

Synthesis, Characterization, Thermogravimetric and Antioxidant Studies of New Cu(II), Fe(II), Mn(II), Cu(II), Zn(II), Co(II) and Ni(II) Complexes with Benzoic acid and 4,4,4-Trifluoro-1-(2-naphthyl)-1,3-butanedione

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Abstract

Six new Mn(II), Fe(II), Co(II), Ni (II), Cu(II) and Zn(II) complexes with benzoic acid (**L**) and 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione (**L**¹), of the molecular formulae [MnLL¹] H₂O (**1**), [FeLL¹] H₂O (**2**), [CoLL¹] (**3**), [NiLL¹] H₂O (**4**), [CuLL¹] (**5**) and [ZnLL¹] (**6**), respectively, have been synthesized. The molecular structures of the complexes were determined by spectrophotometric studies using ir, ¹H and ¹³C nmr, es and mass spectrophotometry revealed that the geometries of the complexes **1**, **2**, **3**, and **6** are tetrahedral, while **4** and **5** have square planar geometry. These geometries were supported by their magnetic moments data. The coordination of the ligands to the metal ion are through their oxygen atoms. TGA studies showed that they are thermally stable. Their antioxidant studies revealed that they are good antioxidants.

Keywords: synthesis, characterization, thermogravimetric, antioxidant

1. Introduction

One of the fascinating features of modern coordination chemistry is the ever increasing academic, commercial and biological interest exhibited by metal complexes of organic molecules, both natural and synthetic (Bonati *et al*, 1967, Chanterjee *et al*, 2011, Chohan *et al*, 2004). This is mainly because of the ability of coordinated metal atom/ion to influence the structure, properties and applications of the organic compound (Chohan *et al*, 2004, Breviglieri *et al*, 2000, Benetti *et al*, 1999).

Thus, numerous highly efficient catalytic systems based on metal complexes for the synthesis of several industrial chemicals are available (Chandra *et al*,). Similarly, several synthetic metal complexes which mimic the behaviour of complex biomolecules are known, and at present, the studies of such compounds are receiving much attention (Grawal *et al*, 2013, Andrae *et al*, 1997).

For a coordination chemist, perhaps the most important aspect of β -diketones is their ability to form diverse types of complexes with various metal and metalloid elements (Avdogdo 2003, Bakre *et al*, 1933, Mandegani *et al*, 2016).

The coordinating abilities of 1,3-diketones were recognized as early as in 1887 with the report of the synthesis of beryllium acetyl acetonates (De Souza *et al*, 2004, Figgs *et al*, 1960, Garnosvskii *et al*, 1999). This was followed by another reported pioneering work of (Kane *et al*, 2016, Kumar *et al*, 2015) which confirmed the bidentate chelating character of these ligands. The diketonate anion, being a powerful chelating agent, form complexes with virtually almost all the metal and metalloid ions in the periodic Table (Bhagat *et al*, 2012).

Owing to their complexing properties, they have also been used in environmental protection, e.g. for metal chelation in sewage (Binnemans *et al*, 2005, Lenice *et al*, 2006). Because of their extensive research and application potentials, large number of them have been investigated (Manuel *et al*, 2005, Nagajothi *et al*, 2013, Gopal *et al*, 2013).

The 1, 3-diketones still serves as the starting material for the design and synthesis of a large number of compound

shaving wide application in many fields (Sreramala *et al*, 2015, Nqombolo *et al*,2016, Osanai *et al*, 2006, Ramzan *et al*, 2017). Therefore, investigation on metal complexes of different types of 1, 3-diketones have considerable importance.

In this present work, six new Cu(II), Fe(II),Cu(II), Zn(II), Co(II), and Ni(II) complexes with benzoic acid (**L**) and 4, 4, 4-trifluoro-1-(2-naphthyl)-1, 3-butanedione were synthesized, characterized and their antioxidant properties were investigated with a view to know the application potentials of these new compounds.

2. Experimental

2.1 Materials and Physical Measurements

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

The melting points were determined using Electrothermal (MEL -TEMP) machine.

The room temperature magnetic susceptibilities of the metal(II) complexes at 302-304 K were measured on Sherwood Susceptibility Balance MSB Mark 1 and various diamagnetic corrections were calculated using Pascal's constants (De Souza *et al*,).

The molar conductance of the metal(II) complexes in DMF (1×10^{-3} M solutions) were obtained using Eutech instruments CON 510 conductivity meter.

