

Synthesis, Characterisation and Biological Activity of New Co, Ni, Zn and Cd Polymeric Complexes Derived from Dithiocarbamate Ligand

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Abstract

Synthesis of a new class of Schiff-base ligand with a tetrazole moiety to form polymeric metal complexes with Co^{II}, Ni^{II}, Zn^{II}, and Cd^{II} ions has been demonstrated. The ligand was synthesised by a multi-steps by treating 5-amino-2-chlorobenzonitrile and cyclohexane -1,3-dione, the 5,5'-(((1E,3E)-cyclohexane-1,3-diylidene)bis(azanylylidene))bis(2-chlorobenzonitrile) was obtained. The precursor (M) was prepared from the reaction 5,5'-(((1E,3E)-cyclohexane-1,3-diylidene)bis(azanylylidene))bis(2-chlorobenzonitrile) with NaN₃ to obtained (1E,3E)-N¹,N³-bis(4-chloro-3-(1H-tetrazol-5-yl)phenyl)cyclohexane-1,3-diimine (N). By reacting the precursor (M) with CS₂/KOH, the required ligand was synthesised. Co (II), Ni (II), Zn (II), Cd (II) ions produce polymeric metal complexes with the formula [M(L)]_n when they react with the ligand (L). These complexes were synthesised using the same methods. The geometrical structure of ligand and their polymeric complexes were determined using FTIR, ¹H, ¹³C-NMR, electronic spectroscopy, ESMS, magnetic susceptibility, metal and chloride contents, micro elemental analysis and conductance. From the results, we conclude that the L-complexes demonstrate the production of four-coordinate complexes with tetrahedral geometry for Co(II), Zn(II), and Cd(II), and square planer geometry for Ni (II). We examined the antibacterial activity of both ligand and complexes with two types of bacteria positive (*Bacillus subtilis* and *Staphylococcus aureus*) and negative (*Escherichia coli* and *Pseudomonas aeruginosa*) with concentration 10⁻².

Keywords: Biological, Ligand, Polymeric, Spectroscopy, Tetrazole.

Introduction

Dithiocarbamates (DTCs) are a class of tiny chemical compounds that chelate metal ions extremely well¹. There has been an abundance of studies and reviews on transition and non-transition

metals, indicating that these compounds come in a wide variety of forms². Dithiocarbamate's ligands are more sophisticated organic sulphur compounds. This may be because the CSS group has a low bite

angle and is capable of reacting with the majority of metals in the periodic table. By adding a single pair of electrons, sulphur atoms can form complexes with metal atoms^{3,4}. Stabilization of DTCs is possible in a wide variety of metal oxidation states, coordination geometries, and compounds. It encompasses a wide range of structural changes, from monomeric to polymeric molecular assemblies. Dithiocarbamates' structural structure is defined by their binding capabilities; their physical and chemical properties are described by their monodentate, bidentate chelating, and bidentate bridging variations^{5,6}. Dithiocarbamate and dithiophosphate complexes have a wide range of applications⁷. Dithiocarbamates are significant materials that have been extensively studied in coordination chemistry, medicine, and radiopharmaceutical chemistry, as well as sensing engineering and materials science, for their peculiarly explanatory⁸, biological⁹, and physico-chemical¹⁰, properties, articulated biological activities¹¹, and utility as models of metallo-enzyme dynamic sites¹². DTCs have been shown to have significant biological activity, including antimicrobial activity¹³. When metal coordination is present, sulphur and nitrogen atoms play a critical role in defining the dynamic destinies of various metallobimolecules¹⁴. Thio macrocyclic applications that have been proposed. The subject of coordination chemistry is Schiff bases and their metal complexes¹⁵. Dithiocarbamates are a class of compounds that are widely employed because they exhibit a strong and selective affinity for a wide

Materials and Methods

Aldrich reagents were used exactly as they were received. Prior to use in the preparation, solvents were dried according to normal procedures. All three tests CHNS were carried out on a Heraeus (Vario-EL) instrument. The spectra of I.R. discs used as KBr discs were measured between 4000 and 400 cm^{-1} using a Shimadzu-8400.S F.T.I.R. spectrophotometer. At a temperature of 25°C, the ultraviolet spectra of 0.001 M solutions of complexes in $(\text{CH}_3)_2\text{SO}$ were investigated using Shimadzu ultra-violet (1800) spectroscopy. ^1H and ^{13}C -NMR spectroscopy, the spectra were collected using a Jeol 300-MHz spectrometer in a $\text{DMSO}-d_6$

range of metal ions. As a result, over the last decade, self-assembly mediated by metal dithiocarbamate coordination has established itself as a feasible supramolecular approach for the construction of macrocycles, cages, catenanes, and nanoparticles. The bulk of applications are based on dithiocarbamate ligands' metal ion complexation capabilities, which have been demonstrated experimentally with transition metal ions.^{16,17}

Two sulphur donor atoms present in dithiocarbamate ligands efficiently form chelating compounds with all metal ions^{18, 19}. Due to the strength of their O-bond, dithiocarbamate molecules are capable of stabilising metal ions with a high oxidation state in metal complexes. While the sulphur atoms in dithiocarbamate ligands exhibit similar O-donor and N-back donation features, those ligands exhibit an unusual property in which an additional n-electron flows from nitrogen to sulphur via a planar delocalized orbital system^{20,21}. The dithiocarbamate ligand can be coordinated to metals in three ways: bidentate, ansio-bidentate, or monodentate²². Numerous metallic elements are essential for the biological system to function properly. Without the appropriate metal ion, a biological reaction catalysed by a particular metallo-enzyme would continue at a snail's pace²³. We want to prepared new dithiocarbamate ligand, and react it with some metal complexes to prepare the polymeric complexes. Also, we want to characterisation the ligand and its metal complexes by spectral techniques and test the biological activity.

solution, with tetra-methylsilan (TMS) serving as an internal standard for ^1H -NMR. (ES) mass spectrometry was used to achieve the spectra of ligand and complexes. Stuart's melting point electro-thermal uncorrected melting points were generated using SMP/40 capillary melting point equipment. A Shimadzu was used to determine the metals. 680-G-(A.A.) 680-G. Chloride content in complexes were determined using the potentiometric titration method with a 686-Titrap processor and 665Dosimat-Metrohim Swiss. A PW 9526 differential conductivity metre was used to determine the conductivity of DMSO solutions, and

a magnetic susceptibility balance was utilised to measure the magnetic moments at ambient temperature.

Synthesis of Precursor(N)

The ligand was isolated adopting a reported procedure in²⁴, as follows:

Cyclohexane-1,3-dione (0.5 g, 4.46 mmol) was added dropwise while stirring to a solution consisting of 1,4-Diazabicyclo[2.2.2]octan (DABCO) (0.66 g, 3.0 mmol), 5-amino-2-chlorobenzonitrile (1.35 g, 8.92 mmol.) and a 6 ml. solution of TiCl_4 (0.089 ml., 0.77 mmol.) (15 mL) (which works to pull a proton from amine to release the nucleophilicity of amine). Three drops of CH_3COOH were added to the reaction mixture, and then solution was refluxed for 8 hours. Filtration and slow evaporation of the reaction mixture. The precursor 5,5'-(((1E,3E)-cyclohexane-1,3-diylidene)bis(azanylylidene)) bis(2-chlorobenzonitrile) obtained as a yellow powder. m.p = 187°C; yield: 0.92 g 59%). FTIR data for the obtained compounds: 2163 $\nu(\text{CN})$, 1627 $\nu(\text{C=N})$, and 1229 $\nu(\text{C-O})$.

