Formation of New Macrocyclic Complexes with Bis (Dithiocarbamate) Ligand;Preparation, Structural Characterisation and Bacterial Activity

Hasan A. Hasan
Enaam I. Yousif
Dept. of Chemistry/ College of Education for Pure Science (Ibn Al-Haitham)/ University of Baghdad

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Abstract

The synthesis and characterisation of new macrocyclic binuclear metal(II) complexes derived from dithiocarbamate (DTC) ligand are reported. The reaction of a bis-secondary amine, CS_2 and KOH resulted in the formation of the free ligand. Two approaches were implemented to synthesis the macrocyclic bis(dithiocarbamate) complexes; (i) from the reaction of the free ligand with a metal ion, and (ii) *via* a one-pot reaction. In the free ligand approach, complexes were obtained by the reaction of dithiocarbamate salt with the metal ions; Co^{II}, Zn^{II} and Cd^{II}. However, the one-pot reaction is based on the mixing of the bis-secondary amine, CS_2, KOH and metal(II) chloride. Physico-chemical analyses were implemented to characterise the ligand and its complexes. These include; elemental analysis, thermal analysis, FTIR, UV-Vis, mass spectroscopy, magnetic susceptibility, conductance, melting points and ^1H, ^{13}C- NMR spectroscopy. These studies indicated the formation of binuclear macrocyclic complexes of the general formula $[M(L)]_2$ (M= Co^{II}, Zn^{II} and Cd^{II}), in which thier geometries about metal centers are tetrahedral. Antibacterial activity of the metal complexes indicated that they have more activity against investigated bacterial strains, compared to the free ligand.

Keywords: Dithiocarbamate complexes; Structural studies; Thermal properties; Bacterial activity.

1.Introduction

Dithiocarbamates (DTCs) are organic species that played a key role in the development of chemistry, in particular coordination chemistry. This is based on their strongly chelating ability towards metal ions [1,2]. Dithiocarbamates (DTCs) are capable to interact with transition metals and representative elements, which allowed them to be useful ligands in both inorganic and bioinorganic chemistry. This is based on the influence of the anionic CS_2^{-} moiety that has a variety of binding modes; monodentate, bidentate or bridging, upon complexation [3-5]. Dithiocarbamates are very interesting ligands that have the capacity to allowing the metal ion to implement its most preferable geometry in different oxidation states [6]. The development of dithiocarbamates and their complexes are due to their role in numerous applications including; medicine [7], materials science [8], environmental applications [9] and in the industry [10]. Further, the influence of dithiocarbamates toward some tumours, fungi, bacteria, and other microorganisms are also investigated [11, 12]. In this work, we report the formation, structural characterisation and bacterial activity of new DTC ligand and its macrocyclic metal-based complexes.

2. Experimental

2.1. Materials

The reagents used without further purification and were available commercially, solvents were distilled with appropriate drying agents, immediately before use.

2.2. Physical measurements

Determination of (C, H, N and S) content for prepared compounds were carried out using Heraeus instrument (Vario EL) and Euro EA 3000. Melting points were measured on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. Infrared spectra were obtained as KBr discs using a Shimadzu 8300s FT-IR spectrophotometer in the range 4000-400 cm^{-1} and as CsI discs in the range 400-200 cm^{-1}. Electronic spectra between 200-1100 nm with solutions of dimethyl sulfoxide (10^{-3})M (DMSO) solvent at 25 °C were measured using a Perkin-Elmer spectrophotometer. Thermogravimetric analysis were carried out using an STA PT-1000 Linseis company / Germany. Mass spectra were obtained by positive electrospray mass spectroscopy technique (ESMS). NMR spectra (^1H, ^{13}C- NMR) were acquired in DMSO-d_6 solutions using a Brucker-300 and a JEOL-400MHz for ^1H-NMR and 75 and 100.61 MHz for ^{13}C-NMR, respectively with tetramethylsilane (TMS) as an internal reference for ^1H NMR. Metal content were measured using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. DMSO solutions used to measure conductivity with a Jenway 4071 digital conductivity meter at room temperature. Magnetic susceptibility balance (Sherwood Scientific) was used to obtain magnetic moments.

3. Synthesis

3.1. Synthesis of the bis-amine precursor

The free bis-amine precursor was prepared using a standard method reported in [13, 14], by two steps, and as follows

:

3.1.1. Preparation of N,N'-(biphenyl-4,4'-diyl)bis(2-chloroacetamide)

Potassium hydroxide (0.78g, 13.24mmol) in H_2O (20mL) was added with stirring to a mixture of benzidine (1.22g, 6.62mmol) dissolved in $CHCl_3$ (50mL). To the above mixture, chloroacetyl chloride (1.49g, 13.24mmol) dissolved in $CHCl_3$ (50mL) was added dropwise with stirring. A white precipitate formed after 15 minutes, filtered off and then washed with Et_2O (20mL). The mixture was air-dried, white product was collected m.p=205-207 ºC. Yield: 2.1g, (94%). FTIR (cm^{-1}), 3296 ν(-CON-H), 1685 ν(C=O), 1587 δ(N-H), 1493 ν_{arom}(C=C).

The electrospray (+) mass spectrum of the N,N'-(biphenyl-4,4'-diyl)bis(2-chloroacetamide) showed the parent ion peak at m/z = 337.6 $(M)^+$ (10%) for $C_{16}H_{14}Cl_2N_2O_2$; requires =337.20 and the following fragments; 245.7 (11%) and 154.4 (80%) correspond to $[M-(NH-CO-CH_2Cl)]^+$ and $[M-(NH-CO-CH_2Cl)+(NH-CO-CH_2Cl)]^+$, respectively, Figure (1). NMR data in (ppm), δ_H(400 MHz, DMSO-d_6): 10.351 (2H, s, N-*H*), 7.56-7.64 (8H, m, $C_{4,4`,6,6`}$-*H*) ($C_{5,5`,7,7`}$-*H*) Ar-*H*,4.24(4H, s, CH_2Cl, ($C_{1,1`}$-*H*)), Figure (2). δ_C(100.63MHz, DMSO-d_6): 41.57 (C*H*$_2$Cl, 2C_1), 119.09 and 126.60 (Ar-$C_{4,5,6,7}$), 164.59 (2C_2=O), Figure (3).

3.1.2. Preparation of bis-amine N,N'-(1,4-phenylene)bis(2-(benzylamino) acetamide)

An excess of benzylamine (5.38g, 50.29mmol) was heated to 40 ºC, then it was added portion-wise with stirring (4.24g, 12.57mmol) of *N,N'*-(biphenyl-4,4'-diyl)bis(2-chloroacetamide). The mixture stirred for 12 h at 40 ºC, then H_2O (200mL) added. The product extracted into CH_2Cl_2 (4 x 50 mL), washed with H_2O (200mL) and dried over K_2CO_3. A light yellow precipitate was obtained by removing the solvent under reduced pressure, Yield: 3.89g, (64%). The IR spectrum showed similar bands to that in the first precursor at 3309 ν(-CON-H), 3157 ν(N-*H*), 1660 ν(C=O), 1603 δ(N-H) and 1556 ν_{arom}(C=C) cm^{-1}. The electrospray (+) mass spectrum showed the parent ion peak at m/z = 480.3 $(M+2H)^+$ (9%) for $C_{22}H_{30}N_4O_2$ as doubly charged species, requires =478.58, Figure (4). NMR data (ppm), δ_H(400 MHz, DMSO-d_6): 2.92(2H, s, *N-H*), 3.29, 3.33 (4H, d, J_{HH}=17.8Hz, ($C_{A,A`}$-*H*)), 3.61(4H, d, $J_{HH}$=16Hz, ($C_{1,1`}$-*H*)), 7.33, 7.65 ($C_{C,C`,D,D`,E,E`,F,F`,G,G`}$-*H*) (8H, d, $J_{HH}$=2.1Hz), 9.81 (2H, s, amidic-*H*), Figure (5). $\delta_C$ (100.63 MHz, DMSO-$d_6$): 51.63 ($C_{A,A`}$), 52.18 ($C_{1,1`}$), 114.03 ($C_{4,4`,6,6`}$), 119.35 ($C_{5,5`,7,7`}$), 135.85; 137.37 ($C_{C,C`,D,D`,E,E`,F,F`,G,G`}$), 169.35,169.61 (C=O)($C_{3,3`}$), Figure (6).

3.2. Synthesis of free ligand

Standard method used in the synthesis of dithiocarbamte compounds [15] was used to prepare the free ligand potassium 2,2'-(biphenyl-4,4'-diylbis(azanediyl))bis(2-oxoethane-2,1-diyl) bis(benzylcarbamodithioate) (L) and as follow:

An excess of KOH (0.140g, 2.50mmol, 4eq) dissolved in H_2O (2mL) was added to a solution of bis-amine (N, N'-(1,4-phenylene) bis(2-(benzylamino) acetamide) (0.30g, 0.626mmol) in 10 mL of a mixture of MeCN: H_2O (9:1). The mixture was stirred in an ice bath, and then a solution of carbon disulfide (0.142g, 1.88mmol, 3 eq) added dropwise and stirred. Then the mixture stirred for 2 h at 0 °C, the potassium dithiocarbamate salt was obtained as a yellow solid, m.p=170-172 ºC. Yield: 0.29g, (65.90 %). Bands at 1500 ν($N-CS_2$) and 1109, 999 attributed to asymmetric and symmetric stretching of (CS_2) (see Table (2)), Figure (7).The electrospray (+) mass spectrum of the L showed the parent ion peak at m/z =707.3 $(M)^+$ (18%) for $C_{32}H_{28}K_2N_4O_2S_4$; requires =707.5, Figure (8).NMR data (ppm), δ_H(300 MHz, DMSO-d_6): 3.32 (4H, s, ($C_{A,A`}$-*H*)), 4.40 (4H, s, ($C_{2,2`}$-*H*)), 7.42,7.44 (4H, d, J_{HH}=5.7 Hz, ($C_{C,C`,G,G`}$-*H*)), 7.46 (4H, t, J_{HH}=12 Hz, ($C_{E,E`}$-*H*)), 7.58 (4H, t, $J_{HH}$=5.1 Hz, ($C_{F,F`,G,G`}$-*H*)), 7.61, 7.64 (4H, d, $J_{HH}$=6.3 Hz, ($C_{5,5`,7,7`}$-*H*)), 7.71, 7.73 (4H, d, $J_{HH}$=5.4 Hz, ($C_{6,6`,8,8`}$-*H*)) (Ar-H), 10.74 (2H, s, amidic-H), Figure (9).$\delta_C$(75 MHz, DMSO-$d_6$): 49.47 ($C_{A,A`}$), 49.84 ($C_{2,2`}$), 118.83, 126.05, 127.37, 127.76, 128.42 ($C_{5,5`,6,6`,7,7`,8,8`}$), ($C_{C,C`,D,D`,E,E`,F,F`,G,G`}$), 170.41 (C=O) ($C_{3,3`}$), 191.72 (C=S) ($C_{1,1`}$) , Figure (10).

