Metal Complexes of Multidentate N₂S₂ Heterocyclic Schiff-base Ligands; Formation, Structural Characterisation and Biological Activity

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Abstract: The synthesis of ligands with N₂S₂ donor sets that include imine, an amide, thioether, thiolate moieties and their metal complexes were achieved. The new Schiff-base ligands; N-(2-((2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-ylidene)amino)ethyl)-2-((2-mercaptoethyl)thio)-acetamide (H₂L₁) and N-(2-((2,4-di-p-tolyl-3-azabicyclo[3.3.1]nonan-9-ylidene)amino)ethyl)-2-((2-mercaptoethyl)thio) acetamide (H₂L₂) were obtained from the reaction of amine precursors with 1,4-dithian-2-one in the presence of triethylamine as a base in the CHCl₃ medium. Complexes of the general formula K₂[M(Ln)Cl₂], (where: M = Mn(II), Co(II) and Ni(II)) and [M(Ln)], (where: M = Cu(II), Zn(II) and Cd(II); n =1 -2, expect [Cu(HL₂)Cl]) were isolated. The entity of ligands and complexes including their purity were confirmed using elemental microanalysis (C,H,N,S), atomic absorption (A.A), chloride content, conductivity measurement’s, melting point and thermal analysis technique. The molecular structures were elucidated with FT-IR, UV-Vis, magnetic susceptibility, ¹H- and ¹³C-NMR and mass spectroscopy. The synthesised compounds were evaluated for their activity against bacterial strains (G+ and G-) and fungi species. The tested compounds indicated that; the ligands have not shown any antimicrobial activity against Escherichia coli. The Cd(II) complexes, for ligands H₂L₁ and H₂L₂, display the higher antimicrobial activity, compared with the other complexes. The H₂L₁ and H₂L₂ have not shown any activity against Candida albicans. All complexes for ligands (H₂L₁ and H₂L₂) exhibited less activity against Candida albicans, compared with other types of fungi.

Keywords: Schiff-bases, N₂S₂ ligand system, Metal complexes, Structural characterisation, Biological activity.

1. Introduction

Compounds incorporate nitrogen and sulfur in their frameworks are a class of organic species that attracted a range of chemist researchers (organic, inorganic and bioinorganic chemists) [1]. The impact of these species on chemistry stimulated researches to investigate and implementing a range of synthetic protocols to increase yields and stability of these materials. These species have shown a range of potential applications, including their role as useful chelating agents for radio-metals of transition and representative elements [2]. They have also used as biomedical agents, in radiopharmaceutical [2], medicine [3] and as a mimic for bioactive molecules, in catalysis, analytical chemistry, coordination chemistry [4], environmental, materials and supramolecular chemistry [5]. Mannich-bases are an important organic species that pronounced a range of uses and applications in chemistry. Compounds derived from 2,4-bis(R-phenyl)-3-azabicyclo[3.3.1]nonan-9-one are interesting materials that used as organic reagents in the fabrication of natural-based blocks including the synthesis of...
phenanthridine-based compounds [6,7]. Further, compounds include N_2S_2 systems are remarkable materials that played a part in the expansion of chemistry and nuclear medicine [8]. Thus, the formation of functionalised Mannich-bases with N, S atoms should be an important class of compounds. They provide a flexible hard/soft system, upon acting as a chelating ligand to the metal centre. In this work, we describe the synthesis and characterisation of two multidentate N_2S_2 heterocyclic ligands N-(2-((2,4-diphenyl-3-azabicyclo[3.3.1] nonan-9-ylidene)amino)ethyl)-2-((2-mercapto ethyl)thio)acetamide (H_2L_1) and N-(2-((2,4-di-p-tolyl-3-azabicyclo[3.3.1]nonan-9-ylidene)amino)ethyl)-2-((2-mercapto ethyl)thio)acetamide (H_2L_2) and their metal complexes. The anti-bacterial and anti-fungi behaviour of ligands and their complexes were also investigated.

2. Experimental

2.1. Materials and methods

All reagents in this work were commercially available and used without further purification. 1,4-Dithian-2-one and ligands were obtained by a reported method [8,9].

2.2. Physical measurements

A Heraeus instrument (Vario EL) and a Perkin-Elmer 2400 Series-II analyser were used to obtain elemental analyses (C,H,N,S) at Materials Research Centre, Ministry for Science and Technology, Baghdad, IRAQ. Uncorrected melting points were recorded using an electro-thermal Stuart SMP40 apparatus. FT-IR spectra were measured as KBr discs using a Biotic 600 FT-IR spectrophotometer in the range 4000-400 cm^{-1} FTIR and as CsI discs in the range 4000-200 cm^{-1} on a Shimadzu 8400s FT-IR at College of Science, University of Baghdad. Electronic spectra were measured from 200-1100 nm for 10^{-3} M solutions in DMSO at room temperature with (UV-Vis) spectrophotometer type Shimadzu 1800, using quartz cell of 1.0 cm length. The measurements were obtained at Ibn Sina Company, Ministry of Industry, Baghdad, Iraq. Mass spectra were obtained as Electrospray (ES) using an LTQ-FIT mass spectrometer (Thermo Fisher Scientific). The spectra were recorded at the University of Manchester Metropolitan, UK. The spectral data were recorded in the positive mode. NMR spectra (^1H, ^13C-NMR) were recorded in DMSO-d_6 solutions using a Brucker-400 MHz and a JEOL-400 MHz for ^1HMR and 100.61 MHz for ^13C-NMR, respectively, and TMS was used as an internal standard for ^1HMR measurement. The samples were recorded at the University of Manchester Metropolitan, UK and Isfahan University, Islamic Republic of Iran. Metals were determined using a Shimadzu atomic absorption spectrophotometer (F.A.A) 680G. Chloride was determined using a 686-titro processor-665 Dosimat-Metrohm Swiss. in Ibn Sina Company, Ministry of Industry Baghdad, Iraq. Conductivity measurements were made with DMSO solutions using a Eutech Instruments Co, 150 digital conductivity meter, and magnetic moments were determined at 298 k with a Sherwood Scientific magnetic susceptibility balance. Thermal analyses were performed under an argon atmosphere on an STA PT-1000 Linseis company /Germany with a heating rate of 10 °C/min at College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad. The evaluation of ligands and their metal complexes against four bacterial strains (Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus and Bacillus subtilis) and four fungi species (Candida albicans, Candida glabrata, Candida tropicalis and Candida parapsilosis) were performed using agar-well diffusion. The results were recorded at College of Science, Baghdad University and at College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad.

2.3. Synthesis

2.3.1. Preparation of precursors (M_1, M_2, A_1 and A_2)

The preparation of M_1 and M_2 was performed according to a published method [10,11] and the preparation of A_1 and A_2 was achieved using a reported method [12].

