



## ORIGINAL ARTICLE

# Novel mono- and binuclear complexes derived from N-benzoyl-N-glycylthiourea (BGH) with some transition metal ions



N. Nawar <sup>a</sup>, I.I. El-Swwah <sup>a</sup>, N.M. Hosny <sup>b</sup>, M.M. Mostafa <sup>a,\*</sup>

<sup>a</sup> Faculty of Science, Mansoura University, Egypt

<sup>b</sup> Faculty of Science, Port Said University, Port Said, Egypt

Received 28 February 2011; accepted 6 June 2011

Available online 22 June 2011

## KEYWORDS

Biological activity;  
Spectroscopic studies;  
N-benzoyl-N-glycylthiourea  
complexes

**Abstract** New metal complexes derived from the reaction of N-benzoyl-N-glycylthiourea (BGH) with Cu(II), Co(II), Ni(II), Zn(II) and Fe(III) chloride and/or acetate salts have been synthesized. The products were characterized by elemental analyses, molar conductivities, spectral (IR, UV–vis., mass, <sup>1</sup>H NMR and <sup>13</sup>C NMR), thermal (TGA, DTG) analyses and magnetic measurements. The IR spectra of the mono- and binuclear complexes have been discussed. The structure of the Zn(II) complex is suggested on the basis of spectral (IR, UV, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass) studies. The geometries of the isolated solid complexes have been suggested on the basis of magnetic and spectral measurements. Also, the data of thermal analysis (TGA) suggests the amounts of solvents existing inside and/or outside the coordination sphere and the mechanism of decomposition for the metal complexes. Finally, the results of biological activity promised to be effective in tumors treatment.

© 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University.

## 1. Introduction

The metal complexes derived from amino acids and their derivatives have important pharmaceutical applications. They have been exploited in cancer multidrug resistance (Sharma and Pivnica-Worms, 1999), tested as antimalarial (Goldberg et al.,

1997) and exhibit antitumor activity (Wang et al., 2005). Also, thiourea derivatives have several important uses in medicine as potent anti-cancer and antiinfluenza agents (Biot et al., 2007; Nair and Sobhia, 2008) but no studies have been carried out recently on the thiourea derivatives involving glycine. The present paper is devoted to study of the coordination chemistry and the spectroscopic behavior of the thiourea and its metal complexes, derived from the reaction of N-benzoyl-N-glycylthiourea (BGH) with Cu(II), Co(II), Ni(II), Zn(II) and Fe(III) chlorides and/or Cu(II), Co(II), Ni(II) and Zn(II) acetates. Also, this study is carried out to shed more light on the behavior of the ligand during complex formation at different pH's.

\* Corresponding author. Tel.: +20 0167446662.

E-mail address: amohsenmostafa@yahoo.com (M.M. Mostafa).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

## 2. Experimental

All the chemicals used in this investigation were of analytical grade and used without further purifications.

### 2.1. Technique

Carbon, hydrogen and metal contents [Cu(II), Co(II), Ni(II), Zn(II) and Fe(III) ions] were determined by the standard methods (Hafez, 1992). Molar conductance measurements of the complexes in DMF and/or water ( $10^{-3}$  M) were carried out with a conductivity bridge YSI model 32. IR spectra were measured using KBr discs on a Mattson 5000 FTIR spectrometer. Calibration of the frequency reading was made with polystyrene film. Electronic spectra were recorded on UV2 Unicam UV/vis. spectrometer using 1 cm stopper silica cells, and the magnetic measurements were carried out at room temperature (25 °C) on a Sherwood magnetic balance. Thermal analyses measurements (TGA, DTG) were recorded on a Shimadzu model 50 instrument using 20 mg samples. The nitrogen flow and heating rates were 20 cm<sup>3</sup>/min and 10 °C/min, respectively. The <sup>1</sup>H NMR spectra of the ligand and Zn(II) complex were determined and recorded on Jeol-90Q Fourier transform (200 MHz) in d<sub>6</sub>-DMSO. <sup>13</sup>C NMR spectrum of the Zn(II) complex was recorded on Bruker FT-100 MHz in d<sub>6</sub>-DMSO at King Abdul Aziz University, Gaddah, Saudi Arabia. Mass spectrum of the ligand was recorded using Shimadzu GC-MS-QP 1000 Ex. at 70 eV Spectrometer.

### 2.2. Biological activity

The ligand was tested as antibacterial agents. Seeded agar plates were prepared by putting 50 ml of inoculated agar into 15 cm petri dishes and allowing them to solidify. Cups were made to receive 25 ml of the solution and allowed to diffuse and incubate at 37 °C for 24 h. Inhibition zone was measured (Gerhardt, 1981) and compared with that of gentamicine solution. The experiment control was DMSO.

### 2.3. Genotoxicity activity

A solution of 2 mg of calf thymus DNA was dissolved in 1 ml of sterile doubly distilled water. Stock concentrations of the investigated ligand were prepared by dissolving 2 mg/ml in DMSO. An equal volume of each compound and DNA were mixed thoroughly and kept at room temperature for 2–3 h. The effect of the chemicals on DNA was investigated using agarose gel electrophoresis. A 2 ml of loading dye was added to 15 ml of the DNA mixture before being loaded into the well of an agarose gel. The loaded mixtures were fractionated by electrophoresis, visualized by UV and photographed.

### 2.4. Preparation of the ligand

The ligand (BGH) was prepared as described earlier in the literature (Li et al., 2003). The elemental analyses of the free ligand (Table 1) as well as the mass (calcd.: 238 and found: 238) and <sup>1</sup>H NMR spectra suggest that the chemical formula is C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>S and a M. Wt. of 238.272.

### 2.5. Metal complexes

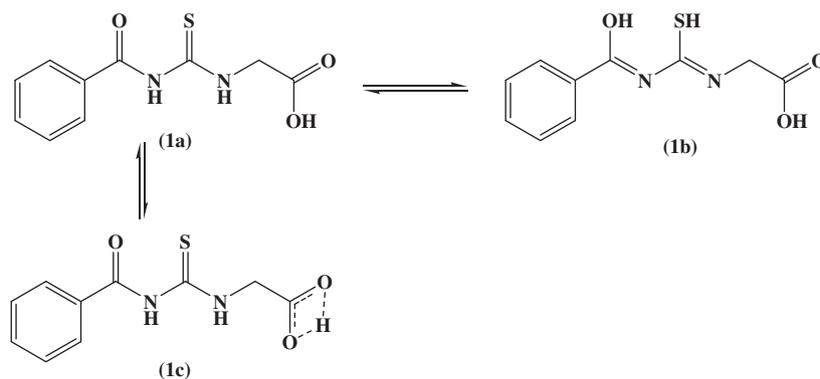
Metal complexes were synthesized by adding equimolar amounts of the hydrated metal salts (0.01 mol) e.g., chloride and/or acetate in 10 cm<sup>3</sup> absolute EtOH to the ligand dissolved in EtOH (25 cm<sup>3</sup>). The reaction mixture was then refluxed on a hot plate for 1 h in case of acetate complexes, but 3–6 h in case of chloride complexes. In case of acetate complexes the pH of the solution ranged from 6 to 6.5 while the pH of the ligand alone was 5. The resulting solid complexes were filtered off, washed successively with EtOH, ether and finally kept in a desiccator over fused calcium chloride. On the other hand, the pH's of complexes derived from the metal chlorides fall in the 1–1.5 region, except for the Ni(II) and Fe(III) complexes in which the pH of the solution reach ~4.0. The reaction mixture was refluxed for at least 3 h then evaporated near dryness and finally the complexes were precipitated by adding dry

