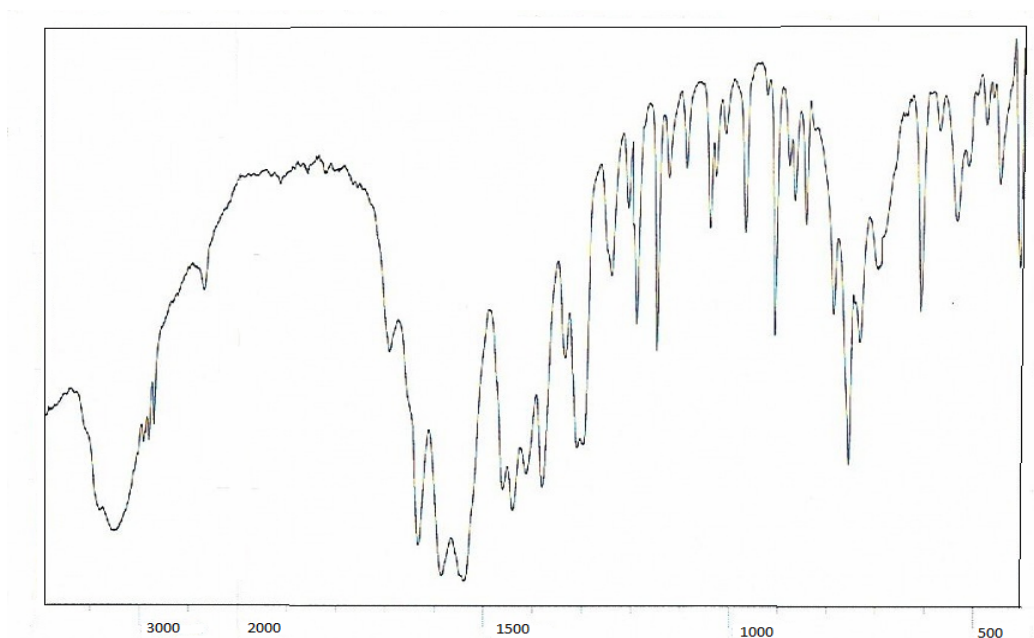


Figure 6.1. Infrared spectrum of the Schiff base caffeine complex $[\text{Ni}(\text{LH})(\text{caf})_2\text{H}_2\text{O}]_n$ in KBr

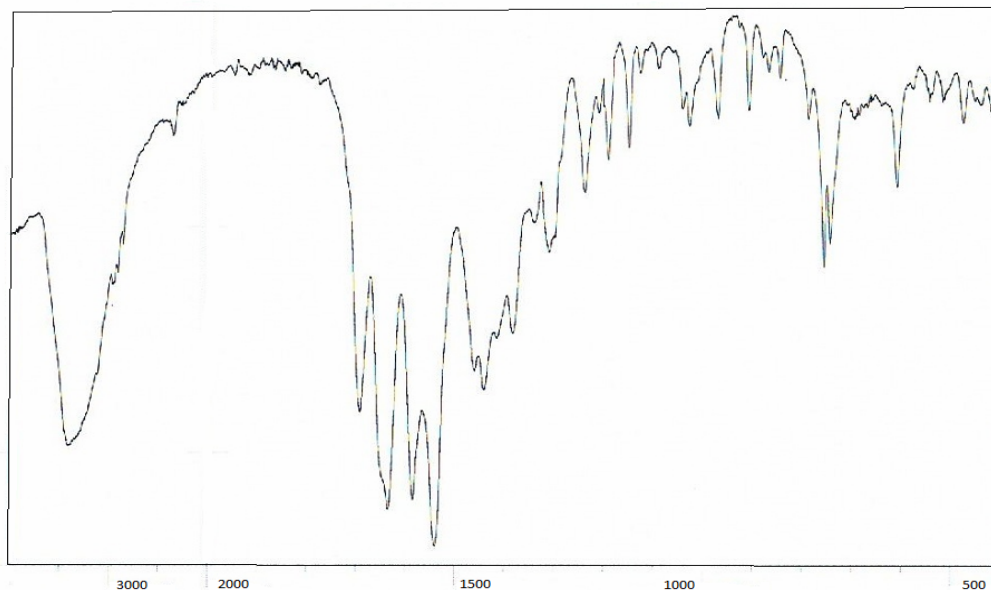


Figure 6.2. Infrared spectrum of the Schiff base caffeine complex
 $[Zn(LH)(caf)_2 H_2O]_n$ in KBr

