



Novel Metal Complexes Derived from Selenosemicarbazone Ligand; Synthesis, Spectral Investigation and Biological Activity

Talib H. Mawat, Mohamad J. Al-Jeboori

Department of Chemistry, College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad, Adhamiyah, Baghdad, Iraq.

Abstract

The formation of a novel bidentate Schiff-base seleno-ligand (HL) and its metal complexes are reported. The title ligand (E)-2-((R)-2-((R)-(4-(dimethylamino)phenyl)((3-nitrophenyl)amino)-methyl)cyclohexylidene)hydrazine-1-carboselenoamide (HL) was prepared from the reaction of 2-((4-(dimethylamino) phenyl) ((3-nitrophenyl)amino) methyl) cyclohexan-1-one with KSeCN and NH_2NH_2 in a 1:1:3 mole ratio using a mixture of CHCl_3 :EtOH (1:3) as a medium. The reaction of the ligand with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) metal ions in a 2:1 (L:M) mole ratio resulted in the isolation of new selenosemicarbazone complexes of general formula $\text{K}_2[\text{ML}_2\text{Cl}_2]$ and $[\text{M}'\text{L}_2]$, (M= Mn(II), Co(II) and Ni(II); M'= Cu, Zn and Cd). A range of physico-chemical methods were used to predict the geometry of complexes. These analyses indicated the formation of octahedral, square planar and tetrahedral geometry about (Mn(II), Co(II) and Ni(II)), Cu(II) and (Zn(II), Cd(II)) ions, respectively. The thermal analysis of the ligand and some metal complexes were investigated to check the stability of tested compounds. Biological activity of the ligand (HL) and its metal complexes against Gram negative bacterial strains; *E. coli*, *B. subtilis* and *K. Pneumoniae* and Gram positive species; *St. aureus* were studied. The compounds displayed various activity towards tested bacteria. Further, selenosemicarbazone compounds were examined against four fungus species (*Candida albicans*, *Candida glabrata*, *Candida tropicalis* and *Candida parapsilisis*). More, the tested compounds showed activity towards all four fungus species (except Co(II)-complex that showed no activity against *Candida tropicalis*).

Keywords: Selenosemicarbazone ligand; Metal complexes; Structural study; Biological activity.

Introduction

Carbazone and semicarbazone species are Schiff-bases that represent an important class of materials that used in the development of organic chemistry [1]. Semicarbazone compounds including seleno-ligands and their complexes have played a key role in the expansion of inorganic and coordination chemistry and showed a range of applications in various fields of chemistry [2]. These species include the "hard", nitrogen, and "soft", selenium, donor atoms [3].

Therefore, these ligands have the ability to coordinate to a range of metal ions. These compounds displayed a range of applications in medicinal and pharmaceutical chemistry. Further, these compounds can be used as reagents in catalysis and in analytical chemistry [4], bioinorganic chemistry [5] in agriculture and in industry (as used as

intermediates in the organic synthesis and in the formation of some dyes) [6].

Selenosemicarbazone ligands and their complexes are excellent agents that used as models in bioinorganic chemistry. This due to the fact that these compounds have low toxicity, high stability, excellent reactivity [7], and have the ability to form stable metal-complexes [7].

Selenosemicarbazone compounds have shown a range of biological and pharmaceutical applications including their antitumor and antibacterial activities. More, these compounds used as antioxidant, anti-inflammatory, antibacterial, antiviral, and antitumor agents [3,8,9]. In this work, we report the synthesis and structural characterisation of a selenosemicarbazone ligand and its metal complexes. The ligand was synthesised from the reaction of a

Mannich precursor 2-((4-(dimethylamino) phenyl) ((3-nitrophenyl)amino) methyl) cyclohexan-1-one with the inorganic reagents (potassium selenocyanate and hydrazine). Further, the prepared compounds were tested for their anti-bacterial and anti-fungal activities.

Experimental

Materials and Methods

All laboratory reagents used in the manipulation and preparation of compounds were commercially available and used without further purification. The precursor 2-((4-(dimethylamino) phenyl) ((3-nitrophenyl)amino) methyl) cyclohexan-1-one was obtained by standard method that reported in [10] which used in synthesis of ligand (HL).

Physical Measurements

Melting points were recorded using an electrothermal Stuart apparatus, model SMP₃₀. FTIR spectra were measured as KBr discs in the range 400-4000 cm⁻¹ on a Biotech FTIR-600 FTIR spectrometer and CsI discs in the range 250-4000 cm⁻¹ on a Shimadzu (FT-IR)-8400S spectrometer. The electronic spectra were performed in the region 200-1100 nm for 10⁻³ M solutions in DMSO at room temperature using a Shimadzu UV-160 spectrophotometer. ¹H- and ¹³C-NMR spectra were acquired in DMSO-d₆ and CDCl₃ solutions using a Brücker 400MHz and 300MHz spectrometer respectively, with tetramethylsilane (TMS) as an internal standard. The ⁷⁷Se-NMR spectra were acquired in DMSO-d₆ solution using a Brücker 400MHz spectrometer with dimethylselenide (Me₂Se) as an internal standard.

The electrospray mass spectra (ESMS) were recorded using Agilent LCms sx spectrometer. Elemental analyses (C, H and N) were carried out on EuroEA 3000. Metals were determined using a (F.A.A) 680G atomic absorption spectrophotometer. A Potentiometric titration method, using a 686-Titro processor-665Dosimat-Metrohm Swiss, was employed to determine chloride content. Conductivity measurements were made with DMSO solutions using a CON 510 digital conductivity meter (Eutech Instruments), and room temperature magnetic moments were measured with a magnetic susceptibility balance (Sherwood

Scientific Devised). Thermal analysis (Thermogravimetry (TG), Differential Thermogravimetry (DTG) and Differential Scanning Calorimetry (DSC)) was performed using a Linseis STA PT-1000 TG-DSC instrument.

Preparation of HL

A solution of 2-((4-(dimethylamino) phenyl) ((3-nitrophenyl)amino) methyl) cyclohexan-1-one (0.3 g, 1 mmol) in a mixture of 20 ml of CHCl₃:EtOH (1:3), was added dropwise with stirring to a mixture of hydrazine hydrate (99.9%, 0.1 ml, 3 mmol), KSeCN (0.1 g, 0.7 mmol) and hydrochloride acid (36%, 0.1 ml, 3 mmol) in ethanol (20 ml). The reaction mixture was allowed to reflux for 3 h, and filtrated while it is hot to remove excess selenium.

The solution was reduced to half under vacuum, and allowed to cool at room temperature during which time a solid was formed that collected by filtration, washed with ether (5 ml) and dried in air, Scheme (1). Yield: 0.12 g (41%), m.p= 265-267 °C. FT-IR data (cm⁻¹): 3558, 3529 (N4-H), 3440 (N3-H), 3383 (N1-H), 1637 (C=N)_{imine}, 1597, 1573 (C=C)_{aromatic}, 3101 (C-H)_{aromatic}, 2970 (C-H)_{aliphatic}, 1257 (C=Se)_{selenone}, 1161 (C-N), 1519 (N-H)_{Bend}. The ¹H-NMR spectrum of the ligand (400MHz, DMSO-d₆) showed peaks at δ_H; 1.61-1.67 (2H, m, C₄-H), 1.71-1.78 (2H, m, C₅-H), 2.00-2.06 (2H, m, C₃-H), 2.08-2.12 (2H, m, C₆-H), 2.58-2.81 (1H, m, C₂-H), 2.82 N(CH₃)₂, 4.19 (2H, s, N4-H), 4.50 (1H, dd, J_{HH}= 6.8, 7.2 Hz, C₇-H), 5.63 (1H, d, J_{HH}= 6.8 Hz N1-H), 6.17 (2H, d, J_{HH}= 8.5 Hz, C_{16,16'}-H), 6.44 (2H, d, J_{HH}= 8.5 Hz, C_{15,15'}-H), 6.47 (1H, dd, J_{HH}= 10.7, 8.1 Hz, C₁₃-H), 6.72 (1H, dd, J_{HH}= 11.7, 8.1 Hz, C₁₁-H), 6.96 (1H, dd, J_{HH}= 10.7, 11.7 Hz, C₁₂-H), 7.17 (1H, s, C₉-H), 7.36 (1H, br, N3-H).

