

## Synthesis, Characterization and Antibacterial of 2,3-Dihydrobenzo Thiazole-2-Carboxylic Acid Complexes with Some Selected Metal Ions

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### Abstract:

A new ligand 2,3-dihydrobenzo [d] thiazole-2-carboxylic acid (L) has been prepared from the reaction of ortho amino phenyl thiol with dichloroacetic acid in mole ratio (1:1). It has been characterized by elemental analysis (C.H.N.), IR, UV-Vis. spectra and  $^1\text{H}$ ,  $^{13}\text{C}$ -NMR. A new series complexes of the bivalent ions (Co, Ni, Cu, Pd, Cd, Hg and Pb) and the trivalent (Cr) have been prepared and characterized too. The structural has been established by elemental analysis (C.H.N.), IR, UV-Vis. spectra, molar conductivity, atomic absorption and magnetic susceptibility measurements.

The synthesized complexes were prepared in (1:2) ratio correspond to (Co(II), Ni(II), Cu(II), Pd(II), Cd(II), Hg(II) and Pb(II) complexes while in case Cr(III) complex is (1:1) ratio (M:L).  $\alpha$ ,  $K_f$  for (Cr(III), Co(II), Ni(II) and Cu(II)) were estimated too. The complexes showed characteristics octahedral geometry with the (O,N) ligand coordinated in bidentate mode except with Pd showed square planer. The study of biological activity of ligand (L) and its complexes showed various activities toward *Staphylococcus aureus* and *E. coli*.

**Key words:** Hydrobenzo, Carboxylic acid, Ligands.

### Introduction:

The interaction of metal complexes with biological system, which is the field of bio-coordination chemistry draws increasing interest[1,2]. It plays many important roles in electron transfer agents, as catalysts, and in photosynthesis[3].

Inorganic elements play crucial roles in biological and biomedical processes and, it is evident that many organic compounds used in medicine do not have a purely organic mode of action[4], some are activated or bio-transformed by metal ions including

metallozymes, other have directed indirect effect on metal ion metabolism[5]. The elements of medical importance (Pd, Cu) offer potential for design of novel therapeutic and diagnostic agents[6] also for treatment and understanding of diseases, which are currently intractable[7]. There have been a lot of studies related to the strong association between metal complexes and antibacterial activities. Attention has been paid during the last decade for the chemistry of the metal complexes of

ligands containing nitrogen and oxygen. This could be due to the stability of such ligands complexes and its biological activity in oxidation catalysis and electro chemical analysis[8]. According to above observation attempt to synthesis anew chelate ligand was done. In present work 2,3-dihydrobenzo [d] thiazole-2-carboxylic acid with (Cr(III), Co(II), Ni(II), Cu(II), Pd(II), Cd(II), Hg(II) and Pb(II)) are synthesized and their physical properties, biological activity were investigated.

### Materials and Methods:

**A- Chemicals;** All reagents used were Analar or chemically pure grade British Drug

Houses (BDH), Merck and Fluka. Materials; ortho amino phenyl thiol ( $C_6H_7NS$ ), dichloro acetic acid ( $C_2H_2O_2Cl_2$ ), Chromium trichloride hexahydrate ( $CrCl_3 \cdot 6H_2O$ ), Cobalt chloride hexahydrate ( $CoCl_2 \cdot 6H_2O$ ), Nickel chloride hexahydrate ( $NiCl_2 \cdot 6H_2O$ ), Copper Chloride Dihydrate ( $CuCl_2 \cdot 2H_2O$ ), Paladium Chloride ( $PdCl_2$ ), Cadmium Chloride Dihydrate ( $CdCl_2 \cdot 2H_2O$ ), Mercury Chloride ( $HgCl_2$ ), Lead Nitrate ( $Pb(NO_3)_2$ ), Ethanol 99% ( $CH_3CH_2OH$ ), Dimethyl Formamide 99.5% (DMF), Dimethyl Sulphoxide 99.5% (DMSO), Carbon tetra Chloride 99.5% ( $CCl_4$ ), Chloroform 99% ( $CHCl_3$ ), Toluene 99% ( $C_7H_8$ ).

**B- Instruments;** Elemental analysis for the new ligand (L) and complexes were determined by calibration type: Linear Regression Euro EA elemental analysis were made in Al-al-Beyt University, Amman-Jordan and Babel University. Melting Points were determined by Gallen-Kamp apparatus.  $^1H$ ,  $^{13}C$ -

NMR spectra were recorded in DMSO using Bruker Model; Ultra shield 300 MHz origin, Switzerland ( Jordan) in  $CH_3OO$  using DMSO as an internal standard. IR spectra were recorded as KBr discs in the range (4000-400)  $cm^{-1}$  using Shimadzu- FTIR.

UV-Visible spectra were recorded by Shimadzu UV-Vis 160 ultraviolet spectrophotometer at 25°C using 1 Cm quartz cell and examined at the range of (200-1100) nm at  $10^{-3}$  M in DMSO. Atomic absorption (A.A.) technique has been measured using a Shimadzu AA680G atomic absorption spectrophotometer at the laboratories of Ibn- Sinaa Company. Molar conductivity of the complexes were measured on PW 9526 digital conductivity in DMSO at  $10^{-3}$  M. Magnetic susceptibility balance, Model, MsB-MK<sub>1</sub> are made in Al-Nahrain University.

