

Research Article

Synthesis and Characterization of the mixed ligand complexes $[M(\text{acac})_2(\text{H}_2\text{O})_n]$ and $[M(\text{acac})_2(\text{caf})_n]$; $n=1$, $M= \text{Zn}^{2+}$, $n=2$, $M= \text{Cu}^{2+}$, Ni^{2+} , Mn^{+2} , Co^{2+} ; acac=acetylacetonate; caf=caffeine

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Abstract

Metal complexes $M(\text{acac})_2(\text{H}_2\text{O})_n$ and $[M(\text{acac})_2(\text{caf})_n]$ $n=1$ of divalent $M= \text{Zn}(\text{II})$, and $n=2$ of divalent $M= \text{Cu}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Mn}(\text{II})$ and $\text{Co}(\text{II})$ with mixed ligands acetylacetonate (acac) and caffeine (caf) were prepared and characterized by molar conductance, infrared, UV-Visible, EPR spectroscopy. The analytical and spectral data depict an octahedral geometry around the metal center where the acetylacetonate ligand is bidentate chelate and the caffeine behaves as a monodentate ligand with N9 donor.

Keywords: UV-Visible, acetylacetonate complexes, caffeine, mixed ligand complexes, infrared, EPR spectroscopy, conductivity

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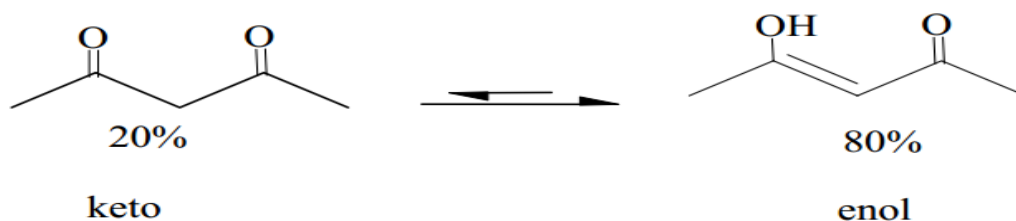
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Introduction

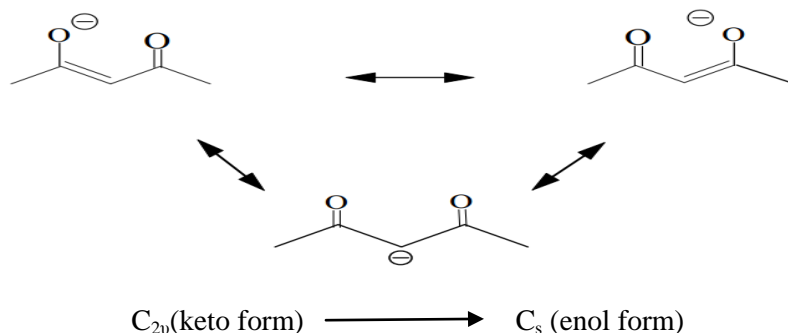
The acetylacetonate is the simplest of the β -diketonates. The presence of β -carbonyl groups with at least one proton on the intermediate carbon atom, allows a tautomeric equilibrium of the keto and enol forms. The acetylacetonate is an intermediate product of organic synthesis reaction, which can be used as an annexing agent in gasoline, lubricant and desiccant in paint [1-3]. Also it has been found to possess fungicidal and insecticidal activities [4, 5]. Complexes of metal ions with acetylacetonate have been the subjects of a wide variety of physical researches for many years. In recent years, the study on metal coordination of β -diketonate and its derivatives has attracted great interest, because metal complexes of β -diketonate derivatives can be good precursors in metalorganic chemical vapour deposition (MOCVD) for growing high T_c superconducting films [6, 7]. The transition metal β -diketonate compounds were used extensively as starting materials in the early days of metallocene chemistry [8, 9], and as electroluminescent materials [10].

Bis(acetylacetonate)cobalt(II) and its derivatives were recently proposed as mediators in controlled radical polymerization (CRP) of olefins [11]. Here in, we report the synthesis and investigation of bis(acetylacetonate) metal(II) complexes with the caffeine ligand $[M(\text{acac})_2(\text{caf})_n]$; $n=1$ of $M= \text{Zn}^{2+}$, and $n=2$ of $M= \text{Cu}^{2+}$, Ni^{2+} , Mn^{+2} , Co^{2+} ; acac= acetylacetonate; caf= caffeine.

The β -diketonates bear two carbonyl groups that are separated by one carbon atom. This carbon atom is the α -carbon which has a quite acidic α -hydrogen, and can be converted essentially completely to enolate anions with bases as mild as hydroxide ion [12].



Then, the acetylacetonate anion can act as a ligand towards the metal divalent to produce $M(\text{acac})_2$ with a six membered weakly aromatic ring.



