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## Synthesis and characterization of 4-(((3-mercapto-5-phenyl-4H-1,2,4-triazole-4-yl)imino)methyl)-2-methoxyphenol and its complexes with Zr(IV), Cd(II) and Sn(II) ions

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### Abstract

A series of coordination compounds of Zr(IV), Cd(II) and Sn(II) ions with 4-(((3-mercapto-5-phenyl-4H-1,2,4-triazole-4-yl)imino)methyl)-2-methoxyphenol, as a ligand has been successfully prepared in alcoholic medium. The prepared complexes were characterized quantitatively and qualitatively by using: elemental analysis CHNS, FT-IR spectroscopy, UV-visible spectroscopy,  $^1\text{H}$  and  $^{13}\text{C}$ NMR, atomic absorption measurements, magnetic susceptibility, thermal analysis(TG and DTG) and conductivity measurements. This ligand coordinates as a bidentate that to the metal ions through sulphur and nitrogen of (azomethine group) atoms. According to the spectral data, Cd(II)- and Sn(II)-complexes have coordination of 6 with octahedral geometry while the Zr(IV)-complex has coordination of 7 with exhibited a pentagonal bipyramid.

**Keywords:** Triazole ring; Triazole complexes; Transition metal complexes

## تحضير وتشخيص 4-((3-مركبتو-5-فني-1,2,4-ترايازول(مئيل)-2-ميثوكسي فينول) ومعداته مع أيونات الزركونيوم (IV) والكاديوم (II) والقصدير (II)

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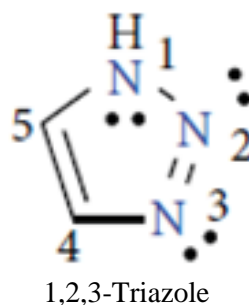
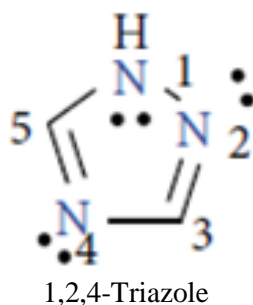
### الخلاصة :

في هذا البحث تم تحضير سلسلة من المركبات التناسقية لأيونات القصدير (II) والكاديوم (II) والزركونيوم (IV) مع الليكاند 4-((3-مركبتو-5-فني-1,2,4-ترايازول(مئيل)-2-ميثوكسي فينول) الذي تم تحضيره باستخدام الايثانول كوسط للتفاعل . شخّصت المعقدات المحضرة كميًا ونوعيًا باستخدام تحليل العناصر CHNS، طيف الأشعة تحت الحمراء ، طيف الأشعة فوق البنفسجية-المرئية، الرنين النووي المغناطيسي، الامتصاص الذري، الخاصية المغناطيسية، التحاليل الحرارية وقياس التوصيلية . يتناسق هذا الليكاند مع الفلز عن طريق ذرتي الكبريت والنيتروجين . طبقًا للنتائج الطيفية المستحصلة ، المعقدات القصدير (II) والكاديوم(II) سداسية التناسق وبشكل هندسي ثماني السطوح اما معدد الزركونيوم (IV) فيكون سباعي التناسق وشكله الهندسي ثنائي الهرم خماسي القاعدة.

### Introduction:

Triazoles are the class of heterocyclic compounds. There are two possible isomers of triazole (1,2,4-triazole and 1,2,3-triazole) depending on the position of nitrogen atom in the ring .

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1, 2, 4-Triazole has the molecular formula  $C_2H_3N_3$ , called triazoles, which have a five-membered ring of two carbon atoms and three nitrogen atoms of azole ring readily able to bind with a variety of enzymes and receptors in biological system via diverse non-covalent interactions, and thus display versatile biological activities. In recent years, the chemistry of triazoles and their fused heterocyclic derivatives has received considerable attention owing to their synthetic and effective biological importance [1].

The derivatization of triazole is considered to be based on the phenomenon of bioisosterism in which replacement of oxygen of oxadiazole nucleus with nitrogen atom yields triazole analogue [2]. 1, 2, 4-Triazole derivatives are readily soluble in polar solvents and only slightly soluble in non-polar solvents. However, the solubility in non-polar solvents can be increased by substitution on the nitrogen atom [3].

Mercaptotriazole derivatives are considered to be good coordinating ligands, because they involved both hard nitrogen and soft sulfur atoms. This ligand has donor groups that coordinate with wide range of metal ions [4-6]. The potential coordinating sites of the NS-type ligand are: sulfur of thiol group, nitrogen of the azomethine group and two nitrogen atoms at position 1 and 2 in triazole ring system [5].

