



Research Paper

# Thermal, antioxidant and spectroscopic studies of six new mixed-ligand metal complexes using benzoyl acetone and dimethyl dithiocarbamates

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## Abstract

Six new mixed-ligand complexes of  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  using dimethyldithiocarbamate (L) and benzoylacetate (L1) as ligands have been prepared. The complexes were obtained in appreciable yields. The spectroscopic studies of the complexes revealed that the complexes all, except, the  $Zn^{2+}$  which is diamagnetic, have octahedral geometries. Mass spectrophotometric studies of the complexes revealed that the  $m/z$  peaks of the  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  complexes are 355.34, 415.24, 394.76, 394.73, 381.97 and 365.81, respectively. The anti-oxidant studies showed that the complexes are good anti-oxidant. They are all thermally stable.

**Keywords:** dithiocarbamate, benzoyl acetone, mixed ligand, antioxidant, thermogravimetric

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## I. Introduction

The availability of new metal-organic complexes that are found to possess new application are frequently reported (Chohan *et al.*, 2000); Deshmukhet *et al.*, 2011), John *et al.*, 2006); Kane *et al.*, 2016). This because most of these new metal complexes present striking structural features and usefulness (Cotton *et al.*, 1990); Geary *et al.*, 1971); Halimehjaniet *et al.*, 2010); Hemmila *et al.*, 1991).

Interestingly, the coordination of metal ions or atoms with ligands have found applications in chemical (Deshmukhet *et al.*, 2011); Housecroft *et al.*, 2005), biological (Deshmukhet *et al.*, 2011), electrochemical (Housecroft *et al.*, 2005), medical, agricultural, environmental, biochemical and catalytic processes or fields; both in nature and industry (Hansen *et al.*, 2017); Heller *et al.*, 2017); Kwiatkowski *et al.*, 1980); Lenice *et al.*, 2006); Pavia *et al.*, 2011).

Carbamates and benzoyl acetones derivatives metal complexes are among these type of compounds that are invoking special interest for their preparation and investigation of properties of their new compounds Heller *et al.*, 2017); Kwiatkowski *et al.*, 1980); Lenice *et al.*, 2006); Pavia *et al.*, 2011).

Organic dithiocarbamates and their metal complexes have been reported to possess: antibacterial (Chohan *et al.*, 2000); antifungal (Ekennia *et al.*, 2015); Kane *et al.*, 2016), antioxidant and anticancer activity ((Chohan *et al.*, 2000); and in the industry, they are used as catalyst in the sulphur vulcanisation of rubber (Kwiatkowski *et al.*, 1980).

Transition metal dithiocarbamate complexes have been synthesized and studied extensively by a large number of researchers (Hogarth *et al.*, 2012). The study of metal dithiocarbamate complexes aroused special interest because of their impressive (due to their resonance structure and various mode of coordination) and distinctive structural features such as the slightly distorted square planar structure reported for Ni(II) bis-dithiocarbamate John *et al.*, 2006); (Methaq e *et al.*, 2013) and diverse areas of applications e.g. industrial (Godwin *et al.*, 20004); biological (John *et al.*, 2006), medical) and agricultural fields (Ekennia *et al.*, 2015); Geary *et al.*, 1971). Several number of aliphatic and aromatic dithiocarbamate transition metal complexes have been synthesized and characterized in the past few years (Bonatiet *et al.*, 1967); Hacker *et al.*, 1993); Hemmila *et al.*, 2006); Lennie *et al.*, 2006).

Recently, we reported the synthesis, characterization and anti-oxidant properties of 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 (Fabiyyet *et al.*, 2019). Our interest in this field has been sustained because of the striking features revealed these complexes.

Hence, in this present studies, we have expanded this field to prepare and study new carbamates and benzoyl acetones metal complexes of Cu(II), Fe(II), Cu(II), Zn(II), Co(II), and Ni(II).

## **II. Reagents and Synthesis**

### **2.1. Reagents**

All reagents used were Analar grade and used as supplied by without further purification.

### **2.2. Synthesis of the mixed ligand metal(II) complexes**

The mixed-ligand metal(II) complexes were prepared using the following concentrations of the solution of the corresponding hydrated salts as follows:

$3.42 \times 10^{-3}$  moles, 0.64 g of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ;  $5.22 \times 10^{-3}$  moles, 0.48 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ;  $4.36 \times 10^{-3}$  moles, 0.74 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ;  $3.83 \times 10^{-3}$  moles, 0.52 g of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ;  $4.64 \times 10^{-3}$  moles, 0.64 g of  $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ .

