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Synthesis, characterization and biological activities of cis-trans complexes $[M(phen)(caf)_2X_2]$ M = Co(II), Fe(II), Mn(II), Cu(II); X: SCN^-, CN^-; caf : caffeine; phen : (1,10)phenanthroline

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Abstract
Mixed ligands complexes of caffeine, phenanthroline, thiocyanato or cyano were prepared and characterized by molar conductivity measurements, FT-IR, UV-Visible, EPR, DTA/DTG and X-ray diffraction studies. The complexes are of 1:1:2:2 (metal:phen:caf:cyano or thiocyanato) stoichiometry of general formula $[M(phen)(caf)_2X_2]$ where X=CN^-, SCN^-, M= Co(II), Fe(II), Mn(II), Cu(II), caf : caffeine ; phen :phenanthroline, are non-electrolytes in dimethylsulfoxide. The ATG/DTG curves provided information on the thermal stabilities and thermal decomposition of new synthesized complexes. The powder-diffraction data for complexes show that these complexes are crystallized in a monoclinic system. The FT-IR, UV-Visible, EPR, spectroscopic data suggested that the complexes have octahedral cis-trans geometry.

Keywords: caffeine, (1,10)phenanthroline, Co(II), Fe(II), Mn(II), Cu(II) complexes, molar conductance, FT-IR, UV-Visible, EPR, DTA/DTG, X-ray .

1. Introduction

Transition metal ions are playing an important role in biological processes in the human body. They are found either at the active sites or as structural components of a good number of enzymes. The study of the coordination chemistry of biologically important metal ions with mixed ligand has been one of the recent developments in the field of bioinorganic chemistry [1-5] in another hand caffeine is the most widely used behavioral active substance in the world. It is well known as hydrotropic agents and has the ability to solubilise a wide variety of therapeutic drugs [6].
The metal caffeine and phenanthroline complexes have many biological processes, antitumor activities, anti-Candida, anti-mycobacterial and antimicrobial activities [7].
Several studies on phenanthroline complexes have shown that both N1 and N10 atoms are electronically favored coordination sites for metals. The major binding site in caffeine would be N9 as shown in Figure (1) [7].The activity of various metal ions, organic compounds and metal complexes in biological system has been explained on the basis of different complex species formed in the living organisms.
Metal ions are also found in several bacterial species and are reported to play an important role in different enzymatic and physiological reactions [8]. Recently, the role of metal complexes has been researched in relation

to antimicrobial activity and studies of transition metal complexes of heterocyclic ligands have gained importance because of their biological significance and interesting spectral and magnetic properties [8].
Certain drugs also play a vital role as bio-ligands in the biological systems. It has been found that the activity of the bio-metals is attained through the formation of complexes with different bio-ligands and the thermodynamic and kinetic properties of the complexes govern the mode of biological action. Sometimes, the permeability, i.e. lipophilicity of drugs is increased through the formation of chelates in vivo and drug action is significantly increased due to much more effective penetration of the drug into the site of action [8].
Thus, the aim of this paper is to synthesize, characterize and evaluate the antibacterial activities of mixed ligands and their complexes [M(phen)(caf)2X2] where X=CN-, SCN-, M= Co(II), Fe(II), Mn(II), Cu(II), caf : caffeine ; phen : phenanthroline.

2. Experimental

2.1. General methods and materials

Materials: all reageants were purchased commercially and used without further purification.The compounds were prepared by mixing at room temperature, with stirring the ethanolic solutions of (1,10)phenanthroline BDH indicators, caffeine Riedl-deHaen.A.G, the chloride of the appropriate metallic ion MCl_2,xH_2O M = Co(II), Fe(II), Mn(II), Cu(II) respectively and potassium thiocyanate or cyanate BDH.
Infrared spectra in the range of 4000-400 cm^{-1} were recorded on Shimadzu 470 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. The X-ray diffraction were performed on XRD-6100 Shimadzu, The thermal decomposition process of complex was studied by DTG and DTA (DTG-60H, Shimadzu).