The presence of (S=C) and (N=C) units allow for bidentate coordination to metal ions through thio substituted and nitrogen of the azomethine to form a stable five member ring [7], which leads to the formation of more stable complexes compared with monodentate ligands [8].

Furthermore, five or six membered chelate is by far the most common and the most stable. The synthesis of thio-triazole complexes with selected metal ions have been reported in the literature [9]. This paper studies the preparation and characterization of Zr(IV), Cd(II) and Sn(II) complexes with 4-(((3-mercapto-5-phenyl-4H-1,2,4-triazole-4-yl)imino)methyl)-2-methoxyphenol.

### Materials and methods

The following reagents, starting materials as well as solvents were purchased commercially and used without any further purification, ( benzoic acid, hydrazine hydrate Hopken & Williams, carbon disulfide (Thomas Baker), Tine (II) chloride (BDH), Zirconium(IV) oxochloride (BDH) and Cadmium (II) chloride (FLUKA).

The melting points were measured using Gallenkamp melting point apparatus. Elemental C.H.N and S analysis were carried out on a (Fison EA 1108 analyzer). The infra-red spectra were recorded in the frequency range (4000-400)  $cm^{-1}$  using KBr disc for ligands and CsI disc in the frequency range (4000-200)  $cm^{-1}$  for their complexes by using (8400 S-FTIR SHIMADZU spectrophotometer). The ultraviolet-visible (U.V-Vis) spectra were recorded on (1800- UV SHIMADZU spectrophotometer in the range of (200–1100) nm.

Magnetic susceptibility measurements for the synthesized complexes were obtained at room temperature using (Auto Magnetic Susceptibility Balance Model Sherwood Scientific). Molar conductivity measurements were obtained using (electrolytic conductivity measuring set model E C 214 Conductivity meter HANNA instrument). Thermal analysis of prepared complexes were performed using (SHIMADZU 60-H Thermo Gravimetric Analyzer). Atomic absorption measurements were obtained by using (Phoenix-986). The spectra of  $^1H$  and  $^{13}C$ NMR were recorded on 400 MHz NMR Spectrometer Avance III 400 Bruker, Germany, using  $DMSO-d_6$  as the solvent and tetramethyl silane (TMS) as the internal standard.

**Experimental:****Synthesis of 4-(((3-mercapto-5-phenyl-4H-1,2,4-triazole-4-yl)imino)methyl)-2-methoxyphenol:****1)- Synthesis of methyl benzoic acid ester(1)[10] :**

To a mixture of benzoic acid (0.15 moles ) in methanol (90 ml ) , was added dropwise conc.  $H_2SO_4$  (16 mL) with stirring and the mixture was refluxed on oil bath at  $80^\circ C$  for 5 hr. The aqueous mixture was extracted with n-hexane (25 mL). The combined organic layer was washed with 5% aqueous  $NaHCO_3$  until the pH reached 7 and then washed with water .The organic layer was dried and filtered. The filtrate was evaporated to dryness to give a colourless oil; methyl benzoate.

**2)- Synthesis of benzoic acid hydrazide(2) [11] :**

A mixture of methyl benzoate (0.01mole) and hydrazine hydrate 80%(0.01mole) was heated with methyl alcohol to obtain a clear solution. The contents were refluxed at  $100^\circ C$  for 4 h. Then the excess methanol was distilled off. A solid product was obtained and recrystallized in methyl alcohol to give benzoic acid hydrazide.

**3)- Synthesis of o-( benzo)-1,3,4-oxadiazole-2-thione(3)[10] :**

This compound was prepared by mixing benzoic acid hydrazide (0.01 mol) with carbon disulfide (0.015mol ) in methanol (150 ml), followed by the addition of potassium hydroxide (0.84 gm) in water. The reaction mixture was stirred and heated under reflux at  $100^\circ C$  for 9 hr. Then excess methanol was distilled off. The crude solid obtained was dissolved in excess water and acidified with dil. hydrochloric acid to (pH= 2-3). The separated product was filtered, washed with water and recrystallized from  $CHCl_3/ EtOH$ .