Each of these were added neat to a stirring 10 mL 50% ethanolic solution of 0.60 g ( $4.189 \times 10^{-3}$  moles) sodium dimethyl dithiocarbamate(**L**) and 0.68 g ( $4.189 \times 10^{-3}$  moles) of benzoyl acetone (**L**<sup>1</sup>) while stirring on a magnetic stirrer in separate flasks. The resulting coloured homogenous solutions were left for 6 hours at room temperature. The respective coloured precipitate formed were filtered under gravity, washed with 50% ethanol, dried with diethyl ether, stored in a clean well-labelled sample containers, kept and further dried over silica gel or  $\text{CaCl}_2$  in a desiccator.

### **2.3. Physicochemical measurements**

The room temperature magnetic susceptibilities of the mixed ligand metal(II) complexes at 302-304 K were measured on Sherwood Susceptibility Balance MSB Mark 1.

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

Absorption spectra of the solution of the ligands and the mixed ligand metal(II) complexes in DMF (1mmol) 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;  $4000\text{-}600 \text{ cm}^{-1}$ ).

The elemental analyses, CHNS of the mixed ligand metal(II) complexes are recorded on ElementarAnalysenSysteme GmbH Vario EL-III instrument.

The thermogravimetric analyses (TGA/DTA) of the mixed ligand 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  $10 \text{ }^\circ\text{C}/\text{min}$ . and a Shimadzu DTG-60 instrument at a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ . under nitrogen atmosphere. Computational work was done by personal computer (PC) with Microsoft Excel Program and Microcal Origin 6.0 software.

The cyclic voltammograms of some of the mixed ligand metal(II) complexes were recorded in DMF ( $1 \times 10^{-3}$  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)

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 determinations of the anti-oxidant properties of the mixed ligand metal(II) complexes were done through the ferrous-ion chelating assay by the standard colorimetric method.

## **III. Results and Discussion**

The summary of the results of the physical properties, percentage metal and CHNS, molar conductance determination, Infrared (IR) and electronic spectra with magnetic moment measurements, mass spectra, <sup>1</sup>H and <sup>13</sup>C NMR spectra, thermal analysis and antioxidant studies are shown in Tables 1 - 7 and Figures 1 - 5.

All the 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. The molar conductance values of the complexes in DMF ( $1 \times 10^{-3}$  M solution) were in the range  $11.28 - 18.24 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  indicating their non-electrolytic nature, since the values were below  $60 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  reported for 1:1 electrolyte (Bonati e *et al.*, 1967).

**Table 1: Physical properties/analytical data of the ligands L, L<sup>1</sup> and their metal complexes.**

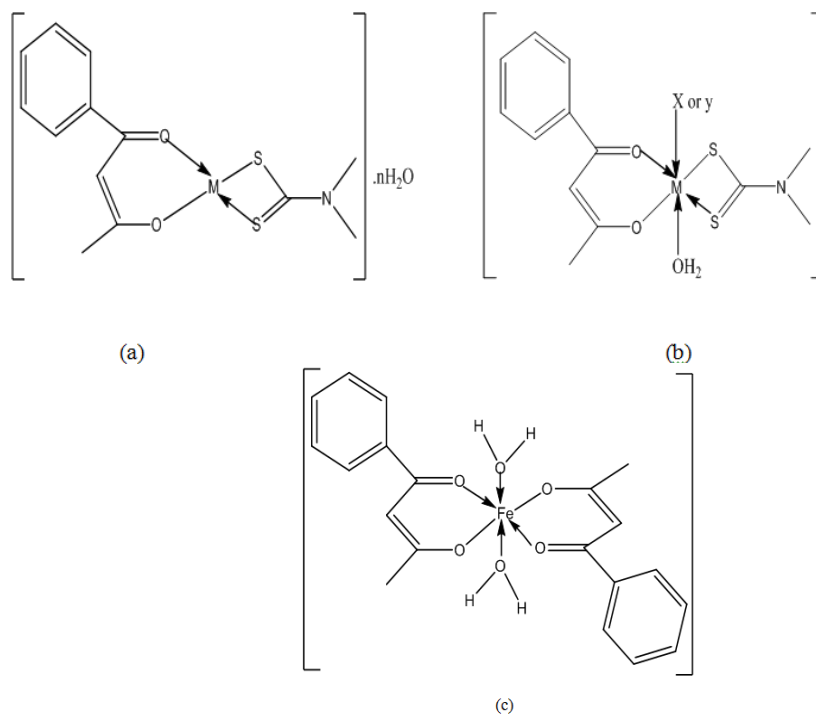
| Ligand/complexes<br>(Molecular formulae)  | Formula Weight<br>(g) | Yield<br>(% yield) | Colour              | M.pt/ *<br>(°C) | % Metal<br>Theo. (Exp) | ^M    |
|---|-----------------------|--------------------|---------------------|-----------------|------------------------|-------|
| BAC (L <sup>1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

