

## Synthesis, Characterization and Biological Activity of Some Transition Metal Complexes with Schiff Bases Derived from 2-Formylindole, Salicylaldehyde, and N-amino Rhodanine

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**Abstract:** The Schiff base ligands (L<sup>1</sup>) and (HL<sup>2</sup>) were prepared from the N-amino rhodanine and each of 2-formylindole (L<sup>1</sup>) and salicylaldehyde (HL<sup>2</sup>), respectively. Moreover, the ligands were characterized by elemental analysis, IR, mass, <sup>1</sup>HNMR and electronic spectra. The Cr(III), Co(II), Ni(II) and Ag(I) complexes of the ligands L<sup>1</sup> and HL<sup>2</sup> were prepared and characterized by the analytical and spectroscopic methods. In addition, the magnetic susceptibility and molar conductance measurements have been made. Tetrahedral geometrical structure was proposed for Ag(I) complex, whereas Cr(III), Co(III), Ni(II) and Cu (II) have octahedral configurations. The free ligands, and their metal complexes were screened for their antimicrobial activities. The results indicated that the ligands do not have any activity, whereas their complexes showed more activity against the same organisms under identical experimental conditions.

**Key words:** Synthesis, characterization, biological activity, Transition Metal, complexes, 2-Formylindole, Salicylaldehyde, Rhodanine

### INTRODUCTION

Schiff bases are important class of ligands due to their synthetic flexibility, their selectivity and sensitivity towards the central metal atom, structural similarities with natural biological substances and also due to presence of imine group (N=CH-) which imports in elucidating the mechanism of transformation and rasemination reaction in biological system (Spinu and Kriza 2000, Sari *et al.* 2003, Cimerman *et al.* 2000).

Rhodanine derivatives are known to possess biological activities such as anticonvulsant, antibacterial, antiviral and antidiabetic (Momose *et al.* 1991). Sudo *et al.* 1997 also reported rhodanine derivatives as hepatitis C virus (HCV) protease inhibitor. El-Bindary *et al.* 2000 have also widely prepared and studied several metal complexes of rhodanine azodyes due to their unusual magnetic properties and relevance to biological system (El-Sonbati *et al.* 2002). On the other hand, it is known that rhodanine plays an important role in biological reactions (Wang *et al.* 2001) e.g. in the inhibition of mycobacterium tuberculosis (El-Dissoky *et al.* 2001). Chemical properties of rhodanines and its derivatives are of interest due to coordination capacity and their use as metal extracting agents (El-Sonbati and El-Bindary 2000).

Many transition elements have been extensively investigated with regard to their potential quality as anticancer agents Petra *et al.* 2006). However, several observations suggest that also other metal-containing compounds might be suitable for the development of new chemotherapeutics, e.g. Lanthanide (III) salts have been reported to exert moderate antiproliferative effects in vitro (Estacion and Mordan 1993, Sato *et al.* 1998) and in vivo (Leopold and Anghileri 1979). Also, some lanthanum compounds possibly represent a new class of potential antitumer agent (Feng-Hua *et al.* 2006). It is, therefore, interesting and convenient to isolate and study some new Ni(II), Co(II), Cu(II), Ag(I), La(III) and Cr(III) Schiff base complexes of N-amino rhodanine.

### MATERIALS AND METHODS

All chemicals used were of the analytical grade (AR) and of highest purity available. They included copper(II)chloride (Aldrich), cobalt(II)chloride (AlfaAesar), nickel(II)chloride (Sigma), silver(I)nitrates(Merck), lanthanum(III) chloride(Merck), chromium(III) chloride(Sigma), indole-3-aldehyde (Sigma), salicylaldehyde (Aldrich) and N-amino Rhodanine (Aldrich).

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**Synthesis of the Schiff base ligand (L<sup>1</sup>):**

Warm solution (~ 40°C) of 3- aldehyde indole (1.45g, 10 mmol) was mixed with warm solution (~ 40°C) of 3-amino rhodanine (1.48g, 10 mmol) in 80 ml ethanol and 5 drops of glacial acetic acid. The resulting mixture was left under reflux for 3 hours and the formed solid product was separated by filtration, purified by crystallization from ethanol, washed with diethylether and dried in a vacuum desiccator over anhydrous calcium chloride. The yellow product is produced in 92% yield.

**Synthesis of the Schiff base ligand HL<sup>2</sup>:**

Hot solution (~ 50°C) of salicylaldehyde (4.884 g, 40 mmol) was mixed with hot solution (5.92 g, 40 mmol) of 3-aminorhodanine (5.92g, 40 mmol.), in 100 ml of hot mixture (~ 50°C) of ethanol-chloroform (1:1). The resulting mixture was left under reflux for 1 hour and the formed solid product was separated by filtration, purified by crystallization from ethanol-chloroform mixture, washed with diethylether and dried in a vacuum desiccator over anhydrous calcium chloride. The yellow product is produced in 78.6% yield. Structure of the ligands L<sup>1</sup> and HL<sup>2</sup> are shown in figure (1).