2.2. General procedure for synthesis

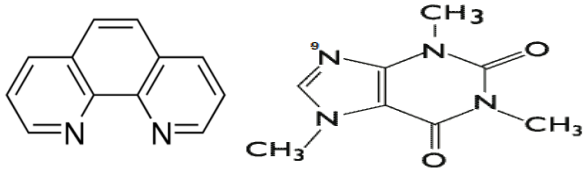
An ethanolic solution of 10^{-3} mol (0,234 g) (1,10)phenanthroline (phen) was added to an ethanolic solution 10^{-3}mol of metal salts in nitrogen atmosphere . This is followed by the addition of an ethanolic solution 2.10^{-3} mol (0,388 g) of caffeine (caf) and an aqueous solution 2.10^{-3} mol of KSCN or KCN. After constant stirring using appropriate amounts of materials needed as decided by the molar ratio 1:1:2:2/2 (M : phen : caf : SCN/CN) of general formula $[M(phen)(caf)_2X_2]$ where $X=CN^-$, SCN^-, M= Co(II) , Fe(II), Mn(II), Cu(II), caf : caffeine ; phen : phenanthroline, the resulting precipitates were filtered, washed several times and recrystallized with 1:3 ethanol : water mixture. Then, they were dried in an oven at 65°C.

3. Results and discussion

The prepared complexes were found to be solids, insoluble in water but they were soluble in some organic solvents such as (DMF) or (DMSO). The lower values observed of molar conductivities in DMSO indicate the non-electrolyte behavior of the complexes [9]**.**

3.1. FTIR Spectroscopy

The Caffeine to a the centrosymmetric Cs point group, the (1,10)phenanthroline free are C_2v symmetry point group.Their structures as shown in Figure 1.



a b

Figure 1: Structure of the (1.10)phenanthroline(a) and the caffeine(b)

It is know from the literature that the caffeine mostly coordinated through its N-donnor atom or even through O-donor atom, which is a rarity [10].
The assignment of different bands of spectra of these complexes $[M(phen)(caf)_2X_2]$ were done comparing with spectra of caffeine, (1,10)phenanthroline and thiocyanato or cyano free ligands. It may be noted that spectra complexes are similar as shown in Figure (2) in the range 4000-400 cm^{-1}. The vibrationnal spectral frequencies for the complexes are shown in Tables 2 and 3.

Table 1: physical properties of the prepared complexes

compound	Colour	M.P. (°C)	Yield (%)	Λ m (Ohm^{-1} cm^2 mol^{-1})
$[Fe(phen)(caf)_2(CN)_2]$	violet	>260	68	38
$[Co(phen)(caf)_2(CN)_2]$	pink	>260	56	15
$[Mn(phen)(caf)_2(CN)_2]$	brown	>260	67	23
$[Cu(phen)(caf)_2(CN)_2]$	Dark green	>260	75	33.6
$[Mn(phen)(caf)_2(SCN)_2]$	brown	>260	70	12
$[Fe(phen)(caf)_2(SCN)_2]$	violet	>260	62	18
$[Co(phen)(caf)_2(SCN)_2]$	pink	>260	60	32
$[Cu(phen)(caf)_2(SCN)_2]$	bleu	>260	58	5.4

