



New Transition Metal(II) Mixed-Ligand Complexes of Phenylbutanedione and Dithiocarbamate: Synthesis, Characterization, Thermal and Antioxidant Studies

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Abstract Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) mixed ligand complexes of 1-phenyl-1,3-butanedione and N,N'-dimethyldithiocarbamate have been synthesized. The complexes were characterized by elemental and percentage metal analyses; magnetic moments, solubility and molar conductance measurements; and spectrophotometrically, by infrared, electronic, ESI mass, ¹H and ¹³C-NMR spectra studies. The percentage metal, CHNS, magnetic moments, molar conductance, electronic, and IR data are corroborative of a non-electrolyte, mononuclear octahedral geometry for Fe(II), Co(II), Ni(II) and Cu(II) complexes and four-coordinate tetrahedral geometry for Mn(II) and Zn(II) complexes. The coordinations to the metal ions were found to be through the S₂O₂ chromophores, with the exception of Fe(II) complex, which was via the O₄ chromophores of bis(1-phenyl-1,3-butanedione) ligand. The thermogravimetric analyses carried out revealed that the complexes are all thermally degradable and support the proposed formulae and, as well the ESI mass data. The antioxidant studies show that the Cu(II) and Co(II) complexes had higher percentage scavenging inhibition of 81.2 % and 71.9 % respectively, compared to the positive standard, ascorbic acid with inhibitory activity of 56.2 %.

Keywords butanedione, chromophores, thermally degradable, mononuclear, ascorbic acid, scavenging inhibition

Introduction

Some transition metals have been reported to be essential metallic elements in the biological systems or processes [1-2]. Manganese and nickel are found to be the major essential elements that are active in the enzymes superoxide dismutase and urease, responsible for ions storage and reactions that involves transfer of electrons [3-4], while iron is essential for haemoglobin and myoglobin responsible for oxygen storage and transport in the body system [5]. Vitamin B₁₂ cobalamin coenzyme that works in the promotion of several molecular transformations in the human body is activated by cobalt as its essential metal ion; while copper is important for the formation of melanin, possesses antioxidant property which removes free radical from the body and prevents cell structure damage in the mammalian body [5-7]. Zinc is an important essential trace metal found in enzymes such as carboxypeptidase, which catalyses digestion process and carbonic anhydrase, which function in the catalysis of the reversible hydration of carbon(IV) oxide [5].

Coordination complexes of mixed-ligand of two different functional groups/chromophores and varied biological/biochemical importance, with first row transition metal elements have been of great interest due to their variations in mode of formation and applications in various areas of life. They have been known to possess



applications in chemical [8], biological [9-10], electrical/electrochemical [11], medical [12-13], agricultural [14], environmental [15-16], biochemical [17-18] and catalytic [19-20] processes or fields. The choice of ligands in forming mixed complexes depend on their adaptability in coordination with the metal ion, flexibility in forming discrete configurations, possibility of tautomerism formation and the ease of reacting in neutral, anionic (deprotonated) or cationic (protonated) forms to produce chelates of various geometries and diverse applications [21].

Metal chelates of different ligands which contain oxygen and sulphur chromophores have been reported [22-25]. β -diketones and dithiocarbamates have been part of captivating ligands found under this category. These two ligands and their metal complexes have shown an interesting chemistry with chemical, biological, medical and industrial applications.

β -diketones, its derivatives and their metal complexes were reported for their various usefulness/ applications in biological [26-28], medical [29-30] and industrial [31-32] fields. In the same vein, dithiocarbamates and their metal chelates have shown antimicrobial, anti-diabetic and anticancer [33-35] activities, as well as additional applications in areas of environmental science, agriculture and industry. They have been used as chelating and analytical agents for abstraction and determination of heavy metals in matters [36-38], fungicides and pesticides that improve the biological activity of the soil and crops [39], and vulcanizers for the sulphur vulcanization of rubber [40-42] in the rubber industry.

Interest has been on the studies of these oxygen and sulphur containing ligands, due to their interesting chemistry of reactions, synthetic flexibility, different resonance forms, bidentate nature, possibility of stable chelates formation and diverse application areas. Therefore, we aim to synthesize and characterize some new mixed ligands of d-block metal(II) complexes of 1-phenyl-1,3-butanedione and N,N'-dimethyldithiocarbamate with a combined and improved properties. Also, the coordination behaviour, magnetic properties in terms of spin cross-over, thermal stability and antioxidant activities of these metal chelates were studied.

Materials and Methods

Materials

All the chemicals used were of AR (analytical reagent) grade from Sigma-Aldrich and BDH chemicals. They were used as received and without further purification.

Physical Measurements and Analytical methods

The melting points/decomposition temperature were determined using Electrothermal (MEL -TEMP) machine, in addition with thermometer and capillary tubes. The molar conductance in DMF (1×10^{-3} M solutions) were obtained with Eutech instruments CON 510 conductivity meter. Elemental analysis (C, H, N, S percentages) were recorded on Elementar Analysen Systeme GmbH Vario EL-III instrument. UV-Visible spectra were recorded with a Perkin Elmer LAMBDA 25 spectrophotometer, in the range 190-600 nm. Infrared spectra were recorded on a Perkin Elmer FTIR C91719 with a Perkin Elmer spectrum-two spectrometer (Zn-Se ATR; $4000-600 \text{ cm}^{-1}$) or a SHIMADZU IR Affinity-1S FTIR spectrophotometer in the range $4000-400 \text{ cm}^{-1}$; the magnetic susceptibilities were measured on Sherwood Susceptibility Balance MSB Mark 1 at 29-31 °C and various diamagnetic corrections were calculated using Pascal's constants [43]. High resolution mass spectra were recorded on an Agilent Technologies 6530 Accurate-Mass LC-HRMS (Q-TOF) system connected with HPLC Agilent technologies 1260 Infinity attached with PC-using Mass Hunter software; the proton and carbon -13 Nuclear Magnetic Resonance (NMR) spectra were recorded on JEOL (JNM-ECX400P) NMR spectrometer at a basic frequency of 400MHz, using tetra methyl silane (TMS) as an internal standard and deuterated dimethylsulfoxide (d_6 -DMSO) as a solvent. Thermogravimetric analysis were carried out on a Perkin Elmer Diamond TG/DTA-Thermogravimetric/Differential Thermal Analyzer, Technology by SII or a Shimadzu DTG-60 instrument, in the range 30 °C-700/800 °C under nitrogen flow rate of 200 mL/min. and at a heating rate of 10 °C/min. The percentage metals were estimated volumetrically by complexometric titration using standardized EDTA solution [44].



Antioxidant Studies

The anti-oxidant properties of the mixed ligand metal(II) complexes were determined through the ferrous-ion chelating assay by the standard colorimetric method [45-46], using a single beam WPA colourwave CO7500 Colorimeter at wavelength 550 nm.