**Synthesis of the Metal Complexes:**

The complexes [Cu<sub>2</sub>(L<sup>1</sup>)Cl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]Cl<sub>2</sub>.6H<sub>2</sub>O, [Ag<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O, [La(L<sup>1</sup>)Cl<sub>3</sub>(H<sub>2</sub>O)].5H<sub>2</sub>O, [Cu(L<sup>2</sup>)Cl(H<sub>2</sub>O)<sub>2</sub>].5H<sub>2</sub>O, [Co(L<sup>2</sup>)(H<sub>2</sub>O)<sub>2</sub>Cl].2H<sub>2</sub>O and [Cr(L<sup>2</sup>)(H<sub>2</sub>O)Cl<sub>2</sub>].H<sub>2</sub>O were synthesized by mixing the warm solution (~ 45°C) of the appropriate metal chloride or nitrate (2 mmol) in an ethanol water mixture (1:1, 10ml) with a warm suspension (~ 45°C) of the Schiff base L<sup>1</sup> (2 mmol) in chloroform (50ml) or a hot solution (~ 50°C) of the Schiff base HL<sup>2</sup> (2mmol) in the same solvent (25 mL). The complexes: [Co (L<sup>1</sup>)<sub>2</sub> Cl<sub>2</sub>]. 2H<sub>2</sub>O and [Ni (L<sub>2</sub>)]. 5H<sub>2</sub>O were prepared by mixing warm solution (45°C) of the metal salt (2mmol of CoCl<sub>2</sub>. 6H<sub>2</sub>O or NiCl<sub>2</sub>. 6H<sub>2</sub>O, respectively) in an ethanol – water mixture (1:1, 10 ml) warm suspension or solution (~ 45°C) of ligand L<sup>1</sup> or the ligand HL<sup>2</sup> (4 mmol) in chloroform (50 ml). The resulting mixture was stirred under reflux for 4h in case of L<sup>1</sup> ligand, except L<sup>1</sup>-Ag, which was precipitated immediately whereupon the complexes precipitated. In case of HL<sup>2</sup> complexes, the mixtures were refluxed with constant stirring for 2h. The solid complexes did not separate on standing but when a few drops of aqueous ammonia solution (1:10) were slowly added with stirring until the pH reached 4-5, the solid metal chelates precipitated. In case of the preparation of all the complexes, the precipitates were collected by filtration, washed with a 1:1 ethanol-water mixture and diethylether and dried over anhydrous CaCl<sub>2</sub>. The analytical data for C, H, N and S were repeated twice (Table 1).

**Instruments:**

Elemental microanalyses of the separated solid chelates for C, H, N, S, Cl and M contents were performed in the Microanalytical Center, Cairo University. Infrared spectra were recorded on a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 400-4000 cm<sup>-1</sup>. The molar conductance of solid complexes in DMF was measured using a model CM – 1K TOA Company (Japan) conductivity meter. Magnetic moments at 25°C were determined using the Gouy method with Hg [Co(SCN)<sub>4</sub>] as calibrant.

The electronic spectra were obtained in Nujol mulls and in saturated ethanol solutions using a Shimadzu UV-240 UV-visible recording spectrophotometer. The mass spectra of the ligands were recorded by the EI technique at 70ev using Fenningan mat SSQ 7000 Thermo. Inst. Sys. Inc., USA spectrophotometer. The <sup>1</sup>HNMR spectra were recorded in DMSO-D<sub>6</sub> using a Jeol EX-270 MH<sub>3</sub> NMR spectrometer from 0-14 ppm with TMS as an internal standard.

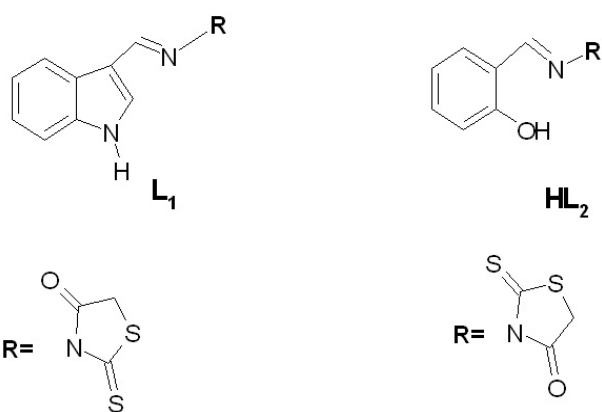
## RESULTS AND DISCUSSIONS

**Schiff Bases Characterization:**

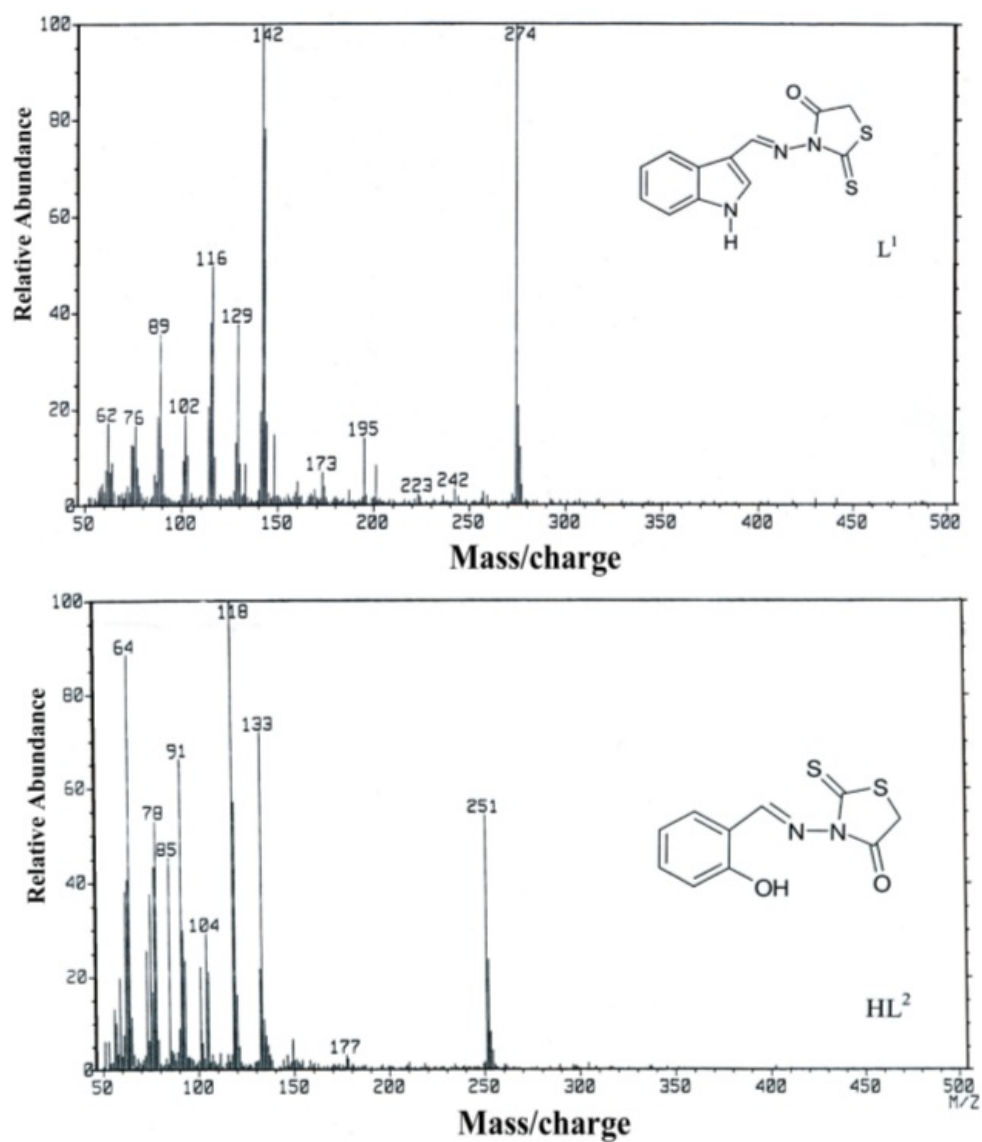
The Schiff bases, L<sup>1</sup> and HL<sup>2</sup> are subjected to elemental analyses. The results of elemental analyses (C, H, N and S) with molecular formulae and melting points are presented in Table (1). The results obtained are in good agreement with those calculated for the suggested formulae. The structures of the Schiff bases under study are given below in figure (1). The structures of these Schiff bases are also confirmed by IR and <sup>1</sup>HNMR spectra, which will be discussed later with metal complexes.

