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\textsuperscript{II}, Ni\textsuperscript{II}, Zn\textsuperscript{II}, and Cd\textsuperscript{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 NaN\textsubscript{3} to obtained (1E,3E)-N\textsubscript{1},N\textsubscript{3}-bis(4-chloro-3-(1H-tetrazol-5-yl)phenyl)cyclohexane-1,3-dimine (N). By reacting the precursor (M) with CS\textsubscript{2}/KOH, the required ligand was synthesised. Co (II), Ni (II), Zn (II), Cd (II) ions produce polymeric metal complexes with the formula [M(L)]\textsubscript{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, \textsuperscript{1}H, \textsuperscript{13}C-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 stubtili and Staphylococcus aureus) and negative (Escherichia coli and Pseudomonas aeruginosa) with concentration 10\textsuperscript{-2}.

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

Introduction

Dithiocarbamates (DTCs) are a class of tiny chemical compounds that chelate metal ions extremely well\textsuperscript{1}. 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 forms\textsuperscript{2}. 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\(^3\). 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 dithiophosphinate complexes have a wide range of applications\(^7\). 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 explanatory\(^8\), biological\(^9\), and physico-chemical\(^10\), properties, articulated biological activities\(^11\), and utility as models of metallo-enzyme dynamic sites\(^12\). DTCs have been shown to have significant biological activity, including antimicrobial activity\(^13\). When metal coordination is present, sulphur and nitrogen atoms play a critical role in defining the dynamic destinies of various metallobimolecules\(^14\). Thio macrocyclic applications that have been proposed. The subject of coordination chemistry is Schi ff bases and their metal complexes\(^15\). Dithiocarbamates are a class of compounds that are widely employed because they exhibit a strong and selective affinity for a wide 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, ansiobidnate, or monodenate\(^22\). 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 pace\(^23\).

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.

**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 (CH\(_2\))\(_2\)SO were investigated using Shimadzu ultra-violet (1800) spectroscopy. \(^1\)H and \(^13\)C-NMR spectroscopy, the spectra were collected using a Jeol 300-MHz spectrometer in a DMSO–d\(_6\) solution, with tetra-methylsilan (TMS) serving as an internal standard for \(^1\)H-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-Titrp 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 in refs. 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 TiCl₄ (0.089 ml., 0.77 mmol.) (15 mL) (which works to pull a proton from amine to release the neocleophility of amine). Three drops of CH₃COOH 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-diyldiene)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 ν(CN), 1627 ν(C=N), and 1229 ν(C=O).

A solution of precursor 5,5’-(((1E,3E)-cyclohexane-1,3-diyldiene)bis(azanylylidene))bis(2-chlorobenzonitrile) (0.751 g, 1.96 mmol.), NaN₃ (0.25 g, 3.84 mmol), Et₃N (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) was obtained using a technique similar to that used with precursor 5,5’-(((1E,3E)-cyclohexane-1,3-diyldiene)bis(azanylylidene))bis(2-chlorobenzonitrile) (0.089 ml., 0.77 mmol.) (15 mL) (which works to pull a proton from amine to release the neocleophility of amine). Three drops of CH₃COOH 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-diyldiene)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 ν(CN), 1627 ν(C=N), and 1229 ν(C=O).

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**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 ¹³C NMR spectra.

\[
\text{C}_3\text{H}_5\text{N}\text{Cl}\text{S} \rightarrow \text{Scheme 1. Synthetic route of the ligand}
\]

