

ORIGINAL ARTICLE

Synthesis and Characterization of the mixed ligand Complexes
[M(Ac)₂(caf)₂]M=Ni(II),Co(II),Zn(II), [Cu₂(μ-Ac)₄(caf)₂]
,Ac=CH₃COO⁻, caf = caffeine

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ABSTRACT

In this work, mixed ligand complexes [M(Ac)₂(caf)_n]; n=2, M= Cu²⁺, Zn²⁺, Co²⁺, Ni²⁺; n=1, M=VO²⁺ Ac= CH₃CO₂⁻, caf= caffeine have been prepared. They have been characterized by molar conductance, infrared, UV-Visible, EPR spectroscopy. The infrared and UV-Visible data suggest that the acetate ligand is bidentate chelate and the caffeine behave a monodentate ligand with N9 donor towards metal ions. The physico-chemical data suggest octahedral divalent metal caffeine diacetato complexes and pyramidal for the dimer copper complex [Cu₂(μ-CH₃COO)₄(caf)₂].

Keywords - Metal Acetate Complexes, caffeine, Co(II), Cu(II), Ni(II), Zn(II), VO(II) conductivity, FT-IR, EPR, UV-Visible.

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INTRODUCTION

Nitrogen donor ligand such as caffeine(1,3,7-trimethylxantine) is one of the main alkaloid formed in various kinds of foods and drinks that we consume in daily life. It is naturally found in leaves, see do of fruits of 63 plant species . The most common sources of caffeine are coffee , coca beans, cola must and tea leaves [1].

The caffeine mostly coordinated through it's N-donor atom or wears through O-donor atom, wich is a rarity. The metal complexes are monomeric, dimeric, several correlations are stabilized and discussed for coordination of caffeine and derivatives [2].

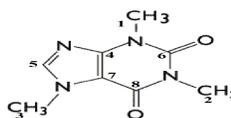


Figure 1. Structure of caffeine

Carboxylate and metal carboxyl are subject of extensive research for few decade. They are used to study as model compounds of metalloenzymes, as the phenomenon of the antiferromagnetic interaction or they show antibacterial proprieties [3].

The carboxylate group has versatile coordination behavior .It can be ionic, monodentate, bidentate, chelating or bridging. One method to determine the mode of the coordination is the infrared spectroscopy [4]. The frequencies of the ν_{as}(CO₂⁻) , ν_s(CO₂⁻) and difference of the carboxylate stretching Δ = ν_{as}(CO₂⁻) - ν_s(CO₂⁻) , are often used as spectroscopic criterions to determine of the carboxylate binding [5]. Generally , the following order is proposed for divalent metal carboxylate.

$$\Delta(\text{chelating}) < \Delta(\text{bridging}) < \Delta(\text{ionic}) < \Delta(\text{monodentate})$$

A number of works use this criteria for the assignment of the carboxylate binding, especially when no structural data are available [6]. Therefore the aim of our study is to investigate the applicability and consistency of the adducts divalent acetates complexes.

In the present work we are reporting studies of $[M(\text{Ac})_2(\text{caf})_n]$; $n=2$, $M= \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$; $n=1$, $M=\text{VO}^{2+}$; $\text{Ac}= \text{CH}_3\text{CO}_2^-$, $\text{caf}= \text{caffeine}$ and $[\text{Cu}_2(\mu\text{-CH}_3\text{COO})_4(\text{caf})_4]$ by using molar conductance, EPR, UV-visible and infrared spectroscopy.

MATERIALS AND METHODS

General methods and materials

All materials were of reagent grade and used without further purification. Anhydrous caffeine was purchased from Riedl-deHaen.A.G. $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{VO}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ used for synthesis were purchased from BDH.

The IR spectra in the range of $4000\text{-}400\text{ cm}^{-1}$ were recorded on Jasco FT/IR-4100 Fourier transform infrared spectrophotometer. UV-Visible spectra were measured in DMSO using Shimadzu UV-Visible recorder spectrophotometer UV-1800. Conductivity measurements were performed at 25°C in DMSO using Hach HQ430d flexi.