**Mass Spectra of the Ligands:**

Mass spectral data confirm the structure of the ligands L<sub>1</sub> and HL<sup>2</sup> as indicated by the peaks corresponding to their molecular mass (Figure 2).



**Fig. 1:** Structure of the Ligand.



**Fig. 2:** Mass Spectra of the Ligand  $L^1$  and  $HL^2$

**Table 1:** Colour, Decomposition Temperature, Conductivities, and Analytical data of the Ligands L<sup>1</sup> and HL<sup>2</sup> and their Metal Complexes.

Ligands and their Complexes	M:L	Colour	D.p. (°C)	Analysis, % Cal.(Found)						Molar Conductance $\Lambda_m$ ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )	Magnetic Moment BM
				%C	%H	%N	%S	%Cl	%M		
Ligand (L <sup>1</sup> )		Orange-yellow	221	52.36 (51.69)	3.27 (3.93)	15.27 (15.35)	23.27 (23.37)	.....	.....	.....	.....
C <sub>12</sub> H <sub>9</sub> N <sub>3</sub> S <sub>2</sub> O											
[Co(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O	1:2	Brown	290	40.22 (40.38)	3.07 (3.16)	11.73 (11.97)	17.87 (18.23)	9.91 (10.05)	8.23 (8.34)	14.82	4.7
[Cu <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>2</sub> .6H <sub>2</sub> O	1:1	Dark - Brown	>300	28.82 (28.16)	3.80 (3.62)	8.40 (8.26)	12.81 (12.56)	14.21 (14.08)	12.72 (12.58)	87.56	3.1
[Ag <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O	1:1	Metallic -Brown	240	28.86 (28.73)	3.01 (3.12)	8.41 (8.45)	12.82 (12.69)	----- (21.68)	21.62	88.78	Dia
[La(L <sup>1</sup> )Cl <sub>3</sub> (H <sub>2</sub> O)].5H <sub>2</sub> O	1:1	Orange Red	260	22.91 (22.34)	3.34 (3.17)	6.68 (6.48)	10.18 (10.47)	16.94 (17.02)	22.10 (21.83)	12.82	Dia
Ligand L <sup>2</sup>	1:1	Yellow	205	47.62 (48.14)	2.52 (2.48)	11.11 (11.23)	25.39 (25.12)	.....	.....	.....	.....
C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> S <sub>2</sub> O <sub>2</sub>											
[Cu(L <sup>2</sup> )Cl(H <sub>2</sub> O) <sub>2</sub> ].5H <sub>2</sub> O	1:1	Greenish Black	268	25.23 (23.59)	4.41 (4.37)	5.88 (5.65)	13.45 (13.28)	7.46 (7.55)	13.36 (13.21)	13.56	1.82
[Co(L <sup>2</sup> )Cl(H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O	1:1	Brown	253	28.78 (28.52)	3.62 (3.38)	6.71 (6.81)	15.35 (15.24)	8.51 (8.60)	14.13 (14.02)	12.00	4.87
[Cr(L <sup>2</sup> )Cl <sub>3</sub> (H <sub>2</sub> O)].H <sub>2</sub> O	1:1	Green	218	29.33 (29.09)	2.68 (2.80)	6.84 (6.67)	15.64 (15.51)	17.35 (17.19)	12.71 (12.80)	10.80	3.7
[Ni(L <sup>2</sup> ) <sub>2</sub> ].5H <sub>2</sub> O	1:2	Greenish Yellow	259	36.87 (36.74)	3.68 (3.73)	8.60 (8.72)	19.66 (19.52)	----- (8.87)	9.05	13.80	3.18

Ligand L<sup>1</sup>: The appearance of final peak at m/e= 274 (C<sub>12</sub> H<sub>8</sub>O S<sub>2</sub>N<sub>3</sub>) [calculated molecular mass at 275] and other peaks at 62, 76, 102, 116, and 142 may be due to different fragments. The intensity of these peaks gives an idea of the stability of these fragments.

Ligand HL<sup>2</sup>: The presence of mass spectral peak at 254 confirms the proposed formula (C<sub>10</sub> H<sub>8</sub> N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>) [calculated molecular mass 252].

A set of peaks observed in the range 78, 85, 91, 104, 118 and 133 are assigned to various fragments. The interpretation of the ligands L<sub>1</sub> and HL<sup>2</sup> fragmentation is shown in schemes 1 and 2.