**Table 1** Analytical and physical data of the ligand (BGH) and its metal complexes.

Compound	Color	M.p. °C	M. wt.	% Found (calcd.)			
				C	H	M	Cl
H <sub>2</sub> L (BGH) = C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> S	Yellow	198	238.3	50.1 (50.4)	3.7 (4.2)	–	–
[Cu(H <sub>2</sub> L)Cl.(H <sub>2</sub> O) <sub>3</sub> ]. ½H <sub>2</sub> O.Cl (1)	Green	255	435.8	28.2 (27.6)	4.6 (3.9)	14.0 (14.6)	16.3 (16.3)
[Co <sub>2</sub> (H <sub>2</sub> L)Cl <sub>3</sub> (EtOH)].H <sub>2</sub> O.Cl (2)	Blue	140	562.0	25.6 (25.6)	3.4 (3.2)	21.6 (21.0)	24.8 (25.2)
[Ni <sub>2</sub> (HL)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ].2H <sub>2</sub> O.Cl (3)	Yellowish–green	230	605.2	19.1 (19.8)	5.1 (4.2)	20.0 (19.4)	17.5 (17.6)
[Fe <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O) <sub>5</sub> ].7H <sub>2</sub> O.Cl <sub>2</sub> (4)	Brown	> 300	742.4	15.5 (16.2)	5.3 (4.5)	14.3 (15.1)	23.8 (23.9)
Cu <sub>2</sub> (L)(Ac) <sub>2</sub> . ½H <sub>2</sub> O (5)	Green	240	490.4	34.7 (34.3)	3.6 (3.1)	25.7 (25.9)	–
[Co <sub>2</sub> (L)(Ac) <sub>2</sub> (H <sub>2</sub> O) <sub>3.5</sub> ] (6)	Green	240	535.3	31.9 (31.4)	4.6 (4.0)	23.0 (22.0)	–
[Ni <sub>2</sub> (L)(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ].4H <sub>2</sub> O (7)	Yellow	200	565.9	21.2 (21.2)	6.1 (5.3)	19.9 (20.7)	–
[Zn <sub>2</sub> (L)(Ac) <sub>2</sub> ].4EtOH (8)	White	220	669.4	40.9 (39.5)	6.6 (5.7)	19.9 (19.5)	–

**Table 2** The most important IR spectral bands of the ligand (H<sub>2</sub>L) and its metal complexes.

Assignments	H <sub>2</sub> L (KBr)	H <sub>2</sub> L (Nujol)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$\nu(\text{OH})$ free $\nu(\text{OH})$ (H <sub>2</sub> O) and/or EtOH	3445	3631	3450	3496	—	—	—	—	—	—
$\nu$ NH (NH—CO)	3237	3245	3334	3246	3300	3343	3260	3394	3200	3282
$\nu$ NH (NH—CS)	3167	3129	3160	3178	3206	3220	—	—	—	—
N(OH) hydrogen-bonded	2874	—	—	—	—	—	—	—	—	—
$\nu(\text{CO})$ free (carboxylic)	1709	1712	1737	1710	—	1666	—	—	—	—
N(C=O) hydrogen-bonded(carboxylic)	1671	1666	1688	1662	—	—	—	—	—	—
$\nu(\text{CO})$ free attached to C <sub>6</sub> H <sub>5</sub> —	1658	1650	1608	1627	1664	1697	—	—	—	—
$\nu_{\text{as}}(\text{COO})$	—	—	—	—	1630	1621	1581	1567	1582	1600
$\nu_{\text{s}}(\text{COO})$	—	—	—	—	1516	1510	1433	1460	1441	1444
$\nu(\text{C} = \text{N}^*)$	—	—	—	—	—	—	1624	1568	1628	1654
$\Delta(\text{NH})$	1547	1550	1580	1577	1592	—	—	—	—	1475
$\nu(\text{C} = \text{S})$	1484	1461	1473	1442	1443	1476	1464	1438	1485	1396
$\Delta(\text{OH})$	1399	1376	1378	—	—	—	—	—	1388	1288
$\nu(\text{C—O})$	1323	1248	1328	1286	1286	1319	1291	1288	1292	1288
$\nu(\text{C} = \text{S})$	1182	1141	1095	1178	1176	1165	1166	1174	1145	1180
$\rho(\text{OH})$	783	785	792	779	780	780	773	786	751	784
$\nu(\text{M—O})$	915	930	908	—	—	—	—	—	—	—
$\nu(\text{M—S})$	—	—	505	540	505	493	473	478	459	472
	—	—	430	450	—	—	—	—	414	430

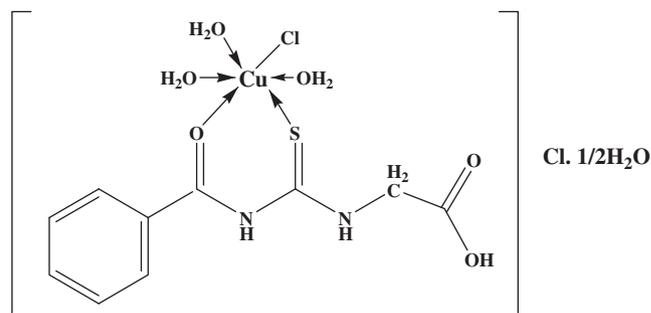
**Figure 1** Scheme represents the tautomeric forms of the ligand.

ether. All the isolated solid complexes were kept in a desiccator over anhydrous CaCl<sub>2</sub>.