General procedure for synthesis

The general procedure for the synthesis of the transition metal (II) complexes was: 2mmol (0,388) g caffeine (caf) was dissolved in a warm environment in 10 mL ethanolic solutions up to 70°C . The obtained solution was treated with a solution that contained 1 mmol of $M(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ dissolved in 10 mL ethanolic solutions. The reaction mixture was refluxed for 4h. The obtained precipitate was filtered using a Büchner funnel washed with diethyl ether.

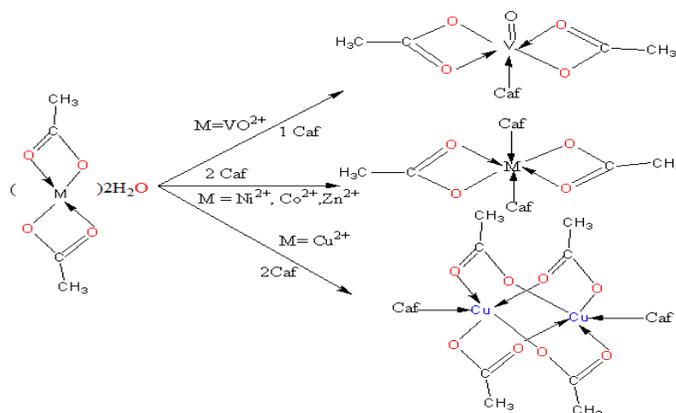


Figure 2. proceeding of synthesis complex

RESULTS AND DISCUSSION

The prepared complexes were found to be solids, insoluble in water but they were soluble in some organic solvents such as dimethylformamide and dimethylsulphoxide. The lower value observed of molar conductivities in DMSO indicates the non-electrolyte behavior of the complexes.

Table 1. The physical properties of the prepared complexes

compound	Colour	M.P. ($^\circ\text{C}$)	Yield (%)	Λ ($\text{Ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$)
$[\text{Zn}(\text{Ac})_2(\text{caf})_2]$	white	>260	80	15.4
$[\text{Co}(\text{Ac})_2(\text{caf})_2]$	pink	>260	76	16.7
$[\text{Ni}(\text{Ac})_2(\text{caf})_2]$	Green	>260	88	19
$[\text{VO}(\text{Ac})_2(\text{caf})]$	Dark green	>260	90	11
$[\text{Cu}(\text{Ac})_2(\text{caf})_2]$	Dark green	>260	86	22

Infrared spectra

The infrared spectrum of caffeine acetate complexes were obtained from spectrometer in the range $(4000\text{-}400)\text{cm}^{-1}$ and compared with that of free caffeine and metal acetates. The infrared data of the complexes are show in table (2).

Caffeine are show in figure (1) , they have a centrosymmetric C_s point group. For the caffeine the numbers of vibrations mode are as a follows $\Gamma_{vib} = 45 A' + 21 A''$. Thus the vibrations of the A' species will be in plane and those the A'' species wile be out of plane. The free acetate in has a very low symmetry C_{2v} and has fifteen fundamental vibration all of which are both infrared active [7]. Of these , the infrared vibrations due to the CO_2^- group are CO_2^- asymmetric stretching $\nu_{as} = 1578 \text{ cm}^{-1}$, CO_2^- symmetric stretching $\nu_s = 1430 \text{ cm}^{-1}$ [8] , CO_2^- bending, CO_2^- out of plane bending and CO_2^- rocking modes . It is well known That the acetate ion, like all other oxyanions, coordinate to the metal through its oxygen [9]. the anion may coordinate with the metal in ionic monodentate, chelate, bidentate bridging [4]

It is known from the literature, that the coordination of the caffeine with nitrogen and oxygen atoms which is accompanied by elimination of the mirror plane σ_h and by a whole series of changes in the infrared spectrum [9].

It may be noted that the spectra of the complexes $[M(Ac)_2(caf)_2]$ $M = Zn^{2+}, Ni^{2+}, Co^{2+}, VO^{2+}$ $Ac = acetate$; $caf = caffeine$, are similar in the ranges $(4000-400) \text{ cm}^{-1}$ [10].

