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# Synthesis and characterization of some bi, tri and tetravalent transition metal complexes of N'-(furan-2-yl-methylene)-2-(p-tolylamino)acetohydrazide HL<sup>1</sup> and N'-(thiophen-2-yl-methylene)-2-(p-tolylamino)acetohydrazide HL<sup>2</sup>

## S.M. Emam, S.A. AbouEl-Enein\*, F.A. El-Saied, S.Y. Alshater

Chemistry Department, Faculty of Science, El-Menoufia University, Shebin El-Kom, Egypt

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#### ABSTRACT

The tetradentate Schiff bases hydrazone ligands HL<sup>1</sup>, HL<sup>2</sup> and their metal complexes have been prepared and characterized by analytical, spectral (IR, UV–vis, <sup>1</sup>H NMR and ESR), molar conductivity, magnetic and TGA measurements. The results show that all the metal complexes are non-electrolytes, except (2, 10 and 20) which have ionic nature. The ligands coordinate in keto-neutral form and act as bidentate or tridentate for all metal complexes, except complexes (4 and 12). The ligands react as monobasic tetradentate and tridentate for complexes (4 and 12), respectively. Octahedral/tetrahedral Co(II) and Ni(II), octahedral/square planar Cu(II), and octahedral Mn(II), Fe(III), Cr(III), Ru(III), Hf(IV) and Zr(IV)O geometries were proposed. The ESR spectra of copper complexes (12 and 14) indicate  $d_{(x^2-y^2)}$  ground state with covalent bond character. The thermal decomposition and the types of crystallized water for some metal complexes were studied. The studied metal complexes are very weakly active against the tested microorganisms.

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#### 1. Introduction

Schiff bases hydrazone derivatives and their metal complexes have been studied for their interesting and important properties, e.g., antibacterial [1,2], antifungal [3], antioxidant [4], anticancer [5] and catalytic activity in oxidation of cyclohexene [6]. Moreover, Schiff bases hydrazone derivatives are versatile ligands and they offer the possibility of different modes of coordination towards transition metal ions. Also, some of these derivatives have been applied as iron chelator drugs in therapy of anemia [7] and treatment of neuropathic pain [8].

Therefore it prompted us to continue our previous work on characterization of some transition metal complexes of aromatic and heterocyclic *N*-anilinoacetohydrazone [1,9,10]. The present investigation deals with synthesis and characterization of Mn(II), Co(II), Ni(II), Cu(II), Cr(III), Fe(III), Ru(III), Hf(IV) and Zr(IV)O metal complexes of *N'*-(furan-2-yl-methylene)-2-(*p*-tolylamino)acetohydrazide, HL<sup>1</sup> and *N'*-(thiophen-2-yl-methylene)-2-(*p*-tolylamino)acetohydrazide, HL<sup>2</sup>. Analytical, spectral, magnetic, molar conductivity and thermogravimetric analysis (TGA) were used to investigate the

chemical structure of these ligands and their metal complexes. The

\* Corresponding author. *E-mail address:* dr.saeyda\_elenein@yahoo.com (S.A. AbouEl-Enein). antibacterial and antifungal tests of some metal complexes were also carried out.

#### 2. Experimental

#### 2.1. Materials

*p*-Toludine, ethylchloroacetate, sodium acetate trihydrate, hydrazine hydrate, 2-furylaldehyde, 2-thiophenealdehyde, absolute ethyl alcohol and metal chloride salts of Cu(II), Ni(II), Mn(II), Cr(III), Fe(III), Ru(III), Hf(IV) and Zr(IV)O, acetate salts of Cu(II), Co(II), Ni(II), Mn(II) and nitrate salts of Cu(II) and Co(II) were used without further purification.

#### 2.2. Synthesis of ligands

The ethyl[(4-methylphenyl)amino]acetate was prepared by refluxing equimolar amounts of a hot ethanolic solution of *p*-toludine, ethylchloroacetate and sodium acetate trihydrate for 6 h. The mixture was poured on cold water and stirred for 30 min. The formed precipitate was filtered off, washed with ethanol and dried over anhydrous CaCl<sub>2</sub>, m.p. =  $43 \degree C$  [11].

The 2-[(4-methylphenyl)amino]acetohydrazide was synthesized by adding ethanolic solution of hydrazine hydrate drop wise to an equimolar amount of ethyl[(4-methylphenyl)amino]acetate in ethanol, with stirring and heating. A white precipitate was

<sup>1386-1425/\$ –</sup> see front matter  $\ensuremath{\mathbb{C}}$  2012 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2012.02.045

formed after about 3 h. The precipitate was filtered off, washed several times with ethanol and dried over anhydrous CaCl<sub>2</sub>, m.p. =  $162 \circ C$  [10,11].

The Schiff bases ligands N'-(furan-2-yl-methylene)-2-(*p*-tolylamino)acetohydrazide  $HL^1$ and N'-(thiophen-2yl-methylene)-2-(p-tolylamino)acetohydrazide  $HL^2$ were prepared by refluxing equimolar amounts of 2 - [(4 methylphenyl)aminolacetohydrazide with 2-furylaldehyde or 2-thiophenealdehyde in 50 mL absolute ethanol for 3 h. The formed solid buff precipitate was filtered off and washed with ethanol. The product was crystallized from ethanol and finally dried over anhydrous CaCl<sub>2</sub>. Melting points are 162 and 140 °C for HL<sup>1</sup> and HL<sup>2</sup>, respectively.

#### 2.3. Synthesis of metal complexes

All the metal complexes were prepared by adding the appropriate metal salts (0.01 mol in 20 mL ethanol) to a hot solution of ligands  $HL^1$  or  $HL^2$  (0.01 mol in 50 mL ethanol). The reaction mixture was magnetically stirred and refluxed for about 3 h. The separated complex was filtered off, washed several times with ethanol and finally dried under vacuum over anhydrous calcium chloride.

#### 2.4. Screening for the antimicrobial activity

The antibacterial activities of metal complexes (10, 12, 14-16 and 19) of HL<sup>2</sup> ligand were evaluated against gram negative bacteria (Escherichia coli and Klebsiella pneumonia) and gram positive bacteria (Bacillus cereus and Staphylococcus aureus) and Candida albicans (as fungs) using the modified disc diffusion method [12]. A nutrient agar (NA) medium was used for bacteria and Sabouroud agar slop was used for fungs. Stock solution of tested compounds was prepared in DMSO at different concentrations (0.25, 0.50, 1.00 and 10.00 mg/mL). To ensure that the solvent had no effect on the growth of microorganisms, a control test was performed with test medium supplemented with DMSO with the same procedures used in the experiments. Ampicillin trihydrate and clorimazole were also screened under similar conditions as reference antibacterial and antifungal drugs, respectively. Minimum inhibitory concentrations (MICs) were determined by the micro-dilution broth method following the procedures recommended by the National Committee for Clinical Laboratory Standards [13,14]. MICs were defined as the lowest concentrations of compounds which inhibit the growth of microorganisms.

#### 2.5. Instruments

Elemental microanalyses (C, H, N and Cl) were performed at the Microanalytical Unit, Cairo University. IR spectra were recorded as KBr discs using a Perkin-Elmer 1430 spectrophotometer. The electronic spectra were measured in nujol mull using a Perkin-Elmer Lambda 4B spectrophotometer. <sup>1</sup>H NMR spectra were carried out in deutrated DMSO and deutrated chloroform (CDCl<sub>3</sub>), using 300 MHz Varian NMR spectrophotometer. The electron spin resonance (esr) spectra were obtained in the X-band at room temperature on Bruker Elexsys 500 E spectrometer with a microwave frequency 9.82 GHz and a modulation frequency 10 kHz. The magnetic susceptibilities were measured at room temperature by a modified Gouy method using a Johnson Matthey magnetic susceptibility balance. Diamagnetic corrections were made using Pascal's constant [15]. Molar conductivity measurements in DMF ( $1 \times 10^{-3}$  M) were measured at room temperature on CM-1K portable conductivity meter. The thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere using a Shimadzu DT-50 thermal analyzer from room temperature to  $800 \degree C$  at a heating rate of  $10 \degree C/min$ .

#### 3. Results and discussion

#### 3.1. The ligands

The prepared ligands  $HL^1$  and  $HL^2$  were investigated by elemental analyses (Table 1), <sup>1</sup>H NMR and IR spectra (Table 2).