### 3. Results and discussion

All the metal complexes are colored, except the Zn(II) complex which was white. Also, they were stable against light and air for more than 12 months and insoluble in most common organic solvents but easily soluble in DMSO and DMF. The molar conductivities in DMF (10<sup>-3</sup> M) at 25 °C for the Cu(II), Co(II), Ni(II) and Zn(II) acetate complexes fall in the range 1.0–10 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicating their non-electrolytic nature. On the other hand, the comparatively high values of molar conductivities of Cu(II), Co(II), Ni(II) and Zn(II) chloride complexes in DMF (40–80 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) suggested 1:1 and/or 1:2 electrolytes (Geary, 1971). The melting points of the metal complexes were in the range of 140–255 °C, except for Fe(III) complex which showed high melting point (> 300 °C). Elemental analyses and some physical properties of the isolated solid complexes are listed in Table 1.

The most important IR spectral bands of the free ligand (BGH) and its metal complexes are recorded in Table 2. The free ligand can be represented in three tautomeric forms, the keto (1a) (free), (1c) (hydrogen-bonded) and the enol (1b) forms as shown in Fig. 1.

**Figure 2** Structure of the Cu(II) complex, [Cu(H<sub>2</sub>L)Cl(H<sub>2</sub>O)<sub>3</sub>]·½H<sub>2</sub>O·Cl (1).

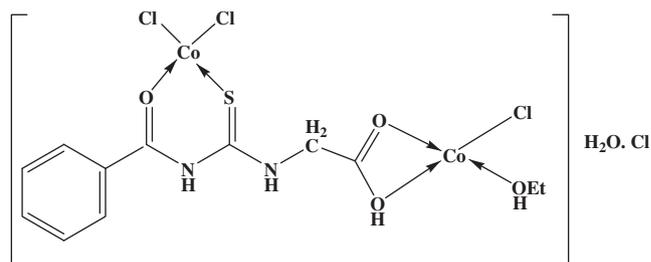
On comparing the IR spectra of the free ligand with that of glycine in Nujol mull, we observed two strong bands at 1712 and 1666  $\text{cm}^{-1}$  in the spectrum of BGH (KBr) assignable to free  $\nu(\text{C}=\text{O})$  and hydrogen-bonded  $\nu(\text{C}=\text{O})$  vibrations, respectively. This indicates the existence of hydrogen bonding between the  $\text{C}=\text{O}$  and  $\text{OH}$  of the carboxylic group. The 1658  $\text{cm}^{-1}$  band is attributed to the  $\text{C}=\text{O}$  attached to  $-\text{C}_6\text{H}_5$  group. The IR spectrum of the free ligand in KBr shows four bands at 3445, 2874, 3237 and 3167  $\text{cm}^{-1}$ . The first two bands are assigned to the  $\nu(\text{OH-free})$  and  $\nu(\text{OH-hydrogen-bonded})$  vibrations while the other two bands are assigned to  $\nu(\text{NH-CO})$  and  $\nu(\text{NH-CS})$  vibrations, respectively. Finally, the two bands observed at 1182 and 783  $\text{cm}^{-1}$  are attributed to  $\nu(\text{C}=\text{S})$  (Nakamoto, 1970) vibrations. The hydrogen bonding between the  $\text{C}=\text{O}$  and the  $\text{OH}$  groups of the carboxylic moiety seems to be strong of the type  $\text{O}-\text{H}\cdots\text{O}$  (Fig. 1c). This is approved by the negative acidity test when the ligand is dissolved in water. On the other hand, the IR spectrum of the free ligand in Nujol mull shows the obscurity of the hydrogen bonding together with the appearance of a strong band at 3631  $\text{cm}^{-1}$  due to the free  $\nu(\text{OH})$  vibration as well as the disappearance of the band at 2874  $\text{cm}^{-1}$  due to the hydrogen-bonded (OH) of the carboxylic group. The most important assignments of the free ligand and its metal complexes are listed in Table 2. The  $^1\text{H}$  NMR spectrum of the free ligand in  $d_6$ -DMSO shows several signals at 4.3 (doublet), 7.5–8.5 (multiplet), 10.83 (singlet), 11.2 (singlet), 11.5 (singlet) and 13.8 (singlet broad) ppm, with respect to TMS, assigned to the protons of  $\text{CH}_2$ ,  $\text{C}_6\text{H}_5$ ,  $(\text{NH}-\text{CH}_2)$ ,  $(\text{NH}-\text{CO})$ ,  $\text{OH}$  (free) and  $\text{OH}$  (hydrogen-bonded), respectively. These may be taken as additional evidence that the ligand is mainly existed in the keto form (Fig. 1a). The broad signal at 13.8 ppm suggests that the  $\text{OH}$  is hydrogen-bonded to the carbonyl oxygen (Fig. 1c). Also, this suggests that the ligand involves a strong hydrogen-bond even on dissolving in  $d_6$ -DMSO. The electronic spectrum of the free ligand in Nujol mull shows seven bands at 36496, 34483, 33557, 31447, 28763, 27933 and 23148  $\text{cm}^{-1}$  assigned to  $n \rightarrow \pi^*$  ( $\text{CO}$ ,  $\text{COOH}$ ),  $n \rightarrow \pi^*$  ( $\text{CO}$ ,  $\text{Ph}$ ),  $n \rightarrow \pi^*$  ( $\text{CS}$ ),  $\pi \rightarrow \pi^*$  ( $\text{CO}$ , carboxylic),  $\pi \rightarrow \pi^*$  ( $\text{CO}$ ,  $\text{Ph}$ ),  $\pi \rightarrow \pi^*$  ( $\text{CS}$ ) and  $\pi \rightarrow \pi^*$  ( $\text{C}=\text{C}$ ,  $\text{Ph}$ ) (Rao, 1975), respectively. This refers to the existence of the free ligand in the keto form.

The modes of coordination in the metal complexes have been determined by comparing the IR spectra of the free ligand (BGH) with those of metal complexes and glycine (Nakamoto, 1970). First, the ligand behaves in a bidentate manner toward the mono-nuclear  $\text{Cu}(\text{II})$  complex (Fig. 2). The IR spectrum in KBr of the  $\text{Cu}(\text{II})$  chloride complex with the general formula,  $[\text{Cu}(\text{H}_2\text{L})\text{Cl}(\text{H}_2\text{O})_3] \cdot \frac{1}{2}\text{H}_2\text{O} \cdot \text{Cl}$  (1), shows that the ligand coordinates in a bidentate manner *via* the (CO) attached to the phenyl and the thione (CS) groups to the  $\text{Cu}(\text{II})$  ion, without displacement of a hydrogen atom, forming a six-member ring around the  $\text{Cu}(\text{II})$  ion. On the basis of the shifts of  $\text{C}=\text{O}$  and  $\text{OH}$  of the  $\text{COOH}$  groups from 1709 and 3445  $\text{cm}^{-1}$  to 1737 and 3450  $\text{cm}^{-1}$ , respectively, indicate that these groups are excluded from bonding. Also, the (CO) attached to the phenyl group and the (CS) groups are shifted to lower wave-numbers at 1608 and 1473  $\text{cm}^{-1}$ , respectively, indicating their participation in coordination. Also, the two  $\text{NH}$  bands are slightly shifted to lower wave-numbers due to their attachment to the donor groups (CO, CS). The observation of two new bands at 505 and 483  $\text{cm}^{-1}$  assigned to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{S})$  vibrations (Ferraro, 1966), respectively, may be