### Preparation:

Synthesis of 2,3-dihydrobenzo[d] thiazole-2-carboxylic acid(L) ortho amino phenyl thiol (0.125gm, 0.001mol) and dichloro acetic acid (0.129gm, 0.001mol) in ethanol ( $15cm^3$ ) was stirred for 6 hours. The precipitate was filtered and recrystallized from hot absolute ethanol, fine yellow crystals were obtained (m.p. 104°C, yield 82%) and it's soluble in most organic solvent as indicated in Table(1).

### Synthesis of metal complexes:

One mole of ethanolic solution of metal salts was added to two moles of the ligand (L) except with Cr-complex the ratio was (1:1)  $[CrCl_3 \cdot 6H_2O]$  (0.26gm, 1.00mmol),  $CoCl_2 \cdot 6H_2O$  (0.24gm, 1.00mmol),  $NiCl_2 \cdot 6H_2O$  (0.24gm, 1.00mmol),  $CuCl_2 \cdot 2H_2O$  (0.169gm, 1.00mmol),  $PdCl_2$  (0.170gm, 1.00mmol),  $CdCl_2 \cdot 2H_2O$  (0.22gm, 1.00mmol),  $HgCl_2$  (0.27gm, 1.00mmol),  $Pb(NO_3)_2$  (0.33gm, 1.00mmol) was

added to (0.181gm. 1.00mmol) in  $\text{Cr}^{+3}$  complex and (0.362gm. 2.00mmol) in the cases of  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Pd}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Hg}^{+2}$  and  $\text{Pb}^{+2}$  of the ligand (L). At room temperature the mixture was stirred for 6 hrs. The product was

filtered and washed with distilled water and dried under vacuum. The color melting point, yield, metal analysis and solubility of the ligand and its complexes are given in Table (1).

**Table (1): Color, melting point, yield, metal analysis and solubility for the ligand (L) and its complexes**

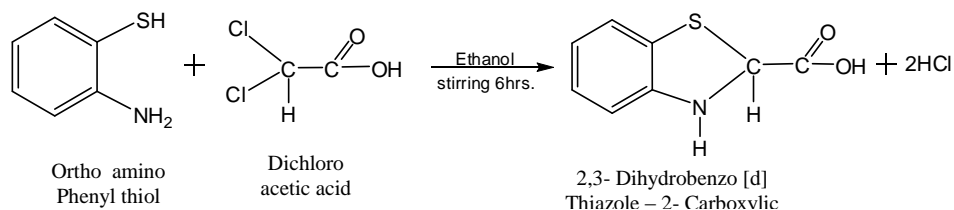
No.	Compound	No. of mol and gm	color	m.p. °c or(dec.)	Yield %	Metal analysis found (Calculated)				solubility
						C%	H%	N%	M%	
1	(L) $\text{C}_8\text{H}_7\text{SNO}_2$	1.00-2.00 0.18-0.36	Yellow	104 °C	82	53.22 (53.03)	3.84 (3.86)	7.68 (7.73)	-	EtOH, $\text{CCl}_4$ , $\text{CHCl}_3$ , DMF, DMSO, $\text{C}_7\text{H}_8$
2	L- $\text{CrCl}_3 \cdot \text{H}_2\text{O}$	1.00 0.26	Green	188°C	75	26.83 (26.85)	1.92 (1.95)	3.9 (3.91)	14.53 (14.54)	DMF, DMSO
3	L <sub>2</sub> - $\text{CoCl}_2$	2.00 0.24	Violet	142°C	62	39.01 (39.02)	2.80 (2.84)	5.98 (5.69)	11.97 (11.99)	DMF, DMSO
4	L <sub>2</sub> - $\text{NiCl}_2$	2.00 0.24	Green	196°C	74	39.01 (39.04)	2.86 (2.84)	5.68 (5.69)	11.89 (11.93)	DMF, DMSO
5	L <sub>2</sub> - $\text{CuCl}_2$	2.00 0.16	Blue	186°C	75	38.65 (38.67)	2.80 (2.81)	5.62 (5.63)	12.76 (12.78)	DMF, DMSO
6	L <sub>2</sub> - $\text{PdCl}_2$	2.00 0.17	Brown	198(dec.)	84	35.57 (35.59)	2.57 (2.59)	5.16 (5.19)	19.70 (19.72)	DMF, DMSO
7	L <sub>2</sub> - $\text{CdCl}_2$	2.00 0.22	Light yellow	192(dec.)	91	35.20 (35.19)	2.53 (2.56)	5.11 (5.13)	20.64 (20.62)	DMF, DMSO
8	L <sub>2</sub> - $\text{HgCl}_2$	2.00 0.27	Brown	204(dec.)	88	30.29 (30.30)	2.19 (2.20)	4.39 (4.41)	31.61 (31.64)	DMF, DMSO
9	L <sub>2</sub> - $\text{Pb}(\text{NO}_3)_2$	2.00 0.33	Light yellow	146°C	78	-	-	-	32.67 (32.8)	DMF, DMSO

Dec.= decomposition.