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 analysis data of the metal complexes**

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

The selected IR data of the ligands **L** and **L<sup>1</sup>** and their complexes **1, 2, 3, 4, 5, and 6** are presented in Table 3.

The IR spectra provide valuable information regarding the type and nature of functional group(s) present in the free ligand(s); and the mode of coordination between the ligand(s) and the metal atom/ ion. The IR spectra of the free ligands **L** and **L<sup>1</sup>** were compared with those of their metal(II) complexes in order to determine the coordination sites at which they were coordinated to the metal atom/ion.

The appearance of broad bands in the spectra of all the metal(II) complexes in the range 3331-3548 cm<sup>-1</sup> were attributed to the presence of coordinated/ crystallization water assigned as  $\nu(\text{OH})$  of H<sub>2</sub>O. The observance of a weak, broad band in the spectrum of ligand **L<sup>1</sup>**, at 3056 cm<sup>-1</sup> has been assigned to the O-H stretching vibration in its enol form (El-Sombatiet al., 2012). This band shifted from 3056 cm<sup>-1</sup> to 3003-3055 cm<sup>-1</sup> in all the metal(II) complexes. The  $\nu(\text{C}=\text{O})$  and the  $\nu(\text{C}-\text{O})$  strong bands of the ligand **L<sup>1</sup>**, suffered bathochromic shift from 1595 cm<sup>-1</sup> and 1256 cm<sup>-1</sup> to 1541- 1586 cm<sup>-1</sup> and 1227-1254 cm<sup>-1</sup> 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 Ekenniaet al., 2015); Osowoleet al., 2015)<sup>(41)</sup> that a weak, broad O-H stretch is observed for enol form of  $\beta$ -diketone at 3200 - 2400 cm<sup>-1</sup> and hydrogen bonded carbonyl groups in enol forms are often observed in the region 1640 - 1570 cm<sup>-1</sup>; and this intra-molecular hydrogen bonding effect was also established by other researchers( Cotton et al., 1999). Thus, ligand **L<sup>1</sup>** behaves as a bidentate ligand by complexation through the carbonyl oxygen and C-3 enolic hydroxyl groups Osowoleet al., 2015).

Furthermore, the appearance of a band at 1234 cm<sup>-1</sup> assigned as  $\nu(\text{C}-\text{N})$  of the ligand **L**, overlapped with the  $\nu(\text{C}-\text{O})$  bands in the metal(II) complexes. The  $\nu(\text{C}=\text{S})$  and  $\nu(\text{C}-\text{S})$  in the ligand **L** at 960 cm<sup>-1</sup> and 845 cm<sup>-1</sup>, experienced hypsochromic shift to 965-998 cm<sup>-1</sup> and 764 - 847 cm<sup>-1</sup> in all the metal(II) complexes due to the coordination of the two sulphur atoms to the metal ion (Furniss, 2011)(10) in a bidentate mode. The bands present in the range 2848- 2927 cm<sup>-1</sup> were assigned due to  $\nu(\text{C}-\text{H})$  stretching vibrations of the methyl group in the ligands and all the metal(II) complexes. The  $\nu(\text{M}-\text{O})$ ,  $\nu(\text{M}-\text{S})$  and  $\nu(\text{M}-\text{Cl})$  bands were absent in the ligands, but they appeared in the spectra of the complexes at the range 515-581 cm<sup>-1</sup>, 411-446 cm<sup>-1</sup>, and <400 cm<sup>-1</sup> respectively, confirming coordination in all the metal(II) complexes. The actual values of  $\nu(\text{M}-\text{Cl})$  were not observed, since it usually falls below 400 cm<sup>-1</sup>, due to the spectral range of our measurements. However, these bands,  $\nu(\text{M}-\text{O})$ ,  $\nu(\text{M}-\text{S})$  and  $\nu(\text{M}-\text{Cl})$  has been reported to be found around 419-586 cm<sup>-1</sup>, 365- 465 cm<sup>-1</sup>, and 352-387 cm<sup>-1</sup> respectively (Chohanet al., 2004); Ekenniaet al., 2015).

