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Formation of macrocyclic complexes with bis(dithiocarbamate) ligand; synthesis, spectral characterisation and bacterial activity

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ABSTRACT

The preparation and characterisation of dithiocarbamate (DTC) ligand and its binuclear metal(II) dithiocarbamate-based macrocyclic complexes are reported. The free ligand was prepared from the reaction of a bis-secondary amine, CS_2 and KOH. The macrocyclic bis(dithiocarbamate) complexes were synthesised using two approaches; (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 prepared by the reaction of potassium dithiocarbamate salt with the metal ions; Mn^{II}, Co^{II}, and Cu^{II}. In the one-pot reaction, the complexes were prepared using a bis-secondary amine, CS_2, KOH and metal(II) chloride. Ligand and its complexes were fully characterised by elemental analysis, thermal analysis, FTIR, UV-Vis, mass spectroscopy, magnetic susceptibility, conductance, melting points, and ^{1}H, ^{13}C- NMR spectroscopy. These studies revealed the formation of binuclear macrocyclic complexes of the general formula $[M(L^n)]_2$ with tetrahedral geometries for Mn^{II}, Co^{II}, and square planar geometry with Cu^{II} complex. Bacterial activity of the ligands and their metal complexes were screened for their antibacterial activity against four bacterial species (Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus and Bacillus stubtilis), which revealed that the complexes are potentially more active against these bacterial strains, compared with the free ligand.

Keywords: Dithiocarbamate macrocyclic complexes; One-pot reaction; Structural studies; Bacterial activity.

INTRODUCTION

Dithiocarbamates (DTCs) are a group of small organic molecules that have strongly chelating ability towards metal ions [1,2]. Their ability to bind transition metals, including lanthanide and actinide and representative elements make them useful ligands in both inorganic and bioinorganic chemistry. This is based on the presence of the anionic CS_2^- moiety that has a range of binding modes; monodentate, bidentate or bridging, upon complexation [3-5]. Dithiocarbamates are flexible ligands that have the ability to stabilize metal ion in a range of oxidation states and allowing the metal ion to implement its most preferable geometry [6]. Dithiocarbamates have been widely investigated due to their numerous applications in medicine [7], materials science [8], environmental applications [9] and in the industry [10]. Many researchers reported the act of dithiocarbamates against some tumours, fungi, bacteria, and other microorganisms [11, 12]. In this paper, we report the preparation, structural characterisation and bacterial activity of new DTC ligand and its macrocyclic metal-based complexes.

MATERIALS AND METHODS

Materials

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use.

Physical measurements

Elemental analyses (C, H, N and S) for ligand and their metal complexes were carried out on a Heraeus instrument (Vario EL) and Euro EA 3000. Melting points were obtained 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 were measured between 200-1100 nm with 10^{-3} M solutions in dimethylsulfoxide (DMSO) spectroscopic grade solvent at 25 °C using a Perkin-Elmer spectrophotometer Lambda. Thermogravimetric analysis was 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. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Conductivity measurements were made with DMSO solutions using a Jenway 4071 digital conductivity meter at room temperature. Magnetic moments were measured with a magnetic susceptibility balance (Sherwood Scientific).

SynthesisPreparation of the bis-amine precursor

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

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). Chloroacetyl chloride (1.49g, 13.24mmol) dissolved in $CHCl_3$ (50mL) was added dropwise with stirring to the above mixture. After 15 minutes a white precipitate that formed was filtered off and then washed with Et_2O (20mL). The mixture was air-dried and a 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 $[M-(NH\text{-}CO\text{-}CH_2Cl)]^+$ and $[M-(NH\text{-}CO\text{-}CH_2Cl)+(NH\text{-}CO\text{-}CH_2Cl)]^+$, respectively, Figure (1).

NMR data (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 (CH_2Cl, $2C_1$), 119.09 and 126.60 (Ar-$C_{4,5,6,7}$), 164.59 ($2C_2$=O), Figure (3).

Preparation of bis-amine N,N'-(biphenyl-4,4'-diyl)bis(2-(propylamino) acetamide)

An excess of propyl-1-amine (2.97g, 50.29mmol) was heated up to 40 ºC, and then *N,N'*-(biphenyl-4,4'-diyl)bis(2-chloroacetamide) (4.24g, 12.57mmol) was added portion-wise with stirring. The mixture was stirred at 40 ºC for 12 h, and then H_2O (200mL) was added. The product was extracted into CH_2Cl_2 (4 x 50 mL), washed with H_2O (200mL) and dried over K_2CO_3. Solvent was removed under reduced pressure and yellow oil was obtained. Yield: 2.96g, (61%). FTIR (cm^{-1}), 3305 ν(N-H), 3236 ν(-CON-*H*), 3236 ν(N-*H*),3045 ν_{arom}(C-H), 1674 ν(C=O), 1583 δ(N-H), 1520 ν_{arom}(C=C). The electrospray (+) mass spectrum of the bis-amine showed the parent ion peak at *m/z* =383.1 $(M+H)^+$ (7%) for $C_{22}H_{30}N_4O_2$; requires =382.50 and the following fragments at *m/z* =298.7 (70%), 184.8(8%) and 154.6(7%) corresponding to $[M-(CH_3CH_2CH{=}CHCH_2CH_3)]^+$, $[M-(CH_3CH_2CH{=}CHCH_2CH_3)+(NH_2\text{-}CH\text{-}CO)_2]^+$ and $[M-(CH_3CH_2CH{=}CHCH_2CH_3)+(NH_2\text{-}CH\text{-}CO)_2+(NH_2NH_2)]^+$, respectively.

NMR data (ppm), δ_H(400 MHz, DMSO-d_6): 0.99 (6H, t, J_{HH}=3Hz, ($C_{A,A`}$-*H*), 1.26 (4H, m, ($C_{B,B`}$-*H*),1.72 (4H, t, J_{HH}=1.8Hz, ($C_{C,C`}$-*H*)), 2.99,3.00 (2H, m, 2NH), 6.78 (2H, s, amidic-*H*),7.42 (4H, d, $J_{HH}$=12Hz, ($C_{4,4`,6,6`}$-*H*)),7.54 (4H, d, $J_{HH}$=6.8Hz, ($C_{5,5`,7,7`}$-*H*)) (Aromatic-H), Figure (4). $\delta_C$ (100.63 MHz, DMSO-$d_6$): 12.11 ($C_{A,A`}$), 31.972 ($C_{B,B`}$), 49.71 ($C_{C,C`}$), 54.15 ($C_{1,1`}$), 119.102 ($C_{4,4`,6,6`}$), 130.23 ($C_{5,5`,7,7`}$), 172.52 (C=O, ($C_{2,2`}$)), Figure (5).