taken as an additional evidence for the participation of the (CO) and the CS groups in bonding. The electronic spectrum of the  $\text{Cu}(\text{II})$  complex in Nujol shows a broad weak band centered at 12469  $\text{cm}^{-1}$  indicating the existence of a distorted-octahedral around the  $\text{Cu}(\text{II})$  ion. This band is mainly attributed to  $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$  transition in distorted-octahedral geometry around the  $\text{Cu}(\text{II})$  ion (Lever, 1968). Also, the normal value of magnetic moment for the  $\text{Cu}(\text{II})$  complex (1.7 B.M.) suggests the absence of any  $\text{Cu}-\text{Cu}$  interactions. On dissolution of the  $\text{Cu}(\text{II})$  complex in DMF the above band is shifted toward lower value and observed at 11655  $\text{cm}^{-1}$  indicating the replacement of water by DMF molecules and the complex has also a distorted-octahedral geometry around the  $\text{Cu}(\text{II})$  ion. Also, the band observed at 22727  $\text{cm}^{-1}$  in Nujol and DMF is assigned to charge-transfer of the type ( $\text{Cu} \rightarrow \text{Cl}$ ) (Rao, 1975). The TGA curve of the  $\text{Cu}(\text{II})$  chloride complex shows that the complex decomposes in four steps. The first step (35–132  $^\circ\text{C}$ ) corresponds to the loss of 2.5 molecules of water of hydration (found: 9.4%; calcd.: 10.3%). The second step (133–295  $^\circ\text{C}$ ) corresponds to the loss of  $2\text{Cl}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_2\text{COOH}$  and phenyl group (found: 52.5%; calcd.: 51.6%). The third step (295–719  $^\circ\text{C}$ ) stands for the loss of  $2\text{NH} + \text{CO}$  (found: 13.8%; calcd.: 13.3%). Finally, the estimated residue corresponds to  $\text{CuCS}$  (found: 24.3%; calcd.: 24.7%).

The IR spectrum of the binuclear  $\text{Co}(\text{II})$  complex with the general formula,  $[\text{Co}_2(\text{H}_2\text{L})\text{Cl}_3(\text{EtOH})] \cdot \text{H}_2\text{O} \cdot \text{Cl}$  (2), shows that the ligand coordinates to two  $\text{Co}(\text{II})$  ions within the same complex. The first  $\text{Co}(\text{II})$  ion coordinates to the (CS) and the (CO) groups attached to the phenyl moiety forming six-member ring while the second  $\text{Co}(\text{II})$  ion is bonded to the (CO) and the (OH) groups of the carboxylic group without displacement of a hydrogen atom forming four-member ring around the second  $\text{Co}(\text{II})$  ion (Fig. 3).

The electronic spectrum of the  $\text{Co}(\text{II})$  complex in Nujol mull shows two bands at 16287 and 15106  $\text{cm}^{-1}$  assigned to  $^4\text{A}_2 \rightarrow ^4\text{T}_1$  ( $\text{P}$ ) ( $\nu_2$ ) transitions in a tetrahedral geometries around the two  $\text{Co}(\text{II})$  ions (Devillanova and Verani, 1979; Nicholls, 1986). The first band may be assigned to the tetrahedral geometry in case of the ring containing both the (CS) and (CO) groups while the second band is assigned to the second ring involving the carboxylic group. The values of  $\nu_1$ ,  $\text{B}$  and  $\beta$  for the first  $\text{Co}(\text{II})$  ion were calculated and found to be 6898  $\text{cm}^{-1}$ , 941 and 0.97, respectively. On dissolution of the  $\text{Co}(\text{II})$  complex in DMF, the two bands observed at 16502 and 14837  $\text{cm}^{-1}$  are assigned to  $^4\text{A}_2 \rightarrow ^4\text{T}_1$  ( $\text{P}$ ) ( $\nu_2$ ) transitions in a tetrahedral geometries around the two  $\text{Co}(\text{II})$  ions (Nicholls, 1986). The blue shift of these bands may be assigned to the substitution of ethanol by DMF molecule in a

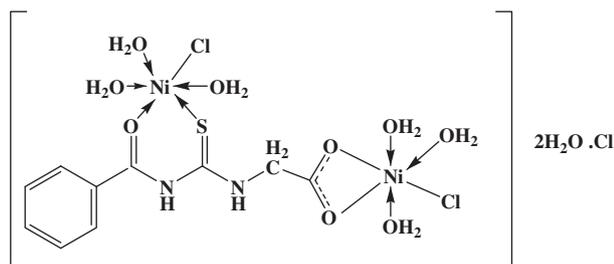


**Figure 3** Structure of the  $\text{Co}(\text{II})$  complex,  $[\text{Co}_2(\text{H}_2\text{L})\text{Cl}_3(\text{EtOH})] \cdot \text{H}_2\text{O} \cdot \text{Cl}$  (2).

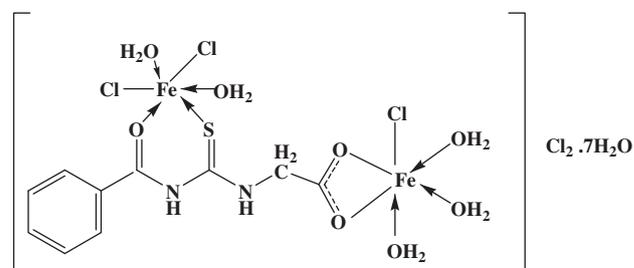
tetrahedral geometry around the two Co(II) ions. The value of the magnetic moment (4.5 B.M.) as well as blue color of the Co(II) complex is taken as strong evidences for the existence of a tetrahedral geometry around the Co(II) ion. The values of  $\nu_1$ ,  $B$  and  $\beta$  for the second Co(II) ion were calculated and found to be  $6775\text{ cm}^{-1}$ , 857 and 0.88, respectively.

The IR spectrum of the binuclear Ni(II) complex with the general formula,  $[\text{Ni}_2(\text{HL})\text{Cl}_2(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}\cdot\text{Cl}$  (3), shows that the ligand acts as a mono negative tetradentate ligand coordinating to two Ni(II) ions within the same complex. The first Ni(II) ion is coordinated to the ligand through the (CS) and (CO) groups attached to the phenyl moiety forming six-member ring while the second Ni(II) ion is bonded to the (CO) and (OH) groups of the carboxylic group with displacement of a hydrogen atom forming four-member ring around the second Ni(II) ion. The ligand forms two octahedral geometries around the two nickel ions (Fig. 4).