The <sup>1</sup>H NMR spectra of ligands  $HL^1$  and  $HL^2$  were carried out at room temperature in DMSO- $d_6$  and CDCl<sub>3</sub>, respectively. The spectra exhibit the signals at 3.40–3.75, 4.20–4.3 and 6.38–7.4 ppm corresponding to methyl group, methylene and aromatic protons (multiples), respectively [16]. The signal of azomethine appears at 7.87–7.97 ppm as a singlet [1,16] and the imide HN–CO signal of the keto form was observed at 9.9–10.8 ppm [17], whereas the signal at 8.43–8.6 ppm was assigned to ph-NH [18]. The spectrum of HL<sup>1</sup> reveals OH signal at 12.38 ppm, indicating a keto–enol tautomerism [9,17].

The infrared spectra of ligands (Table 2) showed bands at 3388–3118, 1676, 1619–1616, 587 and 577 cm<sup>-1</sup>, assigned to  $\upsilon$ (N–H),  $\upsilon$ (C=O),  $\upsilon$ (HC=N), furan and thiophene ring bending, respectively. The elemental analyses (Table 1), infrared and <sup>1</sup>H NMR data are compatible with the structure shown below:



#### 3.2. Metal complexes and characterization

The analytical data of ligands and their metal complexes (Table 1) showed that the reaction of ligand  $HL^1$  or  $HL^2$  with various metal salts in the (1M:1L) molar ratio gives complexes with different stoichiometric 1:1, 1:2 and 2:1 (M:L). All the metal complexes derived from HL<sup>1</sup> and HL<sup>2</sup> are separated with (1M:1L) molar ratio except the chromium chloride, cobalt nitrate (11) and cobalt chloride complexes of HL<sup>2</sup> and HL<sup>1</sup>, respectively, which are formed with (1M:2L) molar ratio. While the binuclear nickel complex  $[Ni_2(L^1)(OAc)_3(H_2O)_3]$  is raised from the reaction of 1 mol nickel acetate with 1 mol HL<sup>1</sup> ligand. The metal complexes are stable, nonhygroscopic, partially soluble in most organic solvents and soluble in DMF and DMSO. The molar conductivity values for all metal complexes were measured in  $(1 \times 10^{-3} \text{ M})$  DMF solution at 25 °C (Table 1). The data showed that the molar conductivities of [Co(HL<sup>1</sup>)<sub>2</sub>]Cl<sub>2</sub>·H<sub>2</sub>O, [Co(HL<sup>2</sup>)<sub>2</sub>]Cl<sub>2</sub>·H<sub>2</sub>O and [Cr(HL<sup>2</sup>)<sub>2</sub>Cl<sub>2</sub>]Cl EtOH complexes are 101.5, 105.2 and  $80.9 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ , respectively. The results indicate that these complexes are ionic in nature and are of the types 2:1 and 1:1 electrolytes, respectively [18,19]. However, the rest of the other metal complexes have small conductance values, indicating that they are non-electrolytes [10,20]. The high molar conductivities of non-electrolytes are due to partial displacement of the anion by DMF molecules [21].

#### 3.2.1. Infrared spectra

The infrared spectral bands with their assignments for the free ligands and their metal complexes are listed in Table 2. The spectra of the free ligands display bands in the range 3392–3118 cm<sup>-1</sup>, assigned to different vibration mode of NH group [20,22]. The bands at 3218–3118 cm<sup>-1</sup> are not greatly affected in complexes

Table	1

Elemental analyses, molar conductivities and colors of ligands and their metal complexes.