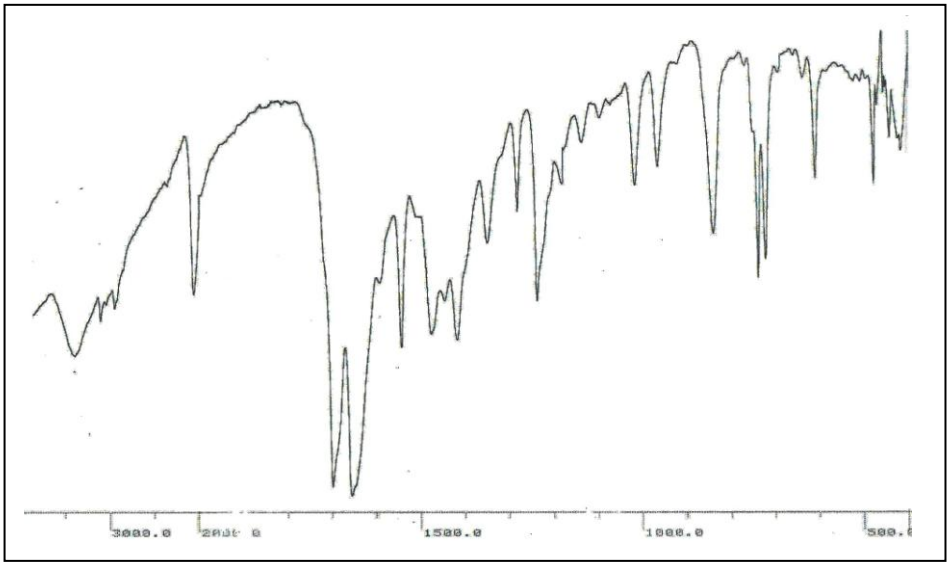


Figure 2: Infrared spectrum of the complex $[Fe(phen)(caf)_2(CN)_2]$ in KBr

The infrared spectra of these complexes exhibited bands in the range 3500-3400 cm^{-1} attributed to stretching vibration υ(OH) of the water hydration , which is confirmed by thermal analysis. The two bands observed at 3100 cm^{-1} and 2950 cm^{-1} can be attributed to stretching vibration υ(CH) and $\upsilon(CH_3)$ aromatic proton and methyl caffeine shifted to lower frequencies [11].

In all complexes, the band at 3050 cm^{-1} attributed to stretching vibration $\upsilon(CH)_{phen}$ phenanthroline ligand [12] . The carbonyl group in caffeine and their complexes exhibit a strong bands due the υ(CO) stretching vibration and is observed in the region (1700-1650) cm^{-1}[11].
In the complexes spectra, the two υ(CO), stretching vibrations (νa(CO), νs(CO)) are shifted to lower frequencies by (2-10) cm^{-1} and (5-20) cm^{-1} respectively. The intensity of the carbonyl is also reduced and inversed upon complexation. The ν(CN) , ν(SCN) frequencies of the thiocyanato and cyano ligands are collected in Tables 2 and 3. The presence of a single and two strong ν(CN) for the complexes indicate the existence of thiocyanato or cyano ligand in two isomers (cis + trans) in octahedral geometry[13].
The band noticed in the caffeine spectrum at 1548 cm^{-1} and which is conferring to the vibrations υ(imidazol)+ υ(pyrimidine) + δ(HCN) and appeared for the caffeine complexes in the range (1540-1542) cm^{-1} [11].
The ν (C-S) occurs in the range 745-746 cm^{-1} is shifted to higher frequencies by (7-8) cm^{-1}. The shifted values are attributed to the fact that the ligands were coordinated with the metal ion.
Some new sharp bands are observed at the range 535-550 cm^{-1} which can be assigned to the υ(M-N) stretching vibration [14]**.**

Table 2: Main vibrations the complexes $[M(phen)(caf)_2(CN)_2]$, M = Co(II), Mn(II), Fe (II), Cu(II)

compound	ν (CH)	ν $(C-H)_{phen}$	ν (CH3)	υ(CN)	νa(CO) νs(CO)	ν $(C=N)_{phen}$	δ(HCN) +υ(imid) +υ(pyri)	δ(CH)phen	ν(M-N)
caffeine	3114	-	2954		1700 1660	1600	1548	-	-
CN^-	-	-	-	2088	-	-	-		-
(1,10)phenanthroline	-	3062	-		-	1616	-	724	-
$[Mn(phen)(caf)_2(CN)_2]$	3105	3050	2950	2150 2120	1695 1650	1618	1542	720	535
$[Fe(phen)(caf)_2(CN)_2]$	3102	3055	2950	2080	1695 1650	1620	1540	722	540
$[Co(phen)(caf)_2(CN)_2]$	3100	3050	2950	2180 2120	1700 1654	1618	1542	726	540
$[Cu(phen)(caf)_2(CN)_2]$	3104	3050	2949	2220 2116	1695 1650	1620	1540	720	550

Table 3: Main vibrations the complexes $[M(phen)(caf)_2(SCN)_2]$, M = Co(II), Mn(II), Fe (II), Cu(II) in KBr

compound	ν (CH)	νC-H_{phen}	ν (CH3)	υ(SCN)	νa(CO) νs(CO)	$\nu(C=N)_{phen}$	δ(HCN) +υ(imid) +υ(pyri)	νC-S	$\delta(CH)_{phen}$	ν(M-N)
caffeine	3114	-	2954		1700 1660	1600	1548	-	-	-
SCN	-	-	-	2051	-	-	-	738		-
(1,10)phenanthroline	-	3062	-		-	1616	-	-	724	-
$[Mn(phen)(caf)_2(SCN)_2]$	3100			2064	1690 1650	1613	1542	745	730	550
$[Fe(phen)(caf)_2(SCN)_2]$	3100	3050	2950	2076 2064	1694 1654	1618	1542	746	724	540
$[Co(phen)(caf)_2(SCN)_2]$	3100	3054	2900	2071 2081	1698 1650	1620	1541	746	725	540
$[Cu(phen)(caf)_2(SCN)_2]$	3100	3050	2950	2130 2110	1695 1650	1625	1540	745	720	550