**4)- Synthesis of 4-(amino)-5-phenyl-4H-1,2,4-triazole-3-thiol (4) [12] :**

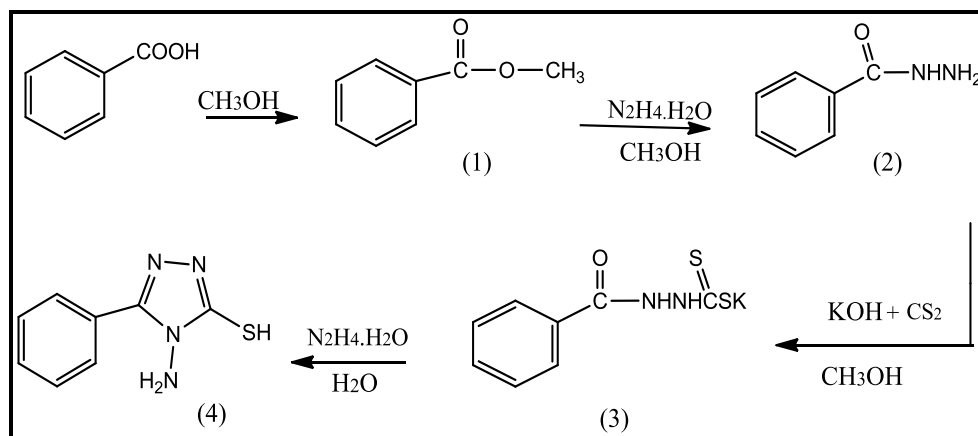
To the potassium salt (0.01mol) which prepared above was added hydrazine hydrate (0.01mol) and water (20ml) and the mixture was refluxed at  $100^\circ C$  for 3 hr. The color of the reaction mixture changed to green, hydrogen disulphide was evolved and a homogenous solution resulted. A white solid was precipitated by dilution with cold water and acidification with conc. hydrochloric acid. The product was filtered, washed with cold water and recrystallized from ethanol.

**Synthesis of ligand [4-(((3-mercapto-5-phenyl-4H-1,2,4-triazole-4-yl)imino) methyl)-2-methoxyphenol] (schiff base)[13] :**

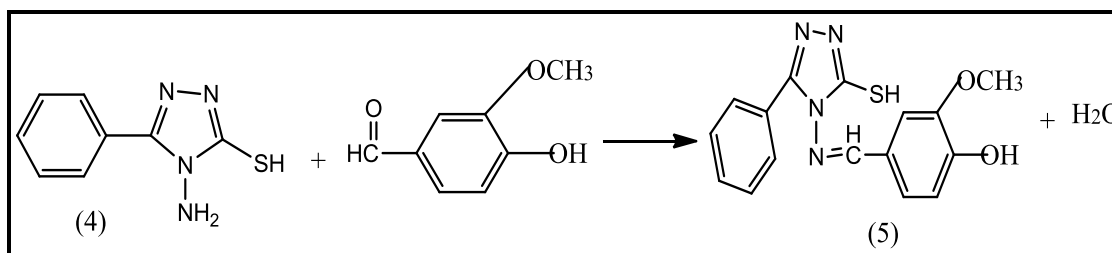
To a solution of triazoles(4) (0.01mole) in glacial acetic acid (10 ml) was added an equimolar amount of the aromatic aldehyde 4-hydroxy-3-methoxy benzaldehyde (0.01mole) and the mixture was refluxed at  $100^\circ C$  for 8 hr. After completion of reaction, the mixture was cooled and poured into the ice cold water. The solid obtained was filtered, washed with ice cold water, dried and recrystallized from ethanol.

**Synthesis of Schiff base metal complexes [14]:**

An ethanolic solution of the suitable metal salt [tine (II) chloride, zirconium (IV)oxo chloride and cadmium (II) chloride] was added to an ethanolic solution of 4-(((3-mercapto-5-phenyl-4H-1,2,4-triazole-4-yl)imino)methyl)-2-methoxy phenol in 1:2 (metal:ligand) ratio and refluxed at  $100^\circ C$  for 4 hr. A colored crystalline solid was formed after cooling to room temperature .The product was filtered, washed with hot methanol and dry then recrystallized from ethanol. The synthesis routes of compounds [1-5] can be shown in schemes 1 and 2.



**Scheme 1-**The synthesis of compounds [1-4].



**Scheme 2**-The synthesis route of ligand [4-((3-mercapto-5-phenyl-4H-1,2,4-triazole-4-yl)imino)methyl)-2-methoxyphenol] (compound 5).

## Results and discussion

### Physical properties

The physical properties, C.H.N.S. analysis and metals content of the prepared compounds are described in table 1. The analytical data are quite agreeable with calculated values. The molecular formula of ligand and its metal complexes have been suggested according to the above-mentioned data together with those obtained from FT-IR, UV-Visible and NMR spectra.