Experimental

Materials and Methods

All chemicals were obtained from commercial sources and were used without purifications: (NiCl₂, 6H₂O BDH; ZnCl₂, 2H₂O BDH; CuCl₂, 6H₂O BDH; MnCl₂, 2H₂O BDH; CoCl₂, 6H₂O BDH), acetylacetonate Sigma Aldrich, salicylaldehyde SAFC, Ethanol and DMSO Sigma Aldrich, double distilled water was used.

Infrared spectra were recorded as KBr pellets on a JASCO FT-IR 660 plus spectrophotometer in the range of 4000-400 cm⁻¹ at 298 K while the electronic spectra (UV-Visible) were obtained on a Shimadzu UV-1800 Spectrophotometer. The EPR spectrum was recorded on a conventional X band Bruker ER 200D spectrometer operating at 9.5 GHz. Conductivity measurements were performed at 25°C in DMSO using Hach HQ430d flexi.

Synthesis of the aquo acetylacetonato complexes [M(acac)₂(H₂O)_n]; n=1 of M= Zn²⁺, and n=2 of M= Cu²⁺, Ni²⁺, Mn²⁺, Co²⁺

The aquo acetylacetonato complexes of divalent metals Zn(II), Cu(II), Ni(II), Mn(II) and Co(II) were synthesized by using the method reported by Harold Golf [13], Bennet [14] and Housecroft [15].

Synthesis of the caffeine acetylacetonato complexes [M(acac)₂(caf)_n]; n=1 of M= Zn²⁺, and n=2 of M= Cu²⁺, Ni²⁺, Mn²⁺, Co²⁺

To a solution of [M(acac)₂(H₂O)_n]; n=1 of M= Zn²⁺, and n=2 of M= Cu²⁺, Ni²⁺, Mn²⁺, Co²⁺ (1 mmol) in boiling ethanol, was added a solution of caffeine (2 mmol) in ethanol. The obtained solution was refluxed for 4 h, after which the solution is concentrated, filtered and washed with small portions of hot water and finally air dried.

Results and Discussion

Characterization of the complexes [M(acac)₂(H₂O)_n] and [M(acac)₂(caf)_n]; n=1 of M= Zn²⁺, and n=2 of M= Cu²⁺, Ni²⁺, Mn²⁺, Co²⁺; acac= acetylacetonato; caf= caffeine

All synthesized complexes are intensively coloured and solids. The solubility of these compounds in water at 25°C was found to be in the range of 10⁻²-10⁻³ mol l⁻¹. Molar conductance values of the complexes in distilled water (10⁻³ M solution at 25°C) were (14.85-22.20) Ω⁻¹ cm² mol⁻¹, indicating, their non-electrolytic nature (**Table 1**).

Table 1 Physico-chemical data of the complexes

Complex	Color	M.P. (°C)	Yield (%)	Λ (Ωm ⁻¹ cm ² mol ⁻¹)
[Co(acac) ₂ (H ₂ O) ₂]	Pink	>260	60	22.20
[Mn(acac) ₂ (H ₂ O) ₂]	Yellow	>260	43	17.91
[Ni(acac) ₂ (H ₂ O) ₂]	Green	>260	54	19.52
[Zn(acac) ₂ (H ₂ O)]	White	>260	60	16.50
[Cu(acac) ₂]	Blue	>260	62	16.28
[Co(acac) ₂ (caf) ₂]	Pink	>260	65	15.59
[Mn(acac) ₂ (caf) ₂]	Brown	>260	40	15.12
[Ni(acac) ₂ (caf) ₂]	Green	>260	50	14.85
[Cu(acac) ₂ (caf) ₂]	Blue	>260	60	16.36
[Zn(acac) ₂ (caf)]	White	>260	65	16.25

Infrared spectroscopy of acetylacetonato ligand and its complexes $[M(acac)_2(H_2O)_n]$; $n=1$ of $M=Zn^{2+}$, and $n=2$ of $M=Cu^{2+}, Ni^{2+}, Mn^{+2}, Co^{2+}$; $acac=$ acetylacetonato

Selection infrared bands of acetylacetonato ligand and its complexes as well as assignments [12] of their frequencies are presented in **Table 2**. The infrared spectrum of $[Zn(acac)_2(H_2O)_2]$ is given in **Figure 1**.