3.2. UV-Visible Spectroscopy

The electronic spectra for free ligands, caffeine, (1,10)phenanthroline and thiocyanato or cyanato showed that the absorption bands in the UV region can be annotated as π→π* and n→π* transitions. The Co(II) complex exhibited bands at 326, 433 and 772 nm for $[Co(phen)(caf)_2(SCN)_2]$ and 348, 454 and 834 nm for the complex $[Co(phen)(caf)_2(CN)_2]$. These transitions could be attributed to the n→π*, $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ respectively and they correspond for Co(II) to a cis-trans octahedral [15].

The spectra were recorded for the Mn(II) complexes figures 4and 5, the resultant data are presented in table 4.The electronic spectral bands observed at 456, 519 and 673nm for $[Mn(phen)(caf)_2(SCN)_2]$, and at 452, 526 and 681 nm for $[Mn(phen)(caf)_2(CN)_2]$ could be assigned to $^6A1g \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4A_{1g}$, ^4Eg, respectively. The electronic spectral data of Mn(II) complexes suggested an octahedral arrangement of ligand atoms around Mn(II) ion [14].

Otherwise, the electronic spectra of the iron(II) complexes bands observed at 693 and 804 nm for $[Fe(phen)(caf)_2(SCN)_2]$ and at 755,905 nm for complex $[Fe(phen)(caf)_2(CN)_2]$ which are attributed to $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, $^6A_1 \rightarrow {}^4T_1(G)$ transitions, are similar to those found for cis-trans octahedral complexes [16].

The spectra of Cu(II) complexes show bands in the visible region at 646 and 797 nm for $[Cu(phen)(caf)_2(SCN)_2]$, and at 484 and 789 nm for $[Cu(phen)(caf)_2(CN)_2$ which are attributed to $^2a_1g(D) \rightarrow {}^2b_1g(D)$, $^2e_2g(D) \rightarrow {}^2b_1g(D)$ [7].

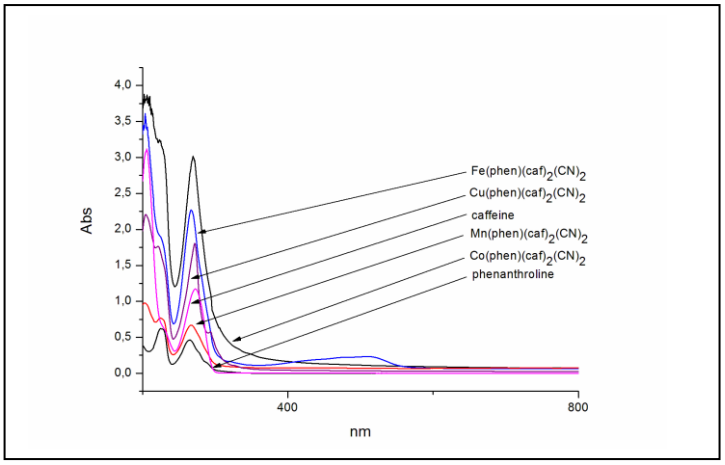


Figure 3: UV-Visible spectra of complexes $[M(phen)(caf)_{2(}CN_2]$, M= Mn(II), Co(II), Fe(II), Cu(II) in DMSO