3.3. General method for synthesis of macrocyclic complexes

A standard methods reported in [16, 17] were used to synthesise the bimetallic macrocyclic dithiocarbamate-based complexes using two approaches; (i) reaction of the free ligand with the metal ion, and (ii) through a one-pot reaction.

3.3.1 .Synthesis of macrocyclic complexes from free ligand

Macrocyclic complexes were synthesised by the reaction of 1equivalent of potassium dithiocarbamate salt, dissolved in 10mL of $MeCN/H_2O$ (9:1) with 1 equivalent of the metal salt; Co^{II}, Zn^{II} and Cd^{II}. The solution was allowed to stir overnight, distilled water was added, if necessary, to precipitate the product. The solid resulted was filtered off then washed with methanol to give the macrocyclic complexes. Elemental analysis data, colors and yields for the complexes are given in Table (1).

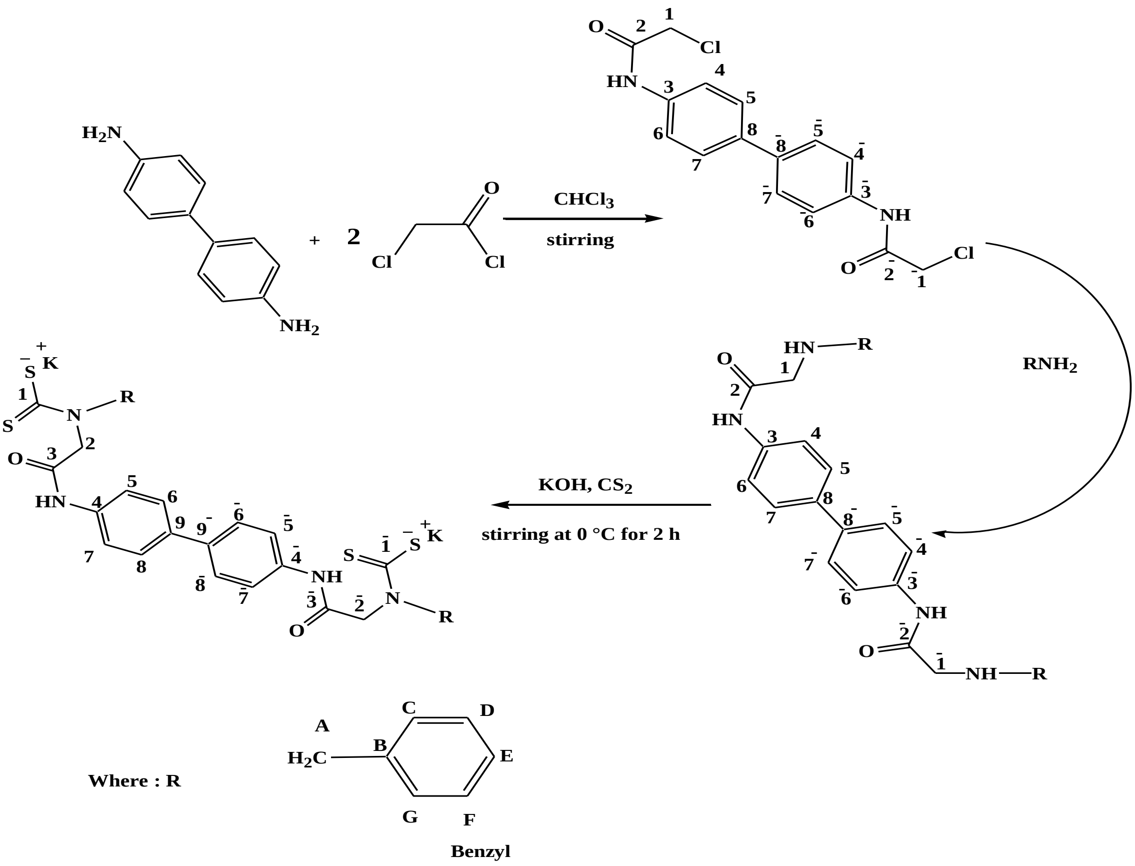
3.3.2. Synthesis of macrocyclic complexes via a one-pot reaction

An excess of KOH (3eq). Carbon disulfide (2.8 equivalents) was added to a solution of the secondary amine in $MeCN/H_2O$ mixture (9:1) with stirring, and the mixture was stirred for 10 minutes to obtain the potassium dithiocarbamate salt. The complexes were synthesised *in situ* (ligand salt was not isolated) by the adding one equivalent of the metal ion. After the mixture stirring overnight, water was added for precipitation, the precipitate filtered and dried to give the macrocyclic complex. Analytical data are similar to the complexes obtained from the free ligand approach.

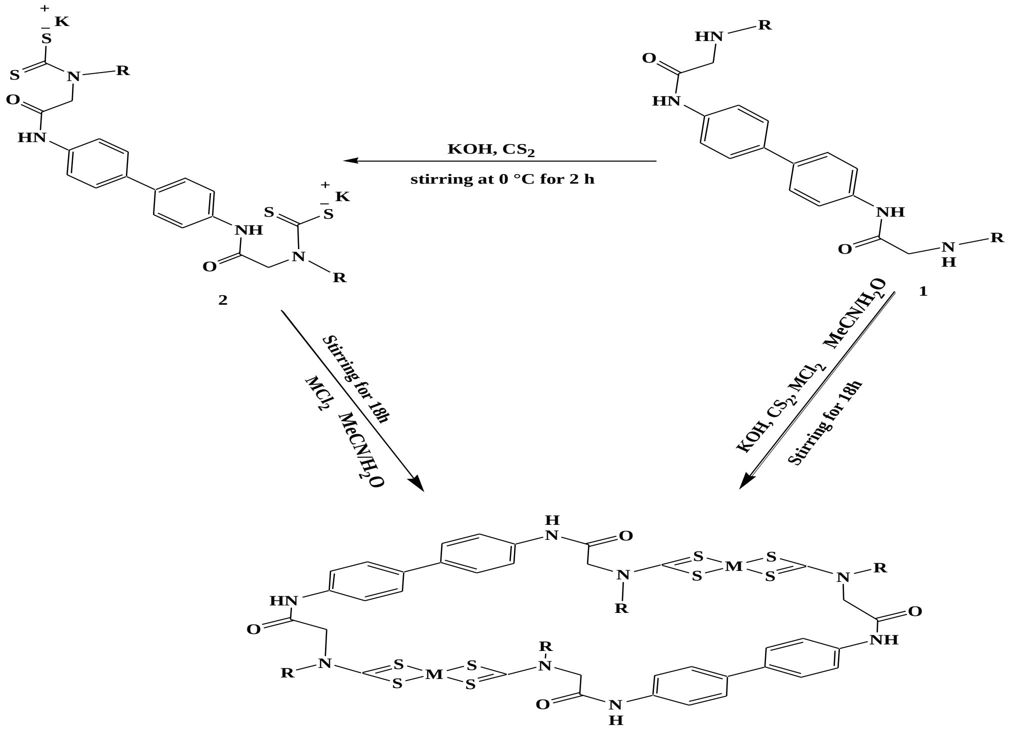
4. Results and discussion

4.1. Synthesis

The free ligand was obtained from the reaction of carbon disulfide and the secondary amine in the presence of KOH (see Scheme (1)). The formation of dithiocarbamate macrocyclic complexes was achieved either through a one-pot approach or from the mixing of the isolated ligand with metal ion, Scheme (2). The ligand and its complexes are isolated in a moderate yield and found to be air stable. The ligand is soluble in most organic solvents. However, its complexes found to be soluble only in DMSO and DMF. They are partially soluble in other common organic solvents. Ligand and its complexes were characterised as required by a range of techniques including; thermal analysis, elemental analysis, UV-Vis, FTIR, mass and ^{1}H, ^{13}C-NMR spectroscopy, magnetic susceptibility, conductance and melting point measurement.



