Synthesis, Spectroscopic and Biological Studies of 2-(N-Phenyl Dithio Carboxamide) Benzothiazole with some Metal Ions

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ABSTRACT

The synthesis of 2(N-phenyl dithio carboxamid) benzothiazol Ligand (L) from reaction of 2-Mercaptobenzothiazol with phenylisothiocyanate using ratio 1:1. The ligand was characterized by elemental analysis (C,H,N), 'H-NMR, IR and UV-Vis. The complexes with bivalent ions (Ni, Cu, Zn, Cd and Hg) have been prepared and characterized. The structural diagnosis was established using IR, UV – Visible spectro photometer, molar conductivity, atomic absorption and molar ratio with selected metal ions (Ni$^{2+}$, Cu$^{2+}$). The complexes of (Ni, Cu) gave octahedral structural while the complexes of (Zn, Cd, Hg) gave tetrahedral structural. The study of biological activity of the ligand (L) and its complexes (Ni, Cu, Hg) in two deferent concentration (1and5) mg/ml with staphylococcus aureus and E-coli. The results showed deference effect towards positive in two concentration (1and5)mg/ml. while the effect towards negative showed variety effect except Hg-complex didn’t
show effect in 1mg/ml but in 5mg/ml the ligand and complexes did show effect except Hg-complex showed effect 5 mm.

INTRODUCTION

Heterocycles bearing nitrogen, sulphur and thiazole moieties constitute the core structure of a number of biologically interesting compound. 2-Mercaptobenzothiazole derivatives are known to possess various pharmacological activities(1-3). Our current interest is in heterocyclic Bis-oxadiazol and trizole derivatives and their complexes have been prepared and reported(4-5). In the present work the efforts have been made to synthesize 2(N-phenyldithiocarboxamide) benzothiazol which has more than one sulphur and nitrogen atoms and study of its reaction with some metal ions and their bactericidal activities.

MATERIALS AND METHODS

a- Chemicals; All reagents used were analar or chemically pure grade by British Drug Houses (BDH).
- The chemical materials: 2-Mercaptobenzothiazol C_2H_5NS_2, phenyl isothiocyanate (C_7H_5NS), Nickelchloridehexahydrate (NiCl_2.6H_2O), Copperchloridedehydrate (CuCl_2.2H_2O), Zincchloride ZnCl_2, Cadmiumchloride dehydrate (CdCl_2.2H_2O), Mercurychloride (HgCl_2).
- Ethanol (CH_3CH_2OH) 99%, Dimethylformamide (DMF) 99%, Dimethylsulphoxide (DMSO) 99%, carbontetrachloride (CCl_4).

b- Instruments;
- Elemental analysis for the new (L) (C. H. N) was determined by calibration type : Linear Regression Euro EA Elemental Analysis.
- Melting points were determind by Gallen-Kamp apparatus.
- 'H-NMR- Bruker, Mondel; Ultra shield 300MHz origin, Swizerland (Jordan) in CH_3OD using TMS as an internal standard.
- IR spectra were recorded as KBr disc in the rang (4000-400)cm^{-1} using shimad Zu-FTIR.
- UV-Visible spectra were recorded by shima Zu-UV-Vis. 160 AUtra violet spectro photometer at 25°C, using 1cm quartz cell and examined at the range of (200-1100)nm in DMF at 10^{-3}M.
- Atomic Absorption (A.A) technique using a shimad Zu AA680G atomic absorption spectrophotometer.
- Molar conductivity of the complexes were measured on pw 9526 digital conductivity in DMF at 10^{-3}M.

Syntheses of 2(N-phenyl dithio carboxamid) benzothiazol (L)

2-Mercaptobenzothiazole (0.17g, 1mmol) in ethanol (10 ml) was added to a solution of phenylisothiocyanate (0.14g, 1mmol) in ethanol
(10ml). The resulting mixture was stirred at room temperature and then followed by refluxing for 4hrs to give a yellow solid. The product filtered and dried. Then it was crystallized by ethanol to give yellowish precipitate.

![Chemical structure](image)

**Figure 1: Preparation of the ligand (L) with formula C\(_{14}\)H\(_{10}\)N\(_2\)S\(_3\)**

**Synthesis of metal complexes.**

An ethanolic solution of the following metal salts NiCl\(_2\).6H\(_2\)O (0.237g, 1mmol), CuCl\(_2\) . 2H\(_2\)O (0.17g, 1mmol), ZnCl\(_2\) (0.136, 1mmol), CdCl\(_2\).H\(_2\)O (0.201 g, 1mmol) and HgCl\(_2\) (0.271g, 1mmol) were added to a solution of the ligand (L) (0.302 g, 1mmol) in ethanol. The mixture was stirred for 30 min. The product was filtered and washed with distilled water and dried under vacuum. Physical properties for the ligand and its complexes are given in Table (1).