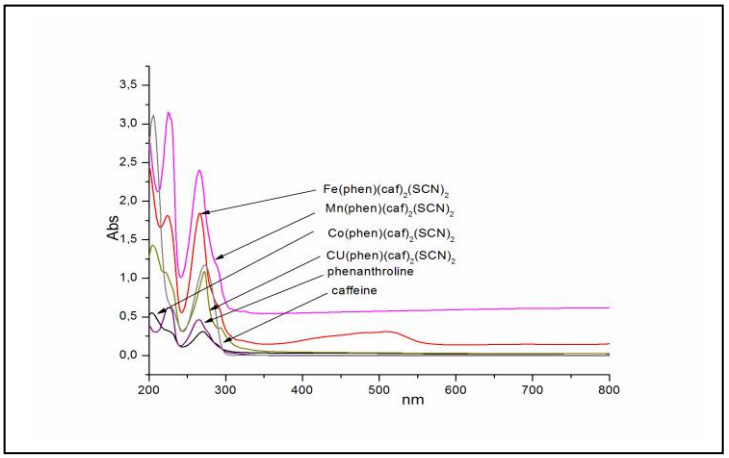


Figure 4: UV-Visible spectra of complexes $[M(phen)(caf)_{2(}SCN_2]$, M= Mn(II), Co(II) ,Fe(II), Cu(II) in DMSO

Table 4: UV Visible data of the complexes[M(phen)$(caf)_2X_2$] (M = Co(II), Ni(II), Fe(II), Mn(II), Cu(II), Ni(II; X = SCN-, CN-) in DMSO

Compound	$\lambda_{max(nm)(abs)}$	Assignement
KCN	270	$\pi\rightarrow\pi^*$
KSCN	276 360	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$
Caffeine	232 ; 273	$\pi\rightarrow\pi^*$
Phenanthroline	222 ; 267; 291 324	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$
[Mn(phen)$(caf)_2(CN)_2$]	225-268-322 452 526 681	$\pi\rightarrow\pi^*$ $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}, {}^4Eg$
[Co(phen)$(caf)_2(CN)_2$]	224-224-269 331 348 454 664	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ $n\rightarrow\pi^*$ $^4T_1g(F) \rightarrow {}^4T_1g(P)$ $^4T_1g(F) \rightarrow {}^4T_2g(F)$
[Fe(phen)$(caf)_2(CN)_2$]	225-267-321 489 755 905	$\pi\rightarrow\pi^*$ C.T $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, $^6A_1 \rightarrow {}^4T_1(G)$
[Cu(phen)$(caf)_2(CN)_2$]	222 ; 272 ; 294 328 484 789	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ $^2a_1g(D) \rightarrow {}^2b_1g(D)$ $^2e_{2g}(D) \rightarrow {}^2b_{1g}(D)$
[Co(phen)$(caf)_2(SCN)_2$]	225-270 326 433 772	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ $^4T_1g(F) \rightarrow T_1g(P)$ $^4T_1g(F) \rightarrow {}^4T_2g(F)$
[Fe(phen)$(caf)_2(SCN)_2$]	224-266-291- 321 483 693 804	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ C.T $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, $^6A_1 \rightarrow {}^4T_1(G)$
[Mn(phen)$(caf)_2(SCN)_2$]	226-265-291-325 456 519 673	$\pi\rightarrow\pi^*$ $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}, {}^4Eg$
[Cu(phen)$(caf)_2(SCN)_2$]	220 -272- 294 328 ; 385 646 797	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ C.T $^2a_{1g}(D) \rightarrow {}^2b_{1g}(D)$ $^2e_{2g}(D) \rightarrow {}^2b_{1g}(D)$

3.3. EPR Spectroscopy

The analysis of EPR spectra of the [Cu(phen)$(caf)_2(CN)_2$] complexes, give the values of $g\| = 2{,}166$ and $g^{\perp} = 2{,}061$. The complex [Cu(phen)$(caf)_2(SCN)_2$] presents an isotropic signal, $g_{isotropic} = 2.0814$).

The EPR spectra (figures 5 and 6) and electronic spectra suggested that the monomer have an octahedral symmetry.