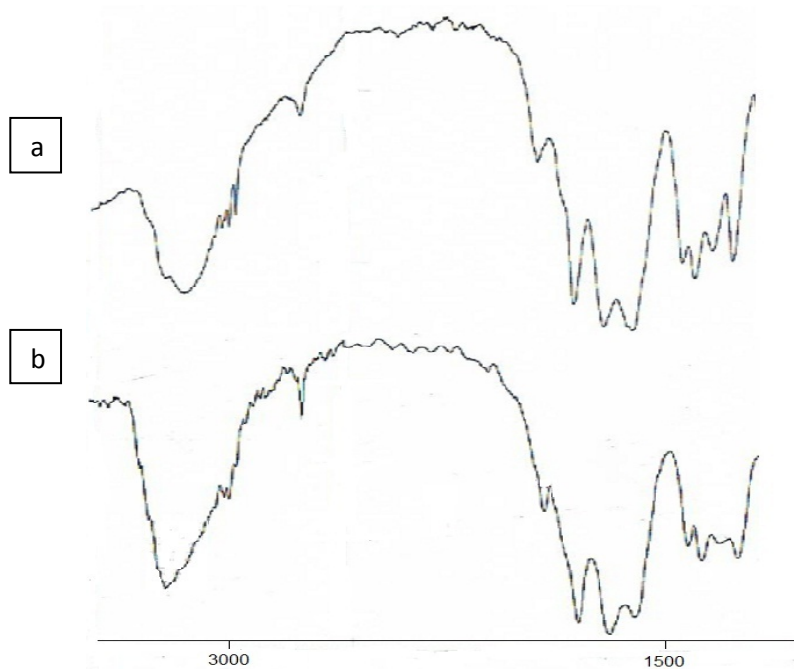


Figure 6.2. Infrared spectrum of the Schiff base caffeine complex
 $[Ni(LH)(caf)_2 H_2O]_n$ (a) and its isotopic exchange by D_2O (b) in the $4000-1400\text{ cm}^{-1}$ range

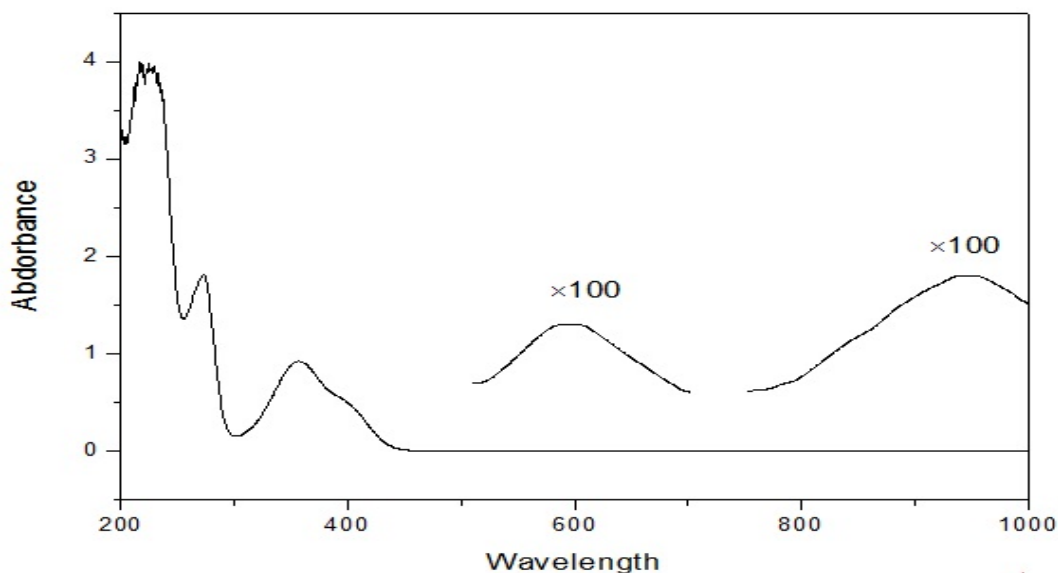


Figure 7.1. Electronic spectrum of the Schiff base caffeine complex $[\text{Ni}(\text{LH})(\text{caf})_2\text{H}_2\text{O}]_n$ in DMSO