The ¹³C-NMR spectrum of HL (75MHz, CDCl₃) exhibits signals at δ_C: 24.77 (C3), 27.89 (C4), 30.61 (C5), 41.97 (C6), 45.23 (N(CH₃)₂) 50.69 (C2), 54.30 (C7, C-H), 103.75 (C9), 110.94 (C11), 113.75 (C13), 115.73 (C_{16,16'}), 125.06 (C14), 129.92 (C_{15,15'}), 134.99 (C12), 147.94 (C8, C-NH), 155.68 (C10, C-NO₂), 142.91 (C₁₇-N(CH₃)₂), 160.64 and 176.94 ppm related to C=N of the imine moiety and the C=Se group. The ⁷⁷Se-NMR spectrum of HL (76MHz, DMSO) showed a singlet at δ_{Se}; 240.51 ppm C=Se group. The positive (ES) mass spectrum of HL showed the parent ion peak m/z= 488.5 amu (M+H)⁺

(23%) and the following fragments; Peaks detected at $m/z = 367.8$ (57%) $[M+H-(CH_3N_2Se+H)]^+$, 212.4 (100%) $[(M+H)-\{(CH_3N_2Se+H)+(C_{11}H_9N)\}]^+$, 128.5 (69%) $[(M+H)-\{(CH_3N_2Se+H)+(C_{11}H_9N)+(C_3H_2NO_2+H)\}]^+$, 55.4 (20%) $[(M+H)-\{(CH_3N_2Se+H)+(C_{11}H_9N)+(C_3H_2NO_2+H)+(C_5H_{12}+H)\}]^+$.

General Synthesis of Metal Complexes with Ligand (HL)

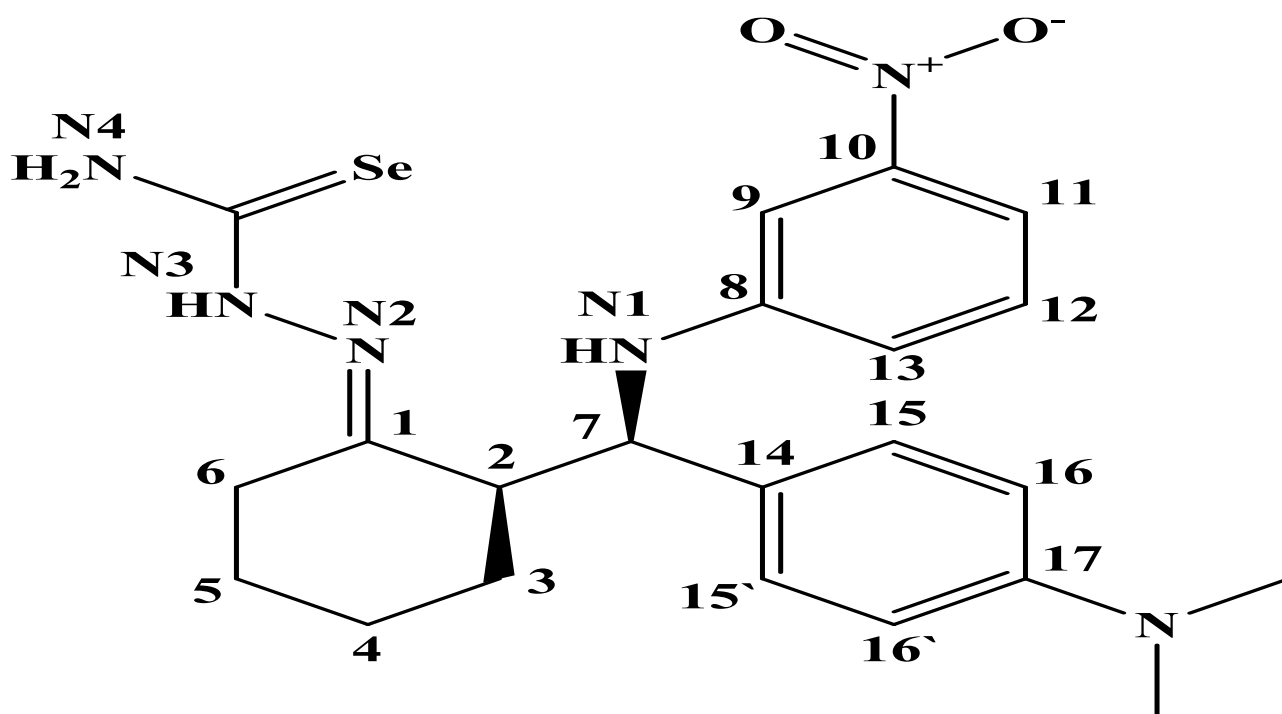
To a solution of the selenosemicarbazone ligand (0.255 mmol) in 20 ml of a mixture of $CHCl_3:EtOH$ (1:3), was added a mixture of metal chloride salt (0.127 mmol) in 10 ml of ethanol. The pH of the reaction mixture was adjusted by adding potassium hydroxide to *ca.* pH= 9, and the reaction mixture was stirring for 3 h. The precipitate that formed was filtered off, washed with cold absolute ethanol (5 ml) and dried on air, Scheme (2). Elemental analysis data, colours and yields of the complexes are given in (Table 1).

NMR Data

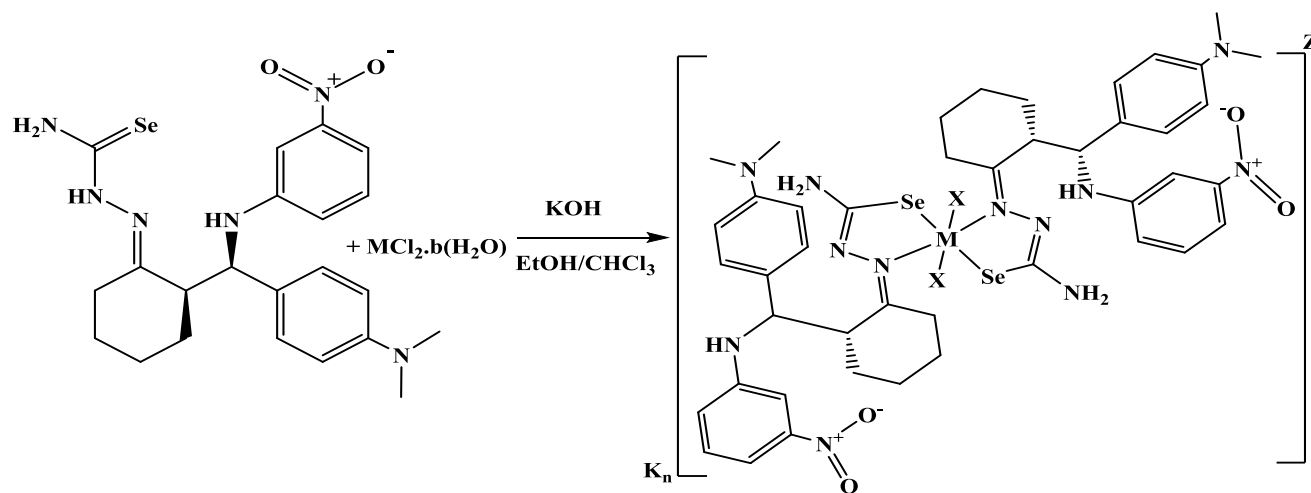
The 1H -NMR spectrum of $[Zn(L)_2]$ (400MHz, DMSO- d_6) showed peaks at δ_H ; 1.03-1.08 (2H, m, C_4-H), 1.40-1.53 (2H, m, C_5-H), 1.63-1.77 (2H, m, C_3-H), 2.04-2.13 (2H, m, C_6-H), 2.83 N(CH $_3$) $_2$, 2.90-3.10 (1H, m, C_2-H), 4.34 (2H, s, N_4-H), 4.62 (1H, dd, $J_{HH} = 4, 8$ Hz C_7-H), 5.80 (1H, d, $J_{HH} = 12$ Hz, N_1-H), 6.07 (2H, d, $J_{HH} = 12$ Hz, $C_{16,16'}-H$), 6.48 (1H, dd, $J_{HH} = 11, 8$ Hz, $C_{13}-H$), 6.62 (2H, d, $J_{HH} = 12$ Hz, $C_{15,15'}-H$), 6.96 (1H, dd, $J_{HH} = 11, 12$ Hz, $C_{12}-H$), 7.06 (1H, dd, $J_{HH} = 12, 8$ Hz, $C_{11}-H$), 7.41 (1H, s,

C_9-H). The ^{13}C -NMR spectrum of $[Zn(L)_2]$ (100MHz, $CDCl_3$) showed peaks at δ_C ; 21.20 (C3), 29.03 (C4), 33.18 (C5), 42.90 (C6), 47.09 N(CH $_3$) $_2$, 54.24 (C2), 55.30 (C7, C-H), 101.68 (C9), 111.28 (C11), 113.91 (C13), 116.01 (C $_{16,16'}$), 125.89 (C14), 127.97 (C $_{15,15'}$), 133.50 (C12), 140.62 (C $_{17-N(CH_3)_2}$), 146.44 (C8, C-NH), 153.25 (C10, C-NO $_2$), 165.11 and 168.36 related to C=N of the imine moiety and C-Se group. The ^{77}Se -NMR spectrum of $[Zn(L)_2]$ (76MHz, DMSO- d_6) exhibited a singlet at δ_{Se} ; 538.86 ppm.

