New Bis(dithiocarbamate) Ligand for Complex Formation; Synthesis, Spectral Analysis and Bacterial Activity

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Abstract

A range of macrocyclic dinuclear metal (II) dithiocarbamate-based complexes are reported. The preparation of complexes was accomplished from either mixing of the prepared ligand with a metal ion or through a template one-pot reaction. The preparation of the bis-amine precursor was achieved through several synthetic steps. The free ligand; potassium 2,2'-(biphenyl-4,4'-diylbis(azanediyl))bis(1-chloro-2-oxoethane-2,1-diyl)bis(cyclohexylcarbamodithioate) (L) was yielded from the addition of CS_2 to a bis-amine precursor in KOH medium.A variety of analytical and physical methods were implemented to characterise ligand and its complexes. The analyses were based on spectroscopic techniques (FTIR, UV-Vis, mass spectroscopy and ^1H, ^{13}C-NMR spectroscopy), melting points, elemental analysis, thermal properties, magnetic susceptibility and conductance. The analytical and physical techniques confirmed the formation of macrocyclic complexes of the general formulae $[M(L)]_2$ (M= Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II}). The proposed structure around Mn^{II}, Co^{II}, Zn^{II} and Cd^{II} is a tetrahedral, while Ni^{II} and Cu^{II} complexes adopt square planar geometries. The prepared compounds were screened against four bacterial species *(Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus and Bacillus stubtilis)*. The anti-bacterial test indicated that the complexes are more active against these bacterial strains, compared with the free ligand.

Keywords: Bis(dithiocarbamate) ligand; Metal complexes; Spectral studies; Thermal properties; Bacterial activity.

1. Introduction

Dithiocarbamates are flexible compounds that have shown a range of applications. These species played a significant role in the expansion of chemistry, due to their importance in synthetic inorganic [1], bioinorganic [2], analytical [3] and environmental chemistry [4]. Dithiocarbamates (DTCs) are flexible ligands that have the ability to bind transition and representative elements. The importance of dithiocarbamates (DTCs) is due to their capability to stabilize metal ion in a variety of oxidation states. This is related to their strongly chelating ability towards metal ions. Further, upon complexation, these species permitting the metal ion to adopt its most preferable geometry [5]. The presence of the anionic CS_2^- moiety allowed DTCs molecules to achieve a range of binding modes; monodentate, bidentate or bridging, upon complexation [6-8]. Dithiocarbamates are essential materials that have been widely explored due to their applications in coordination chemistry [1], materials science [9], medicine and radiopharmaceutical chemistry [10, 11], sensing technology [12] and in the industry [13]. More, the act of dithiocarbamates against some tumours, fungi, bacteria, and other microorganisms [14, 15] make them a hot topic for several research groups. In this paper, we report the preparation, spectral analysis and bacterial activity of a new DTC ligand and its macrocyclic metal-based complexes.

2. Experimental

2.1. Chemicals

Chemicals and solvents were purchased commercially and used as received.

2.2. Instruments

Elemental micro-analyses (C, H, N and S) for ligand and its metal complexes were conducted on a Euro EA 3000. Electrothermal Stuart SMP40 apparatus was used to record melting points. FT-Infrared spectra were recorded as KBr discs with a Shimadzu 8300s FT-IR spectrophotometer in the range 4000-400 cm^{-1} and as CsI discs in the range 400-200 cm^{-1}. UV-Vis spectra were obtained with 10^{-3} M solutions between 200-1100 nm in dimethylsulfoxide (DMSO) spectroscopic grade solvent at 25 °C using a Perkin-Elmer spectrophotometer Lambda. Thermogravimetric analysis was carried out using a STA PT-1000 Linseis company /Germany. Electrospray mass spectroscopy technique (ESMS) was used to measure mass spectra for samples. NMR spectra (^{1}H, ^{13}C-NMR) were acquired in DMSO-d_6 solutions using a Brucker-300 for ^{1}H-NMR and 75 MHz for ^{13}C-NMR, respectively with tetramethylsilane (TMS) for ^{1}H NMR. A Shimadzu (A.A) 680 G atomic absorption spectrophotometer was implemented to determine metal content in complexes. Conductivity measurements were performed using a Jenway 4071 digital conductivity meter with DMSO solutions at room temperature. A magnetic susceptibility balance (Sherwood Scientific) was used to determine magnetic moments of complexes.

3. Synthesis

3.1. Preparation of the bis-amine precursors

In this work, standard methods reported in [16, 17] were used for the preparation of the precursors. The free bis-amine precursor was prepared by two steps, and as follows:

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

To a mixture of benzidine (2.44g, 13.24mmol) dissolved in chloroform (75mL), was added with stirring potassium hydroxide (2.626g, 46.88mmol) in water (35mL). To this mixture, dichloroacetyl chloride (6.90g, 46.88mmol) in chloroform (75mL) was added drop-wise with stirring. The mixture was left to stir for 15 minutes, during which time a white precipitate was formed, which filtered off and then washed with diethyl ether (30mL). The collected white solid was air-dried, m.p=235-237 ºC. Yield: 9.04g, (94%). FTIR (cm^{-1}), 3249 ν(-CON-H), 1674 ν(C=O), 1606 δ(N-H), 1529 ν_{ar}(C=C). The electrospray (+) mass spectrum of the N,N'-(biphenyl-4,4'-diyl)bis(2-dichloroacetamide) exhibited the parent ion peak at *m/z* = 406.1$(M)^+$ (28%) for $C_{16}H_{12}Cl_4N_2O_2$; requires =406.09 and the following fragments; 280.2 (40%) and 154.2 (13%) correspond to $[M-(NH-CO-CHCl_2)]^+$ and $[M-(NH-CO-CHCl_2)+(NH-CO-CHCl_2)]^+$, respectively. NMR data (ppm), δ_H(300 MHz, DMSO-d_6): 8.63 (2H, s, N-*H*), 7.68, 7.69 (4H, d, J_{HH}= 2.1 Hz), 7.40, 7.41 (4H, d, J_{HH}= 2.4 Hz) ($C_{4,\,4`,\,6,\,6`}$-*H*) ($C_{5,\,5`,\,7,\,7`}$-*H*)Ar-*H*, 6.70 (2H, s,$CHCl_2$) ($C_{1,\,1`}$-*H*); δ_C(75MHz, DMSO-d_6): 59.90 (C*H*Cl_2, 2C_1), 120.26 and 126.81 (Ar-$C_{4,\,5,\,6,\,7}$), 161.32 (2C_2=O).

3.1.2. Preparation of bis-amine N,N'-(biphenyl-4,4'-diyl)bis(2-(cyclohexylamine) chloroacetamide)

An excess of cyclohexylamine (3.90g, 39.40mmol) was warmed up to 40 ºC, and then N,N'-(biphenyl-4,4'-diyl)bis(2-dichloroacetamide) (4.00g, 9.85mmol) was added portion-wise with stirring. The reactants was stirred at 40 ºC for 12 h, and then water (200mL) was poured in the mixture. The title compound was extracted into dichloromethane (4 x 50 mL), washed with water (200mL) and dried over K_2CO_3. On removing solvent under reduced pressure, brown oil compound was collected as the required material. Yield: 2.86g (54 %). FTIR cm^{-1}, 3342 ν(N-H), 3222 ν(-CON-*H*), 3032 ν_{ar}(C-H), 2929 and 2858 ν_{ali}(C-H), 1676 ν(C=O), 1622 δ(N-H), 1498 ν_{ar}(C=C) , 700 ν (C-Cl). The electrospray (+) mass spectrum of the bis-amine showed the parent ion peak at *m/z* =532.2 $(M+H)^+$ (7%) for $C_{28}H_{34}Cl_2N_4O_2$, requires =531.52 and the following fragments at *m/z* =343.9 (16%) , 260.8 (90%) and 154.3 (14%), corresponding to $[M-(C_6H_6-NH-Cl-CO-NH)]^+$, $[M-(C_6H_6-NH-Cl-CO-NH)+(C_6H_6)]^+$ and $[M-(C_6H_6-NH-Cl-CO-NH)+(C_6H_6)+(NH_2-Cl-CO-NH)]^+$, respectively. NMR data (ppm), δ_H(300 MHz, DMSO-d_6): 1.09-1.25 (8H, q, J_{HH}=4.8Hz,($C_{B,\,B`\,F,\,F`}$-*H*)), 1.48-1.52 (12H, m, ($C_{C,\,C`,\,D,\,D`,\,E,\,E`}$-*H*)), 3.16-3.17 (2H, m, ($C_{A,\,A`}$-*H*)), 3.91 (2H, t, NH), 5.38 (2H, d, J_{HH}=2.1Hz, ($C_{1,\,1`}$-*H*)), 8.87 (2H, s, amidic-*H*), 7.59 (4H, d, $J_{HH}$=6.3Hz, ($C_{4,\,4`,6,\,6`}$-*H*)), 7.54 (4H, d, $J_{HH}$=6.8Hz, ($C_{5,\,5`,\,7,\,7`}$-*H*)) (Aromatic-H); $\delta_C$ (75 MHz, DMSO-$d_6$): 23.90 ($C_{B,\,B`\,F,\,F`}$-*H*), 25.16 ($C_{C,\,C`,\,E,\,E`}$-*H*), 31.97 ($C_{D,\,D`}$), 56.30 ($C_{A,\,A`}$), 79.18 ($C_{1,\,1`}$), 119.65 ($C_{4,\,4`,\,6,\,6`}$), 131.31 ($C_{5,\,5`,\,7,\,7`}$), 163.64 (C=O, ($C_{2,\,2`}$)).

3.2. Synthesis of free ligand

A conventional procedure that used in the preparation of dithiocarbamte compounds [18] was adopted to obtain ligand and as follows:

3.2.potassium2,2'-(biphenyl-4,4'-diylbis(azanediyl))bis(1-chloro-2-oxoethane-2,1-diyl)bis (cyclohexylcarbamodithioate)