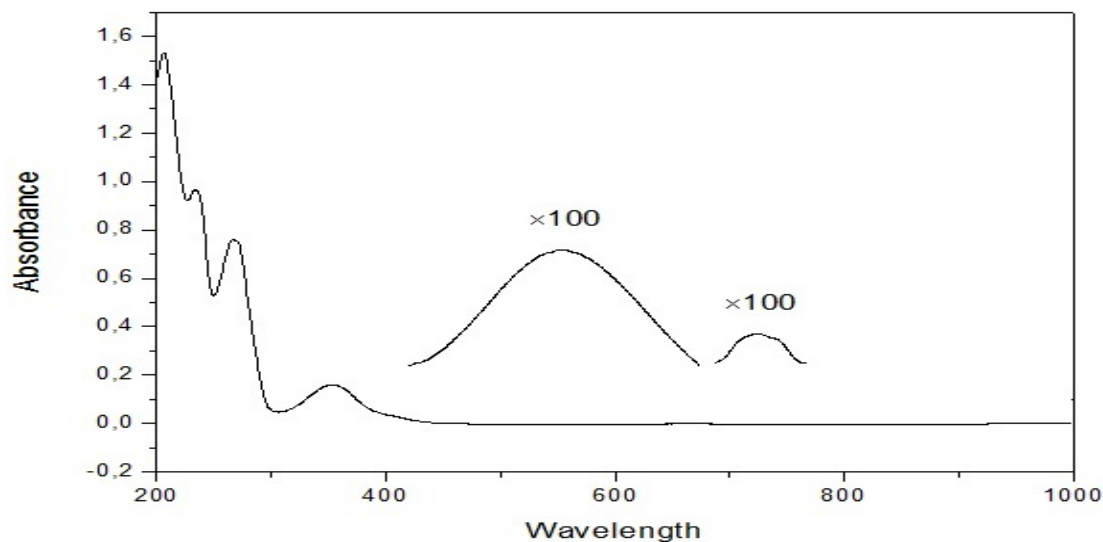


Figure 7.2. Electronic spectrum of the Schiff base caffeine complex $[\text{Cu}(\text{LH})(\text{caf})_2 \text{H}_2\text{O}]_n$ in DMSO

Moreover, the $\nu_s(\text{COO}^-)$ is attributed to the medium-strong peaks appearing in the $1378\text{--}1385\text{ cm}^{-1}$ region. The magnitude of $\Delta\nu = [\nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)]$ for the caffeine complexes falls in the range of $150\text{--}158\text{ cm}^{-1}$, indicating the carboxyl group in all the complexes is bound in bidentate bridging manner [35, 36]. Moreover, for complexes $\Delta\nu$ below 200 cm^{-1} would be expected for chelating carboxylate [35, 36].

Carboxylate is a versatile anion that can assume three types of bridging conformations, syn-syn, syn-anti, and anti-anti [37, 41]. However, the infrared data of $[\text{Cu}(\text{L})(\text{H}_2\text{O})]$ show the carboxylate vibrations $\nu(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ at 1521 cm^{-1} and 1385 cm^{-1} respectively with $\Delta\nu=136\text{ cm}^{-1}$ [25]. Regarding $[\text{Fe}_2\text{L}_2(\text{H}_2\text{O})_4](\text{NO}_3)_2(\text{H}_2\text{O})$, the absorptions of the carboxylate group $\nu(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ are in $1527\text{--}1529\text{ cm}^{-1}$ and $1362\text{--}1372\text{ cm}^{-1}$, respectively. The $\Delta\nu$ has a value of about 170 cm^{-1} , indicative of a bridging carboxylate group between the two metal atoms [42]. Furthermore, the dimeric iron complexes of $[\text{Fe}_2\text{L}_2(\text{H}_2\text{O})_4](\text{NO}_3)_2(\text{H}_2\text{O})_m$ ($m=1\text{--}3$) contain hexacoordinated iron (III), with the metal ion surrounded by water molecules, the salicylideneimine ligand, and the bridging carboxylate groups [43]. On the basis of this all data, we can confirm that the bridging carboxylate group is involved through the two oxygen atoms. New bands, which are not present in the spectrum of ligand appeared in the spectra of complexes in the range of $406\text{--}410\text{ cm}^{-1}$, corresponding to $\nu\text{M-N}$ [44, 45] and $533\text{--}536\text{ cm}^{-1}$ to $\nu\text{M-O}$ vibrations support the involvement of N and O atoms in complexation with metal ions under investigation [46].

These results show on the fact that the ligand is involved in the coordination through the carboxyl group and the azomethine nitrogen. In addition, the caffeine is coordinated with metal ions through the nitrogen atom (N9).