1H -NMR spectrum of $[Cd(L)_2]$ (400MHz, DMSO- d_6) showed peaks at δ_H ; 1.03-1.08 (2H, m, C_4-H), 1.42-1.50 (2H, m, C_5-H), 1.63-1.80 (2H, m, C_3-H), 2.03-2.19 (2H, m, C_6-H), 2.83 N(CH $_3$) $_2$, 2.95-3.17 (1H, m, C_2-H), 4.36 (2H, s, N_4-H), 4.62 (1H, dd, $J_{HH} = 4, 8$ Hz, C_7-H), 5.80 (1H, d, $J_{HH} = 12$ Hz, N_1-H), 6.07 (2H, d, $J_{HH} = 12$ Hz, $C_{16,16'}-H$), 6.47 (1H, dd, $J_{HH} = 11, 8$ Hz, $C_{13}-H$), 6.62 (2H, d, $J_{HH} = 12$ Hz, $C_{15,15'}-H$), 6.96 (1H, dd, $J_{HH} = 11, 12$ Hz, $C_{12}-H$), 7.06 (1H, dd, $J_{HH} = 12, 8$ Hz, $C_{11}-H$), 7.45 (1H, s, C_9-H). The ^{13}C -NMR spectrum of $[Cd(L)_2]$ (100MHz, $CDCl_3$) showed peaks at δ_C ; 22.07 (C3), 29.03 (C4), 32.83 (C5), 41.36 (C6), 46.35 N(CH $_3$) $_2$, 54.24 (C2), 58.62 (C7, C-H), 104.65 (C9), 110.31 (C11), 113.91 (C13), 117.66 (C $_{16,16'}$), 124.72 (C14), 127.97 (C $_{15,15'}$), 132.04 (C12), 140.62 (C $_{17-N(CH_3)_2}$), 146.85 (C8, C-NH), 154.20 (C10, C-NO $_2$), 165.11 and 167.69 related to C=N of the imine moiety and the C-Se group. The ^{77}Se -NMR spectrum of $[Cd(L)_2]$ (76MHz, DMSO- d_6) exhibited singlet at δ_{Se} ; 672.32 ppm.



Scheme 1: Molecular structure of selenosemicarbazone ligand (HL)



M= Mn(II), Co(II), Ni(II); n= 2; X= Cl; Z= -2

M= Cu(II), Zn(II), Cd(II); n= 0; X= 0; Z= 0

b= Number of water molecules

Scheme 2: Synthesis route and proposed structures of complexes HL

Table 1: Colours, yields, elemental analyses and molar conductance values

Compound	Yield (%)	Colour	m.p. °C	Found, (Calc.)%					ΔM ($\text{cm}^2\Omega \text{mol}^{-1}$)
				C	H	N	M	Cl	
HL	41	Brown	265-267	54.12 (54.16)	5.80 (5.74)	17.19 (17.23)	-	-	-
$\text{K}_2[\text{Mn}(\text{L})_2\text{Cl}_2]$	70	Deep brown	288-290	44.92 (44.86)	4.63 (4.59)	14.22 (14.27)	4.61 (4.67)	6.22 (5.95)	67.45
$\text{K}_2[\text{Co}(\text{L})_2\text{Cl}_2]$	63	Dark brown	291-293	44.67 (44.71)	4.62 (4.57)	14.19 (14.23)	5.16 (5.00)	5.86 (5.93)	51.11
$\text{K}_2[\text{Ni}(\text{L})_2\text{Cl}_2]$	54	Deep orange	306-308	44.69 (44.72)	4.55 (4.57)	14.20 (14.23)	4.97 (5.00)	5.90 (5.93)	42.33
$[\text{Cu}(\text{L})_2]$	65	Dark brown	299-301	50.91 (50.94)	5.20 (5.21)	16.18 (16.21)	6.14 (6.18)	-	7.45
$[\text{Zn}(\text{L})_2]$	71	Light brown	309-311	50.83 (50.85)	5.18 (5.20)	16.15 (16.18)	6.24 (6.26)	-	6.23
$[\text{Cd}(\text{L})_2]$	58	Light brown	313-315	48.61 (48.65)	4.96 (4.98)	15.45 (15.48)	10.30 (10.32)	-	5.78

Results and Discussion

The prepared compounds (ligand (HL) and its complexes) are air stable solids, soluble in DMF, CHCl_3 and DMSO, but not soluble in other common organic solvents. The coordination geometries around metal centres were predicted using physico-chemical analysis. The analytical data (Table 1) agree well with the suggested formulae. Conductivity measurements of mononucleating complexes in DMSO lie in the $5.78\text{-}67.45 \text{ cm}^2 \Omega^{-1} \text{mol}^{-1}$ range, indicating their 2:1 electrolytic and neutral behaviour [11].

FT-IR Spectra

The FT-IR spectrum of the free selenosemicarbazone ligand (HL) shows characteristic bands at 3558; 3529, 3440, 3383, 1637, 1597, 3101 and 1257 cm^{-1} that attributed to $\nu(\text{N4-H})$, $\nu(\text{N3-H})$, $\nu(\text{N1-H})$, $\nu(\text{C=N})_{\text{imine}}$, $\nu(\text{C=C})_{\text{aromatic}}$ and $\nu(\text{C=Se})_{\text{selenone}}$, respectively [12,13]. The FT-IR spectrum shows no peak around 2400 cm^{-1} may assign

to $\nu(\text{Se-H})$, indicating the ligand exists in selenone form [14]. The infrared bands of complexes together with their assignments are listed in (Table 2). The FT-IR spectra of complexes exhibited ligand bands with the appropriate shifts due to complex formation. Band appeared at 1637 cm^{-1} that due to $\nu(\text{C=N})$ of imine group in the free ligand (HL) is shifted to lower frequency and appeared around $1623\text{-}1631 \text{ cm}^{-1}$ in the complexes [15]. This shift confirmed the coordination of the ligand through nitrogen atom of the imine moiety to the metal centre indicating a strong bonding nature between the metal ion and the iminic (C=N) group [16,17].

The shift in the $\nu(\text{C-Se})$ may indicate the coordination of the ligand through selenium atoms to the metal ions. This band detected around $702\text{-}759 \text{ cm}^{-1}$ in the spectra of metal complexes, compared with that in HL at 763 cm^{-1} [14]. Band at 3383 cm^{-1} that related to $\nu(\text{N1-H})$ in the free ligand is still existing in the FT-IR spectra of complexes, indicating the non-involvement of nitrogen atoms in the

coordination to the metal centre. Band assigned to $\nu(\text{N3-H})$ that detected at 3440 cm^{-1} in the free ligand (HL) has disappeared in the spectra of complexes, due to the formation $\text{N}=\text{C}-\text{Se}$ moiety that detected in the range $1608-1613\text{ cm}^{-1}$ [18]. The FT-IR spectra of the complexes show new bands in the ranges $405-466$ and $339-375\text{ cm}^{-1}$ assigned to $\nu(\text{M-N})$ and $\nu(\text{M-Se})$, respectively [18,19]. While bands in the range $264-274\text{ cm}^{-1}$ related to $\nu(\text{M-Cl})$ [19] (except complexes Cu(II) , Zn(II) and Cd(II) which showed no peak around 250 cm^{-1} could assign to $\nu(\text{M-Cl})$.