Scheme (1)



Where: R = benzyl
M = Co^{II}, Zn^{II} and Cd^{II}

Scheme (2)

4.2. FTIR and NMR spectra

The FTIR spectrum of L shows characteristic band around 3230cm^{-1} due to ν(N–H) stretching. Bands due to ν(C=O) amide, $\nu_{as}(CS_2)$ and $\nu_s(CS_2)$ functional groups are detected at 1658 , 1009 and 999 cm^{-1} , respectively (see Table (2) Figure (7). The FTIR spectra of the dinuclear-macrocyclic complexes indicated the formation of the dithiocarbamate functions and their coordination to the metal ions. Bands detected around 1441-1495 cm^{-1} are attribute to the stretching of the *C*-*N*-S bonds, C-N single bonds at 1240-1244 cm^{-1}, suggesting a incomplete delocalization of π-electron density within the dithiocarbamate functions [18]. For the CS_2 groups, bands at 1115-1119 cm^{-1} and 970-980 cm^{-1} are assigned to $\nu_{as}(CS_2)$ and $\nu_s(CS_2)$, respectively, which is characteristic to aniso-bidentate coordination mode of the ligand to the metal atoms [19, 20]. Two sets of bands at lower frequency for the complexes around 379-391 cm^{-1} that assigned to the ν(M-S) vibration mode, insuring the anisobidentate coordination mode of the ligand [8], Figures (11-13). The ^{1}H NMR spectrum of L showed a peak at 4.40ppm, assigned to ($CH_{2,}C_{2,\,2}$`-*H*). The downfield appearance of this signal may due to attachment to withdrawing groups, N-H and C=O. The $_{ami}$(N-*H*) peak for the amide moiety is detected as a singlet at resonance δ= 10.74 ppm for L, Figure (9). The ^{13}C NMR spectrum of L shows a number of different carbon nucleuses in molecule indicating the formation of the ligand. The resonance of the carbonyl group detected downfield at δ= 170.41ppm. The formation of the free ligand can be revealed by the signals around δ=191.72ppm, which can be assigned to quaternary carbon in dithiocarbamate moiety C=S in the ligand, Figure (10). The ^{1}H-NMR spectra for $[Zn(L)]_2$ and $[Cd(L)]_2$ in DMSOd$_6$ solution display the $_{ami}$(N-*H*) signal for the amide segment at δ= 10.21 and 9.90 ppm for Zn- and Cd-complexes, respectively that confirming the non-involvement of the amide group upon complex formation [21] Figures (14, 16). The ^{13}C NMR spectra of $[Zn(L)]_2$ and $[Cd(L)]_2$ show a shift in the resonances of carbon nucleus in the complex molecule, compared with that in the free ligand, indicating the formation of the complexes. The chemical shift for C=S moiety is observed downfield at 199.24 and 204.88 ppm in $[Zn(L)]_2$ and $[Cd(L)]_2$, respectively in comparison with that at 191.72 in the isolated ligand confirming the involvement of this moiety in complexation, Figures (15, 17). The downfield shift for the Cd-complex may indicate more thiolate character for the C=S moiety, compared with the Zn-complex [22].

4.3. UV-Vis Spectral data for the complexes, and magnetic susceptibility

The UV-Vis spectrum of the ligand in DMSO solution revealed peaks at 264, 314 and 368 nm may attribute to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively [23-25] (Figure (18)). The electronic spectrum of the Co(II) complex exhibited bathochromic shift of the bands 266, 318 nm associated to the ligand field $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Band at 381 nm may assigned to charge transfer transition (C.T) [26]. The Co(II) complex showed additional peak at 645 nm may assigned to $^4A_2\,^{(F)} \rightarrow\, ^4T_1\,^{(p)}$ transition. This band is distinctive for Co(II)-complex with tetrahedral arrangment about Co ion [27-29], Figure (19). The Co.complex gaveμ_{eff} value of 4.71 B.M, which it is typical for complexes of tetrahedral geometries, indicating a tetrahedral geometry around Co(II) ion [28, 30]. The electronic spectra of the $[Zn(L)]_2$ and $[Cd(L)]_2$ complexes exhibited peaks at 278, 270 and 329, 31 nm that assigned to the ligand field and charge transfer transitions in Zn- and Cd-complexes, respectively [31] (see Figures (20 and 21)). The molar conductance of the complexes in DMSO solutions is indicative of their non-electrolytic nature [32, 33]. (see Table (1)). The UV-Vis bands and magnetic measurements of complexes with their assignments are tabulated in Table (3).

4.4. Thermal analysis

Thermal analysis data for the ligand and its d^{10} metal complexes are summarised in Table (4). The TG-DSC curves of the ligand and its complexes were determined from ambient temperature up to 600 °C in a nitrogen atmosphere. The analysis of thermal data showed ligand is stable up to 118 °C with weight loss 56.68% that attributed to (phenyl-$CH_2NCH_2CONH+2CS_2+$ $K+CH_2N+NH$) segment. This peak is indicated by an exothermic peak by the DSC at 126.5 °C. The final residue of the compound confirmed the mass loss of 40.62% (see Figure (22)). Thermal properties of $[Zn(L)]_2$ and $[Cd(L)]_2$ complexes are listed in Table (4) and exhibit in Figures (23 and 24). Thermal data of $[Zn(L)]_2$ complex consists of three steps. The first step accompanied by an exothermic behaviour as confirmed its DSC curve at 116 °C. Further, $[Cd(L)]_2$ thermal curves indicated two steps with an endothermic peak at 455°C. The weight loss and other thermal properties including lost fragments of the complexes are tabulated in Table (4), [34, 35].

4.5. Bacterial activity

The synthesised dithiocarbamate ligand and its complexes were tested against their bacterial activity against some bacterial strains *(Escherichia coli and Pseudomonas aeruginosa* (G−), *Staphylococcus aureus and Bacillus stubtilis* (G+)). The involvement of DMSO in the biological test was clarified by individual studies that conducted with the solutions of DMSO alone, which indicated no activity towards any bacterial species [36]. The measured inhibition zones against growth of different microorganisms are summarised in Table (5) that displays the effect of the synthesised compounds on bacterial strains. From obtained data, it is clear that, compared with the free ligand, complexes are actually more active against these bacterial species, which means complexation increases antimicrobial activity. Zinc and Cadmium complexes almost have the higher antimicrobial activity compared with the Co-complex. This may be related to their electronic configuration (d^{10} system) and/or their higher molecular weight [37].

5. Conclusion

In this paper, we have investigate the synthesis and characterisation of ligand bis(dirhiocarbamate) ligand and its bimetallic macrocyclic complexes. The macrocyclic complexes were prepared either from the mixing of the isolated ligand with metal ion or through a template one-pot reaction. The overall structure and mode of bonding of the compounds were achieved by analytical and spectroscopic methods. The results indicated formation of four-coordinate complexes in the solid state and in solution. Biological activities indicated that the metal complexes are more active towards these bacterial species, in comparison with the isolated ligand.

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Table (1): Colours, yields, melting points, (C, H, N, S) analysis and molar conductance values for ligand and its bis-dithiocarbamate-based complexes.

Comp.	**Empirical formula**	**m.p**	**Yield %**	**colour**	**Λ_M(Ω^{-1}cm^{2}mol^{-1})**	**Microanalysis found (calc) %**				
						M%	**C**	**H**	**N**	**S**
L	$C_{32}H_{25}K_2N_4O_2S_4$	170 -172	65.90	Yellow	-	-	52.87 (54.36)	3.98 (3.99)	7.98 (7.92)	19.86 (18.14)
[Co (L)]$_2$	$C_{66}H_{62}N_8O_4S_8Co_2$	269	46.25	Deep green	6.01	8.21 (8. 29)	56.12 (56.60)	3.96 (4.68)	7.94 (7.88)	17.67 (18. 04)
[Zn (L)]$_2$	$C_{66}H_{62}N_8O_4S_8Zn_2$	288	41.97	White	4.77	8.75 (9. 22)	55.35 (55.88)	3.88 (4.41)	7.98 (7.90)	17.85 (18. 08)
[Cd(L)]$_2$	$C_{66}H_{62}N_8O_4S_8Cd_2$	245	43.02	Yellow	7.07	14.18 (14.71)	53.97 (52.64)	4.23 (4.35)	7.61 (7.33)	26.96 (16,78)

(calc) = Calculated

Table (2): FT-IR data (wave-number) cm^{-1} of ligand and its metal complexes.

Comp.	ν (N-H)	**ν$_{ar}$(C-H)**	**ν$_{ali}$(C-H)**	**ν (C=O)**	**δ(N-H)**	**ν$_{ar}$(C=C)**	**ν(N-CS$_2$)**	**νas(CS$_2$) ν,s(CS$_2$)**	**ν$_{ar}$(C-N)**
L	3230	3041	2998-2875	1658	1610	1535	1433	1009,999	1275
[Co(L)]$_2$	3324	3091	2974, 2860	1654	1606	1541	1495	1115 ,970	1240
[Zn(L)]$_2$	3309	3041	2912, 2844	1658	1579	1520	1441	1119 ,972	1244
[Cd(L)]$_2$	3294	3037	2912, 2844	1646	1599	1520	1446	1115 ,980	1240

* ν (Co-S) observed at 379.95 and 366.45 cm^{-1}.

* ν (Zn-S) observed at 391.52 and 374.16 cm^{-1}.

Table (3): UV-Vis spectral data of ligand and bisdithiocarbamate-based complexes in DMSO solutions and magnetic moment.

Comp.	**Band Position λ_{nm}**	**Wave number (cm^{-1})**	**Extinction coefficient ε_{max} ($dm^3 mol^{-1} cm^{-1}$)**	**Assignment**	**μ_{eff} (B.M)**
L	264 314 368	37878 31847 27173	562 2391 510	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-
$[Co(L)]_2$	266 318 381 645	37593 31446 26246 15503	2033 1743 1441 256	Intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ C.T ${}^4A_2{}^{(F)} \rightarrow {}^4T_1{}^{(p)}$	4.71
$[Zn(L)]_2$	278 329	35971 30395	2323 923	Intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ C.T	Diamagnetic
$[Cd(L)]_2$	270 331	37037 30211	892 2015	Intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ C.T	Diamagnetic

Table (4): TGA/DTG/DSC data for ligand and its complexes.