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Yield (%)</th>
<th>m.p</th>
<th>Found %, (Calcd. %)</th>
<th>ΛM( cm(^2)Ω-1mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor (N)</td>
<td>Pale</td>
<td>245</td>
<td>-</td>
<td>M: 54.86 C: 3.47 H: 31.87 N: 38.74 Cl: 9.82</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Yellow</td>
<td>237</td>
<td>-</td>
<td>M: 37.67 C: 2.01 H: 19.89 N: 17.92 Cl: 9.82</td>
<td>-</td>
</tr>
<tr>
<td>[Co(II)(L)](n)</td>
<td>Blue</td>
<td>66</td>
<td>294*</td>
<td>M: 8.84 C: 38.71 H: 2.02 N: 20.62</td>
<td>12.67</td>
</tr>
<tr>
<td>[Ni(II)(L)](n)</td>
<td>Green</td>
<td>69</td>
<td>273*</td>
<td>M: 8.46 C: 38.71 H: 2.05 N: 20.59</td>
<td>6.78</td>
</tr>
<tr>
<td>[Zn(II)(L)](n)</td>
<td>Yellow</td>
<td>72</td>
<td>287*</td>
<td>M: 9.43 C: 38.39 H: 2.03 N: 20.26</td>
<td>5.64</td>
</tr>
<tr>
<td>[Cd(II)(L)](n)</td>
<td>Yellow</td>
<td>72</td>
<td>291*</td>
<td>M: 14.83 C: 35.98 H: 1.86 N: 18.87</td>
<td>5.64</td>
</tr>
</tbody>
</table>

*= Decompose
Where $M$ 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 character\(^{26}\). Additionally, because of \(L\) essential structural influence, polymeric complex chain assemblies can be formed\(^{27}\). 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 in 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 $\nu$(N-H), $\nu$(C=N), $\nu$(C=N)tetrazole, $\delta$(N-H), (N=N), and $\nu$(N=N) and (N-N) tetrazole. Bands at 3226 and 1643 cm\(^{-1}\) were discovered as a result of $\nu$(N-H) and $\nu$(C=N) in (\(N\))\(^{28, 29}\). At 1574 cm\(^{-1}\), \(L\) may exhibit bands associated with the tetrazole ring $\nu$(C=N)\(^{30, 31}\). In \(L\) Fig. 1, the tetrazole rings $\nu$(N=N) and $\nu$(N-N) produced bands at 1123 and 1078 cm\(^{-1}\), respectively\(^{32-33}\). The FT-IR spectrum exhibited strong peaks $\nu$(C=N)tetrazole, and functional groups (N=N), (N-N), and (CS\(_2\)). The disappearance of the (N-H) band is thought to be related to the creation of the CS\(_2\) ligand. Due to (C=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 $\nu$(C=N) may be seen. The bands at 1114 and 1031 cm\(^{-1}\) are due to the tetrazole ring’s $\nu$(N=N) and (N-N) configurations in \(L\)\(^{32}\).
After complexation, the polymeric compounds' FT-IR spectra exhibited L bands with the necessary shifts and M-S peaks associated with complexation. Around the moment of complexation, the $\nu$(C=N) of the imine groups is altered and identified. In L complexes, the bands at 1654-1666 cm$^{-1}$ 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 $\nu$(C=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 $\nu$(C-N), (N=N), and (N-N). The FT-IR spectra of complexes exhibited bands between 357-381 cm$^{-1}$ which may be attributed to $\nu$(M-S). These bands show that the metal ion and the dithiocarbamate group are coordinated. The dithiocarbamate CS$_2$ groups, band at 1114-1078 cm$^{-1}$ and 946-991 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, Fig. 2-5 in L complexes, all bands are summarised in Table 2.
Figure 3. IR spectrum of Ni complex