## Results and discussion:

Synthesis and characterization of the ligand 2,3-dihydrobenzo [d] thiazole-2-Carboxylic acid. The ligand

was obtained by the reaction of one mole of the ortho amino phenylthiol and one mole of dichloro acetic acid;



### 1- Elemental analysis (C.H.N) for the ligand:

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

### 2- $^1\text{H-NMR}$ spectrum for the ligand:

The  $^1\text{H-NMR}$  spectrum of the ligand (L) are summarized in the chemical. The chemical shift at ( $\delta$  4.04

ppm) is assigned for (N-H) proton. The chemical shift at ( $\delta$  4.88 ppm) belongs to the (N-C-H). Chemical shift of aromatic protons showed at ( $\delta$  7.1-  $\delta$  7.6 ppm). A weak signal is appeared at higher chemical shift ( $\delta$ 10.67 ppm) for one proton could be attributed of the electron with drawing group (COOH)[8].

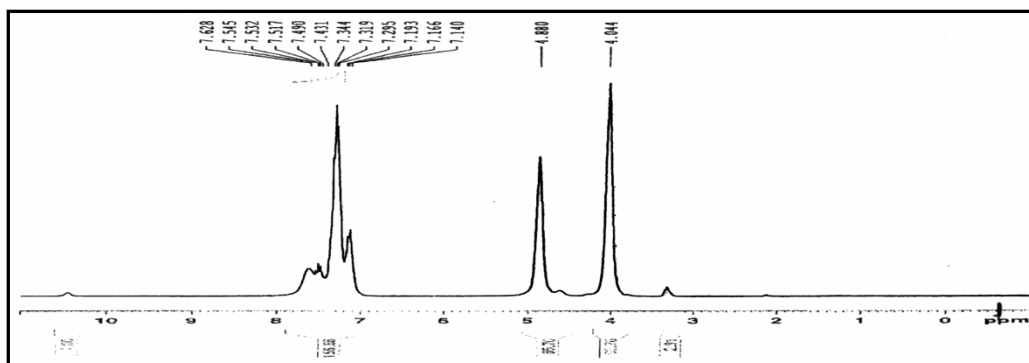


Fig. (1): The  $^1\text{H}$ -NMR spectrum of the ligand (L)

### $^{13}\text{C}$ -NMR spectrum for the ligand (L):

$^{13}\text{C}$ -NMR of the free ligand shows the signals of the  $\text{C}_{\text{aromatic}}$  carbon of the benzene ring were observed at ( $\delta 108$ -  $\delta 136$  ppm.). A signal at ( $\delta 66.22$  ppm.) assigned to the carbon have one

hydrogen (HC-NH). This leaves the signal at ( $\delta 170$  ppm.) correspond to the carboxylic group. The signal at ( $\delta 140$  ppm.) assigned to (=C-NH) and asignal at ( $\delta 40$  ppm.) due to the solvent[9].

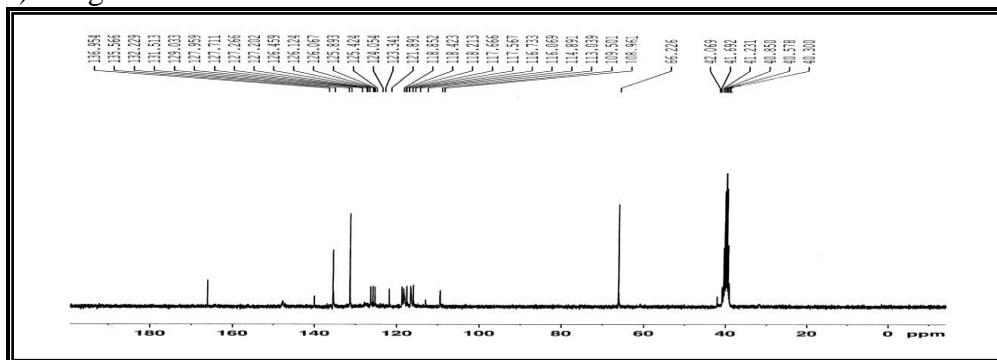


Fig (2): The  $^{13}\text{C}$ -NMR spectrum of the ligand (L). 4-Infrared spectrum for the ligand (L) and complexes.

The infrared spectrum of the ligand in the solid state does not contain the  $\nu(\text{S-H})$  which appears in the starting material orthoaminophenylthiol at ( $2500$ - $2600$ )  $\text{cm}^{-1}$  region. This indicates the displacement of SH hydrogen orthoaminophenylthiol by means of  $>\text{CH-C=O}$ [10], Furthermore new bands were observed at  $2852\text{cm}^{-1}$  due to  $\text{C-H}$  aliphatic[11]. Bands in the

( $3335\text{cm}^{-1}$ , ( $1608\text{cm}^{-1}$ , ( $1307\text{cm}^{-1}$  are diagnostic of primary aromatic amine.

The carboxylate group  $\nu_{\text{as}}(\text{COO}^-)$ , and  $\nu_{\text{s}}(\text{COO}^-)$  appeared at ( $1583\text{cm}^{-1}$  and ( $1560\text{cm}^{-1}$ [12]. Bands at ( $1246\text{cm}^{-1}$ , ( $1020\text{cm}^{-1}$  ( $669\text{cm}^{-1}$  are due to  $(\text{S-CH})$ [13]. Infrared spectra have been used to determine whether coordination occurs through the aromatic( $-\text{NH}-$ ) and  $(\text{S-CH}-)$  or only through aromatic( $-\text{NH}-$ ) in ligand (L).