Compound	**Stable up to °C**	**Stage**	**Decomp. temperature initial-final °C**	**fragments**	**Nature of transformation/intermediate formed% mass found (calc.)**	**Nature of DSC peak and temp. °C**
L	118	1	118-268	(phenyl-$CH_2NCH_2CONH+2CS_2+K+CH_2N+NH$)	2.8343 (2.8115)	126.5 Exo 179.9 Exo
$[Zn(L)]_2$	100	1 2 3	100-195 198-263 265-595	($3CS_2 + CH_3$ CON_2) (phenyl-CH_2NCH_2 CON + NCO +diphenyl) (phenyl-$CH_2NCH_3+CS_2$)	1.4087 (1.4336) 1.6863 (1.7390) 1.0931 (1.1092)	116 Exo - 549.9 Endo
$[Cd(L)]_2$	105	1 2	105-195 200-598	($2CS_2$ + CdN) (phenyl-CH_2NCH_2 CONH+ diphenyl + $NHCOCH_2NCH_2 + CH_2$ +CS)	3.2882 (3.2817) 6.5973 (6.4848)	141.9 Exo 455 Endo

Table (5): Bacterial activity of ligand and bis-dithiocarbamate-based complexes

No.	Sample	Inhibition zone (mm)			
		E. coli	*P. aeruginosa*	*B. sabtuius*	*S. aureus*
1	L	7	5	2	5
2	$[Co(L)]_2$	9	12	_	_
3	$[Zn(L)]_2$	12	14	45	15
4	$[Cd(L)]_2$	10	12	16	14

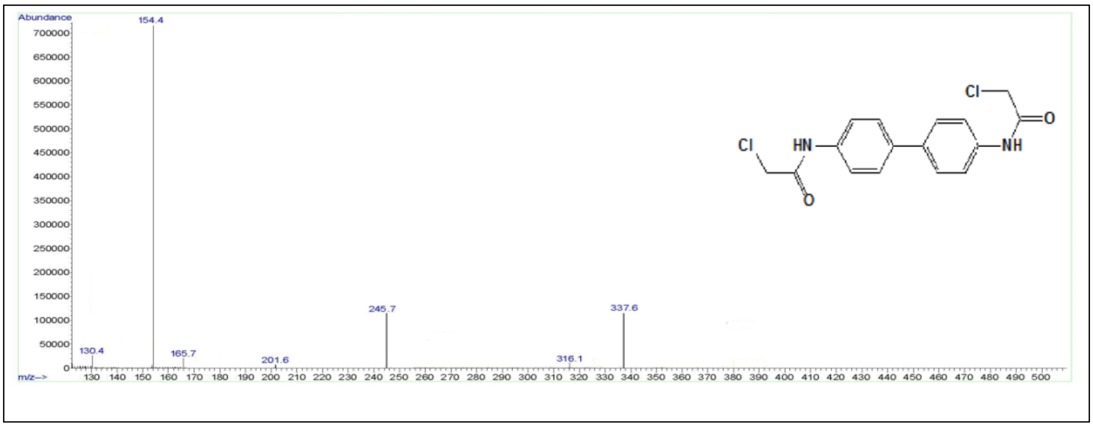

Figure (1): ES (+) mass spectrum of N,N’-(biphenyl-4,4'-diyl)bis(2-chloroacetamid)e

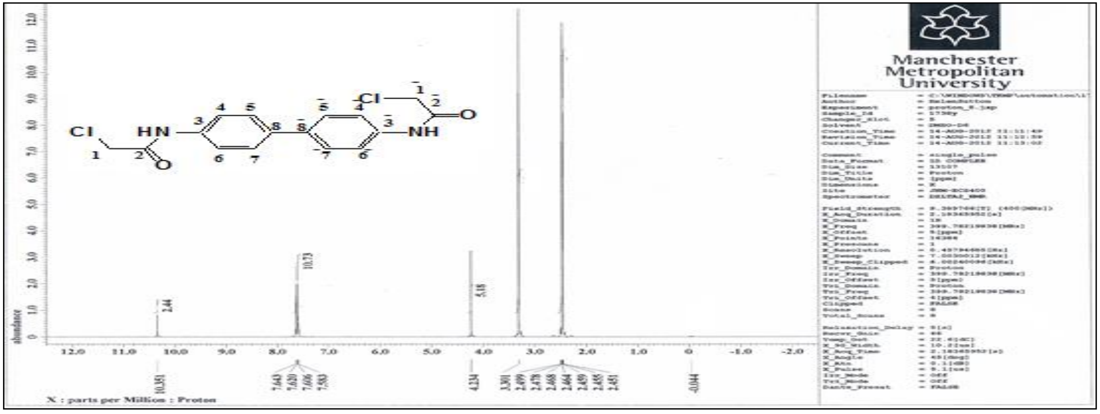

Figure (2): ^{1}H-NMR spectrum of N,N’-(biphenyl-4,4'-diyl)bis(2-chloroacetamide) in DMSO-d_6

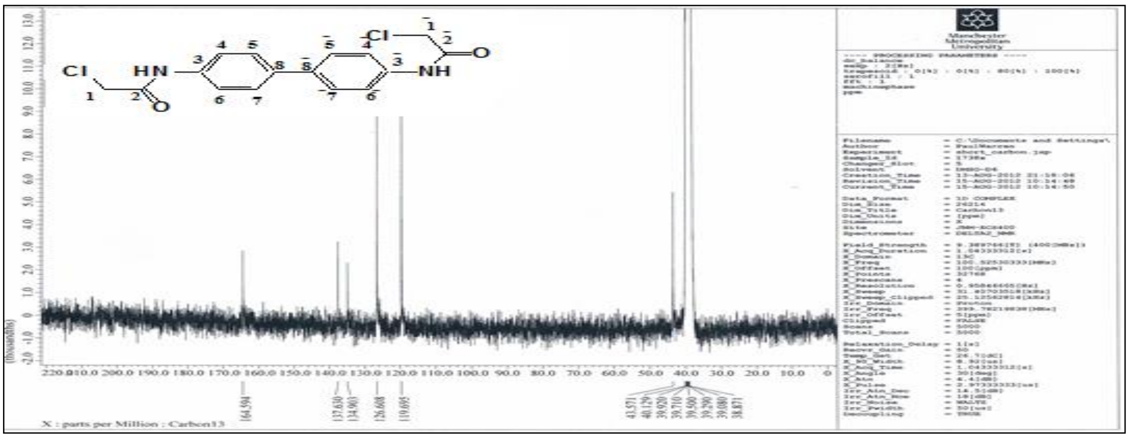

Figure (3): ^{13}C-NMR spectrum of N,N'-(biphenyl-4,4'-diyl)bis(2-chloroacetamide) in DMSO-d$_6$