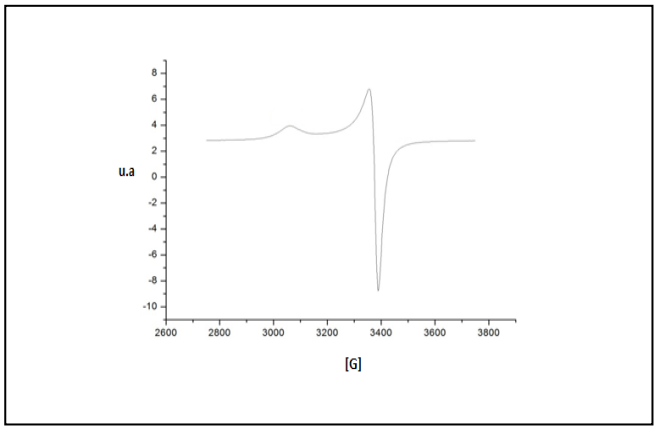


Figure 5: EPR spectrum of complexes $[Cu(phen)(caf)_2(CN)_2]$ in the solid state

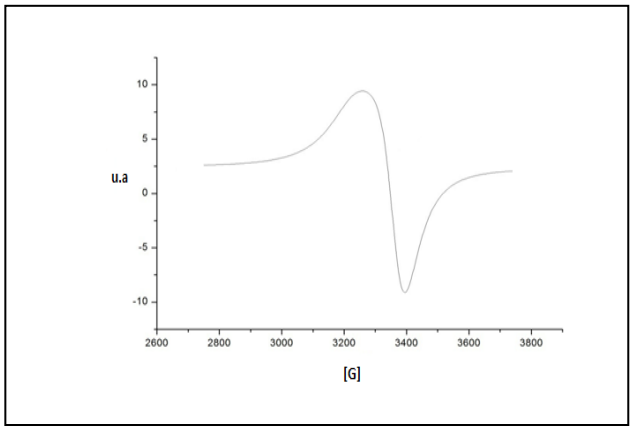


Figure 6: EPR spectrum of complexes $[Cu(phen)(caf)_2(SCN)_2]$ in the solid state

3.4. XRD analysis

The X-ray pattern powder diffractions for $[Cu(phen)(caf)_2(CN)_2]$, $[Cu(phen)(caf)_2(SCN)_2]$, are alike, probably they are isostructural. The pattern diffraction for these compounds are shown in figures 7 and 8 and were indexed using Dicvol 06 program. The two copper complexes are found to crystallize in a monoclinic system having, respectively, the following lattice parameters:

$[Cu(phen)(caf)_2(CN)_2]$: a = 20.729401, b = 3.698700, c = 15.851000 , β = 98.726°, V = 1215 A^3

$[Cu(phen)(caf)_2(SCN)_2]$: a = 19.175600, b = 10.068400, c = 7.159800, β = 90.792999°, V = 1382 A^3

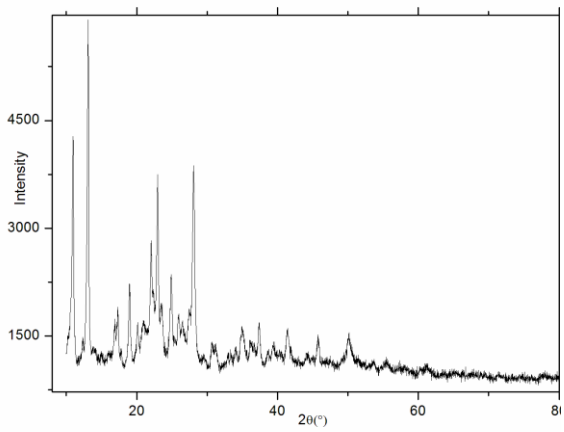


Figure 7: X-ray powder pattern diffraction for $[Cu(phen)(caf)_2(CN)_2]$

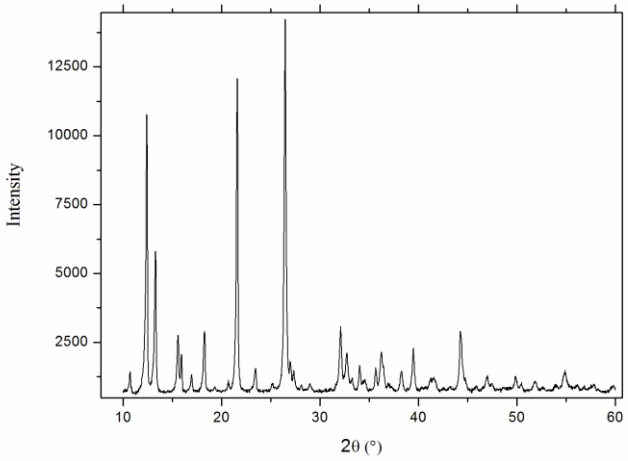


Figure 8: X-ray powder pattern diffraction for $[Cu(phen)(caf)_2(SCN)_2]$

DTA and DTG analysis

Thermal behaviour of the complexes was studied by DTG and DTA in the temperature range (50–600) °C in the static air atmosphere. Thermal decomposition curves of the Iron and Copper complexes are presented in Figure 9 and 10, respectively. The complexes are thermally stable up to 100°C and 125°C, respectively, where the dehydration process commences which are accompanied by endothermic DTA peaks at 104°C for the Iron complex and 157 °C for the Copper complex and then they begin to decompose. The first between 214–309°C