Ferrous ion chelating procedure

1 mL of 1, 10-Phenantroline solution (0.05 g in 100 mL DMSO), 1 mL of FeSO₄.7H₂O solution (0.011 g in 100 mL DMSO) and 1 mL of metal complex sample solution (stock solution = 0.001 g in 1 mL DMSO) were mixed together thoroughly and mechanically stirred for about six minutes, while 2 mL of DMSO solvent was added. The resulting homogenous solution was then stored in the dark cupboard (incubated) for 15 minutes, after which the absorbance of the sample was observed at 550 nm spectrophotometrically. The control or the blank was made up of 1 mL of 1, 10-Phenantroline solution, 1 mL of FeSO₄.7H₂O solution and 2 mL of DMSO solvent, while ascorbic acid was used as the standard. The test was conducted in triplicate and percentage scavenging inhibition of ferrous ion-chelating ability was expressed as:

$$\% \text{ scavenging inhibition} = \frac{A_c - A_s}{A_c} \times 100$$

Where: A_c = Absorbance of control or blank solution,

A_s = Absorbance of sample solution and also

A_s = Absorbance of standard solution separately.

Synthesis

Preparation of the mixed ligand metal(II) complexes

The hydrated metal(II) salts (MnSO₄.H₂O, FeSO₄.7H₂O, CuSO₄.5H₂O, ZnSO₄.7H₂O, CoCl₂.6H₂O and NiCl₂.6H₂O), in the range 0.71-1.20 g (4.189 x 10⁻³ moles), were added neat to a stirring 10 mL 50 % ethanolic solution of 0.60 g (4.189 x 10⁻³ moles) sodium dimethyl dithiocarbamate, **L**, and 0.68 g (4.189 x 10⁻³ moles) of benzoyl acetone, **L**¹, while stirring on a magnetic stirrer. The resulting coloured homogenous solution were left on stirring under reflux for 6 hours at room temperature. The respective coloured precipitates formed were filtered under gravity, washed with 50% ethanol, diethyl ether and further purified by re-crystallization. The products were weighed, stored in a clean well-labeled sample containers, over silica gel in a desiccator. The yields are 0.99 g (67 %), 1.48 g (85 %), 1.15 g (72 %), 1.02 g (67 %), 1.27 g (77 %), and 0.86 g (52 %) respectively.

Results and Discussions

Physical properties/ analytical data of the compounds

The ligand **L**¹, Mn(II) and Zn(II) complexes were of various shades of yellow, Fe(II) and Cu(II) complexes were of brown shades while Co(II) and Ni(II) complexes were of different shades of green. All these complexes, except Zn(II) complex with a d¹⁰ configuration, were expectedly coloured, which might be due to d-d transition. The faint-yellow colour of the Zn(II) complex was attributed to metal-ligand charge transfer.

All the metal(II) complexes of the ligands **L** and **L**¹ have distinct higher melting points/ decomposition temperature compared to the respective free ligands melting points. Furthermore, the percentage metal, as well as that of the C, H, N, S analyses of all the metal(II) complexes are very close to the calculated values corresponding to the respective complexes. This distinction between the melting points of the ligands and that of their various metal(II) complexes, and the closeness of the experimental and theoretical values of the C, H, N, S and percentage metal data are part of evidence of coordination. (Table 1 and Table 2).

All these metal(II) complexes were obtained in a moderate to good yields as powder, and an attempt to grow crystal of all the complexes were not successful as at the time of this research.

Solubility and Conductivity measurements

The compounds were insoluble in water except ligand **L**, which was soluble due to its electrolytic nature. All the complexes were soluble in DMSO and DMF, but almost partially soluble in methanol and acetonitrile. The



complexes solubility in an aprotic, polar solvent like DMSO has been attributed to its unique strength as strong coordinating solvent [47-49], which can dissolve both polar and non-polar compounds.

The molar conductance values of the complexes in DMF (1×10^{-3} M solution) were in the range 11.28 - 18.24 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ indicating their non-electrolytic nature, since the values were below 60 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ reported for 1:1 electrolyte [50-52].

Table 1: Physical properties/analytical data of the ligands and their metal(II) complexes.

Ligand/complexes (Molecular formulae)	Formula Weight (g)	Yield (% yield)	Colour	M.pt/ * (°C)	% Metal Theo. (Exp)	\wedge M
BAC (L ¹) C ₁₀ H ₁₀ O ₂	162.19	-	Pale yellow	57-59	- -	-
SDTC (L) C ₃ H ₆ NS ₂ Na	143.21	-	Off-White	116-118	- -	-
(1) [MnLL ¹].H ₂ O C ₁₃ H ₁₇ N S ₂ O ₃ Mn	354.34	0.99 (67)	Greenish- yellow	150*	15.50 (15.82)	12.26
(2) [Fe(L) ₂ (H ₂ O) ₂] C ₂₀ H ₂₂ O ₆ Fe	414.24	1.48 (85)	Reddish- brown	188*	13.48 (13.40)	13.63
(3) [CoLL ¹ (H ₂ O)Cl] C ₁₃ H ₁₇ NO ₃ S ₂ ClCo	393.79	1.27 (77)	Army-green	129-130	14.97 (15.08)	16.29
(4) [NiLL ¹ (H ₂ O)Cl] C ₁₃ H ₁₇ NO ₃ S ₂ CINi	393.55	0.86 (52)	Crocodile- green	166*	14.92 (15.02)	18.24
(5) [CuLL ¹ (H ₂ O) ₂] C ₁₃ H ₁₉ NO ₄ S ₂ Cu	380.96	1.15 (72)	Burgundy- brown	182*	16.68 (16.27)	11.28
(6) [ZnLL ¹].H ₂ O C ₁₃ H ₁₇ NO ₃ S ₂ Zn	364.78	1.02 (67)	Whitish- yellow	158-160	17.92 (17.78)	14.26

M.pt = Melting point, * = Decomposition temperature, % = percentage, Theo. = theoretical, Exp. = Experimental, \wedge M = molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$).

Table 2: Elemental analysis data of the metal complexes

Complexes (Molecular formulae)	% Calculated (% Found)				
	Metal	C	H	N	S
(1) [MnLL ¹].H ₂ O C ₁₃ H ₁₇ N S ₂ O ₃ Mn	15.50 (15.82)	44.07 (43.98)	4.84 (4.80)	3.95 (3.97)	18.10 (18.22)
(2) [Fe(L) ₂ (H ₂ O) ₂] C ₂₀ H ₂₂ O ₆ Fe	13.48 (13.40)	57.99 (58.03)	5.35 (5.43)	- (0.00)	- (0.00)
(3) [CoLL ¹ (H ₂ O)Cl] C ₁₃ H ₁₇ NO ₃ S ₂ ClCo	14.97 (15.08)	39.65 (39.50)	4.35 (4.29)	3.56 (3.58)	16.28 (16.34)
(4) [NiLL ¹ (H ₂ O)Cl] C ₁₃ H ₁₇ NO ₃ S ₂ CINi	14.92 (15.02)	39.68 (39.64)	4.35 (4.29)	3.56 (3.66)	16.29 (16.35)
(5) [CuLL ¹ (H ₂ O) ₂] C ₁₃ H ₁₉ NO ₄ S ₂ Cu	16.68 (16.27)	40.99 (40.72)	5.03 (4.99)	3.68 (3.65)	16.83 (16.85)
(6) [ZnLL ¹].H ₂ O C ₁₃ H ₁₇ NO ₃ S ₂ Zn	17.92 (17.78)	42.80 (43.12)	4.70 (4.90)	3.84 (3.89)	17.58 (17.70)