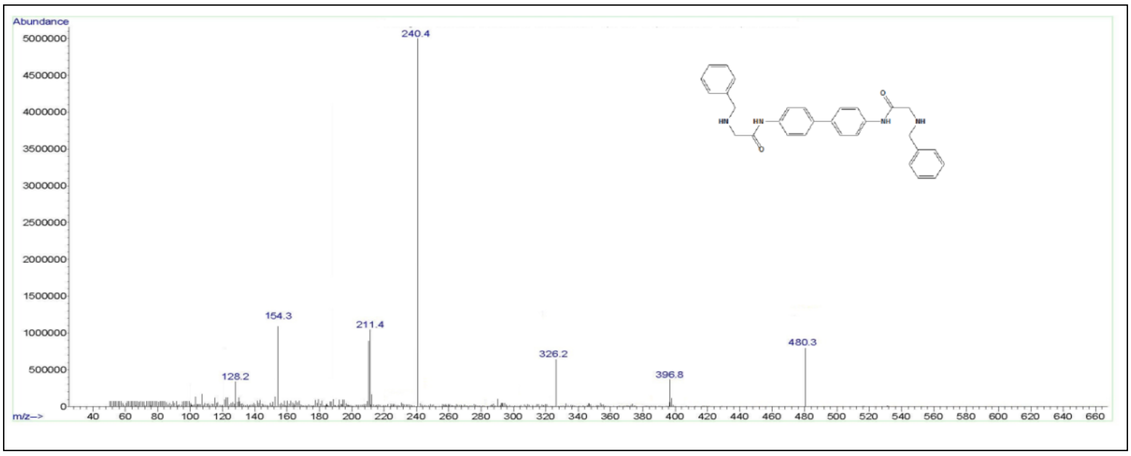

Figure (4): ES (+) mass spectrum of benzylamine precursor

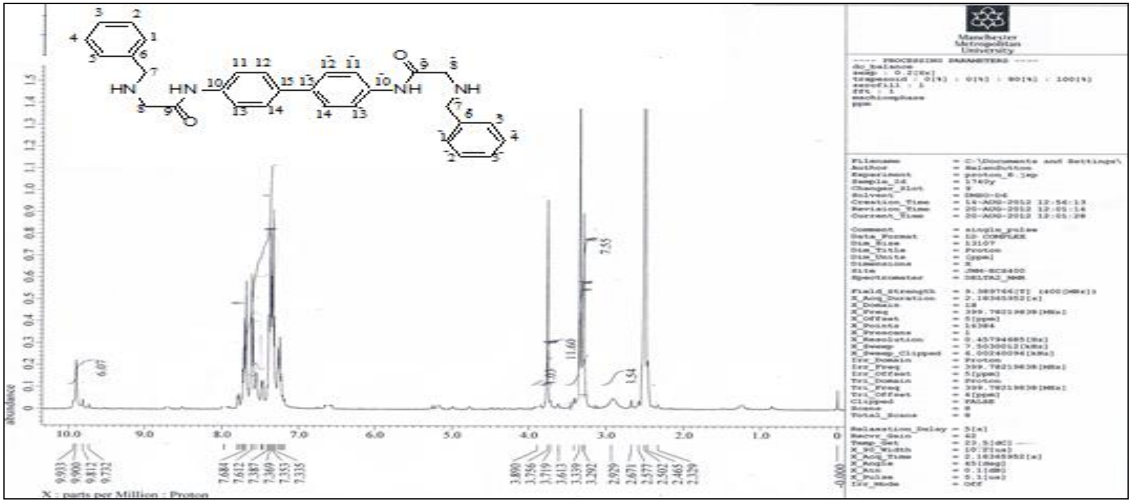

Figure (5): ^{1}H-NMR spectrum of the benzylamine precursor in DMSO-d$_6$

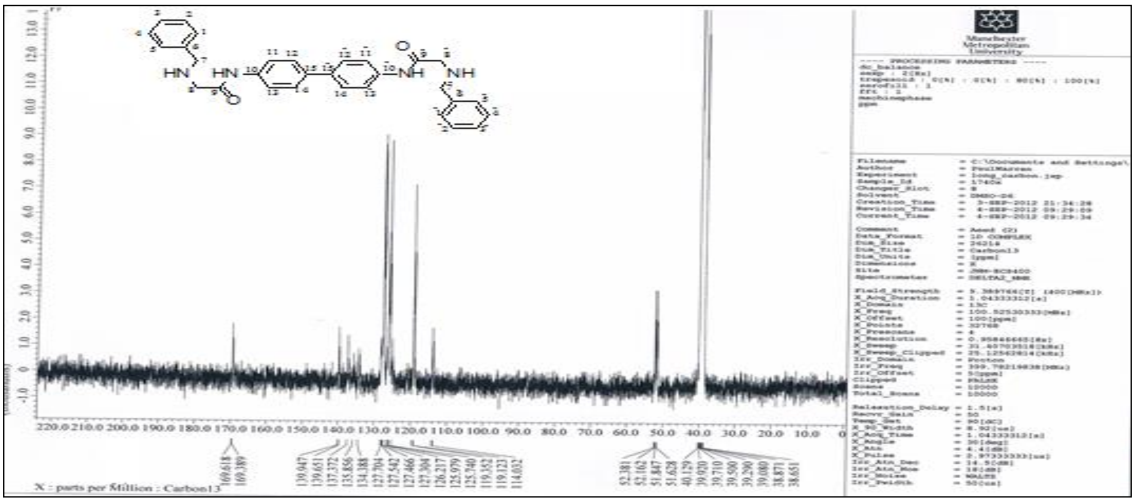

Figure (6): ^{13}C NMR-spectrum of benzylamine precursor in DMSO-d$_6$

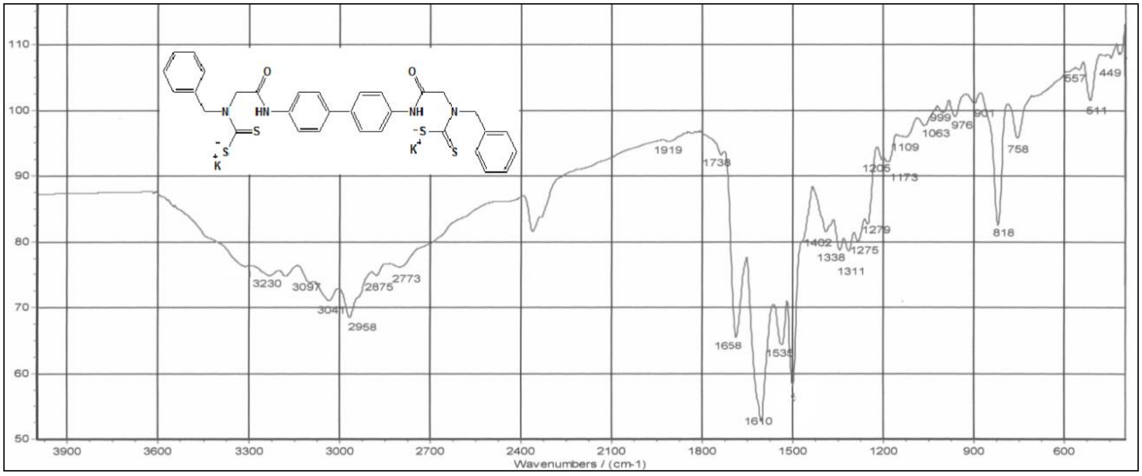

Figure (7): FTIR spectrum of ligand

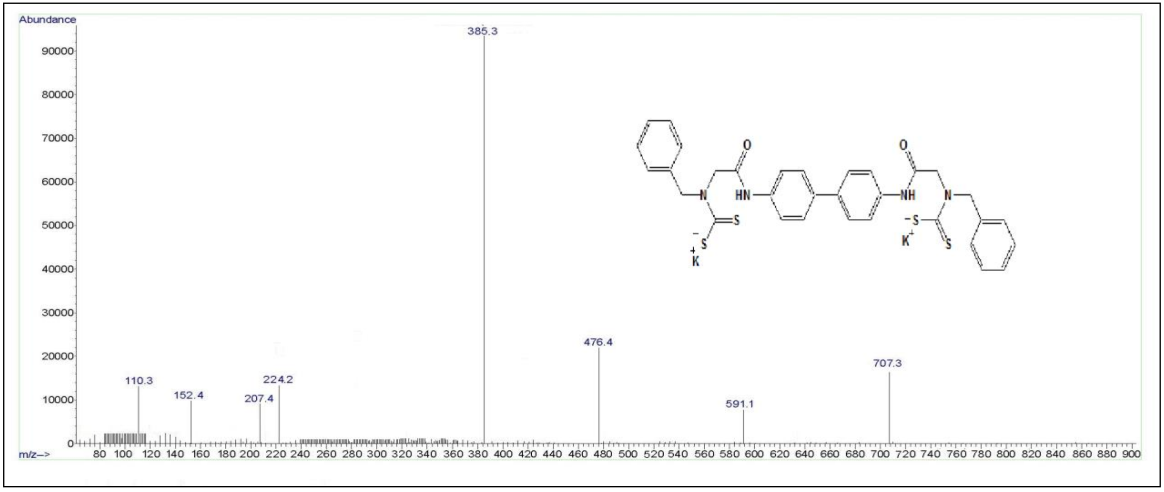

Figure (8): ES (+) mass-spectrum of ligand

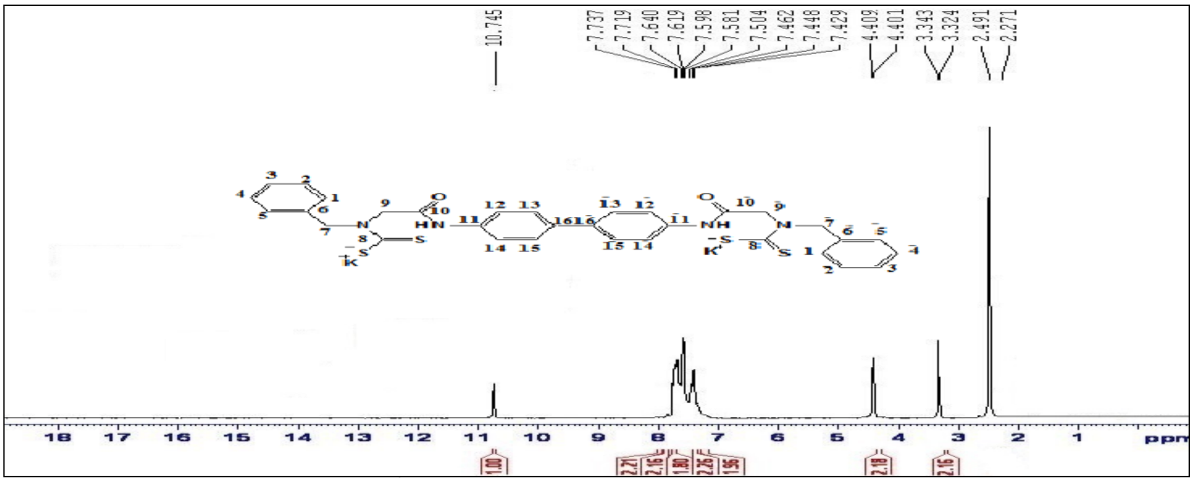

Figure (9): ^{1}H NMR-spectrum of ligand in DMSO-d_6

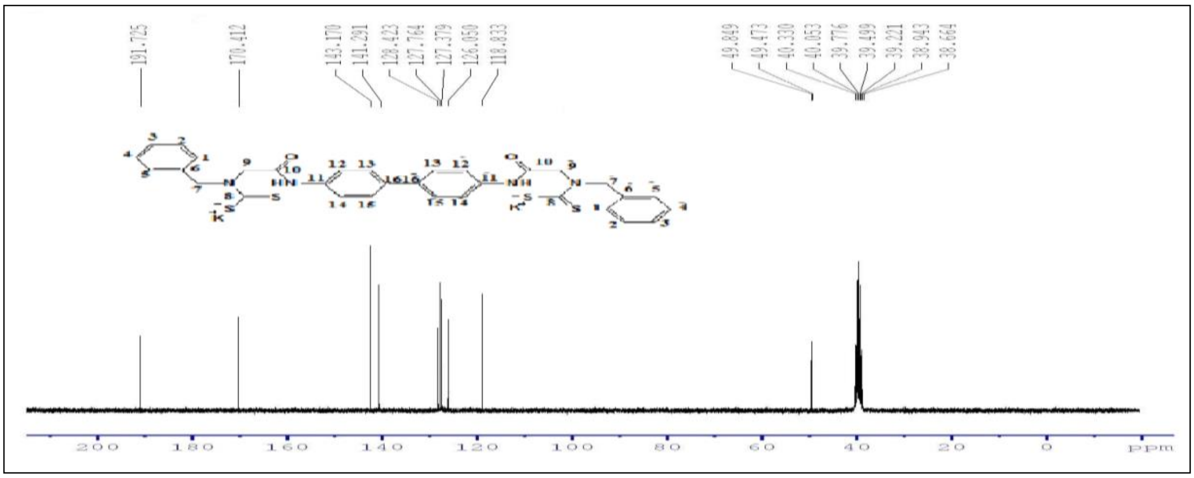

Figure (10): ^{13}C NMR-spectrum of ligand in DMSO-d_6

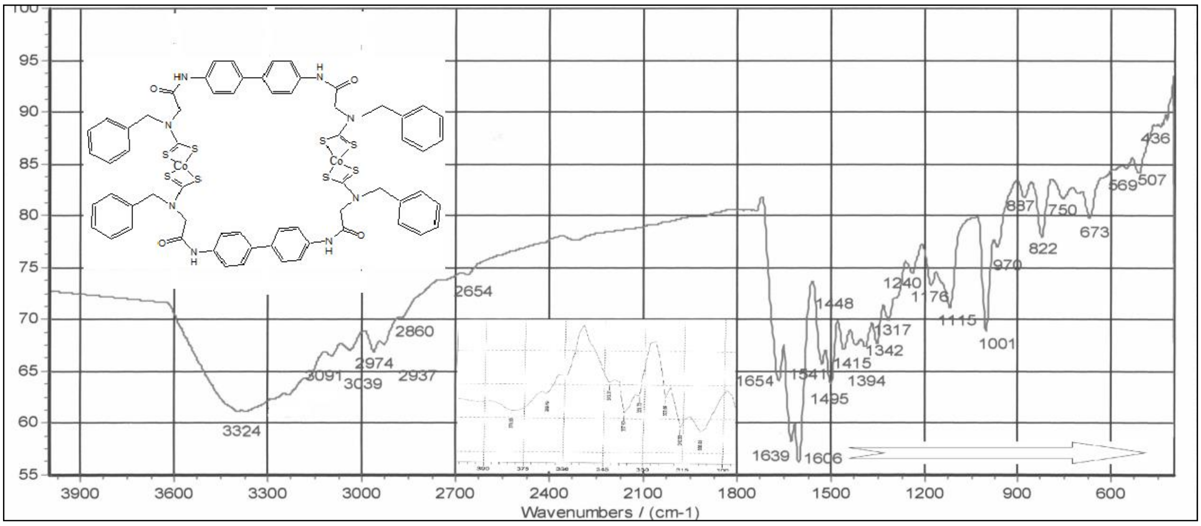

Figure (11): FTIR-spectrum of $[Co(L)]_2$ complex

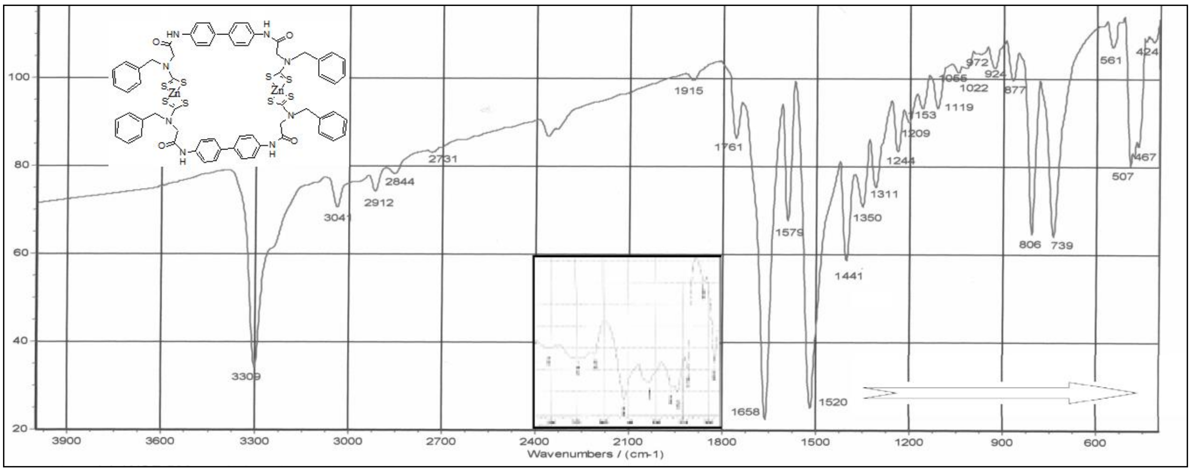

Figure (12): FTIR-spectrum of $[Zn(L)]_2$ complex

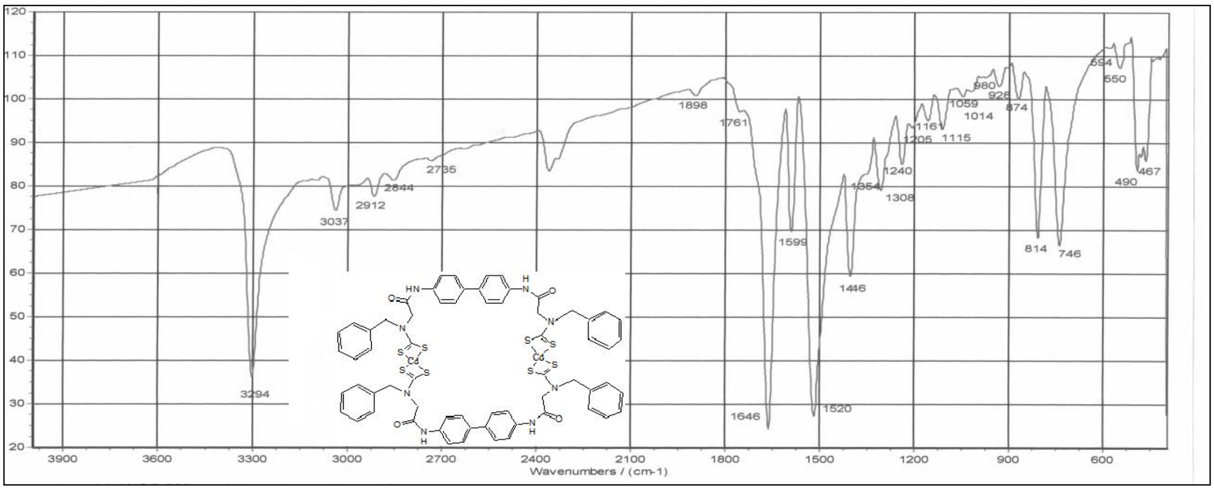

Figure (13): FTIR-spectrum of $[Cd(L)]_2$ complex