Id.         Buff         62         H         N         C           chirsNo         257.30         65.30         5.40         16.370         -         -           1         Coll 100004(10):151b(0         brown 2         49.9         4.07         8.93         -         3.80           2         Coll 110004(10):151b(0         brown 2         49.9         4.07         8.93         -         3.80           2         Coll 110004(10):151b(0         652.30         50.70)         4.87         1.120         10.72           3         Nikh 120(14):10(14):10(14):10(14)         652.90         7.40         8.90         16.00         2.44           4         Coll 120(10):10(14):10(14)         Brown 39.70         5.20         7.40         -         8.20           5         Mid(H1)'Coll+10(1)         Brown 452.0         4.80         8.70         -         4.00           6         Mid(H1)'Coll+10(1)         Brown 452.0         4.80         8.70         -         4.00           7         FerditsMinko         482.37         (4.437)         (5.40)         9.00         2.20         2.20           7         Brown 452.0         4.80         3.80         5.00	No.	Compound	Color, F.W.	Found (Calc)%				$\Lambda - {}^{a}{}_{M}$
				С	Н	Ν	Cl	
Cathis Mode         257.30         (65.36)         (5.88)         (16.33)           Cathis (0x) (1) (1) (2) (1) (1) (2) (1) (1) (2)         Brown         435.00         (5.67)         (8.45)         -         3.80           Cathis (0x) (1) (1) (1) (1) (1) (1)         Deep brown         50.00         (1.80)         11.00         101.50           Cathis (0x) (1) (1) (1) (1) (1) (1) (1) (1)         Geep brown         50.00         (4.37)         (12.70)         (10.72)           Cathis (1) (1) (1) (1) (1) (1) (1) (1) (1) (1)		HL <sup>1</sup>	Buff	66.20	5.40	15.70	_	_
1         Co(HL <sup>1</sup> (DoA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> )1.5H <sub>2</sub> O         Brown         42.00         47.0         8.00         -         3.80           2         Co(HL <sup>1</sup> ) <sub>2</sub> (L <sub>2</sub> )H <sub>2</sub> O         Deep brown         50.90         5.00         1.80         11.00         10.50           3         Co(HC <sup>1</sup> ) <sub>2</sub> (L <sub>1</sub> O, H <sub>2</sub> O)         Deep brown         50.90         5.00         1.80         11.00         23.00           4         N(HC <sup>1</sup> ) <sub>2</sub> (L <sub>1</sub> O, H <sub>2</sub> O)         Green         37.40         5.40         8.90         16.00         23.40           4         N(HC <sup>1</sup> ) <sub>2</sub> (L <sub>1</sub> O, H <sub>2</sub> O)         Green         40.00         5.00         9.90         16.60         15.00           5         (Mn(H <sup>1</sup> ) <sub>2</sub> (L <sub>1</sub> O, H <sub>2</sub> O)         Green         40.00         4.50         8.70         -         34.00           6         (Mn(H <sup>1</sup> ) <sub>2</sub> (L <sub>1</sub> O, H <sub>2</sub> O)         Brown         45.60         4.80         8.70         -         34.00           7         [Fe(H <sup>1</sup> ) <sub>1</sub> (L <sub>1</sub> )         Brown         45.60         4.80         8.70         -         34.00           6         Mn(H <sup>1</sup> ) <sub>2</sub> (L <sub>1</sub> ) <sub>1</sub> O, O         H <sup>1</sup> 60.50         62.01         16.00         -         -         -           7         [Fe((H <sup>1</sup> ) <sub>1</sub> ) <sub>1</sub> O, C)(H <sub>2</sub> O)		C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>	257.30	(65.36)	(5.88)	(16.33)		
c μ <sup>1</sup> / <sub>12</sub> cbv h <sub>0</sub> /cb         model         model         model         model           2         [Cull <sup>1</sup> / <sub>2</sub> ]C <sub>1</sub> / <sub>1</sub> / <sub>1</sub> / <sub>0</sub> O         Deep brow         50.90         5.00         11.80         11.00         101.50           3         [N[(H]/2]([L]/2]_1/ <sub>2</sub> O         Green         37.40         5.40         8.90         16.00         23.40           4         [N[(I]/2](C)/ <sub>1</sub> / <sub>1</sub> / <sub>1</sub> / <sub>1</sub> O)         Brown         39.70         5.20         7.40         -         8.20           5         [M[(II/1/2](C)/ <sub>1</sub> / <sub>1</sub> / <sub>1</sub> / <sub>1</sub> O)]         Brown         39.70         5.20         7.40         -         8.20           C <sub>4</sub> H <sub>3</sub> 0, MN <sub>1</sub> O <sub>4</sub> 49.23         (40.10)         (4.57)         (10.02)         (16.90)         3.400           C <sub>4</sub> H <sub>3</sub> 0, MN <sub>1</sub> O <sub>4</sub> 49.23         (40.10)         (4.57)         (10.02)         (16.90)         3.400           C <sub>4</sub> H <sub>3</sub> 0, MN <sub>1</sub> O <sub>4</sub> 466.23         (46.37)         (5.40)         (9.01)         -         -         3.400           C <sub>4</sub> H <sub>3</sub> 0, MN <sub>1</sub> O <sub>4</sub> 466.23         (46.37)         (5.40)         (9.01)         2.25.00         2.0.10           C <sub>4</sub> H <sub>4</sub> 1, MN <sub>2</sub> O <sub>4</sub> Brown         3.50         6.20         16.50         2.2.50         3.2.70	1	$[Co(HL^{1})(OAc)_{2}(H_{2}O)_{2}] \cdot 1.5H_{2}O$	Brown	42.90	4.70	8.90	-	3.80
2         [Co(UL)_2[C;H_0O)         Beep brown         50.90         5.00         11.80         11.00         10.72           3         [Ni(HJ)C,Q[H_0O)_12H_0O         Green         37.40         5.40         8.90         16.00         23.40           4         [Ni(L <sup>1</sup> )C,Q(H_0O)_12H_0O         Green         37.40         5.05         (9.10)         15.46         -         8.20         15.46           4         [Ni(L <sup>1</sup> )C,Q(H_0O)_12H_0O         604.712         (3.66)         4.83         (6.64)         -         8.20           5         [Min(H <sup>1</sup> )C,Q(H_0O)_12H_0O         604.712         (3.66)         4.83         (5.64)         10.02         (16.94)           6         [Amin(H <sup>1</sup> )C,QAC,(H_0O)_12H_0O         1900.0         4.560         4.80         8.70         -         3.400           6         [Amin(H <sup>1</sup> )CAC,(H_0O)_13H_0O         4663.2         (4.60)         (3.60)         (1.61)         (5.40)         (1.61)         (5.40)         (1.61)         (5.40)         (1.61)         (5.60)         (1.62)         (1.61)         (1.61)         (1.61)         (1.61)         (1.61)         (1.61)         (1.61)         (1.61)         (1.61)         (1.61)         (1.61)         (1.61)         (1.61)         (1.61)<		C <sub>18</sub> H <sub>28</sub> CoN <sub>3</sub> O <sub>9.5</sub>	497.23	(43.50)	(5.67)	(8.45)		
c <sub>µ</sub> h <sub>1</sub> c <sub>1</sub> C <sub>1</sub> CoN <sub>0</sub> O <sub>0</sub> 662.33         (50.70)         (4.87)         (12.70)         (10.72)           a         [N(H))C(f)(A)[b)[2A)         Green         37.40         5.40         8.00         16.00         23.40           a         [N(H))C(f)(A)[b)]         Brown         39.70         5.20         7.40         -         8.20           C <sub>A</sub> H <sub>2</sub> C <sub>5</sub> NN <sub>0</sub> O <sub>1</sub> Brown         39.70         5.20         7.40         -         8.20           C <sub>A</sub> H <sub>2</sub> C <sub>5</sub> NN <sub>0</sub> O <sub>1</sub> Green         40.00         5.00         9.90         16.60         13.50           C <sub>A</sub> H <sub>2</sub> C <sub>5</sub> NN <sub>0</sub> O <sub>1</sub> Green         40.00         (4.87)         (10.02)         (16.94)         34.00           C <sub>A</sub> H <sub>2</sub> C <sub>5</sub> NN <sub>0</sub> O <sub>1</sub> Brown         466.32         (46.37)         (5.40)         (9.01)         -         34.00           C <sub>A</sub> H <sub>2</sub> C <sub>5</sub> NN <sub>0</sub> O <sub>1</sub> Brown         466.32         (46.37)         (5.40)         (9.01)         -         34.00           C <sub>A</sub> H <sub>2</sub> C <sub>5</sub> NN <sub>0</sub> O <sub>5</sub> Brown         48.07         (3.60)         (10.01)         (23.30)         25.00         22.01         25.00         22.01         25.00         25.00         25.00         25.00         25.00         25.00         25.00 </td <td>2</td> <td><math>[Co(HL^1)_2]Cl_2 H_2O</math></td> <td>Deep brown</td> <td>50.90</td> <td>5.00</td> <td>11.80</td> <td>11.00</td> <td>101.50</td>	2	$[Co(HL^1)_2]Cl_2 H_2O$	Deep brown	50.90	5.00	11.80	11.00	101.50
3         [Ni(H) 2(r)(-),0); [2H,0,0)         67.00         5.40         8.90         16.00         23.40           4         [Ni)(1) (OA); (H_0)]         Brown         39.70         5.20         7.40         -         8.20           5         [Min(H) (Oa); (H_0)]         Brown         39.70         5.20         7.40         -         8.20           6         [Min(H) (Oab); (H_0)]         Brown         40.00         5.00         9.90         16.60         13.30           7         [Fe(H) (M),0,1         419.23         (40.10)         (45.7)         (10.02)         (16.94)         -           6         [Min(H) (Oab); (H_0)]         Brown         45.60         4.80         8.70         -         34.00           7         [Fe(H),10,0,1         Brown         45.60         4.80         8.70         25.00         20.10           7         [Fe(H),10,21, H0,0,1         Brown         35.20         3.40         9.00         22.50         32.70           7         [Fe(H),10,21, H0,0]         Brown         35.20         11.70         9.00         -         -         -           7         [Ca,H1,9,0,5,0]         Blue         41.10         5.40         15.20         <		C <sub>28</sub> H <sub>32</sub> Cl <sub>2</sub> CoN <sub>6</sub> O <sub>5</sub>	662.53	(50.70)	(4.87)	(12.70)	(10.72)	
Calls/CD/NNO.6         499.01         (36.3)         (5.0)         (9.15)         (15.4e)           4         (Ni,U)(0A),(Ho))         Brown         39.70         5.20         7.40         -         8.20           5         (Ni,U)(0A),(Ho))         Green         40.00         5.00         9.90         16.60         13.50           6         (Ni,U)(U)(2,(Ho))         Green         40.00         6.00         9.90         16.69         1.20           6         (Ni,U)(U)(2,(Ho))         Brown         45.60         4.80         8.70         -         34.00           6         (Ni,U)(U)(2,(Ho))         Brown         45.60         4.80         9.00         22.50         20.00           7         (F(H1)/C)         Brown         35.20         3.40         9.0         22.50         32.70           7         (F(H1)/C)         Brown         35.20         3.40         9.0         22.50         32.70           8         (Ri(H1)/C)(Ho))         Brown         5.20         1.620         -         -         4.00           9         (CiH2)(A)(A)(Ho)         Brown         5.19         4.870         5.20         1.70         9.80         1.50	3	$[Ni(HL^{1})Cl_{2}(H_{2}O)_{2}]\cdot 2H_{2}O$	Green	37.40	5.40	8.90	16.00	23.40