An excess of KOH (0.126g, 2.25mmol, 4eq) dissolved in H_2O (2mL) was added with stirring to a solution of N, N'-(biphenyl-4,4'-diyl)bis(2-(cyclohexylamine)chloroacetamide) (0.30g, 0.56mmol) in 10 mL of a mixture of acetonitrile:water (9:1). The mixture was placed in an ice bath, and then a mixture of CS_2 (0.128g, 1.69mmol, 3eq) was added portion-wise with stirring. The mixture was kept at 0 °C for 2 h, and then potassium dithiocarbamate salt was collected as a light yellow solid in good yield (0.28g, 66%), m. p=188-190 ºC. FTIR cm^{-1}, 3299 ν(-CON-*H*), 3086 ν_{ar}(C-H), 1676 ν(C=O), 1622 δ(N-H) 1545, ν_{ar}(C=C) , 1441ν($N-CS_2$), 1084, 976 $\nu_{as,\,s}$ (CS_2) 654ν (C-Cl). The electrospray (+) mass spectrum of the L showed the parent ion peak at *m/z*=760.4 $(M+H)^+$ (14%) for $C_{30}H_{34}Cl_2K_2N_4O_2S_4$; requires =759.98 and the following fragments at *m/z*=681.6(12%), 529.7(8%), 341.5(55%) and 153.8 (7%) corresponding to $[M-(K)_2]^+$, $[M-(K)_2+(CS_2)_2]^+$, $[M-(K)_2+(CS_2)_2+(NH-CO-CHCl-N-C_6H_{11})]^+$ and $[M-(K)_2+(CS_2)_2+(NH-CO-CHCl-N-C_6H_{11})+(NH-CO-CHCl-N-C_6H_{11})]^+$. NMR data (ppm), δ_H(300 MHz, DMSO-d_6): 1.79-1.83 (2H, m, $C_{A, A`}$-*H*), 1.50-1.60 (8H, q, $J_{HH}$=3 Hz, $C_{B, B` F, F`}$-*H*), 1.13-1.19 (12H, m, $C_{C, C`, D, D`, E, E`}$-*H*), 5.01-5.02 (2H, s, ($C_{2, 2`}$-*H*)) 7.81-7.82 (4H, d, $J_{HH}$=2.1 Hz, $C_{4, 4`, 6, 6`}$-*H*), 7.13-7.14 (4H, d, $J_{HH}$=2.7 Hz, ($C_{5, 5`, 7, 7`}$-*H*) )(Ar-H), 8.50 (2H, s, amidic-*H*); $\delta_C$ (75 MHz, DMSO-$d_6$): 24.457 ($C_{C, C` E, E`}$), 25.17 ($C_{D, D`}$), 32.32 ($C_{B, B`,F, F`}$), 77.84 ($C_{2, 2`}$), 119.95 ($C_{4, 4`, 6, 6`}$), 128.76 ($C_{5, 5`, 7, 7`}$), 160.33 (C=O) ($C_{3, 3`}$), 189.87 (C=S) ($C_{1, 1`}$).

3.3. General procedure for preparation of macrocyclic complexes

A standard method that reported in [19, 20] were implemented to prepare the binuclear macrocyclic dithiocarbamate-based complexes, which based on two approaches; (i) from the mixing of the free ligand with a metal ion, and (ii) through a one-pot template reaction.

3.3.1 .Formation of macrocyclic complexes from free ligand

The reaction of 1 equivalent of potassium dithiocarbamate salt, dissolved in 20mL of MeCN/H_2O (9:1) with 1 equivalent of the metal salt; Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II}, resulted in the formation of the title complex. The reaction mixture was allowed to stir overnight, and deionised H_2O was added, if necessary, to precipitate the compound. The solid was collected by filtration, washed with MeOH to give the macrocyclic complex. Elemental micro-analysis, colours and yields for the complexes are presented in (Table1). The ^{1}H-NMR data (ppm) for $[Cd(L)]_2$ complex, δ_H(300 MHz, DMSO-d_6): 1.83-1.84 (2H, m, $C_{A, A`}$ -*H*), 1.58 (8H, t, $J_{HH}$=16.1 Hz, $C_{B, B`, F, F`}$-*H*), 1.10-1.16 (12H, m, $C_{C, C`-D, D`-E, E`}$-*H*), 4.09 (2H, s, $C_{2, 2`}$-*H*), 7.70-7.72 (4H, d, $J_{HH}$=8.1Hz, C $C_{4, 4` 6, 6`}$-*H*), 6.87-6.91 (4H, d, $J_{HH}$=12.3 Hz, $C_{5, 5`, 7, 7`}$-*H*), 8.19 (2H, s, NH). The $^{13}$C-NMR spectrum for the $[Cd(L)]_2$, $\delta_C$(75 MHz, DMSO-$d_6$): 25.23 ($C_{B, B` F, F`}$), 25.63 ($C_{D, D`}$), 32.14 ($C_{C, C`, E, E`}$), 76.99($C_{2, 2`}$), 118.996 ($C_{4, 4`, 6, 6`}$), 127.87 ($C_{5, 5`, 7, 7`}$), 159.971 (C=O) ($C_{3, 3`}$), 208.12 (C =S) ($C_{1, 1`}$).