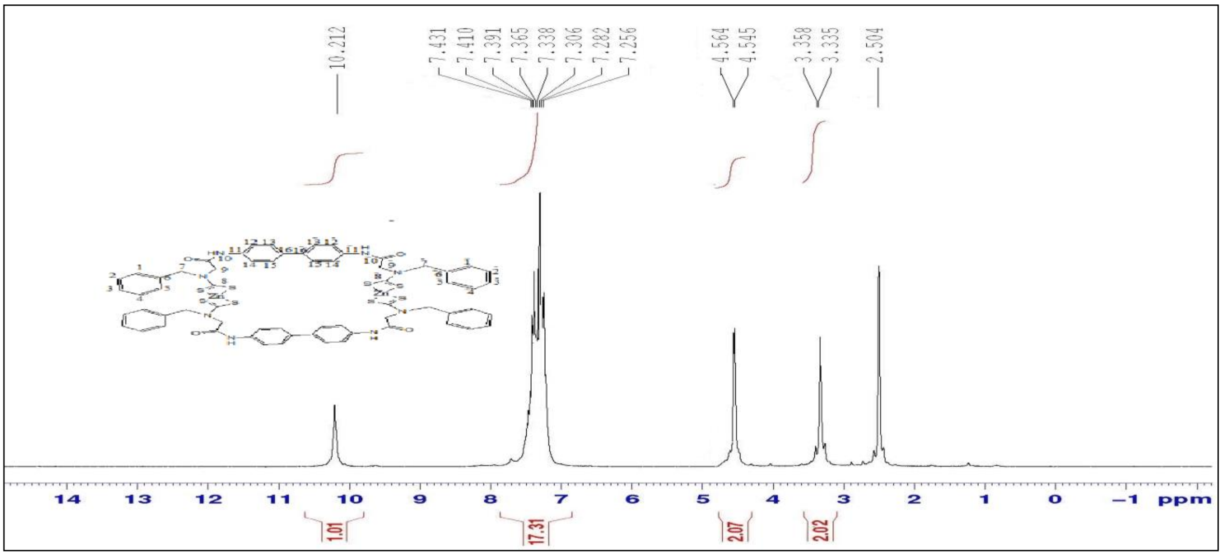

Figure (14): ^{1}H NMR-spectrum for $[Zn(L)]_2$ in DMSO-d_6

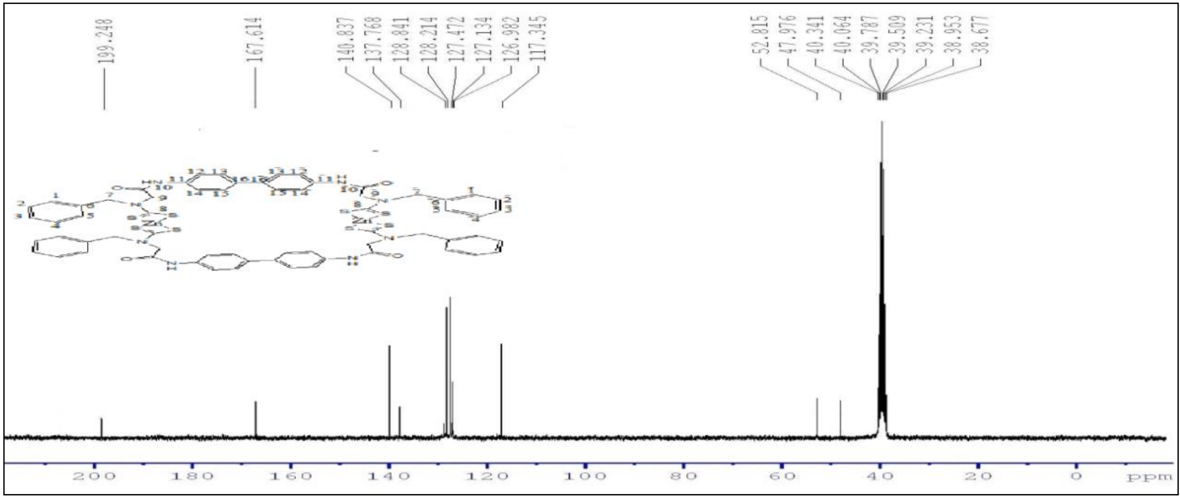

Figure (15): ^{13}C NMR-spectrum for $[Zn(L)]_2$ in DMSO-d_6

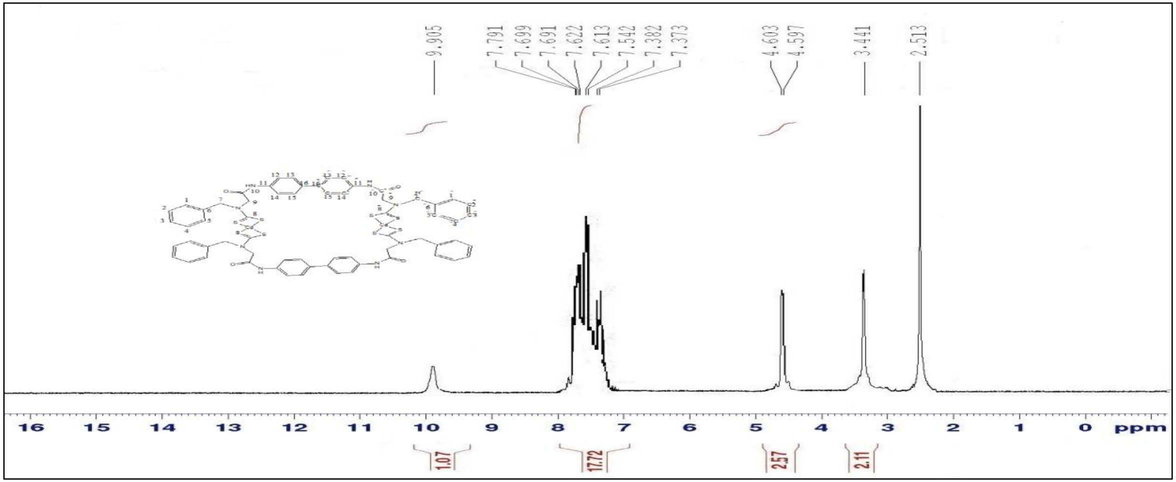

Figure (16): ^{1}H NMR-spectrum for $[Cd(L)]_2$ in DMSO-d_6

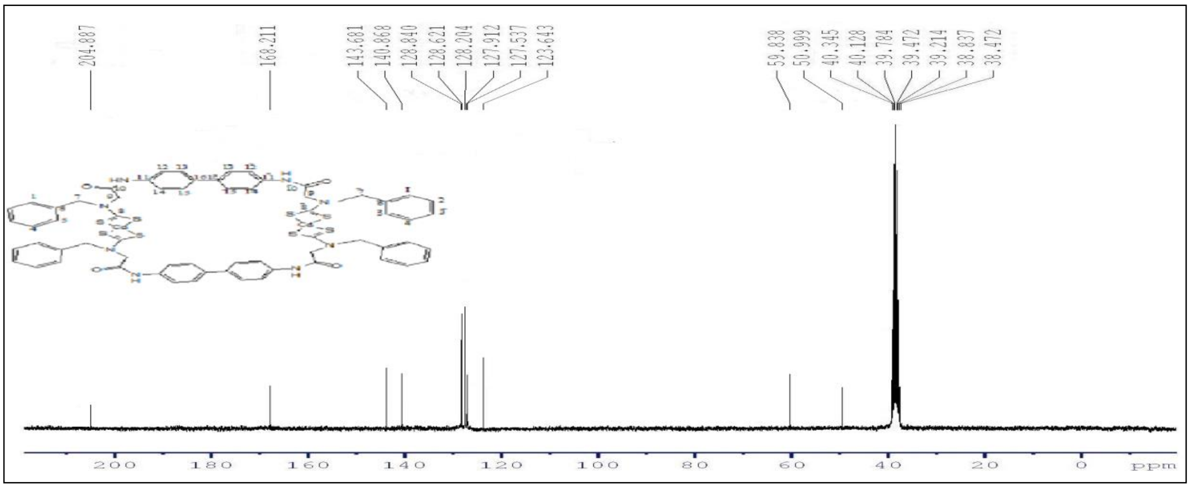

Figure (17): ^{13}C NMR-spectrum for $[Cd(L)]_2$ in DMSO-d_6

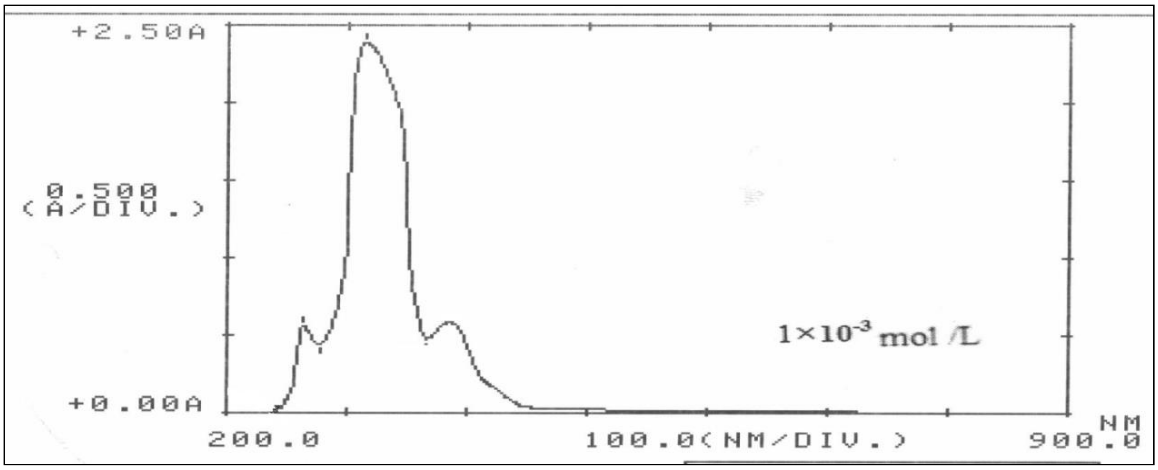

Figure (18): Electronic-spectrum of L in DMSO solution

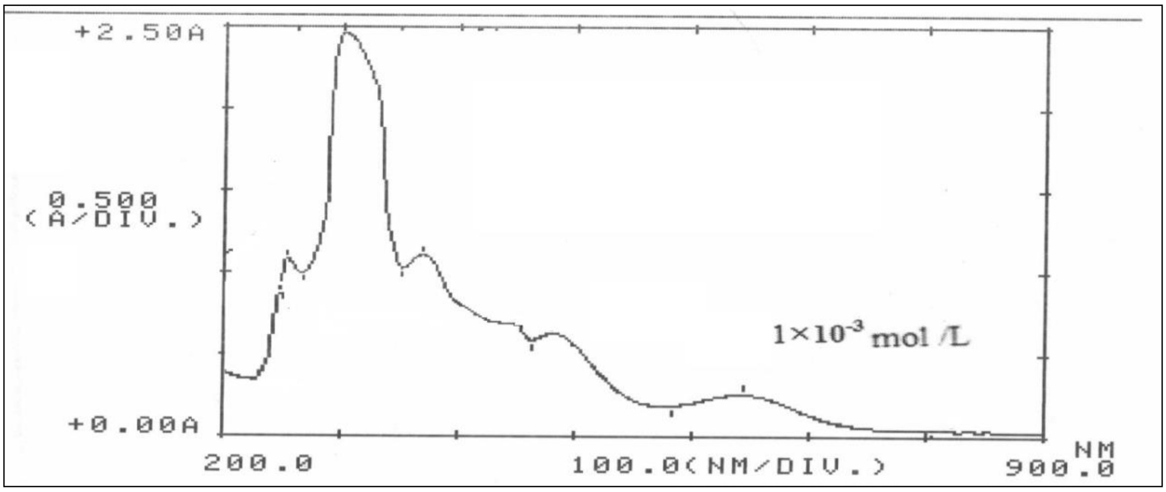

Figure (19): Electronic-spectrum of $[Co(L)]_2$ in DMSO solution

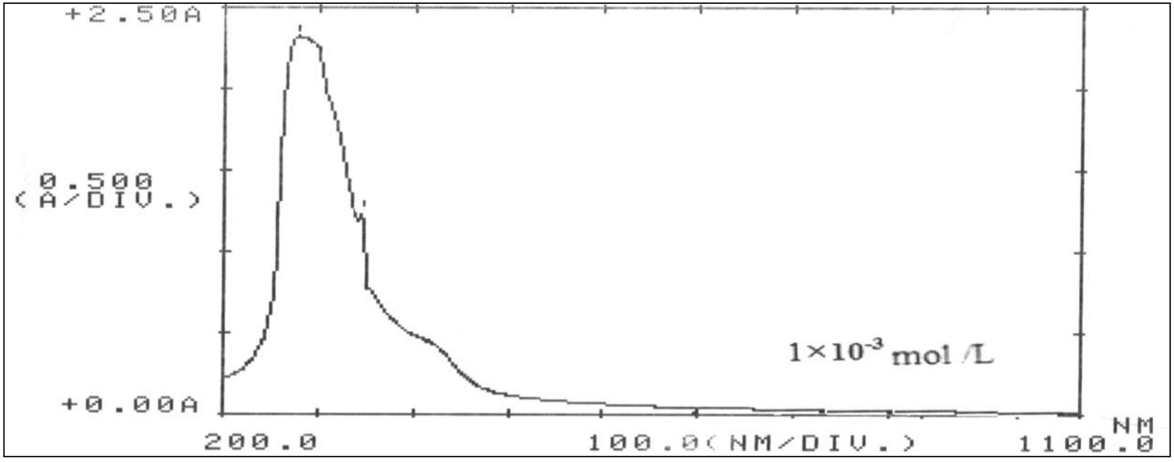

Figure (20): Electronic-spectrum of $[Zn(L)]_2$ in DMSO solution

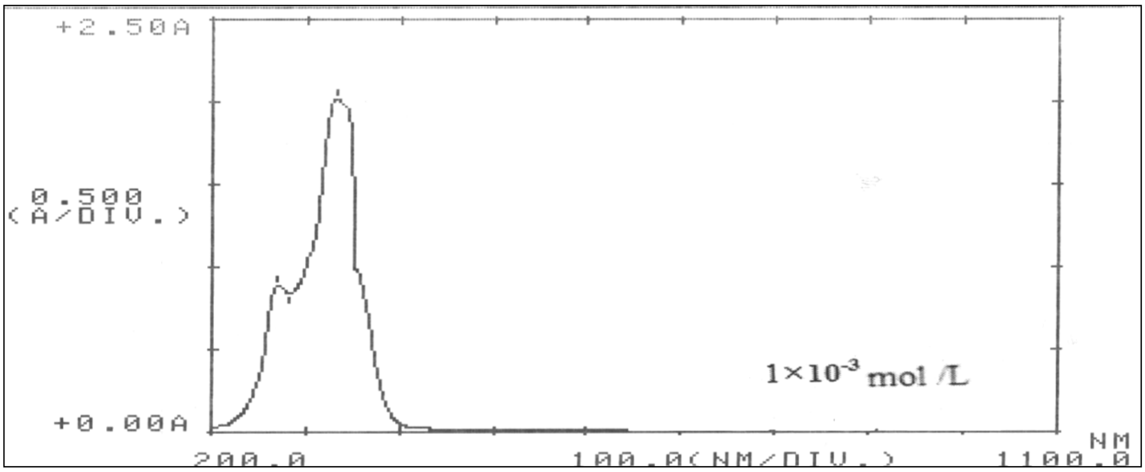

Figure (21): Electronic-spectrum of $[Cd(L)]_2$ in DMSO solution

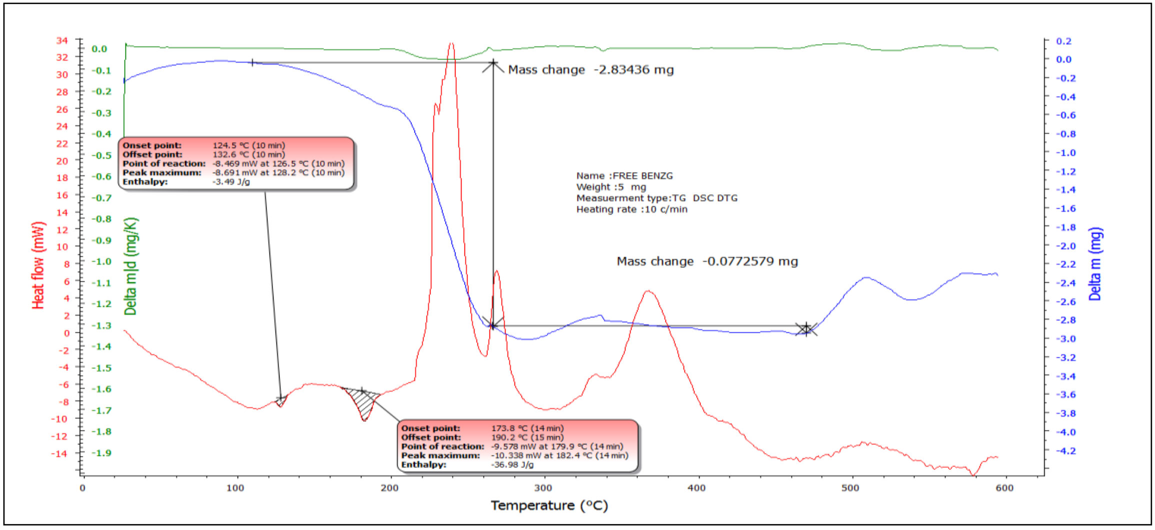

Figure (22): (TG/ DTG and DSC) thermogram of ligand in nitrogen atmosphere