for the Iron complex and 200–303 °C for the Copper complex correspond to release of one phenathroline ligand [17], which are accompanied by endothermic DTA peaks at 284°C for the Iron complex and 223°C for the Copper complex .The following stages, remaining two caffeine and two cyano groups decomposes between 309°C and 515 °C for the Iron complex , 303 and 522 °C for the Copper complex [18,19]. which are accompanied by endothermic DTA peaks at 330, 434,454 and 479°C for the Iron complex and 317, 350,407 and 456°C for the Copper complex , while the final solid product are concluded to be CuO [20] and Fe_2O_3 [21]. The Most probable thermal schèmes could be drawn as follows :

$$[Fe(phen)(caf)_2(CN)_2]XH_2O \xrightarrow{100\ °C} [Fe(phen)(caf)_2(CN)_2] \xrightarrow{214\text{-}309\ °C} [Fe(caf)_2(CN)_2] \xrightarrow{309\text{-}515\ °C} Fe_2O_3$$

$$[Cu(phen)(caf)_2(CN)_2]XH_2O \xrightarrow{125\text{-}200\ °C} [Cu(phen)(caf)_2(CN)_2] \xrightarrow{200\text{-}303°C} [Cu(caf)_2(CN)_2] \xrightarrow{303\text{-}522\ °C} CuO$$

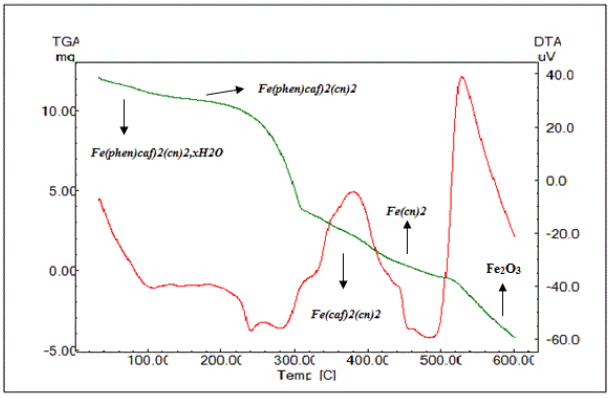


Figure 9: DTG and DTA curves of Complex $[Fe(phen)(caf)_2(CN)_2]XH_2O$

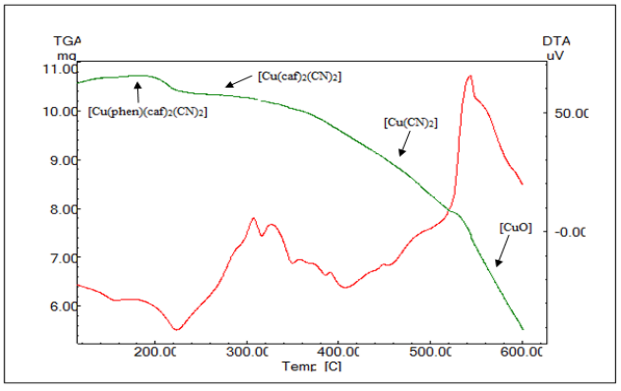


Figure 10: DTG and DTA curves of Complex $[Cu(phen)(caf)_2(CN)_2]XH_2O$

3.6. Antibacterial tests

The new metal complexes were tested for their in vitro antibacterial activity against *Escherichia coli, Staphylococcus aureus, Klebsiella pneumonia, Klebsiella oxytoca and Pseudomonas putida*, using the diffusion method (Fig.11). The diffusion method is simple, yet is routinely used in hospital laboratories; it requires commercial disks, the medium used is Mueller-Hinton agar with 2% of glucose, and the diameter of the zone of

inhibition is visually read 24 h after incubation at 37 °C. The compounds were taken at a concentration of 20 mg/ml using dimethylsulphoxide (DMSO) as solvent. Antibacterial activity was estimated on the basis of the size of the zone of inhibition formed around the paper disks on the seeded agar plates. Gentamecine and imipeneme was used as a standards. The results are presented in Table 5.