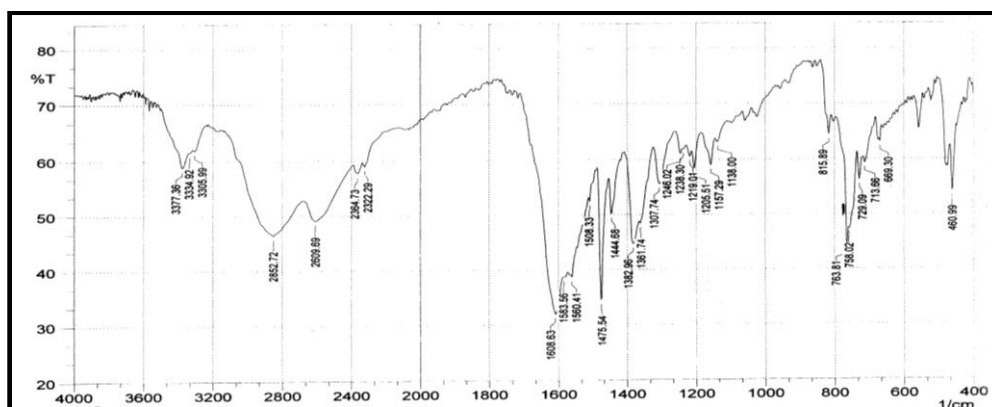


Fig. (3): Infrared Spectrum of the Ligand (L)

The infrared spectra of all complexes showed the multi bands in the range (3587- 3392)  $\text{cm}^{-1}$  are split or broader. The carboxylate group  $\nu_{\text{as}}(\text{COO}^-)$ , and  $\nu_{\text{s}}(\text{COO}^-)$  appeared at (1556-1593)  $\text{cm}^{-1}$  and (1500-1546) $\text{cm}^{-1}$  all that indicated a linkage between the oxygen of carboxylate group with the metal[14]. Bands at (1604-1610) $\text{cm}^{-1}$  and (1301- 1317) $\text{cm}^{-1}$  with the

formation of new absorption bands for the coordination bands (M-N) in the region (503–551) $\text{cm}^{-1}$ . Suggesting the coordination through nitrogen atom[15]. While the bands at (449-486) $\text{cm}^{-1}$  assigned to  $\nu(\text{M-O})$ , these bands confirm the coordination of the oxygen atom of carboxylate group with metal ions in complexes[16].

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

No.	Compound	$\nu(\text{O-H})$ Carboxyl	$\nu(\text{N-H})$	$\nu(\text{C-H})$ Ar.	$\nu(\text{C-H})$ Ali	$\nu(\text{COO}^-)$ asym.	$\nu(\text{COO}^-)$ sym.	$\nu(\text{C-S})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$ + $\nu(\text{OH}_2)$ eq.	$\nu\text{NO}_3^-$
1	(L) $\text{C}_5\text{H}_7\text{SnO}_2$	3377 (m.br)	3335(m.br) 1608(s.s), 1307(s.s)	3306(m.br)	2852 (m.br) 1475(s.s), 1444(m.s)	1583(sh)	1560(w.s)	1246(m.s) 1020(m.s) 669(m.s)			-
2	L-CrCl $_3$ .H $_2$ O	3527 (m.br)	(3350- 3290)(m.br) 1604(s.s), 1301(m.s)	3180, 3061 (m.br)	2885 (m.br) 1469(s.s), 1421(s.s)	1568 (m.s)	1504(s.s)	1232(m.s) 1024(m.s) 677(m.s)	503(m.s)	468(s.s) 825(m.s)	-
3	L $_2$ -CoCl $_2$	3380 (m.br)	(3363)(m.br) 1610(s.s), 1301(s.s)	3160, 3056 (m.br)	2891 (m.br) 1471(s.s), 1420(m.s)	1556 (m.s)	1510(m.s)	1251(sh) 1030(m.s) 671(m.s)	525(m.s)	475(m.s)	-
4	L $_2$ -NiCl $_2$	3392 (m.br)	(3385- 3354)(m.br) 1317(m.s)	3147, 3084 (m.br)	2970(sh) 1473(s.s), 1442(m.s)	1593(s.s)	1546(m.s)	1226(m.s) 1037(m.s) 680(m.s)	551 (m.s)	449(m.s)	-
5	L $_2$ -CuCl $_2$	3587 (m.br)	(3380- 3200)(m.br) 1608(m.S), 1307(m.S)	3150, 3057 (m.br)	2970(sh) 2883(sh) 1473(s.s), 1440(m.s)	1579 (m.s)	1510(m.s)	1249(m.s) 1033(m.s) 665(m.s)	520(w.s)	472(m.s)	-
6	L $_2$ -PdCl $_2$	3570 (m.br)	(3354)(m.br) 1608(m.s), 1305(m.s)	3160, 3053 (m.br)	2989(w.s) 2889(w.s) 1473(s.s), 1444(m.s)	1587 (m.s)	1505(m.s)	1230(m.s) 1031(m.s) 644(m.s)	505(m.s)	470(m.s)	-
7	L $_2$ -CdCl $_2$	3547 (m.br)	(3456)(m.br) 3278,3219(s.s), 1608,1305(s.S)	3160, 3060 (m.s)	2980 (w.br) 2870 (m.br) 1475(s.s), 1444(s.s)	1585 (s.s)	1500(m.s)	1249(m.s) 1055(m.s) 669(m.s)	513(m.s)	486(m.s)	-
8	L $_2$ -HgCl $_2$	3566 (m.br)	(3329- 3282)(m.br) 1608(s.s), 1311(s.s)	3149, 3093 (m.s)	2970 (m.br) 2875 (m.br) 1475(s.s), 1450(m.S)	1570 (m.s)	1510(m.s)	1250(m.br) 1033(m.s) 671(m.s)	512(m.s)	472(m.s)	-
9	L $_2$ -Pb(NO $_3$ ) $_2$	3490 (m.br)	(3375) (m.s) 3302(m.s), 1608(m.s), 1303(s.s)	3178, 3061 (m.s)	2995(m.s) 2890(m.s), 1475(s.s), 1446(M.S)	1583 (m.s)	1500(m.s)	1247(m.s) 1024(m.s) 673(m.s)	540(m.s)	470(m.s)	935 (m.s) 960 (m.s)