C = Carbon, H = Hydrogen, N = Nitrogen, S = Sulphur



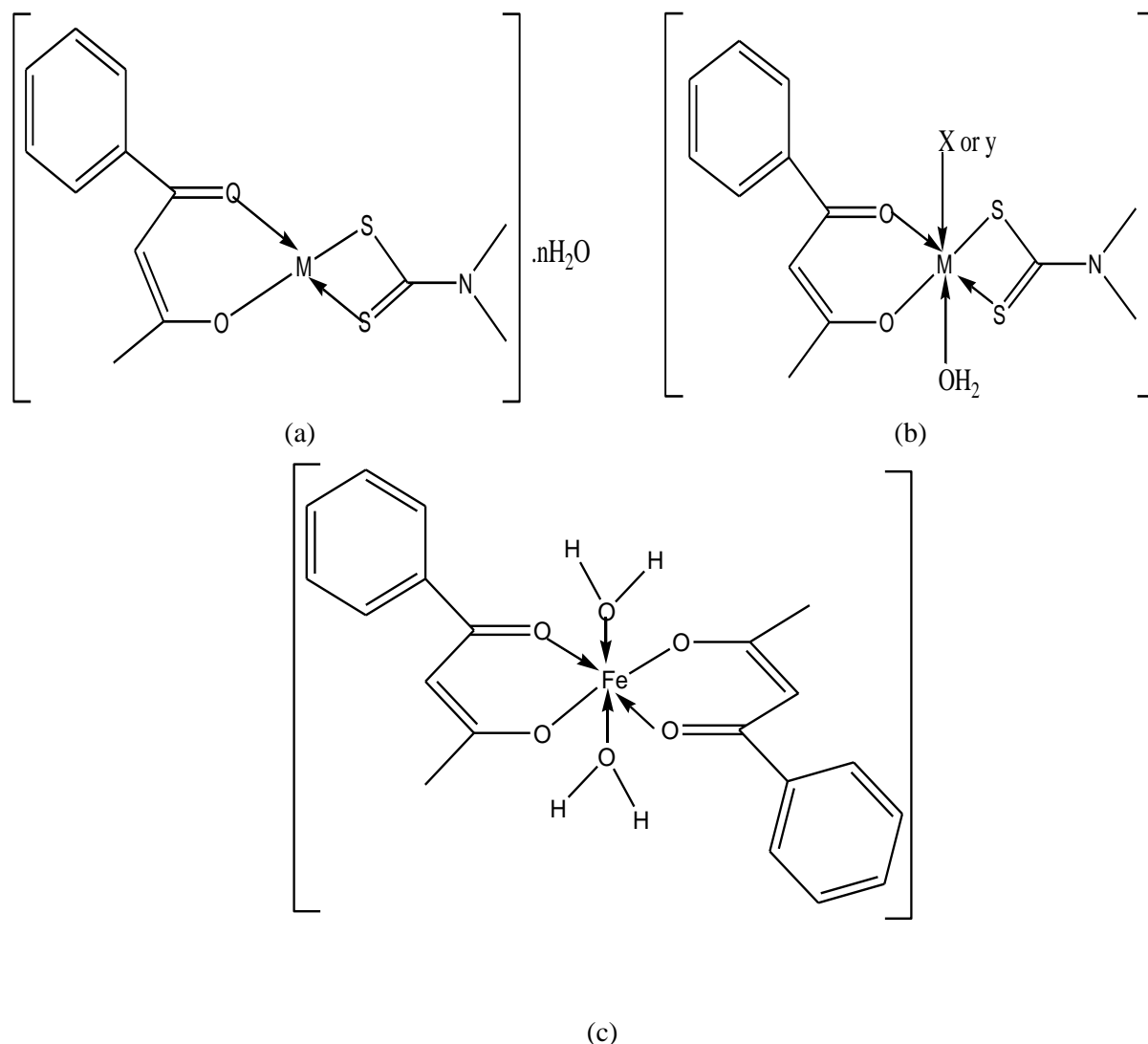


Figure 1: The proposed structures of the $M(II)$ mixed ligands complexes in their assumed geometries. {(a): $M = Mn$ and Zn when $n = 1$; (b): $M = Co$ and Ni when $X = Cl$; $M = Cu$ when $y = H_2O$ }

Infrared spectra studies of the ligands and their metal(II) complexes

The selected IR data of the ligands **L** and **L¹** and their complexes **1**, **2**, **3**, **4**, **5**, and **6** are presented in Table 3. The appearance of broad bands in the spectra of all the metal(II) complexes in the range 3331-3548 cm^{-1} were attributed to the presence of coordinated/ crystallization water assigned as $\nu(\text{OH})$ of H_2O . The observance of a weak, broad band in the spectrum of ligand **L¹**, at 3056 cm^{-1} has been assigned to the O-H stretching vibration in its enol form [53]. This band shifted from 3056 cm^{-1} to 3003-3055 cm^{-1} in all the metal(II) complexes. The $\nu(\text{C}=\text{O})$ and the $\nu(\text{C}-\text{O})$ strong bands of the ligand **L¹**, suffered bathochromic shift from 1595 cm^{-1} and 1256 cm^{-1} to 1541- 1586 cm^{-1} and 1227-1254 cm^{-1} respectively, in all of the metal(II) complexes due to coordination of the carbonyl oxygen atom and C-3 enolic hydroxyl groups. This assignment is based on earlier report by Pavia *et al.*, that a weak, broad O-H stretch is observed for enol form of β -diketone at 3200 - 2400 cm^{-1} and hydrogen bonded carbonyl groups in enol forms are often observed in the region 1640 - 1570 cm^{-1} ; and this intra-molecular hydrogen bonding effect was also

established by other researchers [54-56]. Thus, ligand L^1 behaves as a bidentate ligand by complexation through the carbonyl oxygen and C-3 enolic hydroxyl groups [57].

Furthermore, the appearance of a band at 1234 cm^{-1} assigned as $\nu(\text{C-N})$ of the ligand L , overlapped with the $\nu(\text{C-O})$ bands in the metal(II) complexes. The $\nu(\text{C=S})$ and $\nu(\text{C-S})$ in the ligand L at 960 cm^{-1} and 845 cm^{-1} , experienced hypsochromic shift to $965\text{-}998\text{ cm}^{-1}$ and $764\text{ - }847\text{ cm}^{-1}$ in all the metal(II) complexes due to the coordination of the two sulphur atoms to the metal ion in a bidentate mode [58-59]. The bands present in the range $2848\text{-}2927\text{ cm}^{-1}$ were assigned due to $\nu(\text{C-H})$ stretching vibrations of the methyl group in the ligands and all the metal(II) complexes. The $\nu(\text{M-O})$, $\nu(\text{M-S})$ and $\nu(\text{M-Cl})$ bands were absent in the ligands, but they appeared in the spectra of the complexes at the range $515\text{-}581\text{ cm}^{-1}$, $411\text{-}446\text{ cm}^{-1}$, and $<400\text{ cm}^{-1}$ respectively, confirming coordination in all the metal(II) complexes. The actual values of $\nu(\text{M-Cl})$ were not observed, since it usually falls below 400 cm^{-1} , due to the spectral range of our measurements. However, these bands, $\nu(\text{M-O})$, $\nu(\text{M-S})$ and $\nu(\text{M-Cl})$ has been reported to be found around $419\text{-}586\text{ cm}^{-1}$, $365\text{-}465\text{ cm}^{-1}$, and $352\text{-}387\text{ cm}^{-1}$ respectively [60-63].