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>Color</th>
<th>m.p C° or (D)</th>
<th>Yield %</th>
<th>Metal analysis Found (calculated)</th>
<th>solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mwt</td>
<td>C%</td>
</tr>
<tr>
<td>1</td>
<td>(L)C(<em>{14})H(</em>{10})N(_2)S(_3)</td>
<td>Yellowish</td>
<td>90</td>
<td>75</td>
<td>302.44</td>
<td>55.54 (55.43)</td>
</tr>
<tr>
<td>2</td>
<td>[LNiCl(_2)(H(_2)O)(_2)]5H(_2)O</td>
<td>Green</td>
<td>160</td>
<td>80</td>
<td>558.13</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>[LCuCl(_2)(H(_2)O)(_2)]2H(_2)O</td>
<td>Green</td>
<td>140</td>
<td>87</td>
<td>508.98</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>LZnCl(_2)</td>
<td>White-yellow</td>
<td>165</td>
<td>79</td>
<td>438.83</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>LCdCl(_2)</td>
<td>White-yellow</td>
<td>286</td>
<td>80</td>
<td>524.85</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>LHgCl(_2)</td>
<td>Yellow</td>
<td>110</td>
<td>85</td>
<td>574.03</td>
<td>-</td>
</tr>
</tbody>
</table>

* D = Decomposition
RESULTS AND DISCUSSION

Elemental analysis (C.H.N)
The ligand was characterized by (C.H.N) analysis as shown in Table (1).

$^1$HNMR
The results are summarized in Table (2) Fig.2 displays the $^1$HNMR spectrum of the ligand (L). The chemical shift at 7.0-7.8 ppm are to aromatic protons. The chemical shifts at 4.9 ppm is assigned for (N-H) protons, while the chemical shift at 4.0 ppm is due to solvent(6).

Table 2: $^1$HNMR data for the synthesized ligand

<table>
<thead>
<tr>
<th>L</th>
<th>$\delta$(p.p.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic C-H</td>
<td>7.0 – 7.8</td>
</tr>
<tr>
<td>N-H</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Figure 2: The $^1$HNMR of the ligand(L)

The FTIR spectrum of (L)
Because the ligand consist of the SCNH group which may be available either the thion form (S=C-N-H) or the thiol form (H-S-C=N). from the study of infrared spectroscopy as shown in Fig.3, indicated the ligand can exist in tautomeric thion (H-N-C=S) and thiol (-N=C-SH) forms and hence give characteristic thioamide bands in its IR spectrum(7). Sharp band at 3182 cm$^{-1}$ due to $\nu$(N – H) indicates the thion form while a weak band in the region 2576-2526 cm$^{-1}$ suggests thiol form of the ligand. Another band at 1593, 1535, 1138, 1014 and 676 cm$^{-1}$ are assigned to $\delta$(N – H), $\nu$(C = N), $\nu$(C – N) + $\nu$(C = S), $\nu$(C – S) respectively(7-8).
I.R spectra of L-complexes

The mode of ligand bonding is decided on the basis of shifts of \( \nu(N-H) \), \( \nu(C=S) \) and four thioamide bands on complexation. The thioamide band II and III have contributions from:
\[ \delta(N-H), \delta(N-H)+\nu(C-N)+\nu(C-S) . \]

The high frequency N-H absorption loads in the spectrum of the ligand is appeared in multibands 3186-3300 cm\(^{-1}\) on the formation of the metal-ligand complexes. The infrared absorption bands observed at about 1535 cm\(^{-1}\) assigned to \( \nu(C=\overline{N}) \) stretching vibration. The broaden and increase in frequency observed for the complexes Ni (1545, 1535), Cu (1560, 1543), Zn (1562, 1512), Cd (1558, 1531) and Hg (1550) can be explained as resulting from the greater double bond character of the carbon to nitrogen bond on the complexes formation.

A difference in the spectra of ligand and its metal complexes appears in the region at about 1014 cm\(^{-1}\), which is due \( \nu(C-N)+\nu(C-S) \). A multibands or broaden bands on complexes formation (Table-3). This observation can be explained by the participation of \( \nu(C-N)+\nu(C=S) \) in bonding on complexation. The appearance of \( \nu(M-N) \) and \( \nu(M-S) \) at region (513-410)cm\(^{-1}\) and (489-424)cm\(^{-1}\) respectively, suggesting the coordination through nitrogen and sulphur atom. The bands characteristic of coordinated water and (M-O) are seen in Ni and Cu complexes in (827, 555)cm\(^{-1}\) and (832, 551) cm\(^{-1}\) respectively. Table (3) showed the characteristic stretching vibrational frequencies (cm\(^{-1}\)) located in the FT-IR of the ligand and its complexes.
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Figure 3: a Infrared spectrum of the ligand (L)
b Infrared spectrum of the \([\text{LNiCl}_2\cdot(\text{H}_2\text{O})_2\cdot5\text{H}_2\text{O}]\)

Table 2: Characteristic stretching vibrational frequencies (cm\(^{-1}\)) located in the FT-IR the ligand (L) and its complexes.

