

## RESEARCH ARTICLE

# Synthesis, Physico-chemical Characterization, Biological Activity and Thermal Analysis of Novel Selenosemicarbazone Ligand and its Metal Complexes

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Received: 21st August, 2021, Revised: 11th October, 2021, Accepted: 28th October, 2021, Available Online: 25th December, 2021

## ABSTRACT

Formation of four of mononuclear metals complexes derived from selenosemicarbazone Schiff-base ligand HL have been stated. The (1R,2R,4R,5S)-2,4-diphenyl-3-azabicyclo[3.2.1]octan-8-imine reaction with a mixture of KSeCN and NH<sub>2</sub>NH<sub>2</sub> in aca. 1:1:3 mol ratio has led to the isolation of novel selenosemicarbazone ligand (Z)-2-((1R,2R,4R,5S)-2,4-diphenyl-3-azabicyclo[3.2.1]octan-8-ylidene)hydrazine-1-carboselenoamide (HL). The HL reaction with Mn(II), Cu(II), Ni(II), and Zn(II) ions has led to isolation of new complexes with general formula K<sub>2</sub>[ML<sub>2</sub>C<sub>12</sub>] and [M'L<sub>2</sub>], M= Mn(II) and Ni(II); M'=Cu(II) and Zn(II). The physico-chemical methods were used to indicate the expected structure and type of bonding of ligand and the metal complexes. The analytical and spectroscopic studies of complexes have shown the isolation of octahedral, square planar and tetra-hedral geometry about Mn(II), Ni(II) and Cu(II) and about Zn(II) ion, respectively. The biological evaluation of ligand and its metal complexes have been found against the strains of the Gram(-) bacteria; *Escherichia coli*, and *Klebsiella pneumoniae* and *Bacillus subtilis*, as well as the strains of the gram (+) bacteria *S. aureus*, which has shown the fact that metal complexes potentially have a higher level of resistivity to microbial activities in comparison with free ligand. In addition to that, the seleno-semicarbazone ligand as well as its complexes have been tested against 4 species of fungus (which are *Candida glabrata*, *Candida albicans*, *Candida parapsilosis* and *Candida tropicalis*) that has shown, in general, the fact that the complexes get a higher level of activity in comparison with free ligand HL.

**Keywords:** Biological activity, Selenosemicarbazone bidentate ligand, Schiff-base complexes, Thermal analysis.

International Journal of Drug Delivery Technology (2021); DOI: 10.25258/ijddt.11.4.3

**How to cite this article:** Mawat TH, Atiyah EM. Synthesis, Physico-chemical Characterization, Biological Activity and Thermal Analysis of Novel Selenosemicarbazone Ligand and its Metal Complexes. International Journal of Drug Delivery Technology. 2021;11(4):1130-1137.

**Source of support:** Nil.

**Conflict of interest:** None

## INTRODUCTION

The introductions of new synthetic routes in the preparation of organic molecules that function as ligands had a key impact on development of coordination chemistry.<sup>1</sup> Schiff-base compounds are an interesting class of organic molecules that involved in the development and expansion of inorganic and coordination chemistry. This is because these species are capable of forming stable complexes with transition and non-transition elements.<sup>2</sup> Chalcogenosemicarbazone is a class of organic compounds that incorporate beside the imine moiety heteroatoms such oxygen, sulphur, selenium or tellurium. These compounds showed a range of applications in various fields of chemistry and biological applications.<sup>3</sup> They incorporate the "hard", for example, N, O and "soft", which include the S, Se or Te donor atoms, which gave them the capability to interact with many different metal ions.<sup>4</sup> Organic compounds that incorporate nitrogen and selenium groups on their backbone represent an important class of materials, as they are capable

to form stable metal-complexes. Selenosemicarbazone compounds (ligands and complexes) are Schiff-bases that exhibit a range of biological and pharmaceutical applications including their antitumor and antibacterial activities.<sup>5</sup> Subsequently, these compounds may be used as antioxidant and could serve as biological agents including their role as; anti-inflammatory, antibacterial, antiviral, and antitumor agents.<sup>6</sup> More, they also found applications in agriculture and in the formation of some dyes.<sup>7</sup> As a chelating agent, selenosemicarbazone have the capability for the formation of the stable compounds, with the elements.<sup>1</sup> Seleno-compounds have applications in organic, analytical chemistry and biochemistry as reagents. As a result, introducing the atom of the selenium to homocyclic and heterocyclic compounds was investigated to prepare the seleno-compounds that have a low level of the toxicity, excellent reactivity and high stability.<sup>8</sup> Therefore, seleno-heterocyclic and seleno-homocyclic compound the synthesis turns into one of the significant issues

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in the modern chemistry. Which is a result of their impact on medicinal and biological applications and their utilizations as intermediates in the organic syntheses. Recently, we reported the formation of novel selenosemicarbazone ligand and its metal complexes.<sup>9,10</sup> In this paper, synthesis and structural characterization of a selenosemicarbazone ligand and its metal complexes have been reported. The ligand was synthesis from the reaction of a Mannich precursor (1R,2R,4R,5S)-2,4diphenyl-3azabicyclo[3.2.1]octan-8-imine with the inorganic reagents (potassium selenocyanate and hydrazine).

More, a set of four complexes have been described from reaction of the selenosemicarbazone ligand with M(II) ions (M = Mn, Ni, Cu and Zn) and its metal complexes. Further, the compounds that were prepared had been tested for the anti-bacterial as well as the antifungal activities.