Electronic spectra

The electronic spectra for free ligand and caffeine show that the absorption bands in the UV region can be expressed as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The electronic spectrum of Ni(II) complex exhibited absorption bands at 272, 401, 597 and 950 nm which are attributed to the electronic transition ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ [34].

The spectrum of Cu(II) complex shows that its bands in the visible region is attributed to the electronic transitions of ${}^2\text{a}_{1g}(\text{D}) \rightarrow {}^2\text{b}_{1g}(\text{D})$ and ${}^2\text{e}_{2g}(\text{D}) \rightarrow {}^2\text{b}_{1g}(\text{D})$ at 543 and 740 nm, respectively [34]. Finally, the electronic configuration of Zn(II) and Cd(II) 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 [34]. These absorptions were fully assigned in Table 5 and the electronic spectra of $[\text{Ni}(\text{LH})(\text{caf})_2\text{H}_2\text{O}]_n$ and $[\text{Cu}(\text{LH})(\text{caf})_2\text{H}_2\text{O}]_n$ are shown in Figure 7.1 and Figure 7.

Conclusion

We get to synthesize the Schiff base caffeine complexes from the reaction of $\text{MCl}_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$), caffeine and N-salicylidene- β -alanine (KHL). Then, the ligand of N-salicylidene- β -alanine acts as a tridentate bridging with a (NO_2) -donor set originating from azomethine, and bridging carboxylate. The caffeine is coordinated with metal ions through the nitrogen atom (N9). The spectroscopic studies suggested the octahedral distorted unit structure for the all complexes.

References

- [1] Cimerman Z, Miljanic S, and Galic N, *Croatica Chemica Acta*, 2000, 73 (1), 81- 95.
- [2] Singh P, Goel R L and Singh B P, *J. Indian Chem. Soc.*, 1975, 52, 958.
- [3] Perry B F, Beezer A E, Miles R J, Smith B W, Miller J and Nascimento M G, *Microbois.*, 1988, 45, 181.
- [5] Elmali A, Kabak M and Elerman Y, *J. Mol. Struct.*, 2000, 477, 151.
- [6] Patel P R, Thaker B T and Zele S, *Indian J. Chem.*, 1999, 38 A, 563.
- [7] Valcarcel M and Laque de Castro M D, "Flow-Throgh Biochemical Sensors", Elsevier, 1994, Amsterdam.
- [8] Slin Tascioglu, Bahattin Yalcn, The syntheses, structure and properties of cobalt complexes with β -alanine derivatives, *Polyhedron* 25 ,2006, 1279–1286
- [9] A. S. Gaballa, M. S. Asker, A. S. Atiat and S. M. Teleb, *Spectrochim. Acta*, A, 2007,67,114.
- [10] D.I. Harris, A. Sass-Kortsak, *J. Clin. Invest.* ,1967, (46) 659–667.
- [11] X. S. Tai, X. H. Yin and M. Y. Tan, *Pol. J. Chem.*, 2003, (77) 411.
- [12] L. Xu, R. Yuan, Y. Z. Fu and Y. Q. Chai, *Anal. Sci.*, 2005, (21) 287.
- [13] A. Smith, J. Alam, P.V. Escriba, W.T. Morgan, *J. Biol. Chem.* 1993, (268) 7365–7371.
- [14] L. Xu, R. Yuan, Y. Q. Chai and X. L. Wang, *Anal. Bioanal. Chem.*, 2005, (381) 781.
- [15] Ruchi Verma, Lalit Kumar, Characterization of Caffeine Isolated from Camellia Sinensis Leaves of Sikkim Himalayan Region, *J. Chem. Pharm. Res.*, 2010, 2(4),194-198
- [16] Offiong O.E., NFor E., Ayi A.A. & Martelli S., *Trans. Met. Chem.*,2000,(25),369
- [17] Somnath D., Sujit M. & Animesh C., *Polyhedron*,1995, (14,9)1163
- [18] Polanichany M. & Anbu M., *Proceeding of the Indian Academy of Science: Chemical Science*,1997, (109,2)105
- [19] Armin F., Theodor E., Shahram M. & Wolfgang B., *Journal of Organometallic Chemistry*,2001 (621, 1-2)109
- [20] 19 Sucharita Basak, Amrita M., Deepak C. & Kajal K.R., *Polyhedron*, 2007, (26,13) 3465
- [21] Nasrullayeva T.M., Yaln B., Xudaverdiyev R.A., Aydin A. & Medjidov A.A, *Azerb Chem. J.*, 2005,(1) 22
- [22] Tasciogla S., Yaln B., Nasrullayeva T.M., Anda O., Bykgngr O., Aydin A. & Medjidov A.A., *Polyhedron*, 2006, (25) 1279-1286
- [23] Werner P.E., Valent A., Adelskold V. & Svajlenova O., *Acta Chem. Scand Ser A.*, 1983,(37) 51
- [24] Marck J., Vanco J. & Svajlenova O., *Acta Cryst C.*, 2003, (59) 509
- [25] K. Nakanshi and P. H. Solomon, *Infrared Absorption Spectroscopy*, Holden-Day, Inc., 1977