NMR Spectra

The $^1\text{H-NMR}$ spectrum of the selenosemicarbazone ligand (HL) in DMSO-d_6 solvent showed peak at $\delta_{\text{H}} = 5.63\text{ ppm}$, equivalent to one proton, assigned to (N1-H) group. This peak was detected at $\sim 5.80\text{ ppm}$ in the spectra of Zn(II) and Cd(II) complexes. Peak detected at $\delta_{\text{H}} = 7.36\text{ ppm}$ (1H, s) equivalent to one proton correlated to (N3-H) group, indicating that ligand exists in selenone form (see Figure 1 a). This peak disappeared in the spectra of complexes, conforming the deprotonation of the ligand upon complex formation. Peak detected at $\delta_{\text{H}} = 4.19\text{ ppm}$ in the spectrum of HL, equivalent to two protons, attributed to $(\text{N4-}$

$\text{H})$ group. This signal has detected around $\sim 4.34\text{ ppm}$ in the spectra of Zn(II) and Cd(II) complexes. Peak observed at $\sim 7.06\text{ ppm}$ related to $(\text{C}_{11}\text{-H})$; 1H, dd, $J_{\text{HH}} = 12, 8\text{ Hz}$, in the spectra Zn(II) and Cd(II) complexes. While chemical shifts at 7.41 and 7.45 ppm assigned to $(\text{C}_9\text{-H})$; 1H, s) for Zn(II) and Cd(II) complexes, respectively. These signals were displayed downfield compared with that in the free ligand at 7.17 ppm, indicating complexes formation (Figure 1 b and c). The $^{13}\text{C-NMR}$ spectra in CDCl_3 solvents exhibited signal at $\sim 165\text{ ppm}$ assigned to $\text{C}=\text{N}$ group for Zn(II) and Cd(II) complexes.

This signal detected downfield, compared with that in the free ligand at 160 ppm. Chemical shift at $\sim 168\text{ ppm}$ due to C-Se group appeared upfield in the spectra of complexes, compared with that in the free ligand at 176 ppm [18] (Figure 2 b and c). The $^{77}\text{Se-NMR}$ spectra of Zn(II) - and Cd(II) -complex in DMSO-d_6 solvent showed peaks at 538.86 and 672.32 ppm attributed to C-Se group that appeared downfield compared with the spectrum of the free ligand which showed at 240.51 ppm [18], (Figure 3 a, b and c). The appearance of one single in the examined compounds indicated the purity of compounds and the isolation of one isomer.

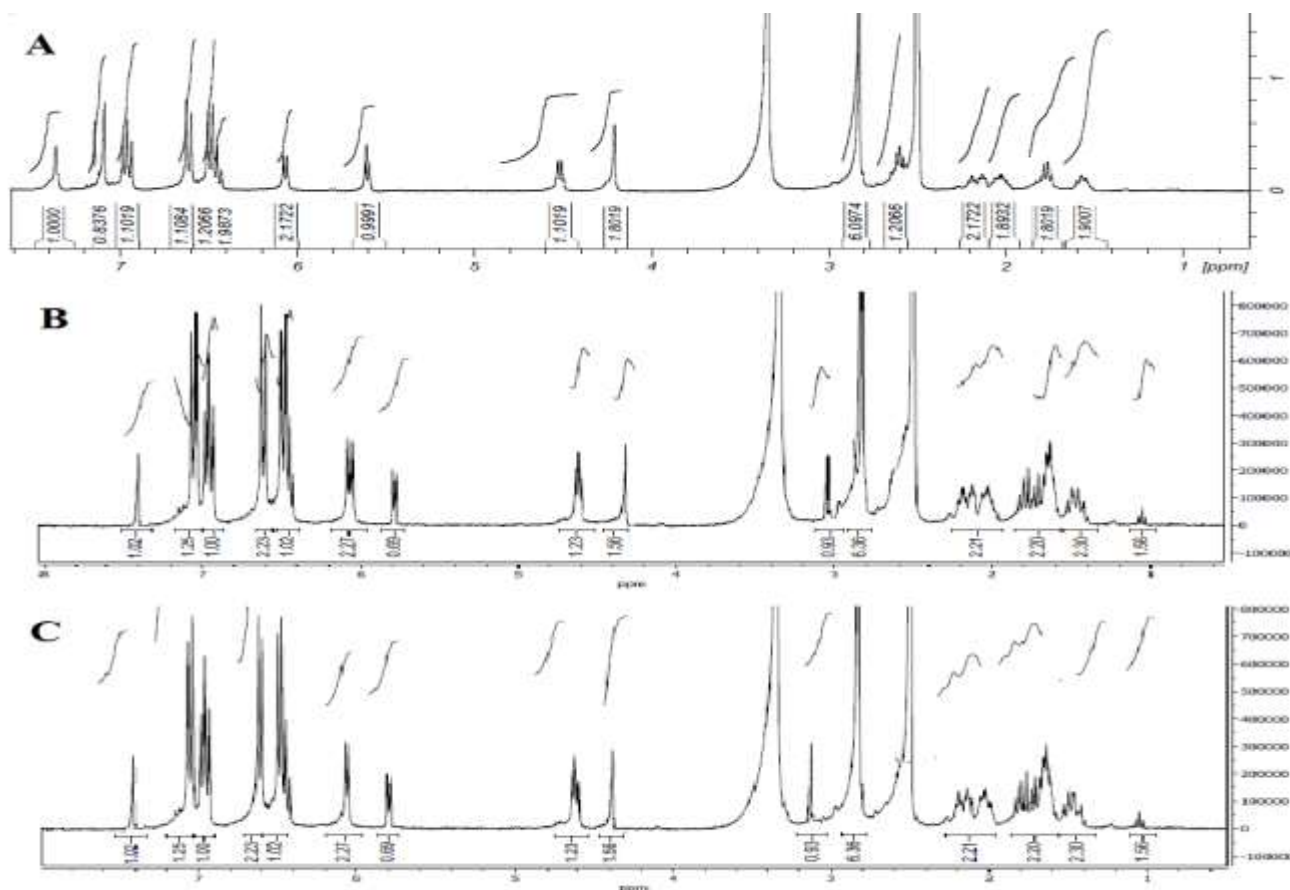


Figure 1: $^1\text{H-NMR}$ spectra in DMSO-d_6 solutions for: a) HL; b) $[\text{Zn(L)}_2]$ and c) $[\text{Cd(L)}_2]$

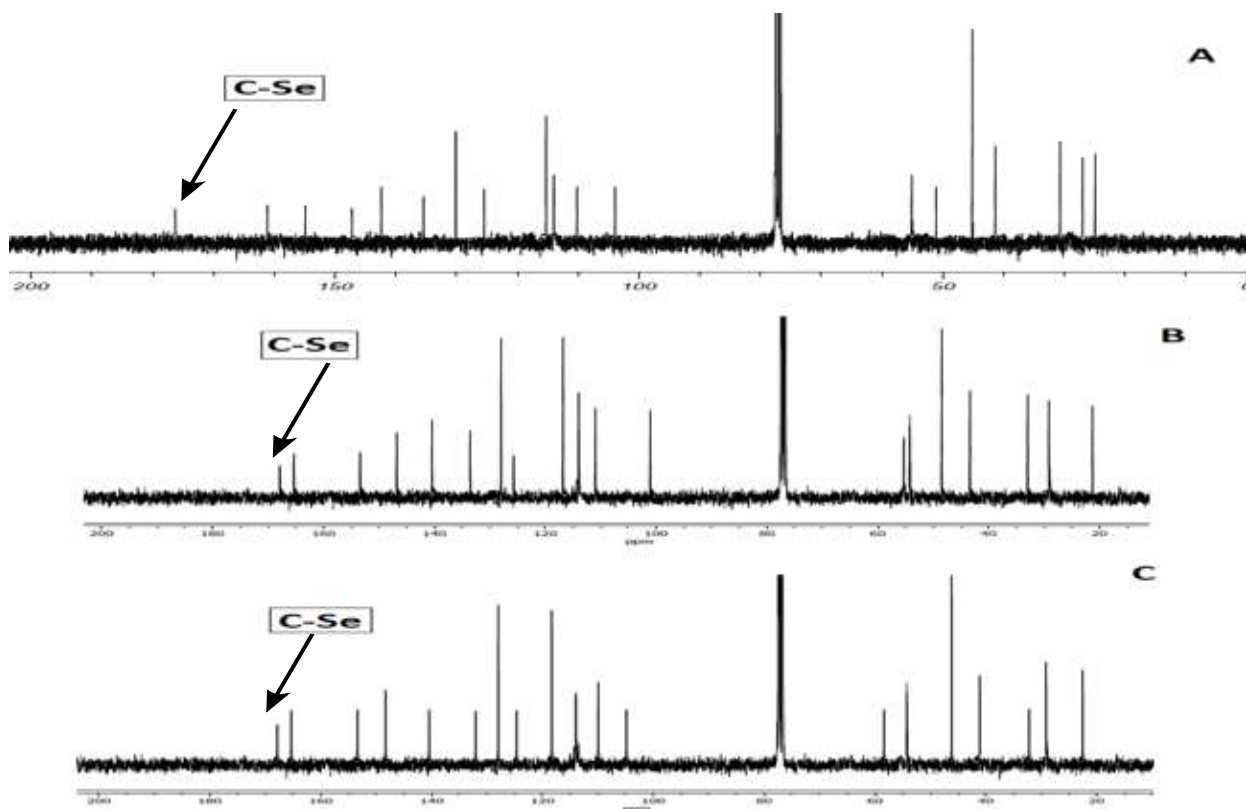


Figure 2: ¹³C-NMR spectra in CDCl₃ solutions DMSO solutions for: a) HL; b) [Zn(L)₂] and c) [Cd(L)₂]