## EXPERIMENTAL

### Materials and Method

All of the laboratory reagents that have been utilized in preparing and analyzing the compounds have been found available commercially and utilized with no additional purifications. The solvents have been distilled from suitable drying agents right before being utilized. (1R,2R,4R, 5S)-2, 4diphenyl-3azabicyclo[3.2.1]octan-8-imine was prepared according to other methods.<sup>11</sup> This compound used as precursor in the synthesis of ligand.

### Physical Measurements

The melting point values have been obtained on electro-thermal Stuart apparatus, SMP-30 model. The spectra of the FTIR have been evaluated as discs of the KBr in a range between 400 and 4000  $\text{cm}^{-1}$  on Bio-tech fourier transform infrared spectroscopy (FTIR) 600 FTIR spectrometer and CsI discs in a range of 250  $\text{cm}^{-1}$  and 4000  $\text{cm}^{-1}$  on Shimadzu (FTIR)-8400-S spectrometer. Electronic spectrum value have been recorded in a range 200 nm-1100 nm for  $10^{-3}$ M solutions in the DMSO at the temperature of the room with the use of Shimadzu UV160 spectro-photometer. The spectra of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR had been obtained in the dimethylsulfoxide (DMSO)- $d_6$  solutions with the use of Bruker 400 MHz spectro-meter respectively, with the tetra-methylsilane (TMS) as internal standard. Spectra of  $^{77}\text{Se}$ -NMR have been obtained in the DMSO- $d_6$  solution with the use of a Bruker 400 MHz spectrometer with dimethylselenide ( $\text{Me}_2\text{Se}$ ) as one of the internal standards. Electrospray mass spectrometry (ESMS) (i.e., electrospray mass spectra) have been recorded with the use of the Agilent LCmsxx spectrometer. Elemental analysis (H, C and N) have been performed upon the EuroEA3000. The metals have been specified with the use of the 4-formylaminoantipyrine (FAA) 680Gatomic absorption spectro-photometer. The approach of the Potentio-metric titration, which uses a 686Titro processor-665Dosimat-Metrohm Swiss, has been utilized for the determination of the content of chloride. The measurements of the Conductivity have been performed with the solutions of the DMSO with the use of CON510 digital meter of conductivity (Eutech Instruments), and magnetic

moments of the room temperature have been evaluated with a balance of the magnetic susceptibilities (Sherwood Scientific Devised). Thermal analyses (Thermo-gravimetry (TG), differential scanning calorimetry (DSC) and differential thermogravimetry (DTG)) has been conducted with the use of Linseis STA PT1000 TG-DSC.

### Preparation of HL

A(1R,2R,4R,5S)-2,4diphenyl-3azabicyclo[3.2.1] octan-8-imine (0.4 g, 1-mmol) has been solution in a mix that includes 20 mL of  $\text{CHCl}_3$ :EtOH (1:3), has been added drop by drop drp, with stirring to a hydrate of the hydrazine (99.90%, 0.1-mL, 3.0 mmol),  $\text{KSeCN}$  (0.2g, 1.0 mmol) and HCl acid (36%, 0.1 mL, 3.0 mmol) in ethanol (20.0 mL). The reaction mix has been left in order to reflux for a 3 hours period, and filtrated when it's still hot for removing the excess selenium. This solution has been reduced to 50% under the vacuum and allowed to when at the temperature of the room throughout which time a solid has been formed that has been obtained through the filtration, washed with ether (5ml) and dried in air, Scheme 1. Yield: 0.25g (63%), m.p= 251-254°C. FTIR data ( $\text{cm}^{-1}$ ): 3460, 3441 (N4-H), 3317 (N3-H), 3248 (N1-H), 1519 (C=C)<sub>aromatic</sub>, 1643 (C=N)<sub>imine</sub>, 3089 (C-H)<sub>aromatic</sub>, 2804 (C-H)<sub>aliphatic</sub>, 1284 (C=Se)<sub>selenone</sub>. The  $^1\text{H}$ -NMR spectrum of ligand (400MHz, DMSO -  $d_6$ ) showed peaks at  $\delta_{\text{H}}$ ; 1.41(4H, m, C<sub>9,9</sub>-H), 2.07 (2H, q, C<sub>8,8</sub>-H), 2,75 (1H, s, N1-H), 3.80 (2H, d,  $J_{\text{HH}} = 8$  Hz, C<sub>7,7</sub>-H), 5.16 (2H, s, N4-H), 6.89 (2H, t,  $J_{\text{HH}} = 8$  Hz, C<sub>1,1</sub>-H), 7.60 (4H, t,  $J_{\text{HH}} = 8$  Hz, C<sub>2,2</sub>, 6,6'-H), 7.88 (4H, d,  $J_{\text{HH}} = 8$  Hz, C<sub>3,3</sub>, 5,5'-H), , 8.54 (1H, s, N3-H) ppm. The  $^{13}\text{C}$ -NMR spectrum (100 MHz, DMSO- $d_6$ ) of HL exhibits signals at  $\delta_{\text{C}}$ ; 27.89 (C<sub>9,9</sub>), 55.10 and 56.44 related to (C<sub>8,8</sub>) which appeared non-equivalent, 64.21 (C<sub>7,7</sub>), 125.26 (C<sub>1,1</sub>), 127.29 (C<sub>3,3</sub>, 5,5'), 128.51 (C<sub>2,2</sub>, 6,6'), 140.82 (C<sub>4,4</sub>) and 158.02 and 171.25 ppm which is associated with the C=N of imine moiety and C=Se group, respectively.  $^{77}\text{Se}$ -NMR spectrum of HL (76MHz, DMSO-  $d_6$ ) exhibits signal at  $\delta_{\text{Se}}$ ; 186.25ppm (C=Se) group.