A solution of precursor 5,5'-(((1E,3E)-cyclohexane-1,3-diylidene)bis(azanylylidene))bis(2-chlorobenzonitrile) (0.751 g, 1.96 mmol.), NaN_3 (0.25 g, 3.84 mmol), Et_3N (0.39 g, 3.93 mmol.), and ammonium chloride in DMF (15 mL) was refluxed at 170 °C for 7 hours, and the L product was obtained using a technique similar to that used with the ligand L. (10 mL). 0.77 g (84%) yield, M. p = 235 °C. The FTIR spectrum of the precursor (N) (1E,3E)-N¹,N³-bis(4-chloro-3-(1H-tetrazol-5-yl)phenyl)cyclohexane-1,3-diimine displayed prominent peaks attributable to the functional groups $\nu(\text{N-H})$, $\nu(\text{C=N})$, $\nu(\text{C=N})$ triazole, $\nu(\text{N-H})$, $\nu(\text{N=N})$ and $\nu(\text{N-N})$ ²⁵⁻²⁷. Bands around 3226 and 1643 cm^{-1} were observed as a result of $\nu(\text{N-H})$ and $\nu(\text{C=N})$ in precursor (N)^{28,29}. At 1574 cm^{-1} , the bands corresponding to the tetrazole ring's $\nu(\text{C=N})$ configuration were detected²⁹⁻³¹. The bands at 1123

and 1078 cm^{-1} are caused by the tetrazole ring in precursor(N) being $\nu(\text{N=N})$ and (N-N), respectively³².

Preparation of Ligand (L)

The free ligand potassium 5,5'-(((1E,3E)-cyclohexane-1,3-diylidene)bis(azanylylidene))bis(6-chloro-3,1-phenylene))bis(1H-tetrazole-1-carbodithioate) (L) was prepared by using a conventional approach for the synthesis of dithiocarbamate compounds¹⁵ and as follows:

To a solution of (1E,3E)-N¹,N³-bis(4-chloro-3-(1H-tetrazol-5-yl)phenyl)cyclohexane-1,3-diimine (0.50g, 1.07mmol) in 10mL of a mixture of $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (9:1), was added an excess of KOH (0.29g, 7.29mmol, 4equivalent) dissolved in H_2O (2mL). The liquid was stirred in an ice bath before adding a carbon disulfide solution (0.99g, 10mmol, 3 equivalent) dropwise with stirring. At 0°C, the mixture was stirred for 2 hours, during which time the potassium dithiocarbamate salt crystallized into a light orange solid., m.p=184-186 °C. Yield: 0.62g, (83.78%).FTIR: 1653 cm^{-1} $\nu(\text{C=N})$, 1575 cm^{-1} $\nu_{\text{arom}}(\text{C=C})$, 1456 cm^{-1} $\nu(\text{N-CS}_2)$, 1031, 985 cm^{-1} $\nu_{\text{as,s}}(\text{CS}_2)$. See Scheme 1.

Synthesis of Complexes

A solution of L (1 mmol) in ethanol (20 mL) was stirred for 3 minutes, and then followed by a dropwise addition of metal chloride a solution of metal chloride (1 mmol) in (10mL) which ($\text{MCl}_2 = \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 and $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$). The reaction mixture was heated at reflux for 2 hours under N_2 atmosphere, and a solid was formed. The solid product was washed with hot ethanol and dried at room temperature, which achieved Co^{II} , Ni^{II} , Zn^{II} , and Cd^{II} as solid polymeric complexes. After that, the solid product was washed in hot ethanol, and dried under vacuum. As shown in Scheme 2, this method produced non-electrolyte complexes with the broad formulas $[\text{M}(\text{L})]_n$ (where $\text{M} = \text{Co}^{\text{II}}$, Ni^{II} , Zn^{II} , and Cd^{II}).

Results and Discussion

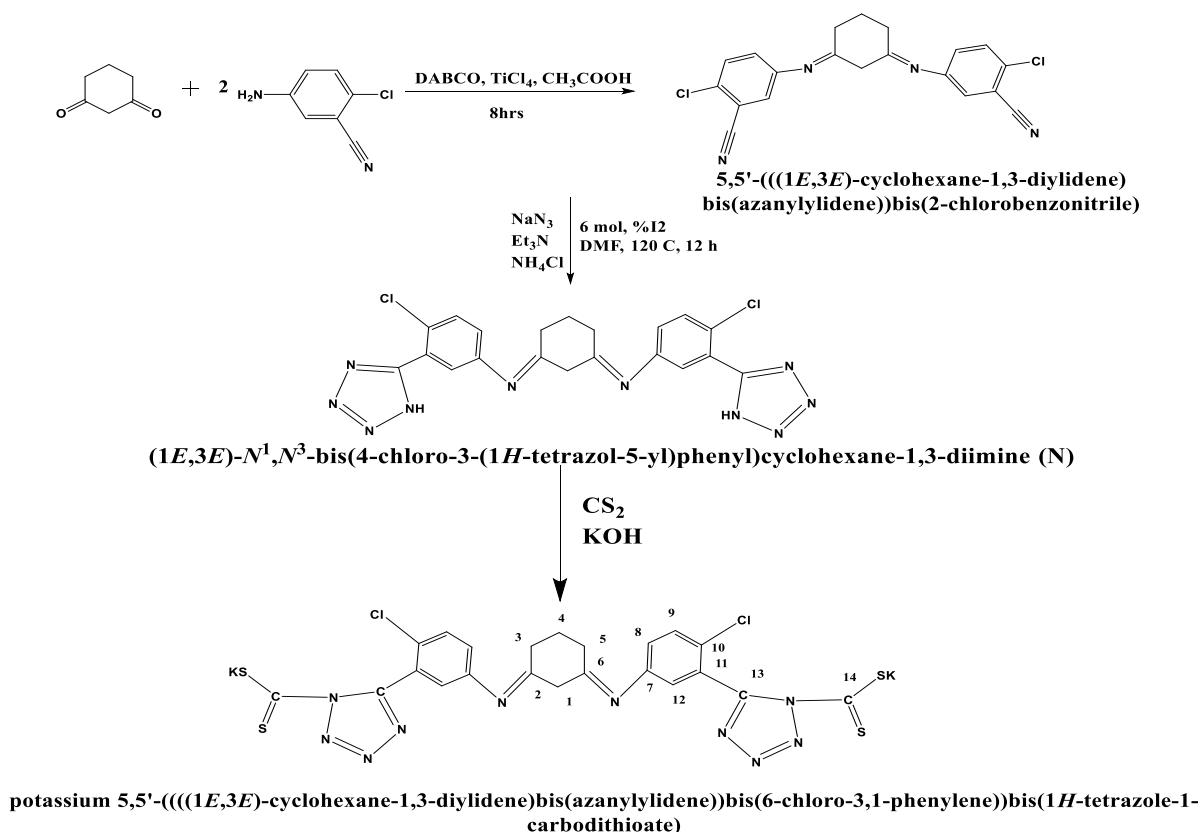
Synthesis

The recently found tetrazole Schiff base ligand L was synthesised in large quantities by

reacting cyclohexane-1, 3-dione with 5-amino-2-chlorobenzonitrile Scheme 1. The ligands were synthesised in three phases, with methanol serving

as the reaction medium. On the other hand, precursor (N) is a neutral precursor. The ligand (L) is a type of electrolyte that can accommodate a single metal ion. The ligand was characterised using

C.H.N.S. Many physical properties are listed in Table 1, FT-IR Table 2, UV-Vis. Table 3, and ^1H and ^{13}C NMR spectra.