Ar=aromatic, Ali=aliphatic,  $\nu_{\text{asym}}$ =Asymmetric, sym=symmetric, sh=shoulder, br=broad, m=medium, s=strong, w=weak

The band characteristic of coordinated water and (M–O) are seen in Cr complex in (825) $\text{cm}^{-1}$  and (468)  $\text{cm}^{-1}$  [17]. The Pb complex spectrum

exhibit bands at (935)  $\text{cm}^{-1}$  and (690) $\text{cm}^{-1}$  due to coordinate nitrate ion[18].

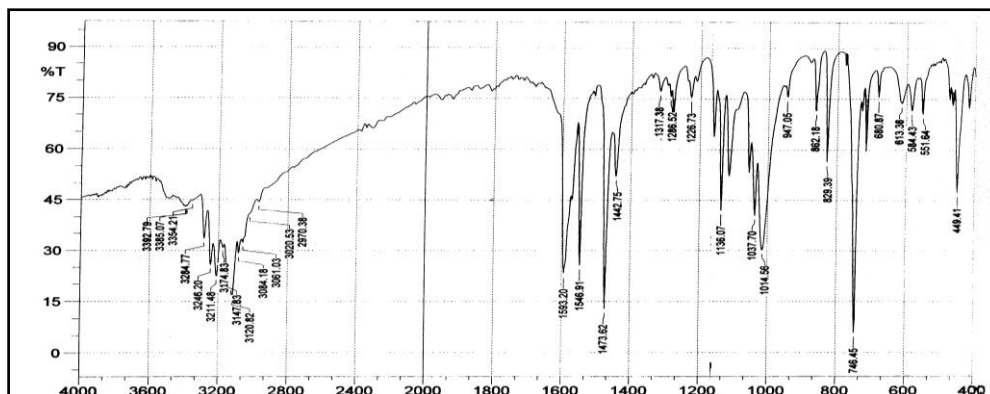


Fig.(4): infrared spectrum of the L<sub>2</sub> – NiCl<sub>2</sub>

**The U.V-Visible spectrum of ligand (L) and complexes:**

The UV-Visible spectrum of ligand (L) in DMSO (10<sup>-3</sup> M) solution exhibited strong absorption peaks at

(268nm, 37313 $\text{cm}^{-1}$ ), (348 nm, 28735 $\text{cm}^{-1}$ ) and (359nm, 27855 $\text{cm}^{-1}$ ). This may attributed to the ( $\pi$ -  $\pi^*$ ) and ( $n$ - $\pi^*$ ) transition[19].

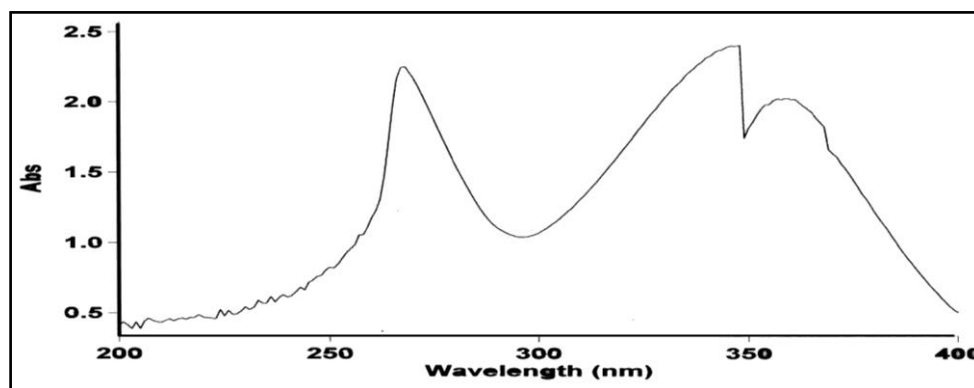


Fig. (5): The UV-Visible spectrum of ligand (L)

The UV-Visible spectrum of Cr<sup>+3</sup> complex showed a peak band in the region (640nm, 15625  $\text{cm}^{-1}$ ) and is due to <sup>4</sup>A<sub>2g</sub>→<sup>4</sup>T<sub>2g</sub>[20]. The UV-Visible spectrum of Co<sup>+2</sup> complex showed two peaks in the region

(600nm, 16666 $\text{cm}^{-1}$ ), (660nm, 15151 $\text{cm}^{-1}$ ) due to <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>A<sub>2g</sub> and (520nm, 19230 $\text{cm}^{-1}$ ) <sup>4</sup>T<sub>1g</sub>(F)→<sup>2</sup>T<sub>1g</sub>(P) [21].