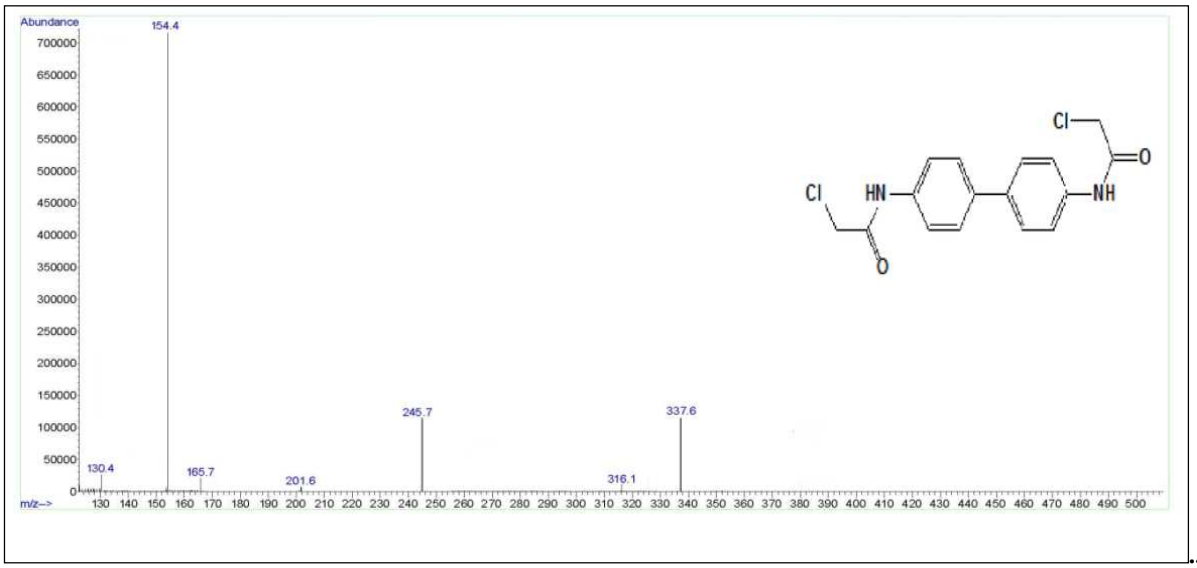


Figure (1): ES (+) mass spectrum of acetamide precursor

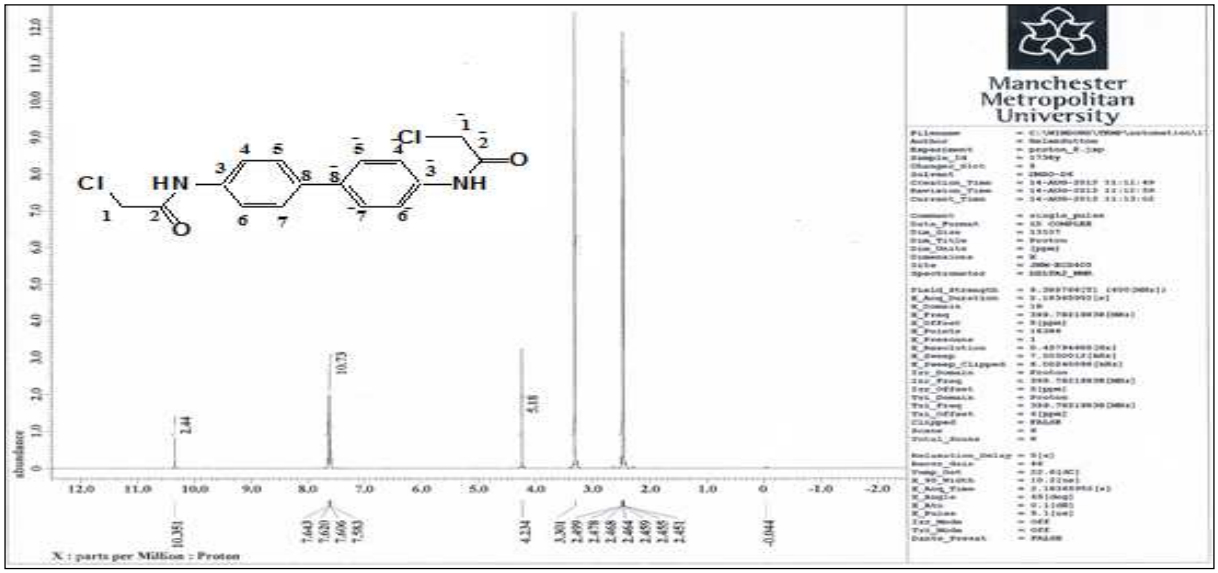


Figure (2): ^{1}H-NMR spectrum of acetamide precursor in DMSO-d$_6$

Synthesis of free ligand

The free ligand potassium2,2'-(biphenyl-4,4'-diylbis(azanediyl))bis(1-chloro-2-oxoethane-2,1-diyl)bis(propyl carbamodithioate) (L) was prepared according to standard method used in the synthesis of dithiocarbamte compounds [15] and as follows:

To a solution of bis-amine(N,N'-(biphenyl-4,4'-diyl)bis(2-(propylamine)acetamide (0.30g, 0.816mmol) in 10 mL of a mixture of MeCN:H_2O (9:1), was added an excess of KOH (0.18g, 3.26mmol, 4eq) dissolved in H_2O (2mL). The mixture was allowed to stir in an ice bath, and then a solution of carbon disulfide (0.18g, 2.44mmol, 3 eq) was added dropwise with stirring. The mixture was allowed to stir at 0 °C for 2 h, during that the formation of the potassium dithiocarbamate salt was obtained as a light orange solid, m.p=165-167 ºC. Yield: 0.31g, (63.26%).FTIR (cm^{-1}), 3298 ν(-CON-*H*), 3097 ν_{ar}(C-H), 1674 ν(C=O), 1591 δ(N-H), 1531 ν_{arom}(C=C), 1416 ν(N-CS_2), 1009, 972 $\nu_{as,s}$(CS_2).. The electrospray (+) mass spectrum of the L showed the parent ion peak at *m/z*=611.8 $(M+H)^+$ (3%) for $C_{24}H_{28}K_2N_4O_2S_4$; requires =610.97 and the following fragments at *m/z*=381.4 (3%), 338.3 (22%), 225.2 (4%) and

154.1(4%) corresponding to $[M-(CS_2K)_2]^+$, $[M-(CS_2K)_2+(CH_3-CH_2-CH_2)]^+$, $[M-(CS_2K)_2+(CH_3-CH_2-CH_2)+(CH_3-CH_2-CH_2)+(NH-CO-CH_2N)]^+$, $[M-(CS_2K)_2+(CH_3-CH_2-CH_2)+(CH_3-CH_2-CH_2)+(NH-CO-CH_2N)]^+$ and $[M-(CS_2K)_2+(CH_3-CH_2-CH_2)+(CH_3-CH_2-CH_2)+(NH-CO-CH_2N)+(NH-CO-CH_2-NH)]^+$. NMR data (ppm), δ_H(300 MHz, DMSO-d_6): 1.54 (6H, t, J_{HH}=8.1Hz, ($C_{A,A}$`-*H*)), 1.68-1.69 (4H, m, ($C_{B,B}$`-*H*),), 3.62 (4H, t, ($C_{C,C}$`-*H*)),3.32 (4H, s,($C_{2,2}$`-*H*)), 7.76, 7.77 (4H, d, J_{HH}=2.4 Hz, $C_{6,6`,8,8`}$-*H*), 8.29, 8.30 (4H, d, J_{HH}=1.8 Hz, ($C_{5,5`,7,7`}$-*H*) (Ar-H), 9.86 (2H, s, amidic-*H*), Figure (8) ; δ_C (75 MHz, DMSO-d_6): 11.21 (CH_3, $C_{A,A}$`), 19.69 ($CH_2$, $C_{B,B}$`), 55.62 (CH_2, $C_{C,C}$`), 66.34 ($CH_2$, ($C_{2,2}$`)), 114.20 ($C_{5,5`,7,7`}$), 123.56 ($C_{6,6`,8,8`}$), 167.25 (C=O) ($C_{3,3}$`), 191.87 (C=S) ($C_{1,1}$`), Figure (9).