2.3.1.1. Preparation of (1R,2R,4R,5S)-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-one (M_1)
A solution of benzaldehyde (1.33ml, 13mmol), ammonium acetate (0.5g, 6.500mmol) and cyclohexanone (0.674ml, 6.500mmol) [2:1:1] in ethanol (20ml) was mixed together. The reaction mixture was allowed heating between 30-40 °C for 6h, during which time a yellow solid was formed. However, upon using MeOH medium for 4h reflux the reaction yielded an identical compound. The solid was collected by filtration, washed with ethanol (5ml), and diethyl ether (10ml) and then dried under vacuum. Yield: 1.26g (93%), m.p = 108-110 °C. FT-IR data (cm⁻¹), 3313 ν(N–H), 3032 ν(C–H)arom, 2920 and 2850 ν(C–H)arom, 1716 ν(C=O), 1581 and 1558 ν(C=O), 1492 ν(N–H). NMR data (ppm), 1H (400 MHz, DMSO-d₆): δH = 1.60 (2H, m, C1₀-H); 1.76 (4H, quar, 3.6 Hz, C7,7`-H); 2.80 (2H, t, JHH = 4.8 Hz, C7,7`-H); 7.80 ppm (1H, s, N-H); 7.02 and 7.11 (C1₁,₁`-H; 2H, t, JHH = 5.2 Hz) and (C2₂,₂`, 6,6`-H); 4H, t, JHH = 5.2 Hz), respectively; 7.43 ppm (4H, d, JH_H = 6 Hz, C7,7`–H) was assigned to (C3,3`, 5,5`-H); 13C NMR (100.63 MHz, DMSO-d₆): δC = 22.89 (C1₀), 25.61 (C₉,₉`), 55.69 (C₇,₇`), 58.93 (C₈,₈`), 124.09 (C₁₁), 131.08 (C₂₂`,₂`, 6,6`) and (C₃,₃`, 5,5`), 139.37 (C₄,₄`), 203.40 (C=O). The electrospray (+) mass spectrum of M₁ shows no molecular ion peak for M₁. Peak detected at m/z = 266.2844 amu assigned to [M-(C₂H₂)+H]+ for C₁₈H₂₀NO, requires = 266.1539. The other peaks detected at m/z = 240.2844, 174.1106 and 107.0409 were assigned to [(M - C₂H₂+C₂)₊]+, [(M - C₂H+C₂+C₆H)₊]+ and [(M - C₂H+C₂ + (CH₃CH₂CH₃))₊].

2.3.1.2. Preparation of (1R,2R,4R,5S)-(1R,2R,4R,5S)-(1R,2R,4R,5S)-(1R,2R,4R,5S)-2,4-di-p-tolyl-3-azabicyclo[3.3.1]nonan-9-one (M₂)

The method used to prepare M₂ was analogous to the starting material M₁, but with the use of 4-methylbenzaldehyde instead of benzaldehyde. The amounts of other reagents used were adjusted accordingly, and a similar workup procedure was used to give compound M₂ as a pale-yellow solid. Yield: 1.53g (54 %), m.p = 168-170 ºC. FT-IR data (cm⁻¹), 3298 ν(N–H), 3020 ν(C–H)arom, 2858 and 2927 ν(C–H)arom, 1715 ν(C=O), 1577 and 1550 ν(C=O), 1512 ν(N–H). NMR data (ppm), 1H (400 MHz, DMSO-d₆): δH = 1.57 (2H, m, C1₀-H); 1.67 (4H, m, C₉,₉`-H); 1.77 and 1.79 (2H, d, JH_H = 6 Hz, C₈,₈`-H); 2.71 (2H, t, JHH = 5.6 Hz, C₇,₇`-H); 2.91 ppm (6H, s, 2CH₃); 4.36 (1H, s, JHH = 6 Hz, C₆,₆`-H); 7.38 (4H, d, JH_H = 7.2 Hz, (C₂₂,₂`, 6,6`-H); and 2.93 ppm (4H, d, JH_H = 7.2 Hz, C₃,₃`, 5,5`-H). 13C NMR (100.63 MHz, DMSO-d₆): δC = 23.75 (C₁₀); 25.98 (C₉,₉`); 44.61 (C methyl); 56.19 (C₈,₈`); 58.79 (C₇,₇`); 124.93 (C₂₂`,₂`, 6,6`); 126.71 (C₂₁`,₂`, 6,6`); 135.61(C₁₁); 138.93 (C₄,₄`); and 209.69 (C=O). The electrospray (+) mass spectrum of M₂ shows the molecular ion peak for M₂ at m/z = 319.0421 amu for C₂₂H₂₅NO, requires = 315.1936. Peaks recorded at m/z = 275.1434 and 151.4732 amu attributed to [M - (CH₃CH₂CH₃)+(C₁₀H)]₊ and [M-(CH₃CH₂)(CH₃)₊] respectively.

2.3.1.3. Preparation of 2-(((1R,2R,4R,5S)-2,4-di-p-tolyl-3-azabicyclo[3.3.1]nonan-9-one (M₃) (A₁)

A solution of ethylenediamine (0.160g, 2.663mmol) dissolved in ethanol (20ml) was added to a mixture of M₁ (0.8g, 2.747mmol) in ethanol (20ml). The reaction mixture was treated with 2ml of concentration hydrochloric acid, and then allowed to reflux for 6h. The reaction mixture was left for a slow evaporation and yellow crystals were obtained that were isolated by filtration, washed with cold ethanol (5ml) and diethyl ether (10ml) and then dried under vacuum. Yield: 0.104g (65%), m.p = 194-196 °C. FT-IR data (cm⁻¹), 3319 ν(N–H), 1639 ν(C=N), 1504 δ(N–H), 119 ν(C–N). NMR data (ppm), 1H NMR (400 MHz, DMSO-d₆): δH = 1.24 (6H, m, C₉,₉` and C₁₀-H); 1.75 (2H, m, C₁₂-H); 2.28-2.41 (5H, m, C₈,₈`-C₁₁-H and N-H); 3.16 (2H, d, JH_H = 7.6 Hz, C₇,₇`-H); 7.25 (C₁₁,₁`-H; 2H, t, JHH = 4.4 Hz); 7.35 (C₂₂,₂`, 6,6`-H); 4H, t, JHH = 4.4 Hz); 7.46 (4H, dd, JH_H = 3.6 and 7.3 Hz) (C₃,₃`, 5,5`-H); 13C NMR (100.63 MHz, DMSO-d₆): δC = 23.80 (C₀,₀`); 27.83 (C₁₀); 28.80 (C₈,₈`); 35.39(C₇,₇`); 46.82 (C₁₂); 49.44(C₁₁); 122.35 (C₁₁); 127.08 (C₁₂); 127.24 (C₆,₆`); 142.49 (C₄,₄`); 152.49 (C=O). The electrospray (+) mass spectrum of A₁ revealed a peak at m/z = 331.1042 amu assigned to (M)₊ for C₂₂H₂₅N₃, requires = 330.2205 and the following fragments at 304.1548 and 264.1742 amu were related to [M-CH₃N]₊ and [M-(CH₃N+(CH₃)₃)]₊, respectively.