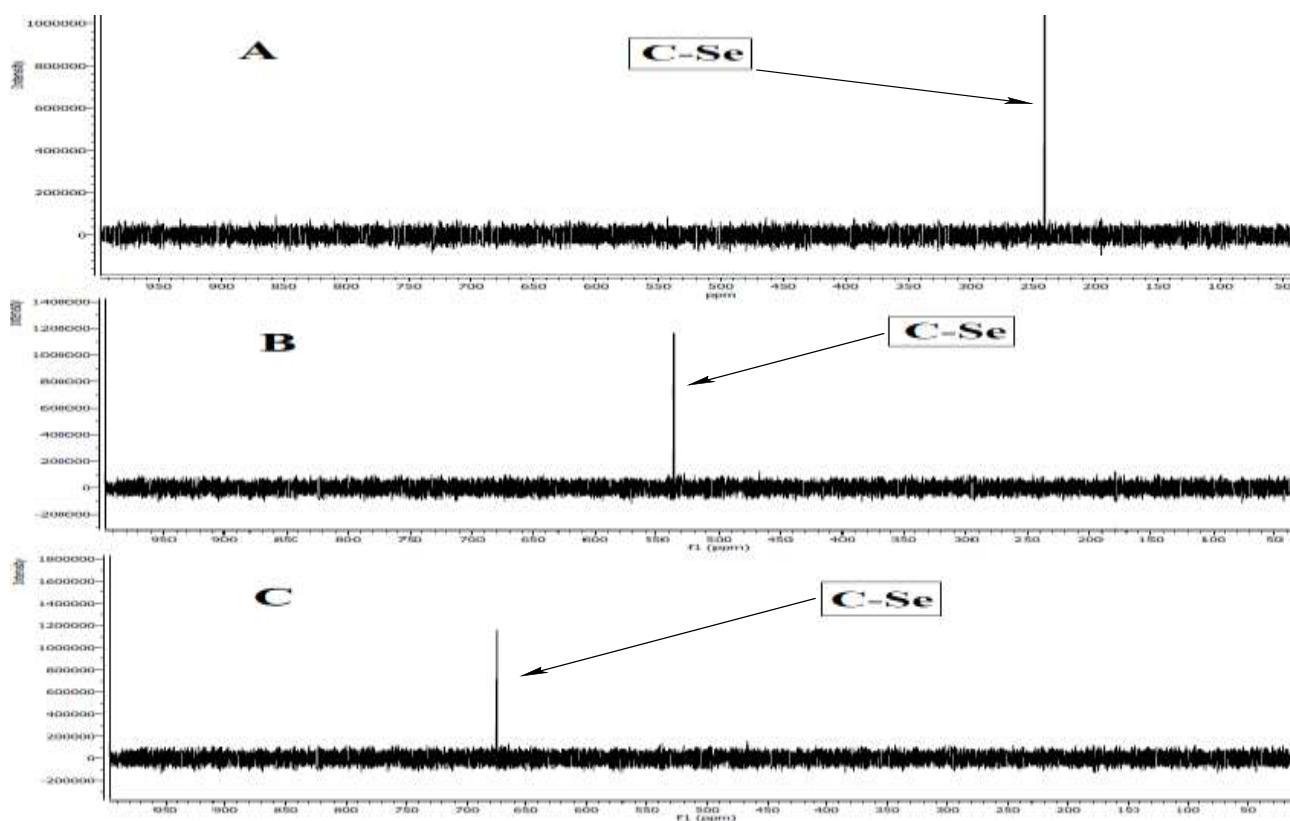


Figure 3: ⁷⁷Se-NMR spectra in for: a) HL; b) [Zn(L)₂] and c) [Cd(L)₂]

Mass Spectra

The mass spectra of complexes indicated the formation of the title compounds. The electrospray (+) mass spectrum of [Zn(L)₂] exhibited several peaks related to successive fragmentations of the molecule. The parent

ion peak is detected at $m/z = 1038.20$ (M^+) (23%) calculated for $C_{44}H_{54}N_{12}O_4Se_2Zn$; requires = 1038.20. The following fragments; 876.11 (35%) ($M-(C_7H_{13}N_2+NO_2)^+$), 711.14 (57%) ($[M-\{(C_7H_{13}N_2+NO_2)+(C_{11}H_{10}N)\}]^+$), 466.71 (100%) ($[M-\{(C_7H_{13}N_2+NO_2)+(C_{11}H_{10}N)+(C_4H_{11}N_3Zn$

Se)}]+, 227.51 (28%) [(M-
 {(C₇H₁₃N₂+NO₂)+(C₁₁H₁₀N)+(C₄H₁₁N₃Zn
 Se)+(C₉H₁₀N₃Se)}]+, 55.91 (20%) [(M-
 {(C₇H₁₃N₂+NO₂)+(C₁₁H₁₀N)+(C₄H₁₁N₃Zn
 Se)+(C₉H₁₀N₃Se)+(C₁₀H₁₀+NO₂)}]+, (see
 Figure 4 b). Whereas, the ESMS spectrum of
 [Cu(L)₂], showed peak at m/z= 1037.21 (M)+
 (24%) assigned to the parent molecular ion,
 calculated for C₄₄H₅₄CuN₁₂O₄Se₂;
 requires= 1037.21. The following fragments;

819.72 (23%), 585.71 (90%), 440.11 (100%),
 180.12 (71%) and 70.90 (30%) assigned to (M-
 (C₁₂H₁₄N+NO₂))+, [(M-
 {(C₁₂H₁₄N+NO₂)+(C₄H₁₁N₃CuSe)}]+, [(M-
 {(C₁₂H₁₄N+NO₂)+(C₄H₁₁N₃CuSe)+(C₅H₁₁N₂
 +NO₂)}]+, [(M-
 {(C₁₂H₁₄N+NO₂)+(C₄H₁₁N₃CuSe)+(C₅H₁₁N₂
 +NO₂)+(C₁₁H₇N₃Se)}]+ and [(M-
 {(C₁₂H₁₄N+NO₂)+(C₄H₁₁N₃CuSe)+(C₅H₁₁N₂
 +NO₂)+(C₁₁H₇N₃Se)+(C₈H₁₄)}]+,
 respectively.