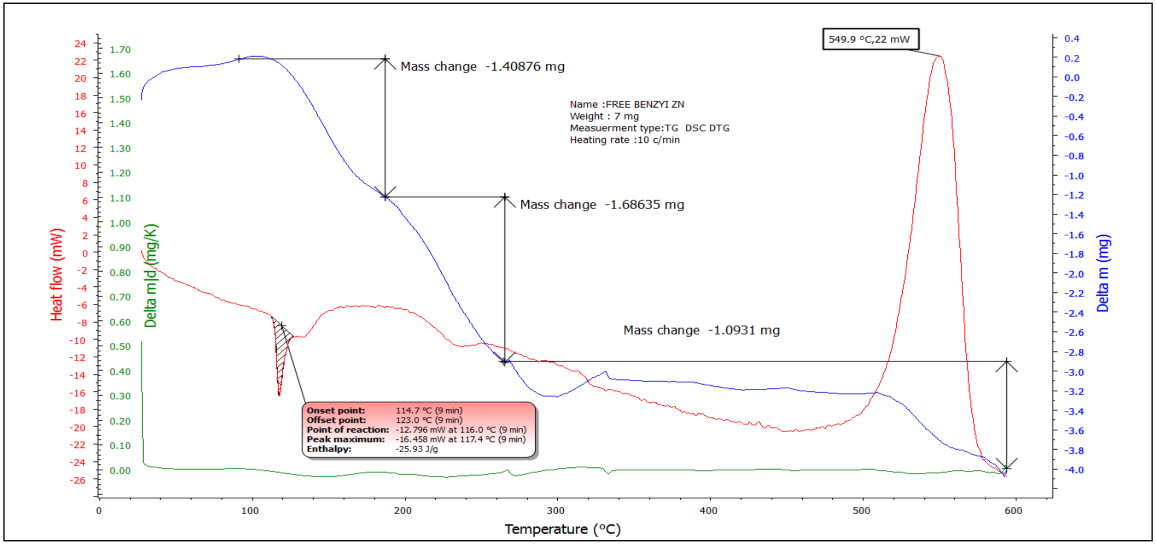

Figure (23): (TG/DTG and DSC) thermogram of $[Zn(L)]_2$ complex in nitrogen atmosphere

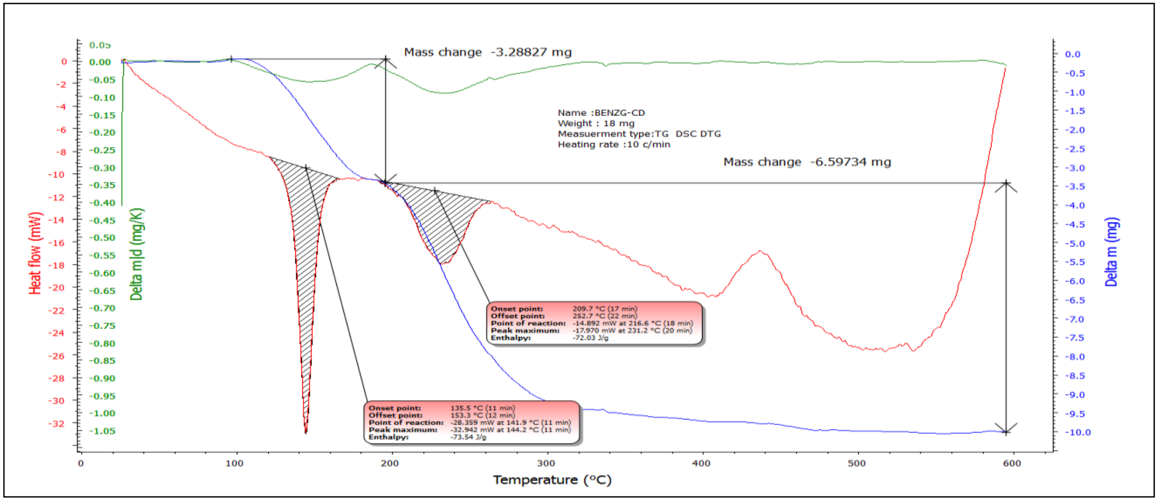

Figure (24): (TG/DTG and DSC) thermogram of $[Cd(L)]_2$ complex in nitrogen atmosphere

تكوين معقدات حلقية جديدة مع ليكاند ثنائي الثايوكارباميت ، تحضير وتشخيص و النشاط البكتيري

حسن احمد حسن
انعام اسماعيل يوسف

قسم الكيمياء/كلية التربية للعلوم الصرفة (ابن الهيثم) /جامعة بغداد

استلم في:21/شباط/2016، قبل في:4/نيسان/2016

الخلاصة

تضمن البحث تحضير وتشخيص ليكاند ثنائي الثايوكارباميت ومعقداته الحلقية ثنائية الفلز حضرت الليكاند بمفاعلة الامين الثانوي مع الكاربون ثنائي الكبريت وبوجود هيدروكسيد البوتاسيوم باستخدام مزيج من الماء والاسيتونايتريل وسطا للتفاعل لنحصل على اللكاند الحر .

حضرت المعقدات باستخدام طريقتين الاولى طريقة الليكاند الحر و الثانية طريقة الاضافة الواحدة للمواد المتفاعلة في دورق التفاعل. حضر المعقد في طريقة الليكاند الحر من تفاعل مكافئ من ملح البوتاسيوم