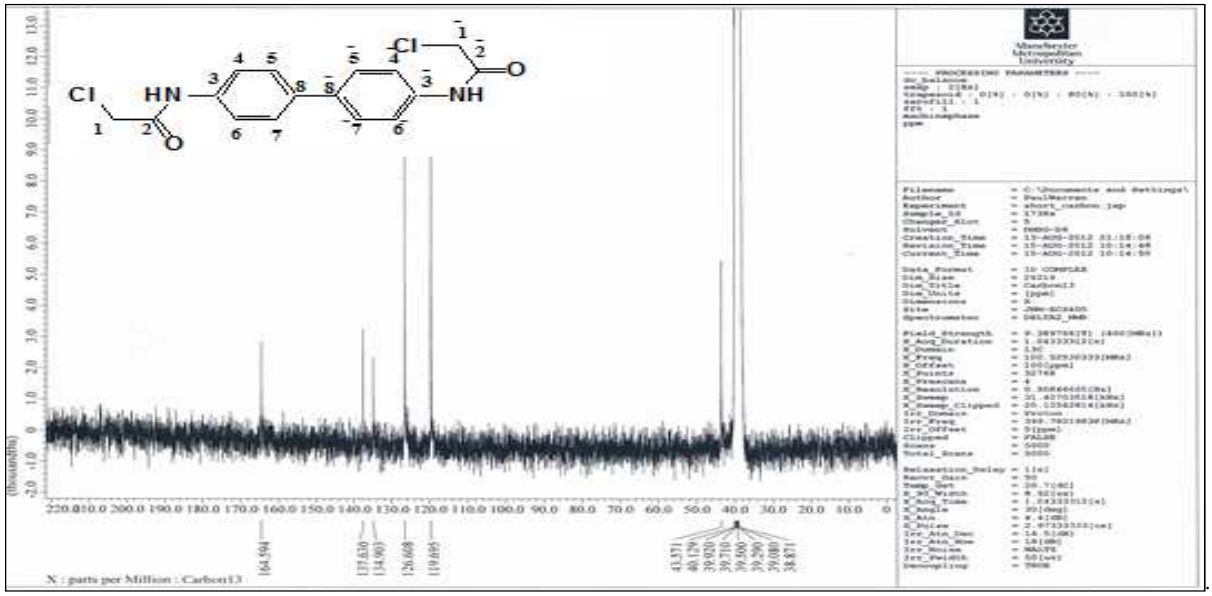


Figure (3): ^{13}C-NMR spectrum of acetamide precursor in DMSO-d_6

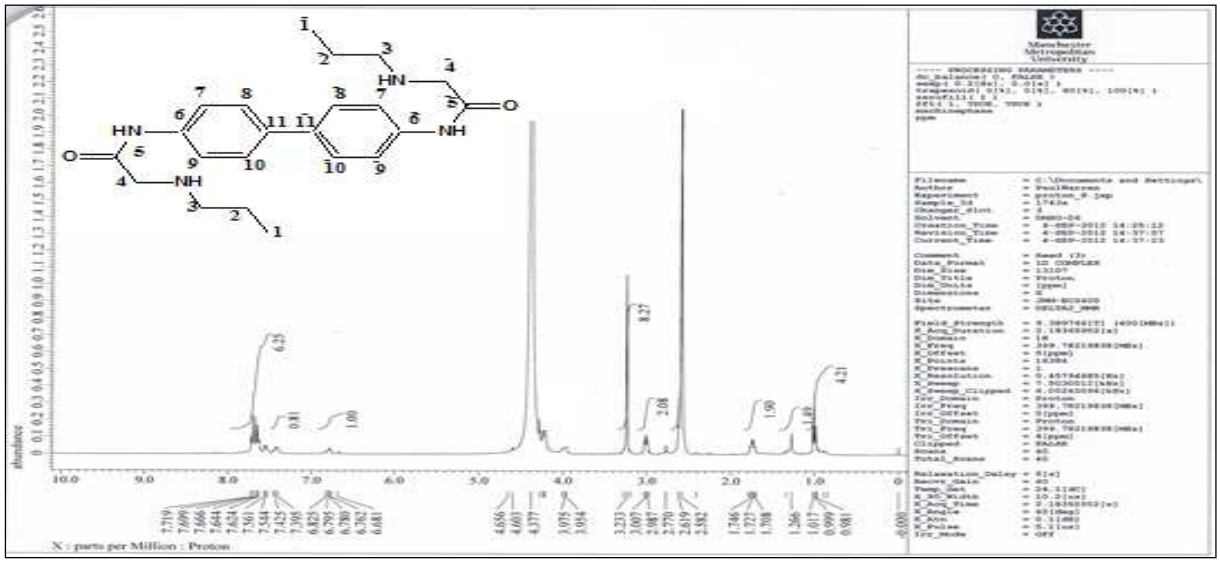


Figure (4): ^{1}H-NMR spectrum of the propyl amine precursor in DMSO-d_6

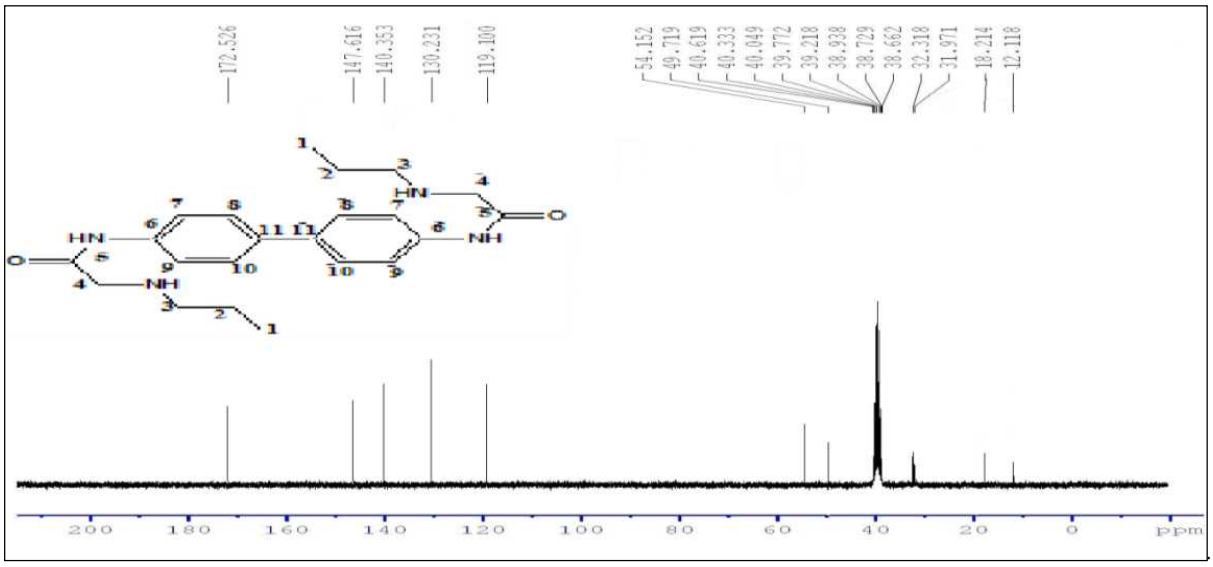


Figure (5): ^{13}C-NMR spectrum of propylamine precursor in DMSO-d_6

General method for synthesis of macrocyclic complexes

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

Synthesis of macrocyclic complexes from free ligand

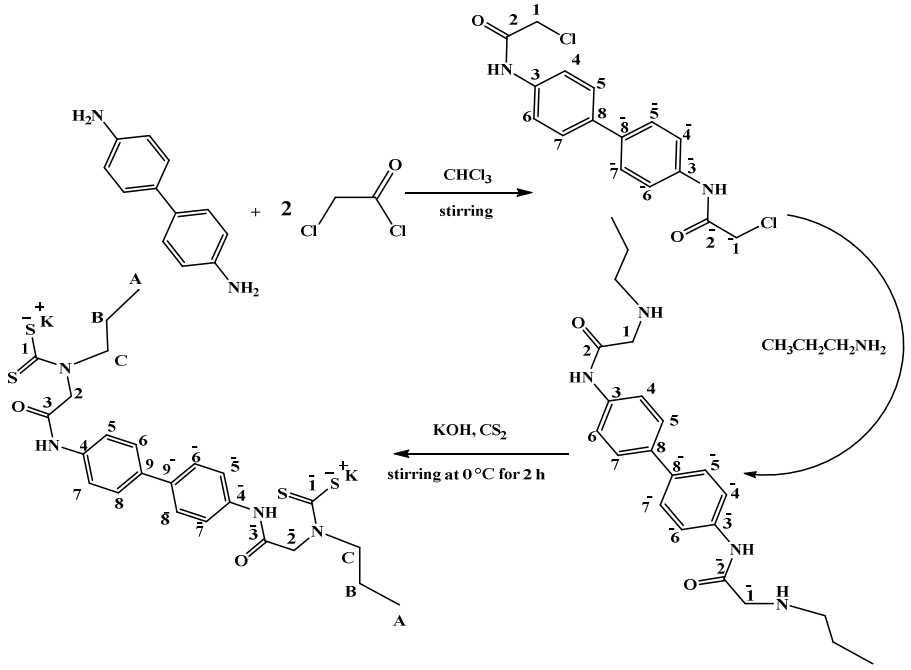
Complexes were prepared from the reaction of 1equivalent of potassium dithiocarbamate salt, dissolved in 10mL of MeCN/H_2O (9:1) with 1 equivalent of the metal salt; Mn^{II}, Co^{II}, and Cu^{II}. The solution mixture was allowed to stir overnight, after that distilled water was added, if necessary, to precipitate the product. The resulted solid was filtered off, washed with methanol to give the macrocyclic complex. Elemental analysis data, colours and yields for the complexes are given in Table (1).

Synthesis of macrocyclic complexes via a one-pot reaction

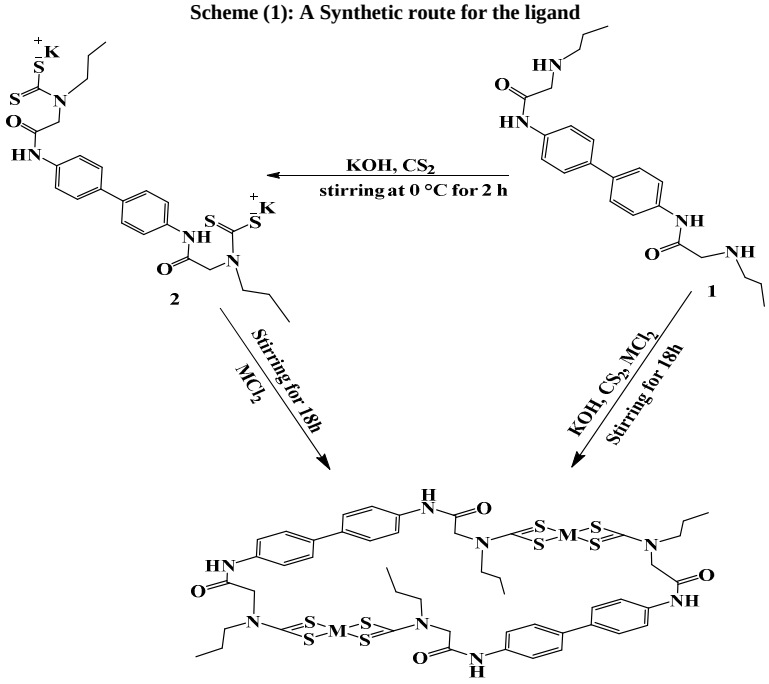
To a solution of the secondary amine in MeCN/H_2O mixture (9:1) was added with stirring an excess of KOH (3eq). Carbon disulfide (2.8 equivalents) was added to the solution, and the mixture was stirred for 10 minutes allowing the formation of the potassium dithiocarbamate salt. The complex was prepared *in situ* (ligand salt was not isolated) by the addition of one equivalent of the metal ion. The mixture was stirred overnight, water was added for precipitation if required, filtered and dried to give the macrocyclic complex. Analytical data are similar to that complexes obtained from the free ligand approach.

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

Comp.	Empirical formula	m.p	Yield %	colour	$\Lambda_M(\Omega^{-1}cm^2mol^{-1})$	Microanalysis; Found (calc) %				
						M%	C	H	N	S
L	$C_{24}H_{28}K_2N_4O_2S_4$	165-167	63.26	light orange	-	-	46.84 (47.18)	3.95 (4.62)	9.99 (9.17)	19.23 (20.99)
$[Mn(L)]_2$	$C_{48}H_{56}N_8O_4S_8Mn_2$	305*	47.36	Deep green	12.08	9.01 (9. 35)	48.57 (49.05)	4.23 (4.80)	9.68 (9.53)	21.17 (21. 82)
$[Co(L)]_2$	$C_{48}H_{56}N_8O_4S_8Co_2$	285*	49.35	Brown	10.99	9.31 (9. 96)	47.88 (48.72)	4.08 (4.77)	9.83 (9.47)	21.57 (21. 68)