Positive electro-spray mass spectrum of HL had shown a peak at  $m/z = 398.4[(\text{M}+\text{H})]^+$  (7%) for  $\text{C}_{20}\text{H}_{22}\text{N}_4\text{Se}$ , requires= 397.4. Peaks detected at  $m/z = 291.4$  (74%), 194.4 (100%), 106.3 (47%) and 55.3 (16%) correspond to  $[(\text{M}+\text{H})-(\text{C}_8\text{H}_{10})]^+$ ,  $[(\text{M}+\text{H})-(\text{C}_8\text{H}_{10}+(\text{C}_6\text{H}_{11}\text{N}))]^+$ ,  $[(\text{M}+\text{H})-(\text{C}_8\text{H}_{10}+(\text{C}_6\text{H}_{11}\text{N}))+(\text{C}_7\text{H}_4)]^+$  and  $[(\text{M}+\text{H})-(\text{C}_8\text{H}_{10}+(\text{C}_6\text{H}_{11}\text{N}))+(\text{C}_7\text{H}_4)+(\text{C}_4\text{H}_2+\text{H})]^+$ , respectively.

### General Metal Complex Synthesis with Ligand (HL)

A mix of the metal chloride salt (0.127 mmol) in ethanol (10.0 mL) has been added drop by stop to an appropriate ligand solution (0.254 mmol) in 20.0 mL of a  $\text{CHCl}_3$ :EtOH (1:3) mix. The reaction mix's pH has been adjusted through the addition of KOH to *ca.* pH= 8, and reaction mix has been stirred for 3 hours. The formed precipitate has been filtered off, washed by cold absolute ethanol (5.0 mL) and dried by air, Scheme 2. Elemental analysis data, colors and yield values of title complexes have been performed.

### NMR Data

$^1\text{H}$ -NMR spectrum (400MHz, DMSO- $d_6$ ) of  $[\text{Zn}(\text{L})_2]$  showed peaks at  $\delta_{\text{H}}$ ; 1.27 (4H, m, C<sub>9,9</sub>-H), 1.93 (2H, q, C<sub>8,8</sub>-H), 2.88 (1H, s, N1-H), 3.85 (C<sub>7,7</sub>-H; d,  $J_{\text{HH}} = 8$  Hz), 5.23 (2H, s, N4-H), 7.20

(2H, t,  $J_{HH}$  = 12 Hz,  $C_{1,1}$ -H), 7.59 (4H, t,  $J_{HH}$  = 8Hz,  $C_{2,2}, 6,6$ -H), 7.93 (4H, d,  $J_{HH}$  = 8Hz,  $C_{3,3}, 5,5$ -H) ppm.  $^{13}\text{C}$ -NMR spectrum of  $[\text{Zn}(\text{L})_2]$  (100MHz, DMSO- $d_6$ ) showed peaks at  $\delta_C$ : 27.89 ( $C_{9,9}$ ), 56.44 ( $C_{7,7}$ ), 65.53 ( $C_{8,8}$ ), 124.67 ( $C_{1,1}$ ), 126.21 ( $C_{2,2}, 6,6$ ), 128.51 ( $C_{3,3}, 5,5$ ), 142.43 ( $C_{4,4}$ ), 164.43 and 168.92 ppm that is associated C=N of the imine moiety and group of C-Se.  $^{77}\text{Se}$ -NMR (76MHz, DMSO- $d_6$ )  $[\text{Zn}(\text{L})_2]$  spectrum exhibits signal at  $\delta_{Se}$ ; 237.20 ppm.

## RESULT AND DISCUSSION

The prepared ligand (HL) and its complexes are the air stable solids, which are soluble in DMF,  $\text{CHCl}_3$  and DMSO (except other common organic solvent types). The expected spatial arrangements of compounds were predicted from their spectroscopic and analytical analyses. Conductivity measurements of HL mononucleating complexes in DMSO, lie in 31.34 to 38.66 and 2.17 to 3.10  $\text{cm}^2/\Omega\text{mol}$  range, respectively that indicates their 2:1 electrolytic and non-electrolytic behavior.<sup>12</sup>

### FTIR Spectra

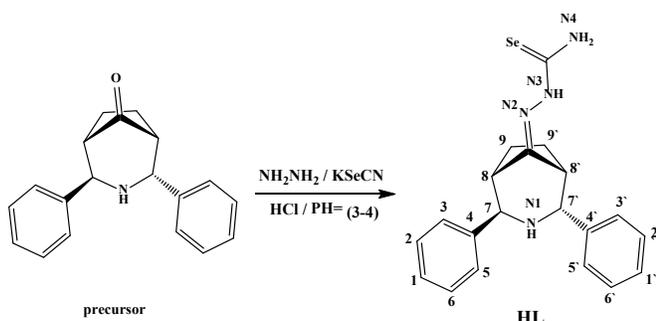
FT-IR spectrum of HL had revealed several characteristic functional group bands at (3460, 3441), 3317, 3248, 1643 and 1284  $\text{cm}^{-1}$  attributed to  $\nu(\text{N4-H})$ ,  $\nu(\text{N3-H})$ ,  $\nu(\text{N1-H})$ ,  $\nu(\text{C=N})_{\text{imine}}$  and  $\nu(\text{C=Se})_{\text{selenone}}$ , respectively.<sup>13-15</sup> The spectrum indicated no peaks around 2400  $\text{cm}^{-1}$  could assign to  $\nu(\text{Se-H})$ , demonstrating the fact that the ligand exists in its selenone form.<sup>13</sup>

The most noticeable infrared bands for ligand HL and its complexes in combination with their assignments have been given in Table 1. The FTIR spectra of HL complexes indicated ligand bands with suitable shifts because of complexation.