Table 2 Characteristic IR frequencies in (cm^{-1}) of the acetylacetonato ligand and its aquo acetylacetonato complexes $[M(acac)_2(H_2O)_2]$; $n=1$ of $M=Zn^{2+}$, and $n=2$ of $M=Cu^{2+}, Ni^{2+}, Mn^{+2}, Co^{2+}$, $acac=$ acetylacetonato

$[Ni(acac)_2(H_2O)_n]$	$[Co(acac)_2(H_2O)_2]$	$[Mn(acac)_2(H_2O)_2]$	$[Zn(acac)_2(H_2O)]$	$[Cu(acac)_2]$	acacH	Attribution
3460s	3424s	3430s	3460s	3458m		$\nu(OH)/H_2O$
	3254w	3267w				
3081w	3074w	3071w	3000w	3100w		$\nu(CH)$
2994w	2987w	2990w	2980w	2921w		$\nu_{as}(CH_3),$
2925w	2922w	2924w	2910w			$\nu_s(CH_3)$
1651w	1656w	1658w		1635w	1729vs	$\nu(C=O)$
1605s	1600s	1595s	1590s	1577s	1710vs,	$\nu(C=C)$
				1552m	1621vs	
1520s	1520s	1520s	1516s	1531s	1421vs	$\nu(C=C)$
1457s	1462s	1460s	1456s	1456m		$+\tau(CH_3)$
1400s	1400s, 1350m	1400s, 1350m	1400s	1416s	1361vs	$\omega(CH_3),$
				1354m		$\nu_{as}(C=C=C)-$
1262m	1261s	1255s	1260m	1275m	1303m,	$\nu_s(C=C=C)$
					1249vs	
1200w	1200m	1200m	1200m	1190w	1171w	$\delta(CH)$
1022m	1020s	1020s	1017m	1020m	1001w	$\omega(CH)-$
934m	932s	925s	930m	937m	956m,	$\delta(C=C=C)$
					915s	
767m	767F	768m	771m	772s	780m	$\gamma(CH)-$
664w	673w	669w	660w	680w		$\rho(CH_3)-$
593w	584m	660w	655w	652m		
	564m	540m	540m	539w		
428w	425m	437w	435w	450m		$\nu(M-O)$

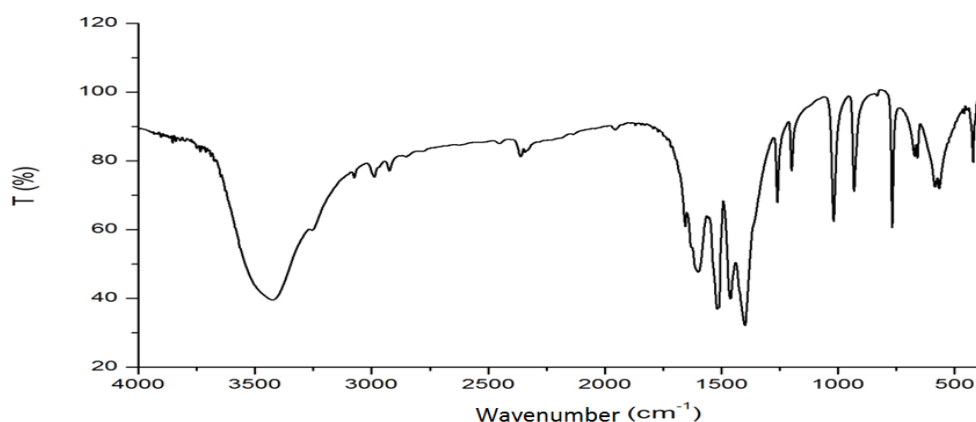


Figure 1 Infrared spectrum of the aquo acetylacetonato complex $[Co(acac)_2(H_2O)_2]$ in KBr

They are thirty nine vibrational modes of acetylacetonato ligand to its internal vibrations in C_s group symmetry [16, 17]. The infrared spectrum of the acetylacetonato ligand shows band at 3005 cm^{-1} which can be attributed to the stretching mode of the methyne group $\nu(CH)$ of the enolic form.

The band at 2960 cm^{-1} is assigned to the asymmetric mode of the methylene $\nu_a(CH_2)$ of the keto form. The band at 2924 cm^{-1} corresponding of the enolic and ketonic forms is attributed to the mode of the methyl [18].

In the region $C=O$ and $C=C$, there are four bands stretching modes of keto and enol forms. The doublet observed at 1729 cm^{-1} and 1710 cm^{-1} is attributed to two carbonyl groups in the keto form. However, a broad band at 1621 cm^{-1} is attributed to the carbonyl group of the enol form [19]

The band at 1431 cm^{-1} can be attributed to the out of plane bending (twisting) δCH_3 for the keto form or the wagging $\omega(\text{CH}_3)$ for the enol form. The band at 1361 cm^{-1} is attributed to the wagging $\omega(\text{CH}_3)$ methyl group of enolic and ketonic forms. The vibrational band at 1303 cm^{-1} is referred to the wagging $\omega(\text{CH}_2)$ and twisting $\delta(\text{CH}_2)$ of the methylene group [12].

The vibration mode at 1171 cm^{-1} is referred to the in plane bending of the methyne group $\delta(\text{CH})$ for the enol form and the stretching mode of the $\nu(\text{C}-\text{CH}_3)$ for the keto form.