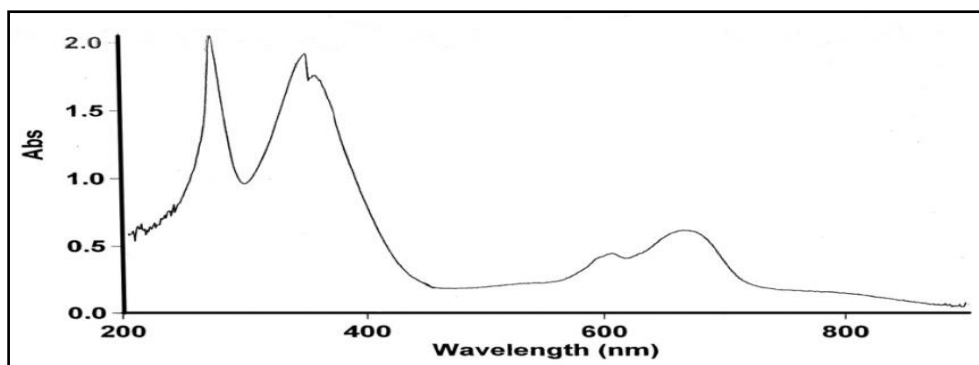


Fig. (6): The UV-Visible spectrum of  $L_2.CoCl_2$

The UV-Visible spectrum of  $Ni^{+2}$  showed a peak at (840nm  $11904cm^{-1}$ ) which is due to  ${}^3A_{2g} \rightarrow {}^3T_{1g}$ [22].  $Cu^{+2}$  complex appeared peak at (610nm,  $16393cm^{-1}$ ) is due to  ${}^2E_g \rightarrow {}^2T_{2g}$ . The brown Palladium complex exhibited a strong peak at (405nm,  $24691cm^{-1}$ ) due to  ${}^1B_{1g} \rightarrow {}^1A_{1g}$  transition[23]. The UV-Visible spectra of  $Cd^{+2}$ ,  $Hg^{+2}$  and  $Pb^{+2}$  complexes showed shifted peaks compared with free ligand (L) are due to charge transfer[24]. The molar conductance were measured in DMSO solvent and concentration  $10^{-3}$  M at room temperature. The molar conductance values of the synthesized complexes were at the range (1.24-11.21  $ohm^{-1}.cm^2.mole^{-1}$ ). These results suggested non-ionic electrolyte for complexes[25].

The magnetic moments of Cr(III) complex were indicative of three unpaired electrons for Cr(III) ion suggesting consistency with their octahedral environment. The magnetic moments measurements for the solid Co(II) complex are also indicative of three unpaired electrons per Co(II) ion suggesting consistency with their octahedral environment. Ni(II) complex showed the magnetic moment value of (2.8- 3.5) B.M. (Octahedral range) suggesting consistency with their octahedral environment. The magnetic susceptibility measurements of Cu(II) complex is 1.98 B.M. which suggests the presence of one unpaired electron with octahedral configuration [26]. Electronic spectra conductance in (DMSO), magnetic moment (B.M) of the ligand and its complexes are given in Table (3).

Table (3): Electronic spectra in (DMSO), conductance in DMSO, magnetic moment (B.M) of the ligand (L) and its complexes

No.	Compound	$\lambda(nm)cm^{-1}$	Assignment bands	$\epsilon_{max}$ ( $L.mol^{-1}.cm^{-1}$ )	$\Lambda S.(ohm^{-1}.cm^2.mol^{-1})$ DMSO ( $10^{-3}M$ )	$M_{eff}$ (B.M)
1	$(L)C_8H_7SNO_2$	37313(268)	$\pi-\pi^*$	2250	-	-
		28735(348)	$n-\pi^*$	2402		
		27855(359)		2025		
2	$L-CrCl_3.H_2O$	36764(272)	L.F	1004	9.34	3.71
		15625(640)	${}^4A_{2g} \rightarrow {}^4T_{2g}$	322		
3	$L_2-CoCl_2$	38314(261)	L.F	2312	9.34	4.42
		19230(520)	${}^4T_{1g(F)} \rightarrow {}^2T_{1g(P)}$	214		
		15151(660)	${}^4T_{1g} \rightarrow {}^4A_{2g}$	543		
4	$L_2-NiCl_2$	35971(278)	L.F	1352	10.52	2.91
		11904(840)	${}^3A_{2g} \rightarrow {}^3T_{1g}$	282		
5	$L_2-CuCl_2$	28985(245)	L.F	1045	8.41	1.98
		16393(610)	${}^2E_g \rightarrow {}^2T_{2g}$	123		
6	$L_2-PdCl_2$	37313(268)	L.F	1440	9.33	Dia
		24691(405)	${}^1B_{1g} \rightarrow {}^1A_{1g}$	987		
7	$L_2-CdCl_2$	26178(382)	Charge-Transfer	1321	10.35	Dia
8	$L_2-HgCl_2$	25641(390)	Charge-Transfer	843	9.45	Dia
9	$L_2-Pb(NO_3)_2$	25125(398)	Charge-Transfer	1031	1.24	Dia

B.M= Bohr magnation.