Thermo gravimetric analyses of complexes have been performed in order to confirm their elemental analysis CHNS as listed in table 1.

As a common behavior, all the TG- DTG curves of the complexes mentioned above does show the stage of mass-loss of water hydration in the stage of mass-loss in the temperature range (50-195°C) as evidenced from calculated and observed mass-loss by use helium as inert gas. Thermo gravimetric analytical data of complexes ( $C_1$ - $C_3$ ) are listed in tables 2,3,4 and their thermographs are shown in figures.1,2 and 3.

**Table 1**-Some physical properties and analytical data for the ligand and its metal complexes.

Compound	Color	decom. temp. or (m.p)°C	Elemental and metal analysis, (theoretical) experimental				
			% C	%H	% N	% S	% M
L=( $C_{16}N_4O_2H_{12}S$ )	yellow	139-142	(58.82) 58.99	(3.67) 4.00	(17.15) 16.50	(9.80) 9.96	-
( $C_1$ ) [Sn(L) $_2$ Cl $_2$ ].H $_2$ O.(0.5)C $_2$ H $_6$ O	dark brown	decom. 121	(44.84) 45.24	(3.51) 3.47	(12.68) 12.72	(7.24) 7.56	(13.44) 13.80
( $C_2$ ) [Cd(L) $_2$ Cl $_2$ ]. H $_2$ O	yellow	decom. 190	(44.95) 45.14	(3.27) 3.51	(13.11) 12.85	(7.49) 7.79	(13.15) 13.10
( $C_3$ ) [ZrO(L) $_2$ Cl $_2$ ].2.5H $_2$ O	yellowish orange	decom. 160	(43.83) 43.25	(3.42) 3.34	(12.78) 12.57	(7.30) 7.11	(10.41) 10.00

**Table 2**-Thermo gravimetric analytical data (TG and DTG) for the complex ( $C_1$ ).

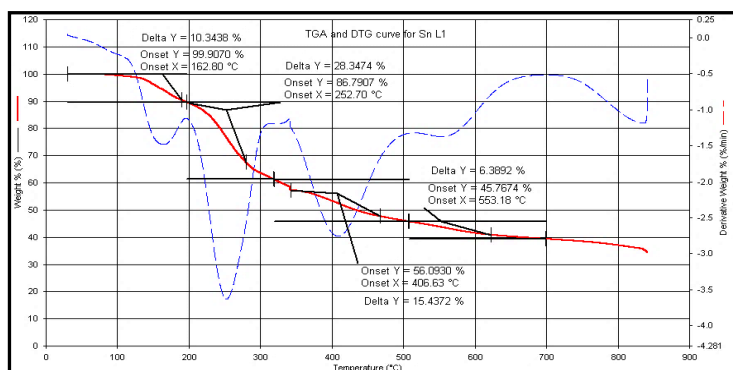
Stable phase [Sn(L) $_2$ Cl $_2$ ].H $_2$ O.(0.5)C $_2$ H $_6$ O (M.wt) (883.35)	Temp. rang of decomp. at TG, °C	Peak temp. at DTG, °C	% Weight loss Found (calc.)
- 0.5 C $_2$ H $_6$ O - H $_2$ O - OCH $_3$ - OH	130-180	162.8	10.34 (10.07)
- OH - 3C $_6$ H $_5$	180-290	252.7	28.34 (28.41)
- OCH $_3$ - C $_6$ H $_5$ - CHN	290-590	406.6	15.43 (15.39)
- Cl - CHN	590-610	553.18	6.30 (7.07)
C $_4$ H $_2$ N $_6$ S $_2$ SnCl	>610	-	(39.86)