$[Cu(L)]_2$	$C_{48}H_{56}N_8O_4S_8Cu_2$	270*	38.46	Dark green	6.77	9.56 (10.66)	48.01 (48.34)	4.12 (4.73)	9.71 (9.40)	20.77 (21.51)



Scheme (1): A Synthetic route for the ligand



M = Mn^{II}, Co^{II} and Cu^{II}

Scheme (2): Synthetic route of macrocyclic complexes; (1) a one pot approach; (2) from free ligand

RESULTS AND DISCUSSION

Chemistry

The free ligand was prepared from the reaction of carbon disulfide and secondary amines in the presence of KOH (see Scheme (1)). Dithiocarbamatemacrocyclic complexes were prepared either via a one-pot approach or from the reaction of the free ligand with metal, Scheme (2). The dithiocarbamate moieties are separated by aromatic amides

spacer. This spacer conferred a degree of rigidity upon the formation of ligand, thus play a role in pre-organising it for self-assembly upon complexation. The complexes are air stable that soluble in hot DMSO rather than other organic solvents.

FTIR and NMR spectra

Ligand and its complexes were characterised as required by elemental analysis, thermal analysis, FTIR, UV-Vis, mass spectroscopy, magnetic susceptibility, conductance, melting points and ^{1}H, ^{13}C-NMR spectroscopy. The FTIR spectrum of L shows characteristic band around 3298cm^{-1} due to ν(N–H) stretching. Band due to ν(C=O) amide is detected at 1674 cm^{-1}. Bands at 1109 and 972cm^{-1} assigned to the $\nu_{as}(CS_2)$ and $\nu_s(CS_2)$ functional groups (see Table (2) Figure (6). The FTIR spectra of the dinuclear-macrocyclic complexes gave evidence for the formation of the dithiocarbamate functions and their coordination to the metal ions. Bands at 1421-1444 cm^{-1} that resulted from the stretching of the *C-N*-S bonds; C-N single bonds at 1221-1238 cm^{-1}, suggesting a partial delocalization of π-electron density within the dithiocarbamate functions [18]. For the CS_2 groups, band at 1015-1122 cm^{-1} and 960-995 cm^{-1} are assigned to $\nu_{as}(CS_2)$ and $\nu_s(CS_2)$, respectively. This is characteristic of an anisobidentate chelation mode of the ligand to the metal atoms [19, 20]. At lower frequency the complexes exhibited two sets of bands around 362-391 cm^{-1}, which are assigned to the ν(M-S) vibration mode, and supporting the anisobidentate chelation mode of the ligand [8]. Figure (7) represents the FTIR spectrum of Mn-complex.