#### Compositions and Structure of the Schiff Base Complexes:

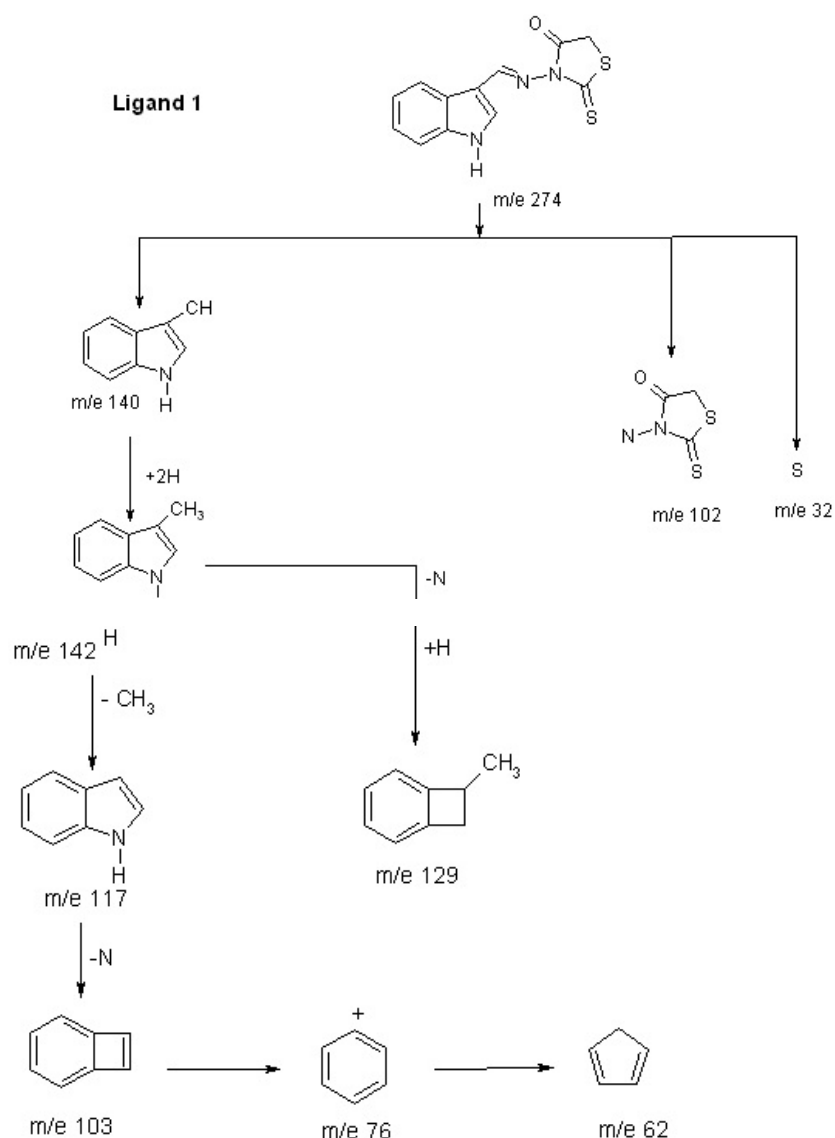
The isolated complexes of Cu(II), Co(II), La(III), and Ag(I) ions with the Schiff base ligand L<sup>1</sup> and those of Co(II), Cu(II), Cr(III) and Ni(II) with the Schiff base ligand HL<sup>2</sup> were subjected to elemental analyses (C, H, N, S and metal content), IR, <sup>1</sup>HNMR, magnetic studies, molar conductance to elucidate their molecular structures. The results of elemental analyses, Table (1), are in good agreement with those required by the proposed formulae.

The formation of the metal complexes of the ligands L<sup>1</sup> and HL<sup>2</sup> may proceed according to the following equations given below:

- 2 CuCl<sub>2</sub> + 2L<sup>1</sup> → [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub> Cl<sub>2</sub> (H<sub>2</sub>O)<sub>4</sub>] Cl<sub>2</sub>. 6H<sub>2</sub>O
- CoCl<sub>2</sub> + 2L<sub>1</sub> → [Co (L<sub>1</sub>)<sub>2</sub> Cl<sub>2</sub>]. 2H<sub>2</sub>O
- LaCl<sub>3</sub> + L<sup>1</sup> → [La (L<sup>1</sup>) Cl<sub>3</sub> (H<sub>2</sub>O)] .5 H<sub>2</sub>O
- 2Ag NO<sub>3</sub> + 2L<sub>1</sub> → [Ag<sub>2</sub> (L<sup>1</sup>)<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] (NO<sub>3</sub>)<sub>2</sub>. 4H<sub>2</sub>O
- MCl<sub>2</sub> + HL<sup>2</sup> → [M (L<sup>2</sup>)Cl(H<sub>2</sub>O)<sub>2</sub>] nH<sub>2</sub>O + HCl
- M= Co (II), (n =2), Cu (II), (n = 5)
- CrCl<sub>3</sub> + HL<sup>2</sup> → [Cr (L<sup>2</sup>) Cl<sub>2</sub> H<sub>2</sub>O]. H<sub>2</sub>O + HCl
- NiCl<sub>2</sub> + 2HL<sup>2</sup> → [Ni (L<sup>2</sup>)<sub>2</sub>]. 5H<sub>2</sub>O + 2HCl