2.3.1.4 Preparation of 2-(((1R,2R,4R,5S)-2,4-di-p-tolyl-3-azabicyclo[3.3.1]nonan-9-one (M₃) (A₂)
An analogous method for the isolation of precursor $A_1$ was used to prepare $A_2$, but $M_2$ was used in place of $M_1$ and other reagents were adjusted accordingly. A yellow solid was obtained, yield = 0.2155g (75%), m.p. = 113-115°C. FT-IR data (cm$^{-1}$), 3421 v(N–H), 1658 v(C=O), 1508 δ(N–H), 1511 v(C–N). NMR data (ppm), $^1H$ NMR (400 MHz, DMSO-d$_6$): $\delta_{H}$ = 1.18 (6H, m, C$_9$, C$_{10}$), C$_{10}$-H); 1.55 (2H, m, C$_{9}$, C$_{10}$-H) and N-H; 3.10 (2H, t, J$_{H, H}$ = 5.2 Hz, C$_{7}$, C$_{7}$-H); 3.76 (6H, s, 2 x CH$_3$); = 7.02 (4H, d, J$_{H, H}$ = 7.6 Hz, C$_{2}$, C$_{2}$, C$_{6}$, C$_{6}$-H); 7.70 (4H, d, J$_{H, H}$ = 7.6 Hz, C$_{3}$, C$_{3}$, C$_{5}$, C$_{5}$-H). $^13C$ NMR (100.63 MHz, DMSO-d$_6$): $\delta_{C}$ = 21.82 (C$_{methyl}$); 22.02 (C$_{9}$, C$_{9}$); 24.50 (C$_{10}$); 29.84 (C$_{8}$, C$_{8}$); 39.28 (C$_{7}$, C$_{7}$); 43.41 (C$_{12}$); 51.36 (C$_{11}$); 124.58 (C$_{2}$, C$_{2}$, C$_{6}$, C$_{6}$); 126.43 (C$_{3}$, C$_{3}$, C$_{5}$, C$_{5}$); 134.34 (C$_{1}$, C$_{1}$); 137.75 (C$_{3}$, C$_{3}$); 153.39 (C=N).

2.3.2. Synthesis of ligands ($H_2L_1$ and $H_2L_2$)

2.3.2.1. Synthesis of $N$-((1R,2R,4R,5S,Z)-2,4-di-p-tolyl-3-azabicyclo[3.3.1]nonan-9-ylidene)amino)ethyl)-2-((2-mercaptoethyl)thio)acetamide ($H_2L_1$)

A mixture of 1,4-dithian-2-one (0.080g, 0.597mmol) in CHCl$_3$ (10ml) was added dropwise, under N$_2$ atmosphere, to a mixture of precursor $A_1$ (0.233g, 0.699mmol) in CHCl$_3$ (10ml). The reaction mixture was stirred under nitrogen atmosphere for 3h. A white solid that formed was collected by filtration, washed with diethylether (10ml) and then allowed to dry under vacuum. Yield: 0.2155g (75 %), m.p. = 113-115°C. FT-IR data (cm$^{-1}$), 3398 ν(C=O), 2921 ν(C-H), 1682 ν(C=O), 1542 ν(N–H) and ν(C–H), 1464 ν(C–H), 1371 ν(C–H), 1265 ν(C–S), 1195 ν(C–O–S) and ν(C–O–N), 1105 ν(C–O–C). NMR spectra (ppm), $^1H$ NMR (400 MHz, DMSO-d$_6$), Figure 1; $^13C$ (100 MHz, DMSO-d$_6$), Figure 2; δ = 24.49 (C$_{10}$); 25.52 (C$_{10}$); 28.80 (C$_{8}$); 32.56 (C$_{13}$); 41.18 (C$_{13}$); 46.42 (C$_{13}$); 48.13 (C$_{13}$); 56.79 (C$_{11}$); 60.97 (C$_{7}$, C$_{7}$); 125.10(C$_{1}$, C$_{1}$); 126.43 (C$_{3}$, C$_{3}$, C$_{5}$, C$_{5}$); 134.34 (C$_{1}$, C$_{1}$); 137.75 (C$_{3}$, C$_{3}$); 153.39 (C=N).

2.3.2.2. Synthesis of N-((1R,2R,4R,5S,Z)-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-ylidene)amino)ethyl)-2-((2-mercaptoethyl)thio)acetamide ($H_2L_2$)

The method adopted to prepare $H_2L_2$ was similar to that for $H_2L_1$, but with precursor $A_2$ instead of $A_1$. Other reaction reagents were adjusted accordingly and an analogues workup procedure that implemented resulted in the isolation of the required ligand. Yield: 0.2155g (75 %), m.p. = 320-322°C. IR data (cm$^{-1}$), 3398 ν(N–H), 1674 ν(C=O), 1616 ν(C–N), 2619 ν(S-H), 1577 and 1523 ν(C=O)$_{amide}$, 1323 ν(C–N), 1033 and 9254 ν(C–S). NMR data (ppm), $^1H$ NMR (400 MHz, DMSO-d$_6$), see Figure 1; $^13C$ (100 MHz, DMSO-d$_6$), Figure 2; δ = 24.49 (C$_{10}$); 25.52 (C$_{10}$); 28.80 (C$_{8}$); 32.56 (C$_{13}$); 41.18 (C$_{13}$); 46.42 (C$_{13}$); 48.13 (C$_{13}$); 56.79 (C$_{11}$); 60.97 (C$_{7}$, C$_{7}$); 125.10(C$_{1}$, C$_{1}$); 126.43 (C$_{3}$, C$_{3}$, C$_{5}$, C$_{5}$); 134.34 (C$_{1}$, C$_{1}$); 137.75 (C$_{3}$, C$_{3}$); 153.39 (C=N);

Table 1.

| Precursor | Colour | Yield | Melting Point |
|-----------|--------|-------|---------------|
| A1        |        |       |               |
| A2        |        |       |               |

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Figure 1. $^1$HNMR spectra of H$_2$L$^1$ and H$_2$L$^2$ in DMSO-d$_6$. 
Figure 2. $^{13}$CNMR spectra of ligands $\text{H}_2\text{L}^1$ and $\text{H}_2\text{L}^2$ in DMSO-$d_6$.

Table 1. Microanalyses data and physical properties for precursors and ligands.

| Comp. | Empirical formula | M. wt g/mol | Yield (%) | m.p. ºC | Colour   | Found/(Calc.)/% | C | H | N | S |
|-------|------------------|-------------|-----------|--------|----------|------------------|---|---|---|---|
| $\text{M}_1$ | $\text{C}_{26}\text{H}_{33}\text{NO}_2$ | 467.68 | 70 | 312-315 | White | 66.22 (66.77) | 7.75 (7.11) | 8.44 (8.98) | 13.48 |
| $\text{H}_2\text{L}^1$ | $\text{C}_{26}\text{H}_{33}\text{N}_2\text{O}$ | 495.74 | 75 | 320-322 | White | 67.11 (67.84) | 7.95 (7.52) | 8.27 (8.48) | 12.11 |
| $\text{H}_2\text{L}^2$ | $\text{C}_{26}\text{H}_{33}\text{N}_2\text{O}_2$ | 523.78 | 50 | 325-328 | White | 68.04 (68.67) | 7.75 (7.29) | 8.27 (8.89) | 12.11 |
2.3.3. Synthesis of the complexes with $\text{H}_2\text{L}^1$ and $\text{H}_2\text{L}^2$

A mixture of the title ligand (0.1g, 0.180mmol) in 20ml of a mixture solution of ethanol:chloroform 1:1 and potassium hydroxide (0.03g, 0.541mmol) in ethanol (5ml) was stirred for 10 min. To the above mixture was added dropwise an ethanol solution (10ml) of the metal chloride (0.043g, 0.180mmol). The resulting mixture was refluxed under N$_2$ atmosphere for 3h. A solid that formed was filtered, washed by ethanol and diethyl ether, and dried under vacuum. Elemental analysis data, colours, and yields for the ligands and their complexes are given in Table (2).