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		C14H23Cl2NiN3O6	459.01	(36.63)	(5.05)	(9.15)	(15.46)	
Cadhawinaboli         G00.712         (3966)         (4.8)         (6.4)           5         Cadhawinaboli         419.23         (40.10)         (5.00)         9.90         (16.04)           6         Min(HL) Cachy(14.50);         Brown         45.60         4.80         8.70         -         \$3.400           7         [Fe(HL)CI;]         Brown         46.63         (40.37)         (5.40)         (9.01)         2.50         2.50         2.50           8         [Ru(HL)CI;]         Brown         35.20         3.40         9.00         2.50         2.70           6         (44.7), Cla(HN,05)         43.57         (3.47.7)         (3.54)         (8.70)         2.250         2.70           1         Mit         50.5         5.22.3         (41.7)         (5.60)         (5.70)         (17.8)         3.40           1         [Ca(HL <sup>2</sup> )(Ac);]4H <sub>2</sub> O         Biue         41.10         5.40         7.00         1.02           1         [Ca(HL <sup>2</sup> )(Ac);]4H <sub>2</sub> O         Brown         51.15         (5.21)         1.170         9.80         1.050           1         [Ca(H <sup>2</sup> )(Ac);]4H <sub>2</sub> O         Brown         51.15         (5.21)         1.170         9.80         1.050 <td>4</td> <td><math>[Ni_2(L^1)(OAc)_3(H_2O)_3]</math></td> <td>Brown</td> <td>39.70</td> <td>5.20</td> <td>7.40</td> <td>_</td> <td>8.20</td>	4	$[Ni_2(L^1)(OAc)_3(H_2O)_3]$	Brown	39.70	5.20	7.40	_	8.20
5         [Ma((HL)')Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> )         Green         40.00         5.00         9.00         16.60         13.50           6         [CaH <sub>3</sub> Cl <sub>3</sub> MN <sub>5</sub> O <sub>4</sub> 412.32         (40.10)         (45.7)         (10.02)         (16.00)         -         34.00           CaH <sub>3</sub> MN <sub>1</sub> O <sub>6</sub> 460.37         (5.40)         (3.01)         (2.50)         (2.10)           7         [Fe(HL')Cl <sub>1</sub> ]         Brown         40.40         3.80         9.50         (2.50)         (2.10)           CaH <sub>1</sub> S(HN <sub>3</sub> O <sub>4</sub> )         Brown         35.20         3.40         9.0         2.500         2.500         2.70           CaH <sub>1</sub> (HL')Cl <sub>1</sub> H <sub>2</sub> O)         Brown         35.20         3.40         9.0         2.203         2.270           CaH <sub>2</sub> (HL')Cl <sub>2</sub> H <sub>2</sub> O)         Brown         43.57         (34.77)         (3.54)         (8.70)         (2.02)         -           H <sup>2</sup> Buff         6.50         6.50         (5.20)         (15.3)         -         -         3.40           CaH <sub>2</sub> H <sub>2</sub> (NAN,50         S22.23         (41.39)         (5.60         (8.55)         -         -         3.40           CaH <sub>2</sub> (CoNA,55         694.53         (48.70)         (4.80)         (10.22)         -		$C_{20}H_{29}Ni_2N_3O_{11}$	604.712	(39.66)	(4.83)	(6.94)		
C4H μC(MN/h)O <sub>4</sub> (h)O <sub>2</sub> )         H023         (40.0)         (47)         (10.2)         (16.34)           G         C4H <sub>2</sub> (MNh)O <sub>4</sub> 465.23         (46.37)         (5.40)         9.01         -         3.400           C <sub>14</sub> H <sub>2</sub> (MNh)O <sub>6</sub> 466.23         (46.37)         (5.40)         9.01         -         3.400           C <sub>14</sub> H <sub>2</sub> (MNh)O <sub>5</sub> 419.64         (40.07)         (3.60)         (10.10)         (25.33)         -           Ru((HL)/C3(H20))         M357         (34.77)         (3.54)         (8.70)         (22.02)         -           H <sup>2</sup> Buff         60.50         6.20         16.20         -         -         -           C <sub>14</sub> H <sub>1</sub> NGN         8137         (34.77)         (3.54)         (8.70)         -         3.40           C <sub>14</sub> H <sub>1</sub> NGN         8107         63.00         63.00         (13.30)         -         -         3.40           C <sub>14</sub> H <sub>1</sub> NGN <sub>2</sub> (MA <sub>2</sub> )         Hite         411.00         5.40         (8.60)         -         -         -         3.40           C <sub>14</sub> H <sub>1</sub> NGN <sub>2</sub> (MA <sub>2</sub> )         Hite         48.70         5.20         11.70         9.80         -         -         -         -         -         - </td <td>5</td> <td><math>[Mn((HL^1)Cl_2(H_2O)_2]</math></td> <td>Green</td> <td>40.00</td> <td>5.00</td> <td>9.90</td> <td>16.60</td> <td>13.50</td>	5	$[Mn((HL^1)Cl_2(H_2O)_2]$	Green	40.00	5.00	9.90	16.60	13.50
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{14}H_{19}Cl_2MnN_3O_4$	419.23	(40.10)	(4.57)	(10.02)	(16.94)	
C <sub>μ</sub> H <sub>2</sub> MN <sub>2</sub> O <sub>8</sub> 466.23         (46.37)         (5.40)         (9.01)           7         C <sub>μ</sub> (H <sub>2</sub> C)L <sup>1</sup> )         Brown         40.40         3.80         9.50         25.00         20.10           8         [Ru((H1,Cl <sub>2</sub> (H <sub>2</sub> O)]         Brown         35.20         3.40         9.0         22.50         22.00           1         HL <sup>2</sup> Buff         60.50         6.20         16.20         -         -           9         [Co(H <sup>2</sup> / <sub>2</sub> )OA <sub>2</sub> / <sub>2</sub> ] 4H <sub>2</sub> O         Buff         60.50         (5.50)         (15.00)         - <td< td=""><td>6</td><td><math>[Mn((HL^1)(OAc)_2(H_2O)_2]</math></td><td>Brown</td><td>45.60</td><td>4.80</td><td>8.70</td><td>-</td><td>34.00</td></td<>	6	$[Mn((HL^1)(OAc)_2(H_2O)_2]$	Brown	45.60	4.80	8.70	-	34.00
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{18}H_{25}MnN_{3}O_{8}$	466.23	(46.37)	(5.40)	(9.01)		
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	7	$[Fe((HL^1)Cl_3]$	Brown	40.40	3.80	9.50	25.00	20.10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{14}H_{15}Cl_3FeN_3O_2$	419.64	(40.07)	(3.60)	(10.01)	(25.38)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	$[Ru((HL^1)Cl_3(H_2O)]$	Brown	35.20	3.40	9.0	22.50	32.70
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{14}H_{17}Cl_3RuN_3O_3$	483.57	(34.77)	(3.54)	(8.70)	(22.02)	
$ \begin{array}{c} { { { c} } { $		HL <sup>2</sup>	Buff	60.50	6.20	16.20	-	-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> OS	273.30	(61.50)	(5.50)	(15.38)		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	9	$[Co(HL^2)(OAc)_2]\cdot 4H_2O$	Blue	41.10	5.40	7.90	-	3.40
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		C <sub>18</sub> H <sub>29</sub> CoN <sub>3</sub> O <sub>9</sub> S	522.23	(41.39)	(5.60)	(8.05)		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10	$[Co(HL^2)_2]Cl_2 \cdot H_2O$	Blue	48.70	5.20	11.70	9.80	105.20
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		C <sub>28</sub> H <sub>32</sub> Cl <sub>2</sub> CoN <sub>6</sub> O <sub>3</sub> S <sub>2</sub>	694.53	(48.42)	(4.64)	(12.10)	(10.22)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11	$[Co(HL^2)_2(OH)_2] \cdot H_2O$	Brown	51.19	4.80	13.14	-	10.30
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{28}H_{34}CoN_6O_5S_2$	657.53	(51.15)	(5.21)	(12.80)		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	12	$[Cu(L^2)(OAc)(H_2O)_2] \cdot H_2O$	Buff	43.40	4.93	9.60	-	8.50
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{16}H_{23}CuN_3O_6S$	448.83	(42.82)	(5.16)	(9.36)		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	13	$[Cu(HL^2)Cl_2(H_2O)_2]\cdot H_2O$	Brown	36.61	4.20	8.80	14.90	9.50
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{14}H_{21}Cl_2CuN_3O_5S$	461.84	(36.41)	(4.58)	(9.1)	(15.36)	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	14	[Cu(HL <sup>2</sup> )(NO <sub>3</sub> ) <sub>2</sub> ]·0.5EtOH	Green	37.28	3.9	15.00	-	4.90
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{15}H_{18}CuN_5O_{7.5}S$	483.84	(37.24)	(3.75)	(14.47)		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	15	$[Ni(HL^2)(OAc)_2(H_2O)_2]$	Buff	44.90	5.00	8.45	-	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		C <sub>18</sub> H <sub>25</sub> NiN <sub>3</sub> O <sub>7</sub> S	486.01	(44.49)	(5.18)	(8.65)		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	16	$[Ni(HL^2)Cl_2]\cdot 7H_2O$	Brown	31.17	4.95	8.20	13.00	32.10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{14}H_{29}Cl_2NiN_3O_8S$	529.01	(31.80)	(5.53)	(7.94)	(13.42)	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	17	$[Mn(HL^2)(OAc)_2(H_2O)_2]$	Pale brown	44.11	4.40	8.45	-	7.4
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		$C_{18}H_{25}MnN_{3}O_{7}S$	482.23	(44.83)	(5.23)	(8.71)		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	18	$[Mn(HL^2)Cl_2(H_2O)_2] \cdot 1.5H_2O$	Brown	36.20	3.90	8.79	16.00	26.7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		C <sub>14</sub> H <sub>22</sub> Cl <sub>2</sub> MnN <sub>3</sub> O <sub>4.5</sub> S	462.34	(36.37)	(4.76)	(9.09)	(15.36)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	19	$[Fe(HL^2)Cl_3]\cdot 2H_2O$	Deep brown	35.75	3.99	8.50	22.00	3.5
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		$C_{14}H_{19}Cl_3FeN_3O_3S$	471.64	(35.65)	(4.06)	(8.91)	(22.58)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	20	[Cr(HL <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]Cl·EtOH	Brown	48.60	4.80	11.60	13.85	80.9
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{30}H_{36}Cl_3CrN_6O_3S_2$	751.10	(48.00)	(4.83)	(11.17)	(14.18)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	21	[Ru(HL <sup>2</sup> )Cl <sub>3</sub> ]·0.5EtOH	Brown	35.40	3.80	8.21	20.70	25.3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{15}H_{18}Cl_{3}RuN_{3}O_{1.5}S$	504.57	(35.71)	(3.60)	(8.33)	(21.1)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22	$[ZrO(HL^2)Cl_2(H_2O)_2] \cdot 5H_2O$	Brown	28.40	4.70	7.60	11.70	20.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_{14}H_{29}Cl_2ZrON_3O_8S$	577.52	(29.12)	(5.00)	(7.27)	(12.29)	
$C_{14}H_{25}Cl_2HIN_3O_7S$ 628.79 (26.74) (4.01) (6.68) (11.29)	23	$[Hf(HL^2)Cl_2(OH)_2]\cdot 4H_2O$	Brown	27.20	4.20	6.46	10.90	22.5
		$C_{14}H_{25}Cl_2HtN_3O_7S$	628.79	(26.74)	(4.01)	(6.68)	(11.29)	