The vibrational modes at 1001 cm^{-1} can be attributed to the rocking of the methylene $\rho(\text{CH}_2)$ for the ketonic form and is assigned to the wagging $\omega(\text{CH})$ for the enolic form [12].

For the enolic form, this band is due to $\delta(\text{OH})$ in plane bending. The band at 780 cm^{-1} can be assigned to $\gamma(\text{OH})$ and $\nu(\text{C}-\text{CH}_3)$ for the enolic and/or keto forms [20].

Upon coordination, the enol form was stabilized by chelation to metal divalent and formation of $[\text{M}(\text{acac})_2(\text{H}_2\text{O})_n]$; $n=1$ of $\text{M}=\text{Zn}^{2+}$, and $n=2$ of $\text{M}=\text{Cu}^{2+}$, Ni^{2+} , Mn^{2+} , Co^{2+} . Their infrared spectra show the strong bands in the $(1635-1655)\text{ cm}^{-1}$, $(1516-1605)\text{ cm}^{-1}$ and $(1456-1460)\text{ cm}^{-1}$ ranges which are assigned to the stretching vibrations $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{C})$, $\tau(\text{CH}_3)$ respectively.

The bands observed in $(1350-1354)\text{ cm}^{-1}$ and $(1255-1275)\text{ cm}^{-1}$ are due to the asymmetrical and symmetrical stretching vibrations of $\nu_{\text{as}}(\text{C}=\text{C}=\text{C})$ and $\nu_{\text{s}}(\text{C}=\text{C}=\text{C})$ respectively [12].

The bending $\delta(\text{CH})$ and the wagging $\omega(\text{CH})$ bands were observed in the $(1190-1200)\text{ cm}^{-1}$ and $(1017-1020)\text{ cm}^{-1}$ ranges respectively.

The chelation of the acetylacetonato ligand to divalent metals is shifted in the infrared spectra to lower frequencies.

New bands in $(425-450)\text{ cm}^{-1}$ range are attributed to $\nu(\text{M}-\text{O})$ stretching vibrations [21]

Infrared spectroscopy of the complexes $[\text{M}(\text{acac})_2(\text{caf})_n]$; $n=1$ of $\text{M}=\text{Zn}^{2+}$, and $n=2$ of $\text{M}=\text{Cu}^{2+}$, Ni^{2+} , Mn^{2+} , Co^{2+} ; $\text{acac}=\text{acetylacetonato}$; $\text{caf}=\text{caffeine}$

The infrared spectrum of $[\text{M}(\text{acac})_2(\text{caf})_2]$ is given in **Figure 2**. The absorption bands observed in the infrared spectra of the different complexes studied as solid in KBr are given in **Table 3**.

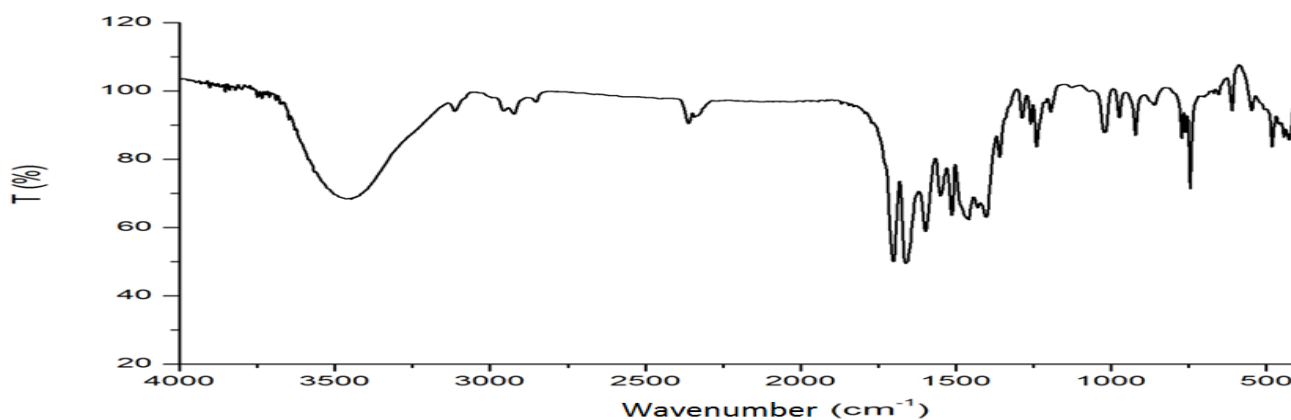


Figure 2 Infrared spectrum of the caffeine acetylacetonato complex $[\text{Zn}(\text{acac})_2(\text{caf})_2]$ in KBr

The characteristic frequencies of the free acetylacetonato, caffeine ligand and their complexes were readily assigned based on comparison with the literature [12, 22].