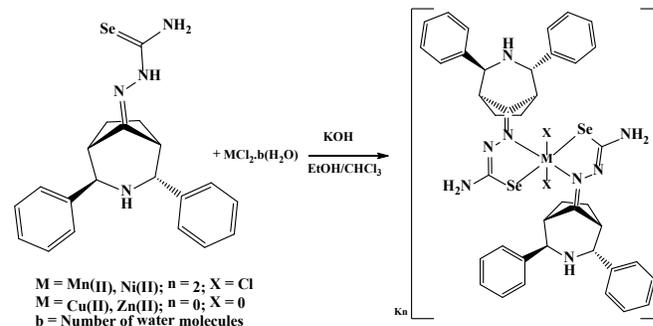
The  $\nu(\text{C=N})$  of imine group that detected at 1643  $\text{cm}^{-1}$  in free ligand HL was shifted to lower wavenumber and appeared about 1629–1636  $\text{cm}^{-1}$  in complexes HL. The shift to lower wavenumber that is associated with the metal electron density delocalization into ligand  $\pi$ -system. Such shifting had confirmed the coordination of imine moieties' nitrogen to metal ions and indicating strong nature of the bonding between metal ions and iminic (C=N) group.<sup>15,16</sup> The  $\nu(\text{C-Se})$  bands for the complexes recorded around 702–736  $\text{cm}^{-1}$  in both complexes, compared with the free ligand HL at 771  $\text{cm}^{-1}$ .<sup>14</sup> The  $\nu(\text{N3-H})$  band detected around 3317  $\text{cm}^{-1}$  in HL is no longer exist in complexes' spectra, confirming the deprotonation of ligand upon complexation.<sup>16</sup> The spectra of complexes showed absorption band around 1608–1618  $\text{cm}^{-1}$  related to formation (N=C-Se) moiety. The  $\nu(\text{N1-H})$  and  $\nu(\text{N4-H})$  stretching bands remain existing in complexes' spectra, indicating the non-involvement of atoms of nitrogen of these groups in coordination to metal center.<sup>17</sup> The FTIR spectra of complexes had shown the bands around 420 to 459 and 333 to 364  $\text{cm}^{-1}$  have been assigned to  $\nu(\text{M-N})$  and  $\nu(\text{M-Se})$ , respectively.<sup>18,19</sup> Peaks recorded around 254 to 275  $\text{cm}^{-1}$  attributed to  $\nu(\text{M-Cl})$ ,<sup>19</sup> (except complexes Cu(II) and Zn(II) that did not show any peaks around 250  $\text{cm}^{-1}$  may assign to  $\nu(\text{M-Cl})$ .

### NMR Spectra

$^1\text{H}$ -NMR spectrum of selenosemicarbazone ligand (HL) in DMSO- $d_6$  solvent indicated peak at  $\delta_H$  = 2.75, ppm equivalent to one proton assigned to (N1-H) group that derived from (1R,2R,4R,5S)-2,4-diphenyl-3-azabicyclo[3.2.1]octan-8-imine. Peak detected at  $\delta_H$  = 8.54 ppm (1H, br) equivalent to one proton



**Scheme 1:** Chemical structure of seleno-semicarbazone ligand HL



**Scheme 2:** Synthesis route and suggested structures of HL complexes

**Table 1:** FT-IR frequency values in ( $\text{cm}^{-1}$ ) of compounds

Compounds	$\nu(\text{N4-H})$	$\nu(\text{N3-H})$	$\nu(\text{N1-H})$	C=N	$\nu(\text{N-C-Se})$					
					$\nu(\text{N=C-Se})$	C=C	C-Se	M-N	M-Se	M-Cl
HL	3460 3441	3317	3248	1643	1593	1519	1284 771	–	–	–
$\text{K}_2[\text{Mn}(\text{L})_2\text{Cl}_2]$	3444 3433	–	3305	1636	– 1618	1585 1512	1240 736	420 459	364	275
$\text{K}_2[\text{Ni}(\text{L})_2\text{Cl}_2]$	3501 3464	–	3410	1630	– 1610	1581 1512	1249 736	420 443	333	254
$[\text{Cu}(\text{L})_2]$	3460 3444	–	3394	1630	– 1608	1597 1554	1234 702	412 451	334	–
$[\text{Zn}(\text{L})_2]$	3486 3433	–	3394	1629	– 1608	1585 1512	1249 736	420 459	350	–

attributed to (N3-*H*) group, confirming the existence of the ligand in its selenone form Figure 1. Peak detected at  $\delta_{\text{H}}=5.16$  ppm that is equivalent to 2 protons that have been assigned to (N4-*H*) group. The triplet signal that at  $\delta_{\text{H}}=6.89$  ppm due to (C<sub>1,1</sub>-*H*) protons. Peak observed at  $\delta_{\text{H}}=7.60$  ppm that equivalent to four protons assigned to (C<sub>2,2</sub>, 6,6'-*H*) protons. Resonance recorded at  $\delta_{\text{H}}=7.88$  ppm related to (C<sub>3,3</sub>, 5,5'-*H*) protons. The <sup>13</sup>C-NMR spectrum of HL in DMSO-d<sub>6</sub> solvent displays peak at  $\delta_{\text{C}}=171.25$  ppm assigned to (C=Se) group.<sup>18</sup> The <sup>77</sup>Se-NMR spectrum of HL in DMSO-d<sub>6</sub> solvent shows peak at  $\delta_{\text{Se}}=186.25$  ppm attributed to C=Se group.<sup>18</sup>