The solution absorption spectra of the ligands and the metal(II) complexes in DMF (1 mmol) were recorded with a Perkin Elmer LAMBDA 25 spectrophotometer, in the range 190-600 nm.

The infrared spectra of the ligands and the metal(II) complexes were recorded on a Perkin Elmer FTIR C91719 with a Perkin Elmer spectrum-two spectrometer (Zn-Se ATR; $4000-600 \text{ cm}^{-1}$) and a Shimadzu IR Affinity-1S FTIR spectrophotometer in the range $4000-400 \text{ cm}^{-1}$.

The elemental analyses, CHNS of the metal(II) complexes were recorded on Elemental Analysen Systeme GmbH Vario EL-III.

The thermogravimetric analyses (TGA/DTA) of the metal(II) complexes were done using a Perkin Elmer Diamond TG/DTA-Thermogravimetric/Differential Thermal Analyzer, Technology by SII, with nitrogen flow rate of 200 mL/min and heating rate of $10^\circ\text{C}/\text{min}$. and a Shimadzu DTG-60 instrument at a heating rate of $10^\circ\text{C}/\text{min}$. under nitrogen atmosphere.

The cyclic voltammograms of some of the mixed ligand metal(II) complexes were recorded in DMF (1×10^{-3} solutions), using a CH Electrochemical Analyser with three electrode system and TBAP (tetrabutylammonium perchlorate) as supporting electrolyte, under nitrogen atmosphere. The three electrodes are Ag/AgCl (as reference electrode), platinum wire (as counter or auxiliary electrode) and glassy carbon (as working electrode). The measurements were carried out using Personal Computer (PC) with Microsoft Excel program and CHI 1120A Electrochemical Analyzer software.

High resolution mass spectra of the mixed ligand metal(II) complexes 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 anti-oxidant properties of the mixed ligand metal(II) complexes were determined through the ferrous-ion chelating assay by the standard colorimetric method using a single beam WPA colourwave CO7500 Colorimeter at wavelength 550 nm (Ramzan *et al*,).

2.2 Preparation of the Metal(II) Ions Complexes

The mixed ligand complexes of Mn(II), Fe(II),Cu(II), Zn(II), Co(II), and Ni(II) ions were prepared by adding gradually and neatly 0.68-1.15 g (4.01×10^{-3} moles) of the respective metal(II) salts ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), to the stirring homogenous solution of 0.49 g (4.01×10^{-3} moles) benzoic acid (**L**) and 0.65 g (4.01×10^{-3} moles) of 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione (**L**¹) in 15 mL of ethanol. The resulting coloured solutions were buffered to a pH of 9 with 2-3 drops of aqueous ammonia and were refluxed for 6 hours at $35-40^\circ\text{C}$. The various coloured products formed were filtered, washed with 50 % ethanol, recrystallized twice using absolute ethanol, and then dried in a vacuum over phosphorous pentoxide (P_2O_5) They were stored in borosilicate containers and further dried over silica gel in a desiccator.

3. Results and Discussion

Table 1 shows the physical properties measurements carried out on the metal complexes.

The complexes were obtained in the range 37-58% yields in powdered form.

All the metal(II) complexes, except Zn(II) complex with a d^{10} configuration, are expectedly coloured due to d-d

transitions. Mn(II) and Co(II) complexes are yellow, Ni(II) and Cu(II) complexes are of different shades of green, while Fe(II) complex is brown.

They all exhibited distinct higher melting points temperature in the range 126-182 °C compared to the respective free ligands melting points temperature in the range 72-121 °C. The experimental values for percentage metal and elemental analyses (C, H) of all the metal(II) complexes are very close to their theoretical values and in good agreement with their respective molecular formulae and formulae masses. These are presented in Table 2.

The complexes were obtained in the range 37-58% yields in powdered form. The molar conductance values of the complexes in DMF (1 mM solution) were in the range 12.15 - 19.40 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, indicating their non-electrolytic nature, since values above 60 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ are expected for 1:1 electrolyte.^[29] Unfortunately, attempts to grow single crystals for X-ray diffraction studies for all the complexes were not successful.