The IR spectrum suggests the disappearance of the OH band of the carboxylic group together with the appearance of two new bands at  $1630$  and  $1516\text{ cm}^{-1}$  assigned to the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  vibration, respectively. This indicates the participation of the carboxylic group in bonding with displacement of a hydrogen atom toward the second Ni(II) ion. Also, the spectrum shows the negative shifts of both the CO and CS groups to lower wave-numbers (Sallam et al., 2006; Cakir et al., 2001) suggesting the participation of these groups in coordination to the first Ni(II) ion. The electronic spectrum of the Ni(II) complex in Nujol mull shows bands at  $27933$ ,  $23256$ ,  $16556$  and  $14245\text{ cm}^{-1}$ . The first and the third bands are attributed to  $\nu_3$  and  $\nu_2$  transitions for the first Ni(II) ion while the second and fourth bands are attributed to  $\nu_3$  and  $\nu_2$  transitions for the second Ni(II) ion. The values of  $\nu_1$ ,  $B$  and  $\beta$  for the first Ni(II) ion were calculated and found to be  $6467\text{ cm}^{-1}$ , 995 and 0.95, while these values were calculated and found to be  $7386\text{ cm}^{-1}$ , 995 and 0.95, respectively, for the second Ni(II) ion. The value of the magnetic moment for each Ni(II) ion (2.5 B.M.) was taken as an evidence for the existence of octahedral geometry around the two Ni(II) ions. Thermal analyses (TGA, DTG) of the Ni(II) chloride complex showed that the complex decomposes in five stages. The first step ( $30\text{--}91\text{ }^\circ\text{C}$ ) indicates the loss of  $5\text{H}_2\text{O}$  molecules (found: 15.5%; calcd.: 14.9%). The second step ( $91\text{--}265\text{ }^\circ\text{C}$ ) corresponds to the loss of  $3\text{H}_2\text{O}$  of coordination and  $3\text{Cl}$  ions in two successive stages (found: 26.1%; calcd.: 26.5%). The third step ( $266\text{--}441\text{ }^\circ\text{C}$ ) corresponds to the loss of  $\text{CH}_2\text{COOH}$  and  $\text{NH}$  moieties (found: 13.2%; calcd.: 12.2%). The fourth step ( $442\text{--}574\text{ }^\circ\text{C}$ ) indicates the loss of Ph and HN (found: 15.9%; calcd.: 15.2%). The residue is a mixture of NiCS and  $6\text{C}$  (found: 29.4%; calcd.: 28.9%).



**Figure 4** Structure of the Ni(II) complex,  $[\text{Ni}_2(\text{HL})\text{Cl}_2(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}\cdot\text{Cl}$  (3).



**Figure 5** Structure of the Fe(III) complex,  $[\text{Fe}_2(\text{HL})\text{Cl}_3(\text{H}_2\text{O})_5]\cdot\text{Cl}_2\cdot 7\text{H}_2\text{O}$  (4).

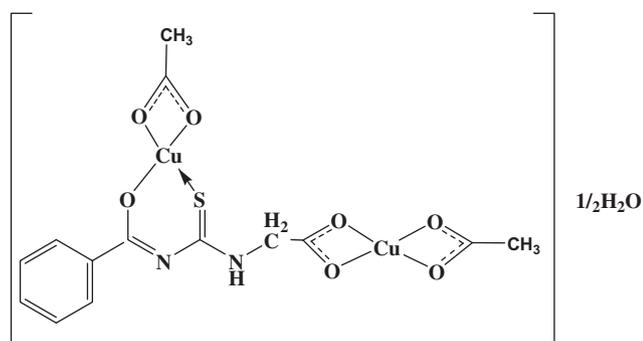
Also, BGH acts as a mono negative tetradentate ligand coordinating to two Fe(III) ions at the same time as in the Fe(III) complex,  $[\text{Fe}_2(\text{HL})\text{Cl}_3(\text{H}_2\text{O})_5]\cdot\text{Cl}_2\cdot 7\text{H}_2\text{O}$  (4). It binds to the first Fe(III) atom through the amidic carbonyl (CO) and (CS) groups, while it coordinates to the second Fe(III) atom through the carboxylate group after displacement of the hydrogen atom. This behavior is supported by the shifts of the bands in the regions,  $1619\text{--}1630$ ,  $1662\text{--}1666$ ,  $1173\text{--}1178\text{ cm}^{-1}$  and  $779\text{--}789$  to lower wave-numbers (Cakir et al., 2001) assigned to the  $\text{C}=\text{S}^*$ , CO and CS groups, respectively. The new two bands in the  $1690\text{--}1722$  and  $1442\text{--}1476\text{ cm}^{-1}$  regions assigned to  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  groups, respectively, are taken as an evidence for the participation of the carboxylic group with replacement of a hydrogen atom (Fig. 5). The electronic spectrum of Fe(III) chloride complex in Nujol shows two bands at  $16666$  and  $20746\text{ cm}^{-1}$  assigned to d-d transitions and a band at  $29325\text{ cm}^{-1}$  assigned to LMCT (Lever, 1968; Sutton, 1968). The value of magnetic moment (3.13 B.M.) falls in between the values expected for the high spin  $\text{Fe}^{\text{III}}$  with  $S = 5/2$  and for the low spin Fe(III) with  $S = 1/2$  and the possibility of spin state equilibrium between  ${}^6\text{A}_2$  and  ${}^2\text{T}_2$  states (Sutton, 1968). The TGA of the ferric chloride complex shows six stages of decomposition. The first step ( $51\text{--}150\text{ }^\circ\text{C}$ ) is due to the loss of one molecule of water (found: 2.1%; calcd.: 2.4%). The second step ( $151\text{--}356\text{ }^\circ\text{C}$ ) indicates the loss of 11  $\text{H}_2\text{O}$  molecules hydrated and coordinated molecules (found: 27.7%; calcd.: 26.7%). The third step ( $357\text{--}788\text{ }^\circ\text{C}$ ) corresponds to the loss of  $3\frac{1}{2}\text{Cl}_2$  (found: 15.7%; calcd.: 16.8%) leaving a residue (found: 54.5%; calcd.: 54.1%) corresponding to  $\text{Fe}_2\text{C}_{10}\text{H}_9\text{O}_3\text{N}_2\text{SCl}_{1\frac{1}{2}}$ .

The high melting point of the Fe(III) ( $> 300\text{ }^\circ\text{C}$ ) in comparison to the other metal complexes suggests the strong bonding between the Fe(III) ion and the ligand. The strong bond is also confirmed from the data of TGA which indicate that the complex is not completely decomposed up to  $788\text{ }^\circ\text{C}$ .