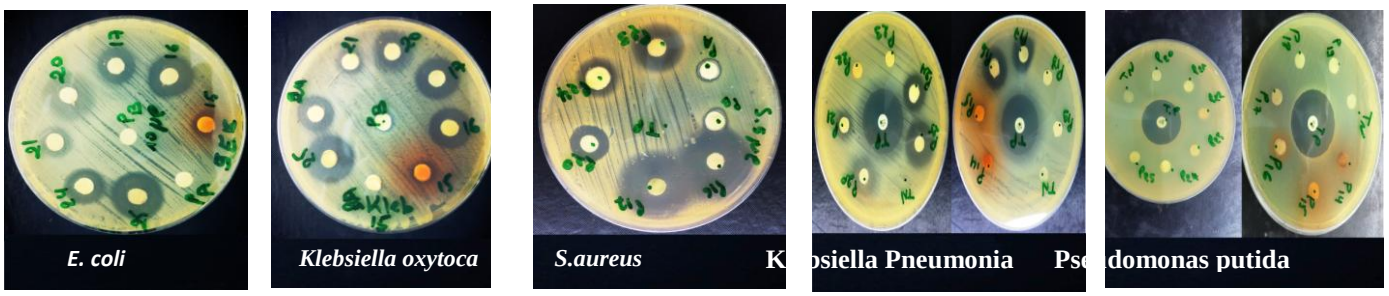


Figure 11: Photographes Showing the Antibacterial Activity

Table 5: Biological activity of compound

	Microbial species (Zone of inhibition in mm)				
Ligand/Complex	*E. coli*	*S.aureus.*	*Klebsiella pneumoniae*	*Pseudomonace putida*	*Klebsiella oxytoca*
caffeine	0	0	0	0	0
1,10-phenanthroline	30	23	30	20	33
KSCN	0	0	0	0	0
$[Mn(phen)(caf)_2(SCN)_2]$	15	14	16	0	16
$[Fe(phen)(caf)_2(SCN)_2]$	0	0	0	0	0
$[Co(phen)(caf)_2(SCN)_2]$	0	0	0	0	0
$[Cu(phen)(caf)_2(SCN)_2]$	18	28	17	0	17
KCN	0	0	0	0	0
$[Mn(phen)(caf)_2(CN)_2]$	20	17,5	19	0	21
$[Fe(phen)(caf)_2(CN)_2]$	8	0	0	0	11
$[Co(phen)(caf)_2(CN)_2]$	0	0	0	0	0
$[Cu(phen)(caf)_2(CN)_2]$	17	28	17	0	18
gentamecine	26	23	27	0	20
IPM	-	-	-	24	-
DMSO	0	0	0	0	0

Results in table 5 show that the free ligands, and their complexes are found to have potent activities against the tested bacteria, 1,10-phenanthroline ligand have slightly more antibiotic activitie than their complexes against the tested microorganisms under identical experimental conditions. It is known that chelation tends to make ligands act as more powerful and potent bactericidal agents [8]**.** All complexes synthesized have insignificant effect on Pseudomonace putida specie. [M(Phen)(caf)2X2] where X = CN-, SCN-, M= Mn(II), Cu(II) have the greatest inhibitory effect against Escherichia coli, Staphylococcus aureus, Klebsiella pneumonia, Klebsiella oxytoca , while [M(Phen)(caf)2X2] where X=CN-, SCN-, M= Co(II), Fe(II) have insignificant effect on all species.

Conclusion

We reported the synthesis and characterization of a series of mixed ligand complexes. Spectral data (infrared, UV-Visible, X-ray, EPR, DTG/DTA, molar conductance) we can conlude that the caffeine behave a mono-

dentate ligand with N9 donor, and the (1,10)phenanthroline is bidentate chelate with N1,N10 donor in cis-trans octahedral symmetry. This study shows that the antimicrobial activity of ligands (caffeine, phenanthroline and cyano or thiocyanato) are modified in the presence of metal ions. Free phenanthroline exhibit more antimicrobial properties against all species as compared to the complexes.

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