#### <sup>1</sup>HNMR:

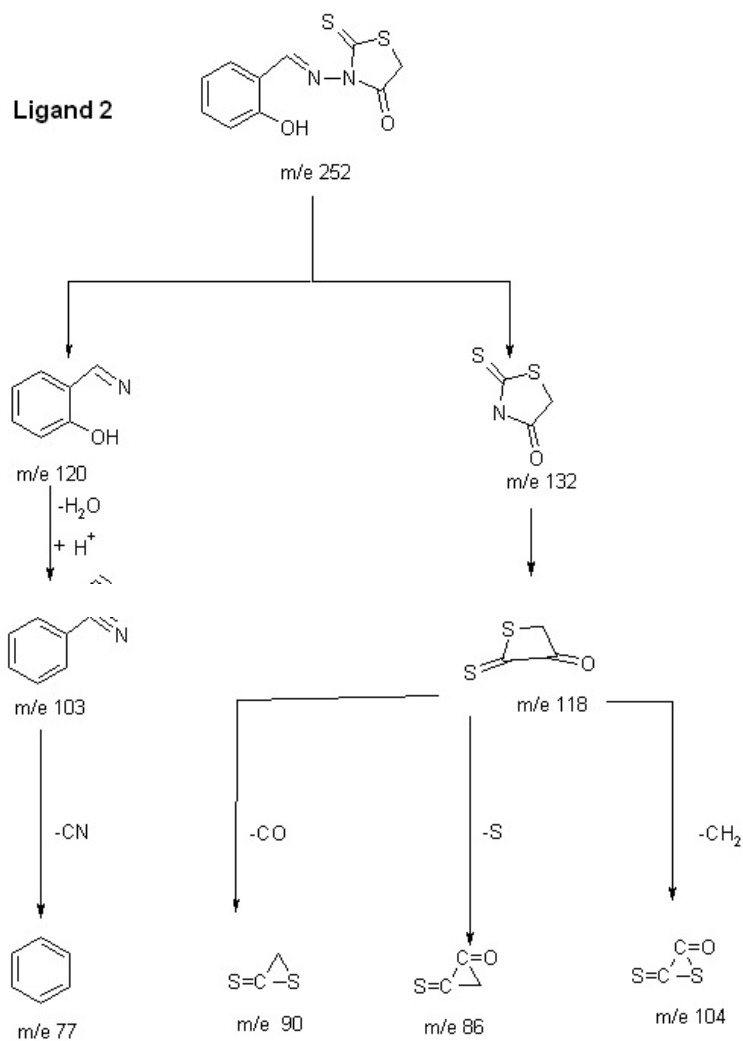
The <sup>1</sup>HNMR spectra of the ligands L<sup>1</sup> and HL<sup>2</sup> in DMSO solutions with assignments are collected in Table (2). The <sup>1</sup>HNMR spectra of the free ligands (Fig.5 for L<sup>1</sup>),(Fig.6 for HL<sup>2</sup>), showed besides the aromatic proton signals appearing at 7.0-7.5 and 6.9-7.8 ppm, 5-methylene protons at 4.3 ppm and the azomethine proton at 8.1 and 8.9, in case of ligands L<sup>1</sup> and HL<sup>2</sup>, respectively. The phenolic OH proton has a signal at 10.7 ppm in case of ligand HL<sup>2</sup>, whereas in case of ligand L<sup>1</sup> the signals due to NH and CH of the indole moiety appear at 12.1 and 8.7ppm, respectively.

**Scheme 1:****Table 2:** <sup>1</sup>H NMR data for the ligands L<sup>1</sup> and HL<sup>2</sup> in DMSO solution (δ, ppm)

Ligand	Phenolic OH	δ (CH <sub>2</sub> of the ring)	NH (Indole)	CH (indole)	CH=N (azomethine)	Aromatic protons
L <sup>1</sup>	-----	4.3	12.1	8.7	8.1	7.0-7.5
HL <sup>2</sup>	10.7	4.3	-----	-----	8.9	6.9-7.8

**Infrared Spectra:**

The significant IR bands of the ligands and their metal complexes and their assignments are given in Table (3). The spectra of all studied complexes show a broad band in the range 3157-3500 cm<sup>-1</sup> assigned to n(OH), suggesting the presence of water molecules<sup>16</sup>. The bands due to n(CS) and n(CS) + n(CN) at 673-889 cm<sup>-1</sup> and 1023-1049 cm<sup>-1</sup> respectively, in the free ligands L<sup>1</sup> and H L<sup>2</sup> are either shifted, split, or weakened in all of their complexes except L<sup>1</sup>-La, indicating the participation of the S atom in complex formation (Casas *et al* 1995). Moreover, coordination of the azomethine N to the metal ion is suggested by the shift of the ν(C=N) band (Kovala-Demertzi *et al* 2001). The N-bonding is also indicated by the shift of the strong bands at 1234 and 1272 cm<sup>-1</sup> in case of L<sup>1</sup> and HL<sup>2</sup> spectra, respectively, assignable to a (C-N-C) mode (Casas *et al* 1995, Fabretti and Peyronel 1978), to high or lower frequencies in their complexes. All the L<sup>1</sup> complexes show significant shifts to lower frequencies for ν(C=O) band, suggesting coordination of the metal ion through the carbonyl oxygen atom (Casas *et al* 1995). The strong phenolic ν(C-O) band (Chatterjee and Ghosh 1998) at 1202 cm<sup>-1</sup> in the free HL<sup>2</sup> ligand is shifted towards lower wave numbers in its complexes, consistent with coordination via the deprotonated phenolic oxygen (Jayabalakrishnan and Natarajan 2001).



**Scheme 2:**

**Table 3:** IR Spectra (4000-400 cm<sup>-1</sup>) of the ligands L<sup>1</sup> and HL<sup>2</sup> and their metal complexes.

Compound	v(OH)(H <sub>2</sub> O)	v(C=O)	v(C=N)	v(CNC)	v(C=S)	v(CS)+n(CN)	v(C-O) <sub>phenolic</sub>
L <sup>1</sup>	1742s	1661m	1234s	673s	1023s	-----	
[Co(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ·2H <sub>2</sub> O	----- 3261 b	1590s 1725m	1572m 1585w	1226m	603w 566w	1015s	-----
[Cu <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>2</sub> ·6H <sub>2</sub> O	3291b	1690w	1580w	1224w	667w 596w	1041w	-----
[Ag <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	3157b	1693m	1563m 1542m	1193m	600b 561b	1045w	-----
[La(L <sup>1</sup> )Cl <sub>3</sub> (H <sub>2</sub> O)]·5H <sub>2</sub> O	3309b -----	1714w 1728s	1624s 1614m	1240-1167w 1272s	676m 889s	1023m 1049m	----- 1202s
HL <sup>2</sup>	1716s	1597s		767s			
[Cu(L <sup>2</sup> )Cl(H <sub>2</sub> O) <sub>2</sub> ·5H <sub>2</sub> O	3417b	1730m	1602m	1199w	811w 755w	1022s	1151w
[Co(L <sup>2</sup> )Cl(H <sub>2</sub> O) <sub>2</sub> ·2H <sub>2</sub> O	3426b	1728s	1599s	1293m	876w 751m	1027m	1162s
[Cr(L <sup>2</sup> )Cl <sub>2</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O	3500b	1728m 1716m	1615w 1600vw	1272vw	880vw 760w	1022w	1202w
[Ni(L <sup>2</sup> ) <sub>2</sub> ·5H <sub>2</sub> O	3335b	1767s	1595m	1240s	875w 779w	1034w	1139m

**Molar Conductivity:**

The molar conductivity values of  $L^1$ -Co,  $L^1$ -La complexes and all  $L^2$  complexes in DMF solutions [ $\Lambda_m = 10.80-14.82 \Omega^{-1}cm^2mol^{-1}$ ] confirmed the non-electrolytic nature of these complexes, whereas, the molar conductivities of  $L^1$ -Cu and  $L^1$ -Ag complexes (Table 1) show that they are electrolytes.