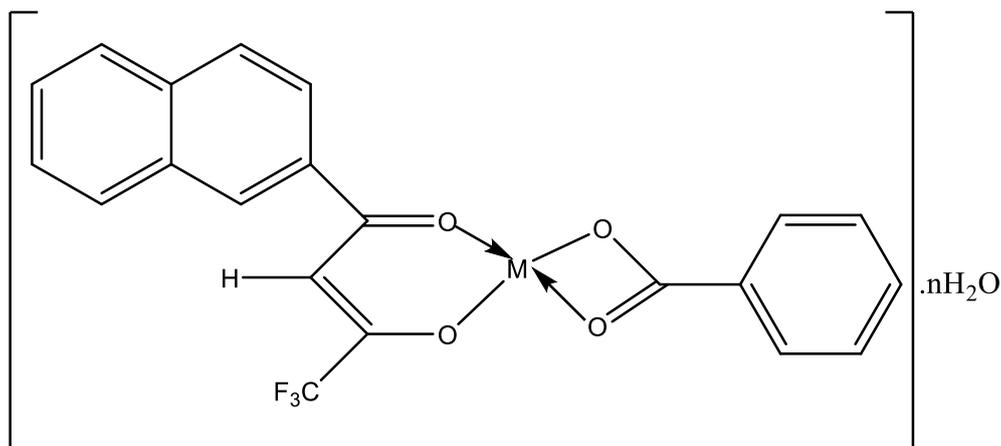


Figure 1. Structure of complexes 1, 2, 3, 4, 5 and 6. [M = Mn, Fe and Ni when n = 1, M = Co, Cu and Zn when n = 0]

The selected IR data of the ligands **L** and **L**¹ and the six complexes are presented in Table 3.

The appearance of broad bands in the spectra of all the metal(II) complexes in the range 3367-3544 cm^{-1} were attributed to the presence of coordinated/ crystallization water and assigned as $\nu(\text{OH})$ of H_2O . A weak and broad band observed in the spectrum of ligand **L** at 3074 cm^{-1} was assigned to O-H stretching vibration of the acid. While the one observed at 3066 cm^{-1} in the spectrum of **L**¹ has been assigned to the O-H stretching vibration in its enol form. These bands shifted to between 3056-3071 cm^{-1} in all the metal(II) complexes, corroborating coordination of the deprotonated phenol oxygen atom of **L** and enolic oxygen atom of **L**¹ to the metal(II) ions.

The $\nu(\text{C}=\text{O})$ strong bands of the ligands **L**¹ and **L**, at 1597 cm^{-1} and 1673 cm^{-1} respectively, experienced a shift to between 1588 - 1603 cm^{-1} in all the metal(II) complexes due to coordination of the carbonyl oxygen atom to the metal(II) ions (Bhaghat *et al*, 2012).

In addition, the appearance of a new sharp band in all the metal(II) complexes in the range 403 - 583 cm^{-1} , attributed to $\nu(\text{M}-\text{O})$ vibrations, which were completely absent in the ligands **L**³ and **L**^b, was another confirmation of the involvement of the oxygen atoms of the phenol, enol, carbonyl and carboxylic acid in complexation or coordination with the metal atoms (Grawal *et al*, 2013, Andrae *et al*, 1997).

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

The ultraviolet spectra of the compounds were characterized by two peaks between 339 - 331 nm (29,499 - 30,211 cm^{-1}) and 294 - 267 nm (34,014 - 37,453 cm^{-1}), assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively. The absorption bands in the two ligands **L**¹ and **L**, experienced a red shift (bathochromic shift i.e longer wavelengths) in all the metal(II) complexes due to coordination/ complexation (Lenice *et al*, 2006).

The complex **1**, showed an absorption band at 417 nm (23,981 cm^{-1} , $\epsilon = 150 \text{ Lcm}^{-1}\text{mol}^{-1}$), assigned to ${}^6\text{A}_1 \rightarrow {}^4\text{E}(\text{G})$ transition, which was suggestive of a four coordinate tetrahedral geometry. 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. An observed magnetic moments of 5.92 B.M is usually expected for the Mn(II) complexes at room temperature, regardless of stereochemistry since the ground term is ${}^6\text{A}_1$ and thus, there is no orbital contribution. In this study, the Mn(II) complex has a magnetic moment of 5.82 B.M, indicative of anti-ferromagnetism and complementary of the proposed tetrahedral geometry(Manuel *et al*, 2005, Osanai *et al*, 2006).

The electronic spectrum of complex **2**, displayed an absorption band at 472 nm ($21,186\text{ cm}^{-1}$, $\epsilon = 400\text{ Lcm}^{-1}\text{mol}^{-1}$), which indicated a four coordinate tetrahedral geometry and is assigned as ${}^5\text{T}_2 \rightarrow {}^5\text{E}$ transition. The electronic configuration of Fe(II) is d^6 , and it has a spectroscopic ground term of ${}^5\text{D}$. An observed magnetic moment in between 5.0 - 5.5 B.M is usually expected for high spin Fe(II) complexes and low spin complexes are expected to be diamagnetic. However, magnetic moment of 4.49 B.M was observed for this Fe(II) complex.