لليكاند مع مكافئ من ملح الفلز ،اما الطريقة الثانية فهي طريقة الاضافة الواحدة حيث يتم تحضير المعقد من خلال مزج ثنائي الامين الثانوي مع الكاربون ثنائي الكبريت و ملح الفلز و بوجود هيدروكسيد البوتاسيوم باستخدام مزيج من الماء والاسيتونايتريل وسطا للتفاعل لنحصل على المعقدات. شخص الليكاند والمعقدات بوساطة التحليل الدقيق للعناصر وتقنية اطياف الاشعة تحت الحمراء واطياف الاشعة فوق البنفسجية والمرئية والحساسية المغناطيسية والتوصلية المولارية وقياس درجة الانصهار وتقنية طيف الكتلة واطياف الرنين المغناطيسي:

^{1}H, ^{13}C -NMR spectroscopy.

تم دراسة الفعاليه البكتيرية لليكاند والمعقدات وكانت المعقدات اكثر فعالية من اليكاند .

كشفت القياسات (الفيزو-كيميائية) ان التناسق حول الايونات الفلزية في المعقدات الحلقية المحضرة هو رباعي التناسق.

ناتج التفاعل في الطريقتين اعطى معقدات حلقية ذات الصيغة العامة :

$[M(L)]_2$
(where M = (Co^{II}, Zn^{II} and Cd^{II}) .

الكلمات المفتاحية: معقدات ثنائي الثايوكارباميت، دراسة التراكيب ، الخواص الحرارية ، الفعالية البكتيري.