2.4. Determination of biological activity

The evaluation of compounds (ligands and complexes) against four bacterial strains (Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus and Bacillus) and four fungi species (Candida albicans, Candida glabrata, Candida tropicalis and Candida parapsilis) were performed using agar-well diffusion. In this method, the wells were dug in the media with the help of a sterile metallic borer with centres at least 6 mm. A 100 µl concentration of the title specimen 1 mg/mL in DMSO was placed in the individual wells ($^*$). The Petri dishes were incubated in the incubator for 24h at 37 ºC. The biological activity was observed by measuring the diameter of inhibition zones (mm).

Table 2. Elemental analyses, some physical properties, yields and colours of ($\text{H}_2\text{L}^1$ –$\text{H}_2\text{L}^2$) complexes.

| Chemical Formula          | M.wt g/mol | Yield (%) | Colour | m.p. °C | $\mu_{\text{eff}}$ per one atom | C   | H   | N    | S    | M   | Cl  | 659.7  |
|---------------------------|------------|-----------|--------|--------|-------------------------------|-----|-----|------|------|-----|-----| -------|
| K$_2$[Mn(L$^1$)]Cl$_2$    | 673.7      | 40        | Brown  | 295°   | 4.96                          | 46.3 | 46.0| 9.73 | 9.87 | 8.30| 10.0| 58.69 |
| K$_2$[Co(L$^1$)]Cl$_2$    | 673.4      | 62        | Pale-blue | 285°   | 3.83                          | 46.8 | 46.3| 9.73 | 9.71 | 8.97| 10.7| 58.30 |
| K$_2$[Ni(L$^1$)]Cl$_2$    | 670.7      | 42        | Brown  | 275°   | 1.79                          | 48.6 | 48.5| 9.43 | 9.43 | 7.48| 10.4| 54.30 |
| K$_2$[Co(L$^2$)]Cl$_2$    | 701.7      | 71        | Green-blue | 280°   | 4.90                          | 47.6 | 47.8| 9.30 | 8.82 | 9.89| 10.1| 63.70 |
| K$_2$[Ni(L$^2$)]Cl$_2$    | 701.5      | 85        | Pale-blue | 290°   | 3.31                          | 47.3 | 47.8| 9.31 | 8.90 | 9.89| 10.2| 63.70 |
| [Cu(HL$^2$)]Cl           | 558.2      | 41        | Blue   | 310°   | 1.69                          | 60.5 | 60.1| 11.72| 11.72| 6.16| 6.34| 558.2  |
Results and discussion

Ligands were prepared from the reaction of amine precursors with 1,4-dithian-2-one. The preparation of the precursors was achieved into two steps; the first step includes Mannich-reaction of benzaldehyde or its derivative with ammonium acetate and cyclohexanone in the presence of ethanol to isolate precursors M1 and M2. The second step focused on the reaction of precursors with ethylenediamine to obtain amine compounds A1 and A2. The ligands were synthesised from the reaction of 1,4-dithian-2-one and amine precursors in the presence of triethylamine as a base in CHCl3 medium, which gave the title ligands (H2L1 and H2L2), see Scheme (1). Elemental analysis Table 1, FT-IR (Table 3), NMR (1H- and 13C-NMR) and mass spectra were implemented to determine the entity of compounds (precursors and ligands).

Complexes of the ligands with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions were synthesised by heating 1 mmole of each ligand with 1 mmole of metal chloride using a mixture of ethanol/chloroform medium at reflux using KOH as a base. In the ethanol/chloroform solution of KOH, the deprotonation of the ligands is occurred that facilitated the formation of K2[Co(HLn)Cl2], K2[Mn(HLn)Cl2], K2[Ni(HLn)Cl2], [Cu(HLn)], [Zn(HLn)] and [Cd(HLn)] (M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II), Ln = L1 or L2), Scheme 2. The complexes are air-stable and soluble in DMSO (bar other organic solvents). Elemental analysis and other physical properties of the complexes are placed in Table 4. Physico-chemical data agree well with the proposed formulas. The prominent infrared peaks and their assignments for the ligands and complexes are included in Table 3. The electronic data (UV-Vis) with their assignments for ligands and complexes are placed in Table 4.
Scheme 2. General synthetic route of (H$_2$L$_1$ and H$_2$L$_2$) complexes.

3.1. FT-IR and NMR spectra

The FT-IR spectra of free ligands display bands due to $\nu$(C=O)$_{amide}$, $\nu$(C=N)$_{imine}$ and $\nu$(C-N)$_{groups}$. The distinct frequency around 2555-2619 cm$^{-1}$ related to $\nu$(S–H)$_{},$ confirms the presence of the ligands in the thiol form [14]. The FT-IR spectra of the complexes exhibited H$_2$L$_1$ and H$_2$L$_2$ bands with the proper shifts due to complex formation (Table 3). Band assigned to $\nu$(S–H) in the free ligands was disappeared in the spectra of complexes, due to the involvement of sulfur atom, as a thiolate moiety, in complex formation. The $\nu$(C=O)$_{amide}$ and $\nu$(C=N)$_{imine}$ at ca. 1662, 1674 cm$^{-1}$ and at ca. 1604-1616 cm$^{-1}$ in the free ligands were recorded at lower frequencies, indicated a reduced bond order, and observed around 1631-1651; 1600 and 1639-1651; 1600 cm$^{-1}$ for H$_2$L$_1$ and H$_2$L$_2$ complexes, respectively. This shift confirmed the involvement of the N atoms of these moieties in the coordination to the metal centre. Bands detected around 1056-1029; 898-855 cm$^{-1}$ and 1083-1033; 898-855 cm$^{-1}$ were attributed to $\nu$(C–S) for complexes of H$_2$L$_1$ and H$_2$L$_2$, respectively indicating the involvement of sulfur atoms upon coordination to metal centre [15]. At lower frequency, the complexes exhibited bands around 416-493 and 333-383 cm$^{-1}$ attributed to $\nu$(M–N) and $\nu$(M–S), respectively. Bands observed around 244-262 and 243-277 cm$^{-1}$ in the spectra of K$_2$[Mn(L$_1$)$_2$Cl$_2$], K$_2$[Co(L$_1$)$_2$Cl$_2$], K$_2$[Mn(L$_2$)$_2$Cl$_2$] and K$_2$[Ni(L$_2$)$_2$Cl$_2$] are related to $\nu$(M–Cl) [16]. The appearance of two bands indicated the coordination of the Cl atoms in the cis conformation.

| Compound | $\nu$(N-H)$_{amide}$ cm$^{-1}$ | $\nu$(C=O)$_{amide}$ cm$^{-1}$ | $\nu$(C=O)$_{imine}$ cm$^{-1}$ | $\nu$(C–N)$_{arom}$ cm$^{-1}$ | $\nu$(C–N)$_{arom}$ cm$^{-1}$ | $\nu$(M–N)$_{coordination}$ cm$^{-1}$ | $\nu$(M–S)$_{coordination}$ cm$^{-1}$ | $\nu$(M–Cl)$_{coordination}$ cm$^{-1}$ |
|----------|-------------------------|-------------------------------|-----------------------------|-------------------------------|-------------------------------|---------------------------------|---------------------------------|--------------------------------|
| H$_2$L$_1$ | 3417                   | 1662                          | 1604                        | 1531                          | 1323                          | 1056                             | -                               | -                              |