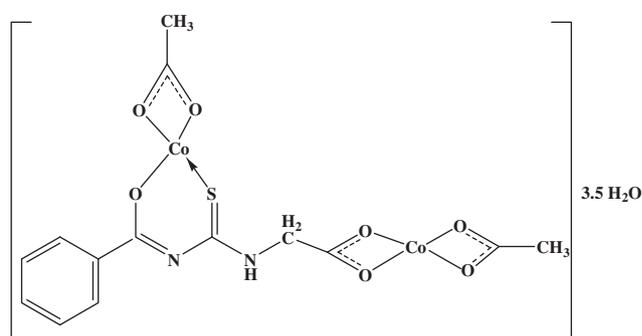
All the chloride complexes show the participation of the thioketo and the carbonyl oxygen (amidic) in bonding and the inertness of the carboxylic group toward coordination except for the Ni(II) and Fe(III) complexes. This can be explained on the basis of the low pH (1–1.5) of the solution during complex formation which prevented the removal of a hydrogen atom from the carboxylic group. On the other hand, the comparatively high pH value ( $\sim 4$ ) for the Ni(II) and Fe(III) complexes assisted the participation of this group in bonding.

Also, the ligand (BGH) behaves as a binuclear binegative tetradentate ligand in the enol form as in case of the Cu(II), Co(II), Ni(II) and Zn(II) acetate complexes. The ligand

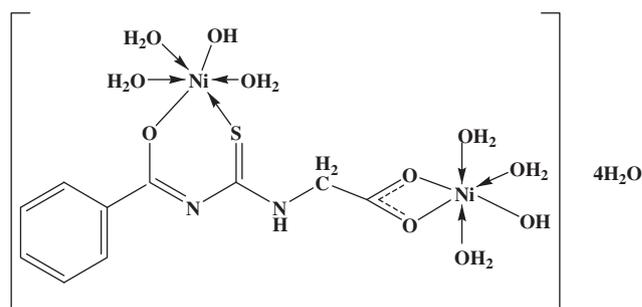
coordinates to the first atom through the CS and (CO) groups in the enol form with replacement of a hydrogen atom from the enolized OH group and it coordinates to the second metal atom through the (COOH) with replacement of a hydrogen atom. This mode of coordination is supported by the disappearance of the band assigned to amidic carbonyl and the appearance of new band in the region  $1568\text{--}1654\text{ cm}^{-1}$  assigned to the  $(\text{C}=\text{N}^*)$  group. Also, the shifts of the bands in the regions  $1145\text{--}1180$  and  $751\text{--}786\text{ cm}^{-1}$  are assigned to  $\nu(\text{CS})$  vibrations to lower wave-numbers. The ligand binds the second atom through carboxylic group after replacement of a hydrogen atom. The bands observed in the  $1567\text{--}1600$  and  $1433\text{--}1460\text{ cm}^{-1}$  regions are assigned to  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  vibrations. First, the IR spectrum of the Cu(II) acetate complex with the general formula,  $[\text{Cu}_2\text{L}(\text{Ac})_2] \cdot \frac{1}{2}\text{H}_2\text{O}$  (5), shows that the ligand coordinates to two Cu(II) ions. The results indicate that the ligand coordinates to the first Cu(II) ion through the thioketo (CS) and the enolized ( $\text{C}=\text{O}$ ) with the displacement of a hydrogen atom from the latter group forming six-member ring around the first Cu(II) ion, while it coordinates to the second Cu(II) ion *via* the carboxylate group with displacement of a hydrogen atom forming four-member ring around the second Cu(II) ion. Also, the IR spectrum shows a broad band centered at  $3406\text{ cm}^{-1}$  assigned to  $\nu(\text{OH})$  vibration of the water molecule. The disappearance of the carbonyl oxygen at  $1658\text{ cm}^{-1}$  together with the appearance of a new band at  $1624\text{ cm}^{-1}$  assigned to the  $\text{C}=\text{N}^*$  group may be taken as an evidence for the enolization of the carbonyl oxygen together with the displacement of a hydrogen atom. The negative shifts of the CS groups at  $1464$  and  $1166\text{ cm}^{-1}$  to lower wave numbers (Table 2) suggest the participation of this group in bonding. On the other hand, the results show the obscurity of both the OH and the CO groups of the carboxylic group together with the appearance of two new bands at  $1581$  and  $1433\text{ cm}^{-1}$  assigned to  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  vibrations, respectively. The electronic spectrum of the Cu(II) complex, in Nujol mull, shows a broad band centered at  $15290\text{ cm}^{-1}$  which may be assigned to  ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{E}_{\text{g}}$  and  ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{A}_{1\text{g}}$  transitions in a square-planar geometries (Sutton, 1968) around the two Cu(II) ions. This band is blue shifted in DMF and observed at  $15923\text{ cm}^{-1}$ . Also, the normal value of magnetic moment for the Cu(II) complex (1.74 B.M.) suggests the absence of any Cu–Cu interactions. All these foundations suggest a square-planar geometry around the two Cu(II) ions (Fig. 6).



**Figure 6** Structure of the Cu(II) acetate complex,  $[\text{Cu}_2\text{L}(\text{Ac})_2] \cdot \frac{1}{2}\text{H}_2\text{O}$  (5).



**Figure 7** Structure of the Co(II) acetate complex,  $[\text{Co}_2(\text{L})(\text{Ac})_2] \cdot 3\frac{1}{2}\text{H}_2\text{O}$  (6).



**Figure 8** Structure of the Ni(II) acetate complex,  $[\text{Ni}_2\text{L}(\text{OH})_2(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}$  (7).

Second, the electronic spectrum of Co(II) acetate complex of the general formula,  $[\text{Co}_2(\text{L})(\text{Ac})_2] \cdot 3\frac{1}{2}\text{H}_2\text{O}$  (6), in Nujol and DMF shows three bands at  $19380$ ,  $16393$  and  $14970\text{ cm}^{-1}$ . These bands are assigned to  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$  (P) transition in a tetrahedral geometry around the second Co<sup>II</sup> ion (Sutton, 1968). The value of magnetic moment (4.1 B.M.) is taken as an evidence for the existence of a tetrahedral geometry around the two Co(II) ions (Fig. 7).