**Table 3-**Thermo gravimetric analytical data (TG and DTG) for the complex (C<sub>2</sub>).

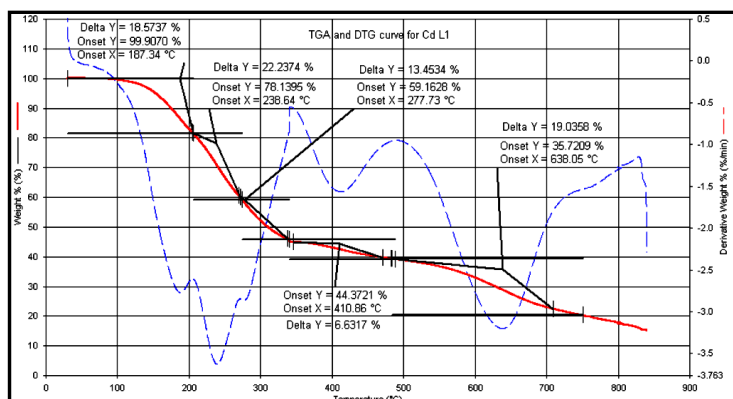
Stable phase [Cd(L) <sub>2</sub> Cl <sub>2</sub> ].H <sub>2</sub> O (M.wt) (854.02)	Temp. rang of decomp. at TG, °C	Peak temp. at DTG, °C	%Weight loss Found (calc.)
- H <sub>2</sub> O - 2 OCH <sub>3</sub> - C <sub>6</sub> H <sub>5</sub>	100-210	187.34	18.57 (18.37)
- 2 OH - 2C <sub>6</sub> H <sub>5</sub>	210-275	238.64	22.23 (22.00)
-C <sub>6</sub> H <sub>5</sub> - Cl	275-340	277.73	13.45 (13.16)
-2 CHN	340-470	410.86	6.63 (6.32)
- Cl -2 C <sub>2</sub> HN <sub>3</sub>	470-715	638.05	19.03 (19.84)
-S, -CdS	>715	-	20.82

**Table 4-**Thermo gravimetric analytical data (TG and DTG) for the complex (C<sub>3</sub>).

Stable phase [ZrO(L <sub>1</sub> ) <sub>2</sub> Cl <sub>2</sub> ].2.5H <sub>2</sub> O (M.wt) (876.02)	Temp. rang of decomp. at TG, °C	Peak temp. at DTG, °C	%Weight less Found (calc.)
- 0.5H <sub>2</sub> O	50-85	68.55	1.47 (1.02)
- 2H <sub>2</sub> O - 2C <sub>6</sub> H <sub>5</sub>	85-195	173.37	22.41 (21.68)
-2C <sub>6</sub> H <sub>5</sub> - 2 OCH <sub>3</sub> - 2 OH -H <sub>2</sub> C <sub>3</sub> N <sub>3</sub>	195-255	226.15	37.75 (37.65)
-2Cl	255-550	444.26	8.52 (8.10)
ZrOS <sub>2</sub> C <sub>3</sub> H <sub>2</sub> N <sub>5</sub>	>550	-	(31.87)



**Figure 1-** Thermographs of C<sub>1</sub>.



**Figure 2-**Thermographs of C<sub>2</sub>.

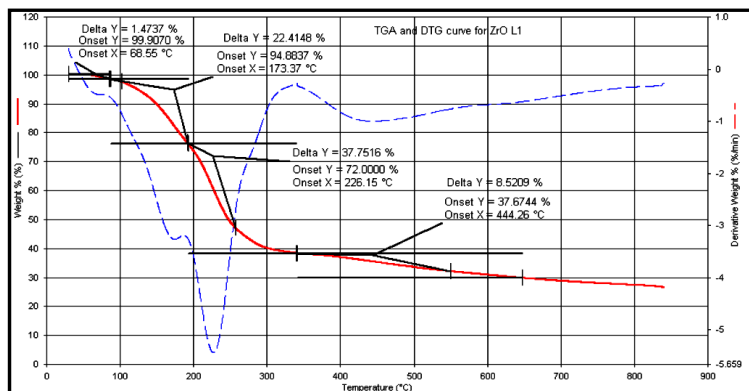


Figure 3-Thermographs of  $C_3$ .

### Infra-red spectroscopy

The FTIR spectrum of the prepared ligand showed the characteristic stretching vibration bonds at the following frequency with their corresponding assignments : ( $3540\text{ cm}^{-1}$ ) stretch for  $\text{-NH}$  group, ( $3139\text{ cm}^{-1}$ ) for C-H aromatic, ( $1595\text{ cm}^{-1}$ ) for (C=N) group , ( $1172/698\text{ cm}^{-1}$ ) for  $\nu(\text{C}=\text{S})/\nu(\text{C}-\text{S})$  groups, ( $3600\text{ cm}^{-1}$ ) for O-H phenol, ( $1153\text{ cm}^{-1}$ ) for (O- $\text{CH}_3$ ) group and ( $2756\text{ cm}^{-1}$ ) for S-H [15]. The tautomerism form could occur in triazole. It is responsible to expect deprotonation of ligand molecule before complexation, the complete disappearance of the band due to  $\nu(\text{S}-\text{H})$  in the spectra of complexes unambiguously support this view. After deprotonation, the ligand can link with the metal ion at N of azomethine and S of thiol group. Bonding at S is more favorable because such a thing would result in a stable five membered chelate ring [5], which could be found in complexes ( $C_1$ - $C_3$ ) [16-19]. FTIR spectral data of compounds  $[\text{L}, \text{Sn}(\text{L})_2, \text{Cd}(\text{L})_2$  and  $\text{Zr}(\text{L})_2]$  are listed in table 5.