- [26] Ja'n Vanc'o, Jaromír Marek, Zdeněk Tra'vníček, Eva Račanská, Jan Muselík, Olga Švajlenová, *Journal of Inorganic Biochemistry*, 2008, (102) 595–605
- [27] Shayma A. Shaker & Yang Farina, *Modern applied science*, 2009, Vol 3 N°2
- [28] Sülin Tascıoğlu, Bahattin Yalcı, Tarana M. Nasrullayeva, Ömer Andac,
- [29] Orhan Bu'yu'kgü'ngör, Adnan Aydın, Ajdar Akber Medjidov, *Polyhedron*, 2006,(25) 1279–1286
- [30] A.S.P.Azzouz, R.T. Ali, *Synthesis of Schiff Bases Derived From Benzaldehyde and*
- [31] *Salicylaldehyde With Some Amino Acids by a New Develop Method*, *National Journal of Chemistry*, 2010, Volume 37, 158-168
- [32] B. Jezowska, J. Lisowski, and P. Chmielewski, *Polyhedron*, 1988, (7) 337
- [33] a- Thomas Nelson and Sons a-Kettle.S.F.A.Coordination compounds., London. 1975,p.165
- [34] Quaglian J.V., Fujita J. and Franz G.. *J. Am. Chem. Soc.*, 1961, (81), 3770.
- [35] A.L. El-Ansary, A.A. Soliman, O.E. Sherif, J.A. Ezzat, *Synth. React. Inorg. Met-Org. Chem.*, 2002, 32 (8) 1301.
- [36] A.A. Soliman, W. Linert, *Thermochim. Acta.*, 1999, (338) 67.
- [37] Ja'n Vanc'o, Jaromír Marek, Zdeněk Tra'vníček, Eva Račanská, Jan Muselík, Olga Švajlenová, *Journal of Inorganic Biochemistry*, 2008, (102) 595–605
- [38] Shayma A. Shaker, Yang Farina, Sadia Mahmmod and Mohean Eskender, , *ARNP Journal of Engineering and Applied Sciences*, 2009, (4), NO. 9,
- [39] P. C. Junk, C. J. Kepert, L. Wei-min, B. W. Skelton and A. H. White, *Aust. J.Chem.*, 1999, (42) 437
- [40] Har Lal Singh, Jangbhadur Singh, *Nature Science*, 2012, (4), 170-178.
- [41] Romerosa, J. Ruiz, *Inorg. Chim. Acta* 1993, 212, 1152121 *Dalton Trans.* 1993, (11),7921184.
- [42] Z. N. Chen, S. X. Liu, J. Qiu, Z. M. Wang, J. L. Huang, W. X. *Inorg. Chem.* 1995, (34), 4082411.
- [43] J. P. Costes, F. Dahan, J. P. Laurent, *Inorg. Chem.* 1985, 24
- [44] M. Kato, Y. Muto, *Coord. Chem. Rev.* 1988, (92), 45.
- [45] M. Inoue, M. Kubo, *Inorg. Chem.* 1970,(9), 231022314.
- [46] V.Pardes-Garcia, D.Vengegas-Yazigi, R.O.Latorre, E.Spodine, *Polyhedron*, 2006, (25) 2026-2032.
- [47] Veronica Pardes-Garcia, Ramon O. Latorre, Evgenia Spodine, *Polyhedron*, 2004, (23)1869-1876
- [48] M. Thomas, M. K. M. Nair, and P. K. Radhakrishnan, *Synth. React. Inorg. Met Org. Chem.*, 1995, (25), 471
- [49] K. Nakamoto, *Infrared and Raman Spectra of inorganic and coordination compound* 3rd Edition (Wile, New York, 1997).
- [50] A. Jain, R. Goyal, and D. D. Agarwal, *J. Inorganic Nuclear Chem.*, 1981, (43), 2005