**Electronic Spectra and Magnetic Susceptibility:**

Listed in Table (4) are the electronic transitions for  $L^1$  and  $HL^2$  and their metal complexes, whereas the magnetic moments of these complexes are given in Table 1. The observed magnetic moment of the Co (II) complexes fall in the range 4.7-4.87 BM. The molar conductance of these complexes in DMF is  $12.00-14.82 \Omega^{-1}cm^2 mol^{-1}$ , which shows that the chloride ions are coordinated to the cobalt (II) ion Douglas *et al* 1999. The electronic spectra of these complexes display two electronic spectral bands at 525 nm and 420-445 nm assignable to  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)$  transitions, respectively, characteristic of octahedral geometry (Chandra and Kumar 2005).

**Table 4:** Electronic Absorption Spectral Bands of the Ligands  $L^1$  and  $HL^2$  and their Complex in Ethanol.

Ligands and their Complexes	Intra ligand & Transfer bands (nm)	d-d Bands (nm)
$L^1$	255,270,295	
$[Co(L^1)_2Cl_2] \cdot 2H_2O$	240,250,255,265,290,330,40,390,410,	445,525
$[Cu_2(L^1)_2(H_2O)_4]Cl_2 \cdot 6H_2O$	245,255,295,360	425,450
$[Ag_2(L^1)_2(H_2O)_2](NO_3)_2 \cdot 4H_2O$	390,410,	
$[La(L^1)Cl_3(H_2O)] \cdot 5H_2O$	225,255,290,350,370	
$HL^2$	215,290,350	
$[Cu(L^2)Cl(H_2O)_2] \cdot 5H_2O$	210,230,345	420,455
$[Co(L^2)Cl(H_2O)_2] \cdot 2H_2O$	210,230,345	420
$[Cr(L^2)Cl_2(H_2O)] \cdot H_2O$	220,250,290,390	410
$[Ni(L^2)_2] \cdot 5H_2O$	210,220,310,330,390	410

A presumably tetrahedral structure is suggested for the diamagnetic  $L^1$ -Ag (I) complex (Ping *et al* 1999). The  $HL^2 - Ni$  (II) complex shows electronic spectral band at 410 nm attributable to  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  transition (Fostiak *et al* 2002). This complex has magnetic moment value of 3.18 BM which indicates that it is of high-spin octahedral type (Garcia *et al* 2002), whereas its molar conductance is consistent with a non-electrolyte. The  $HL^2$ -Cr (III) complex shows a magnetic moment corresponding to three unpaired electrons (i.e 3.7 B.M) which is approximately equal to spin only value. The electronic spectra of this complex shows a band at 410 nm which can be assigned to the  ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ , suggesting an octahedral geometry. The broadness of this band suggests distortion in the octahedral structure to this chelate (Youssef and Hegab 2005).

The magnetic moment of  $HL^1$ -Cu (II) complex is 3.1 B.M, which is smaller than the calculated value for two Cu(II) ions in octahedral geometries and may indicate slight antiferromagnetic interactions between adjacent Cu(II) ions in this complex.  $HL^2$ -Cu (II) complex is a non-electrolyte with a magnetic moment of 1.82 B.M. The magnetic moment of this complex at room temperature, given in Table (1), lie in the range normally observed for octahedral Cu (II) complexes corresponding to one unpaired electron (Mohammad and El-Wahab 2005). This indicates that this complex is monomeric in nature and the absence of metal-metal interaction.

**Suggested Structural Formulae of the Complexes:**

From the spectral data and the elemental analyses, the structure of the prepared complexes may be formulated as shown in Figures 3 and 4.

**Antimicrobial Activity:****Microorganisms used:**

The microorganisms used in this study are shown in Table (5). Four bacterial and one fungal species were subjected to antimicrobial activity test of the  $L^1$  and  $HL^2$  ligands and their complexes. These microorganisms were obtained from Microbial chemistry Department, National Research Center, Giza, Egypt.

**Media Used:**

Nutrient broth/ agar medium. It contains (g/L), (5) peptone, (3) beef extract. For solid medium 15 g/L agar was added.

Malt broth/agar medium: It contains (g/L), (5) peptone (24) malt extract. For solid medium 15g/L agar was added.