The <sup>1</sup>H-NMR spectra for [Zn(L)<sub>2</sub>] complex in DMSO-d<sub>6</sub> solvent has not shown any peaks around  $\delta_{\text{H}}=8.00$  ppm can be assigned to (N3-*H*) group, which indicates the deprotonation of N-H group at the moment of the complex formation. Peak detected at  $\sim 5.02$  ppm equivalent to 2 protons that are associated with (N4-*H*) group, indicating non-involvement of those groups upon the complexation.<sup>18</sup> The triplet around 7.20 ppm that equivalent to 2 protons that have been assigned to (C<sub>1,1</sub>-*H*) aromatic protons in the complex. Those protons have appeared as expected triplet because of the rigidity that has been occurred upon the formation of the complex, in comparison to upfield chemical shift that has been noticed in free ligand HL.

The <sup>13</sup>C-NMR spectra of [Zn(L)<sub>2</sub>] complex in DMSO-d<sub>6</sub> solvents exhibit a peak at 168.92 ppm assigned to (C-Se) moiety (Figure 2). The significant upfield shift of C-Se is a result of the complexations, compared with that in free ligand, which indicates involvement of C-Se groups in the coordination. Metal center can de-localize the density of the electrons to ligand  $\pi$ -system (particularly selenium d $\pi$ -system), and consequently C-Se exhibited lower bond order and shows more selenide character. A peak correlated to the imine moiety appeared at  $\sim 164$  ppm, confirming the 2 moieties of the imine have been equivalent and appeared with higher chemical shifting in comparison with free ligands. Which has been a result of involvement of imine groups in complexation. The <sup>77</sup>Se-NMR spectra of [Zn(L)<sub>2</sub>] complex in DMSO-d<sub>6</sub> solvents exhibit peak at 237.20 ppm related to (C-Se) group. The chemical shift of signals appeared downfield. In comparison to

that in free ligand indicated complex formation and the ligand coordinated to the metal centre in their selenide forms.<sup>18</sup>

### 3.3 Mass Spectra

The electro-spray (+) mass spectrum of HL displayed a peak  $\text{atm/z}=398.4$  [(M+H)<sup>+</sup>] (7%) for C<sub>20</sub>H<sub>22</sub>N<sub>4</sub>Se, requires= 397.4. Peaks detected at  $\text{m/z}=291.4$  (74%), 194.4 (100%), 106.3 (47%) and 55.3 (16%) correspond to [M+H-(C<sub>8</sub>H<sub>10</sub>)]<sup>+</sup>, [(M+H)-(C<sub>8</sub>H<sub>10</sub>)+(C<sub>6</sub>H<sub>11</sub>N)]<sup>+</sup>, [(M+H)-{(C<sub>8</sub>H<sub>10</sub>)+(C<sub>6</sub>H<sub>11</sub>N)}+(C<sub>7</sub>H<sub>4</sub>)]<sup>+</sup> and [(M+H)-{(C<sub>8</sub>H<sub>10</sub>)+(C<sub>6</sub>H<sub>11</sub>N)+(C<sub>7</sub>H<sub>4</sub>)+(C<sub>4</sub>H<sub>2</sub>+H)}]<sup>+</sup>, respectively.

The electro-spray (+) mass spectrum of K<sub>2</sub>[Mn(L)<sub>2</sub>Cl<sub>2</sub>] shows peak  $\text{atm/z}=998.61$  [(M+H)<sup>+</sup>] (14%) for C<sub>40</sub>H<sub>42</sub>Cl<sub>2</sub>K<sub>2</sub>MnN<sub>8</sub>Se<sub>2</sub>, requires= 997.6 amu. Peaks detected at  $\text{m/z}=728.8$  (32%), 626.8 (100%), 448.3 (55%), 346.3 (86%) and 116.8 (24%) related to [(M+H)-(C<sub>11</sub>H<sub>10</sub>+CH<sub>3</sub>Cl+C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup>, [(M+H)-{(C<sub>11</sub>H<sub>10</sub>+CH<sub>3</sub>Cl+C<sub>6</sub>H<sub>6</sub>)+(C<sub>7</sub>H<sub>4</sub>N)}]<sup>+</sup>, [(M+H)-{(C<sub>11</sub>H<sub>10</sub>+CH<sub>3</sub>Cl+C<sub>6</sub>H<sub>6</sub>)+(C<sub>7</sub>H<sub>4</sub>N)+(C<sub>4</sub>H<sub>9</sub>N<sub>3</sub>Se)}]<sup>+</sup>, [(M+H)-{(C<sub>11</sub>H<sub>10</sub>+CH<sub>3</sub>Cl+C<sub>6</sub>H<sub>6</sub>)+(C<sub>7</sub>H<sub>4</sub>N)+(C<sub>4</sub>H<sub>9</sub>N<sub>3</sub>Se)+(C<sub>7</sub>H<sub>4</sub>N)}]<sup>+</sup> and [(M+H)-{(C<sub>11</sub>H<sub>10</sub>+CH<sub>3</sub>Cl+C<sub>6</sub>H<sub>6</sub>)+(C<sub>7</sub>H<sub>4</sub>N)+(C<sub>4</sub>H<sub>9</sub>N<sub>3</sub>Se)+(C<sub>7</sub>H<sub>4</sub>N)+(C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>SeMn)}]<sup>+</sup>, respectively, (Figure 3).