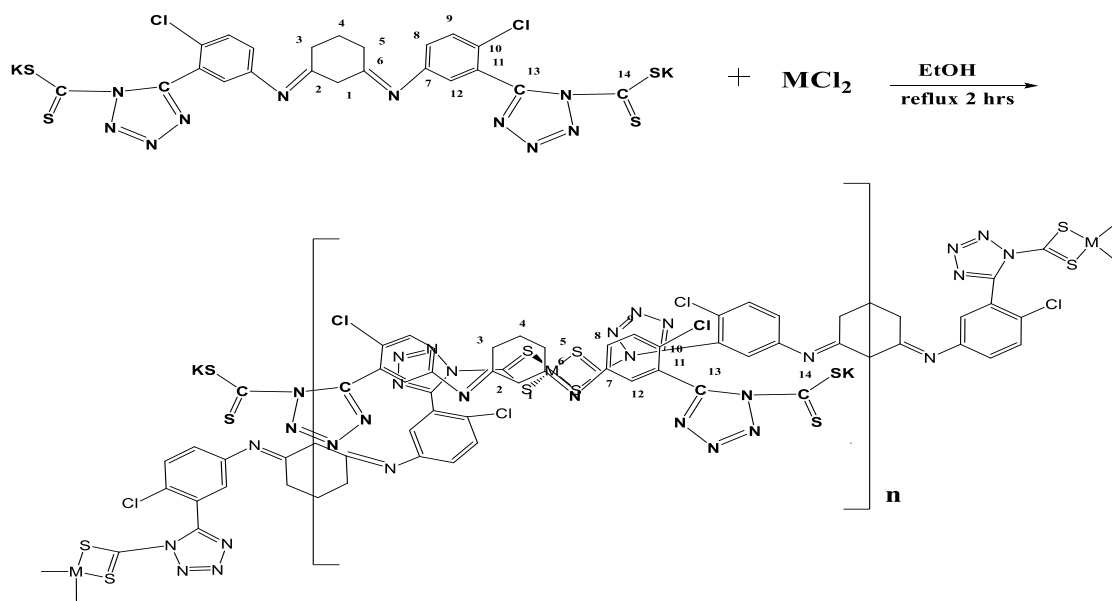


Scheme 1. Synthetic route of the ligand

Table 1. The Colours, yields, elemental analyses, and molar conductance in DMSO values for compounds

Compound	Colour	Yield (%)	m.p °C	Found %, (Calcd. %)						$\Delta\text{m}(\text{cm}^2\Omega^{-1}\text{mol}^{-1})$
				M	C	H	N	S	Cl	
Precursor (N)	Pale Yellow		245	-	54.86 (55.30)	3.47 (3.71)	31.87 (32.24)	-	-	-
L	Yellow		237	-	37.67 (37.98)	2.01 (2.03)	19.89 (20.13)	17.92 (18.43)	9.82 (10.19)	-
[Co ^{II} (L)] _n	Blue	66	294*	8.84 (8.71)	38.74 (39.06)	2.02 (2.09)	20.62 (20.71)	18.73 (18.96)	10.27 (10.48)	12.67
[Ni ^{II} (L)] _n	Green	69	273*	8.46 (8.68)	38.71 (39.07)	2.05 (2.09)	20.59 (20.71)	18.75 (18.96)	10.26 (10.48)	6.78
[Zn ^{II} (L)] _n	Yellow	72	287*	9.43 (9.57)	38.39 (38.69)	2.03 (2.07)	20.26 (20.51)	18.54 (18.78)	10.14 (10.38)	5.64
[Cd ^{II} (L)] _n	Yellow	72	291*	14.83 (15.40)	35.98 (36.20)	1.86 (1.93)	18.87 (19.19)	17.24 (17.57)	9.53 (9.71)	5.64

*= Decompose



where $M = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Zn}^{\text{II}}$ and Cd^{II}

Wh

ere M denotes cobalt, nickel, zinc, and cadmium.

Scheme 2. The general chemical structure of polymeric complexes

After heating, the complex formation was solid compounds, inert to air and soluble in DMF and DMSO, but not soluble in other solvents. Insolubility may refer to the polymeric character²⁶. Additionally, because of L essential structural influence, polymeric complex chain assemblies can be formed²⁷. As a result, the sulphur atom in the dithiocarbamate segment is required for the vacant position on the unsaturated metal centre to be filled, resulting in ladder-like structures. The complexes' anticipated geometries were obtained by analysing their spectra and other analytical data. The analytical results corroborated the formulas provided Table 1, FT-IR peaks Table 2, UV-Vis spectra are presented Table 3.

FT-IR and NMR Spectra

The FT-IR of precursor (N) and free ligand revealed strong peaks for the functional groups $\nu(\text{N}-$

$\text{H})$, $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{N})$ tetrazole, $\delta(\text{N}-\text{H})$, $(\text{N}=\text{N})$, and $\nu(\text{N}=\text{N})$ and $(\text{N}-\text{N})$ tetrazole. Bands at 3226 and 1643 cm^{-1} were discovered as a result of $\nu(\text{N}-\text{H})$ and $\nu(\text{C}=\text{N})$ in (N)^{28, 29}. At 1574 cm^{-1} , L may exhibit bands associated with the tetrazole ring $\nu(\text{C}=\text{N})$ ^{30,31}. In L Fig. 1, the tetrazole rings $\nu(\text{N}=\text{N})$ and $\nu(\text{N}-\text{N})$ produced bands at 1123 and 1078 cm^{-1} , respectively³²⁻³³. The FT-IR spectrum exhibited strong peaks $\nu(\text{C}=\text{N})$ tetrazole, and functional groups $(\text{N}=\text{N})$, $(\text{N}-\text{N})$, and (CS_2) . The disappearance of the $(\text{N}-\text{H})$ band is thought to be related to the creation of the CS_2 ligand. Due to $(\text{C}=\text{N})$ in L, bands were identified about 1653 cm^{-1} ³⁰⁻³¹. At 1575 cm^{-1} in L, bands associated with the tetrazole ring's $\nu(\text{C}=\text{N})$ may be seen. The bands at 1114 and 1031 cm^{-1} are due to the tetrazole ring's $\nu(\text{N}=\text{N})$ and $(\text{N}-\text{N})$ configurations in L³².

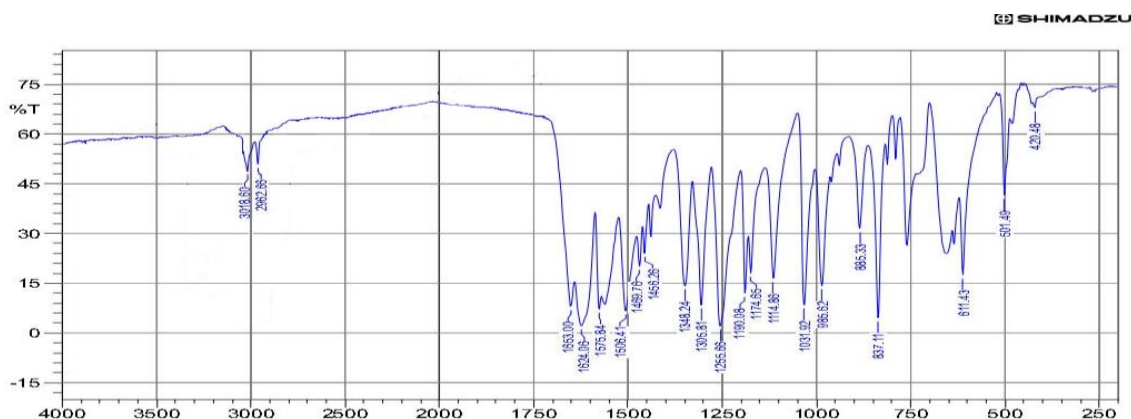


Figure 1. IR spectrum of L

After complexation, the polymeric compounds' FT-IR spectra exhibited L bands with the necessary shifts and M-S peaks associated with complexation Table 2. Around the moment of complexation, the $\nu(\text{C}=\text{N})$ of the imine groups is altered and identified. In L complexes, The bands at 1654-1666 cm^{-1} ³¹, do not coordinate the metal atoms. These bands have been shifted to a higher frequency in compared to the free ligands. The bands at 1552-1566 cm^{-1} , which corresponds to the tetrazole ring's $\nu(\text{C}=\text{N})$ in L. Complexes have bands in their FT-IR

spectra 1149-1178, 1091-1114, and 1006-1078 cm^{-1} which can be assigned to $\nu(\text{C}-\text{N})$, $(\text{N}=\text{N})$, and $(\text{N}-\text{N})$ ³². The FT-IR spectra of complexes exhibited bands between 357-381 cm^{-1} which may be attributed to $\nu(\text{M}-\text{S})$. These bands show that the metal ion and the dithiocarbamate group are coordinated. The dithiocarbamate CS₂ groups, band at 1114-1078 cm^{-1} and 946-991 cm^{-1} are assigned to $\nu_{\text{as}}(\text{CS}_2)$ and $\nu_{\text{s}}(\text{CS}_2)$, respectively. This is characteristic of an anisobidentate chelation mode of the ligand to the metal atoms, Fig. 2-5 in L complexes, all bands are summarised in Table 2.