Three less intense bands in the region $(3100-2950) \text{ cm}^{-1}$, which can be attributed to ν_{CH} and ν_{CH_3} stretching vibrations for acetate and caffeine coordinated .

The changes in the spectrum of caffeine and acetate is observed in the $(1700-400) \text{ cm}^{-1}$ region corresponding of stretching and bonding vibration of the carbonyl, imidazol(imid), carboxylate(Ac), pyrimidine(pyrimi) and methyl (CH_3) fragments.

A strong bands ν_{CO} for the carbonyl group in the caffeine are observed in the region $(1700-1650) \text{ cm}^{-1}$.this region is a characteristic of aromatic lactones for one and two carbonyl as in the quinine [10]. Caffeine contain two carbonyl vibration in the meta position , the strong band observed at 1700 cm^{-1} and 1650 cm^{-1} considered to be due to asymmetric $\nu_{as}(CO)$ and symmetric $\nu_s(CO)$ stretching vibration in caffeine [10] . The infrared spectra of the caffeine acetate complexes are characterised by insignificant shift frequencies for $\nu_{as}(CO)$ but $\nu_s(CO)$ is shifted to lower frequencies by 10 cm^{-1} .

The band noticed in the free caffeine spectrum at 1548 cm^{-1} is attributed to the $\nu(\text{imid}) + \nu(\text{pyrimi}) + \delta(\text{HCN})$ [10] and appeared for the caffeine acetate complexes at 1540 cm^{-1}

Corresponding to the vibration $\nu(\text{imid}) + \nu(\text{pyrimi}) + \nu_{as}(CO_2^-) + \delta(\text{HCN})$. On the thesis of the direction of the shift of $\nu_{as}(CO)$ is lower in comparison for their complexes $[M(Ac)_2(caf)_2]$.

For all complexes acetate it can be seen that the band of the $\nu(\text{imid}) + \nu(\text{pyrimi}) + \nu_{as}(CO_2^-) + \delta(\text{HCN})$ is displaced toward lower frequencies by $(10-15) \text{ cm}^{-1}$ indicated the coordination of caffeine to metal through the nitrogen imidazol N9 atom , in comparison to the free caffeine [11].

For example , in copper acetate hydrate and copper acetate caffeine, the value of separation Δ of the carboxylate $\Delta = 175 \text{ cm}^{-1}$, This value characterizes the bidentate bridge and it is in agreement with the results of X-Ray diffraction and EPR spectra [12].

The EPR spectra of solid, were measured at room temperature .The EPR spectrum at ambient temperature were observed in figure (3), for complex $[Cu_2(\mu-CH_3COO)_4(caf)_4]$. this spectrum, characteristic of two interacting Cu(II), already studied in detail, can be described by the spin Hamiltonian, given by the following expression. $H = \beta H_g S + D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2)$

where D and E are the zero-field splitting parameters, x, y and z are the principal coordinate axes and $S = 1$. The other symbols have their usual meaning. Because of the strong antiferromagnetic interaction, the spin Hamiltonian parameter D contains the exchange parameter J, arising from the exchange and dipole-dipole interactions.

$$D = -J/8[1/4(g_{\parallel} - 2)^2 - (g_{\perp} - 2)^2] - [g_{\parallel}^2 + 1/2(g_{\perp}^2)] \beta^2 / r^3$$

where r is the distance between two interacting paramagnetic centers. It was shown for dimeric copper(II) carboxylate [4-11-12]

Data obtained for complex Cu(II) are: $H_{z1} = 241$, $H_{\perp} = 4738$, and $H_{z2} = 5996 \text{ G}$, which are in good accordance of axially symmetric binuclear copper(II) [4-11-12]

g-values ($g_{\parallel} = 2.24$, $g_{\perp} = 1.47$) were calculated taking into account the simplified model for moderate interacting dinuclear Cu(II) centers. The calculated magnetic parameters are in agreement with the previous reports for dinuclear copper complexes [11-12].