Table 3: Infrared Spectra data of the ligands and the metal complexes

Ligands / Complexes	$\nu(\text{OH})$ / H_2O	$\nu(\text{C=O})$	$\nu(\text{C-O})$ / $\nu(\text{C-N})$	$\nu(\text{C=S})$	$\nu(\text{C-S})$	$\nu(\text{O-H})$ enol	$\nu(\text{C-H})$ Alkyl	$\nu(\text{M-O})$	$\nu(\text{M-S})$ / $\nu(\text{M-Cl})$
L^1 (BAC)	-	1595s	1256s	-	-	3056wb	2921s	-	-
L (SDTC)	-	-	1234s	960s	845s	-	2923s	-	-
Complex 1	3331b	1584s	1227s	998s	846s	3055w	2912m	569s	417s
Complex 2	3514b	1584s	1277s	-	-	3052wb	2913s 2857m	575s	-
Complex 3	3403b	1586s	1254s	977s	847s	3050w	2920m 2848m	581s 515s	438s, 422s /
Complex 4	3509b	1541s	1236s	969s	764s	3003w	2902m 2854s	569s 546s	440s, 411s /
Complex 5	3548b	1586s	1240s	969s	847s	3039w	2920s 2854m	554s	446s -
Complex 6	3437b	1577s	1239s	965s	838s	3054w	2927s 2850m	563s	442s

s = sharp or strong, b = broad, m = medium, w = weak

Electronic spectra and magnetic moments of the complexes

The electronic spectra of the ligands and their metal(II) complexes **1, 2, 3, 4, 5, and 6** were obtained in DMF. The results are presented in Table 4.

The ultraviolet spectra of the compounds were characterized by strong absorption maxima between $330\text{ - }267\text{ nm}$ ($30,303\text{ - }37,453\text{ cm}^{-1}$) and two shoulder bands at 356 nm ($28,090\text{ cm}^{-1}$) and 318 nm ($31,446\text{ cm}^{-1}$), assigned to $\pi \rightarrow \pi^*$ transitions. The two ligands L^1 and L , exhibited absorption bands at 310 nm , 300 nm and 267 nm ; with the energies of $32,258\text{ cm}^{-1}$, $33,333\text{ cm}^{-1}$, and $37,453\text{ cm}^{-1}$ respectively, assigned to $\pi \rightarrow \pi^*$ transitions. These bands have been shifted to shorter and longer wavelengths, depending upon the central metal atom/ ion in all the metal(II) complexes due to coordination/ complexation [64].

The complex **1**, $[\text{Mn}(\text{L})(\text{L}^1)]\cdot\text{H}_2\text{O}$ showed one absorption band at 330 nm ($30,303\text{ cm}^{-1}$, $\epsilon = 850\text{ Lcm}^{-1}\text{mol}^{-1}$). The spectroscopic ground term symbol of Mn(II) is ${}^6\text{S}$ and a ${}^4\text{G}$ upper term, with a d^5 electronic configuration. The Mn(II) complexes are characterized by weak spin forbidden transitions. These weak transitions for an octahedral complex are assigned as: ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$, and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ transitions [65]. The ${}^6\text{S}$ orbital is non-degenerate, being in a singlet state and cannot split by either a tetrahedral or an octahedral field [66], hence no d-d



transition is expected in the visible spectrum of this complex. Therefore, the absorption peak at 330 nm ($30,303 \text{ cm}^{-1}$, $\epsilon = 8500 \text{ Lcm}^{-1}\text{mol}^{-1}$) is assigned to $\pi \rightarrow \pi^*$ transition. The effective magnetic moment of high spin Mn(II) complexes are expected to be close to the spin-only value of 5.90 B.M., regardless of stereochemistry since the ground term is ${}^6A_{1g}$ and thus, there is no orbital contribution [67-68]. However, the room temperature magnetic moment of 4.77 B.M obtained in this study, indicating presumably a spin-free tetrahedral geometry [64, 69].

The electronic spectrum of complex **2**, $[\text{Fe}(\text{L})_2(\text{H}_2\text{O})_2]$ revealed three bands at 301 nm ($33,222 \text{ cm}^{-1}$, $\epsilon = 5200 \text{ Lcm}^{-1}\text{mol}^{-1}$), 404 nm ($24,752 \text{ cm}^{-1}$, $\epsilon = 1100 \text{ Lcm}^{-1}\text{mol}^{-1}$), 482 nm ($20,747 \text{ cm}^{-1}$, $\epsilon = 500 \text{ Lcm}^{-1}\text{mol}^{-1}$) and a shoulder band at 356 nm ($28,090 \text{ cm}^{-1}$, $\epsilon = 1600 \text{ Lcm}^{-1}\text{mol}^{-1}$). The Fe(II) has electronic configuration of d^6 , with a spectroscopic ground term of 5D . The band at 301 nm ($33,222 \text{ cm}^{-1}$, $\epsilon = 5200 \text{ Lcm}^{-1}\text{mol}^{-1}$) is assigned to $\pi \rightarrow \pi^*$ transition, while the bands at 482 nm ($20,747 \text{ cm}^{-1}$, $\epsilon = 500 \text{ Lcm}^{-1}\text{mol}^{-1}$) and 404 nm ($24,752 \text{ cm}^{-1}$, $\epsilon = 1100 \text{ Lcm}^{-1}\text{mol}^{-1}$) are d-d transitions, assignable to ${}^5T_{2g} \rightarrow {}^5E_g$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions respectively. These type of d-d transitions have earlier been reported for a 6-coordinate, high spin and low spin octahedral geometry [70-71], with an observed magnetic moment in between a moment of 5.0 - 5.5 B.M usually expected for high spin octahedral Fe(II) complexes and low spin octahedral complexes which are expected to be diamagnetic. In this study, a moment of 5.02 B.M was observed for the Fe(II) complex, indicative of a high spin octahedral geometry.

The complex **3**, $[\text{CoLL}^1(\text{H}_2\text{O})\text{Cl}]$ in its electronic spectrum exhibited three bands at 320 nm ($31,152 \text{ cm}^{-1}$, $\epsilon = 7400 \text{ Lcm}^{-1}\text{mol}^{-1}$), assigned to $\pi \rightarrow \pi^*$ transition; 405 nm ($24,691 \text{ cm}^{-1}$, $\epsilon = 1200 \text{ Lcm}^{-1}\text{mol}^{-1}$), assigned to ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ (ν_3); and 479 nm ($20,747 \text{ cm}^{-1}$, $\epsilon = 200 \text{ Lcm}^{-1}\text{mol}^{-1}$), assigned to ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ (ν_1). The Co(II) has a d^7 electronic configuration, and a ground term symbol of 4F . It has been reported that the 6-coordinated octahedral and pseudo-octahedral cobalt(II) complexes typically display three transitions in the visible region as: ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ (ν_1), ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$ (ν_2) and ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ (ν_3) [72-74]. The (ν_2) transition is often not observed but only occurs when the two states cross is very weak. Therefore, ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ (ν_1) and ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ (ν_3) transitions are usually observed in the visible region. Magnetic moments value in the range 4.7-5.2 B.M. and 1.9-2.4 B.M. are expected and have been reported for high and low spin octahedral cobalt (II) complexes respectively [75-76]. The magnetic moment of 3.47 B.M. obtained for this complex, was indicative of spin equilibrium between high spin and low spin octahedral geometry [77].