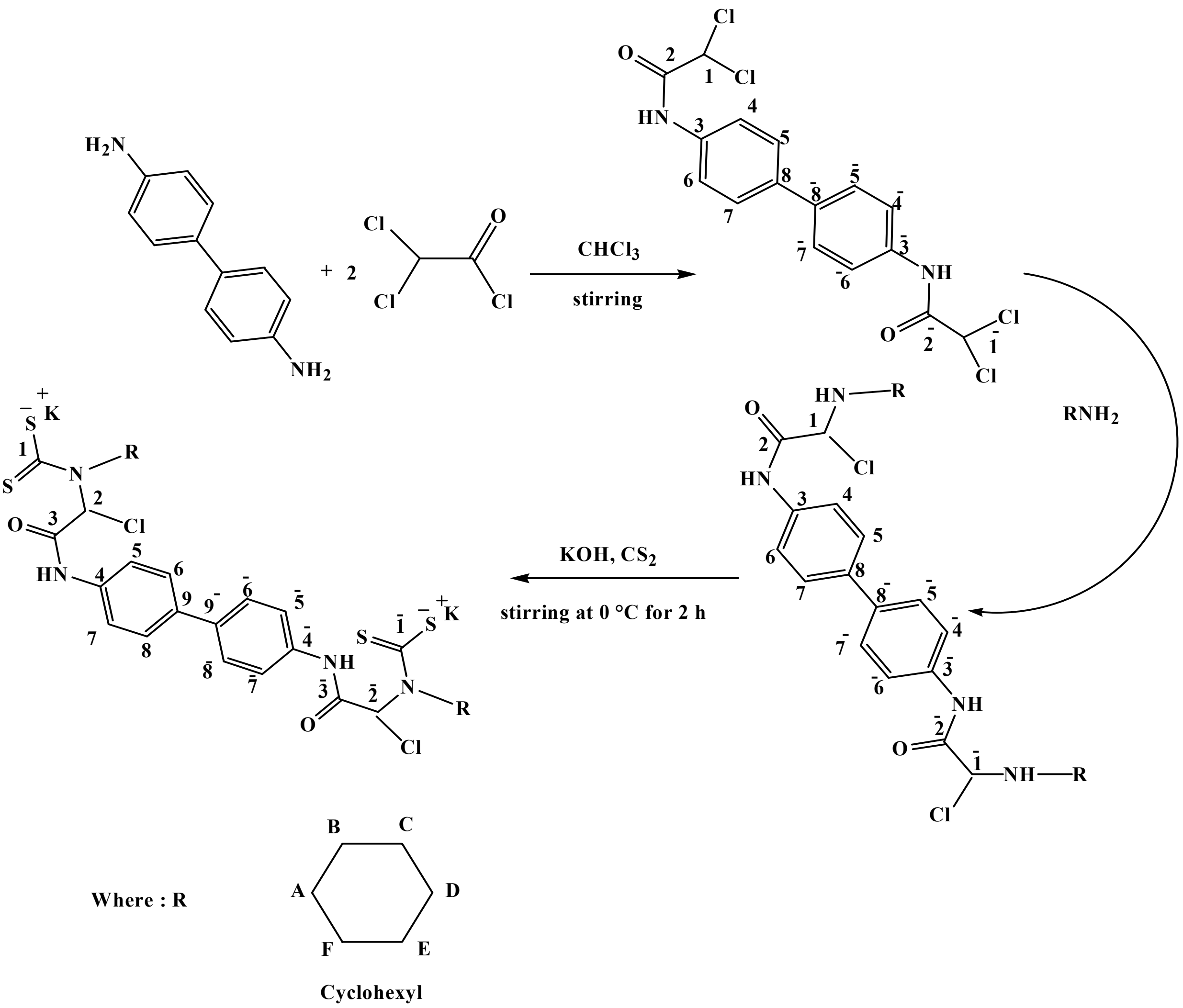
3.3.2. Formation of macrocyclic complexes through a one-pot template reaction

An excess of KOH (3eq) was added with stirring to a mixture of the secondary amine in acetonitrile/water medium (9:1). To the above solution, carbon disulfide (2.8 equivalents) was added slowly and the mixture was allowed to stir for 10 minutes during which time potassium dithiocarbamate salt was formed. The complex was synthesised *in situ* (ligand salt was not isolated) by the addition of one equivalent of the metal ion. The obtained mixture was stirred overnight, H_2O was poured for precipitation if required. Solid was collected by filtration and allowed to dry in air to yield the macrocyclic complex. Analytical data are similar to that complexes obtained from the free ligand approach.