**Table3: Infrared Spectra data of the ligands and the metal complexes**

| Ligands / Complexes        | $\nu(\text{OH})$ / H <sub>2</sub> O | $\nu(\text{C}=\text{O})$ | $\nu(\text{C}-\text{O})$ / $\nu(\text{C}-\text{N})$ | $\nu(\text{C}=\text{S})$ | $\nu(\text{C}-\text{S})$ | $\nu(\text{O}-\text{H})$ enol | $\nu(\text{C}-\text{H})$ Alkyl | $\nu(\text{M}-\text{O})$ | $\nu(\text{M}-\text{S})$ / $\nu(\text{M}-\text{Cl})$ |
|----------------------------|-------------------------------------|--------------------------|---|--------------------------|--------------------------|-------------------------------|--------------------------------|--------------------------|--|
| <b>L<sup>1</sup></b> (BAC) | -                                   | 1595s                    | 1256s   | -                        | -                        | 3056wb                        | 2921s                          | -                        | -  |
| <b>L</b> (SDTC)            | -                                   | -                        | 1234s   | 960s                     | 845s                     | -                             | 2923s                          | -                        | -  |
| <b>1</b>                   | 3331b                               | 1584s                    | 1227s   | 998s                     | 846s 762s                | 3055w                         | 2912m                          | 569s<br>519s             | 417s   |
| <b>2</b>                   | 3514b                               | 1584s                    | 1277s   | -                        | -                        | 3052wb                        | 2913s<br>2857m                 | 575s                     | -  |
| <b>3</b>                   | 3403b                               | 1586s                    | 1254s   | 977s                     | 847s 756s                | 3050w                         | 2920m<br>2848m                 | 581s<br>515s             | 438s, 422s /<br>< 400                                |
| <b>4</b>                   | 3509b                               | 1541s                    | 1236s   | 969s                     | 764s                     | 3003w                         | 2902m<br>2854s                 | 569s 546s                | 440s, 411s /<br>< 400                                |
| <b>5</b>                   | 3548b                               | 1586s                    | 1240s   | 969s                     | 847s 768s                | 3039w                         | 2920s<br>2854m                 | 554s                     | 446s   |
| <b>6</b>                   | 3437b                               | 1577s                    | 1239s   | 965s                     | 838s 761s                | 3054w                         | 2927s<br>2850m                 | 563s                     | 442s   |

S = strong or sharp, b = broad, m = medium, w = weak, wb = weak, broad.

The electronic spectra of the ligands and their metal(II) complexes 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 - 267 nm (30,303 - 37, 453 cm<sup>-1</sup>) and two shoulder bands at 356 nm (28,090 cm<sup>-1</sup>) and 318 nm (31,446 cm<sup>-1</sup>), assigned to  $\pi \rightarrow \pi^*$  transitions. The two ligands **L<sup>1</sup>** and **L**, exhibited absorption bands at 310 nm, 300 nm and 267 nm; with the energies of 32,258 cm<sup>-1</sup>, 33,333 cm<sup>-1</sup>, and 37,453 cm<sup>-1</sup> 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 (Georgievaet al., 2007).

The complex **1**, [Mn(L)(L<sup>1</sup>)]<sub>2</sub>.H<sub>2</sub>O showed one absorption band at 330 nm (30,303  $\epsilon = 850 \text{ Lcm}^{-1}\text{mol}^{-1}$ ). The spectroscopic ground term symbol of Mn(II) is <sup>6</sup>S and a <sup>4</sup>G upper term, with a d<sup>5</sup> electronic configuration. The Mn(II) complexes are characterized by weak spin forbidden transitions. These weak transitions for an octahedral complex are assigned as: <sup>6</sup>A<sub>1g</sub> →

${}^4T_{2g}(G)$ ,  ${}^6A_{1g} \rightarrow {}^4E_g(G)$ , and  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  transitions (Ekennia et al, 2015)(8). The  ${}^6S$  orbital is non-degenerate, being in a singlet state and cannot split by either a tetrahedral or an octahedral field (Cotton *et al.*, 1966)<sup>(5)</sup>; 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 (Saha *et al.*, 2000). 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 (Raman et al (2004). However, the room temperature magnetic moment of 4.77 B.M obtained in this study, indicating presumably a spin-free tetrahedral geometry ( Chohan *et al.*, 2004).