Similarly, the complex **4**, $[\text{NiLL}^1(\text{H}_2\text{O})\text{Cl}]$ showed three absorption bands at 324 nm ($30,864 \text{ cm}^{-1}$, $\epsilon = 7700 \text{ Lcm}^{-1}\text{mol}^{-1}$), 384 nm ($26,042 \text{ cm}^{-1}$, $\epsilon = 1300 \text{ Lcm}^{-1}\text{mol}^{-1}$) and 425 nm ($23,529 \text{ cm}^{-1}$, $\epsilon = 300 \text{ Lcm}^{-1}\text{mol}^{-1}$). The Ni(II) is a transition metal with d^8 electronic configuration and a ground state term symbol 3F . The band at 324 nm ($30,864 \text{ cm}^{-1}$, $\epsilon = 7700 \text{ Lcm}^{-1}\text{mol}^{-1}$) is assigned to $\pi \rightarrow \pi^*$ transition, while the other two bands; 425 nm ($23,529 \text{ cm}^{-1}$, $\epsilon = 300 \text{ Lcm}^{-1}\text{mol}^{-1}$) and 384 nm ($26,042 \text{ cm}^{-1}$, $\epsilon = 1300 \text{ Lcm}^{-1}\text{mol}^{-1}$) were assigned to ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ and ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ transitions respectively [78]. The room temperature magnetic moments expected for high spin octahedral Ni(II) complexes is in the range 2.9 - 3.3 B.M; while low spin octahedral Ni(II) should be diamagnetic. However, moment in the range 0.5 - 2.7 B.M were reported for Ni(II) complexes with spin-equilibria [79-80]. Thus, an observed moments of 2.55 B.M for this complex under study, corroborates the existence of spin-crossover and the proposed octahedral geometry.

The complex **5**, $[\text{CuLL}^1(\text{H}_2\text{O})_2]$, gave two absorption bands at 327 nm ($30,581 \text{ cm}^{-1}$, $\epsilon = 3800 \text{ Lcm}^{-1}\text{mol}^{-1}$), 434 nm ($23,041 \text{ cm}^{-1}$, $\epsilon = 1500 \text{ Lcm}^{-1}\text{mol}^{-1}$). The electronic configuration of Cu(II) is d^9 ; thus, a spectroscopic ground state term symbol 2D . The absorption band at 327 nm ($30,581 \text{ cm}^{-1}$, $\epsilon = 380 \text{ Lcm}^{-1}\text{mol}^{-1}$) is assigned to $\pi \rightarrow \pi^*$ transition, and an absorption band 434 nm ($23,041 \text{ cm}^{-1}$, $\epsilon = 1500 \text{ Lcm}^{-1}\text{mol}^{-1}$) at the visible region of the spectrum, assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition of an octahedral geometry. For mononuclear Cu(II) complexes, a moment in the range 1.9-2.3 B.M is usually observed, regardless of stereochemistry, expectedly higher than the spin - only value ($\mu_{\text{so}} = 1.73$ B.M), due to orbital contribution and spin-orbit coupling. For this study, the Cu(II) complex had a moment of 1.96 B.M, indicative of an octahedral geometry.

The complex **6**, $[\text{ZnLL}^1]\cdot\text{H}_2\text{O}$, UV-visible spectrum had one band and a shoulder at 279 nm ($35,842 \text{ cm}^{-1}$, $\epsilon = 320 \text{ Lcm}^{-1}\text{mol}^{-1}$), and 318 nm ($31,446 \text{ cm}^{-1}$, $\epsilon = 2300 \text{ Lcm}^{-1}\text{mol}^{-1}$). The Zn(II) has a completely filled 3d orbital, that is, d^{10} electronic configuration and thus; no d-d transition is expected in the visible region of its spectrum. And if any absorption band appears at this region, then it would be a metal-ligand charge transfer. Therefore, the bands at 279



nm (35,842 cm^{-1} , $\epsilon = 3200 \text{ Lcm}^{-1}\text{mol}^{-1}$), and 318 nm (31,446 cm^{-1} , $\epsilon = 2300 \text{ Lcm}^{-1}\text{mol}^{-1}$) were assigned to MLCT and $\pi \rightarrow \pi^*$ transitions respectively. The Zinc(II) metal complexes are expectedly diamagnetic in nature with a magnetic moment less than zero Bohr Magneton and mostly adopt a four-coordinate tetrahedral geometry [81]. The magnetic moment value obtained for this complex under study was negative, and tetrahedral geometry has been proposed.

Table 4: Electronic Spectra data of the ligands and the metal(II) complexes

Ligands /Complexes	Absorption regions			Assigned Transitions	Geometry	μ_{eff} (B.M)
	(nm)	(cm^{-1})	(ϵ)			
BAC (L^1) $\text{C}_{10}\text{H}_{10}\text{O}_2$	310	32,258		$\pi \rightarrow \pi^*$	-	-
SDTC (L) $\text{C}_3\text{H}_6\text{NS}_2\text{Na}$	267	37,453		$\pi \rightarrow \pi^*$	-	-
	300	33,333		$\pi \rightarrow \pi^*$		
(1) $[\text{MnLL}^1]\cdot\text{H}_2\text{O}$ $\text{C}_{13}\text{H}_{17}\text{N S}_2\text{O}_3\text{Mn}$	330	30,303	8500	$n \rightarrow \pi^*$	Tetrahedral	4.77
(2) $[\text{Fe}(\text{L}^1)_2(\text{H}_2\text{O})_2]$ $\text{C}_{20}\text{H}_{22}\text{O}_6\text{Fe}$	301	33,222	5200	$\pi \rightarrow \pi^*$	Octahedral	5.02
	356 sh	28,090	1600	$n \rightarrow \pi^*$		
	404	24,752	1100	$^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$		
	482	20,747	500	$^5\text{T}_{2g} \rightarrow ^5\text{E}_g$		
(3) $[\text{CoLL}^1(\text{H}_2\text{O})\text{Cl}]$ $\text{C}_{13}\text{H}_{17}\text{NO}_3\text{S}_2\text{ClCo}$	320	31,152	7400	$\pi \rightarrow \pi^*$	Octahedral	3.47
	405	24,691	1200	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$		
	479	20,877	200	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$		
(4) $[\text{NiLL}^1(\text{H}_2\text{O})\text{Cl}]$ $\text{C}_{13}\text{H}_{17}\text{NO}_3\text{S}_2\text{ClNi}$	324	30,864	7700	$\pi \rightarrow \pi^*$	Octahedral	2.55
	384	26,042	1300	$^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})$		
	425	23,529	300	$^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$		
(5) $[\text{CuLL}^1(\text{H}_2\text{O})_2]$ $\text{C}_{13}\text{H}_{19}\text{NO}_4\text{S}_2\text{Cu}$	327	30,581	3800	$\pi \rightarrow \pi^*$	Octahedral	1.96
	434	23,041	1500	$^2\text{E}_g \rightarrow ^2\text{T}_{2g}$		
(6) $[\text{ZnLL}^1]\cdot\text{H}_2\text{O}$ $\text{C}_{13}\text{H}_{17}\text{NO}_3\text{S}_2\text{Zn}$	279	35,842	3200	MLCT	Tetrahedral	D
	318 sh	31,446	2300	$\pi \rightarrow \pi^*$		

nm = nanometer (unit of wavelength (λ)), cm^{-1} = per centimeter or reciprocal centimeter, (unit of wavenumber ($\bar{\nu}$)), ϵ = Molar absorptivity ($\text{Lcm}^{-1}\text{mol}^{-1}$), $1000\text{cm}^{-1} = 1 \text{ kK}$, MLCT = Metal to Ligand Charge transfer, μ_{eff} = effective magnetic moment, sh = shoulder, B.M. = Bohr Magnetons. D = Diamagnetic.