<sup>a</sup>  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>.

(1, 4, 6, 8, 9, 10, 12, 13, 14, 16, 18, 21 and 22), whereas the higher wave number bands at 3392–3388 cm<sup>-1</sup> appeared at different positions with a very broad nature due to overlapping with  $\upsilon$ (OH) of water of crystallization [20,23]. The infrared spectra of metal complexes (1, 8, 10, 13, 14 and 18) show shift to lower wave number for  $\upsilon$ (C=O) and  $\upsilon$ (HC=N). This is consistent with coordination of carbonyl oxygen and azomethine nitrogen atoms [9,24]. The  $\upsilon$ (HC=N) band of free ligand (1619 cm<sup>-1</sup>) exhibits a bathchromic shift of 19–51 cm<sup>-1</sup> for complexes (2, 6, 9, 17 and 22). Also, the vibrations due to hetero-ring atoms undergo hypsochronic shift of 28–45 cm<sup>-1</sup> upon complexation. The spectra of these complexes show that the  $\upsilon$ (C=O) remains unchanged. The above arguments indicate that the ligands in these complexes behave as neutral bidentate and coordination occurs via the azomethine nitrogen atom and the hetero-oxygen or sulphur atoms.

The absorption band due to v(C=0) at 1676 cm<sup>-1</sup> and the thiophene ring bending band at 577 cm<sup>-1</sup> of free ligand HL<sup>2</sup> appear at the same position or are slightly affected upon complexation for

(11, 15, 20 and 23). On the other hand, the vibration of NH and (HC=N) is perturbed upon complexation, which indicate that the coordination takes place via anilino nitrogen atom and azomethine nitrogen atom.

The complexes (7, 16, 19 and 21) show that the v(C=0) of free ligands HL<sup>1</sup> or HL<sup>2</sup> were shifted to lower frequency by 18–40 cm<sup>-1</sup>, whereas the hetero-ring bending exhibited positive or negative shifts by 11–25 cm<sup>-1</sup> upon complexation. Moreover, the band due to v(HC=N) of free ligands is strongly affected in shape and position upon complexation. The above discussion reveals that the metal ions (except Ni(II)) form neutral coordination compounds through carbonyl oxygen, azomethine nitrogen and hetero-atoms. However, for Ni(II) complex (16) the ligand was binding with Ni(II) ion through azomethine nitrogen atom and carbonyl oxygen atom or hetero-atom.

The infrared spectra of complexes (3 and 5) display that the bands due to v(HC=N) and hetero-atom do not participate in coordination. While, the v(C=O) band shows shift to higher frequency

Table 2

Infrared spectral bands and their assignments for ligands and their metal complexes.

No.	Compound	$\upsilon(H_2O)$	$\upsilon(\rm NH)$	<i>∪</i> (C=0)	$\upsilon$ (C=N)	R.b. F/S	υ(M−−0)	U(M-N)	∪(M—S)	v(Anion)
	HL <sup>1</sup>	-	3392(s), 3200(s),	1673(vs)	1619(s)	587(m)	_	-	-	-
1	$[Co(HL^1)(OAc)_2(H_2O)_2] \cdot 1.5H_2O$	3440(w) 671*	3390(b), 3200(w), 3120(w)	1615(w)	1550(w)	583(w)	515(w)	450(sh)	_	(1600, 1400) <sup>b</sup>
2	$[Co(HL^1)_2]Cl_2{\cdot}H_2O$	3461(s)	3354(s), 3215(w), 3120(w)	1673(m)	1568(m)	632(w)	518(m)	450(sh)	-	330(w) <sup>a</sup>
3	$[Ni(HL^1)Cl_2(H_2O)_2] \cdot 2H_2O$	3500 666*	3391(s.b), 3250(sb),	1701(s)	1616(s)	588(m)	512(w)	430(w)	-	330(w) <sup>a</sup>
4	$[Ni_2(L^1)(OAc)_3(H_2O)_3]$	3480(w) 676*	– 3200(b), 2118(w)	_	1605, 1545	628	540	460(w)	-	(1600, 1417) <sup>b</sup>
5	$[Mn((HL^1)Cl_2(H_2O)_2]$	3375(s) 667*	-	1701(s)	1615(s)	586(w)	510(w)	445(sh)	-	330(w) <sup>a</sup>
6	$[Mn((HL^1)(OAc)_2(H_2O)_2]$	3430 668*	3392, 3200(m),	1673(s)	1568(s)	615, 590(w.sp)	517(w)	485(w)	-	(1600, 1392) <sup>b</sup>
7	[Fe((HL <sup>1</sup> )Cl <sub>3</sub> ]	-	3420, 3250(sh), 3125(sh)	1655(w)	1610(w)	619, 576(sh)	505(m)	410(s)	-	371(s) <sup>a</sup>
8	$[Ru((HL^1)Cl_3H_2O]$	643*	3390(w), 3202(w), 2122(w)	1655(m)	1600(w)	589(m)	546(w)	450(w)	-	371(w) <sup>a</sup>
	HL <sup>2</sup>	-	3388(m), $3218(w)$	1676(s)	1619(m)	577(m)	_	-	-	-
9	$[Co(HL^2)(OAc)_2]$ ·4H <sub>2</sub> O	3442(b)	- 3222(sh)	1676(m)	1600(sh)	616(w)	518(w)	450(w)	437(w)	(1515, 1330) <sup>b</sup>
10	$[\text{Co}(\text{HL}^2)_2]\text{Cl}_2{\cdot}\text{H}_2\text{O}$	3423(b)	- 3209(sh)	1649(s)	1600(sh)	583(m)	516(w)	455(w)	-	327(w) <sup>a</sup>
11	$[Co(HL^2)_2(OH)_2] \cdot H_2O$	3420(s)	- 3185, 3167(w.sp)	1674(s)	1610(m)	580(m)	520(s)	435(m)	-	-
12	$[Cu(L^2)(OAc)(H_2O)_2] \cdot H_2O$	3427(b)	- 3220(sh)	-	1610(w) 1595(sh)	614(m)	515(w)	464(w)	415(w)	(1580, 1388) <sup>b</sup>
13	$[Cu(HL^2)Cl_2(H_2O)_2]\cdot H_2O$	3442(b)	- 3213(w)	1655(s)	1595(sh)	584(m)	518(w)	464(w)	_	380(w) <sup>a</sup>
14	$[Cu(HL^2)(NO_3)_2]$ ·0.5EtOH	3442(b)	- 3200(w)	1651(m)	1608(w)	579(w)	530(m)	489(m) 420(w)	-	(1389, 1300) <sup>c</sup>
15	$[Ni(HL^2)(OAc)_2(H_2O)_2]$	3449(b.w)	3403(s), 3167(w)	1674(s)	1610(m)	581(m)	522(s)	430(w)	_	(1584, 1402) <sup>b</sup>
16	$[Ni(HL^2)Cl_2]$ ·7H <sub>2</sub> O	3400(w)	3358(b), 3197(sh)	1635(w)	1610(w)	602(w)	490(s)	452(w)	415(w)	-
17	$[Mn(HL^2)(OAc)_2(H_2O)_2]$	3420	3383(w), 3222(w)	1677(m)	1555(b)	581(m)	517(w)	470(sh)	-	(1600, 1344) <sup>b</sup>
18	[Mn(HL <sup>2</sup> )Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]·1.5H <sub>2</sub> O	3413(b)	– 3222(sh)	1631(w)	1590(w)	582(m)	513(sh)	462(sh)	-	372(w) <sup>a</sup>
19	[Fe(HL <sup>2</sup> )Cl <sub>3</sub> ]·2H <sub>2</sub> O	3418(b)	3304(m), 3222(w)	1649(m)	1587(m)	564(m)	508(m)	470(sh)	436	-
21	[Cr(HL <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]Cl·EtOH	3404(m)	- 3170(w)	1676(s)	1608(w)	583(w)	-	495(w)	-	-
21	[Ku(HL <sup>2</sup> )Cl <sub>3</sub> ]·0.5EtOH	3422(b.w)	3317(w.b), 3200(m)	1654(m)	1620(w)	588(w)	490(w)	466(w)	417(w)	-
22	$[ZrO(HL^2)Cl_2(H_2O)_2] \cdot 5H_2O$	3180(b) 653*	3197(w) 3187(w)	1679(w)	1594(w)	615(w)	_	464	417(w)	-
23	$[Hf(HL^2)Cl_2(OH)_2]\cdot 4H_2O$	3403(m)	-	1673(m)	1611(w) 1582(w)	579(w)	-	466(w)	-	370(w) <sup>a</sup>