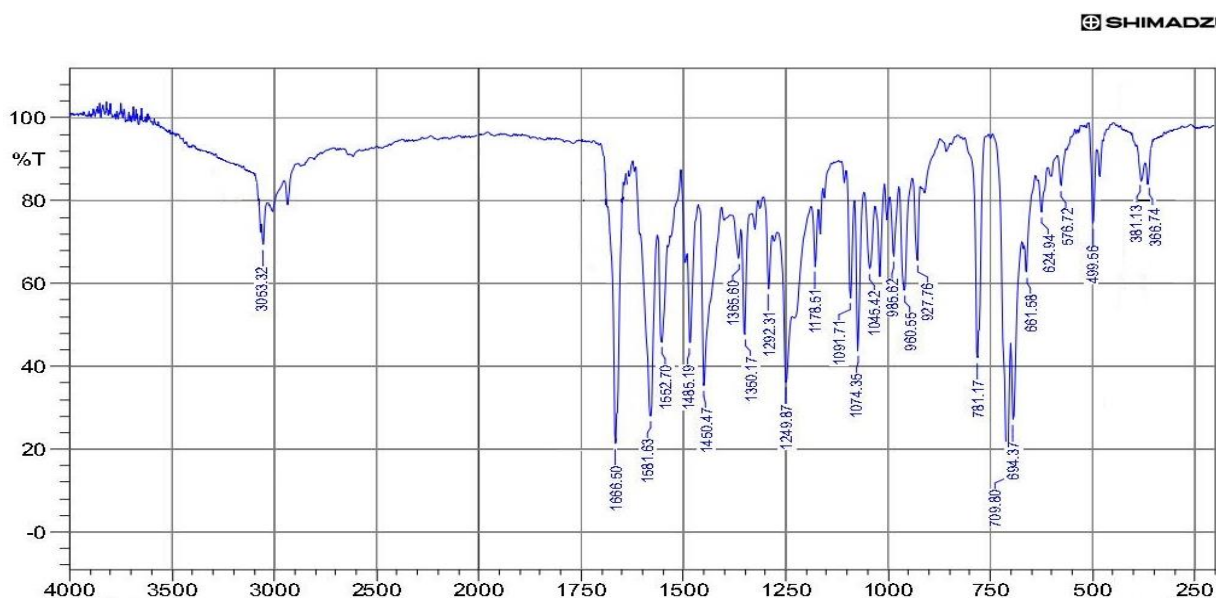


Figure 2. IR spectrum of Co complex

SHIMADZU

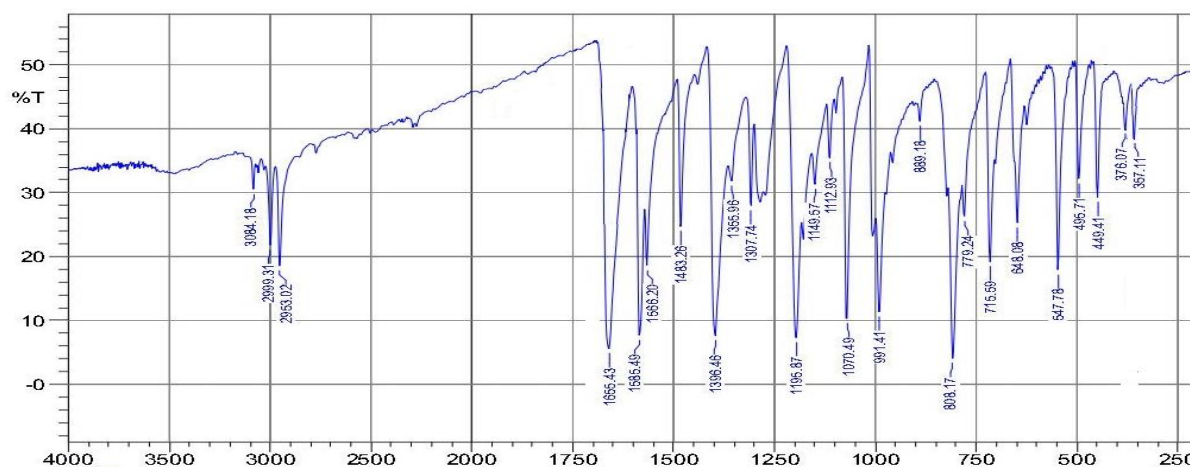


Figure 3. IR spectrum of Ni complex

SHIMADZU

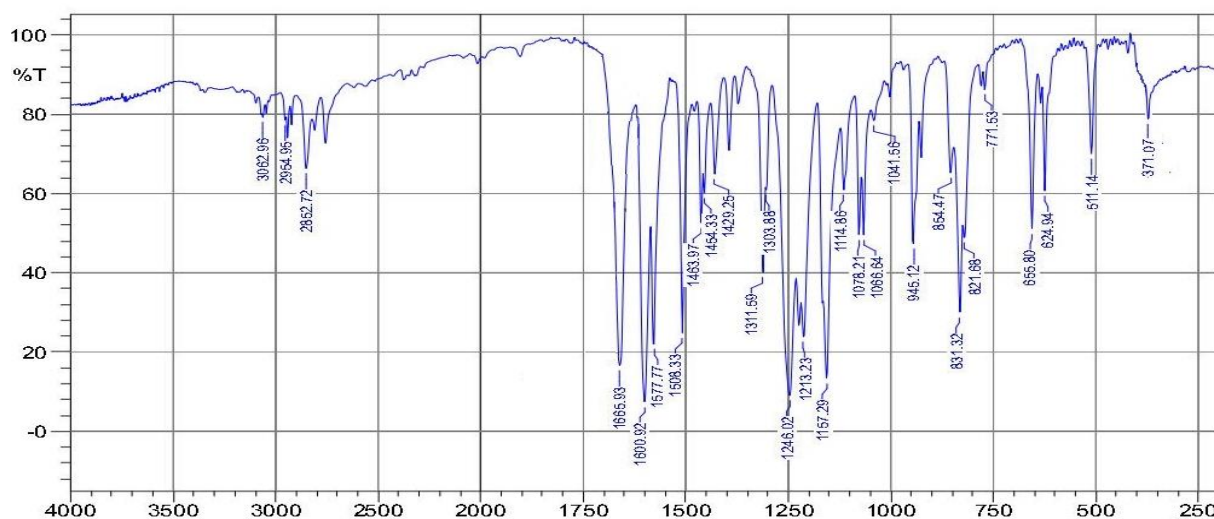


Figure 4. IR spectrum of Zn complex

SHIMADZU

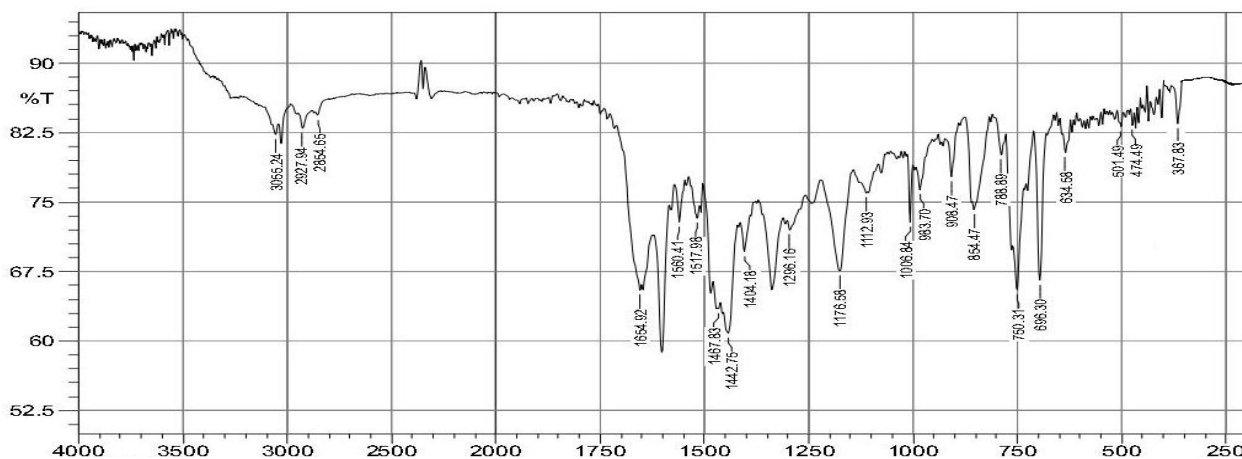


Figure 5. IR spectrum of Cd complex

Table 2. FTIR frequencies (cm⁻¹) of the compounds.