Mass Spectroscopic studies of the metal(II) complexes 1, 2, 3, 4, 5 and 6

The relative molecular mass of the metal(II) complexes **1**, **2**, **3**, **4**, **5** and **6** were determined by Liquid Chromatography-High Resolution Mass Spectrometry with ElectroSpray Ionization method {LC-HRMS (ESI)}. The results are presented in Table 5.

The LC-HRMS (ESI) spectra of all the metal(II) mixed-ligand complexes revealed the m/z value for their observed masses ($M+1$) as single peaks. These were in close range to the m/z value for the calculated masses (M) of all the complexes (Table 5). The complexes **1**, **2**, and **3** showed peak at m/z 355.0102 (found), 354.34 (calc.); 415.2720 (found), 414.24 (calc.) and 394.7602 (found), 393.79 (calc.) respectively.



Furthermore, the m/z peak at 394.7297 (found), 393.55 (calc.); 381.9688 (found), 380.96 (calc.) and 365.8134 (found), 364.78 (calc.) were attributed to complexes **4**, **5** and **6** respectively.

Thus, the mass spectral studies corroborate the formulae and the proposed structures of the complexes.

Table 5: Mass spectra data of the metal(II) complexes 1, 2, 3, 4, 5 and 6

Complexes/ Chemical formulae	Molecular Mass (Calculated)	Observed Mass (Found) (M+1)
(1) [MnLL ¹].H ₂ O C ₁₃ H ₁₇ N S ₂ O ₃ Mn	354.34	355.0102
(2) [Fe(L ¹) ₂ (H ₂ O) ₂] C ₂₀ H ₂₂ O ₆ Fe	414.24	415.2720
(3) [CoLL ¹ (H ₂ O)Cl] C ₁₃ H ₁₇ NO ₃ S ₂ ClCo	393.79	394.7602
(4) [NiLL ¹ (H ₂ O)Cl] C ₁₃ H ₁₇ NO ₃ S ₂ ClNi	393.55	394.7297
(5) [CuLL ¹ (H ₂ O) ₂] C ₁₃ H ₁₉ NO ₄ S ₂ Cu	380.96	381.9688
(6) [ZnLL ¹].H ₂ O C ₁₃ H ₁₇ NO ₃ S ₂ Zn	364.78	365.8134

Nuclear Magnetic Resonance spectra data of the mixed ligands complex

The proton NMR and carbon-13 NMR were recorded in deuterated DMSO and only the diamagnetic Zn(II) mixed ligand complex **6** was determined (Figure 2). The ¹H NMR spectra showed a sharp singlet characteristic peak at 2.20 ppm, corresponding to three protons directly attached to C-10 of the benzoyl acetone moiety of the complex. Another singlet peak appeared at 2.53 ppm and was ascribed to the six protons of the di-methyl group attached to the N atom of the dithiocarbamate moiety of the complex. Also, a singlet peak at 6.56 ppm in the spectra was assigned to one proton attached to the C-8 contained in the benzoyl acetone moiety of the complex. The characteristic multiplet and singlet peaks in the region 7.49-7.57 ppm and 7.87 ppm, were assigned to three protons and two protons of the phenyl ring (C₆H₅) of the whole complex respectively.

The carbon-13 NMR spectra of the complex **6** revealed signals at 26.08 ppm and 45.21 ppm, assigned to C-10 of the benzoyl acetone moiety and di-methyl group carbon atoms (-NC₂H₆) of dithiocarbamate moiety respectively. Also, the C-8 of the benzoyl acetone moiety appeared in the spectra at 97.41 ppm while the signals observed in the region 128.61-134.79 ppm were attributed to the carbons of the phenyl ring (C₆H₅) in the complex.

Furthermore, C-7 and C-9 of the benzoyl acetone moiety exhibited two different signals at 183.07 ppm and 195.23 ppm respectively, whereas, the C-11 (C-N) of the dithiocarbamate moiety showed up at a very high signal of 204.41 ppm.

Although, the actual structure of the complexes can be correctly deduced and confirmed by X-ray crystallographic data, but no single crystal growth were successful for all the complexes.

Therefore, based on this information of the proton NMR and carbon-13 NMR assignments of the Zn(II) mixed ligands complex and some other spectroscopic measurements data, the structure or geometry was proposed.

Thermal analysis studies of the metal(II) complexes 1, 2, 3, 4, 5 and 6

Thermo gravimetric analysis (TGA/DTA) provides useful information about the thermal stability of the metal complexes at specific temperatures. A systematic order for the thermal degradation or decomposition of the complexes, and the percentage or weight/mass loss of water molecules and other molecules attached to the central metal ion, inside or outside the coordination sphere could also be determined.

The thermal gravimetric analysis (TGA) curves of the complexes **1**, **2**, **3**, **4**, **5** and **6** are presented in figures 3 and 4. The heating rates were properly controlled at 10°C per minute under nitrogen atmosphere at a flow rate of 200 mL per minute and the temperature range from 30°C - 700°C or 800°C.



The thermal stability of the metal complexes at specific temperatures are greatly considered in this study. It is evident from the thermogravimetric curves (Figure 3) that each of the complexes **1**, **2**, **3**, **5** and **6** exhibit a three steps decomposition pattern, while complex **4** only decomposes in two phases. The decomposition temperatures of the complexes **1**, **2**, **3**, **5** and **6** are 140 °C, 170 °C, less than 100 °C, 210 °C, 160 °C, and 150 °C respectively.

In all cases, the decomposition starts by the loss of coordinated / crystallized water molecule of the complexes alone or with the other part of ligands moiety or molecule at a temperature range of 70 °C – 210 °C, which corroborate the composition of the complexes. They are all thermally stable.

Thus, the comparative TGA curves (Figure 4) of the metal complexes reveal their thermal stability in the order: Co(II) < Mn(II) < Zn(II) < Cu(II) < Fe(II) < Ni(II). The Ni(II) complex, being the most thermally stable with its smaller ionic radius has been reported [82].