R.b.: ring bending; F: furan; S: thiophene; s: strong; b: broad; w: weak; sh: shoulder; m: medium; \*: coordinated water; a: v(M-Cl); b: monodentate acetate  $v(COO)^{-}$ ; c: monodentate nitrate  $v(NO_3)^{-}$ .

by 28 cm<sup>-1</sup> relative to that of free ligand. Also, the band due to  $\upsilon$ (NH) is perturbed upon complexation. This indicates that the ligand in these complexes reacts as a bidentate molecule and coordination occurs via the carbonyl oxygen atom and anilino nitrogen atom.

The infrared spectra of metal complexes (4 and 12) reveal that the disappearance of  $\upsilon$ (C=O) band in free ligands HL<sup>1</sup> and HL<sup>2</sup> and the formation of a new band at about 1605–1610, 1545–1595 cm<sup>-1</sup> are attributed to the  $\upsilon$ (C=N–N=C) and  $\upsilon$ (N=C–O), respectively. This is in agreement with the deprotonated nature of ligands [9,17,25]. The  $\upsilon$ (HC=N) band of free ligands HL<sup>1</sup> and HL<sup>2</sup>

exhibited shifts to lower frequency, whereas the hetero-atoms, oxygen or sulphur atom displayed shifts to higher frequency by  $37-41 \text{ cm}^{-1}$  upon complexation. According to this assumption, the azomethine nitrogen atom and hetero-atoms become involved in coordination to form complexes (4 and 12). In addition, the band due to v(NH) ( $3118 \text{ cm}^{-1}$ ) for HL<sup>1</sup> ligand is absent in complex (4) while, the v(NH) ( $3218 \text{ cm}^{-1}$ ) for HL<sup>2</sup> is unchanged upon complexation (12). This indicates that the anilino NH group takes place in coordination to form binuclear complex (4) and is not involved in complex (12). The above discussion, along with elemental analyses, suggests that the ligand HL<sup>1</sup> reacts as enolic tetradentate with

T	a	b	le	

Magnetic moments  $\mu_{\mathrm{eff}}$  (B.M.) and electronic spectral bands for metal complexes in solid state.

No.	Compound	$\mu_{ m eff}$ (B.M.) <sup>a</sup>	d-d transitions (nm)
1	[Co(HL <sup>1</sup> )(OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]·1.5H <sub>2</sub> O	5.01	626(w), 584(w)
2	$[Co(HL^1)_2]Cl_2 \cdot H_2O$	3.44	692(s), 668(s), 632(s).
3	$[Ni(HL^1)Cl_2(H_2O)_2]\cdot 2H_2O$	3.01	628(w), 574(w), 526(s)
4	$[Ni_2(L^1)(OAc)_3(H_2O)_3]$	1.10	624(w), 588(w), 528(s)
5	$[Mn((HL^1)Cl_2(H_2O)_2]$	5.80	529(w), 568(w)
6	$[Mn((HL^1)(OAc)_2(H_2O)_2]$	6.01	594(w), 554(m), 532(m)
7	$[Fe(HL^1)Cl_3]$	4.62	626(w), 604(w), 566(s)
8	$[Ru((HL^1)Cl_3(H_2O)]$	1.74	746(w), 600(w), 564(s)
9	$[Co(HL^2)(OAc)_2]\cdot 4H_2O$	4.40	584(s), 538(s)
10	$[Co(HL^2)_2]Cl_2 \cdot H_2O$	4.60	688(s), 658(s), 626(s), 604(w)
11	$[Co(HL^2)_2(OH)_2] \cdot H_2O$	4.20	626(w), 566(w)
12	$[Cu(L^2)(OAc)(H_2O)_2] \cdot H_2O$	1.75	652(br), 580(w)
13	$[Cu(HL^2)Cl_2(H_2O)_2]\cdot H_2O$	1.68	664(br), 586(w)
14	[Cu(HL <sup>2</sup> )(NO <sub>3</sub> ) <sub>2</sub> ]·0.5EtOH	1.08	680(br), 584(m), 550(w)
15	$[Ni(HL^2)(OAc)_2(H_2O)_2]$	3.35	766(w), 700(w), 625(w), 578(m)
16	$[Ni(HL^2)Cl_2]\cdot7H_2O$	4.30	875(w), 830(w),760(w), 690(w), 570(m)
17	$[Mn(HL^2)(OAc)_2(H_2O)_2]$	5.70	600(w), 572(w), 542(m)
18	$[Mn(HL^2)Cl_2(H_2O)_2] \cdot 1.5H_2O$	1.70	624(w), 552(w), 526(m)
19	$[Fe(HL^2)Cl_3]\cdot 2H_2O$	5.90	600(w), 576(s), 560(m)
20	[Cr(HL <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]Cl·EtOH	2.30	622, 592, 570, 532(m)
21	[Ru(HL <sup>2</sup> )Cl <sub>3</sub> ].0.5EtOH	1.65	762(w), 600(w), 570(s)

w: weak; m: medium; s: strong; b: broad.

<sup>a</sup> Per metal atom.

nickel acetate to form binuclear complex (4). However, the ligand  $HL^2$  reacts as enolic tridentate with copper acetate to form mononuclear complex (12).

New bands are found in spectra of complexes in the regions 546-490, 492-410 and 366-415 cm<sup>-1</sup> assigned to v(M-O), v(M-N)and  $\upsilon$ (M–S), respectively [10,24]. The spectra of acetato complexes show two bands near 1600–1575 and 1400–1325 cm<sup>-1</sup>, due to  $v_{\rm as}(\rm COO^-)$  and  $v_{\rm s}(\rm COO^-)$ , respectively, suggesting that the acetate ligand coordinates as a monodentate ligand [3]. The spectrum of complex [Cu(HL<sup>2</sup>)(NO<sub>3</sub>)<sub>2</sub>]·0.5EtOH (14) shows two bands at 1389 and 1300 cm  $^{-1}$  , assigned to  $\upsilon_{as}(\text{NO}_3{}^-)$  and  $\upsilon_{s}(\text{NO}_3{}^-)$  , respectively, indicating that the  $NO_3^-$  group reacts as a monodentate ligand [9,25]. The spectra of chloro-complexes display a new band in the range 330–380 cm<sup>-1</sup> assigned to v(M-Cl) [26]. The spectra of complexes which contain water molecules show a broad band near 3480–3380 cm<sup>-1</sup>, assigned to v(OH) of crystallization water involved in the complexes [2,27]. Moreover, the spectra of complexes containing coordinated water molecules show additional two bands near 960 and 640 cm<sup>-1</sup>, owing to  $\rho_{\rm rock}({\rm H_2O})$  and  $\rho_{\text{wagg}}(\text{H}_2\text{O})$ , respectively [1,25]. The appearance of the latter two modes indicates coordinated water rather than hydrated water.

#### 3.2.2. Electronic spectra and magnetic moments

The electronic spectral data of the metal complexes in nujol mull and their room temperature magnetic moment values ( $\mu_{eff}$  B.M.) per metal ion are given in Table 3.

The electronic spectra of cobalt(II) complexes (2, 9 and 10) reveal ( $\upsilon_3$ ) band as a high intensity multiple bands, assigned to tetrahedral arrangement around the cobalt(II) ion [28]. The magnetic moment values ( $\mu_{\rm eff}$  = 3.44–4.6 B.M.) provide further evidence for tetrahedral geometry for cobalt(II) complexes [10,25], while the cobalt(II) complexes (1 and 11) display the ( $\upsilon_3$ ) as a weak intensity broad bands at 626 and 584–566 nm [27,28]. These bands, gathered with ( $\mu_{\rm eff}$  values = 4.2–5.01 B.M.), suggest spin free octahedral geometry [19,27,29].