Upon substitution of the water coordination by caffeine ligand, the infrared spectra of studied complexes show that the stretching vibrations $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ of the acetylacetonato ligand were shifted to lower frequencies. These vibrations occurred as multiple bands in $(1600-1698)\text{ cm}^{-1}$ range for the caffeine ligand and in $(1510-1620)\text{ cm}^{-1}$ range for the acetylacetonato ligand [23].

The carbonyl group in the the caffeine acetylacetonato complexes exhibit a strong absorption band in the $(1694-1700)\text{ cm}^{-1}$ range due to $\nu(\text{CO})$ asymmetric. Another strong band in the $(1656-1659)\text{ cm}^{-1}$ range belong to $\nu(\text{CO})$ symmetric and $\nu(\text{C}=\text{N})$ is shifted to lower frequencies, compared with the free caffeine, indicating coordination of the caffeine through the azomethine nitrogen atom (N9) [24]. In addition, the band at 1550 cm^{-1} is assigned to $(\delta\text{HCN}+\text{oring imid}+\text{oring pyrimi})$ which is shifted to lower frequencies compared with the free caffeine.

Table 3 Characteristic IR frequencies in (cm^{-1}) of the caffeine ligand and its caffeine acetylacetonato complexes $[\text{M}(\text{acac})_2(\text{caf})_n]$; $n=1$ of $\text{M}=\text{Zn}^{2+}$, and $n=2$ of $\text{M}=\text{Cu}^{2+}$, Ni^{2+} , Mn^{2+} , Co^{2+} ; acac= acetylacetonato; caf= caffeine

$\text{Ni}(\text{acac})_2\text{caf}_2$	$\text{Co}(\text{acac})_2\text{caf}_2$	$\text{Mn}(\text{acac})_2\text{caf}_2$	$\text{Zn}(\text{acac})_2\text{caf}$	$\text{Cu}(\text{acac})_2\text{caf}_2$	Caféine	Attribution
3445s	3431s, 3254w	3450s	3452s	3448m		$\nu(\text{OH})$
3117w	3116w	3110w	3114w	3115w		$\nu(\text{CH})$, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_3)$
2991w	2991w	2920w	2993w	2920w		
2925w	2922w	2925w	2923w			
2955w	2960w	2950w	2954w	2957w	2954w	$\nu_{\text{s}}(\text{CH}_3)\text{caf}$
1698s	1700s	1694s	1698s	1700s	1700s	$\nu(\text{C}=\text{O})\text{caf}$
1656s	1658s	1657s	1660s	1656s	1660s	$\nu_{\text{as}}(\text{C}=\text{O})\text{caf}$ $+\nu_{\text{s}}(\text{C}=\text{C})$ $\nu(\text{C}=\text{O})$
1620s	1608s	1590s	1598s	1579s 1551m		
1550m	1545m	1543m	1549m	1541m	1550s	$\delta(\text{HCN}) +$ $\nu(\text{imid}) + \nu(\text{pyri})$ $+ \nu(\text{C}=\text{C})$
1518s	1518s	1510m	1512s	1529s	1487m,	$\nu(\text{C}=\text{C}) +$
1464s	1461s	1455m	1459s	1457w	1456m, 1432m	$\delta(\text{CH}_3) +$ $\tau(\text{CH}_3)$
1400s	1400s, 1360w	1380m, 1358w	1400s, 1358w	1416s, 1356w		$\omega(\text{CH}_3) +$ $\nu_{\text{as}}(\text{C}=\text{C}=\text{C})$
1288w	1286 w	1284m	1287w	1284m	1286m	$\nu(\text{pyri})$
1260m	1260 m	1256m	1258m	1273m		$\nu_{\text{s}}(\text{C}=\text{C}=\text{C})$
1240w	1238s	1238m	1240w	1240w	1237m	$\delta(\text{C}-\text{H})$
1200w	1200m	1195w	1194w	1190w		$\omega(\text{CH})$
1022m	1020s	1021m	1020s	1020m		$\omega(\text{CH})$
974w	974m	974m	974w	974w	973m	$\nu(\text{N}-\text{CH}_3)$ $+\delta(\text{imid})$ $+\rho_{\text{r}}(\text{CH}_3)$
933m	931m	921m	922m	938m		$\delta(\text{C}=\text{C}=\text{C})$
861w	860w		860w		862w	$\rho_{\text{r}}(\text{CH}_3) + \nu(\text{N}-\text{CH}_3) + \delta(\text{C}=\text{O})$
765m	768m	760w	775m	780s		$\gamma(\text{CH})$
744m	744 m	744m	746m	745fw	745m	$\gamma(\text{pyri}) + \gamma(\text{imid})$
663w	673w	669w 660w	660w 655w	680w 652m		$\rho(\text{CH}_3)$
609f	610 m	610 m	611 f	611f	611f	$\nu(\text{imid})$
593f	583 f 566 f	541 f	540 m	539f		$\delta(\text{C}-\text{CH}_3) + \nu(\text{M}-\text{O})$
576f	510f	548f	550f	555f		$\nu(\text{M}-\text{N})$
482f	482m	480f	482f	482f	481f	τ (caffeine)
427f	422 m	435 f	433 f	448m		$\nu(\text{M}-\text{O})$