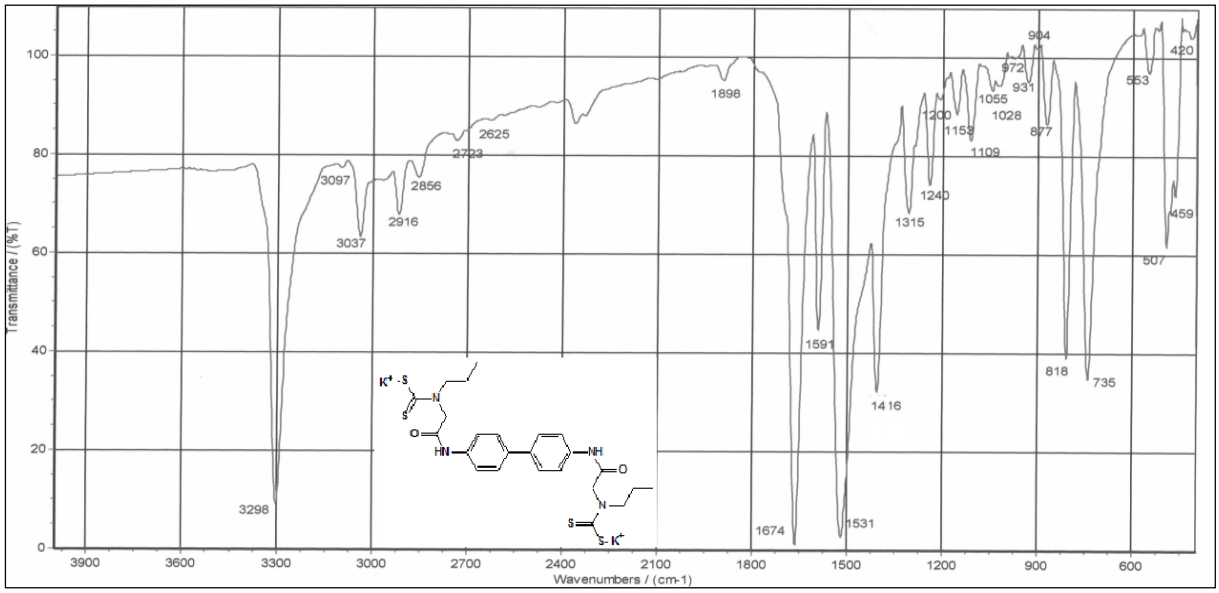


Figure (6): FTIR spectrum of ligand

Table (2): FTIR spectral data (wave number) cm^{-1} of ligand and its 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^1	3298	3097	2916-2856	1674	1591	1531	1416	1109, 972	1240
$[Mn(L)]_2$	3313	3032	2964, 2862	1662	1604	1500	1421	1015,960	1238
$[Co(L)]_2$	3334	3018	2920	1670	1606	1496	1444	1122 ,995	1228
$[Cu(L)]_2$	3330	3003	2889	1656	1550	1493	1433	1059 ,972	1221

** ν(Mn-S) observed at 376.75 and 362.59cm^{-1}*
ν(Cu- S) observed at 385.74 and 378.02cm^{-1}

The ^{1}H NMR spectrum of L showed a peak at 3.32 ppm, assigned to ($CH_{2,}C_{2,\,2}$`-*H*). The downfield appearance of this signal may due to attachment to withdrawing groups (C=O and N-H). The $_{ami}$(N-*H*) signal for the amide segment is seen as a singlet at its expected resonance at δ= 9.86 ppm for L, Figure (8). The ^{13}C NMR spectrum of L shows a number of different carbon nucleuses in molecule indicating the formation of the ligand. The chemical shift of the carbonyl moiety appears as expected downfield at δ= 167.25 ppm in L. The formation of the free ligand has been revealed by detecting signals around δ=191.87 ppm, which can be attributed to quaternary carbon in dithiocarbamate moiety C=S in the ligand, Figure (9).