The nickel(II) complexes (3, 4 and 15) display three bands in range 766–700 ( $\upsilon_1$ ), 628–624 ( $\upsilon_2$ ) and 578–526 ( $\upsilon_3$ )nm attributable to  ${}^{3}A_{2}g \rightarrow {}^{3}T_{2}g$ ,  ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(F)$  and  ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(p)$  transitions, respectively, characteristic of octahedral geometry [27]. The room temperature magnetic moment values are 1.1–3.35 B.M. (Table 3) [28,29]. The low magnetic moment value 1.1 B.M. for complex (4) is due to a super magnetic exchange interaction via bridging of enolic oxygen atom, which binds two nickel(II) atoms forming the binuclear complex. The spectrum of nickel(II) complex (16) and the magnetic moment value 4.3 B.M. are compatible with tetrahedral nickel complex. The spectrum displays multiple bands near 875 and 570 nm, assigned to the  ${}^{3}T_{1}(F) \rightarrow {}^{3}A_{2}(\upsilon_{2})$  and  ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(\upsilon_{3})$  transitions, respectively [30].

The spectra of copper(II) complexes (12 and 13) consist a broad, weak band centered at 664–652 and 586–580 nm, and assigned to  ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$  and  ${}^{2}B_{1} \rightarrow {}^{2}E_{g}$ , indicating tetragonally distorted octahedral structure [22,28]. The copper complex (14) shows a multiple band near 550 nm which states a square planar geometry around Cu(II) ion [6,25]. The magnetic moment value of complexes (12 and 13) is 1.68–1.73 B.M., corresponding to the spin value (1.73 B.M.), indicating the monomeric nature [17]. The low magnetic moment of the copper(II) complex (14) (1.08 B.M.), suggests the presence of magnetic exchange interaction between adjacent Cu(II) atoms [28,30].

The manganese(II) complexes display three absorption bands in 624–592, 572–552 and 542–532 nm region, characteristic of octahedral geometry. These bands are assigned to  ${}^{6}A_{1}g \rightarrow {}^{4}T_{1}g({}^{4}G)(\upsilon_{1})$ ,  ${}^{6}A_{1}g \rightarrow {}^{4}Eg({}^{4}G)(\upsilon_{2})$  and  ${}^{6}A_{1}g \rightarrow {}^{4}Eg({}^{4}D)(\upsilon_{3})$  transitions, respectively [10,31]. The  $\mu_{eff}$  values (5.7–6.1 B.M.) for manganese(II) complexes (5, 6 and 17) are compatible with high-spin octahedral Mn(II) complexes [26]. Complex (18) has ( $\mu_{eff}$  = 1.7 B.M.), indicative of low spin octahedral geometry for Mn(II) complex.

The electronic spectra of iron(III) complexes (7 and 19) show absorption bands near 626–600 and 576–560 nm, assigned to the  ${}^{6}A_{1}g \rightarrow {}^{4}T_{2}g$  and  ${}^{6}A_{1}g \rightarrow {}^{4}A_{1}g$  (*G*) transitions in octahedral stereochemistry [32]. The observed magnetic moment value of iron(III) complex (19) is 5.9 B.M., indicating high spin octahedral of iron(III) complexes [3,9]. The lower magnetic value 4.6 B.M. of complex (7) is due to the presence of equilibrium between high and low spin state [33].

The electronic spectrum of chromium(III) complex (20) displays four bands at 622, 592, 570 and 532 nm. These bands are consistent with octahedral stereochemistry [31]. The low  $\mu_{\rm eff}$  value (2.3 B.M.) of Cr(III) complex is attributed to existence of magnetic exchange interaction between adjacent Cr(III) atoms.

Compound	$^{a} \varDelta_{1}$	$^{a} \varDelta_{2}$	$g_{  }$	$g_{\perp}$		<g></g>	G	<i>K</i> //	$K_{\perp}$	Κ	$\alpha^2$	$\beta^2$	$A_{//}(G)$	$g_{//}/A_{//}({ m cm}^{-1})$
12	17,065	15,037	2.239	2.057		2.12	4.19	0.73	0.75	0.74	0.64	1.65	120.0	179.12
Compound	$^{a} \varDelta_{1}$	$^{a}\Delta_{2}$	$g_x$	$g_y$	gz	R	<i>K</i> <sub>//</sub>	$K_{\perp}$	I	ĸ	$\alpha^2$	$\beta^2$	$A_{//}(G)$	$g_{  }/A_{  }$ (cm <sup>-1</sup> )
14	-	-	2.23	2.09	2.03	0.43	-	-	-	-	-	-	-	-

 Table 4

 ESR spectral parameter of copper(II) complexes.

<sup>a</sup> Unit of  $\Delta$  is cm<sup>-1</sup>.

The ruthenium(III) complexes (8 and 21) gave three absorption bands in the regions 762, 600 and 576–560 nm. These bands, in connection with  $\mu_{\text{eff}}$  values (1.74–1.65 B.M.), indicate a low spin octahedral geometry [3,26].

#### 3.2.3. Electronic spin resonance spectral studies

The esr spectrum pattern of the solid copper(II) complex (12) at room temperature exhibits an axial type symmetry (Table 4), where  $g_{||} > g_{\perp} > 2.0023$ , indicating  $d_{(\chi^2 - \chi^2)}$  ground state for tetragonal copper(II) complexes [34]. The calculated  $\langle g \rangle = (g_{||} + 2g_{\perp})/3 = 2.12$ , suggests the high covalence property of complex with distorted symmetry [23]. In an axial symmetry, the g-values are related by  $G = (g_{||} - 2.003)/(g_{\perp} - 2.003) = 4.0$ , if G > 4, the exchange interaction between copper(II) centers in the solid state is negligible. Whereas G < 4, a considerable exchange interaction occurs in the solid state complexes. The G value of complex is 4.19, ruling out the exchange interactions [10] and assigning the tetragonal distorted geometry [35,36]. This result is in agreement with the magnetic moment value (1.73 B.M.) for complex (12). The hyperfine coupling constants  $A_{||}$  = 120G and  $A_{\perp}$  = 25G indicate the dynamic tetragonal distortion for  $d_{(x^2-y^2)}$  ground state [23]. Also  $g_{//} = 2.23$ corresponds to covalence character of metal-ligand bond [30,32]. The  $(g_{||}/A_{||})$  values indicate the stereochemistry of the copper(II)

#### Table 5

TGA data for some metal complexes.

complexes [30,37]. The range reported for square planar complexes is 105–135 cm<sup>-1</sup> and for tetragonal distorted complexes is >135–250 cm<sup>-1</sup>. The complex (12) has  $(g_{//}/A_{//} = 179.12 \text{ cm}^{-1})$ , which lies in the range reported for tetragonal distorted copper(II) complexes [30,38]. The *g*-value of the copper complexes with a <sup>2</sup>B<sub>1g</sub> ground state can be related to  $k_{//}$  and  $k_{\perp}$  components of the orbital reduction factor (k) as follows [39,40]:

$$\begin{aligned} k_{//}^2 &= \frac{(g_{//} - 2.0023)\Delta_2}{8\lambda_0}, \quad k_{\perp}^2 &= \frac{(g_{\perp} - 2.0023)\Delta_1}{2\lambda_0} \\ k^2 &= \frac{(k_{//}^2 + 2k_{\perp}^2)}{3} \end{aligned}$$

where  $\lambda_o$  is the spin–orbit coupling of the free copper(II) ion  $(\lambda_o = -828 \text{ cm}^{-1})$ ,  $\Delta_1$  and  $\Delta_2$  are the electronic transitions,  ${}^2B_{1g} \rightarrow {}^2E_g$  and  ${}^2B_{1g} \rightarrow {}^2B_{2g}$ , respectively. The calculated values of  $k_{//}^2$ ,  $k_{\perp}^2$  and  $k^2$  (Table 4) exhibit the lower value of k than the unity (0.74), due to covalent nature [30,40], which is in agreement with the lower value of  $g_{//}$ .