The bands in $(1356-1360) \text{ cm}^{-1}$ and $(1256-1273) \text{ cm}^{-1}$ ranges due to $\nu_{\text{as}}(\text{C}=\text{C}=\text{C})$ and $\nu_{\text{s}}(\text{C}=\text{C}=\text{C})$ respectively are shifted to lower frequencies. Therefore, the bands in $(1455-1464) \text{ cm}^{-1}$, $(1190-1200) \text{ cm}^{-1}$ and $(1020-1022) \text{ cm}^{-1}$ ranges were assigned to $\tau(\text{CH}_3)$, $\delta(\text{CH})$ and $\omega(\text{CH})$ respectively [12].

New bands in $(510-576) \text{ cm}^{-1}$ and $(422-448) \text{ cm}^{-1}$ ranges are attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ respectively, indicating that the caffeine and acetylacetonato ligands coordinated to metals [25, 26].

The similarity among infrared spectra of the complexes $[\text{M}(\text{acac})_2(\text{H}_2\text{O})_n]$ and $[\text{M}(\text{acac})_2(\text{caf})_n]$; $n=0,1,2$; $\text{M}=\text{Zn}^{2+}$, Cu^{2+} , Ni^{2+} , Mn^{2+} , Co^{2+} ; acac= acetylacetonato; caf= caffeine might imply that all complexes are the same and the only differences are due to presence of different counter ions.

Electronic spectra of the complexes $[M(acac)_2(H_2O)_n]$ and $[M(acac)_2(caf)_n]$; $n=1$ of $M= Zn^{2+}$, and $n=2$ of $M= Cu^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}$; $acac= acetylacetonato$; $caf= caffeine$

The UV-Visible data of the acetylacetonato and caffeine ligands [12, 27] were compared with those of the complexes. The electronic spectra of the acetylacetonato and caffeine ligands [12, 27] show the absorption bands in the UV region can be expressed as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

Upon coordination, the absorption bands attributed to $\pi - \pi^*$ and $n \rightarrow \pi^*$ transitions were found to be shifted to higher wavelength compared with acetylacetonato and caffeine ligands [28-30].

Therefore, new bands at longer wavelength observed in (310-354) nm range may be assigned to d-d transitions. All absorptions were fully assigned in **Table 4** and the electronic spectra of $[M(acac)_2(H_2O)_2]$ and $[M(acac)_2(caf)_2]$ are shown in **Figures 3** and **4** respectively.

Table 4 UV-Visible data of the complexes $[M(acac)_2(H_2O)_2]$ and $[M(acac)_2(caf)_2]$; $n=1$ of $M= Zn^{2+}$, and $n=0, 2$ of $M= Cu^{2+}$, $n=2$ of $M= Ni^{2+}, Mn^{2+}, Co^{2+}$ in water

Complexes	λ_{max} (nm)	Assignment	Complexes	λ_{max} (nm)	Assignment
$[Co(acac)_2(H_2O)_2]$	284	$n \rightarrow \pi^*$	$[Co(acac)_2(caf)_2]$	225	$\pi \rightarrow \pi^*$
	321	$n \rightarrow \pi^*$		277	$\pi \rightarrow \pi^*$
	356	$n \rightarrow \pi^*$		358	$n \rightarrow \pi^*$
	493	d→d		494	d→d
$[Mn(acac)_2(H_2O)_2]$	284	$n \rightarrow \pi^*$	$[Mn(acac)_2(caf)_2]$	230	$\pi \rightarrow \pi^*$
	310	$n \rightarrow \pi^*$		271	$\pi \rightarrow \pi^*$
	346	$n \rightarrow \pi^*$		368	$n \rightarrow \pi^*$
	731	d→d		621	d→d
$[Ni(acac)_2(H_2O)_2]$	292	$n \rightarrow \pi^*$	$[Zn(acac)_2(caf)]$	750	d→d
	305	$n \rightarrow \pi^*$		245	$\pi \rightarrow \pi^*$
	372	$n \rightarrow \pi^*$		277	$\pi \rightarrow \pi^*$
	682	d→d		355	$n \rightarrow \pi^*$
$[Zn(acac)_2(H_2O)]$	290	$n \rightarrow \pi^*$	$[Ni(acac)_2(caf)_2]$	227	$\pi \rightarrow \pi^*$
	299	$n \rightarrow \pi^*$		277	$\pi \rightarrow \pi^*$
	364	$n \rightarrow \pi^*$		360	$n \rightarrow \pi^*$
$[Cu(acac)_2]$	237	$\pi \rightarrow \pi^*$	$[Cu(acac)_2(caf)_2]$	621	d→d
	290	$n \rightarrow \pi^*$		234	$\pi \rightarrow \pi^*$
	296	$n \rightarrow \pi^*$		281	$n \rightarrow \pi^*$
	368	$n \rightarrow \pi^*$		306	$n \rightarrow \pi^*$
	609	d→d		366	$n \rightarrow \pi^*$
			636	d→d	