Figure 4. IR spectrum of Zn complex

Figure 5. IR spectrum of Cd complex
Table 2. FTIR frequencies (cm\(^{-1}\)) of the compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(C=N)</th>
<th>ν(C=C)</th>
<th>ν(C=N- \text{tetrazole})</th>
<th>ν(C-N)</th>
<th>ν(N=CS(_2))</th>
<th>ν(N=N)</th>
<th>ν(M-S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N tetrazole</td>
<td>1632</td>
<td>1602, 1493</td>
<td>1568</td>
<td>1185</td>
<td>1107</td>
<td>1078</td>
<td>-</td>
</tr>
<tr>
<td>LCS(_2)</td>
<td>1653</td>
<td>1624</td>
<td>1575</td>
<td>1386</td>
<td>1190</td>
<td>1114</td>
<td>1031</td>
</tr>
<tr>
<td><a href="L">Co(_{II})</a>(_n)</td>
<td>1666</td>
<td>1581, 1485</td>
<td>1552</td>
<td>1398</td>
<td>1178</td>
<td>1091, 985</td>
<td>1091</td>
</tr>
<tr>
<td><a href="L">Ni(_{II})</a>(_n)</td>
<td>1656</td>
<td>1585, 1483</td>
<td>1566</td>
<td>1386</td>
<td>1149</td>
<td>1112, 991</td>
<td>1112</td>
</tr>
<tr>
<td><a href="L">Zn(_{II})</a>(_n)</td>
<td>1665</td>
<td>1600, 1483</td>
<td>1577</td>
<td>1429</td>
<td>1157</td>
<td>1078, 946</td>
<td>1114</td>
</tr>
<tr>
<td><a href="L">Cd(_{II})</a>(_n)</td>
<td>1654</td>
<td>1608, 1467</td>
<td>1560</td>
<td>1404</td>
<td>1176</td>
<td>1112, 983</td>
<td>1112</td>
</tr>
</tbody>
</table>

The ligand's \(^1\)H and \(^{13}\)C-NMR spectra indicated signals corresponding to the both proton, and carbon, nuclei (see experimental section). \(^1\)H-NMR spectrum of L Fig. 6, contained a peak between 1.83 and 2.05 ppm, corresponding to two methylen group protons (C\(_{3,5}\)-H, m, CH\(_2\), 2H). Between 2.94 and 3.08 ppm, a signal is assigned to (C\(_{3,5}\)-H, CH\(_2\), 4H, t), whereas the chemical shift between 3.61 and 3.61 ppm is attributed to (C\(_{1,2}\)-H, CH\(_2\), s, 2H). The chemical shift of 7.28 ppm indicates that two protons have been assigned to the (C\(_8\)-H, d, CH\(_{aro}\), 2H). The chemical shift of 7.52 ppm indicates that two protons have been assigned to the (C\(_{12}\)-H, d, CH\(_{aro}\), 2H), whereas the signal at 7.86 ppm indicates that two protons have been assigned to the (C\(_9\)-H, d, CH\(_{aro}\), 2H). Due to its connection to the chloro atom, this peak was moved downfield in compared to the (C\(_8\)-H) peak (electron withdrawing group). By eliminating the N-H group, the dithiocarbamate group is generated. \(^{13}\)C NMR showed chemical shifts at 19.991 (C\(_4\)) and 31.121 (C\(_4\)) Fig. 7. (C\(_{3,5}\), at 119.706 and 126.562, the chemical shift may be assigned to (C\(_8\), 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 (C\(_{11}\)). The resonance at 162.868ppm may be assigned to (C\(_{13}\)). 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 CS\(_2\) group.
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) + (CS₂)]⁺, [M-(2K)⁺ + (CS₂)]⁺, [M-(2K)⁺ + (CS₂)⁺ + (N₃⁺CN)]⁺, [M-(2K)⁺ + (CS₂)⁺ + (N₃⁺CN)⁺]⁺, [M-(2K)⁺ + (CS₂)⁺ + (N₃⁺CN)⁺ + (C₆H₄)]⁺.
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$_2$)$_2$]+, [M- (CS$_2$)$_3$]+, [M- (CS$_2$)+(N$_3$+CN)]+, [M- (CS$_2$)+(N$_3$+CN)$_2$]+, [M- (CS$_2$)+(N$_3$+CN)$_2$]+ (C$_6$H$_4$Cl)$_2$]+, [M- (CS$_2$)+(N$_3$+CN)$_2$]+ (C$_6$H$_4$Cl)$_2$]+.