The fraction of the unpaired electron density on copper(II) ion, in plane  $\sigma$ -bond coefficients  $\alpha^2$  was calculated by [23,41]:

$$\alpha^2 = \frac{A_{//}}{0.036} + (g_{//} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04$$

No.	Complex	Temperature range (°C)	Weight loss Found/(Calcd.)	Assignment	<i>T</i> <sub>s</sub> (°C)
1	[Co(HL <sup>1</sup> )(OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]·1.5H <sub>2</sub> O	32-159 159-218 218-441 441-700 700	5.10 (5.43) 6.95 (7.24) 23.81 (23.73) 46.00 (46.11) 16.65 (16.30)	Loss 1.5 molecules of hydrated water <sup>(a)</sup> s.d. Loss two molecules of coordinated water <sup>(d)</sup> Loss two molecules of coordinated acetate <sup>(d)</sup> Decomposed of organic ligand <sup>(d)</sup> CoO + C <sup>(f)</sup>	159
3	$[Ni(HL^1)Cl_2(H_2O)_2]\cdot 2H_2O$	49–127 127–190 190–267 267	4.9 (3.9) 3.6 (3.9) 24.0 (23.3)	Loss one molecule of hydrated water <sup>(a)</sup> Loss second molecule of hydrated water <sup>(a)</sup> s.d. Loss two molecules of coordinated water and two chloride ions <sup>(d)</sup> Decomposed of organic ligand <sup>(d)</sup>	190
9	[Co(HL <sup>2</sup> )(OAc) <sub>2</sub> ]·4H <sub>2</sub> O	147-181 181-241 241-315.75 315.75-600 600	7.09 (6.89) 4.87 (5.17) 22.27 (22.59) 34.88 (34.14) 30.89 (31.19)	Loss two molecules of hydrated water <sup>(a)</sup> Loss one and half molecules of hydrated water <sup>(a)</sup> s.d. Loss two molecules of coordinated acetate <sup>(d)</sup> Decomposed of organic ligand and loss $0.5H_2O^{(d)}$ CoS + $6C^{(f)}$	241
12	$[CuL^2(OAc)(H_2O)_2]\cdot H_2O$	50–160 160–191 191–241 241–500 500	4.5 (4.1) 8.2 (8.0) 13.69 (13.15) 48.0 (48.4) 26.9 (26.62)	Loss one molecule of hydrated water <sup>(a)</sup> s.d. Loss two molecules of coordinated water <sup>(d)</sup> Loss of coordinated acetate <sup>(d)</sup> Decomposed of organic ligand <sup>(d)</sup> CuS + 2C <sup>(f)</sup>	160
13	$[Cu(HL^2)Cl_2(H_2O)_2] \cdot H_2O$	112–161 161–200 200–300 300–790 790–800	4.0 (3.9) 8.2 (7.8) 15.8 (15.4) 44.2 (44.4) 27.9 (28.5)	Loss one molecule of hydrated water <sup>(a)</sup> s.d. Loss two molecules of coordinated water <sup>(d)</sup> Loss two coordinated chloride ions <sup>(d)</sup> Decomposed of organic ligand <sup>(d)</sup> CuS + 3C <sup>(f)</sup>	161
16	[Ni(HL <sup>2</sup> )Cl <sub>2</sub> ]·7H <sub>2</sub> O	35–85 85–148 150–258 255–650 650	16.8 (17.01) 7.3 (6.81) 13.35 (13.43) 48.46 (48.64) 14.05 14.08	Loss five molecules of hydrated water <sup>(a)</sup> Loss of the remaining two molecules of hydrated water <sup>(a)</sup> s.d. Loss two coordinated chloride ions <sup>(d)</sup> Decomposed of organic ligand <sup>(d)</sup> NiO <sup>(f)</sup>	148

s.d.: start of decomposition; <sup>(a)</sup>: dehydration; <sup>(d)</sup>: decomposition; <sup>(f)</sup>: final product; *T*<sub>s</sub>: thermal stability.

### Table 6

Minimal inhibitory co	oncentrations (MICs:	mg/mL) of metal	complexes of HL	<sup>2</sup> ligand.
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Compound	Gram-negative bacte	ria	Gram-positive bacte	Fungs	
	Escherichia coli	Klebsiella pneumonia	Bacillus cereus	Staphylococcus aureus	Candida albicans
(10)	25.0	ND	30.0	ND	ND
(12)	ND	15.0	45.0	ND	ND
(14)	20.0	15.0	30.0	25.0	ND
(15)	ND	ND	ND	ND	ND
(16)	12.0	10.0	12.0	50.0	15.0
(19)	10.0	10.0	15.0	10.0	10.0
Ampicillin	0.025	0.050	0.0125	0.0125	_
Clorimazole	-	-	-	-	0.025

ND: non detected.



Comple	x M	Х	Y	Ζ	n	m
(1)	Co(III)	0	$\rm H_2O$	OAc	1.5	-
(13)	Cu(II)	S	$\rm H_2O$	C1	1	-
(14)	Cu(II)	S	-	NO <sub>3</sub>	-	0.5
(18)	Mn(II)	S	$H_2O$	Cl	1.5	-



Complex (8)













Complex (4)



Scheme 1.



The calculated value,  $\alpha^2 = 0.61$ , suggests the covalent character [30,42].

The in-plane and out-plane  $\pi$ -bonding coefficients ( $\beta_1$  and  $\beta_2$ ) are dependent upon the values of  $\Delta_1$  and  $\Delta_2$  as in these expressions [39,40]:

$$\alpha^2 \beta^2 = \frac{(g_{\perp} - 2.0023)\Delta_1}{2\lambda_o}, \quad \alpha^2 \beta_1^2 = \frac{(g_{//} - 2.0023)\Delta_2}{8\lambda_o}$$

The value of  $\beta_1^2 = 0.84$  indicates a moderate degree of covalency of the in-plane  $\pi$ -bonding; while  $\beta^2 = 1.65$ , assigns ionic character of the out-of-plane  $\pi$ -bonding [3,43].

The approximate orbital population for the d orbital was estimated by [44,45]:

$$A_{iso} = \frac{(A_{//} + 2A_{\perp})}{3}, \quad A_{//} = A_{iso} - 2B\left(1 + \frac{7}{4}\right) \Delta g_{//},$$
$$\Delta g_{//} = g_{//} - 2.0023, \quad a_{p,d}^2 = \frac{2B}{2B^0}$$

where  $2B^o$  is the calculated dipolar coupling for unit occupancy of the d orbital. The parallel component of the dipolar coupling (2B = -272G) is negative and the orbital population is 81%, indicating that the ground state is  $d_{(x^2-y^2)}$  [3,30].

The spectrum of copper complex (14) shows non-axial parameter (Table 4) where  $g_x = 2.23$ ,  $g_y = 2.09$  and  $g_z = 2.03$ . The geometric parameter,  $R = (g_y - g_z)/((g_x - g_y) = 0.43$ , means that a  $d_{(x^2 - y^2)}$  ground state prevails [25,46]. The  $g_y$  value <2.3 was reported for covalent bond character [25,47,48].

#### 3.2.4. Thermal studies

The infrared spectra and elemental analyses show the presence of water molecules in the chemical structures of metal complexes. Therefore, the thermogravimetric analysis TGA was undertaken for some of the investigated metal complexes. The TGA data and their assignments are summarized in (Table 5). The TGA data show that the investigated complexes (1, 3, 9, 12, 13 and 16) display a weight loss within the temperature range 32-241 °C assignable to the loss of water of hydration [49,50]. The TGA curves also show the loss of coordinated water molecules in complexes (1, 3, 12 and 13) within the temperature range 159–267 °C [51,52]. The acetato complexes (1,9 and 12) also reveal the loss of coordinated acetate group within the temperature range 218–414 °C [1]. The three complexes (3, 13 and 16) show a weight loss within temperature range 150–300 °C, corresponding to the loss of coordinated chloride ions [28,29]. The decomposition of the organic ligand takes place within temperature range 241-840 °C [19,53]. The thermal decomposition process ended with the formation of metal oxide from complexes (1 and 16), or metal sulphide from complexes (9, 12 and 13) [19,28]. The TGA data of complexes (3,9 and 16) point out to the loss of hydrated water molecules at two ranges of temperature (Table 5), indicating that not all molecules of hydrated water bind similarly within the solid crystal [30,52].

The obtained data are consistent with the proposed chemical structure of complexes as shown in Scheme 1.

#### 3.2.5. Antibacterial activity

Minimum inhibitory concentrations (MICs) of metal complexes of HL<sup>2</sup> are given in Table 6. All tested metal complexes (10, 12, 14–16 and 19) are very weakly active against all tested microorganisms, *E. coli* and *K. pneumonia* (as gram negative bacteria) and *B. cereus* and *S. aureus* (as gram positive bacteria) and *C. albicans* (as fungs). The MIC values of these compounds are of 10000.0–50000.0 µg/mL when compared with the reference antibacterial agent, ampicillin (12.5–50.0 µg/mL) and antifungal agent; clorimazole (25.0 µg/mL) but complex (15) lacks any virtually microbial activity towards all tested microorganisms.

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