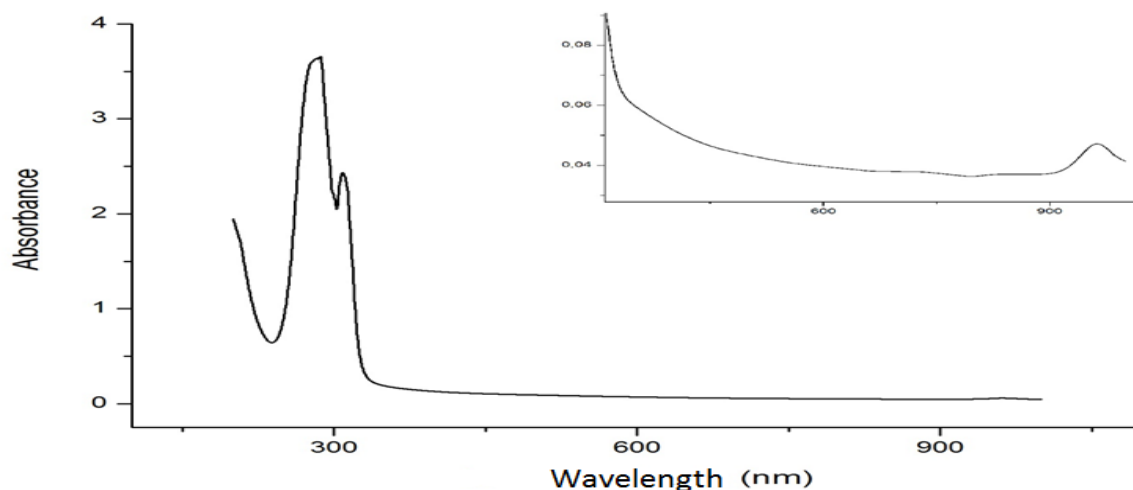


Figure 3 Electronic spectrum of the aquo acetylacetonato complex $[Mn(acac)_2(H_2O)_2]$ in distilled water

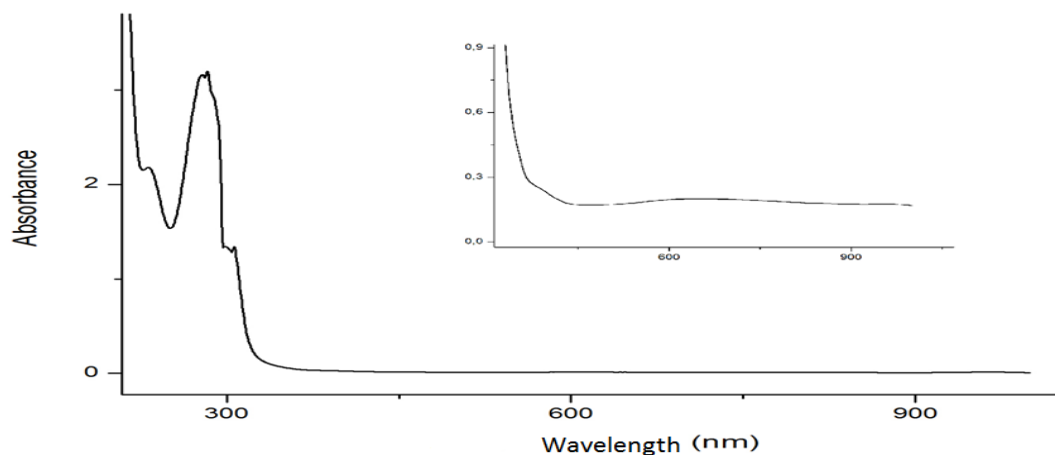


Figure 4 Electronic spectrum of the caffeine acetylacetonato complex $[\text{Mn}(\text{acac})_2(\text{caf})_2]$ in distilled water

EPR spectra of the complexes $[\text{M}(\text{acac})_2(\text{H}_2\text{O})_n]$ and $[\text{M}(\text{acac})_2(\text{caf})_n]$; $n=0, 2$ of $\text{M}=\text{Cu}^{2+}$, and $\text{M}=2$ of $\text{M}=\text{Ni}^{2+}$, Co^{2+} .in solid state