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>(\nu(N-H)) cm(^{-1})</th>
<th>(\delta(N-H)) cm(^{-1})</th>
<th>(\nu(C-N)) cm(^{-1})</th>
<th>(\nu(C-S)) cm(^{-1})</th>
<th>(\nu(C=S)) cm(^{-1})</th>
<th>(\nu(M-N)) cm(^{-1})</th>
<th>(\nu(M-S)) cm(^{-1})</th>
<th>(\nu(M-O)) cm(^{-1})</th>
<th>Other band (\nu(O-H)) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((L)\text{C}<em>{14}\text{H}</em>{10}\text{N}_2\text{S}_3)</td>
<td>3182 1593</td>
<td>1535 1138 1014</td>
<td>667 - - - -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>([\text{LNiCl}_2\cdot2\text{H}_2\text{O}]\cdot5\text{H}_2\text{O})</td>
<td>3186 1610</td>
<td>1545 1138 1014</td>
<td>671 525 430 555 3387</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>([\text{LCuCl}_2\cdot2\text{H}_2\text{O}]\cdot2\text{H}_2\text{O})</td>
<td>3186 1600</td>
<td>1560 1543 1520 1130 1010</td>
<td>678 532 432 551 3398</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(\text{LZnCl}_2)</td>
<td>3059 1599</td>
<td>1562 1512 1134 1026</td>
<td>671 581 432 - -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(\text{LCDCl}_2)</td>
<td>3059 1589</td>
<td>1558 1531 1130 1010</td>
<td>694 536 424 - 3525</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(\text{LHgCl}_2)</td>
<td>3182 1597</td>
<td>1550 1138 1037</td>
<td>690 532 420 - -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
UV-Visible spectra of the ligand (L) and complexes

The UV-Visible spectra of the ligand (L) in dimethyl formamide solution (Table-4) exhibited strong absorption bands at (220 nm, 4545 cm\(^{-1}\)), (279 nm, 35842 cm\(^{-1}\)) and (326 nm, 30675 cm\(^{-1}\)). This may be attributed to the \((\pi-\pi^*)\) and \((n-\pi^*)\) transition (15).

The UV-Visible spectrum of Ni\(^{2+}\)-complex showed multibands in the region (640 nm, 15625 cm\(^{-1}\)) are due to \(^2E_g \leftrightarrow ^3A_{2g}\) (\(\nu_2\)) and (430 nm, 23256 cm\(^{-1}\)) is due to \(\tau_{1g(p)} \leftrightarrow ^3A_{2g}\) (\(\nu_3\)). The absence of transition (\(\nu_1\)) which is equal to (10 Dq) was calculated by fitting the ratio \((\nu_3/\nu_2)\) to the Tanabe-sugans digram for d\(^8\) ion (15-16). The ratio 23256 to 15625 equal 1.49 \(E(\nu_2)/B=30\), B = 23256 / 30 = 775 and \(\Delta 0 / B = 9\). \(\Delta 0 = 6975\) cm\(^{-1}\). B for free Ni\(^{2+}\) = 775 \(\beta\) (nephelauxetic effect) = B complex / B Ni\(^{2+}\) = 755/1030 = 0.756, which indicates of d-electron delocalization on the ligand hence a some covalent character in complex Bonds. Cu\(^{2+}\) complex appeared band at (650nm, 15385 cm\(^{-1}\)) is due to \(^2T_{2g} \leftrightarrow ^2E_{(g)}\). The yellowish L-complexes (Zn, Cd, Hg) spectra that have d\(^{10}\) configuration have shifting from a free ligand band, which presented at (316 nm, 31645 cm\(^{-1}\)), (379 nm, 26385 cm\(^{-1}\)) and (311 nm, 32102 cm\(^{-1}\)) are due to charge transfer (17-18).

The molar conductance

The molar conductance of all complexes in DMF Table(4) was found to be low which suggested coordination of anion to the metal (18).