### Electronic Spectral Data and Magnetic Moment Measurement

The UV-Vis spectral data of ligand as well its complexes have been given in Table 2. Free ligand HL along with its complexes exhibited two intra ligand,  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  peaks at 263 and 315 nm, respectively.<sup>13</sup>

The electronic spectra of HL complexes exhibit additional peaks in the range 275 to 467 nm assigned to  $\pi \rightarrow \pi\pi$ ,  $\pi \rightarrow \pi\pi$  and charge transfer (C.T).<sup>20</sup> The electronic Mn(II) complex spectrum had shown a peak at 845nm that has been assigned to <sup>6</sup>A<sub>1g</sub>(F)  $\rightarrow$  <sup>4</sup>T<sub>1g</sub>(G) transitions that indicate distorted octa-hedral geometry about Mn(II) ion.<sup>21</sup> The magnetic moment value 5.86BM of Mn(II)-complex has been typical for high spin Mn(II) ion that was assigned to the a distorted octahedral geometry Mn(II) complex structures.<sup>22,23</sup> The Ni(II)-complex electronic spectrum had shown peaks at 451, 650 and 815 nm assigned to <sup>3</sup>A<sub>2g</sub>  $\rightarrow$  <sup>3</sup>T<sub>1g</sub>(P), <sup>3</sup>A<sub>2g</sub>  $\rightarrow$  <sup>3</sup>T<sub>2g</sub>(F) and <sup>3</sup>A<sub>2g</sub>  $\rightarrow$  <sup>3</sup>T<sub>1g</sub>(F) transitions, respectively, which indicate a distorted octahedral geometry

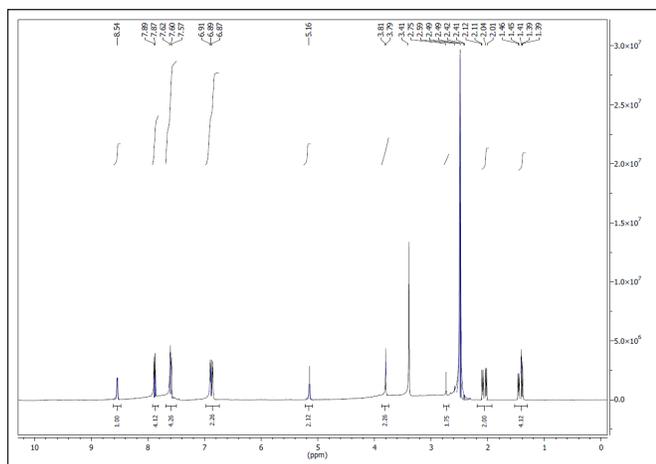


Figure 1: <sup>1</sup>H-NMR spectrum of ligand (HL).

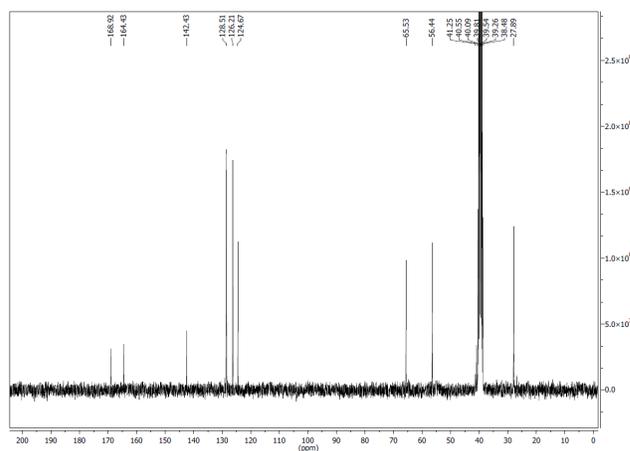


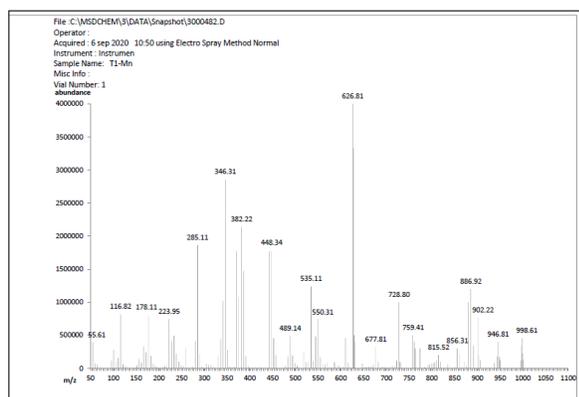
Figure 2: <sup>13</sup>C-NMR spectra for [Zn(L)<sub>2</sub>]

about Ni atom.<sup>21</sup> The magnetic moment value 2.64 B.M of the Ni(II)-complex has confirmed a distorted octa-hedral geometry about Ni atom.<sup>21</sup> Cu(II) complex displays peaks in d-d region at 762 and 871 nm attributed to d-d transition type  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2A_{2g}$ , respectively, which confirm distorted square planar arrangements about Cu atom.<sup>24</sup> This spectrum is in agreement with proposed geometry and value of the Cu(II)-complex magnetic moment which indicated a distorted square planar arrangement about Cu atom.<sup>25</sup> The Zn(II) complex spectrum had shown bands that have been assigned to the ligand field  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and C.T.<sup>26</sup> The structure of the tetra-hedral geometry has been proposed for Zn(II) center.<sup>27</sup>