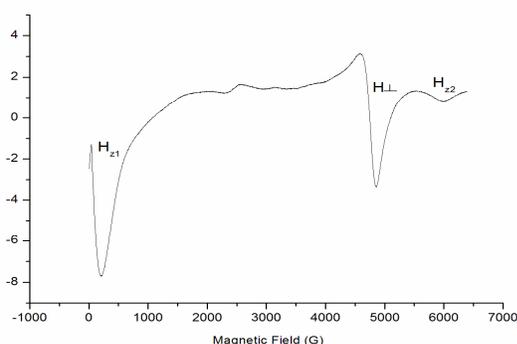


Figure 3. EPR spectrum of the complex $[\text{Cu}_2(\mu\text{-CH}_3\text{COO})_4(\text{caf})_4]$

The signals and values of G is similar of $[\text{Cu}(\text{CCl}_3\text{COO})_2(\text{caf})_2]_2$ complex in polycrystalline EPR spectra. The complexes has the structure usually formed in dimeric type $[\text{Cu}(\text{CH}_3\text{COO})_2\text{L}]_2$ in the centrosymmetric dimer having distorted square pyramidal symmetry with N9 of the caffeine molecule in the apical position [12].

Infrared for the zinc acetate dihydrate and zinc acetate caffeine [13], the values of magnitude $\Delta=110\text{ cm}^{-1}$ and 121 cm^{-1} respectively. This value characterizes the bidentate chelate mode of carboxylate coordination [13].

The infrared spectra of the three acetate caffeine complexes, $[\text{M}(\text{Ac})_2(\text{caf})_n]$ $n=2$, $\text{M}=\text{Ni}^{2+}, \text{Co}^{2+}$; $n=1$ $\text{M}=\text{VO}^{2+}$ are very similar. The EPR spectrum of the complex $[\text{VO}(\text{Ac})_2(\text{caf})]$ in the solid state, is shown in Figure (4). This species shows $g=1,967$ which is typical of complex monomer an cubic structure.

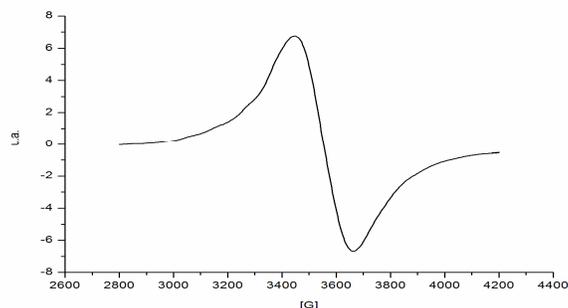


Figure 4. EPR spectrum of the complex $[\text{VO}(\text{Ac})_2(\text{caf})]$

In these spectra contain asymmetric and symmetrical stretching vibrations due to the COO^- group appearing in the acetate caffeine are found at 1555 cm^{-1} , 1420 cm^{-1} for nickel at 1540 cm^{-1} , 1418 cm^{-1} for zinc, at 1540 cm^{-1} , 1426 cm^{-1} for cobalt, at 1540 cm^{-1} , 1425 cm^{-1} for vanadyl.

As for the coordination of the carboxylate ion is concerned the information is show from the position and differentia Δ of asymmetric and symmetric CO_2^{2-} frequencies. In this case $\nu_{\text{as}}\text{CO}_2^-$ decreased, $\nu_{\text{s}}\text{CO}_2^-$ increased and Δ occurring at about $90\text{-}125\text{ cm}^{-1}$ for the complexes. This is clear indication of the involvement conservation of the mode chelate bidentate in this complexes.

The band noticed in the caffeine free at 1405 cm^{-1} which can attributed to the bending vibrations disappear for these complexes.

The bending vibrations are usually found at lower frequencies.

The frequencies noticed in the range $(760\text{-}740)\text{ cm}^{-1}$ and 475 cm^{-1} are due to bending $\gamma\text{CO}_2^- + \gamma\text{NCO} + \gamma\text{pyrimi} + \gamma\text{imid}$ and $\tau(\text{caffeine})$ respectively.