**Table 3.** Infrared spectral data (wavenumber, $\nu$ cm$^{-1}$) of (H$_2$L$_1$ and H$_2$L$_2$) and their complexes
The $^1$H and $^{13}$C NMR spectra of ligands revealed peaks related to the various proton and carbon nuclei consistent with the proposed structural formula. The $^1$H NMR spectrum of [Cd(L$^1$)] Figure 3; in DMSO-d$_6$ solution indicated two characteristic sets of chemical shifts in the aliphatic and aromatic regions. In the aromatic region, the spectrum indicated signals at: 7.57 ppm (4H, d, $J_{HH} = 4$ Hz, H$_3$,3$'$; 5,5$'$); 7.17 (4H, t, $J_{HH} = 8$ Hz, H$_2$,2$'$; 6,6$'$); 7.02 ppm (2H, t, $J_{HH} = 8$ Hz, H$_1$,1$'$). The aliphatic region shows chemical shifts at: 3.99 (2H, s, H 13); 3.41 (2H, t, H 12, $J_{HH} = 8$ Hz); 2.68 (2H, s, H 7,7); 2.34 (2H, t, H 15); 1.60 (9H, m, H 8,8$'$, H9,9$'$, H11 and N-H); 1.14 (2H, t, H 14, $J_{HH} = 8$ Hz); 1.01 (2H, m, H10). The spectrum indicated no signals may attribute to N-H of the amide groups and S-H of thiol, confirming the involvement of these moieties in complexation, and making the ligand behaves as -2 species upon complexation. 22.61 (C10); 23.50 (C9,9$'$); 28.36 (C8,8$'$) 29.61 (C15); 38.07 (C14); 39.81 (C13); 41.10 (C12) 44.27 (C11); 67.52 (C1,1$'$); 128.27 (C3,3$'$); 128.60 (C2,2$'$, 6,6$'$); 131.63 (C4,4$'$; 137.43 (C4$'$); 167.06 (C=N); 188.12 (C=O). The $^{13}$C-NMR spectrum of [Cd(L$^2$)] displayed signals at: 22.30 (Cmethyl); 23.80 (C 9,9$'$); 28.24 (C 8,8$'$); 34.49 (C15); 43.95 (C 7,7$'$); 50.28 (C14); 55.42 (C13) and (C 12); 55.76 (C 11); 128.21 (C2,2$'$, 6,6$'$); (C3,3$'$, 5,5$'$) 132.55; 134.45 (C 4,4$'$; 135.17 (C 1,1$'$); 159.76 (C=N); (C=O) 188.87 ppm. The chemical shift for the imine and amide groups by ca. 10-13 and 11-13 ppm, respectively in comparison with that in the free ligand confirmed the involvement of the nitrogen atoms of the imine and amide groups in complexation. This shift is related to the deshielding occurred to these moieties by the Cd(II) centre upon complexation.
3.2. Mass spectra

The obtained mass spectra of the ligands agreed with the suggested structural formula (see experimental section and ‘Figure 4’).

The accurate electrospray (+) mass spectrum of K₂[Ni(L¹)Cl₂] Figure 5; indicated a peak at m/z = 671.4532 amu, requires = 670.9913 corresponding to (M)⁺. The successive fragments at 487.3041, 374.2201, 261.1360 and 160.8402 were assigned to [M-(C₆H₅S)+(C₄H₂S)]⁺,[M-(C₆H₅S)+(C₄H₂S)+(CHCl₂NO)]⁺, [M-(HCN)+(2HCl)+(2C₄H₈S₂)+(HCN)+(C₆H₄O)+(C₅H₂C₅H₆S)+(C₄H₂S)+(CHCl₂NO)+(HCN)+(C₇H₂)]⁺ and [M- (C₅H₆S)+(C₄H₂S)+(CHCl₂NO)+(HCN)+(C₈H₃N)+(C₆H₁₃N)]⁺, respectively.
3.3. Electronic spectra, magnetic moments, and conductivity measurements

The electronic data of H$_2$L$^1$ and H$_2$L$^2$ display absorption peak at 260, 265 and 345, 360 nm, respectively related to overlaps of $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The spectra of H$_2$L$^1$ complexes showed hypsochromic shift peaks correlated to the ligand field transitions ($\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$) [17-19], bar Cu(II) complex that exhibited a bathochromic shift. The electronic spectrum of Mn(II) complex revealed peaks in the d-d region at 441 and 762 nm assigned to $^6$A$_{1g}(F) \rightarrow ^4$T$_{2g}(G)$ and $^6$A$_{1g} \rightarrow ^4$T$_{2g}(G)$ transitions, respectively indicating a distorted octahedral geometry about Mn(II) ion [20-21]. These data with the magnetic moment value confirmed an octahedral geometry around the Mn(II) atom. The Co(II) complex displays more peaks in the d-d region at 413, 537 and 674 nm due to $^2$E$_{g} \rightarrow ^2$T$_{2g}$ or $^2$T$_{2g} \rightarrow ^2$T$_{1g}^{(F)}$ and $^4$T$_{2g}^{(F)} \rightarrow ^4$A$_{2g}^{(F)}$, respectively. This spectrum is characteristic for Co(II) complexes with distorted octahedral geometries around Co atom [22-24]. The $\mu_{eff}$ value for this complex is included at the range of octahedral confirming octahedral geometry about metal centre. The Ni(II) complex showed peaks at 417, 610 and 681 nm related to $^3$A$_{2g} \rightarrow ^3$T$_{1g}^{(P)}$, $^3$A$_{2g} \rightarrow ^3$T$_{1g}^{(p)}$ and $^3$A$_{2g} \rightarrow ^3$T$_{1g}^{(F)}$ transitions, respectively confirmed a distorted octahedral geometry around Ni atom [16]. The paramagnetic behaviour of the Ni(II) complex suggested a distorted octahedral geometry. The Cu(II) complex displayed a peak in the d-d region at 828 nm attributed to d-d transition attributed to $^2$B$_{1g} \rightarrow ^2$A$_{2g}$, confirming a distorted square planar arrangement about Cu atom [25-27]. The proposed distorted square planar arrangement for the pale-green Cu(II) complex is supported by its magnetic measurement value and other analytical data. The spectra of the Zn(II) and Cd(II) complexes revealed peaks related to ligand field ($\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$). These, diamagnetic complexes (d$^{10}$ system) normally prefer tetrahedral structures. The conductance values of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes were in the range of 13.1-76.99 $\Omega^{-1}$cm$^{-2}$mol$^{-1}$ indicating 2:1 electrolytic behaviour of the Mn(II), Co(II) and Ni(II), while those of the Cu(II), Zn(II) and Cd(II) complexes were indicating nonelectrolytes [27-28].
and other analytical data. The spectra of the Zn(II) and Cd(II) compounds indicated peaks attributed to ligand field (π→π* and n→π*). These diamagnetic complexes (d^0 system) normally prefer tetrahedral structures. The molar conductance values of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes were in the range of 7.07-78.21 Ω^−1cm^mol^−1 indicating 2:1 electrolytic behaviour of the Mn(II), Co(II) and Ni(II), while those of the Cu(II), Zn(II) and Cd(II) complexes were indicating nonelectrolytes, except Cu(II) complex that indicated a 1:1 electrolytic behaviour [27-28].