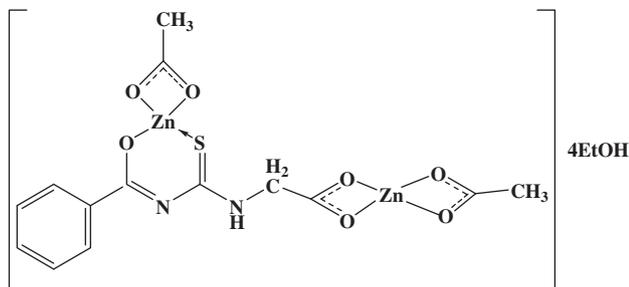
The thermal analyses curves of Co(II) acetate complex show four stages of decomposition. The first step ( $40\text{--}109\text{ }^\circ\text{C}$ ) corresponds to the loss of one molecule of one and half water of hydration (found: 4.5%; calcd.: 5.0%). The second step ( $109\text{--}378\text{ }^\circ\text{C}$ ) corresponds to the loss of two coordinated water molecules, two acetate groups and  $\text{CH}_2\text{COOH}$  (found: 40.9%; calcd.: 39.8%). The third step ( $380\text{--}555\text{ }^\circ\text{C}$ ) stands for the loss of NH molecule (found: 3.1%; calcd.: 2.8%). The last step corresponds to the decomposition of the remaining organic ligand leaving a residue (found: 51.5%; calcd.: 52.4%) for  $\text{Co}_2\text{C}_8\text{SNOH}_5$ .

The UV spectra of Ni(II) acetate complex of the general formula,  $[\text{Ni}_2\text{L}(\text{OH})_2(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}$  (7), in DMF and Nujol, show bands at  $16611$  and  $23364\text{ cm}^{-1}$  assigned to  ${}^3\text{A}_{2\text{g}} \rightarrow {}^3\text{T}_{1\text{g}}$  ( $\nu_2$ ) and  ${}^3\text{A}_{2\text{g}} \rightarrow {}^3\text{T}_{1\text{g}}$  (P) ( $\nu_3$ ) respectively. The presence of these bands suggests an octahedral geometry around Ni(II) ion (Fig. 8). Also, the spectrum shows a band at  $29069\text{ cm}^{-1}$  assigned to LMCT (Sutton, 1968). The relatively low magnetic moment value (2.5 B.M.) supports the absence of any Ni–Ni interaction (Nawar et al., 2001).

The thermal analyses curves (TGA, DTG) show that the Ni(II) acetate complex decomposes in five steps. The first ( $38\text{--}122\text{ }^\circ\text{C}$ ) stands for the loss of two molecules of water of

hydration (found: 6.3%; calcd.: 6.3%). The second step (123–241 °C) corresponds to the loss of 2H<sub>2</sub>O one of them is hydrogen bonded but not participated in crystal lattice (Jasinski et al., 2003) (found: 7.0%; calcd.: 6.3%). The next step (243–381 °C) corresponds to the decomposition of 6H<sub>2</sub>O + OH (found: 22.8%; calcd.: 22.1%). The fourth step (382–531 °C) stands for the loss of C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>O<sub>4</sub> (found: 25.6%; calcd.: 25.4%). The remaining corresponds to Ni<sub>2</sub>C<sub>6</sub>S (found: 38.3%; calcd.: 39.1%).

The IR spectrum shows that the ligand coordinates to Zn(II) acetate forming binuclear complex with the general formula, [Zn<sub>2</sub>(L)(Ac)<sub>2</sub>·4EtOH (8). The ligand behaves as a mono-



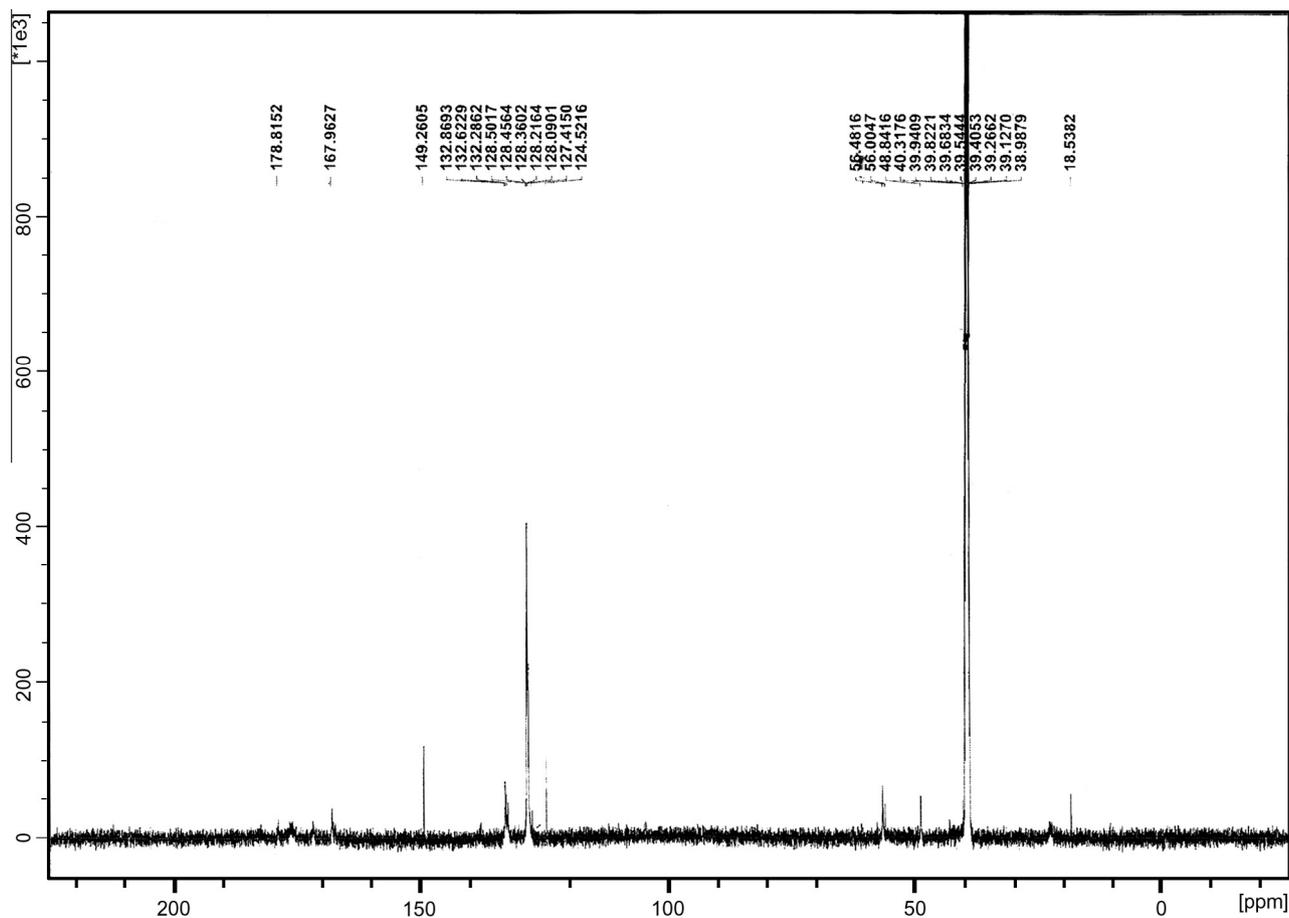
**Figure 9** Structure of the Zn(II) acetate complex, [Zn<sub>2</sub>(L)(Ac)<sub>2</sub>·4EtOH (8).

negative bidentate ligand in the enol form toward the first Zn(II) ion coordinating via the CS and C–OH groups with replacement of a hydrogen atom from the latter group. The second Zn(II) ion is coordinated to the ligand through the carboxylic group with replacement of a hydrogen atom. Also, the spectrum shows two bands in the region 1583 and 1423 cm<sup>-1</sup> assigned to the ν<sub>as</sub>(COO) and ν<sub>a</sub>(COO) vibrations, respectively. The difference between these two groups is 160 cm<sup>-1</sup> indicating the bidentate nature of the carboxylate group (Fig. 9).