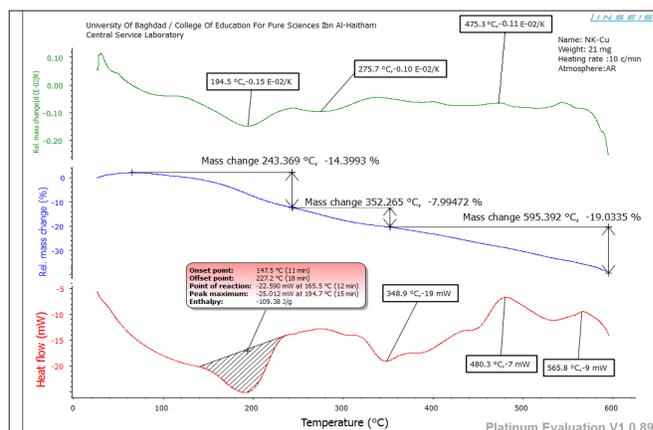
### Thermal Analyses

The thermal analysis data (DSC, DTG and TGA) of ligands HL and some metal complexes have been registered. The thermal analysis curves of TG, DSC and DTG of ligand as well as its metal complexes have been determined

from ambient temperatures to 600°C in argon atmosphere. The thermal analysis data of HL revealed the ligand is stable up to 90.2°C. The DSC curves show four peaks that recorded over temperatures 108.4, 172.3, 250.7, 345.1 and 472.3°C. Peak observed between 90.2-259.7°C attributed to the loss of ( $C_6H_{13}$ ) fragments (obs.= 4.4723 mg; calc.= 4.4961 mg, 21.41%). The second step recorded at 361.5°C assigned to the loss of ( $NH_3 + C_5H_{11}$ ) fragment (obs.= 4.6668mg; calc.= 4.6550mg, 22.17%). The third peak that detected at 595.2°C is related to the loss of ( $N_2H_4 + C_4H_9 + H_2$ ) fragments (obs.= 4.8769 mg; calc.= 4.8136 mg, 22.92%). The thermal decomposition data of  $K_2[Mn(L)_2Cl_2]$  complex appeared to be stable up to 78.1°C. The DSC analysis recorded peaks at 180.1, 348.9, 480.3 and 565.8°C which included exothermic and endothermic phases, (Figure 4). In TGA curve, first step that detected between 78.1–243.4°C, correlated to the removal of ( $N_2H_4 + C_6H_6 + C_2H_6 + 2H_2$ ) molecules (OBS.= 3.0239 mg; calc.= 3.0331 mg, 14.44%). Peaks detected at 352.3 and 595.4°C attributed to the loss of



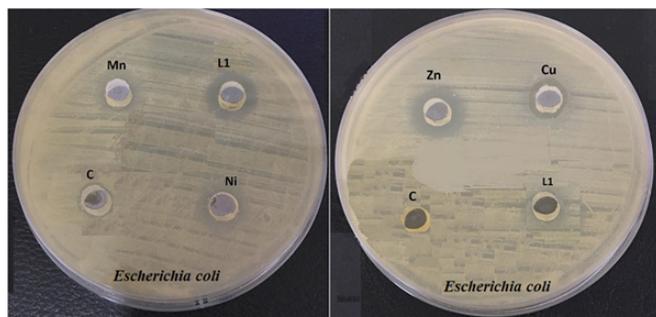
**Figure 3:** The electrospray (+) mass spectrum for  $K_2[Mn(L)_2Cl_2]$  complex



**Figure 4:** TGA, DSC and DTG analyses of Mn(II) complex

**Table 2:** Magnetic moments and UVvis spectral data in the solutions of the DMSO.

Compounds	$\mu_{eff}$ (BM)	$\lambda_{nm}$	$\epsilon_{max}$ $dm^3 mol^{-1} cm^{-1}$	Assignment
HL	-	263	560	$\pi \rightarrow \pi^*$
		315	1234	$n \rightarrow \pi^*$
$K_2[Mn(L)_2Cl_2]Cl$	5.86	275	670	$\pi \rightarrow \pi^*$
		305	1465	$n \rightarrow \pi^*$
		467	280	C.T.
		845	30	${}^6A_{1g}(F) \rightarrow {}^4T_{1g}(G)$
$K_2[Ni(L)_2Cl_2]$	2.64	290	2190	$\pi \rightarrow \pi^*$
		351	2310	$n \rightarrow \pi^*$
		451	176	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$
		650	66	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$
		815	34	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
$[Cu(L)_2]$	1.72	295	2432	$\pi \rightarrow \pi^*$
		380	1456	$n \rightarrow \pi^*$
		762	35	${}^2B_{1g} \rightarrow {}^2B_{2g}$
		871	57	${}^2B_{1g} \rightarrow {}^2A_{2g}$
$[Zn(L)_2]$	Diamagnetic	284	844	$\pi \rightarrow \pi^*$
		340	932	$n \rightarrow \pi^*$
		375	1345	C.T.