Table 4. Electronic spectral data of (H₂L¹⁻, H₂L²⁻) complexes in DMSO solutions.

| Comp. | Band Position | Wavenumber (cm⁻¹) | Extinction coefficient (εmax/cm² mol⁻¹) | Assignment | M(Ω⁻¹cm²mol⁻¹) | Suggested geometry |
|-------|---------------|-------------------|---------------------------------------|------------|----------------|-------------------|
| H₂L¹⁻| 285           | 35087             | 2197                                  | π→π        |                |                   |
|       | 360           | 27777             | 545                                   | n→π*       |                |                   |
| K₂[Mn(L¹)Cl] | 275           | 36363             | 1146                                  | π→π*       | 75.08          | Distorted         |
|       | 345           | 28985             | 33                                    | n→π*       |                | Octahedral        |
|       | 441           | 22675             | 32                                    | 6A₁g→T₂g(G) |                |                   |
|       | 762           | 13123             | 20                                    | 6A₁g→T₂g    |                |                   |
| K₂[Co(L¹)Cl] | 269           | 37174             | 1724                                  | π→π*       | 76.99          | Distorted         |
|       | 350           | 28571             | 70                                    | n→π*       |                | Octahedral        |
|       | 413           | 24213             | 72                                    | 4T₁g(P)→A₁g(F) |                |                   |
|       | 537           | 18621             | 71                                    | 4T₁g(P)→A₁g(F) |                |                   |
|       | 674           | 14836             | 51                                    | 4T₁g(P)→A₁g(F) |                |                   |
| K₂[Ni(L¹)Cl] | 265           | 37735             | 1033                                  | π→π*       | 74.65          | Distorted         |
|       | 350           | 28571             | 36                                    | n→π*       |                | Octahedral        |
|       | 417           | 23980             | 126                                   | 3A₁g→T₁g(P) |                |                   |
|       | 610           | 16393             | 120                                   | 3A₁g→T₁g(F) |                |                   |
|       | 681           | 14684             | 206                                   | 3A₁g→T₁g(F) |                |                   |
| [Cu(L¹)] | 290           | 34482             | 2312                                  | π→π*       | 16.77          | Distorted         |
|       | 828           | 12077             | 78                                    | 2B₁g→2A₁g  |                | Square Planar     |
| [Zn(L¹)] | 264           | 37878             | 646                                   | π→π*       | 14.11          | Distorted         |
|       | 350           | 28571             | 48                                    | n→π*       |                | Tetrahedral       |
| [Cd(L¹)] | 270           | 37037             | 1484                                  | π→π*       | 13.1           | Distorted         |
|       | 341           | 29325             | 53                                    | n→π*       |                | Tetrahedral       |
| H₂L²⁻| 265           | 37735             | 1254                                  | π→π*       |                |                   |
|       | 345           | 28985             | 45                                    | n→π*       |                |                   |
| K₂[Mn(L²)Cl] | 268           | 37313             | 1696                                  | π→π*       | 78.21          | Distorted         |
|       | 350           | 28571             | 300                                   | n→π*       |                | Octahedral        |
|       | 434           | 23041             | 308                                   | 6A₁g→T₂g(G) |                |                   |
|       | 639           | 15649             | 25                                    | 6A₁g→T₂g(G) |                |                   |
| K₂[Co(L²)Cl] | 270           | 37037             | 1957                                  | π→π*       | 76.01          | Distorted         |
|       | 438           | 22831             | 123                                   | 4T₁g(P)→2A₁g(F) |                |                   |
|       | 680           | 14705             | 102                                   | 4T₁g(P)→2A₁g(F) |                |                   |
| K₂[Ni(L²)Cl] | 268           | 37313             | 1684                                  | π→π*       | 74.54          | Distorted         |
|       | 350           | 28571             | 195                                   | n→π*       |                | Octahedral        |
|       | 641           | 15600             | 188                                   | 3A₁g→T₁g(F) |                |                   |
| [Cu(HL²)]Cl | 266           | 37594             | 1469                                  | π→π*       | 32.27          | Distorted         |
|       | 300           | 33333             | 45                                    | n→π*       |                | Square Planar     |
|       | 794           | 12594             | 36                                    | 2B₂g→2B₁g  |                |                   |
| [Zn(L²)] | 267           | 37453             | 1600                                  | π→π*       | 13.77          | Distorted         |
|       | 350           | 28571             | 75                                    | n→π*       |                | Tetrahedral       |
| [Cd(L²)] | 269           | 37174             | 1832                                  | π→π*       | 7.07           | Distorted         |
|       | 350           | 28571             | 85                                    | n→π*       |                | Tetrahedral       |