The newly appeared vibrations observed in the infrared spectrum of the complexes acetate caffeine in $(550\text{-}540)\text{ cm}^{-1}$ corresponding to M-N stretching vibrations [14]

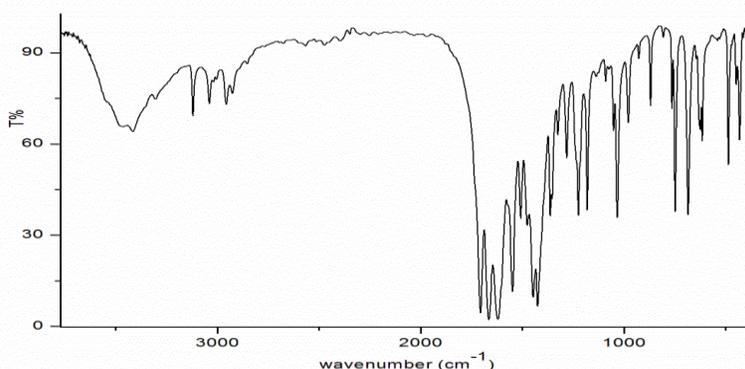


Figure 5. Infrared spectrum of the complex $\text{Cu}_2(\mu\text{-CH}_3\text{COO})_4(\text{caf})_4$ in KBr

Table 2. Main vibrations of the complexes $[\text{M}(\text{Ac})_2(\text{caf})_n]$; $n=2$, $\text{M} = \text{Cu}(\text{II}), \text{Zn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$; $n=1$, $\text{M} = \text{VO}(\text{II})$ $\text{Ac} = \text{CH}_3\text{CO}_2^-$, $\text{caf} = \text{caffeine}$ and $[\text{Cu}_2(\mu\text{-CH}_3\text{COO})_4(\text{caf})_4]$ in KBr

$\text{Cu}_2(\text{AC})_4(\text{caf})_2$	$\text{VO}(\text{AC})_2(\text{caf})$	$\text{Zn}(\text{AC})_2(\text{caf})_2$	$\text{Ni}(\text{AC})_2(\text{caf})_2$	$\text{Co}(\text{AC})_2(\text{caf})_2$	Assignment
3470			3450	3460	(OH) _{H2O}
3118	3100	3100	3100	3100	v (CH)caf
3039	3050		3000	3000	v (CH ₃)Ac
2956	2950	2952	2950	2950	v (CH ₃)caf
1706	1694	1695	1695	1690	vs (CO)caf
1664	1646	1650	1650	1650	vas (CO)caf
1620	1595	1590	1600	1590	vas (COO ⁻)Ac
1549	1540	1540	1555	1540	(C=C)+ (HCN)+ vas (CO ₂)
1507	1479	1478	1478	1478	δ(HCN)+δ(CH ₃)
1445	1445	1440	1440	1440	(CH ₃)+δ(CH ₃)+ δ(CH ₃)Ac
1424	1425	1418	1420	1426	vs (CO ⁻)ac
1362	1360	1350	1350	1350	s(CH ₃)ac
1281	1285	1285	1290	1285	(pyri)
1225	1238	1240	1240	1240	(CN) +ρr(CH ₃)
1051	1075	1050	1070	1078	out of plane CH ₃ rocking
1032	1020	1025	1025	1022	in- plane CH ₃ rocking
927	930	930	940	930	υ(C-C)ac
746	742	745	745	742	γ(pyrimi)+γ(imid)+γ CO ₂ ⁻ + γ NCO
683	680	690	690	700	δ (COO)ac
650	610	612	610	610	γ(imidazol)
539	535	550	542	550	(M-N)
486	482	480	478	478	τ (caffeine)
431	420	420	420	420	ρr(C=O)

UV-visible

The electronic spectrum of the Co(II) complex displayed three bands at 504 nm, and 966 nm, attributed to the d-d transitions: ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ respectively. These transitions are consistent with the characteristic octahedral geometry [15].