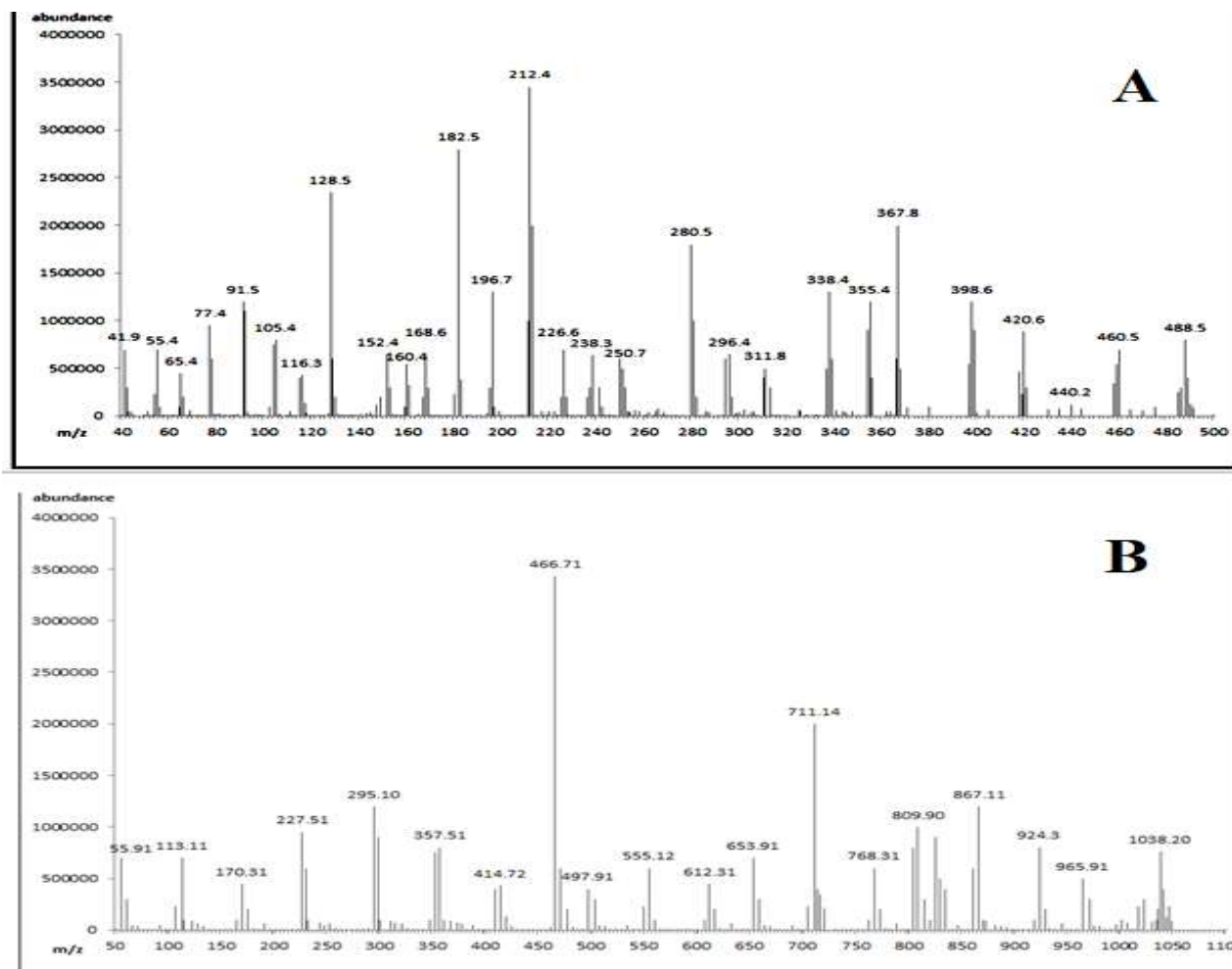


Figure 4: The electrospray (+) mass spectrum for: a) HL and b) [Zn(L)₂]

Electronic Spectra and Magnetic Moment Measurements

The UV-Vis spectrum of HL exhibits an intense absorption peak at 272 nm (36765 cm⁻¹; ε_{max}= 1443 dm³ mol⁻¹ cm⁻¹) and 318 nm (31447 cm⁻¹; ε_{max}= 1366 dm³ mol⁻¹ cm⁻¹) assigned to π→π* and n→π* transitions, respectively [20]. The electronic spectra and magnetic moments data of the ligand (HL) and its complexes are collected in (Table 3). The electronic spectra of the complexes display various peaks around 276-298 and 352-390 nm attributed to π→π* and n→π*, respectively [20]. The electronic spectrum of the Mn(II) complex showed peak in the d-d

region at 540 nm (18519 cm⁻¹; ε_{max}= 39 dm³ mol⁻¹ cm⁻¹) and 766 nm (13055 cm⁻¹; ε_{max}= 87 dm³ mol⁻¹ cm⁻¹) that assigned to ⁶A_{1g}(F)→⁴T_{2g}(G) and ⁶A_{1g}(F)→⁴T_{1g}(G) transitions, respectively indicating a distorted octahedral structure about Mn(II) ion [21]. The magnetic moment value of the Mn(II)-complex is consistent with octahedral assignment [22]. The electronic spectrum of the Co(II) complex displays peak in the d-d region at 752 nm (13298 cm⁻¹; ε_{max}= 107 dm³ mol⁻¹ cm⁻¹) related to ⁴T_{1g}(F)→⁴T_{2g}(F) transition. This spectrum is characteristic for Co(II) complexes with distorted octahedral geometries around Co atom [21]. The electronic spectrum of the Ni(II) complex

exhibited peaks in the d-d region at 640 nm (15625 cm^{-1} ; $\epsilon_{\text{max}} = 77 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 839 nm (11919 cm^{-1} ; $\epsilon_{\text{max}} = 112 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) due to type transitions ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$, respectively, indicating a distorted octahedral geometry about Ni atom [21]. The electronic spectra of Co(II) and Ni(II) complexes and their magnetic moment values are consistent with the formation of distorted octahedral structure [21]. The Cu(II) complex showed one peak in the d-d

region at 740 nm (13514 cm^{-1} ; $\epsilon_{\text{max}} = 52 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) attributed to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transition, confirming a distorted square planar arrangement about Cu atom [23]. This spectrum and the μ_{eff} value is in agreement with the suggested geometry. The spectrum of the Zn(II) and Cd(II) complexes exhibited bands assigned to ligand field $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [24]. The tetrahedral geometry structure is suggested for the Zn(II) and Cd(II) centre [25].

Table 2: FT-IR frequencies in (cm^{-1}) of the compounds.

Compound	$\nu(\text{N4-H})$	$\nu(\text{N3-H})$	$\nu(\text{N1-H})$	$\nu(\text{C=N})$	$\nu(\text{N-C=Se})$ $\nu(\text{N=C-Se})$	$\nu(\text{C=C})$	$\nu(\text{C-Se})$	$\nu(\text{M-N})$	$\nu(\text{M-Se})$	$\nu(\text{M-Cl})$
HL	3558 3529	3440	3383	1637	1597 -	1573 1519	1257 763	-	-	-
$\text{K}_2[\text{Mn}(\text{L})_2\text{Cl}_2]$	3501 3464	-	3410	1623	- 1611	1581 1548	1249 752	405 432	360	274
$\text{K}_2[\text{Co}(\text{L})_2\text{Cl}_2]$	3501 3464	-	3410	1630	- 1613	1580 1512	1226 759	416 466	339	264
$\text{K}_2[\text{Ni}(\text{L})_2\text{Cl}_2]$	3501 3464	-	3410	1630	- 1610	1581 1512	1245 736	420 443	350	270
$[\text{Cu}(\text{L})_2]$	3436 3433	-	3394	1629	- 1608	1585 1512	1249 736	420 459	344	-
$[\text{Zn}(\text{L})_2]$	3501 3460	-	3394	1631	- 1608	1581 1519	1226 759	424 451	375	-
$[\text{Cd}(\text{L})_2]$	3460 3444	-	3394	1630	- 1608	1597 1554	1234 702	412 451	353	-

Table 3: Magnetic moment and UV-VIS spectral data in DMSO solutions.

Compound	μ_{eff} (BM)	λ_{nm}	ϵ_{max} $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	Assignment
HL	-	272 318	1443 1366	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
$\text{K}_2[\text{Mn}(\text{L})_2\text{Cl}_2]$	5.92	279 363 540 766	876 1098 39 87	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ ${}^6\text{A}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{G})$ ${}^6\text{A}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{G})$
$\text{K}_2[\text{Co}(\text{L})_2\text{Cl}_2]$	3.90	294 352 752	988 846 107	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$
$\text{K}_2[\text{Ni}(\text{L})_2\text{Cl}_2]$	2.53	298 380 640 839	769 879 77 112	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$
$[\text{Cu}(\text{L})_2]$	1.63	281 376 740	1234 968 52	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$
$[\text{Zn}(\text{L})_2]$	Diamagnetic	295 390	1064 976	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
$[\text{Cd}(\text{L})_2]$	Diamagnetic	276 302	1123 1645	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$

Thermal Analysis

TGA, DSC and DTG analysis data for the ligand (HL) and some metal complexes are summarised in (Table 4), (Figures 5 a and b). The TG, DSC and DTG curves of HL and its complexes were determined from ambient temperature to 600°C in an argon atmosphere. The analysis of the thermal data showed that the ligand (HL) is stable up to 70.2°C . Peaks detected at 80.9, 130.5, 155.7 and 455.3°C revealed to DSC analysis. The TGA peak between $70.2\text{-}225.8^\circ\text{C}$. This decomposition process attributed to the loss of $(\text{N}_2\text{H}_2 + \text{C}_4\text{H}_4\text{O} + \text{CH}_4)$ segments (obs.=