3.4. Thermal gravimetric analysis

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This technique was implemented to study the thermal properties of compounds (stability and chemical composition of ligands and some complexes). TGA analysis supported the determination of the melting points of compounds and identifying their decomposition steps, see Table (5). The TGA peak of the ligand Figure 6; observed at 399.9 °C indicated the loss of (C9H7N2) fragment, (det. = 12.364 mg, 60.904 %; calc. = 12.357 mg). The other step occurred at 521.8 °C revealed the loss of (C5H6NO) portion, (det. = 1.941 mg, 9.562 %; calc. = 1.921 mg). The third step of the decomposition of the compound at 593.3 °C is linked to the evolving of (C7H4) segment, (obs. = 1.956 mg, 9.633 %; calc. = 1.958 mg). The remaining deposit of the compound above 598.0 °C is associated with the loss of (C10H10S), (obs. = 4.040 mg, 19.901 %; calc. = 3.668 mg). The differences in the weight may be related to a sublimation process that occurred at high temperature. The DSC curve recorded peaks at 317.1, 337.0, 524.1 and 593.3 °C, which refer to an endothermic decomposition process. While the peak at 344.0 °C was referred to an exothermic decomposition process. The exothermic and endothermic peaks may specify combustion of the organic ligand in an argon environment [29-30]. The thermogram for K2[Co(L1)Cl2] Figure 7; which confirmed the Co(II) complex is stable up to 285.0 °C. In the TGA curve, peak detected at 408.6 °C is related to the loss of (CnHm, CnHnNO and 2HCl) segments, (det. = 9.954 mg, 54.997 %; calc. = 9.941 mg). The second step at 594.0 °C that indicated the loss of (2C) fragment, (obs. = 0.619 mg, 3.429 %; calc. = 0.646 mg). The final residue of the compound that recorded above 598.0 °C is correlated to the (Co, 2K, N2, 2H2S, CH4 and C2H6), (det. = 7.534 41.573 %; calc. = 7.512 mg). The DSC curve indicated peaks at 283.0, 325.4, 353.6, 419.2 and 594.0 °C correlated to an endothermic decomposition process. The endothermic peaks may show combustion of the organic ligand in the inert atmosphere [29-30]. The last endothermic peak may indicate the braking of the metal-ligand bond. The thermogram for [Cu(L1)] Figure 8; which shows the Cu(II) complex is stable up to 220.0 °C. The TGA peak at 259.9 °C indicated the loss of (C20H22N2) fragment, (det. = 12.364 mg, 60.904 %; calc. = 12.357 mg). The final residue of the compound at 598.0 °C is assigned to the (Cu, HCN and Co, 2K, N2, 2H2S, CH4 and C2H6), (det. = 7.534 41.573 %; calc. = 7.512 mg). The DSC curve indicated peaks at 283.0, 325.4, 353.6, 419.2 and 594.0 °C correlated to an endothermic decomposition process. The endothermic peaks may show combustion of the organic ligand in the inert atmosphere [29-30]. Peaks at 436.1 and 459.4 °C attributed to exothermic decomposition steps. The exothermic and endothermic curves may relate to the combustion of the organic ligand in the inert atmosphere [29-30]. The last endothermic peak may signify the metal-ligand bond breaking. While the thermogram for H2L2 is shown in Figure 9; The analysis chart indicated the ligand is intact up to 325.0 °C. The TGA curve measured at 336.9 °C attributed to the mass loss of (C10H8N2O) segment, (obs. = 3.845 mg, 19.612 %; calc. = 3.844 mg). The second step took place at 399.3 °C confirmed the loss of (C9H7N2, C4H6N and C4H6) portions, (obs. = 7.698 mg, 40.092 %; calc. = 7.711 mg). The third step of the decomposition of the compound is accounted for the loss of (2H2 and NH3) fragments, (obs. = 0.771 mg, 4.016 %; calc. = 0.765 mg). The final residue of the compound recorded above 598.0 °C is assigned to the (Cu, HCN and C3H7NO), (obs. = 9.896 mg, 51.543 %; calc. = 9.778 mg). The DSC curve indicated endothermic decomposition processes at temperatures 220.4, 280.4, 334.6 and 515.5 °C. Peaks at 436.1 and 459.4 °C attributed to exothermic decomposition steps. The exothermic and endothermic curves may relate to the combustion of the organic ligand in the inert atmosphere [29-30]. The thermogram for [Mn(L2)Cl2] Figure 10; that revealed the Mn(II) complex is steady up to 272.0 °C. The TGA curve observed at 399.3 °C related to the loss of (C9H7N2O) segment, (obs. = 3.845 mg, 19.612 %; calc. = 3.844 mg). The second and third steps occurred at 485.3 and 580.28 °C indicated the evolving of (HCN) compound, (obs. = 1.146 mg, 5.847 %; calc. = 1.110 mg). The final residue that observed above 598.0 °C is attributed to the elimination of (C4H6O) portion, (obs. = 1.631 mg, 8.322 %; calc. = 1.664 mg). In the DSC curve, peaks at 331.3, 363.1 and 577.5 °C indicate endothermic decomposition processes. Peaks at 535.0 and 568.8 refer to exothermic decomposition processes. The exothermic and endothermic curves may relate to the pyrolysis of the organic ligand in the inert environment [29-30]. The thermogram for K2[Ni(L2)Cl2] Figure 11; which revealed the Ni(II) complex is stable up to 288.8 °C. The TGA peak observed at 411.9 °C.
confirmed the loss of \((\text{C}_7\text{H}_11\text{N}, \text{C}_4\text{H}_8\text{S}_2\text{ and C}_8\text{H}_{10})\) segments, \((\text{obs.} = 10.070 \text{ mg, } 47.952 \% ; \text{calc.} = 10.069 \text{ mg})\). The second and third step occurred at 443.9 and 594.8 \(\degree\text{C}\) indicated the loss of \((\text{C}_3\text{H}_1\text{ and HCN})\) fragments, \((\text{det.} = 1.663 \text{ mg, } 7.919 \% ; \text{calc.} = 1.655 \text{ mg})\). The remaining residue above 598.0 \(\degree\text{C}\) related to the \((\text{NiO, 2K, Cl}_2, \text{HCN and 4C})\), \((\text{det.} = 9.267 \text{ mg, } 44.128 \% ; \text{calc.} = 8.978 \text{ mg})\). The DSC analysis shows peaks at 288.8, 347.7, 502.7 and 594.8 \(\degree\text{C}\) refer to endothermic decomposition processes. The peak at 477.0 \(\degree\text{C}\) refers to an exothermic decomposition step. The exothermic and endothermic peaks may conclude combustion of the organic compound in the inert atmosphere [29-30]. The final endothermic peak attributed to the metal-ligand bond breaking.

**Figure 6.** (TGA/DTA and DSC) thermogram of \(\text{H}_2\text{L}^1\) in an argon atmosphere.

**Figure 7.** (TGA/DTA and DSC) thermogram of \(\text{K}_2[\text{Co(L}^1\text{)}\text{Cl}_2]\) in an argon atmosphere.
Figure 8. (TGA/DTA and DSC) thermogram of [Cu(L1)] in an argon atmosphere.

Figure 9. (TGA/DTA and DSC) thermogram of ligand H2L2 in an argon atmosphere.

Figure 10. (TGA/DTA and DSC) thermogram of K2[Mn(L2)Cl2] in an argon atmosphere.
Figure 11. (TGA/DTA and DSC) thermogram of K$_2$[Ni(L$^2$)Cl$_2$] in an argon atmosphere.

Table 5. TGA/DTA/DSC data for ligands (H$_2$L$^1$-H$_2$L$^2$) and complexes.

| Compound          | Stable up to °C | Decomposition temp. °C | Nature of transformation/intermediate formed% mass found (calc.) | DTG peak temp. °C |
|-------------------|-----------------|------------------------|---------------------------------------------------------------|-----------------|
| H$_2$L$^1$        | 317.1           | 399.9                  | 12.364 (12.357)                                               | 317.1 Endo      |
|                   |                 |                        |                                                               | 337.0 Endo       |
|                   |                 |                        |                                                               | 344.0 Exo        |
|                   |                 |                        |                                                               | 593.3            |
|                   | 2               | 521.1                  | 1.941 (1.921)                                                | 524.1 Endo       |
|                   |                 |                        |                                                               | 283.0 Endo       |
|                   |                 |                        |                                                               | 594.0            |
|                   | 3               | 533.9                  | 1.956 (1.958)                                                | 325.4 Endo       |
|                   |                 |                        |                                                               | 353.6 Endo       |
|                   |                 |                        |                                                               | 419.2 Endo       |
| K$_2$[Co(L$^1$)Cl$_2$] | 285.0           | 408.6                  | 9.954 (9.941)                                                | 220.4 Endo       |
|                   |                 |                        |                                                               | 280.4 Endo       |
|                   |                 |                        |                                                               | 334.6 Endo       |
|                   |                 |                        |                                                               | 436.1 Exo        |
|                   |                 |                        |                                                               | 459.4 Exo        |
|                   | 1               | 594.0                  | 0.619 (0.646)                                                | 331.3 Endo       |
|                   |                 |                        |                                                               | 363.1            |
|                   |                 |                        |                                                               | 577.7            |
| [Cu(L$^1$)]      | 220.0           | 391.9                  | 7.698 (7.711)                                                | 272.0 Endo       |
|                   |                 |                        |                                                               | 351.8 Endo       |
|                   |                 |                        |                                                               | 418.3 Endo       |
|                   |                 |                        |                                                               | 449.2 Exo        |
|                   |                 |                        |                                                               | 504.3 Exo        |
|                   |                 |                        |                                                               | 284.8 Endo       |
|                   |                 |                        |                                                               | 325.8 Endo       |
| H$_2$L$^2$        | 325.0           | 399.3                  | 12.979 (12.985)                                              | 419.0 Endo       |
|                   |                 |                        |                                                               | 513.8            |
|                   |                 |                        |                                                               | 595.7            |
|                   | 3               | 577.7                  | 1.146 (1.110)                                                | 288.8 Endo       |
|                   |                 |                        |                                                               | 347.7 Endo       |
| K$_2$[Mn(L$^2$)Cl$_2$] | 272.0           | 393.3                  | 11.014 (11.010)                                              | 284.8            |
|                   |                 |                        |                                                               | 347.7 Endo       |
|                   | 2+3             | 485.3 and 580.2        | 0.779 (0.779)                                                | 375.8 Endo       |
|                   |                 |                        |                                                               | 449.2 Exo        |
| K$_2$[Co(L$^2$)Cl$_2$] | 284.8           | 406.2                  | 9.774 (9.784)                                                | 419.0 Endo       |
|                   |                 |                        |                                                               | 513.8            |
|                   | 2               | 595.7                  | 0.619 (0.621)                                                | 288.8 Endo       |
|                   |                 |                        |                                                               | 347.7 Endo       |
| K$_2$[Ni(L$^2$)Cl$_2$] | 288.8           | 411.9                  | 10.070 (10.069)                                              | 477.0            |
|                   |                 |                        |                                                               | 594.3            |
4. Antimicrobial activity