### The Study of Cr<sup>+3</sup>, Co<sup>+2</sup>, Ni<sup>+2</sup>, Cu<sup>+2</sup> complexes formation in solution:

The complexes of the ligand (L) with selected metal ion (Cr<sup>+3</sup>, Co<sup>+2</sup>, Ni<sup>+2</sup>, Cu<sup>+2</sup>) were studied in solution using ethanol as solvent, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method[27]. A series of solutions were prepared having a constant

concentration (C) 10<sup>-3</sup> 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) for (Cr<sup>+3</sup>) complex while(1:2) for (Co<sup>+2</sup>, Ni<sup>+2</sup>, Cu<sup>+2</sup>) complexes. The results of the complexes formation in solutions are shown in Tables (4 and 5).

V<sub>M</sub> = volume of metal in (ml) V<sub>L</sub> = volume of ligand in (ml)

Table (4): Continuous variation slop for Cr <sup>+3</sup> ion λ (368nm)		
L- CrCl <sub>3</sub> .H <sub>2</sub> O		
V <sub>M</sub>	V <sub>L</sub>	Abs
1 ml	0.25	0.28
1	0.5	0.59
1	0.75	0.91
1	1	1.2
1	1.25	1.19
1	1.5	1.21
1	1.75	1.22
1	2	1.19
1	2.25	1.18
1	2.5	1.21
1	2.75	1.19
1	3	1.22

Table (5): Continuous variation slop for Co <sup>+2</sup> ion λ (261nm)		
L <sub>2</sub> - CoCl <sub>2</sub>		
V <sub>M</sub>	V <sub>L</sub>	Abs
1 ml	0.25	0.12
1	0.5	0.17
1	0.75	0.24
1	1	0.27
1	1.25	0.37
1	1.5	0.39
1	1.75	0.39
1	2	0.4
1	2.25	0.41
1	2.5	0.39
1	2.75	0.39
1	3	0.41

The stability constant (K<sub>f</sub>) of the (1:1) [metal: Ligand] (eq.1) or (1:2) [metal: Ligand] (eq.2) complex was evaluated using the following equations:

$$K_f = 1 - \alpha / \alpha^2 C \dots (1), K_f = 1 - \alpha / 4\alpha^3 C^2 \dots (2), \alpha = A_m - A_s / A_m \dots (3).$$

(α) is the degree of the dissociation (C) is the concentration of the complex (10<sup>-3</sup> M). (A<sub>m</sub>) and (A<sub>s</sub>) are absorbance of the partially and fully formed complex respectively

Table (6). The solutions were measured at (λ<sub>max</sub>) of the maximal absorption. The molar absorptivity (ε<sub>max</sub>)(eq.4) has been calculated using equation; A= ε<sub>max</sub>. b.C..... (4)

(A) is the average of three measurement of the absorption containing the same amount of metal ion and three fold excess of ligand, (b) is the path way of the quartz cell usually equal (1cm).

Table (6): A<sub>s</sub>, A<sub>m</sub>, K<sub>f</sub>, λ<sub>max</sub>, of the Cr<sup>+3</sup>, Co<sup>+2</sup>, Ni<sup>+2</sup>, Cu<sup>+2</sup>

No.	Compound	A <sub>s</sub>	A <sub>m</sub>	α	Formation constant (K <sub>f</sub> )	λ <sub>max</sub> nm
1	Cr-complex	1.2	1.22	0.016	3.843×10 <sup>6</sup>	368
2	Co-complex	0.27	0.41	0.341	4.140×10 <sup>6</sup>	261
3	Ni-complex	0.20	0.31	0.354	3.640×10 <sup>6</sup>	397
4	Cu-complex	0.50	1.01	0.504	9.680×10 <sup>5</sup>	362

### Antibacterial activity study:

The antibacterial activity of the prepared new ligand and it's complexes were studied against selected types of microorganisms which include gram positive bacteria like *staphylococcus aureus* and gram negative bacteria like *E.coli*, in a gar diffusion method<sup>[28]</sup>, which is used (DMSO) as a solvent,

and we are used these Antibiotics disc which include cephalosporin as control. Agar 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 Table (7).