The electronic spectrum of complex **2**,  $[\text{Fe}(\text{L}^1)_2(\text{H}_2\text{O})_2]$  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 ( $28,090\text{ cm}^{-1}$ ,  $\epsilon = 1600\text{ Lcm}^{-1}\text{mol}^{-1}$ ). Shown in Table 4 and Figure 2. 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 (Howard et al 2015(21), Methaqet *et al.*, 2013), 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  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  ( $\nu_3$ ); and 479 nm ( $20,747\text{ cm}^{-1}$ ,  $\epsilon = 200\text{ Lcm}^{-1}\text{mol}^{-1}$ ), assigned to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  ( $\nu_1$ ). 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:  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  ( $\nu_1$ ),  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  ( $\nu_2$ ) and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  ( $\nu_3$ ). The ( $\nu_2$ ) transition is often not observed but only occurs when the two states cross is very weak. Therefore,  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  ( $\nu_1$ ) and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  ( $\nu_3$ ) transitions are usually observed in the visible region. (Halimehjaniet *et al.*, 2019); Lim *et al.*, 2007). 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. 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 (Ekennia *et al.*, 2015).

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  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  transitions respectively (Halimehjaniet *et al.*, 2010). 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 (Hemnila *et al.*, 1991); Howard *et al.*, 2015); Kumar *et al.*, 2015). 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 ( $\mu_{so} = 1.73\text{ B.M}$ ), due to orbital contribution and spin-orbit coupling. For this study, the Cu(II) complex had a moment of 1.96 B.M, indicative of an octahedral geometry.

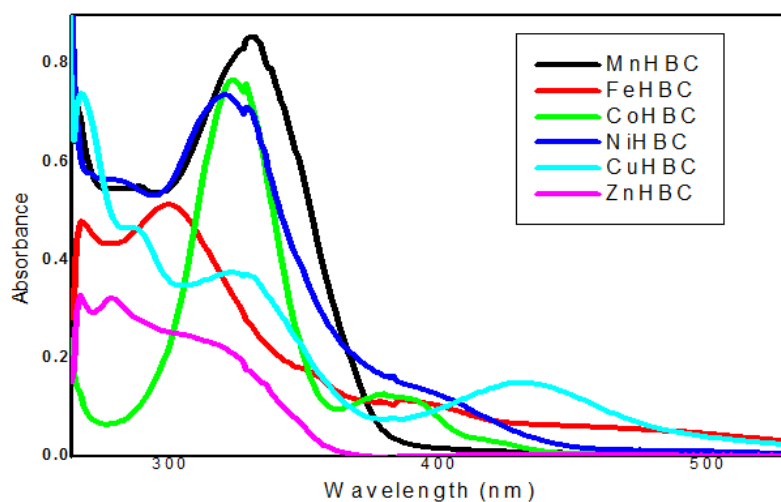
The complex **6**,  $[\text{ZnLL}^1].\text{H}_2\text{O}$ , UV-visible spectrum had one band and a shoulder at 279 nm ( $35,842\text{ cm}^{-1}$ ,  $\epsilon = 320\text{ Lcm}^{-1}\text{mol}^{-1}$ ), and 318 nm ( $31,446\text{ cm}^{-1}$ ,  $\epsilon = 2300\text{ Lcm}^{-1}\text{mol}^{-1}$ ). The Zn(II) has 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 ( $35,842\text{ cm}^{-1}$ ,  $\epsilon = 3200\text{ Lcm}^{-1}\text{mol}^{-1}$ ), and 318 nm ( $31,446\text{ cm}^{-1}$ ,  $\epsilon = 2300\text{ Lcm}^{-1}\text{mol}^{-1}$ ) 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 (Kavitha *et al.*, 2017); Lineceet *et al.*, 2006). The magnetic moment value

obtained for this complex under study was negative, and this indicated that the geometry is tetrahedral geometry.