The EPR spectra of $[\text{M}(\text{acac})_2(\text{H}_2\text{O})_n]$ and $[\text{M}(\text{acac})_2(\text{caf})_n]$; $n=0, 2$ of $\text{M}=\text{Cu}^{2+}$, and $\text{M}=2$ of $\text{M}=\text{Ni}^{2+}$, Co^{2+} , provide information of importance in studying the metal ion environment. The X-band EPR spectra of the complexes $[\text{Cu}(\text{acac})_2]$ and $[\text{Ni}(\text{acac})_2(\text{caf})_2]$ in the solid state recorded at room temperature are shown in **Figures 5** and **6** respectively. All spectra of the copper, nickel and cobalt aquo/caffeine acetylacetonato complexes at room temperature show one intense absorption band in the high field and is isotropic due to the tumbling motion of the molecules. The calculated g_i values were found to be in (2.114-2.117) range (**Table 5**), which are compared to that of free electron ($g = 2.0023$). These values suggest an appreciable covalency of metal ligand bonding characteristic of octahedral stereochemistry [31, 32].

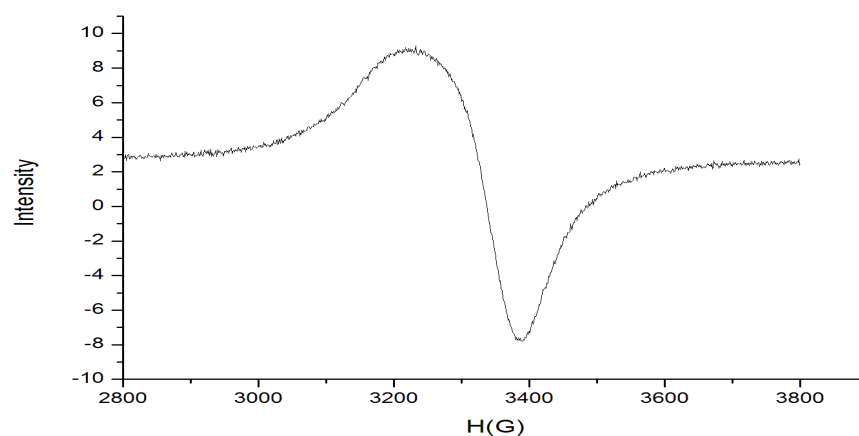


Figure 5 EPR spectrum of $[\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2]$

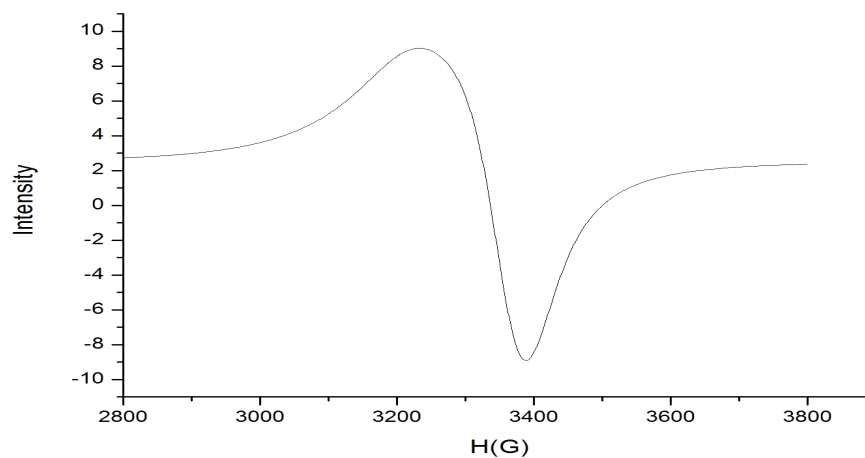


Figure 6 EPR spectrum of $[\text{Cu}(\text{acac})_2(\text{caf})_2]$

Table 5 The calculated g_i -values of $[M(\text{acac})_2(\text{H}_2\text{O})_n]$ and $[M(\text{acac})_2(\text{caf})_n]$; $n=0, 2$ of $M= \text{Cu}^{2+}$, and $M=2$ of $M= \text{Ni}^{2+}, \text{Co}^{2+}$

complexes	g_i
$[\text{Cu}(\text{acac})_2]$	2.117
$[\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2]$	2.116
$[\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2]$	2.115
$[\text{Cu}(\text{acac})_2(\text{caf})_2]$	2.116
$[\text{Ni}(\text{acac})_2(\text{caf})_2]$	2.114
$[\text{Co}(\text{acac})_2(\text{caf})_2]$	2.115

Conclusion

In this work, the synthesized complexes were characterized by molar conductance, infrared, UV-Visible and EPR spectroscopy. The results suggested the octahedral symmetry for the all complexes. Then, we can conclude that the aquo acetylacetonato complexes and the caffeine acetylacetonato complexes were found to have the general formulae $[M(\text{acac})_2(\text{H}_2\text{O})_n]$ and $[M(\text{acac})_2(\text{caf})_n]$; $n=1$ of $M= \text{Zn}^{2+}$, and $n=2$ of $M= \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}$ respectively.

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