Table 5-FTIR most diagnostic bands of the ligand and its metal complexes ( $\text{cm}^{-1}$ ).

Group	L	$[\text{Sn}(\text{L})_2], C_1$	$[\text{Cd}(\text{L})_2], C_2$	$[\text{Zr}(\text{L})_2], C_3$
$\nu(\text{N}-\text{H})$ stretch	3540	3417	3500	3357
$\nu(\text{-C}=\text{N})$	1595	1573	1581	1571
$\nu(\text{C}=\text{S})/\nu(\text{C}-\text{S})$	1172/698	1186	1193	1145
$\nu(\text{S}-\text{H})$	2756	-	-	-
$\nu(\text{O}-\text{H})$	3600	3417	3415	3357
$\nu(\text{O}-\text{CH}_3)$	1153	1120	1160	1170
$\nu(\text{C}=\text{C})_{\text{arom.}}$	1502	1500	1512	1515
$\nu(\text{C}-\text{O}-\text{C})$	1267	1290	1296	1267
$\nu(\text{-C}-\text{N})$ trz.	1668	1666	1649	1649
M-N	-	523	520	532
M-S	-	453	459	453
M-Cl	-	330	312	304

arom.=aromatic

The FTIR spectra of the complexes ( $C_1$ - $C_3$ ) exhibited the shift of  $\nu(\text{C}=\text{N})$  band to lower frequencies. This gave an indication that the coordination of the ligand with the metal ion took place via the nitrogen atom of (C=N) group [20]. The band of  $\nu(\text{S}-\text{H})$  in the ligand was disappeared and the bond order of carbon-sulfur increased (C=S), indications that the metal ion coordinates with the ligand through the sulfur atom also [21]. The FTIR spectra for compounds  $[\text{L}, \text{Sn}(\text{L})_2, \text{Cd}(\text{L})_2$  and  $\text{Zr}(\text{L})_2]$  are shown in figures. 4,5,6 and 7.

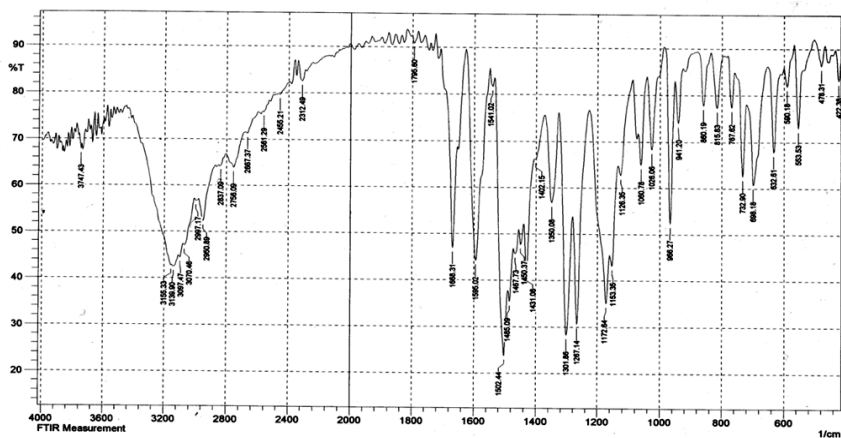


Figure 4-FTIR Spectrum for the ligand (L) .