**Table (7) The effect of ligand and its complexes on gram positive and gram negative bacteria**

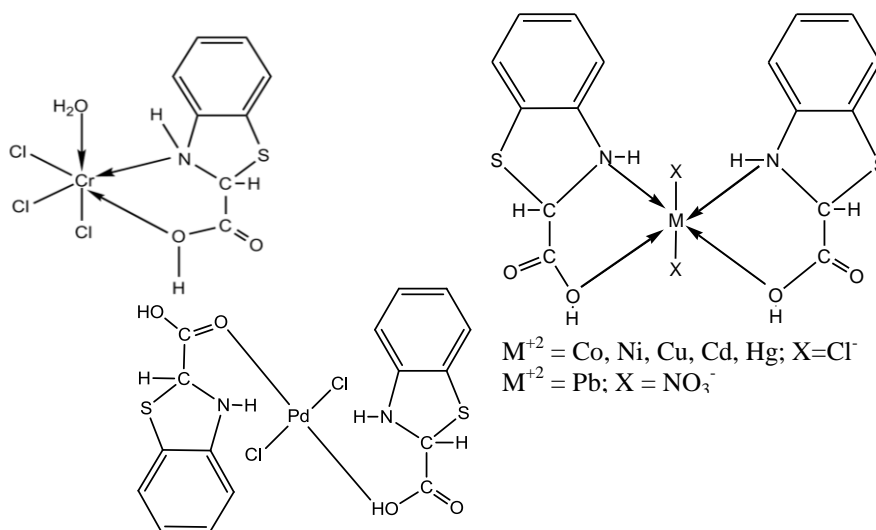
Compound	Diameter of inhibition zone (mm)at concentration 1mg/ml		Diameter of inhibition zone (mm)at concentration 5mg/ml	
	<i>E. coli</i>	<i>Staphylococcus aureus</i>	<i>E. coli</i>	<i>Staphylococcus aureus</i>
Cephalosporin	26.4	25.8	28.8	26.2
(L) $C_8H_7SNO_2$	16.6	16.4	17.2	17.8
L-CrCl <sub>3</sub> .H <sub>2</sub> O	12.6	12	13.4	14.2
L <sub>2</sub> -CoCl <sub>2</sub>	14.4	14	15.6	14.2
L <sub>2</sub> -NiCl <sub>2</sub>	16	15.8	16.4	15.6
L <sub>2</sub> -CuCl <sub>2</sub>	15	11.6	13.8	14.6
L <sub>2</sub> -PdCl <sub>2</sub>	17.4	17	18.4	17

### Conclusions:

The measurements (elemental analysis, infrared and electronic spectra, magnetic susceptibility measurements, atomic absorption spectroscopy and molar conductivity) are used to determined geometry of synthesized.

A new series of complexes of Cr<sup>+3</sup>, Co<sup>+2</sup>, Ni<sup>+2</sup>, Cu<sup>+2</sup>, Pd<sup>+2</sup>, Cd<sup>+2</sup>, Hg<sup>+2</sup>,

Pb<sup>+2</sup> with 2,3-dihydrobenzo [d] thiazole-2-carboxylic acid (L) have been prepared and characterized. The bidentate ligand (L) (N,O) is binding metal forming octahedral structure except Pd<sup>+2</sup> forming square planer structure as follow;



Antibacterial effects of new ligand and its complexes indicated that the new ligand than its complexes exhibited almost equal or more antibacterial activity against both gram positive and gram negative bacteria.

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## تحضير، تشخيص ومضاد بكتيري لمعقدات 3,2- ثنائي هايدروبنزو ثايوزول-2- حامض كاربوكسيللي مع بعض ايونات الفلزات المنتخبة

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### الخلاصة:

حضر الليكاند الجديد (L)3,2- ثنائي هايدرو بنزو [d] ثايوزول -2- حامض كاربوكسيليمن من تفاعل أورثو أمينو فنيل ثايول مع ثنائي كلورو حامض ألكليك و بنسبة 1:1 و شخص بواسطة التحليل الدقيق للعناصر (كاربون، هايدروجين، نيتروجين)، الأشعة تحت الحمراء، والأشعة فوق البنفسجية- المرئية وطيف الرنين النووي المغناطيسي، كما حضرت وشخصت معقدات جديدة لليكاند مع أملاح بعض أيونات العناصر الثنائية التكافؤ (كوبلت، نيكل، نحاس، بلاديوم، كاديوم، زئبق و رصاص) والثلاثي التكافؤ (الكروم). استخدمت تقنيات التحليل الدقيق للعناصر (كاربون، هايدروجين، نيتروجين)، طيف الأشعة تحت الحمراء، الأشعة فوق البنفسجية- المرئية، التوصيلية الكهربائية، الامتصاص الذري أللهبي والخواص المغناطيسية. بينت النسبة المولية ان نسبة (فلز: ليكاند) كانت (2:1) لمعقدات الكوبلت، النيكل، النحاس، البلاديوم، الكاديوم، الزئبق والرصاص و(1:1) بالنسبة لمعقد الكروم. واستنتج من التحاليل ان المعقدات لها شكل ثماني السطوح مع الليكاند (L) (ثنائي السن (N,O) ما عدا البلاديوم مكوناً مربع مستوي. وقد تم حساب قيم  $K_f$ ،  $\alpha$  لمعقدات (الكروم، كوبلت، نيكل والنحاس). كما تم دراسة الفعالية البايولوجية لليكاند ومعقداته وقد أظهرت النتائج امتلاكها فعالية متفاوتة اتجاه أنواع البكتريا *E. coli* و *Staphylococcus aureus*.

الكلمات المفتاحية: هايدروبنزو، حامض كاربوكسيللي، معقدات.