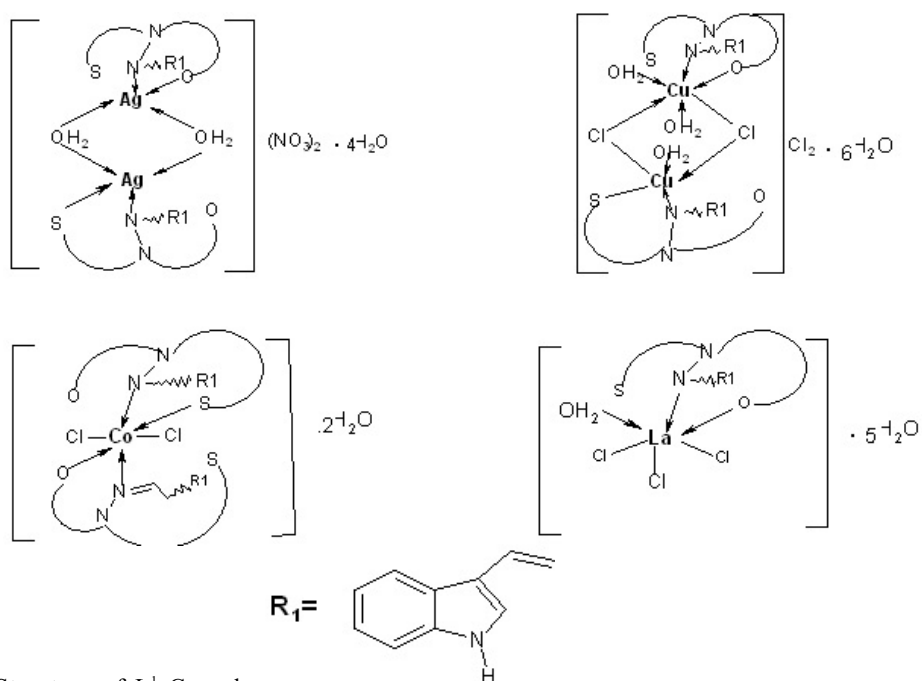


Fig. 3: Suggested Structure of  $L^1$  Complex.

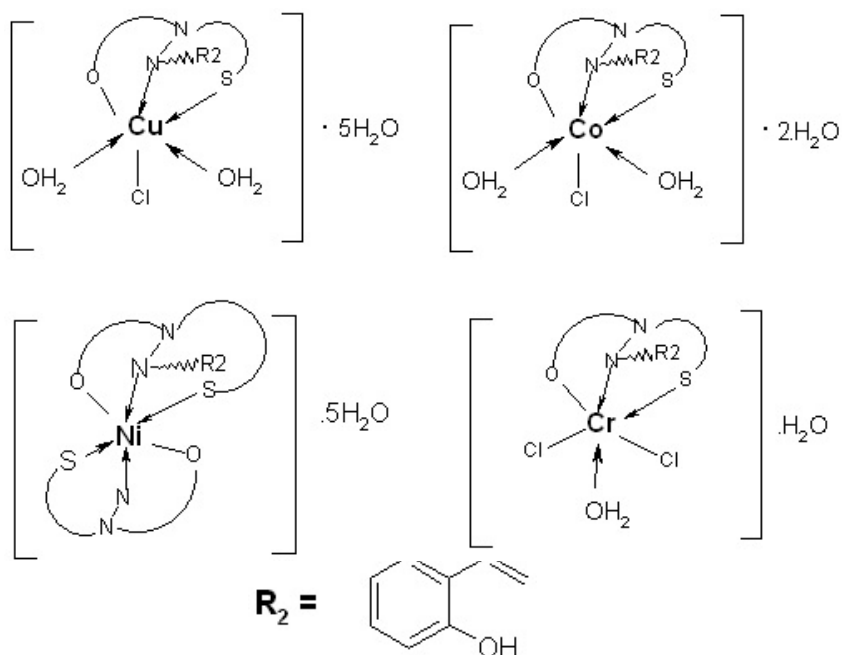


Fig. 4: Suggested Structure of  $HL^2$  Complex.

**Growth Conditions:**

An inoculum of each bacterial strain was suspended in 25 ml of nutrient broth medium and was shaken for 24 h at 37 °C. For yeast, malt broth was inoculated with test organism and incubated at 28°C for 24h.

**Antimicrobial Activity:**

Disc diffusion method was used for screening the ligands and their complexes. Nutrient agar (for bacteria) or malt agar (for yeast) plates were inoculated with 0.1 mL of an appropriate dilution of the tested culture. Samples (1 cm diameter) were suspended in 100 mL of sterile distilled water. About 20 ml of each

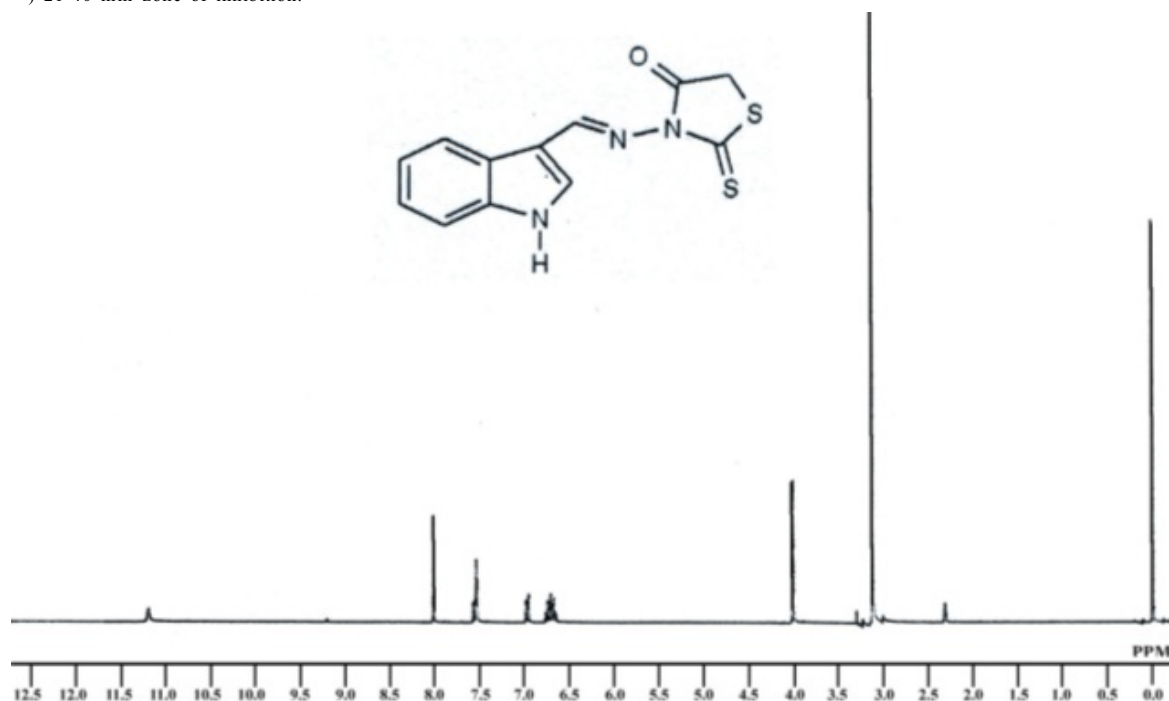
**Table 5:** The classification of microorganisms used in this study.