The compounds (ligands and complexes) were screened against four bacterial strains (*Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Bacillus*) and four fungi species (*Candida albicans*, *Candida glabrata*, *Candida tropicalis* and *Candida parapsilis*). The measured areas of inhibition against the growth of different microorganisms were listed in Tables (6 and 7). These data show the inhibition capacity of the prepared compounds on the tested bacteria and fungi species. It is found that metal complexes have antimicrobial activity against bacterial strains and fungi species. This attributed to the complexation influence that allows the participation of the inherent positive charge of the metal ion in complexes with the negative charge provided by the donor atoms of the ligand. Subsequently, the π-electron will distribute over the entire chelate ring resulting in the increases of the lipophilic character of the metal chelate system. This shall help its mobility through the cell membranes [31-32].

**Table 6.** The bacterial activity of (H$_2$L$_1$ - H$_2$L$_2$) and their complexes.

| No. | Compound          | Gram-negative (G−) | Gram-positive (G+) |
|-----|-------------------|---------------------|--------------------|
|     |                   | Escherichia coli   | Pseudomonas        | Bacillus stabulis | Staphylococcus aureus |
|     |                   | Av.    | SD±     | Av.    | SD±     | Av.     | SD±     | Av.    | SD± |
| 1   | Control           | ---    | ---     | ---    | ---     | ---     | ---     | 0      | ---  |
| 2   | H$_2$L$_1$        | 0      | 1.18    | 11.67  | 1.65    | 10      | 7.07    | 10     | 0    |
| 3   | K$_2$[Mn(L$_1$)Cl$_2$] | 14.5   | 0       | 14.33  | 0.47    | 0       | 0       | 0      | 0    |
| 4   | K$_2$[Co(L$_1$)Cl$_2$] | 19.67  | 0.24    | 12.00  | 0.71    | 4       | 5.66    | 10.33  | 0.24 |
| 5   | K$_2$[Ni(L$_1$)Cl$_2$] | 13.67  | 2.36    | 11.33  | 0.94    | 9.67    | 3.77    | 13.67  | 2.36 |
| 6   | [Cu(L$_1$)]       | 14     | 1.41    | 0      | 0       | 14.33   | 0.47    | 11.33  | 1.15 |
| 7   | [Zn(L$_1$)]       | 44.67  | 2.01    | 21.33  | 1.08    | 25      | 0       | 36.67  | 0.76 |
| 8   | [Cd(L$_1$)]       | 0      | 1.65    | 16.67  | 1.02    | 16.67   | 0       | 17     | 0.71 |
| 9   | H$_2$L$_2$        | 6.67   | 9.43    | 6.67   | 0.24    | 6.67    | 2.36    | 16.67  | 0.24 |
| 10  | K$_2$[Mn(L$_2$)Cl$_2$] | 3.67   | 2.60    | 3.67   | 0       | 4.33    | 3.06    | 0      | 0    |
| 11  | K$_2$[Co(L$_2$)Cl$_2$] | 15.67  | 2.60    | 15.67  | 0.24    | 3       | 4.24    | 9.33   | 0.47 |
| 12  | K$_2$[Ni(L$_2$)Cl$_2$] | 14.67  | 6.60    | 14.67  | 4.01    | 0       | 0       | 9      | 1.41 |
| 13  | [Cu(HL$_2$)]Cl    | 15     | 0       | 15     | 0       | 10      | 2.83    | 14     | 1.41 |
| 14  | [Zn(L$_2$)]       | 23.67  | 0.94    | 23.67  | 1.18    | 12      | 0.71    | 15.67  | 3.77 |

5. Conclusions

In the present publication, we have investigated the synthesis, structural characterisation and coordination bonding mode of metal complexes isolated from the reaction of multidentate N$_2$S$_2$ heterocyclic ligands (H$_2$L$_1$ and H$_2$L$_2$) with a range of metal ions. The coordination chemistry and overall structure of the complexes were concluded using a range of analytical and spectroscopic techniques. Further, thermal properties of the ligands and some complexes were established using TGA, DTA and DSC analyses. Biological activities revealed that the ligands and their metal complexes showed different
activity effect on both types of the Gram-positive (G+) and Gram-negative (G-) of the tested bacteria and four species of fungi.

Table 7. Fungi activity of ligands and their complexes.

| No. | Compound         | Candida albicans | Candida glabrata | Candida tropicalis | Candida parapsilosis |
|-----|------------------|------------------|------------------|-------------------|---------------------|
| 1   | Control          | 0                | 0                | 0                 | 0                   |
| 2   | $H_2L_1^1$       | 13               | 10               | 10                | 13                  |
| 3   | $K_2[Mn(L_1^1)Cl_2]$ | 0               | 14               | 10                | 10                  |
| 4   | $K_2[Co(L_1^1)Cl_2]$ | 10            | 18               | 20                |                     |
| 5   | $K_2[Ni(L_1^1)Cl_2]$ | 8              | 22               | 19                | 16                  |
| 6   | $[Cu(L_1^1)]^+$  | 0                | 14               | 11                | 15                  |
| 7   | $[Zn(L_1^1)]$    | 0                | 10               | 18                | 0                   |
| 8   | $[Cd(L_1^1)]$    | 8                | 24               | 33                | 30                  |
| 9   | $H_2L_2^1$       | 0                | 0                | 0                 | 0                   |
| 10  | $K_2[Mn(L_2^1)Cl_2]$ | 0              | 13               | 15                | 16                  |
| 11  | $K_2[Co(L_2^1)Cl_2]$ | 0              | 0                | 18                | 12                  |
| 12  | $K_2[Ni(L_2^1)Cl_2]$ | 9              | 11               | 0                 | 10                  |
| 13  | $[Cu(HL_2^1)]$   | 0                | 0                | 16                | 12                  |
| 14  | $[Zn(L_2^1)]$    | 0                | 12               | 10                | 15                  |
| 15  | $[Cd(L_2^1)]^+$  | 13               | 22               | 22                | 22                  |

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