The complex **3**, in its electronic spectrum at visible region exhibited a lone band at 431 nm ($23,202\text{ cm}^{-1}$, $\epsilon = 150\text{ Lcm}^{-1}\text{mol}^{-1}$), typical of a four coordinate geometry and was assigned to ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ (ν_1). The Co(II) has a d^7 electronic configuration, and a ground term symbol of ${}^4\text{F}$. Magnetic moments value in the range 4.2-4.8 B.M. are expected for a tetrahedral Co(II) compounds. The magnetic moment of 4.01 B.M. obtained for this complex corroborated its geometry (Grawal *et al*, 2013, Kane *et al*, 2016).

Ni(II) complexes usually exhibit a complicated equilibria between a six-coordinate (octahedral) and four-coordinate (tetrahedral/square-planar) geometries (De Souza *et al*, 2004, Manuel *et al*, 2005). The complex **4** showed a single absorption band at 423 nm ($23,641\text{ cm}^{-1}$, $\epsilon = 160\text{ Lcm}^{-1}\text{mol}^{-1}$), typical of a four coordinate geometry and assigned to ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$ transition (Kumar *et al*, 2015, Nagajothi *et al*, 2013). The Ni(II) is a transition metal with d^8 electronic configuration and a ground state term symbol ${}^3\text{F}$. The room temperature magnetic moments expected for tetrahedral Ni(II) complex is in the range 3.7 - 4.0 B.M; while low spin octahedral or tetrahedral/square-planar Ni(II) should be diamagnetic. The observed moments for this complex is 3.39 B.M, and a four coordinate tetrahedral/square-planar geometry was proposed (Chohan *et al*, 2004, Andrae *et al*, 1997).

The complex **5**, gave an absorption band at 423 nm ($23,641\text{ cm}^{-1}$, $\epsilon = 800\text{ Lcm}^{-1}\text{mol}^{-1}$), assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_{1g}$ transition of a four coordinate square-planar geometry (Bennetti *et al*, 1999, Bennemans *et al*, 2005, Nagojothi *et al*, 2013). The electronic configuration of Cu(II) is d^9 ; thus, a spectroscopic ground state term symbol ${}^2\text{D}$. 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 ($\mu_{\text{so}} = 1.73\text{ B.M}$), due to orbital contribution and spin-orbit coupling. For this study, the Cu(II) complex had a moment of 1.75 B.M, complimentary of a square-planar geometry (Grawal *et al*, 2013, DeSouza *et al*, 2004, Gopal *et al*, 2013).

Complex **6**, showed one absorption band at 334 nm ($29,940\text{ cm}^{-1}$, $\epsilon = 7900\text{ Lcm}^{-1}\text{mol}^{-1}$), assigned to MLCT transition. (Figure 2). Since Zn(II) has a completely filled 3d orbital, no d-d transition is expected. Its diamagnetic nature confirmed the tetrahedral geometry proposed (Kane 2016, Figs 1960, Kumor 2015, Manuel 2005).

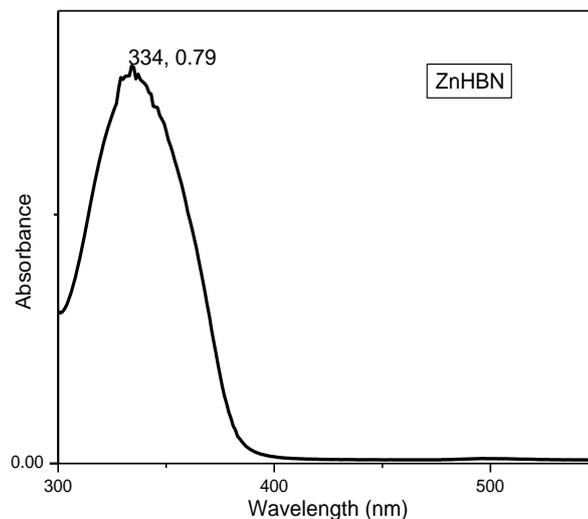


Figure 2. Electronic spectrum of complex 6

The relative molecular mass of the six complexes were determined by Liquid Chromatography-High Resolution Mass Spectrometry with Electro Spray Ionization method {LC-HRMS (ESI)}. The results of the mass spectra for the complexes are presented in Table 5.