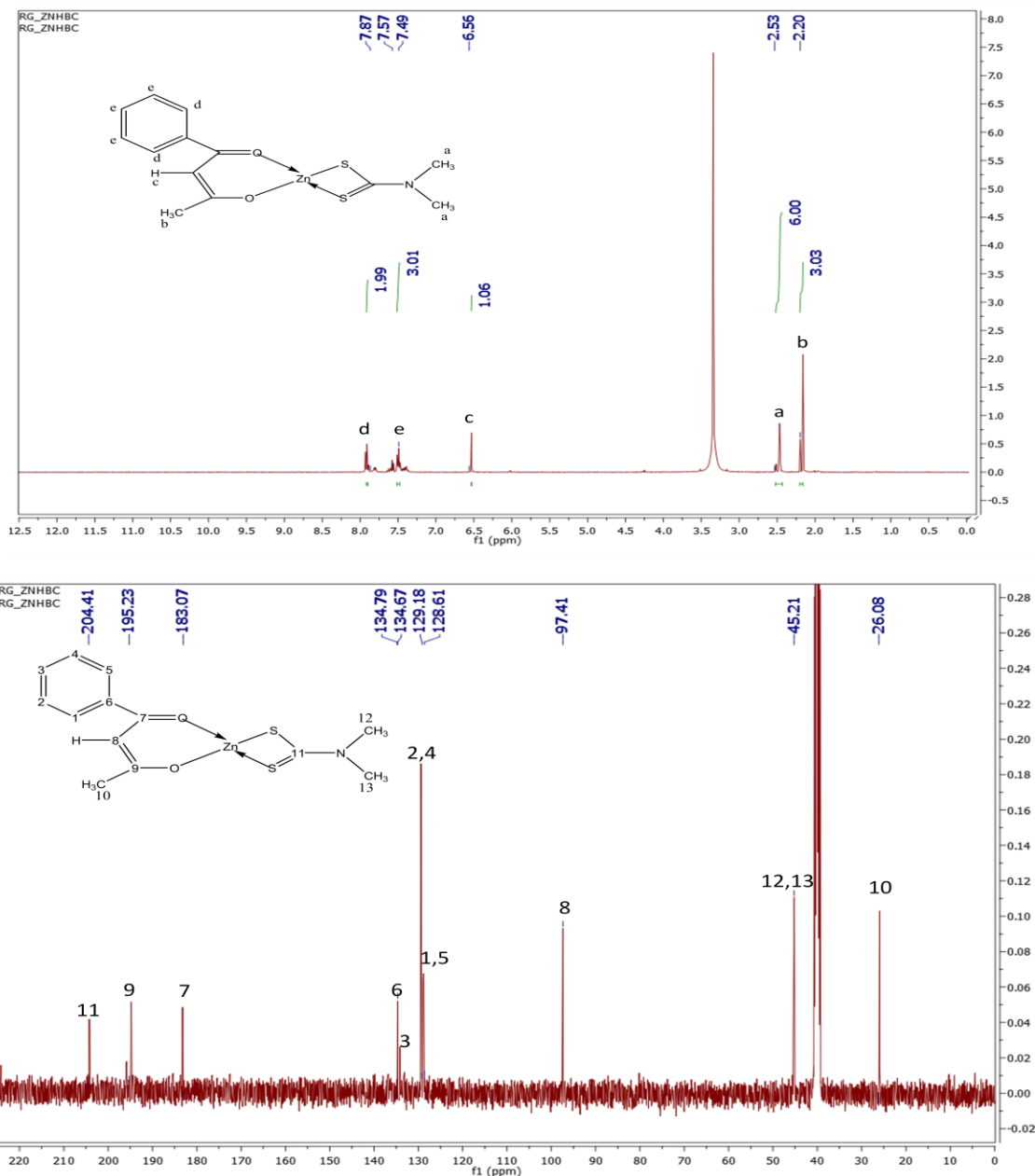
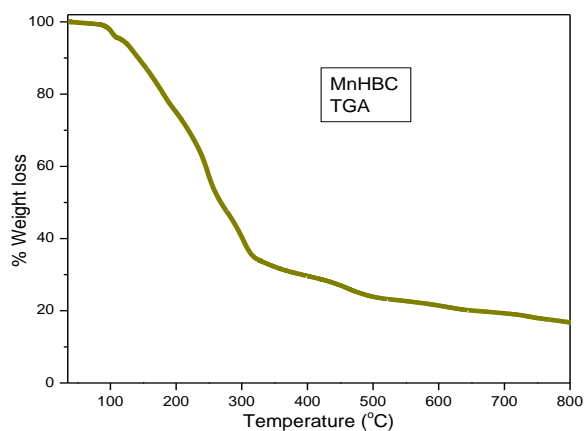
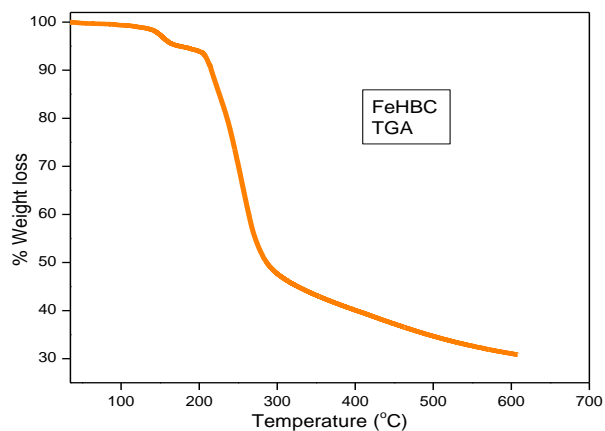
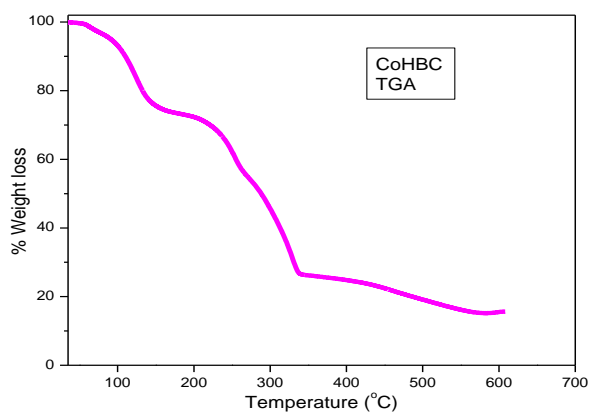
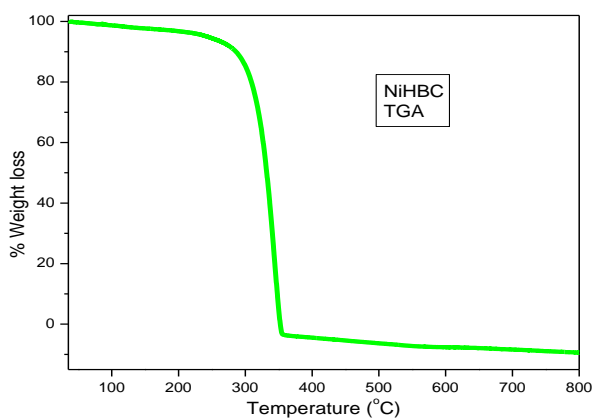
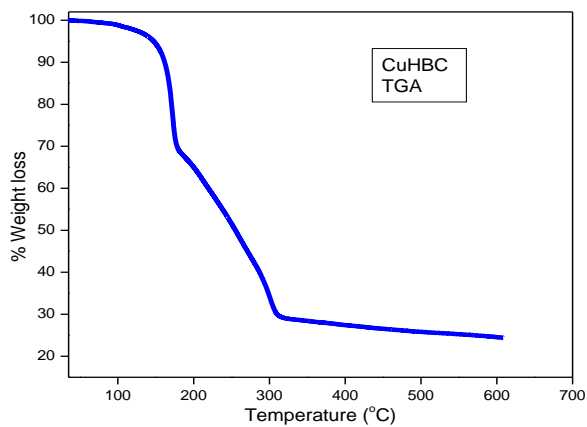
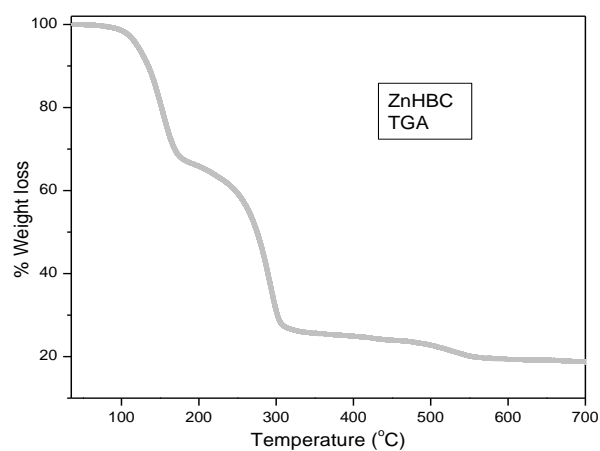