Table-4: Electronic spectra and conductance in DMF of ligand (L) and its complexes

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>(\lambda (nm)) (\lambda (cm^{-1}))</th>
<th>Assignment bands</th>
<th>(\Lambda) S.cm(^{-1}) DMF (10(^{-3})M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(L)C(<em>{14})H(</em>{10})N(_2)S(_3)</td>
<td>4545 (220) 35778(279.5) 30627(326.5)</td>
<td>(\pi \rightarrow \pi^<em>) (n \rightarrow \pi^</em>)</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>[LNiCl(_2)(H(_2)O)(_2)] 5H(_2)O</td>
<td>23256(430) 15625 (640)</td>
<td>(\tau_{1g(p)} \leftrightarrow ^3A_{2g}) (^2E_g \leftrightarrow ^3A_{2g})</td>
<td>10.4</td>
</tr>
<tr>
<td>3</td>
<td>[LCuCl(_2)(H(_2)O)(_2)] 2H(_2)O</td>
<td>15385 (650)</td>
<td>(\tau_{1g} \leftrightarrow ^2E_{(g)})</td>
<td>12.4</td>
</tr>
<tr>
<td>4</td>
<td>LZnCl(_2)</td>
<td>31645 (316)</td>
<td>Charge-transfer</td>
<td>2.26</td>
</tr>
<tr>
<td>5</td>
<td>LCdCl(_2)</td>
<td>26385 (379)</td>
<td>Charge-transfer</td>
<td>0.20</td>
</tr>
<tr>
<td>6</td>
<td>LHgCl(_2)</td>
<td>32102 (311.5)</td>
<td>Charge-transfer</td>
<td>3.98</td>
</tr>
</tbody>
</table>
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Figure 4(a): uv-visible spectrum of the ligand (L)
(b): uv-visible spectrum of the [LNiCl₂(H₂O)₂]5H₂O the [LNiCl₂.2H₂O]5H₂O
(c): uv-visible spectrum of the [LCdCl₂]2H₂O
Molar ratio

The complexes of the ligand (L) with selected metal ions (Ni$^{2+}$ and Cu$^{2+}$) were studied in solution using ethanol as a solvent, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method (19). A series of solutions were prepared having a constant concentration (C) $10^{-3}$M of the hydrated metal salts and the ligand (L). The (M:L) ratio was determined from the relationship between the absorption of the observed light and the mole ratio (M:L) found to be (1:1). Fig-5 (a),(b). The result of complexes formation in solution are show in Table(5).

Table 5: (a,b): VM, VL and absorption of (L), VM= volume of metal in ml, VL= volume of ligand in ml

<table>
<thead>
<tr>
<th></th>
<th>[LNiCl$_2$2H$_2$O] 5H$_2$O</th>
<th>[LCuCl$_2$2H$_2$O] 2H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VM</td>
<td>VL</td>
</tr>
<tr>
<td>1ml</td>
<td>0.25</td>
<td>0.32</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.68</td>
</tr>
<tr>
<td>1</td>
<td>0.75</td>
<td>0.94</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1.4</td>
</tr>
<tr>
<td>1</td>
<td>1.25</td>
<td>1.38</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>1.39</td>
</tr>
<tr>
<td>1</td>
<td>1.75</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Figure 5: (a): molar ratio slop for Ni$^{2+}$ ion $\lambda$(352 nm)
(b): molar ratio slop for Cu$^{2+}$ ion $\lambda$(617 nm)

Study of biological activity

The biological activity of the prepared new ligand and its complexes were studied against selected type of microorganisms which include gram positive bacteria like staphylococcus aureus and gram Negative bacteria like E.coli, in agar diffusion method (20), which is used (DMF) as a solvent,
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and we are used these Antibiotics disc which include cephalosporin and Amoxicillin as control. Agar diffusion method involves the exposure of the Zone of inhibition toward the diffusion of microorganisms on agar plate. The plates were incubated for (24)hrs at (37°C). The Zone of inhibition of bacterial growth around the disc was observed.

Biological effects of new ligand and its complexes exhibited antibacterial activity against gram positive bacteria in two different concentration (1 and 5) mg/ml while with gram negative, the effect was clear in 1 mg/ml concentration except Hg-complex did not have effect but in 5 mg/ml the ligand and its complexes did not show any effect except Hg-complex gave 5 mm. Fig-6.

Figure 6: (a): Effect of ligand and its complexes on *Staphylococcus aureus*.

(b): Effect of ligand and its complexes on *E.coli*.

CONCLUSION

A series of complexes (Cu²⁺, Ni²⁺, Zn²⁺, Cd²⁺ and Hg²⁺) with 2(N-phenyldithio carboxamide) benzothiazol (L) have been prepared and
characterized. The bidentate ligand (L) (N, S) is binding metal ions (M$^{2+}$ = Cu, Ni) and with two molecule H$_2$O forming octahedral structure while with metal ion (M$^{2+}$=Zn, Cd, Hg$^{2+}$), forming tetrahedral structure and as follow; Fig-7.

![Diagram](image)

$M^{2+}$ = Ni, Cu

$M^{2+}$ = Zn, Cd, Hg

**Figure 7:** The structure of these complexes may thus be represented

**REFERENCES**