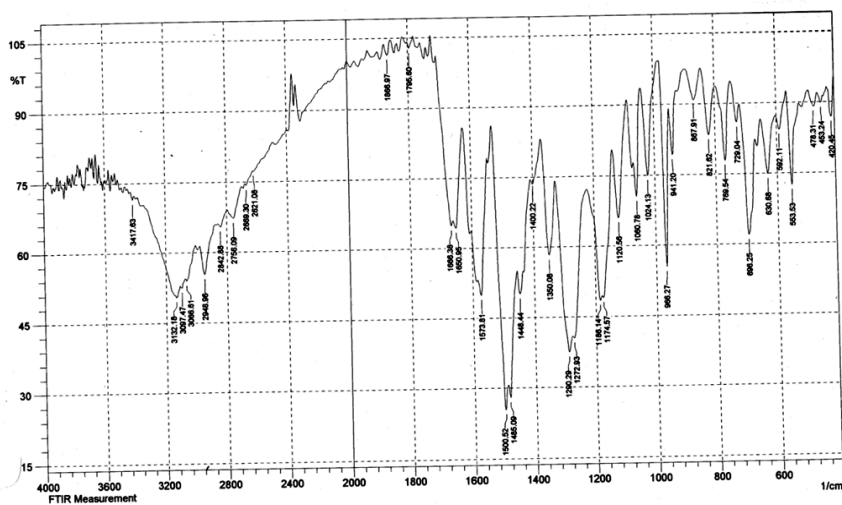


Figure 5-FTIR Spectrum for the complex [Sn(L)<sub>2</sub>], (C<sub>1</sub>) .

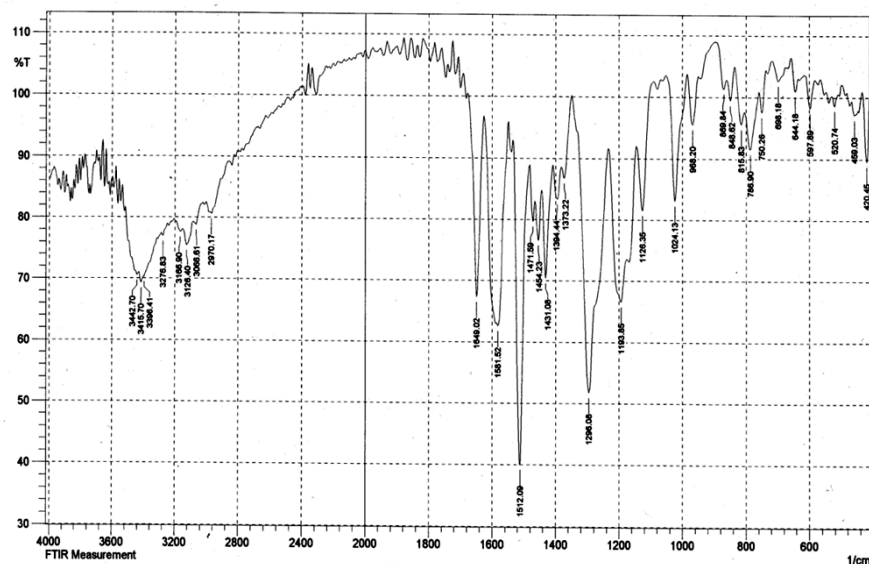


Figure 6-FTIR spectrum for the complex [Cd(L)<sub>2</sub>], (C<sub>2</sub>) .

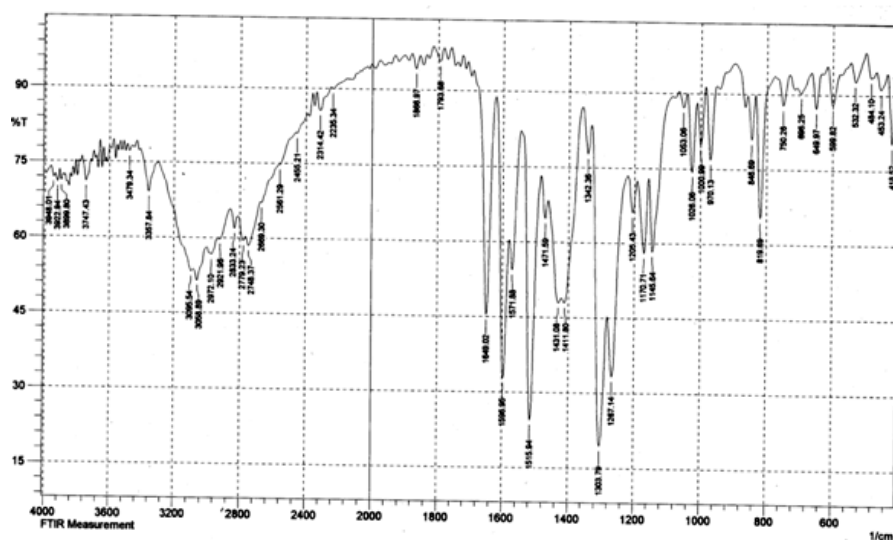


Figure 7-FTIR spectrum for the complex  $[Zr(L)_2] \cdot (C_3)$ .