Test Microorganism	Classification	Abbreviation
Bacillus cerens	Gram-positive bacteria	BC
Escherichia coli	Gram-negative bacteria	EC
Pseudomonas aeruginosa	Gram-negative bacteria	Pa
Staphylococcus aureus	Gram-positive bacteria	Sa
Candida albicans	Yeast	Ca

**Table 6:** Antimicrobial activity of the Ligands L<sup>1</sup> and HL<sup>2</sup> and their corresponding metal complexes

Compound	Ec	Pa	Bc	Sa	Ca
L <sup>1</sup>	-	-	-	-	-
[Co(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ·2H <sub>2</sub> O	-	-	-	-	-
[Cu <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>2</sub> ·6H <sub>2</sub> O	-	+++	+	+	+
[Ag <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	++	-	+	+++	+
[La(L <sup>1</sup> )Cl <sub>3</sub> (H <sub>2</sub> O)]·5H <sub>2</sub> O	++	+	+	++	++
HL <sup>2</sup>	-	-	-	-	-
[Cu(L <sup>2</sup> )Cl(H <sub>2</sub> O) <sub>2</sub> ]·5H <sub>2</sub> O	+++	+++	+++	+++	+++
[Co(L <sup>2</sup> )Cl(H <sub>2</sub> O) <sub>2</sub> ]·2H <sub>2</sub> O	++	-	-	-	-
[Cr(L <sup>2</sup> )Cl <sub>2</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O	+++	+++	+++	+++	+++
[Ni(L <sup>2</sup> ) <sub>2</sub> ]·5H <sub>2</sub> O	+++	+++	+++	+++	+++

(-) n zone of inhibition, (+)1-10 mm zone of inhibition(++), 11-20 mm zone of inhibition, (+++) 21-40 mm zone of inhibition.



**Fig. 5:** <sup>1</sup>HMR spectrum of ligand L<sup>1</sup>.

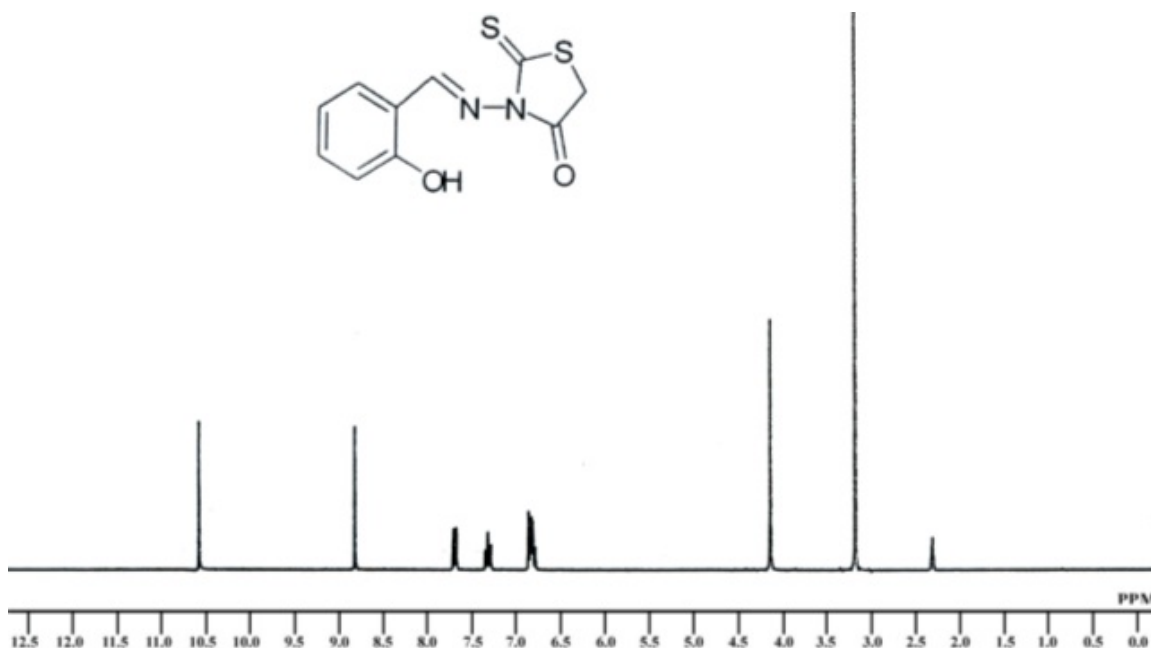
suspension was added to filter paper discs (6 mm diameter), which were placed on the surface of the previously inoculated plates. The plates were incubated at the appropriate temperature for 24h.

**Biological Activity:**

The results of biological activity tested for ligands and their complexes are given in Table (6). Diameter of inhibition zone (mm) including the disc diameter was measured for each treatment. The L<sup>1</sup> and HL<sup>2</sup> ligands showed no antimicrobial activity at all against EC, Pa, Bc, Sa and Ca.

The HL<sup>2</sup>- Cu, HL<sup>2</sup> - Cr, and HL<sup>2</sup>- Ni complexes exhibited the maximum antimicrobial activity against EC, Pa, Bc, Sa and Ca, while L<sup>1</sup>-La complex showed moderate antimicrobial activity against all organisms used in this study. Moreover, the L<sup>1</sup>-Ag and -Cu complexes produced +ve antimicrobial activity on some organisms and -ve activity on the others. In addition, Co complexes did not show any activity on the microorganisms.

The results indicate that the complexes show more activity and the ligands do not have any activity against some organisms under identical experimental conditions. This would suggest that the chelation could facilitate the ability of a complex to cross a cell membrane and can be explained by Tweedy's chelation theory



**Fig. 6:** <sup>1</sup>HMR spectrum of ligand HL<sup>2</sup>.

(Fahmi *et al* 1998). Chelation considerably reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible electron delocalization over the whole chelate ring. Such chelation could also enhance the lipophilic character of the central metal atom, which subsequently favours its permeation through the lipid layer of the cell membrane (Tumer *et al* 2007).

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