Both electronic spectra of the Ni(II) complexes, exhibited three bands at: 391 nm, 592 nm and 722 nm, attributed to the transitions ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$, ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ respectively, which are characteristic of an octahedral geometry [15].

The solution of Zn(II) complex, shown high intensity peak at 368 nm which is attributed to (M→L) charge transfer transition. This value is accepted for octahedral complex.

Therefore, one expects 3 d → d transitions for $[\text{VO}(\text{AC})_2\text{caf}]$ at 854; 778; 590 nm attributed to the transitions ${}^2\text{B}_2(\text{dxy}) \rightarrow {}^2\text{E}(\text{dxz, yz})$, ${}^2\text{B}_2(\text{dxy}) \rightarrow {}^2\text{B}_1(\text{dx}^2 - \text{y}^2)$, and ${}^2\text{B}_2(\text{dxy}) \rightarrow {}^2\text{A}_1(\text{dz}^2)$ respectively, which are characteristic of a Square Pyramid Geometry [15].

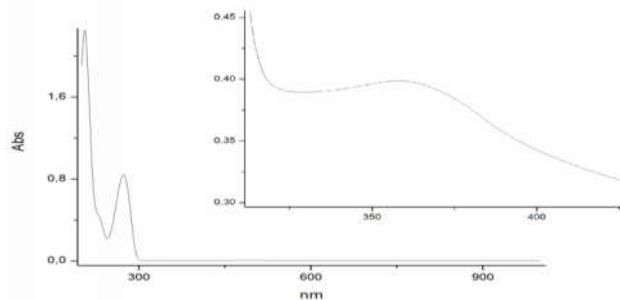


Figure 6. uv-visible spectrum of the complex $[Zn(AC)_2(caf)_2]$ in DMSO

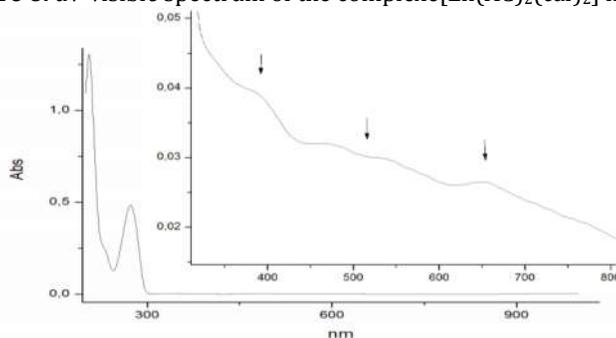


Figure 7. uv-visible spectrum of the complex $[Ni(AC)_2(caf)_2]$ in DMSO

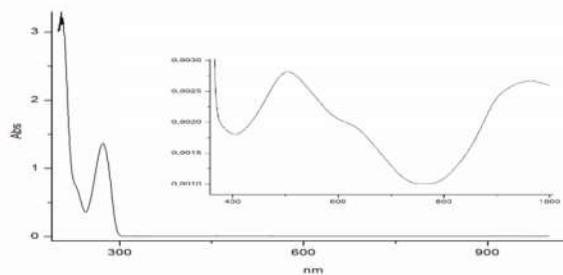


Figure 8. uv-visible spectrum of the complex $[Co(AC)_2(caf)_2]$ in DMSO

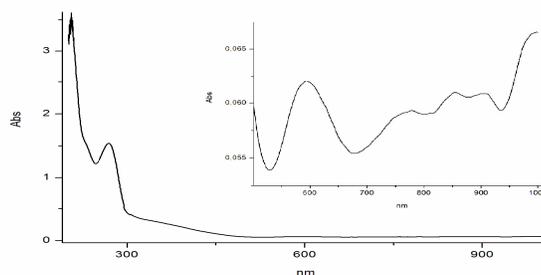


Figure 9. uv-visible spectrum of the complex $[VO(AC)_2(caf)]$ in DMSO

The electronic spectrum of the complex Cu show a broad absorption band in the visible region at 674 nm, which could be assigned to a $dxy \rightarrow dx^2 - y^2$ transition. Moreover, the spectrum displays a shoulder at 384 nm has been assigned to a charge transfer LMCT absorption and is believed to be indicative of a binuclear complex [4].