4.6499 mg; calc.= 4.6721 mg, 23.36%). The second process at 304.9°C is related to the loss of $(\text{C}_4\text{H}_4\text{N})$ molecule, (obs.= 2.7712 mg; calc.= 2.7049 mg, 13.53%). While, the third process at 363.0°C is due to the removal of $(\text{NH}_3 + \text{H}_2)$ molecule, (obs.= 0.7717 mg; calc.= 0.7787 mg, 3.89%). The fourth process at 527.6°C is related to the loss of $(\text{C}_3\text{H}_6 + \text{H}_2\text{Se})$ fragment, (obs.= 5.0002 mg; calc.= 5.0410 mg, 25.21%). The final process, which detected at 594.3°C is related to the loss of (CH_4) molecule (obs.= 0.5817 mg; calc.= 0.6557 mg, 3.27%). The analysis thermal data of Ni(II) and Zn(II) selenosemicarbazone complexes

appeared to be stable up to 170.2 °C. The exothermic and endothermic for temperatures were appeared at 219.0, 295.4 and 496.4 °C which due to the DSC analysis. The first process showed between 170.2-260.9 °C assigned to the mass loss of (N₂H₂+2C₄H₄O) molecules (obs.= 2.6899 mg; calc.= 2.6706 mg, 14.10%) represented first process. Whereas, the second process showed at 350.9 °C due to loss of (2N₂H₄+2C₆H₆+2C₄H₄N+Cl₂+C₄H₄Se) fragments (obs.= 8.9128 mg; calc.= 8.8967 mg, 46.83%). Peak which represents third step recorded at 594.4 °C attributed to the remove of (N₂+2C₆H₆+C₄H₄Se) (obs.= 5.0446

mg; calc.= 5.0677 mg, 26.67%) for Ni (II)-complex. While Zn(II)-complex appeared is stable up to 110.1 °C. Peaks observed at 127.9, 274.7 and 480.1 °C which due to the DSC analysis. The first process showed between 110.1-282.4 °C related to the mass loss of (N₂+C₆H₆) molecules (obs.= 2.0398 mg; calc.= 2.0424 mg, 10.21%). The second process that detected at 372.1 °C related to the mass loss of (2N₂H₄) (obs.= 1.2068 mg; calc.= 1.2331 mg, 6.17%). The third peak, which represents the third step is recorded at 594.5 °C attributed to the remove of (C₂H₄) (obs.= 0.5542 mg; calc.= 0.5395 mg, 2.70%).

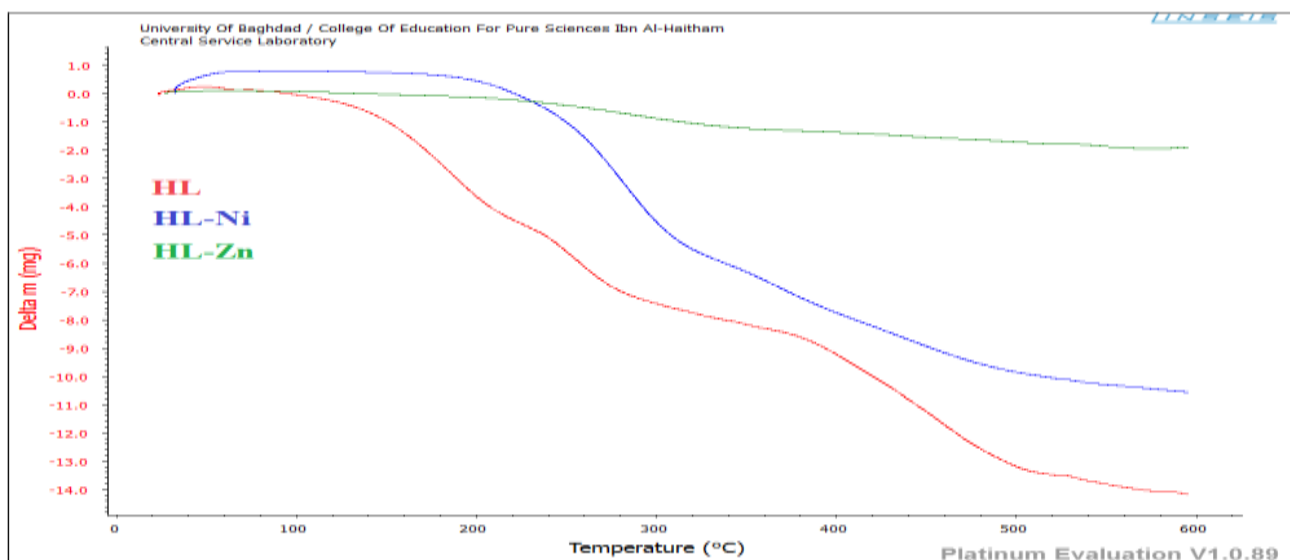


Figure 5 a: TGA analysis of ligand (HL) and its complexes

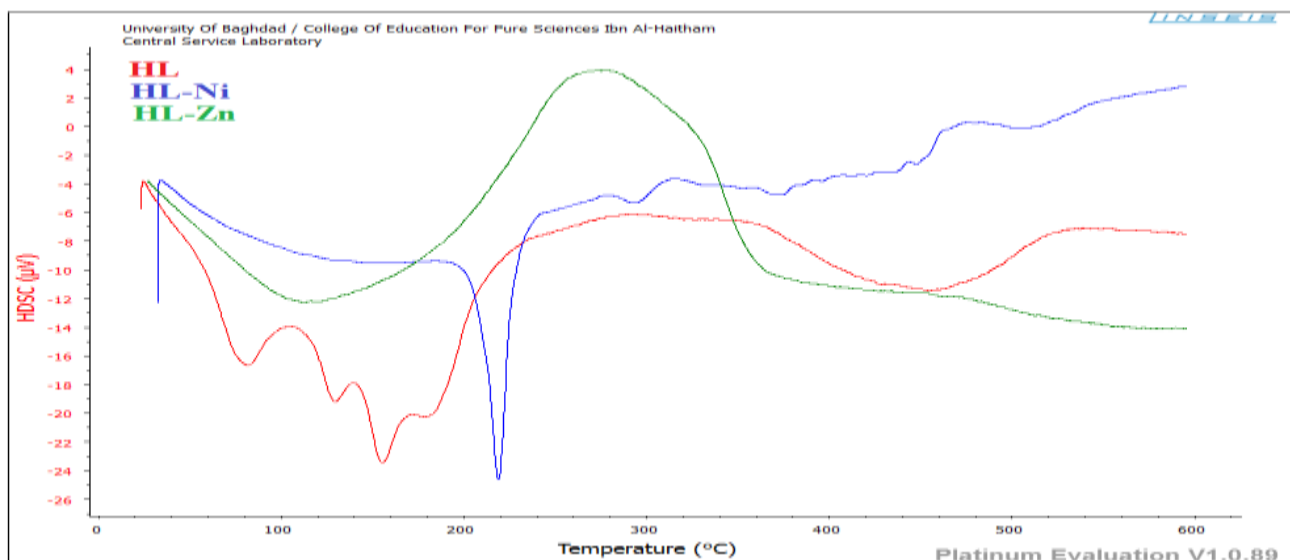


Figure 5 b: DSC analysis of ligand (HL) and its complexes

Table 4: TGA/DSC/DTG/ data of ligand (HL) and its metal complexes.

Compound	Stable up to °C	Stage	Decomposition temperature initial-final °C	Nature of transformation/intermediate formed% mass found (calc.)	Nature of DSC peak and temp. °C	DTG peak temp. °C
HL	70.2	1	70-226	4.6499 (4.6721)	80.9 Exo 130.5 Exo 155.7 Exo	185.2
		2	227-305	2.7712 (2.7049)		256.1

		3	306-363	0.7717 (0.7787)		
		4	364-528	5.0002 (5.0410)	455.3 Exo	452.3
		5	529-594	0.5817 (0.6557)		556.2
K ₂ [Ni(L) ₂ Cl ₂]	170.2	1	170-261	2.6899 (2.6706)	219.0 Exo	278.0
		2	262-351	8.9128 (8.8967)	295.4 Exo	
		3	353-594	5.0446 (5.0677)	496.4 Endo	
[Zn(L) ₂]	110.1	1	110-282	2.0398 (2.0424)	127.9 Exo	284.0
		2	283-372	1.2068 (1.2139)	274.7	
		3	373-595	0.5542 (0.5395)	Endo 480.1 Endo	

Biological Activity

Selenosemicarbazone ligand (HL) and its complexes were tested against four types of bacterial species: Gram negative including *Escherichia coli*, *Bacillus sabtuius* and *Klebsiella pneumoniae* and Gram positive covering *Staphylococcus aureus*. Mueller Hinton agar is a method, which used to examine compounds [26]. DMSO solvent showed no effect on the tested compounds. The concentration that used is 100 ppm in DMSO solvent.