Compound	v(C=N)	v(C=C)	v(C=N) tetrazole	v(N- CS ₂)	v(C-N)	Nas, (CS ₂)	s	v(N=N)	v(N-N)	v(M- S)
N tetrazole	1632	1602, 1493	1568		1185			1107	1078	-
LCS₂	1653	1624	1575	1386	1190	1114,986		1114	1031	-
[Co^{II}(L)]_n	1666	1581, 1485	1552	1398	1178	1091, 985		1091	1074	366, 381
[Ni^{II}(L)]_n	1656	1585, 1483	1566	1386	1149	1112, 991		1112	1070	357, 376
[Zn^{II}(L)]_n	1665	1600, 1483	1577	1429	1157	1078, 946		1114	1078	371
[Cd^{II}(L)]_n	1654	1608, 1467	1560	1404	1176	1112, 983		1112	1006	367

The ligand's ¹H and ¹³C-NMR spectra indicated signals corresponding to the both proton, and carbon, nuclei (see experimental section). ¹H-NMR spectrum of L Fig. 6, contained a peak between 1.83 and 2.05 ppm, corresponding to two methylene group protons (C₄-H, m, CH₂, 2H). Between 2.94 and 3.08 ppm, a signal is assigned to (C_{3,5}-H, CH₂, 4H, t), whereas the chemical shift between 3.61 and 3.61 ppm is attributed to (C₁-H, CH₂, s, 2H). The chemical shift of 7.28 ppm indicates that two protons have been assigned to the (C₈-H, d, CH_{aro.}, 2H). The chemical shift of 7.52 ppm indicates that two protons have been assigned to the (C₁₂-H, d, CH_{aro.}, 2H), whereas the signal at 7.86 ppm indicates that two protons have been assigned to the (C₉-H, d, CH_{aro.}, 2H). Due to its

connection to the chloro atom, this peak was moved downfield in compared to the (C₈-H) peak (electron withdrawing group). By eliminating the N-H group, the dithiocarbamate group is generated. ¹³C NMR showed chemical shifts at 19.991 (C₄) and 31.121 (C₄) Fig. 7. (C_{3,5}). at 119.706 and 126.562, the chemical shift may be assigned to (C₈, ₁₂). The resonances at 137.457 and 137.486 ppm, can be attributed to (C_{9,10}). The chemical shift at 144.332, may be attributed to (C₁₁). The resonance at 162.868ppm may be assigned to (C₁₃). While it is possible to ascribe the chemical signal at 169.988ppm to (C_{2,6}). The signal with a strong chemical shift at 188.749ppm could be assigned to CS₂ group.

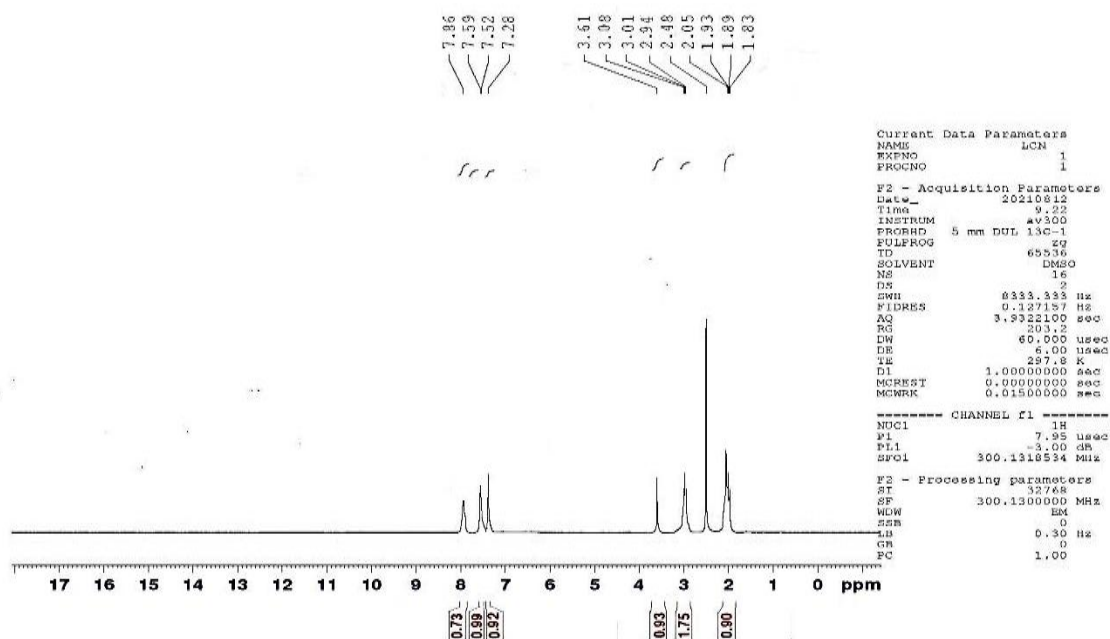


Figure 6. ¹H NMR spectrum of L

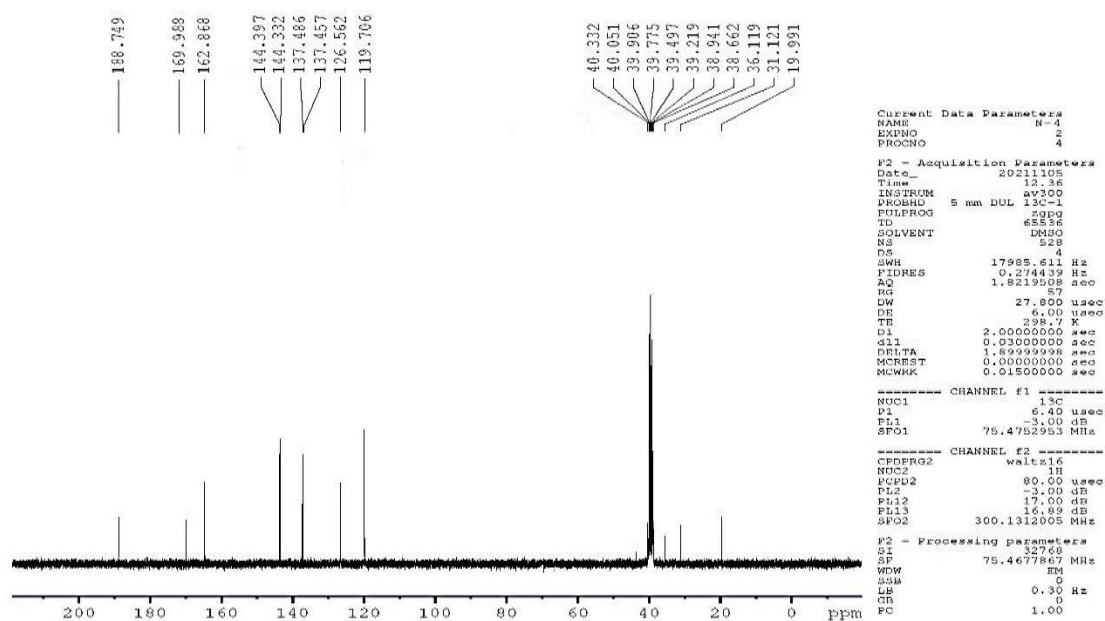


Figure 7. ¹³C NMR spectrum of L

Mass Spectra of Ligand and Complexes

The E.S.M.S. analysis of L Fig. 8, showed peaks associated with the molecule's sequential fragmentation. The ligand's molecular ion peak was determined to be m/z 696.51 (19 percent) $(M+1)^+$. The spectra suggested the presence of additional peaks at m/z 657.53 (7%), 617.82 (17%),

542.24(25%), 466.15(22%), 398.37(18%), 330.32(100%), , 236.19(26%) that assigned to the $[M-K]^+$, $[M-2K]^+$, $[M-(2K) + (CS_2)]^+$, $[M-(2K)_2 + (CS_2)_2]^+$, $[M-(2K) + (CS_2) + (N_3 + CN)]^+$, $[M-(2K) + (CS_2) + (N_3 + CN)_2]^+$, $[M-(2K) + (CS_2) + (N_3 + CN)_2]^+$, $(C_6H_4F)^+$.