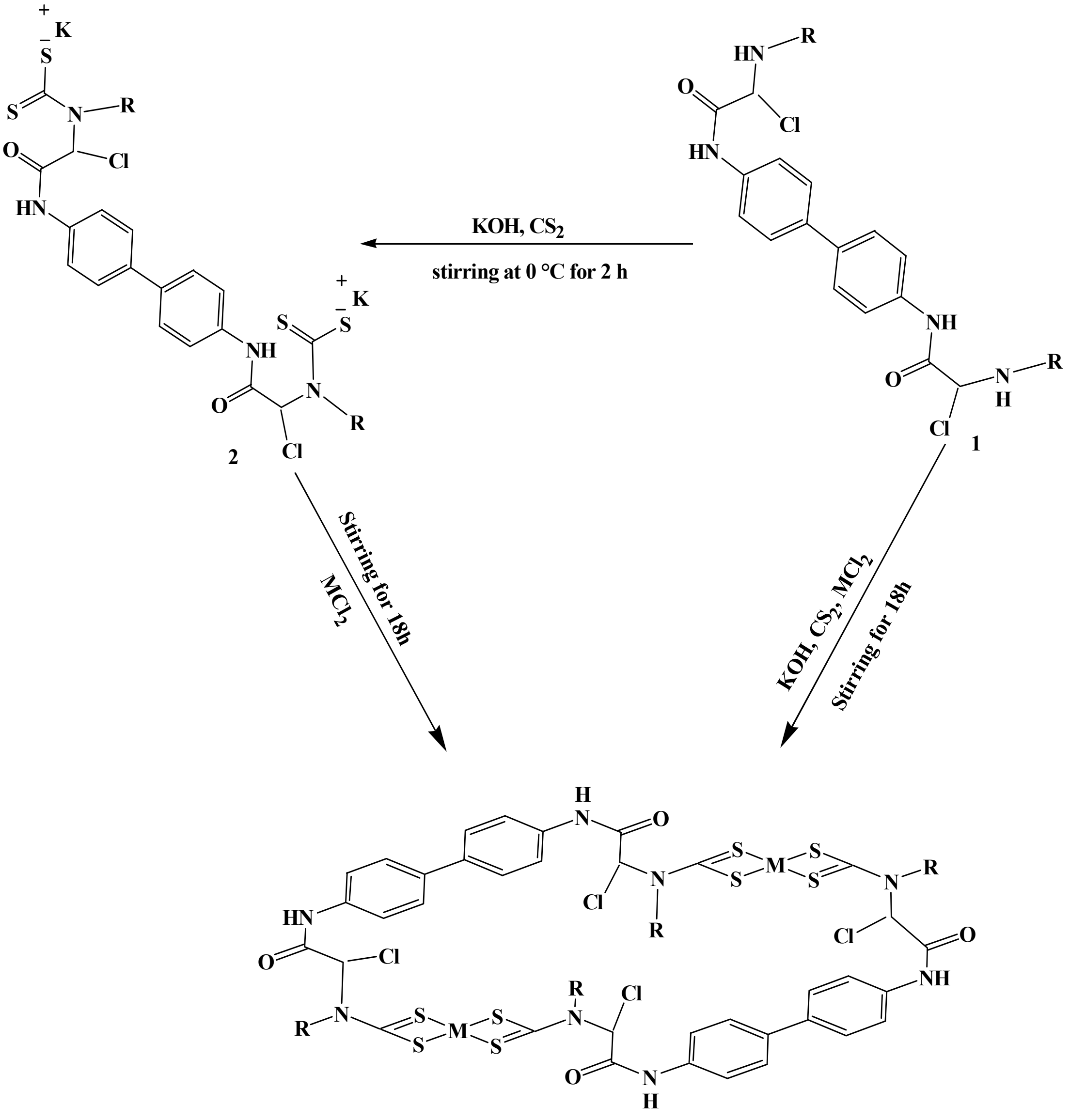
4. Results and discussion

4.1. Chemistry

The addition of carbon disulfide to a secondary bis-amine in the presence of KOH resulted in the formation of the free ligand, see Scheme (1). The ligand was characterised by elemental analysis (Table 1), FTIR (Table 2), UV–Vis (Table 3), mass and ^{1}H, ^{13}C NMR spectroscopy. The formation of dithiocarbamate-based macrocyclic complexes were obtained either via a one-pot approach or from the addition of a metal ion to the free ligand. In the later, the method was based on heating 1 equivalent of the ligand with 1 equivalent of metal chloride, using a mixture of MeCN/H_2O as a solvent, see Scheme (2). The objective of this work is to achieve the formation of macrocyclic complexes, in which the metal ion plays a key role in the self-assembly. Complexes, that are stable in air, are not soluble in the common organic solvents. However, they are soluble in hot DMSO. Spectroscopic analyses were used to predict geometries about metal centres. The analytical data (Table 1) support well the suggested formulae. The important FT-IR bands of the ligand and its complexes together with their assignments are tabulated in (Table 2). The electronic spectra for the ligand and its complexes are collected in (Table 3).



Scheme (1)



Where: R = Cyclohxyl = L

M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II}

Scheme (2)

4.2. FTIR and NMR spectra

The FTIR spectral data is collected in Table (2). FTIR spectrum of L exhibits band at 3299cm^{-1} due to ν(N–H) stretching. Band related to ν(C=O) amide is observed at 1676 cm^{-1}. Bands assigned to $\nu_{as}(CS_2)$ and $\nu_s(CS_2)$ functional groups were observed at 1084, 976 cm^{-1}, while peak related to ν(C-Cl) was detected at 654 cm^{-1}. Evidence for the formation of dinuclear-macrocyclic complexes was deduced from their FTIR spectra. Bands at 1424-1498 cm^{-1} that resulted from the stretching of the *C*-*N*-S bond indicated a partial delocalization of π-electron density within the dithiocarbamate moieties [21]. Peaks detected at 1084-1151 cm^{-1} and 933-984cm^{-1} were assigned to $\nu_{as}(CS_2)$ and $\nu_s(CS_2)$, respectively indicating an anisobidentate chelation approach of the ligand to the metal atoms [22, 23]. Complexes exhibited two sets of bands around 374-389cm^{-1}, which attributed to ν(M-S) vibration mode, and supporting the asymmetrical chelation mode of the ligand [9]. The ^{1}H and ^{13}C NMR spectra of the ligand exhibited signals related to the various protons and carbon nucleus indicating the formation of the ligand (See Experimental section). The ^{1}H NMR spectrum in DMSO-d_6 solution of the ligand shows peak at ca. 5.00 ppm assigned to CH ($C_{2,\,2`}$-*H*). The downfield appearance of this signal may be due to attachment to withdrawing groups (C=O, N-H and Cl). The (N-*H*) peak for the amide moiety appears as expected around 8.50 ppm. The ^{13}C NMR spectrum in DMSO-d_6 solution of L shows a chemical shift of the carbonyl moiety at δ= 160.33. The preparation of the free ligand was confirmed by detecting resonance around δ=189.87 ppm, which assigned to quaternary carbon in dithiocarbamate moiety C=S. The ^{1}H-NMR spectrum for $[Cd(L)]_2$ in DMSO-d_6 solution displays the (N-H) signal for the amide moiety at δ= 8.19 ppm, confirming the non-involvement of the amide group upon complexation [24]. The ^{13}C NMR spectrum of $[Cd(L)]_2$ exhibits a number of different carbons in a molecule with the appropriate shifting to that observed in the free ligand, indicating the formation of the Cd-complex. The chemical shift for C=S moiety is detected at 208.12 ppm in $[Cd(L)]_2$, compared with that at 189.87 in the free ligand confirming the involvement of this moiety in complexation [25] (see Figure (1)).