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

| Ligands /Complexes                                      | Absorption regions |                      |                | Assigned Transitions                      | Geometry    | $\mu_{\text{eff}}$ . (B.M) |
|---|--------------------|----------------------|----------------|---|-------------|----------------------------|
|   | (nm)               | ( $\text{cm}^{-1}$ ) | ( $\epsilon$ ) |   |             |                            |
| BAC ( $L^1$ )<br>$C_{10}H_{10}O_2$                      | 310                | 32,258               |                | $\pi \rightarrow \pi^*$                   | -           | -                          |
| SDTC (L)<br>$C_3H_6NS_2Na$                              | 267                | 37,453               |                | $\pi \rightarrow \pi^*$                   | -           | -                          |
|   | 300                | 33,333               |                | $\pi \rightarrow \pi^*$                   |             |                            |
| (1) $[MnLL^1]_2 \cdot H_2O$<br>$C_{13}H_{17}N S_2O_3Mn$ | 330                | 30,303               | 8500           | $n \rightarrow \pi^*$                     | Tetrahedral | 4.77                       |
| (2) $[Fe(L^1)_2(H_2O)_2]$<br>$C_{20}H_{22}O_6Fe$        | 301                | 33,222               | 5200           | $\pi \rightarrow \pi^*$                   | Octahedral  | 5.02                       |
|   | 356 sh             | 28,090               | 1600           | $n \rightarrow \pi^*$                     |             |                            |
|   | 404                | 24,752               | 1100           | ${}^1A_{1g} \rightarrow {}^1T_{2g}$       |             |                            |
|   | 482                | 20,747               | 500            | ${}^5T_{2g} \rightarrow {}^5E_g$          |             |                            |
| (3) $[CoLL^1(H_2O)Cl]$<br>$C_{13}H_{17}NO_3S_2ClCo$     | 320                | 31,152               | 7400           | $\pi \rightarrow \pi^*$                   | Octahedral  | 3.47                       |
|   | 405                | 24,691               | 1200           | ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ |             |                            |
|   | 479                | 20,877               | 200            | ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ |             |                            |
| (4) $[NiLL^1(H_2O)Cl]$<br>$C_{13}H_{17}NO_3S_2ClNi$     | 324                | 30,864               | 7700           | $\pi \rightarrow \pi^*$                   | Octahedral  | 2.55                       |
|   | 384                | 26,042               | 1300           | ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$    |             |                            |
|   | 425                | 23,529               | 300            | ${}^3A_{2g} \rightarrow {}^3T_{1g}$       |             |                            |
| (5) $[CuLL^1(H_2O)_2]$<br>$C_{13}H_{19}NO_4S_2Cu$       | 327                | 30,581               | 3800           | $\pi \rightarrow \pi^*$                   | Octahedral  | 1.96                       |
|   | 434                | 23,041               | 1500           | ${}^2E_g \rightarrow {}^2T_{2g}$          |             |                            |
| (6) $[ZnLL^1]_2 \cdot H_2O$<br>$C_{13}H_{17}NO_3S_2Zn$  | 279                | 35,842               | 3200           | MLCT                                      | Tetrahedral | D                          |
|   | 318 sh             | 31,446               | 2300           | $\pi \rightarrow \pi^*$                   |             |                            |

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



**Figure 2:** UV-visible spectra of the ligands,  $L$ ,  $L^1$  and their complexes.

The relative molecular mass of the metal(II) complexes 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 . 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.**

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

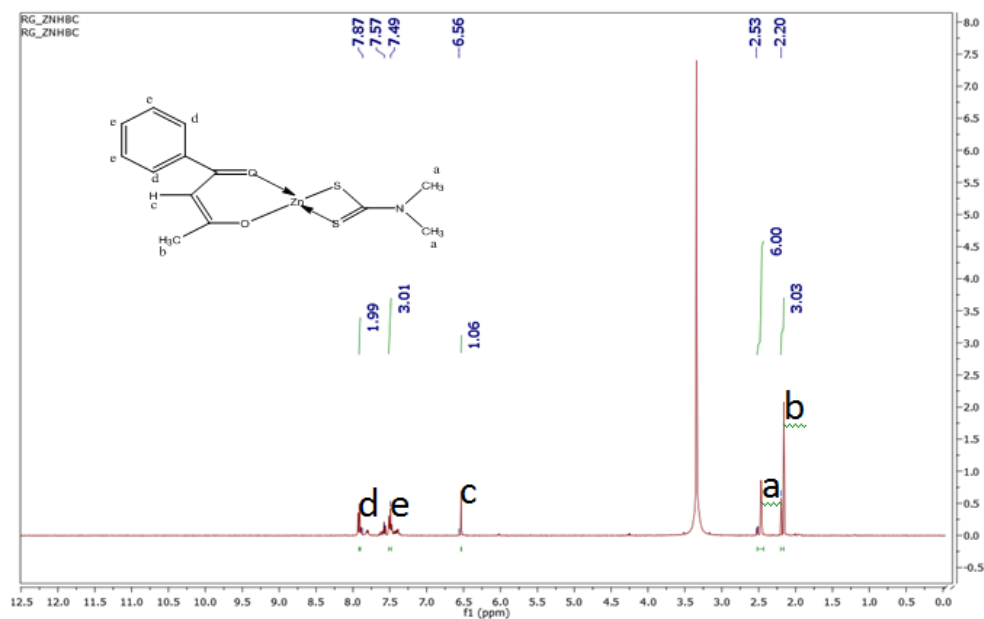
The proton NMR and carbon-13 NMR (Figures 3 and 4) were recorded in deuterated DMSO and only the diamagnetic Zn(II) mixed ligand complex **6** was determined. The <sup>1</sup>H NMR spectra showed a sharp singlet characteristic peak at 2.20 ppm, corresponding to three protons directly attached to C-10 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 dimethyl 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 (C<sub>6</sub>H<sub>5</sub>) 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 (-NC<sub>2</sub>H<sub>6</sub>) 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 (C<sub>6</sub>H<sub>5</sub>) in the complex Sahaet *al.*, 2000)<sup>(44)</sup>.