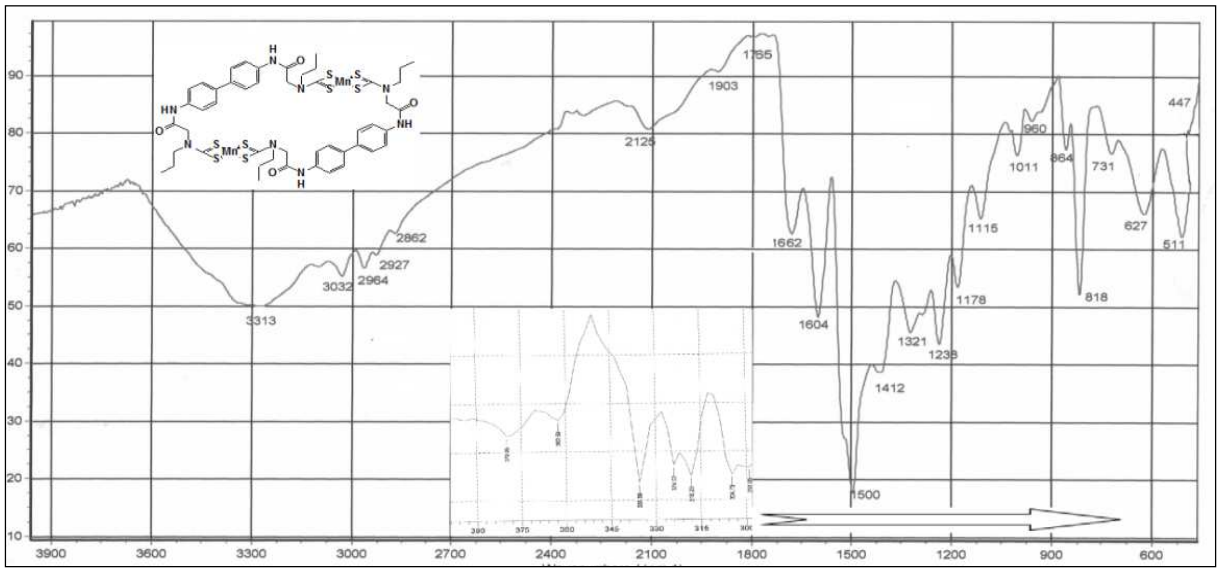


Figure (7): FTIR spectrum of $[Mn(L)]_2$ complex

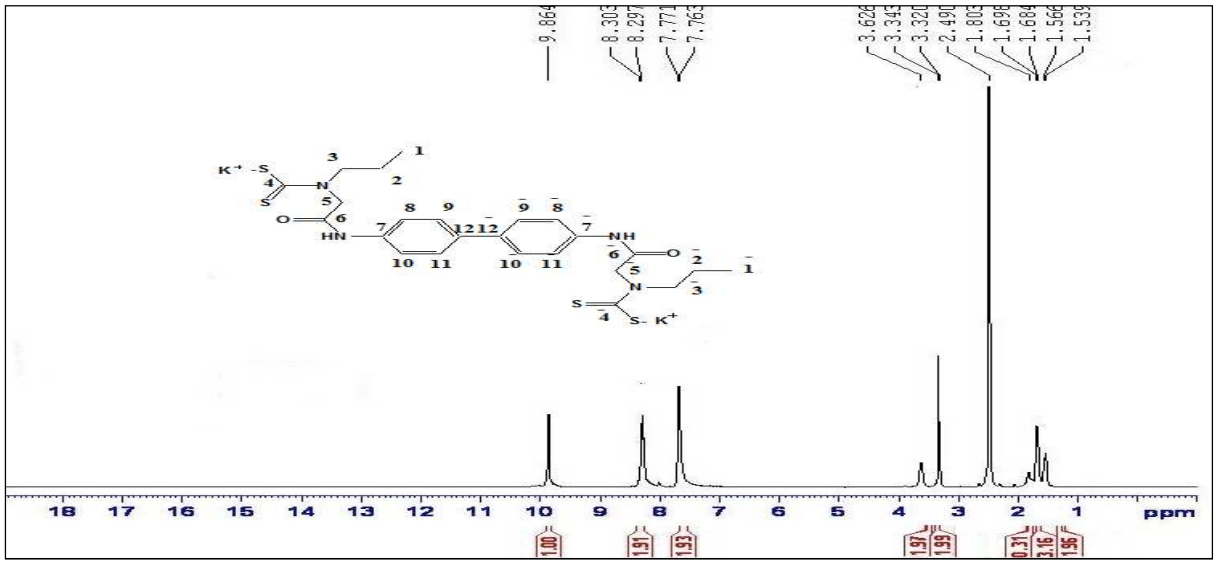


Figure (8): ^{1}H-NMR spectrum of the ligand in DMSO-d_6

UV-Vis Spectral data for the complexes and magnetic susceptibility

The UV-Vis spectra of L in DMSO solutions revealed peak at 268 and 328 nm assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively [21-23], Figure (10). The electronic spectra of the complexes exhibited various extents of bathochromic shift of bands at 269-273 nm related to the ligand field $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in L complexes. Bands at 344-384 nm related to the charge transfer transitions (CT) in L complexes [24]. The spectrum of the Mn(II)-complex showed a peak in the d-d region at 432 nm assigned to $^6A_1 \rightarrow {}^4A_1$ transition, indicating tetrahedral geometry about Mn(II) ion [25, 26]. The magnetic moment measurement of $[Mn^{II}(L)]_2$ reveals μ_{eff} value of 5.29 B.M. This value is typical for a high spin Mn(II) ion, which assigned to tetrahedral geometries for Mn(II)-complexes [25, 27]. The Co(II) complex displays additional peaks in the d-d region at 616 and 679 nm due to $^4T_1{}^{(F)} \rightarrow {}^4T_1{}^{(P)}$ and $^4A_2{}^{(F)} \rightarrow {}^4T_1{}^{(p)}$ transitions, respectively. This spectrum is characteristic for Co(II)-complexes with tetrahedral geometry around Co atom [26-28], Figure (11). Co.complex gaveμ_{eff} value of 4.69 B.M, which it is typical for complexes of tetrahedral geometries, indicating a high spin geometry around Co(II) ion [27, 29]. The spectrum of

the Cu(II)-complex showed a peak in the d-d region at 644 nm attributed to d-d transition type $^2B_1g \rightarrow {}^2B_2g$, confirming square planar geometry about Cu atom [24-26], Figure (12). The magnetic moment value of 1.7 B.M for $[Cu^{II}(L)]_2$ complex confirms the square planar geometry around Cu(II) ion [25, 27]. The molar conductance of the complexes in DMSO solutions is indicative of their non-electrolytic nature [30, 31], see Table (1). The UV-Vis bands and magnetic moment measurements of ligand complexes with their assignments are tabulated in Table (3).