4.3. Mass spectrum

The electrospray (+) mass spectrum of $[Zn(L)]_2$ complex. Reveals that the parent ion peak is not observed upon fragmentation. For $C_{60}H_{68}Cl_4N_8O_4S_8Zn_2$, requires1494.39. Peaks detected at m/z=1307.3 (9%), 1062.8 (9 %) 748.2 (19 %), 560.8 (8 %) and 245.3 (10 %) related to $[M\text{-}(NH\text{-}CO\text{-}CHCl\text{-}(N\text{-}C_6H_{11}))]^+$, $[M\text{-}(NH\text{-}CO\text{-}CHCl\text{-}(N\text{-}C_6H_{11}))+((Ph)_2NH\text{-}CO\text{-}CHCl)]^+$, $[M\text{-}(NH\text{-}CO\text{-}CHCl\text{-}(N\text{-}C_6H_{11}))+((Ph)_2NH\text{-}CO\text{-}CHCl)+((N\text{-}C_6H_{11})(CS_2)_2Zn)]^+$, $[M\text{-}(NH\text{-}CO\text{-}CHCl\text{-}(N\text{-}C_6H_{11}))+((Ph)_2NH\text{-}CO\text{-}CHCl)((N\text{-}C_6H_{11})+(CS_2)_2Zn)+(NH\text{-}CO\text{-}CHCl\text{-}(N\text{-}C_6H_{11}))]^+$ and $[M\text{-}(NH\text{-}CO\text{-}CHCl\text{-}(N\text{-}C_6H_{11}))+((Ph)_2NH\text{-}CO\text{-}CHCl)+((N\text{-}C_6H_{11})+(CS_2)_2Zn)+(NH\text{-}CO\text{-}CHCl\text{-}(N\text{-}C_6H_{11})+((N\text{-}C_6H_{11})+(CS_2)_2Zn)]^+$.

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

The electronic spectrum of L in DMSO solution revealed peaks at 268 and 359 nm assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively [26-28]. The electronic spectra of the complexes exhibited bands at 265-268 nm associated to the ligand field $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Bands at 321-343 nm attributed to the charge transfer transitions (CT) in L complexes [29]. The spectrum of the Mn(II)-complex showed a peak at 435 nm related to $^6A_1 \rightarrow {}^4A_1$ transition, indicating tetrahedral geometry about Mn(II) ion [30, 31]. The magnetic moment value 5.76 B.M of $[Mn^{II}(L)]_2$ is typical for a high spin Mn(II) ion, which related to tetrahedral structures for Mn(II)-complexes [30, 32]. The Co(II) complex exhibits an additional peak at 670 nm correlated to $^4A_2{}^{(F)} \rightarrow {}^4T_1{}^{(p)}$ transition, indicating tetrahedral structure around Co ion [31-32]. The μ_{eff} value of 4.87 B.M for Co-complex indicates a four-coordinate complex with a tetrahedral arrangement about metal centre [30, 32]. The spectrum of the Ni(II)-complex displayed peaks in the forbidden region at 478 and 645 nm attributed to $^1A_1g^{(F)} \rightarrow {}^1B_1g^{(F)}$ and $^1A_1g^{(F)} \rightarrow {}^1A_2g^{(F)}$, respectively confirming square planar structure around Ni atom [31, 32]. The magnetic moment measurement for $[Ni^{II}(L)]_2$ complex reveals a diamagnetic arrangement. The experimental magnetic value of Ni(II) complex along with other analytical data indicated square planar geometry about Ni ion. The spectrum of the Cu(II)-complex exhibited peaks in the d-d region at 721 and 835 nm related to $^2B_1g \rightarrow {}^2B_2g$ and $^2B_1g \rightarrow {}^2A_2g$ transitions, respectively indicating square planar geometry around Cu ion [29-31]. The magnetic moment value of 1.64 B.M for $[Cu^{II}(L)]_2$ complex confirms the square planar geometry around Cu(II) ion [30, 31]. The electronic spectra of the $[Zn(L)]_2$ and $[Cd(L)]_2$ complexes exhibited peaks at 267, 267 and 339, 330 nm that assigned to the ligand field and charge transfer transitions in Zn- and Cd-complex, respectively [28, 29]. The electronic data, molar conductance and magnetic moment measurements of L complexes with their assignments are listed in (Table 3).

4.5. Thermal analysis

Thermal properties of the ligand and some metal complexes are summarised in Table (4). The TG-DSC curves of the ligand and their complexes were measured from ambient temperature up to 600 °C in the atmosphere of nitrogen. The analysis of thermal data showed ligand L is stable up to 85 °C with a weight loss of 15.87%, which attributed to (KCS_2) fragment.The peak detected at 128-238ºC related to the (diphenyl-NCOCHClNphenyl+C+CS_2) segment with 63.85% weight loss. The third step occurs at 240-590ºC is related to the loss of (C_2H_2) fragments with a weight loss of 3.50%. This peak accompanied by an endothermic behaviour in the DSC curve at 574.4 °C. The final residue of the compound is related to the (phenyl-CHOCl) with 12.26% weight loss. Thermal data of $Mn(L)]_2$, $[Co(L)]_2$, $[Ni(L)]_2$ complexes consists of two steps. The weight loss and other thermal properties including lost fragments of the complexes are listed in Table (4), [35, 36].