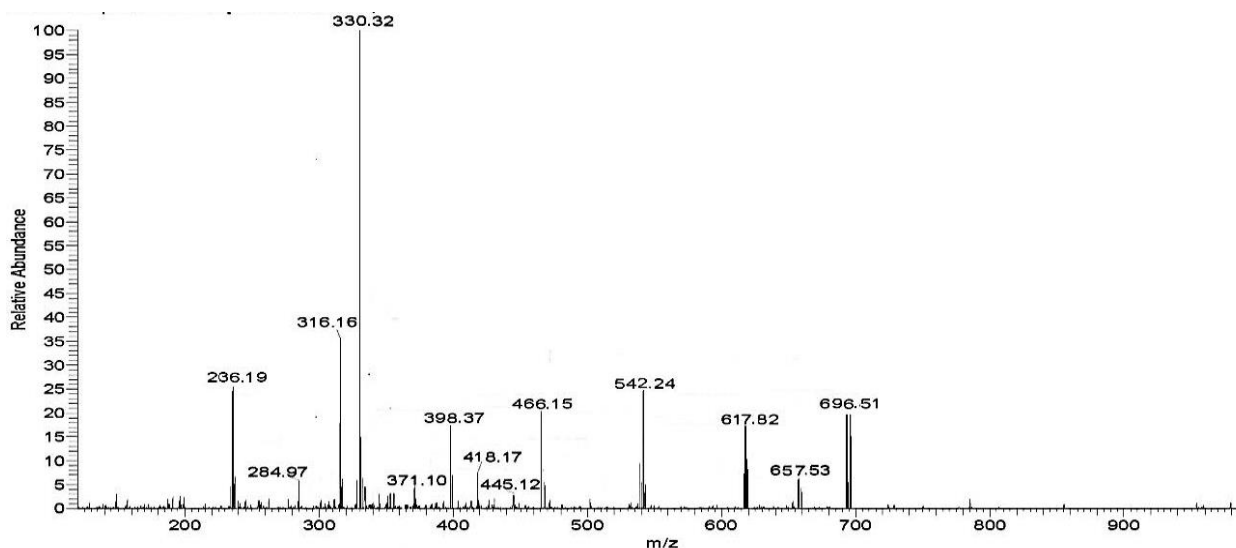


Figure 8. Mass spectrum of L

The ESMS of Co, Fig. 9, showed peaks that corresponded to the molecule's fragmentation. At m/z 677.11 (8 percent) (M)⁺, the ligand's molecular ion peak was found. There were other peaks in the spectrum at m/z 601.38 (10%), 525.24 (13%),

457.37(20%), 389.42(22%), 295.56(100%), 201.63(24%), that assigned to the $[M - (CS_2)]^+$, $[M - (CS_2)_2]^+$, $[M - (CS_2) + (N_3 + CN)]^+$, $[M - (CS_2) + (N_3 + CN)_2]^+$, $[M - (CS_2) + (N_3 + CN)_2 + (C_6H_4Cl)]^+$, $[M - (CS_2) + (N_3 + CN)_2 + (C_6H_4Cl)_2]^+$.

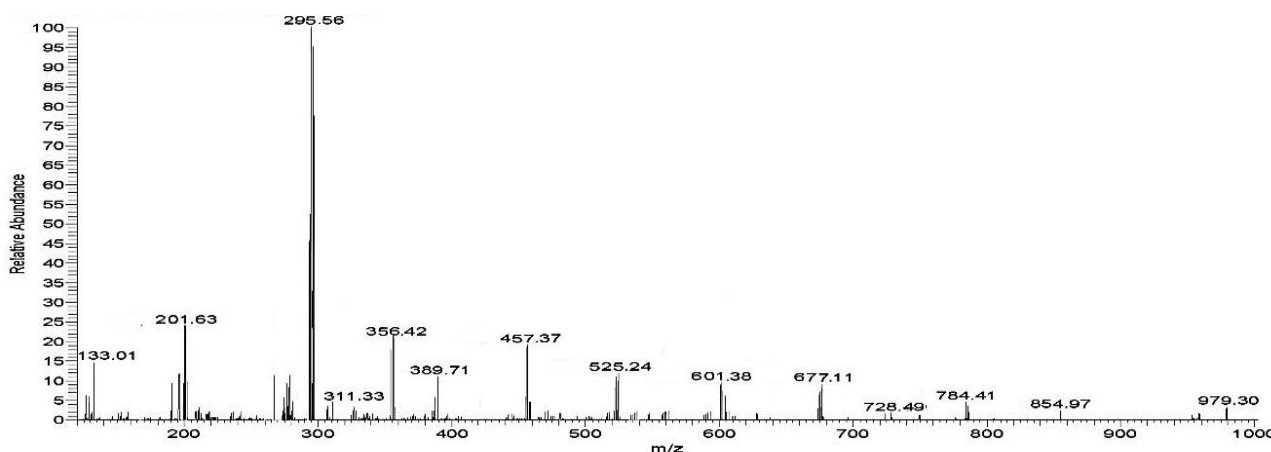


Figure 9. Mass spectrum of Co

The ESMS of Ni, Fig.10 exhibited peaks that corresponded to the molecule's successive fragmentations. The ligand's molecular ion peak was discovered at m/z 676.03 (19 percent) (M)⁺. Other peaks in the spectrum could be found at m/z

600.12 (22%), 524.46 (18%), 457.39(36%), 388.43(40%), 294.59(100%), 200.64(29%), that assigned to the $[M - (CS_2)]^+$, $[M - (CS_2)_2]^+$, $[M - (CS_2) + (N_3 + CN)]^+$, $[M - (CS_2) + (N_3 + CN)_2]^+$, $[M - (CS_2) + (N_3 + CN)_2 + (C_6H_4Cl)]^+$, $[M - (CS_2) + (N_3 + CN)_2 + (C_6H_4Cl)_2]^+$.

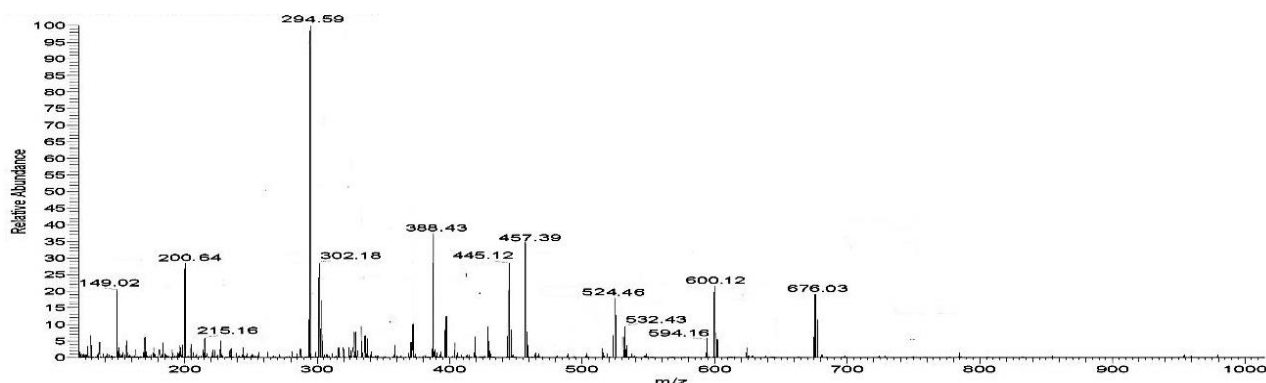


Figure 10. Mass spectrum of Ni

The ESMS of Zn, Fig. 11, showed peaks that correlated to the molecule's fragmentation. At m/z 682.18 (12 percent) $(M-1)^+$, the ligand's molecular ion peak was found. There were other peaks in the spectrum at m/z 606.32 (9%), 530.48 (13%),

462.57(5%), 394.63(11%), 300.74(100%), 206.62(19%), that assigned to the $[M-(CS_2)]^+$, $[M-(CS_2)_2]^+$, $[M-(CS_2)+(N_3+CN)]^+$, $[M-(CS_2)+(N_3+CN)_2]^+$, $[M-(CS_2)+(N_3+CN)_2+(C_6H_4Cl)]^+$, $[M-(CS_2)+(N_3+CN)_2+(C_6H_4Cl)_2]^+$.