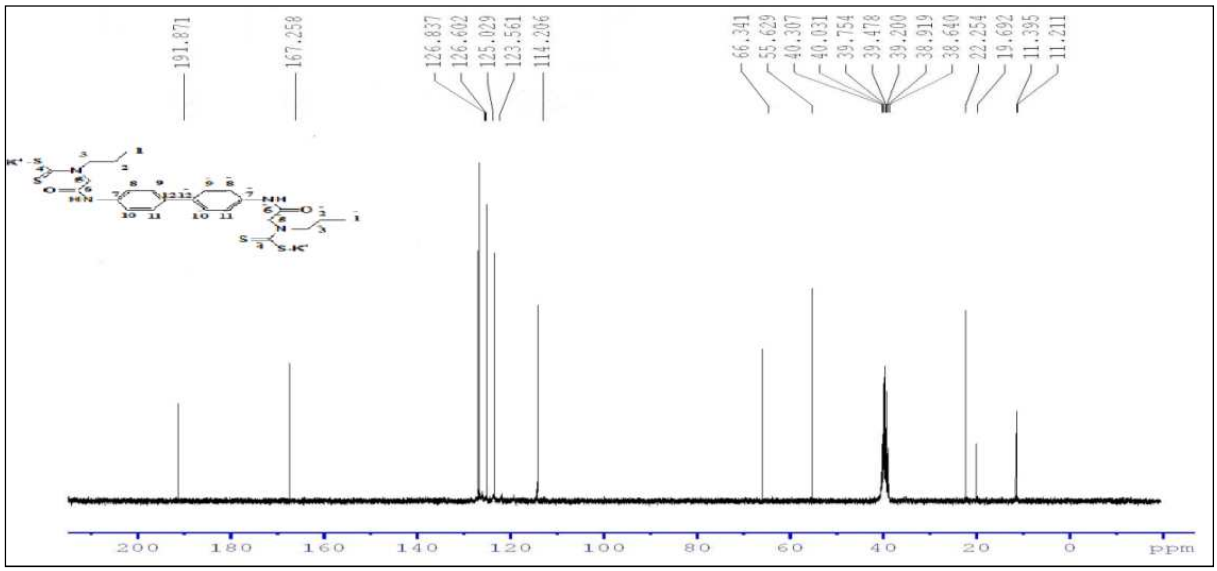


Figure (9): ^{13}C-NMR spectrum of the ligand in DMSO-d_6

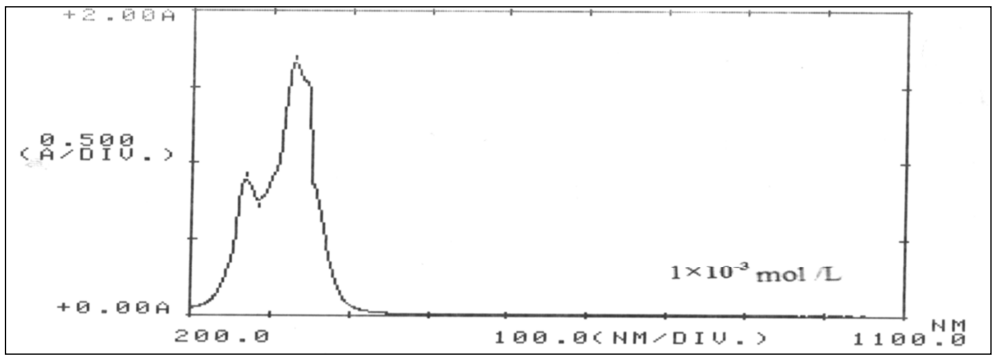


Figure (10): Electronic spectrum of L^1 in DMSO solution

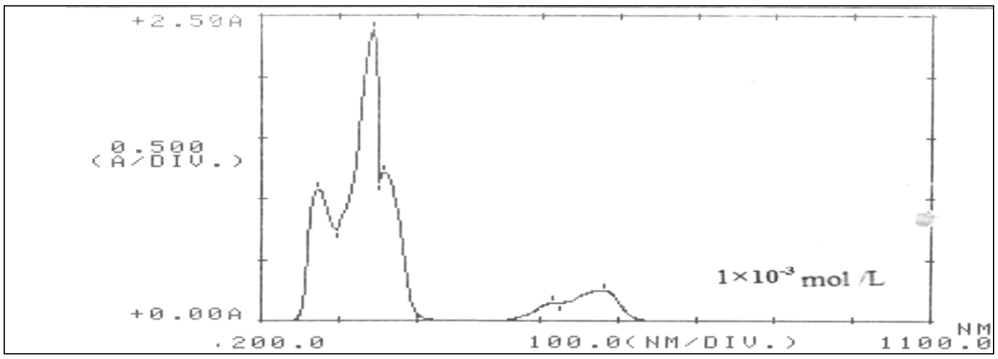


Figure (11): Electronic spectrum of $[Co(L)]_2$ in DMSO solution

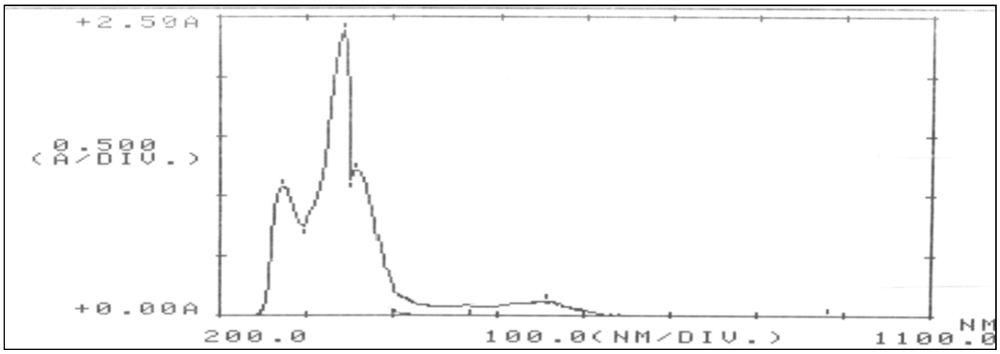


Figure (12): Electronic spectrum of $[Cu(L)]_2$ in DMSO solution

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

Comp.	Con. m/L	Band Position λ_{nm}	Wave number (cm^{-1})	Extinction coefficient ε_{max} ($dm^3 mol^{-1} cm^{-1}$)	Assignment	μ_{eff} (B.M)
L	1×10^{-3} 1×10^{-3}	268 328	37313 30487	894 1658	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	-
$[Mn(L)]_2$	1×10^{-3} 1×10^{-3} 1×10^{-3}	269 344 432	37174 29069 23148	1441 2263 180	Intra-ligand $\pi \rightarrow \pi^*$, n→π*C.T $^6A_1 \rightarrow {}^4T_1$	5.29
$[Co(L)]_2$	1×10^{-3} 1×10^{-3} 1×10^{-3} 1×10^{-3} 1×10^{-3}	273 344 380 616 679	36630 29069 26315 16233 14727	1073 2380 1090 136 185	Intra-ligand $\pi \rightarrow \pi^*$, n→π* C.T $^4T_1{}^{(F)} \rightarrow {}^4T_1{}^{(P)}$ $^4A_2{}^{(F)} \rightarrow {}^4T_1{}^{(p)}$	4.69
$[Cu(L)]_2$	1×10^{-3} 1×10^{-3} 1×10^{-3} 1×10^{-3}	273 344 384 644	36630 29069 26041 15527	1070 2378 1150 23	Intra-ligand $\pi \rightarrow \pi^*$, n→π* C.T $^2B_1g \rightarrow {}^2B_2g$	1.7

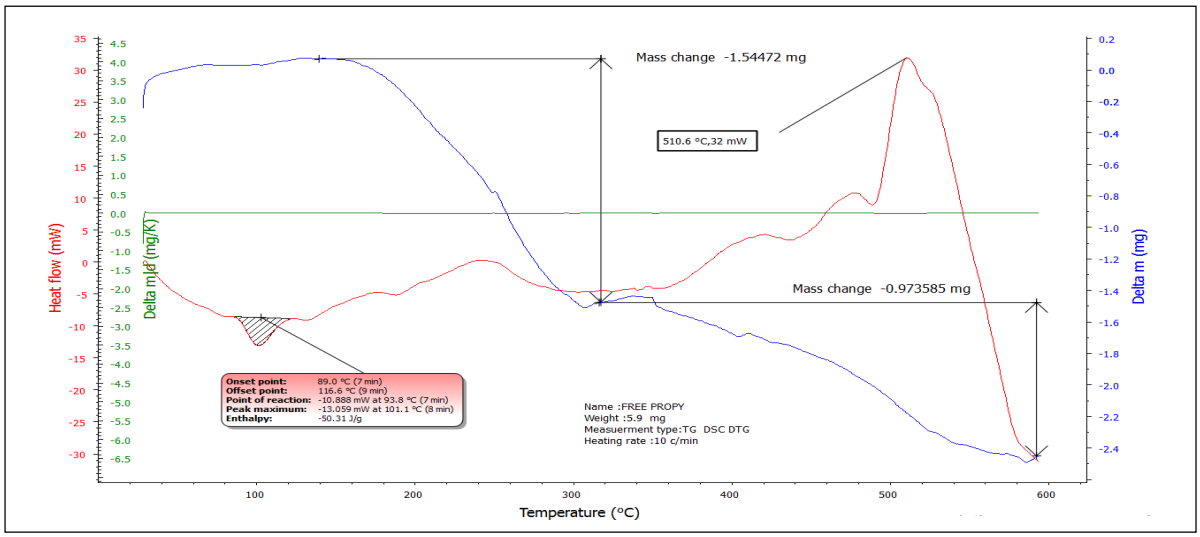


Figure (13): TG/ DTG and DSC thermogram of ligand in a nitrogen atmosphere

Thermal analysis

Thermal analysis data for the ligand and selected 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 the atmosphere of nitrogen. The analysis of thermal data showed the ligand is stable up to 148 °C with a weight loss of 26.18%, which attributed to (CS_2+$COCH_2NCH_2CH_3$) fragment. The peak detected at 340-595 °C related to ($CH_3CH_2CH_2CH_2CS$) segment with 16.56% weight loss. This peak accompanied by the endothermic effect in the DSC curve at 510.6 °C.

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

Compound	Stable up to °C	Stage	Decomp. Temp. initial-final °C	fragments	Nature of transformation /intermediate formed% mass found (calc.)	Nature of DSC peak and temp. °C	DTG peak temp. °C
L^1	148	1 2	148-320 340-595	(CS_2+$COCH_2NCH_2CH_3$) ($CH_3CH_2CH_2CH_2CS$)	1.5447 (1.5475) 0.9735 (0.9771)	93.8 Exo 510.6 Endo	- -
$[Mn(L^1)]_2$	108	1 2 3	108-503 210-316 220-503	($2CS_2$) ($HNCOCH_2NCH_2CH_2CH_3$) (3diphenyl+2$HNCOCH_2NCH_2CH_2CH_3$+$HNCCH_2NCH_2CH_2CH_3$)	1.0241 (1.0364) 0.7532 (0.7769) 5.0470(5.0618)	183.4 Endo 243.8 Endo 477.3Endo	- - -
$[Co(L^1)]_2$	255	1 2 3	255 260-360 668-765	($2CS_2$) ($CS_2NCH_2CH_2CH_3$) (diphenyl+2$HNCOCH_2N$+$HNCOCH_2$+$HNCOCH_2NCH_2CH_2CH_3$+CS_2)	1.3611 (1.4154) 1.3057 (1.3284) 5.0205 (5.0535)	55 Exo 456 Endo 497.2 Endo 559.8 Endo	360 - -

The final residue of the compound is attributed to the (diphenyl-NH, S, N, 2K and CO) with 54.91% weight loss, Figure (13).Thermal data of $Mn(L^1)]_2$ (Figure (14)) and $[Co(L)]_2$ (Figure (15)) complexes consists of three steps. The first step accompanied by exothermic behaviour as confirmed by the DSC at 55 °C for $[Co(L)]_2$ complex. However, $[Mn(L)]_2$ exhibits an endothermic peak at 183.4 °C [32, 33]. The weight loss and other thermal properties including lost fragments of the complexes are tabulated in Table (4).