4.6. Bacterial activity

Dithiocarbamate ligand and its metal complexes were tested for their antimicrobial activity towards four bacterial species (*Escherichia coli, Pseudomonas aeruginosa* (G−), *Staphylococcus aureus and Bacillus stubtilis* (G+)). The involvement of DMSO in the biological activity was clarified by separate studies carried out with the solutions of DMSO alone, which showed no activity against any bacterial strains [37]. The measured zones of inhibition against the growing of different microorganisms are tabulated in Table (5). Biological data showed that complexes become potentially more active against these tested bacteria (except $[Zn(L)]_2$ with *E. coli* and, *P. aeruginosa*) compared with the free ligand. 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 through the whole chelate ring that enhances the lipophilic character of the metal chelate structure. This will favour its spread through the lipid of the cell membranes [38, 39].

5. Conclusion

The work is based on the formation of new bimetallic macrocyclic dithiocarbamate complexes. The synthesis of these complexes was accomplished by adopting two routes; (i) from the mixing of the free ligand with a metal ion, or (ii) through a one-pot template reaction. In these complexes, the metal ion plays a key role in the self-assembly. The nature of bonding and proposed structures of the complexes were established by analytical and spectroscopic techniques. These results indicated the isolation of four-coordinate complexes.

Bacterial activities revealed that complexes found to be more active towards these bacterial strains in comparison with the free ligand.

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

Metal ion	Molecular formula	Colour	m.p. ºC	Yield (%)	Found (Calca%)					
L	$C_{30}H_{34}Cl_2K_2N_4O_2S_4$	Light yellow	188 - 190	66.00	-	46.56 (47.41)	4.21 (4.51)	7.82 (7.37)	16.26 (16.88)	9.11 (9.33)
$[Mn(L)]_2$	$C_{60}H_{68}Cl_4N_8O_4S_8Mn_2$	Brown	242	42.85	7.22 (7.46)	48.08 (48.91)	4.33 (4.65)	7.95 (7.60)	17. 18 (17.41)	9.55 (9.62)
$[Co(L)]_2$	$C_{60}H_{68}Cl_4N_8O_4S_8Co_2$	Dark green	255	50	-	-	-	-	-	-
$[Ni(L)]_2$	$C_{60}H_{68}Cl_4N_8O_4S_8Ni_2$	Green	286	46.15	7.42 (7.93)	48.15 (48.66)	4.07 (4.63)	7.85 (7.57)	17.21 (17.32)	9.05 (9.58)
$[Cu(L)]_2$	$C_{60}H_{68}Cl_4N_8O_4S_8Cu_2$	Brown	278	41.02	-	-	-	-	-	-
$[Zn(L)]_2$	$C_{60}H_{68}Cl_4N_8O_4S_8Zn_2$	Pale yellow	256	44.87	-	-	-	-	-	-
$[Cd(L)]_2$	$C_{60}H_{68}Cl_4N_8O_4S_8Cd_2$	Pale yellow	263	44.57	13.82 (14.15)	45.11 (45.37)	4.07 (4.63)	7.85 (7.25	16.09 (16.15)	8.25 (8.93)

Table (2) FTIR spectral data (wave number) cm^{-1} of ligand and their complexes.

Comp.	ν (N-H)	ν_{ar}(C-H)	ν_{ali}(C-H) ν (CH-Cl)	ν (C=O)	δ(N-H)	ν_{ar}(C=C)	ν(N-CS_2)	ν (C- Cl	vas(CS_2) ν,s(CS_2)	ν (C- N
L	3299	3086	2922, 2844	1676	1622	1545	1441	654	1084 ,976	1223
$[Mn(L)]_2$	3293	3095	2933, 2850	1682	1628	1550	1498	768	1151, 980	1255
$[Co(L)]_2$	3249	3010	2939, 2850	1650	1514	1494	1488	798	1090 ,980	1255
$[Ni(L)]_2$	3224	3012	2931, 2848	1656	1512	1446	1424	667	1070 ,984	1265
$[Cu(L)]_2$	3265	3005	2927, 2856	1644	1576	1520	1452	752	1105 ,933	1240
$[Zn(L)]_2$	3290	3010	2927, 2850	1685	1612	1550	1498	773	1078 ,976	1228
$[Cd(L)]_2$	3296	3010	2922, 2856	1628	1550	1498	1452	773	1084 ,980	1228

*= ν (Ni-S) observed at 389.59 and 374.16 cm^{-1}.

*= ν (Cd-S) observed at 385.74 cm^{-1}.

Table (3) UV-Vis spectral data of ligand and bis(dithiocarbamate)-based complexes in DMSO solutions, molar conductance and magnetic moment.

Comp.	Band Position λ_{nm}	Wave number (cm^{-1})	Extinction coefficient ε_{max} ($dm^3 mol^{-1} cm^{-1}$)	Assignment	Λ_M($\Omega^{-1} cm^2 mol^{-1}$)	μ_{eff} (B.M)
L	268 342 359	37313 41322 27855	1239 2247 1280	Intra-ligand $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
$[Mn(L)]_2$	267 324 435	37458 30864 23148	884 393 77	Intra-ligand $\pi \rightarrow \pi^*$ C.T ${}^6A_1 \rightarrow {}^4T_1$	19.9	5.76
$[Co(L)]_2$	268 328 670	37313 30487 14925	1028 1613 44	Intra-ligand $\pi \rightarrow \pi^*$ C.T ${}^4A_2{}^{(F)} \rightarrow {}^4T_1{}^{(p)}$	8.47	4.87
$[Ni(L)]_2$	265 343 478 645	37735 29154 20920 15503	1223 2501 455 187	Intra-ligand $\pi \rightarrow \pi^*$ C.T ${}^1A_1g^{(F)} \rightarrow {}^1B_1g^{(F)}$ ${}^1A_1g^{(F)} \rightarrow {}^1A_2g^{(F)}$	5.86	Diamagnetic
$[Cu(L)]_2$	266 321 721 835	37593 31152 13869 11976	740 669 18 16	Intra-ligand $\pi \rightarrow \pi^*$, C.T ${}^2B_1g \rightarrow {}^2B_2g$ ${}^2B_1g \rightarrow {}^2A_2g$	9.77	1.64
$[Zn(L)]_2$	267 339	37458 29498	1226 2419	Intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ C.T	3.72	Diamagnetic
$[Cd(L)]_2$	267 330	37458 30303	976 1795	Intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ C.T	2.09	Diamagnetic