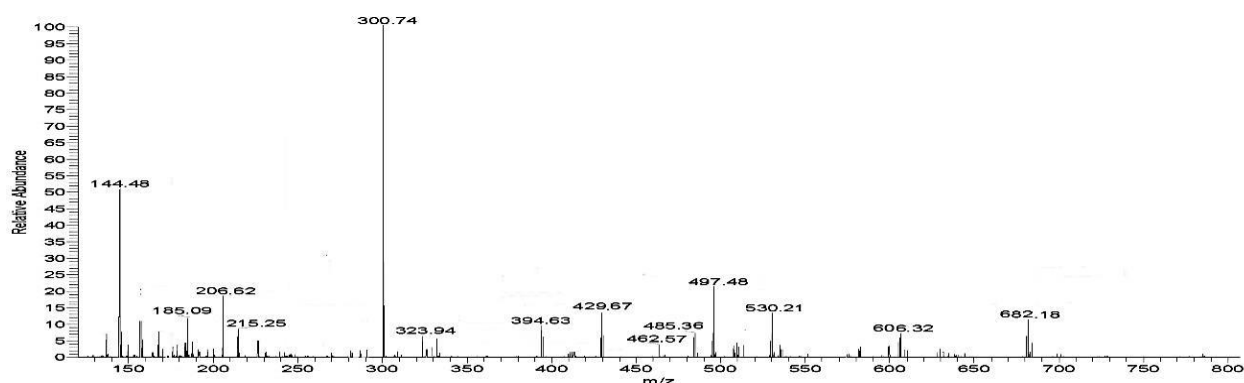


Figure 11. Mass spectrum of Zn

The ESMS of Cd, Fig.12, revealed peaks that matched to the fragmentation of the molecule. The ligand's molecular ion peak was found at m/z 731.03 (12 percent) $(M+1)^+$. Other peaks in the spectrum could be found at m/z 655.35 (16%),

579.54 (20%), 511.59(26%), 443.76(23%), 349.82(100%), 255.74(24%), that assigned to the $[M-(CS_2)]^+$, $[M-(CS_2)_2]^+$, $[M-(CS_2)+(N_3+CN)]^+$, $[M-(CS_2)+(N_3+CN)_2]^+$, $[M-(CS_2)+(N_3+CN)_2+(C_6H_4Cl)]^+$, $[M-(CS_2)+(N_3+CN)_2+(C_6H_4Cl)_2]^+$.

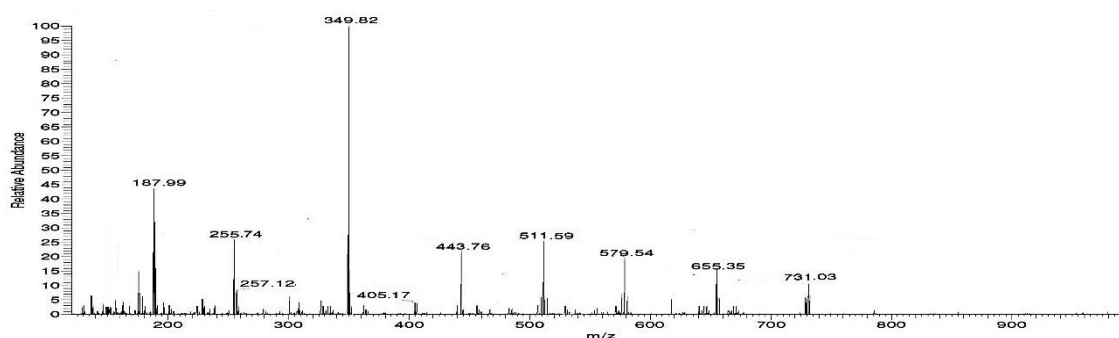


Figure 12. Mass spectrum of Cd

Electronic Spectra, Magnetic Moments and Conductivity Measurements

L's electronic spectrum, Fig. 13, revealed a peak at 289 nm attributable to $\pi \rightarrow \pi^*$. The electronic spectra of the L polymeric complexes demonstrated a hypsochromic shift of the bands associated with the intra-ligand $\pi \rightarrow \pi^*$ transition and charge transfer (C.T) peak. The tetrahedral structure is consistent with the spectrum of the Co(II) complex^{33, 34} Fig. 14. The μ_{eff} value of magnetic moment indicates a tetrahedral structure with a high spin number. Due to the diamagnetic nature of the Ni(II) complex, a square planar form surrounding the Ni atom has been proposed³⁵ Fig. 15. When compared to the

projected values, the polymeric compounds demonstrated low magnetic moment values at room temperature. This could be a result of metal-metal interactions mediated by dithiocarbamate. Additionally, the assembly of polymeric structures may result in considerable electron delocalization between structures³⁶. In the spectra of Zn(II) and Cd(II) complexes, bands associated with intraligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ have been found³⁷ Figs. 16 and 17. The diamagnetic compounds, as expected, have a d^{10} system, implying a tetrahedral structure. L complexes are non-electrolytes based on their molar conductivities³⁸, see Table 3.

Table 3. The Magnetic moment and U.V-Visible spectral data.

Compound	μ_{eff} (BM)	λ_{nm}	Wave number (cm^{-1})	$\epsilon_{\text{max}}(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$	Assignments	Suggested structure
L	-	289	34602	2119	$\pi \rightarrow \pi^*$	
		365	27397	532	$n \rightarrow \pi^*$	
[Co ^{II} (L)] _n	3.11	278	35971	2014	Intra-ligand	tetrahedral
		323	30959	2156	C.T	
		425	23529	365	C.T	
		663	15082	74	${}^4A_2(F) \rightarrow {}^4T_1(P)$	
[Ni ^{II} (L)] _n	Diamagnetic	277	36101	1385	Intra-ligand	square planar
		326	30674	394	C.T	
		657	15220	47	${}^1A_1g(F) \rightarrow {}^1A_2g(F)$	
[Zn ^{II} (L)] _n	Diamagnetic	275	36363	1360	Intra-ligand	tetrahedral
		301	33222	1437	C.T	
		384	26041	832	C.T	
[Cd ^{II} (L)] _n	Diamagnetic	285	35087	1278	Intra-ligand	tetrahedral
		381	26246	589	C.T	