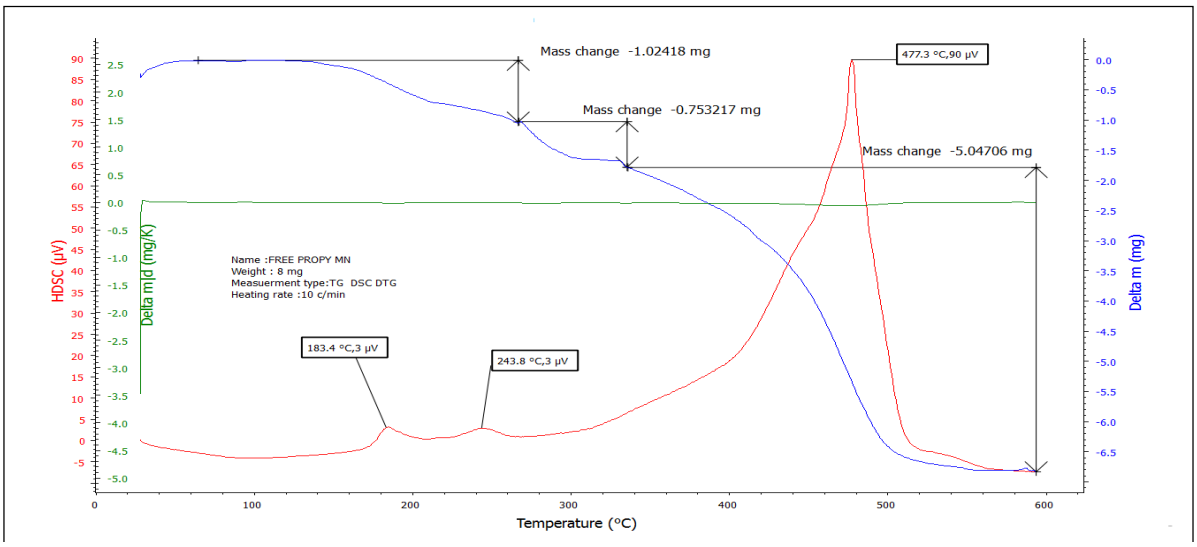


Figure (14): TG/DTG and DSC thermogram of $[Mn(L)]_2$ complex in nitrogen atmosphere

Biological activity

The synthesised dithiocarbamate ligand and its- metal complexes were screened for their antimicrobial activity against four bacterial species *(Escherichia coli, Pseudomonas aeruginosa* (G−), *Staphylococcus aureus and Bacillus stubtilis* (G+)). The role of DMSO in the biological screening was clarified by separate studies carried out with the solutions of DMSO alone, which showed no activity against any bacterial strains [34]. The measured zones of inhibition against the growth of different microorganisms are listed in Table (5) that displays the effect of the synthesised compounds on bacterial strains. Table (5) indicated that complexes found are potentially more active against these bacterial strains, compared with the free ligand, which means complexation increases antimicrobial activity (except Mn-complex with *B. Sabtilis and S aureus* strains). This may be explained by chelation effect in which the partially sharing of the positive charge of the metal in complexes by the donor atoms present in the ligand

and there may be π-electron delocalization over the whole chelate ring that increases the lipophilic character of the metal chelate system. This will favour its permeation through lipid layer of the cell membranes [35, 36].

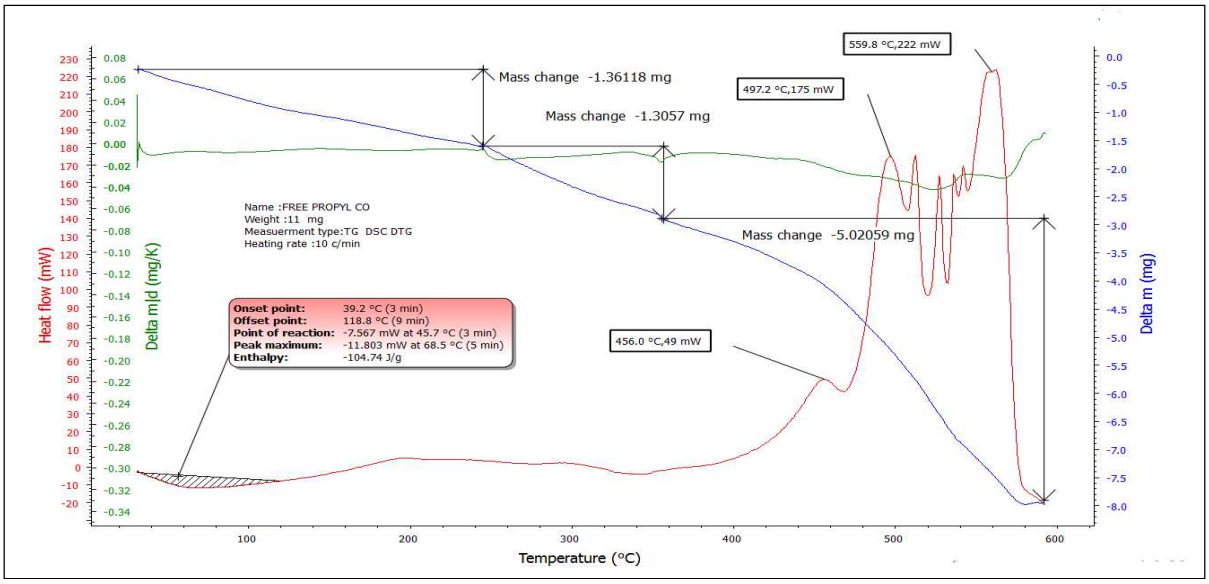


Figure (15): TG/DTG and DSC thermogram of $[Co(L)]_2$ complex in nitrogen atmosphere

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

No.	Sample	Inhibition zone (mm)			
		E. coli	*P. aeruginosa*	*B. sabtilis*	*S. aureus*
1	L	6	4	6	6
2	$[Mn(L)]_2$	11	10	-	-
3	$[Co(L)]_2$	12	11	11	10
5	$[Cu(L)]_2$	10	10	9	11

CONCLUSION

In this paper, we have explored the synthesis and characterisation of ligand and its bimetallic dithiocarbamate macrocyclic complexes. The macrocyclic complexes were prepared using two approaches; (i) from the reaction of the free ligand with a metal ion, and (ii) *via* a one-pot reaction. The mode of bonding and overall structure of the complexes were determined by physico-chemical and spectroscopic methods. These results indicated the formation of four-coordinate complexes in the solid state and in solution. Biological activities revealed that complexes found to be potentially more active against these bacterial strains, compared with the free ligand.

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