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

Comp	Stable up to °C	Stage	Decomposition temperature initial-final °C	fragments	Nature of transformation/intermediate formed% mass found (calc.), mg	Nature of DSC peak and temp. °C	DTG peak temp. °C
L	85	1	85-125	(KCS_2)	2.3807 (2.2745)	85 Exo	-
		2	128-238	(diphenyl-NCOCHClNphenyl+C+CS_2)	9.5780 (9.4936)	132.2,173.3,215.0,404.7,483.8 Endo	-
		3	240-590	(C_2H_2)	0.5254 (0.5139)	574.4 Endo	-
$[Mn(L)]_2$	110	1	110-264	($2CH_2$ CH_2 CH_2 CH_2 $CH_2CHNCHCl$ HN+ $HNCOCHClNCHCH_2CH_2$ CH_2 +$4CS_2$ +CHCONH)	5.1091 (5.0773)	120,185 Exo	-
		2	265-598	(Cl+CONH)	0.4753 (0.4288)	241, 400.6 Endo	-
$[Co(L)]_2$	105	1	105-218	($HNCOCHClNCHCH_2CH_2CH_2CH_2CH_2$+$4CS_2$+$CH_2CH_2CH_2CH_2CH_2CHNCH_2$ CO +CHCOHN)	4.2179 (4.2117)	185.8 Endo	200
		2	220-560	(diphenyl-NHCONCHCl + $CH_2CH_2CH_2CH_2CH_2CH_2$)	2.0267 (2.0039)	455 Endo	-

Table (5) Bacterial activity of ligand and bisdithiocarbamate-based complexes

No.	Sample	Average inhibition zone (mm)			
		E. coli	*P. aeruginosa*	*B. sabtuius*	*S. aureus*
1	L	6	5	5	3
2	$[Mn(L)]_2$	12	11	13	15
3	$[Co(L)]_2$	13	12	16	15
4	$[Ni(L)]_2$	12	13	12	12
5	$[Cu(L)]_2$	10	12	9	10
6	$[Zn(L)]_2$	-	-	13	11
7	$[Cd(L)]_2$	12	17	25	16

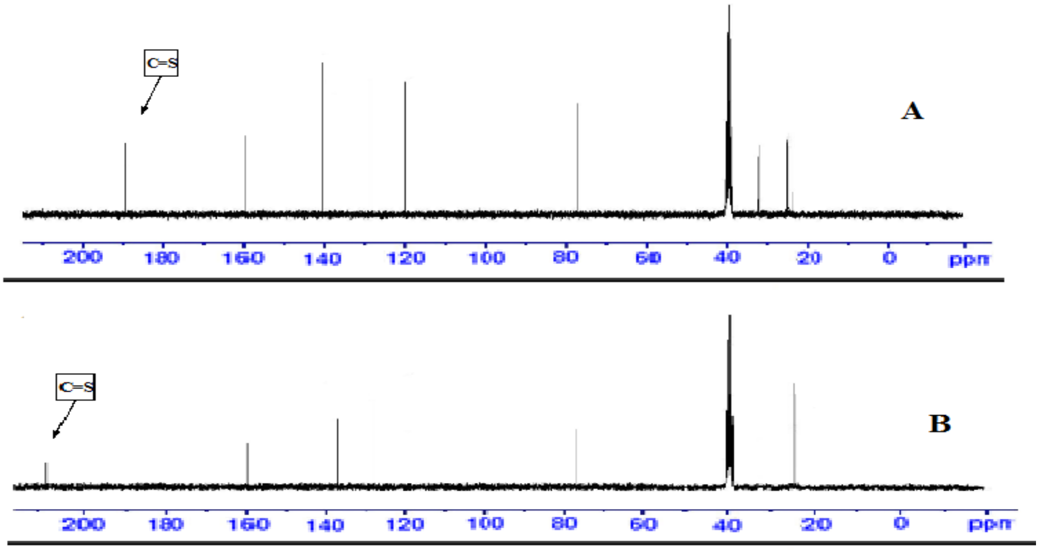

Figure (1) ^{13}C NMR spectra in DMSO-d_6 solutions for: A) L; B) $[Cd(L)]_2$

ليكاند جديد ثنائي داي ثايو كارباميت في تكوين المعقدات، تحضير وتشخيص طيفي والفعالية البكتيرية

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استلم في:21/شباط/2016، قبل في:5/نيسان/2016

الخلاصة

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

حضرت المعقدات باستعمال 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 باستعمال 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 = (Mn^{II} ,Co^{II}, Ni^{II} ,Cu^{II} , Zn^{II} and Cd^{II}) .

الكلمات المفتاحية: معقدات ثنائي الثايوكارباميت , دراسة التراكيب, الفعالية البكتيرية