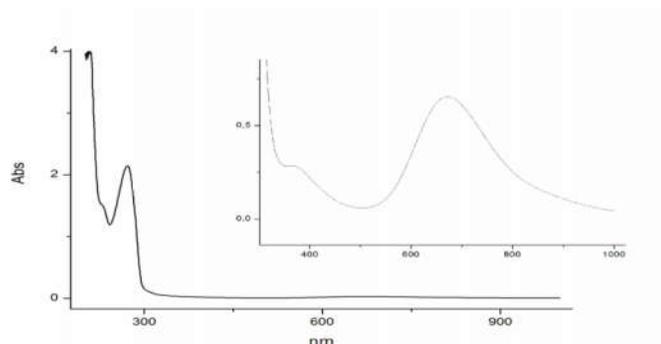


Figure 10. uv-visible spectrum of the complex $[\text{Cu}(\text{AC})_4(\text{caf})_2]$ in DMSO

Tableau 2. Electronic spectra of the complexes $[\text{M}(\text{Ac})_2(\text{caf})_n]$; $n=2$, $\text{M} = \text{Cu}(\text{II}), \text{Zn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$; $n=1$, $\text{M} = \text{VO}(\text{II})$ $\text{Ac} = \text{CH}_3\text{CO}_2^-$, $\text{caf} = \text{caffeine}$ and $[\text{Cu}_2(\mu\text{-CH}_3\text{COO})_4(\text{caf})_4]$ in DMSO.

Compound	$\lambda_{\text{max}}(\text{nm})_{(\text{abs})}$	Assignment
caféine	273	$\pi \rightarrow \pi^*$
	271	$\pi \rightarrow \pi^*$
	384	C.T
$[\text{Co}(\text{AC})_2(\text{caf})_2]$	504	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$
	965	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$
	271	$\pi \rightarrow \pi^*$
$[\text{Ni}(\text{AC})_2(\text{caf})_2]$	391	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$
	592	${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$
	722	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$
$[\text{Zn}(\text{AC})_2(\text{caf})_2]$	270	$\pi \rightarrow \pi^*$
	368	CT
	270	$\pi \rightarrow \pi^*$
	377	$n \rightarrow \pi^*$
$[\text{VO}(\text{AC})_2(\text{caf})]$	590	${}^2\text{B}_2(\text{dxy}) \rightarrow {}^2\text{A}_1(\text{dz}^2)$
	778	${}^2\text{B}_2(\text{dxy}) \rightarrow {}^2\text{B}_1(\text{dx}^2 - \text{y}^2)$
	854	${}^2\text{B}_2(\text{dxy}) \rightarrow {}^2\text{E}(\text{dxz}, \text{yz})$
$[\text{Cu}_2(\text{AC})_4(\text{caf})_2]$	271	$\pi \rightarrow \pi^*$
	381	C.T
	673	$\text{dxy} \rightarrow \text{dx}^2 - \text{y}^2$

CONCLUSION

In this study the complexes acetate of $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Zn}(\text{II})$, $\text{VO}(\text{II})$ and $\text{Cu}(\text{II})$ with caffeine ligand were synthesized and characterized. On the basis of conductance, caffeine analysis, infrared, UV-visible, EPR the spectral data suggested the formula of the complexes are $[\text{M}(\text{Ac})_2\text{caf}_2]$ $\text{M} = \text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Zn}(\text{II})$, $[\text{VO}(\text{Ac})_2\text{caf}]$, $[\text{Cu}(\text{Ac})_2\text{caf}]_2$. The results suggested the octahedral symmetry of $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Zn}(\text{II})$, $\text{VO}(\text{II})$ complexes.

The complex of copper characterized on basis of spectroscopic data FT-IR, EPR, and UV-Visible indicate the complex of formula $[\text{Cu}_2(\mu\text{-CH}_3\text{COO})_4(\text{caf})_2]$, the copper centre are bridged bidentate acetate groups, the two copper atom are pyramidal.

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