Figure 2: ^1H (upper) and ^{13}C NMR (lower) spectra of Zn(II) mixed ligand complex **6** in d_6 -DMSO.



**Complex 1****Complex 2****Complex 3****Complex 4****Complex 5****Complex 6***Figure 3: TGA curves of complexes 1, 2, 3, 4, 5 and 6*

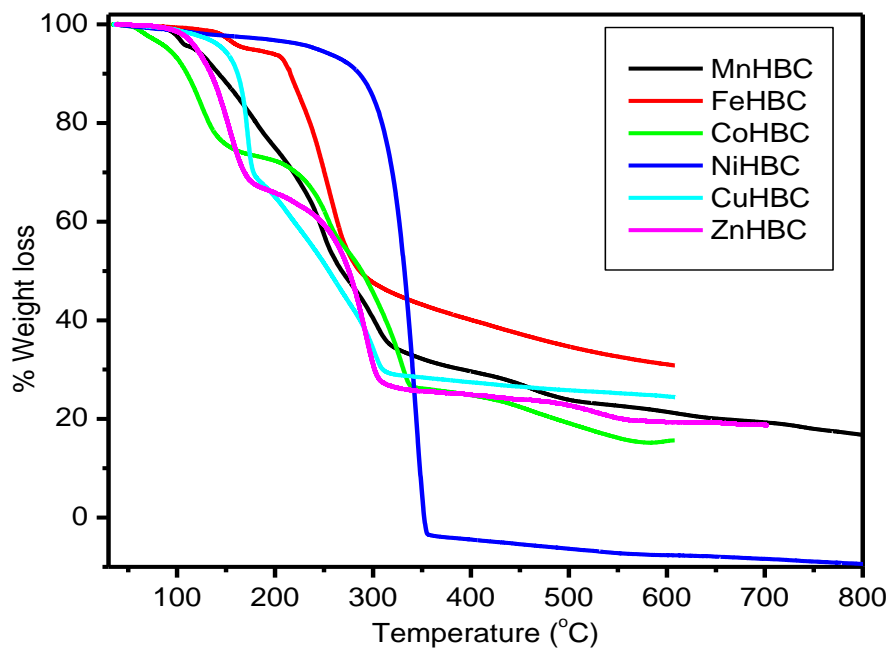


Figure 4: Comparative TGA curves of complexes 1, 2, 3, 4, 5 and 6

Antioxidant studies of the metal(II) mixed ligands complexes of L and L¹

Table 6: Antioxidant data of the mixed ligand metal(II) complexes of L and L¹

Complexes/ Chemical formulae	Absorbance (Standard Deviation)	% Scavenging Inhibition
(1) [MnLL ¹].H ₂ O C ₁₃ H ₁₇ N S ₂ O ₃ Mn	0.09(±0.01)	42.2
(2) [Fe(L ¹) ₂ (H ₂ O) ₂] C ₂₀ H ₂₂ O ₆ Fe	0.06(0)	28.1
(3) [CoLL ¹ (H ₂ O)Cl] C ₁₃ H ₁₇ NO ₃ S ₂ ClCo	0.153(±0.00577)	71.9
(4) [NiLL ¹ (H ₂ O)Cl] C ₁₃ H ₁₇ NO ₃ S ₂ ClNi	0.12(0)	56.3
(5) [CuLL ¹ (H ₂ O) ₂] C ₁₃ H ₁₉ NO ₄ S ₂ Cu	0.163(±0.01155)	81.2
(6) [ZnLL ¹].H ₂ O C ₁₃ H ₁₇ NO ₃ S ₂ Zn	0.07(0)	32.8
Ascorbic acid (standard)	0.12(±0.01)	56.2

The antioxidant studies of all the metal(II) complexes of dimethyldithiocarbamate, L and Benzoyl acetone, L¹ were carried out by ferrous ion chelating assay. The tests were run in triplicate, while the mean absorbance alongside standard deviation and the percentage scavenging inhibition results are presented in Table 6.



The study shows that the Cu(II) and Co(II) complexes had higher percentage scavenging inhibition of 81.2 % and 71.9 % respectively, compared to the positive standard, ascorbic acid with inhibitory activity of 56.2 %. It was so remarkable that the Ni(II) complex and the positive standard had the same scavenging inhibition percentage of approximately 56 %; while Mn(II), Zn(II) and Fe(II) complexes had inhibitory activities of 42.2 %, 32.1 % and 28.1 % respectively.

Thus, these complexes might find application in medical area as therapeutic agents in treatment of some neurodegenerative or heart diseases and cancer. Also, they might be relevant in the food and pharmaceutical industries as preventive agents against oxidation and damage of industrial materials that are exposed to light and oxygen.

Conclusion

The mixed ligand metal(II) complexes of iron, cobalt, nickel and copper assumed an octahedral geometry, while Mn(II) and Zn(II) complexes exhibit a 4-coordinate tetrahedral geometry through the S₂O₂chromophores as supported by electronic, infrared, and other spectral analyses. All the complexes were non-electrolytes and mononuclear. However, the Co(II) and Ni(II) complexes show spin equilibrium between the high spin and low spin octahedral geometry, while others are high spin paramagnetic in nature as corroborated by molar conductance and magnetic moment measurements. The complexes were all thermally degradable, air-stable and followed a three steps decomposition pattern, except Ni(II) complex with a two step pattern. The presence of hydrated/coordinated water molecules in the complexes, with their proposed structural/molecular formulae and compositions were supported by the thermogravimetric analysis, IR and ESI mass spectra. The antioxidant studies show that the Cu(II) and Co(II) complexes had higher percentage scavenging inhibition of 81.2 % and 71.9 % respectively, compared to the positive standard, ascorbic acid with inhibitory activity of 56.2 %, proving them as potential therapeutic and preventive agents against diseases and oxidation of some industrial materials respectively.

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Authors Contributions

AAO- the corresponding author, carried out the research, analyzed the data, funded the project, and wrote the manuscript. FSF supervised the work, read through the manuscript and edited it. RG hosted, supervised, provided some reagents and analytical tools used for the study, when AAO visited his laboratory and Chemistry Department, University of Delhi, Delhi, India, as a doctoral candidate. EGK co-supervised the research.

Conflict of interest

The authors declare no conflict of interest

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