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$_2$)$_2$]+, [M- (CS$_2$)$_3$]+, [M- (CS$_2$)+(N$_3$+CN)]+, [M- (CS$_2$)+(N$_3$+CN)$_2$]+, [M- (CS$_2$)+(N$_3$+CN)$_2$]+ (C$_6$H$_4$Cl)$_2$]+, [M- (CS$_2$)+(N$_3$+CN)$_2$]+ (C$_6$H$_4$Cl)$_2$]+.
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- (CS₂)]^+, [M- (CS₂)₂]^+, [M- (CS₂)+(N₃+CN)]^+, [M- (CS₂)+(N₃+CN)₂], [M- (CS₂)+(N₃+CN)+ (C₆H₄Cl)]^+, [M- (CS₂)+(N₃+CN)₂+ (C₆H₄Cl)]^+

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- (CS₂)]^+, [M- (CS₂)₂]^+, [M- (CS₂)+(N₃+CN)]^+, [M- (CS₂)+(N₃+CN)₂], [M- (CS₂)+(N₃+CN)+ (C₆H₄Cl)]^+, [M- (CS₂)+(N₃+CN)₂+ (C₆H₄Cl)]^+.
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) complex33, 34 Fig. 14. The 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.

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

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Gram-negative (G+)</th>
<th>Gram-negative (G-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bacillus stutli</td>
<td>Staphylococcus aureus</td>
</tr>
<tr>
<td>L</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>[CoII(L)]n</td>
<td>13</td>
<td>6</td>
</tr>
<tr>
<td>[NiII(L)]n</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>[ZnII(L)]n</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>[CdII(L)]n</td>
<td>17</td>
<td>22</td>
</tr>
</tbody>
</table>

### Conclusion

The synthesis coordination chemistry of novel tetrazole Schiff-base ligands capable of polymerizing with Co\textsuperscript{II}, Ni\textsuperscript{II}, Zn\textsuperscript{II} and Cd\textsuperscript{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\textsuperscript{II}, Zn\textsuperscript{II}, and Cd\textsuperscript{II}, and square planar surrounding metal centers for Ni\textsuperscript{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

### References


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تحضير والتشخيص والنشاط البيولوجي لمعقدات بوليمرية جديدة

Dithiocarbamate المشتقة من ليكاند

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قسم الكيمياء، كلية التربية للعلوم الصرفة (بان الهيثم)، جامعة بغداد، بغداد، العراق

الخلاصة

تم تحضير فئة جديدة من ليكاند قادعة شف حاوي على تترازول علية تترازول على تكوين معقدات بوليمرية مع أيونات Co II و Ni II و Zn II و Cd II. تم تحضير الليكاند بعدة خطوات عن طريق إضافة chlorobenzonitrile - 2-amino-5-tetrazol على تكوين معقدات بوليمرية مع أيونات Co II و Ni II و Zn II و Cd II. تم تحضير المادة الأولية (L) عن طريق تفاعل أيونات 

\[\text{Na}_2\text{CS}_2/\text{KOH} \]

مع (M) من خلال تفاعل المشتق ((1E,3E)phenyl)cyclohexane-1,3-diimine (N). عندما تتفاعل مع [M(L)_n] المطلوب. تنتج أيونات (Cd II و Zn II و Ni II و Co II) معقدات فازية بوليمرية ذات الصيغة [Cd(L)_n] NMR والمغناطيسية ومحتوى ESMS والتحليل الطيفي الإلكتروني وطيف الكتلة وحالة الكتلة المغناطيسية، مما ينتج مقدرات رباعية التناسق مع شكل فلز مربع مستوي لـ Ni (II) و شكل مربع مستوي لـ Cd (II) و Zn (II) و Co (II) و Cd (II) و Zn (II) و Co (II). قمنا بفحص النشاط المضاد للبكتيريا لكل الليكاند ومعقداته ضد نوعين من البكتيريا الموجهة (0.01. (Escherichia coli and Pseudomonas aeruginosa)

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