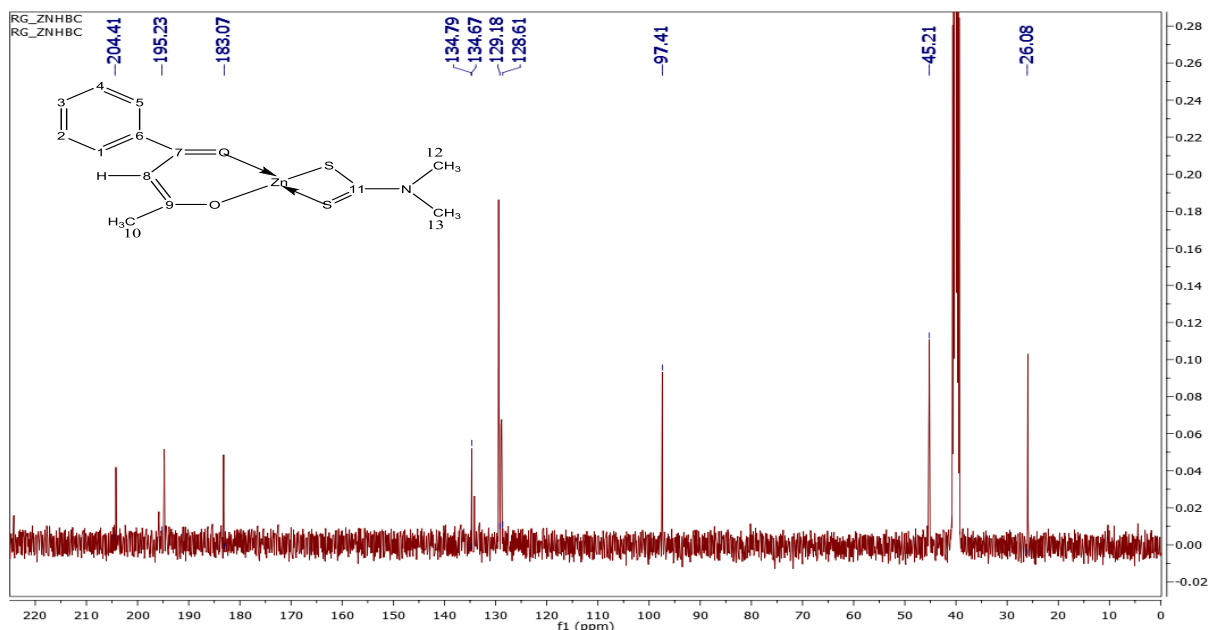
Furthermore, C-7 and C-9 of the benzoyl acetone moiety exhibited two different signals at 183.07 ppm and 195.23 ppm respectively, whereas, the C-11 (C-N) of the dithiocarbamate moiety showed up at a very high signal of 204.41 ppm.

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.



(a)



**Figures 3 (a) and (b):**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of Zn(II) mixed ligand complex **6** in  $d_6$ -DMSO.