The LC-HRMS (ESI) spectra of all the 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. The complexes **1**,

2, and **3** exhibit peak at m/z 460.2768 (found), 459.28 (calc.); 461.2811 (found), 460.19 (calc.) and 446.2899 (found), 445.26 (calc.) respectively.

Furthermore, the m/z peak at 464.1249 (found), 463.03 (calc.); 450.80 (found), 449.87 (calc.) and 452.67 (found), 451.71 (calc.) were assigned to complexes **4**, **5** and **6** respectively.

Thus, the mass spectral studies in addition to other spectroscopic measurements, corroborate the molecular formulae and the proposed structures of the complexes.

The proton NMR and carbon-13 NMR were recorded in deuterated DMSO and only the diamagnetic Zn(II) mixed ligand complex **6** was determined. The results are presented in Figures I and II. The ^1H NMR spectra gave a sharp singlet characteristic peak at 2.51 ppm (s, 6H, $-\text{NC}_2\text{H}_6$) which corresponds to the six protons of the two methyl group attached to the N atom of the dithiocarbamate moiety of the complex. The one proton attached to the C-12 contained in the β -diketone moiety of the complex showed up at a peak of 7.87 ppm.

Moreover, peaks in the region 7.56-7.85 ppm were assigned to three protons of the naphthyl ring in the 4,4,4-trifluoro-(2-naphthyl) butanedione moiety of the complex, other three protons appeared in the region 8.05-8.12 ppm; while the signal at 8.52 ppm established the seventh proton of the naphthyl ring in the whole complex.

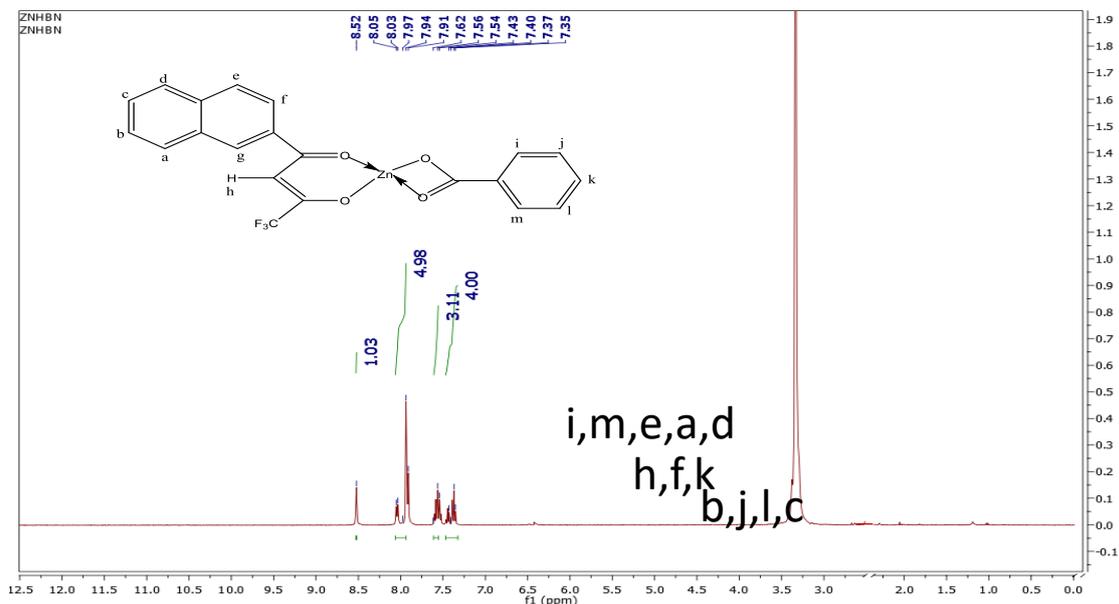
The carbon-13 NMR spectra of the complex **6** exhibited signals at 45.30 ppm, assigned to C-16 and C-17 ($-\text{NC}_2\text{H}_6$) of dithiocarbamate moiety of the complex while the signal for C-12 of the β -diketone moiety appeared in the spectra at 90.74 ppm. The naphthyl ring plus the β -diketone moiety carbons showed signals at different chemical shifts, because of their different environment. The C-1, C-6, C-4 and C-14 signals appeared in the region 124.27-128.08 ppm; C-2, C-5 and C-7 in the region 128.50-129.58 ppm, whereas signals for C-9, C-8, C-3 and C-10 showed up in the region 130.28-136.20 ppm.

Furthermore, signals at 172.21, 190.39 and 197.40 ppm were ascribed to C-11, C-13 and C-15 of the whole complex respectively.