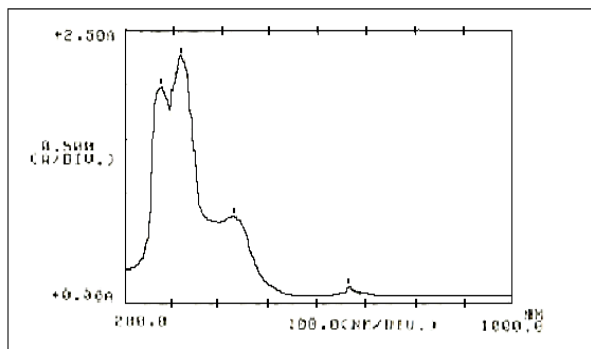


Figure 13. UV-Vis spectrum of L

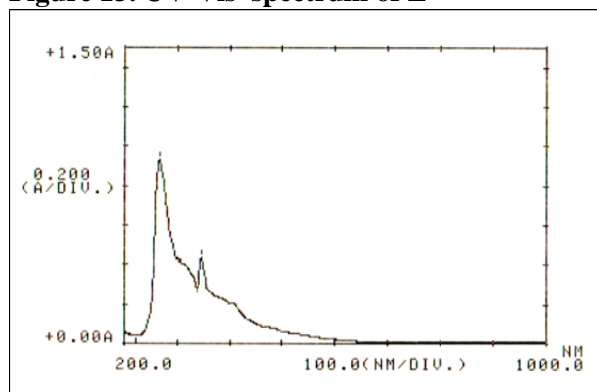


Figure 14. UV-Vis spectrum of Co complex

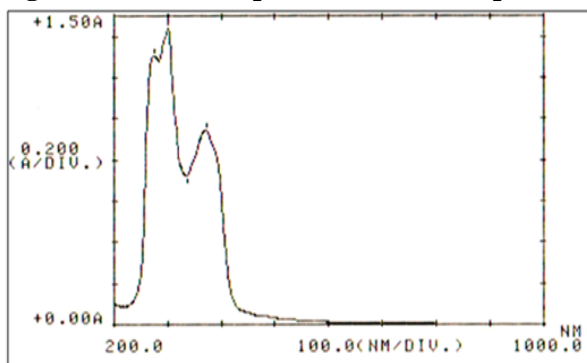


Figure 15. UV-Vis spectrum of Ni complex

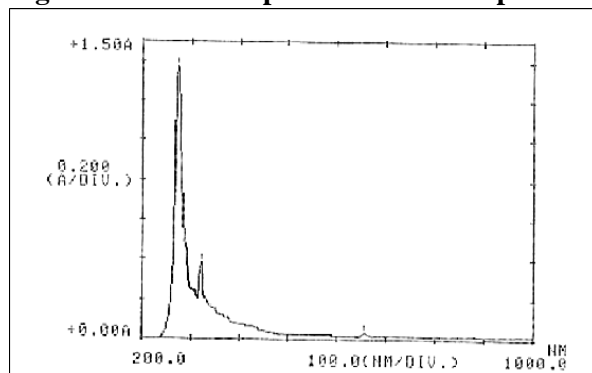


Figure 16. UV-Vis spectrum of Zn complex

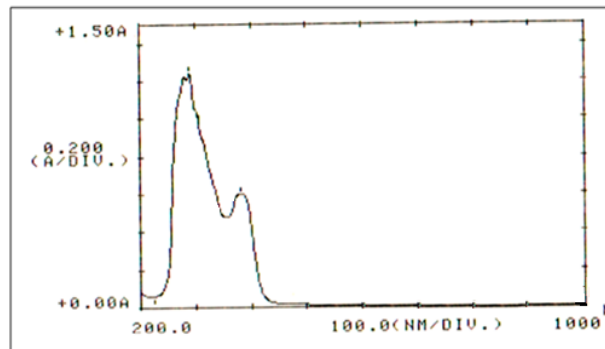


Figure 17. UV-Vis for Cd complex

Biological Activity

The bacterial activity of the synthesised ligands and their complexes was investigated using gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) with concentration 10^{-2} .

Individual tests using DMSO alone found no activity against any bacterial species. The effect of the preparation compounds on bacterial species is described in Table 4, which displays the size of inhibition zones measured against the development of various bacterial strains by mm. According to the findings, the ligands had no antibacterial activity against *Escherichia coli* and *Escherichia coli*.

As a result, the formation of complexes boosts antibacterial activity when compared to free ligands. The chelation idea may be able to explain why complex activity has risen so much. Chelation decreases the polarity of the metal, allowing it to share some of its positive charge with the donor group and allowing for π -electron delocalization across the ring. The cadmium complex is approximately twice as effective against bacteria. This may be explained by the Cd atom's toxicity, as well as its molecular weight and electronic configuration (d^{10} system) in comparison to other metal ions.^{39,40}

Table 4. The bacterial activity of compounds

Compounds	Gram-negative (G+)		Gram-negative (G-)	
	<i>Bacillus stultili</i>	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>	<i>Pseudomonas aeruginosa</i>
L	3	2	3	–
[Co ^{II} (L)] _n	13	6	4	-
[Ni ^{II} (L)] _n	3	10	-	-
[Zn ^{II} (L)] _n	18	21	12	20
	3	5	-	-
[Cd ^{II} (L)] _n	17	22	15	26

Conclusion

The synthesis coordination chemistry of novel tetrazole Schiff-base ligands capable of polymerizing with Co^{II}, Ni^{II}, Zn^{II} and Cd^{II} ions. Polymeric complexes were formed when the tetrazole ligand was combined with metal chloride. Many measurements are used to the ligand and its complexes. These techniques indicated the development of polymeric complexes with

tetrahedral geometries surrounding metal centers for Co^(II), Zn^(II), and Cd^(II), and square planar surrounding metal centers for Ni^(II) complexes. The low magnetic values and solubility of these chemicals indicate their polymeric nature. Also, the effects of L and its complexes on gram-positive and gram-negative bacteria were tested.

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Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for

- re-publication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors' Contribution Statement

All the authors participated in performing different roles as follows: Conception, design,

acquisition of data, analysis, interpretation, drafting the MS, revision and proofreading

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التحضير والتشخيص والنشاط البيولوجي لمعقدات بوليمرية جديدة Cd و Zn و Ni و Co المشتقة من ليكاند Dithiocarbamate

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الخلاصة

تم تحضير فئة جديدة من ليكاند قاعدة شيف حاوي على تترازول على تكوين معقدات فلزية بوليمرية مع أيونات Zn^{II} و Ni^{II} و Co^{II} و Cd^{II} . تم تحضير الليكاند بعدة خطوات عن طريق اضافة 5-amino-2-chlorobenzonitrile الى سايكلو هكسان -1,3-ديون للحصول على 5,5'-(((1E,3E)-cyclohexane-1,3-diylidene)bis(azanylylidene))bis(2-chlorobenzonitrile). تم تحضير المادة الأولية (M) من تفاعل 5,5'-(((1E,3E)-cyclohexane-1,3-diylidene)bis(azanylylidene))bis(2-chlorobenzonitrile) مع NaN_3 للحصول على: (1E,3E)- N^1, N^3 -bis(4-chloro-3-(1H-tetrazol-5-yl)phenyl)cyclohexane-1,3-diimine (N). من خلال تفاعل المشتق (M) مع CS_2 / KOH ، تم تحضير الليكاند المطلوب. تنتج أيونات (Cd^{II} و Zn^{II} و Ni^{II} و Co^{II}) معقدات فلزية بوليمرية ذات الصيغة $[\text{M}(\text{L})_n]$ عندما تتفاعل مع الليكاند (L). تم تحضير هذه المعقدات واستخدمت نفس الطريقة، لتحديد هوية الليكاند ومعقداته. تم تحديد الشكل الهندسي لليكاند ومعقداته البوليمرية باستخدام FTIR و NMR والتحليل الطيفي الإلكتروني وطيف الكتلة ESMS والقابلية المغناطيسية ومحتوى الفلز ومحتوى الكلوريد وتحليل العناصر الدقيقة والتوصيلة. من النتائج تبين ان الليكاند L ينتج معقدات رباعية التناسق مع شكل هندسي رباعي السطوح لـ Co^{II} و Zn^{II} و Cd^{II} وشكل مربع مستوي لـ Ni^{II} . قمنا بفحص النشاط المضاد للبكتيريا لكل من الليكاند ومعقداته ضد نوعين من البكتيريا الموجبة (*Bacillus subtilis* and *Staphylococcus aureus*) والسالبة (*Escherichia coli* and *Pseudomonas aeruginosa*) 0.01.

الكلمات المفتاحية: بايولوجي، ليكاند، بوليمرية، التحليل الطيفي، تترازول.