According to results presented in Table (5), the ligand (HL) showed antimicrobial activity towards all Gram negative and Gram positive bacterial strains. Complexes of HL have shown more antimicrobial activity against all types bacterial, compared with the free ligand (HL). Additionally, Zn(II)-complex exhibited an excellent activity against *Escherichia coli* strains, compared with free ligand and other complexes. While, Mn(II), Cu(II) and Zn(II) complexes displayed less activity against *Staphylococcus aureus* strains than other complexes, (see Figure (6)). The enhanced activity of the complexes can

be discussed on the basis of chelation theory and Overtone's model [27]. About chelation approach, complexation may increase the ability of metal complex to cross the cell layer of bacteria. Then, this process will lead to decrease of the positive charge of the metal centre towards the coordinated ligand through nitrogen and selenium atoms. Therefore, will increase the lipophilic nature of the metal chelate system which favours its penetration through lipid layer of the cell membranes of microorganism.

The antifungal activities of selenosemicarbazone ligand (HL) and its complexes were studied against four types fungi species, Table (6). Generally, the ligand (HL) with its complexes revealed activity against all fungi species (except Co(II)-complex showed no active against *Candida tropicalis* strains). While, Cu-complex showed the highest activity against *Candida glabrata* strains, compared with other complexes. The collected data indicated the cobalt complex exhibited less active against *Candida parapsilsis* strains than other compounds, (see Figure (7)).

Table 5: Biological activity of ligand (HL) and its complexes

No.	Sample	Inhibition zone (mm)			
		<i>E. coli</i>	<i>B. sabtuius</i>	<i>S. aureus</i>	<i>K. pneumoniae</i>
1	HL	15	14	12	13
2	K ₂ [Mn(L) ₂ Cl ₂]	16	17	13	15
3	K ₂ [Co(L) ₂ Cl ₂]	20	21	14	16
4	K ₂ [Ni(L) ₂ Cl ₂]	19	18	16	14
5	[Cu(L) ₂]	20	22	13	14
6	[Zn(L) ₂]	29	21	13	15
7	[Cd(L) ₂]	23	21	19	20

Table 6: Fungi activity of ligand (HL) and its complexes.

No.	Sample	Inhibition zone (mm)			
		<i>Candida albicans</i>	<i>Candida glabrata</i>	<i>Candida tropicalis</i>	<i>Candida parapsilsis</i>
1	HL	17	16	12	11
2	K ₂ [Mn(L) ₂ Cl ₂]	13	17	11	9
3	K ₂ [Co(L) ₂ Cl ₂]	19	18	-	8
4	K ₂ [Ni(L) ₂ Cl ₂]	20	19	19	15
5	[Cu(L) ₂]	22	20	20	14
6	[Zn(L) ₂]	21	21	18	13
7	[Cd(L) ₂]	20	11	17	11

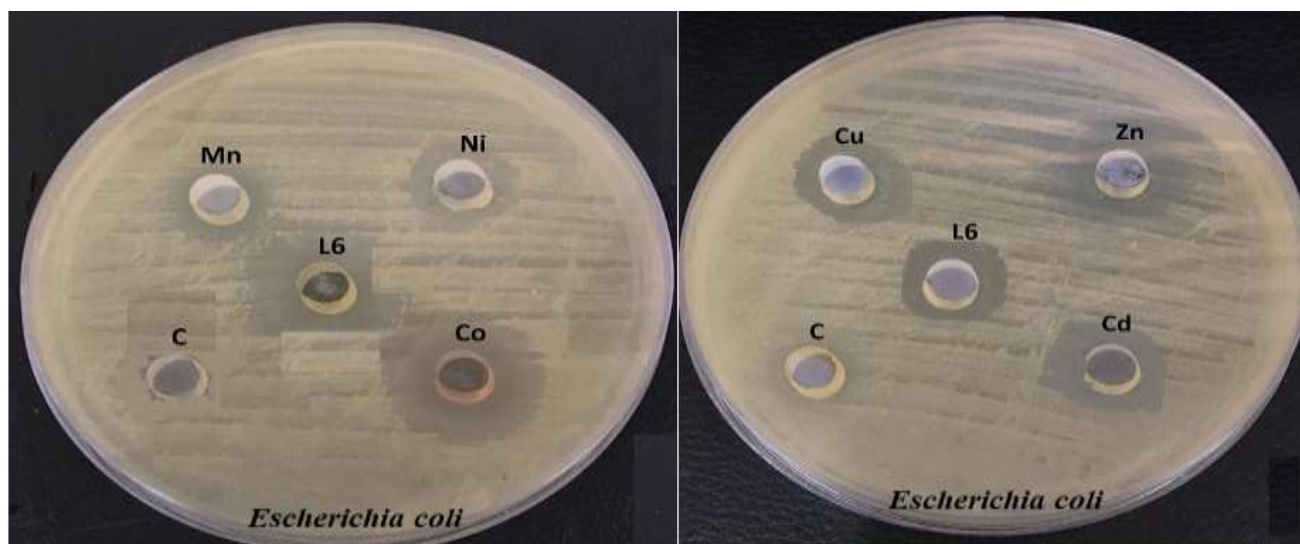


Figure 6: Inhibition diameter (mm) of HL and its complexes against *Escherichia coli*

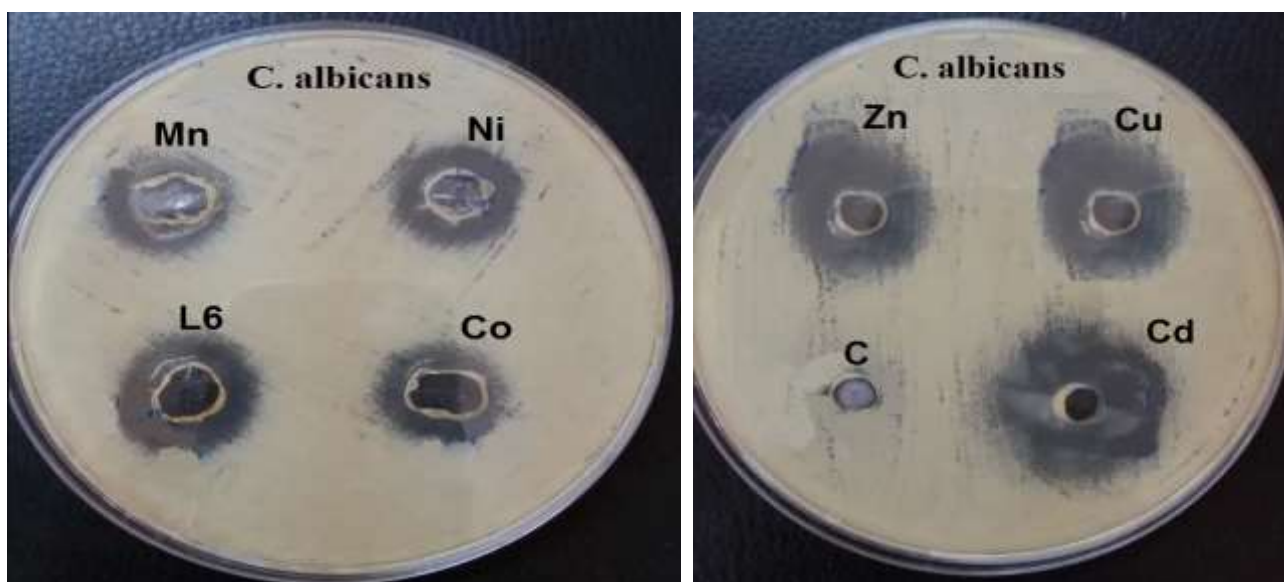


Figure 7: The influence of HL and its complexes on *Candida albicans*

Conclusions

In this paper, a novel selenosemicarbazone ligand (HL) and its metal complexes were synthesised and characterised using a range of physico-chemical techniques. Upon complexation, selenosemicarbazone ligand was deprotonated and coordinated to metal centre *via* nitrogen and selenium atoms. An octahedral geometry was predicted for Mn(II), Co(II) and Ni(II) complexes in which two ligands bound to the metal centre and the remaining two vacant orbitals occupied by chlorido atoms. While, a square-planar geometry and a tetrahedral arrangement

were suggested for Cu(II) and Zn(II) and Cd(II) complexes. The biological activity of the ligand and its complexes against bacterial species and fungi pathogens were also tested. Generally, selenosemicarbazone complexes showed more antimicrobial activities, compared with the free ligands.

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