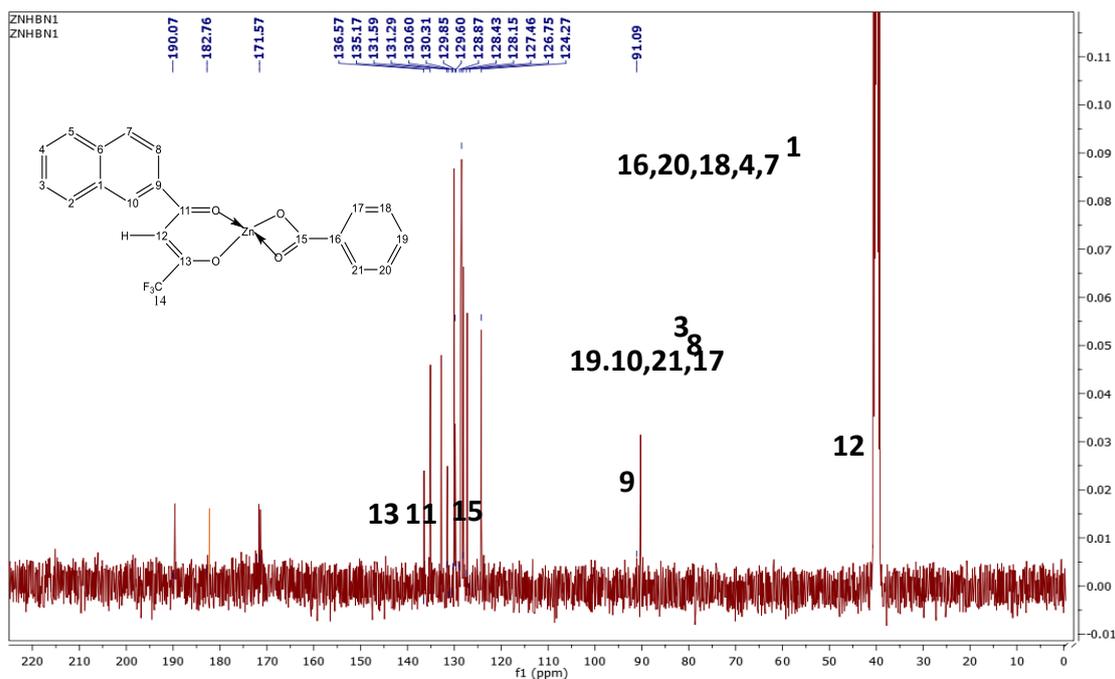
Based on this information of the proton NMR and carbon-13 NMR assignments of the Zn(II) mixed ligands complex and some other spectroscopic measurements data, the proposed structure or geometry was formulated as shown in Fig.1.

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 the six complexes are presented in Fig. 3. 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 – 700 °C or 800 °C.



(a)



(b)

Figure 3. ^1H (a) and ^{13}C NMR (b) spectra of Zn(II) mixed ligand complex in d_6 -DMSO

The thermal stability of the metal complexes at specific temperatures are greatly considered in this study. Three phases decomposition pattern were observed for all the complexes except complex **5**, which only exhibit two stage decomposition pattern. Complex **1** starts with loss of hydrated water and part of ligand **L** moiety at temperature range 30-140 °C in its first stage of decomposition. The complete removal of ligand **L**¹ moiety at 170-370 °C characterized its second stage while the final stage was attributed to the loss of the remaining part of ligand **L** moiety at temperature range of 370-700 °C. In the first stage of complexes **2** and **4**, a detectable change in the curves at 45 to 100 °C, corroborate the loss of 1 mole of hydrated water. The second stage correspond to loss of ligand **L** moiety at temperature range of 100-300 °C; while at the final stage, the ligand **L**¹ moiety were completely removed within 300-700 °C. For complexes **3** and **6**, ligand **L**¹ moiety were first removed at 30-210 °C, followed by the loss of fraction of ligand **L** moiety within temperature range of 210-360 °C; and finally the remaining fractions of **L** moiety were removed at

360-610 °C.

In all cases, the final products left as residue are either oxides of the metal or metal with carbon fragment oxidized to CO₂, and hydrogen being lost as a gas.

Thus, the thermal studies of all these complexes from their curves were in good agreement with their proposed structures and their molecular formulae.

Antioxidant property studies

The antioxidant studies of all the metal(II) complexes of Benzoic acid, **L** and 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione, **L**¹ were carried out using 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.