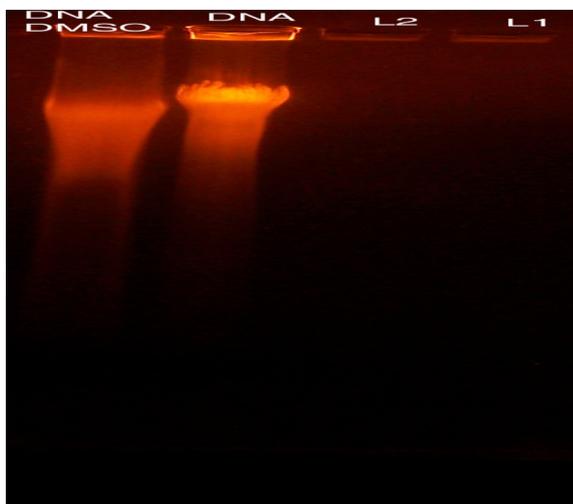
The <sup>13</sup>C NMR spectrum of the Zn(II) complex in d<sub>6</sub>-DMSO shows several signals at 178, 168, 149, 124–132, 56 and 18.5 ppm, down field of TMS, assigning to the carbon of CO, C=N, C=S, C=C (phenyl), CH<sub>2</sub>NH and CH<sub>3</sub>, respectively. The existence of these signals as shown in Fig. 10 confirms the proposed for the Zn(II) complex (Fig. 9).

The participation of the carboxylic group in coordination in case of the acetate complexes is mainly attributed to the high pH of the solution (6–6.5) during complex formation. On the other hand, the carboxylic remains inert in case of chloride complexes, except the Ni(II) chloride complex, since the pH of the solution is very low (1–1.5) which prevents the ionization and the participation of this group.

Finally, one of our goals is to study the antimicrobial activities of the ligand against *B. subtilis* and *P. aeruginosa*. The data suggest that the Gram positive and Gram negative bacteria were affected by the ligand under investigation. Moreover, the effects of the genotoxicity on the DNA for the ligand in



**Figure 10** <sup>13</sup>C NMR spectrum of [Zn<sub>2</sub>(L)(Ac)<sub>2</sub>·4EtOH (8).



**Figure 11** The degradation powers of the tested ligand on calf thymus DNA.

comparison to the control sample indicate interesting results. The degradation powers of the tested ligand on calf thymus DNA is high for all complexes supporting the selective action of the ligand against bacteria and the human or related eukaryotic organisms as shown in Fig. 11. The results are promising toward the use the ligand as anti-tumor.

#### Acknowledgements

The authors are thankful to Pro. Y. Osman at Botany Department, Mansoura University for the measurements of biological activity. Also, we gratefully acknowledge Prof. Sief at King Abdul Aziz University, Saudi Arabia, for doing the  $^{13}\text{C}$  NMR spectrum.

#### References

- Biot, Christophe, Pradines, Bruno, Sergeant, Marie-Hélène, Gut, Jiri, Rosenthal, Philip J., Chibale, Kelly, 2007. *Bio. Org. Med. Chem. Lett.* 17, 6434–6438.
- Cakir, S., Coskun, E., Naumov, P., Bicer, E., Bulut, I., Icbudak, H., Cakir, O., 2001. *J. Mol. Str.* 608, 101–107.
- Devillanova, F.A., Verani, G., 1979. *J. Inorg. Nucl. Chem.* 41, 1111–1114.
- Ferraro, J.R., 1966. *Low Frequency Vibrations of Inorganic and Coordination Compounds.* Plenum Press, New York.
- Geary, W.J., 1971. *Coord. Chem. Rev.* 7, 81–122.
- Gerhardt, P. 1981. *Manual Methods of general bacteriology.* American Chemical Society for Microbiology, Castello.
- Goldberg, D.E., Sharma, V., Oksman, A., Gluzman, I.Y., Wellems, T.E., Pivnica-Worms, D., 1997. *J. Biol. Chem.* 272, 6567–6572.
- Hafez, M.H., 1992. *Anal. Lett.* 255, 1779–1796.
- Jasinski, J.P., Bianchani, J.R., Cueva, J., El-Saied, F.A., El-Asmy, A.A., West, D.X., 2003. *Z. Anorg. Allg. Chem.* 629, 202–206.
- Lever, A.B.P., 1968. *Electronic Spectroscopy.* Elsevier, Amsterdam.
- Li, Z., Zhang, Y., Wang, Y., 2003. *Phosph. Sulf. Silic.* 178, 293–297.
- Nair, P.C., Sobhia, M.E., 2008. *Eur. J. Med. Chem.* 43, 293–299.
- Nakamoto, K., 1970. *Infrared Spectra of Inorganic and Coordination Compounds.* John Wiley, New York.
- Catineriras, A., Bermejo, E., Valdes-Martinez, J., Espinosa, G., West, D.X., . *J. Mol. Struct.* 522, 271–278.
- Nawar, N.A., Shallaby, A.M., Hosny, N.M., Mostafa, M.M., 2001. *Trans. Met. Chem.* 26, 180–185.
- Nicholls, D., 1986. *Complexes and First-Row Transition Elements.* Macmillan, UK.
- Rao, C.N.R., 1975. *Ultraviolet and Visible Spectroscopy.* Plenum Press, New York.
- Sallam, S.A., Bahgat, K.M., El-Tanany, A.Z., Mahmoud, M.A., 2006. *J. Coord. Chem.* 59, 2055–2073.
- Sharma, V., Pivnica-Worms, D., 1999. *Chem. Rev.* 99, 2545–2560.
- Sutton, D., 1968. *Electronic Spectra of Transition Metal Complexes.* McGraw-Hill, London.
- Wang, M.Z., Meng, Z.X., Liu, B.L., Cai, G.L., Zhang, C.L., Wang, X.Y., 2005. *Inorg. Chem. Comm.* 8, 368–371.