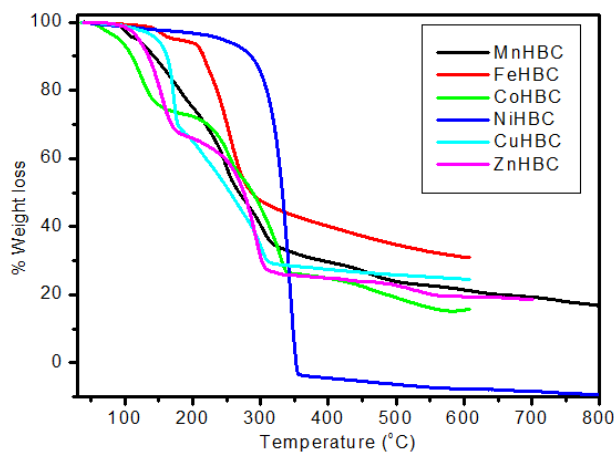
Thermo gravimetric analysis (TGA/DTA) provides useful information about the thermal stability of the metal complexes at specific temperatures. A systematic order for the thermal degradation or decomposition of the complexes, and the percentage or weight/mass loss of water molecules and other molecules 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 Figure 4. The heating rates were properly controlled at  $10\text{ }^\circ\text{C}$  per minute under nitrogen atmosphere at a flow rate of  $200\text{ mL}$  per minute and the temperature range from  $30\text{ }^\circ\text{C}$  –  $700\text{ }^\circ\text{C}$  or  $800\text{ }^\circ\text{C}$ .

The thermal stability of the metal complexes at specific temperatures are greatly considered in this study. It is evident from the thermogravimetric curves (Figure 4.5) 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  $140\text{ }^\circ\text{C}$ ,  $170\text{ }^\circ\text{C}$ , less than  $100\text{ }^\circ\text{C}$ ,  $210\text{ }^\circ\text{C}$ ,  $160\text{ }^\circ\text{C}$ , and  $150\text{ }^\circ\text{C}$  respectively (Perrin *et al.*, 1980)<sup>(42)</sup>.

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  $70\text{ }^\circ\text{C}$  –  $210\text{ }^\circ\text{C}$ , which corroborate the composition of the complexes. They are all thermally stable.

Thus, the comparative TGA curves (Figure 4.6) of the metal complexes reveal their thermal stability in the order:  $\text{Co(II)} < \text{Mn(II)} < \text{Zn(II)} < \text{Cu(II)} < \text{Fe(II)} < \text{Ni(II)}$ . The Ni(II) complex, being the most thermally stable with its smaller ionic radius has been reported (Ekennia *et al.* 2015)(8).



**Figure 5:** Comparative TGA curves of complexes.



### Antioxidant studies

The antioxidant studies of all the metal(II) complexes of dimethyldithiocarbamate, **L** and Benzoyl acetone, **L**<sup>1</sup> 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.

**Table 6: Antioxidant data of the mixed ligand metal(II) complexes of L and L<sup>1</sup>**

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

### IV. Conclusion

The mixed-ligands Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of various β-diketones with N,N'-dimethyl dithiocarbamic and benzoic acids were synthesized. The complexes were characterized by melting point, solubility, magnetic moments and conductivity measurements, percentage metal, elemental (CHNS) analysis, thermal analysis (TGA), UV-Visible, Infrared, Nuclear Magnetic Resonance (<sup>1</sup>H and <sup>13</sup>C), and Mass spectroscopies. The spectroscopic results, most especially infrared spectroscopy, revealed that all the ligands: β-diketones, dithiocarbamic and benzoic acids were bidentate, coordinating to the metal ions through the oxygen atoms of the carbonyl and the enol/hydroxyl groups in β-diketones/benzoic acid and the two sulphur atoms in dithiocarbamic acid.

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.

Furthermore, the antioxidant studies for all the complexes confirm the position of most of these

metal(II) mixed-ligand complexes having the same activity (NiHBC, NiHAC and ZnHBN) as the standard, ascorbic acid (56.20 %) or greater percentage scavenging inhibition (e.gCuHBC, ZnHPC, CoHNC, CoHAC, CoHBN, CuHBP, CuHBA and NiHBB) in the range 56.20 - 81.24 %. The Ni(II) complexes of mixed-ligands; benzoyl acetone/acetyl acetone with dithiocarbamate; and Zn(II) complex of mixed-ligands of benzoic acid with 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione in each case had the same activity as the standard, ascorbic acid. Thus, these complexes had potential as therapeutic agents that could be used as supplement in the treatment of some diseases such as cancer and neurodegenerative ones.

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