In this study, all the metal(II) complexes show good inhibitory activities in the range 54.62 - 79.65 % with the Co(II) as the highest and Fe(II) the lowest. The Zn(II) complex had exactly the same activity (56.20 %) with the standard, ascorbic acid while Fe(II) complex was only 1.58 % difference below it.

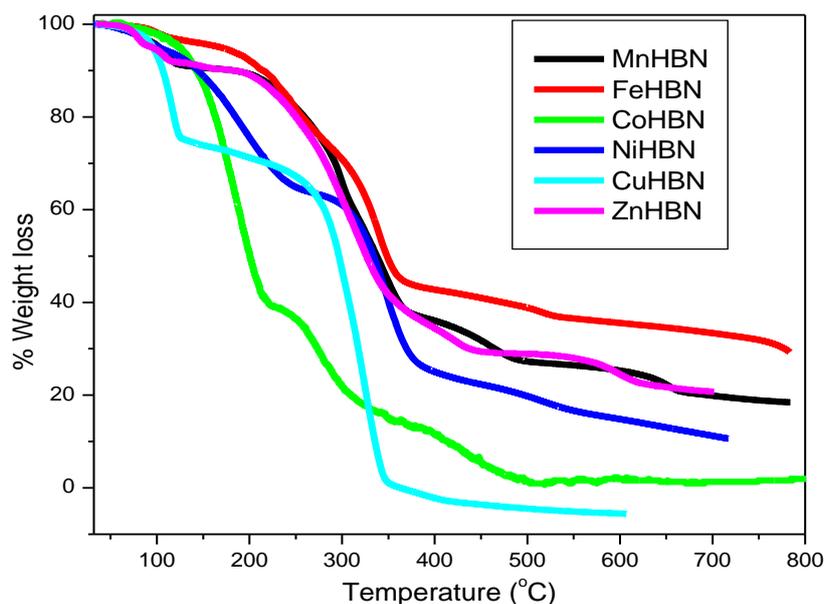


Figure 4. Comparative TGA plots of the complexes 1, 2, 3, 4, 5 and 6 showing their stability order

Thus, the metal complexes of **L** and **L**¹ might be potential therapeutic agents in treatment of some neurodegenerative or heart diseases and cancer in the medical field. Also, they might find application in the industries as preventive agents against oxidation and damage of industrial materials that are exposed to light and oxygen.

4. Conclusion

The spectroscopic results, most especially infrared spectroscopy, revealed that the β -diketones and benzoic acids were bidentate, coordinating to the metal ions through the oxygen atoms of the carbonyl and the enol/hydroxyl groups.

The assignment of six-coordinate (octahedral) and four-coordinate (tetrahedral/square-planar) geometries for the metal(II) mixed-ligand complexes, and in some, occurrence of an interesting magnetic properties of spin-crossover and antiferromagnetism were supported by electronic spectral measurements, magnetic moments, percentage metal and elemental analysis. Their relative molecular masses, the formulations for each complexes and their thermal stability were corroborated by mass spectroscopy, elemental analysis and thermal studies.

The complexes were all mostly soluble in DMF and DMSO. However, all the complexes were non-electrolytic in nature as confirmed by conductivity measurements.

The antioxidant studies for all the complexes confirm the position of most of these metal(II) mixed-ligand complexes having the same activity as the standard, ascorbic acid (56.20%) or greater percentage scavenging inhibition in the range 56.20-81.24%. The Zn(II) complex of mixed-ligand of benzoic acid with

4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione has the same activity as the standard, ascorbic acid. Thus, these complexes have potential as therapeutic agents that could be used as supplement in the treatment of some diseases such as cancer and neurodegenerative ones.