**Figure 5:** Inhibition diameter of HL and its complexes against *E. coli*

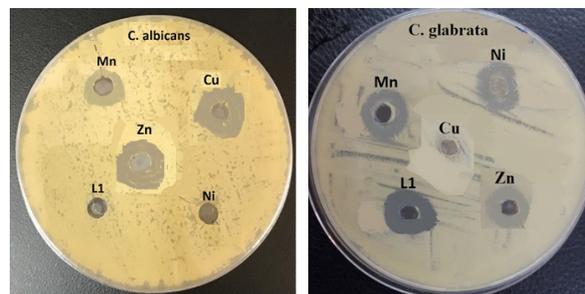
( $H_2+C_6H_6$ ) (obs. = 1.6851 mg; calc. = 1.6789 mg, 8.02%) and ( $N_2+2H_2Se$ ) (obs. = 3.9970 mg; calc. = 4.0020 mg, 19.06%), respectively. While Cu(II) complex appeared is stable up to 97.2°C. The DSC curve appeared peaks at 208.7, 291.7 and 415.2 °C which included exothermic and endothermic for above temperatures. In TGA analysis displayed peaks between 97.2-257.0°C indicated the elimination of ( $H_2N_2+C_7H_7$ ) molecules (obs.= 2.8315 mg; calc.= 2.8271 mg, 14.14%). Peaks detected at 382.4 and 595.3°C attributed to the loss of ( $2N_2+C_6H_6+C_5H_6$ ) (obs.= 4.6631 mg; calc. = 4.6729 mg, 23.37%) and ( $H_2N_2+C_4H_9$ ) (obs.= 2.0398 mg; calc. = 2.0327 mg, 10.16%), respectively.

### Biological Activity

Biological activities of ligand as well as its metal complexes had been examined against 4 bacterial strains, which are; *E. coli*, *S. aureus*, *K. pneumoniae* and *B. subtilis* and 4 species of fungi; *C. glabrata*, *C. albicans*, *C. parapsilosis* and *C. tropicalis* utilizing the medium Mueller Hinton agar approach.<sup>28</sup> The concentration of sample, in DMSO solvent, that used in the test is 100 ppm. The plates have been immediately incubated at 37°C for 24 hours.

Samples have been checked through the measurement of the width of the zones of inhibition in mm, utilizing the DMSO solution as control in an experiment that did not show any activities against any bacterial and fungal strains. Generally, the biological activities of selenosemicarbazone complexes were reported to increase upon coordination with the metal ions, compared with the free selenosemicarbazone ligands. Metal complexes appear more active in comparison with free ligand, and also exhibited biological activities that no display in the free ligand.

The free selenosemicarbazone ligand HL as well as its complexes with Cu(II), Mn(II), Ni(II), and Zn(II) ions have been screened against the Gram negative strains of the bacteria *E. coli*, *B. acillus subtilis* and *K. pneumoniae* and Gram positive strains of bacteria *S. aureus* utilizing the approach of disc diffusion. Ligand showed antimicrobial activities against Gram negative strains (*E. coli*, *B. subtilis*) only. The metal complexes had shown anti-microbial activities against all types of bacterial strains, compared with the free ligand (except Mn(II), Ni(II) and Cu(II) complexes showed no active against *S. aureus* strain.). Further, complex of Zn(II) exhibited higher activity against *E. coli*, *B. subtilis* and *K. pneumoniae*, compared with other complexes and the



**Figure 6:** The influence of HL and its complexes on *Candida albicans* and *Candida glabrata*

free ligand. The increase in the activities of complexes may be discussed according to the theory of the chelation and Overtone's model.<sup>29,30</sup> Based on the method of the chelation, the formation of the complex could be supporting complex to cross the micro-organism's cell membrane. Which results from the chelation results in considerably decreasing metal ion polarity and allowing of partially sharing the positive charge of the metal with the donor groups. Which might take place through delocalising metal charge into ligand  $\pi$ -system, over entire chelate system. Which will results in increasing lipophilic metal chelate system nature, favouring its movement through the cell membranes' lipid layer of the micro-organism (Figure 5).

The biological activity of examined compounds against fungi species have been performed and have shown the following trend:

- HL ligand and its complexes were found active against *C. glabrata* and showed no activity against *C. parapsilosis* strain.
- Complex of Ni(II) display no activity against *C. albicans*. However, this complex showed activity against *C. glabrata*.
- Complexes of Mn(II) and Ni(II) showed no activity against *C. tropicalis* strain.
- HL ligand and its complexes showed no active against *C. parapsilosis* strain (Figure 6).

### CONCLUSIONS

The synthesis and characterisation of novel selenosemicarbazone ligand and its four coordination metal complexes (where M = Mn(II), Ni(II), Cu(II) and Zn(II)) are reported. The formation of the ligand was accomplished *in situ* from direct Mannich-based compound reactions with KSeCN and  $NH_2NH_2$  precursors. During complexation, the title ligand functioned as mono-basic species and coordinated to center of the metal through selenium atom and imine nitrogen. Ligand as well as its metal complexes have been entirely identified with the use of many different physicochemical analyses, which include the thermal characteristics spectroscopic and analytical analyses have shown formation of 6 coordinate complexes with for HL with Mn(II) and Ni(II) metal ions. In addition to that, Cu(II) and Zn(II) complex with the ligand HL has been an indication of a square-planar and tetrahedral arrangement formations, respectively. Biological activities of title compounds against the

species of the bacteria and the pathogens of the fungi have been tested as well. In general, the seleno-semicarbazone complexes have shown more anti-microbial activities in comparison to free ligand.

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