Table 1. Physical properties/analytical data of the ligands and their complexes

Ligand/complexes (Molecular formulae)	Formula weight (g)	Yield wt (%)	Colour	M.pt/ *(°C)	% Metal Theo.(Exp)	^M
TfNBD (L ¹) (C ₁₄ H ₉ O ₂ F ₃)	266.22	-	Light yellow	72-74	- -	-
BZA (L) (C ₇ H ₆ O ₂)	122.12	-	White	120-121	- -	-
[MnLL ¹].H ₂ O (1) (C ₂₁ H ₁₅ F ₃ MnO ₅)	459.2808.31	1.02 (45)	yellow	148-150	11.96 (12.31)	12.15
[Fe LL ¹].H ₂ O (2) (C ₂₁ H ₁₅ F ₃ FeO ₅)	460.19	1.04 (46)	Brown	138-140	12.14 (12.51)	19.40
[CoLL ¹] (3) (C ₂₁ H ₁₃ CoF ₃ O ₄)	445.26	0.81 (37)	Yellow	126-128	13.24 (13.20)	19.16
[NiLL ¹].H ₂ O (4) (C ₂₁ H ₁₅ F ₃ NiO ₅)	463.03	0.98 (43)	Mint- green	152-154	12.68 (12.21)	15.44
[CuLL ¹] (5) (C ₂₁ H ₁₃ CuF ₃ O ₄)	449.87	1.03 (47)	Olive- green	218-220	14.13 (14.24)	16.40
[ZnLL ¹] (6) (C ₂₁ H ₁₃ F ₃ O ₄ Zn)	451.71	1.30 (59)	White	180-182	14.47 (14.65)	12.60

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

Table 2. Elemental analyses data of the metal complexes

Complexes	% Calculated (% Found)		
1	11.96 (12.31)	54.92 (54.69)	3.29 (3.17)
2	12.14 (12.51)	54.81 (54.60)	3.29 (3.16)
3	13.24 (13.20)	56.65 (56.67)	2.94 (2.96)
4	12.68 (12.21)	54.47 (54.80)	3.27 (3.41)
5	14.13 (14.24)	56.07 (55.99)	2.91 (2.87)
6	14.47 (14.65)	55.84 (55.70)	2.90 (2.86)

C = Carbon, H = Hydrogen.

Table 3. Infrared spectra data of the ligands and complexes

Ligands/Complex	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{O}-\text{H})$	$\nu(\text{C}-\text{F})$	$\nu(\text{M}-\text{O})$
L ¹	-	1597, s	1189, s	3066, b	1274, s	
L	-	1673, s	1285, s	3074, b	-	
1	3389, b	1595, s 1660, s	1179, s 1183, s	3068, wb	1292, s	583, s 467, s 403, s
2	3418, b	1588, s	1178, s 1198, s	3056, wb	1299, s	583, s 467, s 409, s
3	3544, b	1603, s	1190, s	3063, wb	1299, s	547, s 467, s
4	3375, b	1603, s	1183, s	3071, wb	1292, s	583, s 467, s
5	-	1595, s	1183, s	3063, wb	1292, s	525, s
6	3367, b	1599, s	1183, s	3060, wb	1295, s	583, s 467, s

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

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

Ligands /Complexes	Absorption regions (nm)(cm ⁻¹) (ϵ)			Assigned Transitions	Geometry	μ_{eff} . (B.M)
L ¹	267 283 333	37,453 35,336 30,030		$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
L	272 280	36,765 35,714		$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	-	-
1	267 294 339 417	37,453 34,014 29,499 23,981	7100 3600 7200 150	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ ${}^6A_1 \rightarrow {}^4E(G)$	Tetrahedral	5.82
2	294 350 472	34,014 28,571 21,186	2100 2400 400	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ ${}^5T_2 \rightarrow {}^5E$	Tetrahedral	5.49
3	281 331 431	35,587 30,211 23,202	6000 8000 150	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ ${}^4T_1(F) \rightarrow {}^4T_2(F)$	Tetrahedral	4.01
4	292 344 423	34,247 29,070 23,641	5700 8900 160	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ ${}^3A_2 \rightarrow {}^3T_2$	Tetrahedral/ Square-planar	3.39
5	293 339 423	34,130 29,499 23,641	4800 5900 130	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ ${}^2B_{1g} \rightarrow {}^2E_{1g}$	Tetrahedral/ Square-planar	1.75
6	334	29,940	7900	MLCT	Tetrahedral	D

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

Table 5. Mass spectra data of the metal(II) complexes

Complexes Chemical formulae	Molecular Mass (Calculated)	Observed Mass (Experimental) M+1
1	459.2808.31	460.2768
2	460.19	461.2811
3	445.26	446.2899
4	463.03	464.1249
5	449.87	450.8051
6	451.71	452.6739

Table 6. Antioxidant data of the metal(II) complexes

Complexes Chemical formulae	Absorbance (STDEV)	% Scavenging Inhibition
1	0.133(\pm 0.005774) 0.110	62.48
2	0.117(\pm 0.005774)	54.62
3	0.17(\pm 0.01)	79.65
4	0.163(\pm 0.005774)	76.55
5	0.153(\pm 0.005774)	71.86
6	0.12(\pm 0.01)	56.20
Ascorbic acid (standard)	0.12(\pm 0.01)	56.20

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