### Nuclear magnetic resonance spectra of ligand and metal complexes.

The  $^1\text{H}$ NMR chemical shifts,  $\delta$ (ppm) of the above mentioned compounds which are described in the following sections showed a good support to the suggested structures and agreement with those obtained from other triazole derivatives [7], [22-25].

#### [4-(((3-mercapto-5-phenyl-4H-1,2,4-triazole-4-yl)imino)methyl)-2-methoxyphenol](L).

The signals assignments of  $^1\text{H}$ NMR spectrum of L in  $\text{DMSO}-d_6$  are given in table 6 and the spectrum is shown in figure.8. Chemical shifts of the (N=CH) proton of azomethine exhibited a signal at  $\delta = (9.76)$  ppm' while that of the proton of methoxy group and phenolic proton appeared at  $\delta = (3.83)$  ppm and  $\delta = (4.09)$  ppm respectively. Chemical shifts of aromatic and triazole ring protons appeared at  $\delta = (6.9-8.05)$  ppm and  $\delta = (8.6)$  ppm respectively. The spectrum exhibited signal at lower field at  $\delta = (14.77)$  ppm and it is assigned to S-H proton of thiole

Table 6-  $^1\text{H}$ NMR spectral data of ligand.

Assignment	Chemical shift (ppm)
$\delta$ O-CH <sub>3</sub>	3.83
$\delta$ O-H phenol	4.09
$\delta$ C-H aromatic	6.9-8.05
$\delta$ N=CH	9.76
$\delta$ N-H	8.6
$\delta$ S-H	14.77



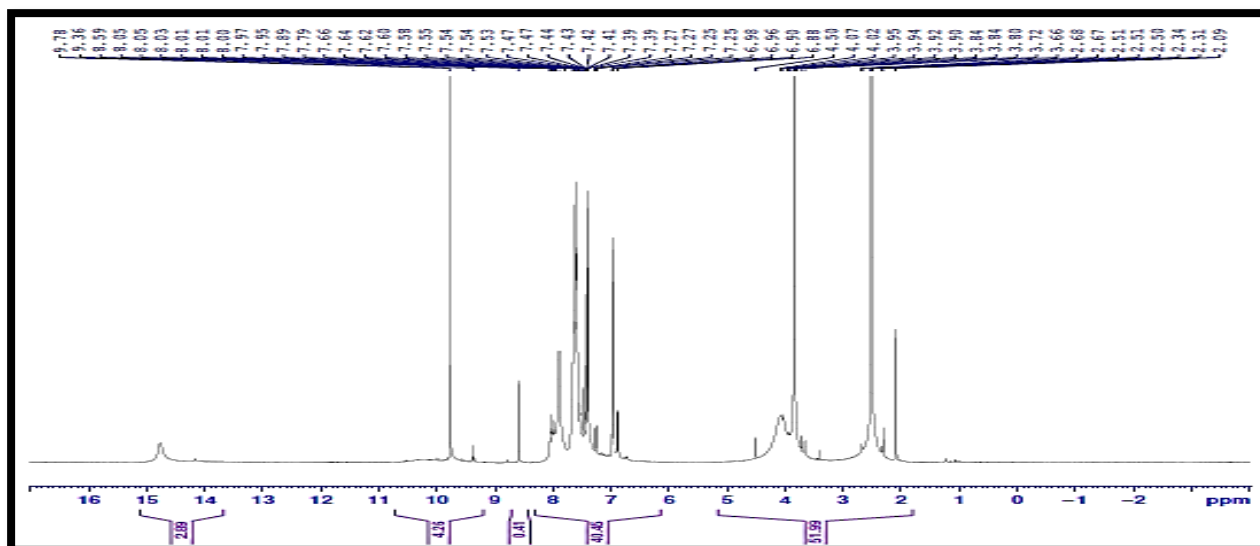


Figure 8-<sup>1</sup>H NMR spectrum of L in DMSO-*d*<sub>6</sub>.

### <sup>13</sup>C NMR data of ligand

The <sup>13</sup>C NMR spectrum of the ligand in DMSO-*d*<sub>6</sub> is shown in figure.9 and the signal assignments of the chemical shifts are described in table 7. The spectrum of L is characterized by the presence of (N=C) group of azomethine which appeared as a signal at  $\delta = (153-160)$  ppm and the chemical shift of carbon aromatic ring appeared at  $\delta = (110-132)$  ppm. The spectrum shows a signal at lower fields  $\delta = (190.9)$  ppm was assigned to (C=S) group, while chemical shifts of (O-CH<sub>3</sub>) appeared at  $\delta = (56.0)$  ppm.

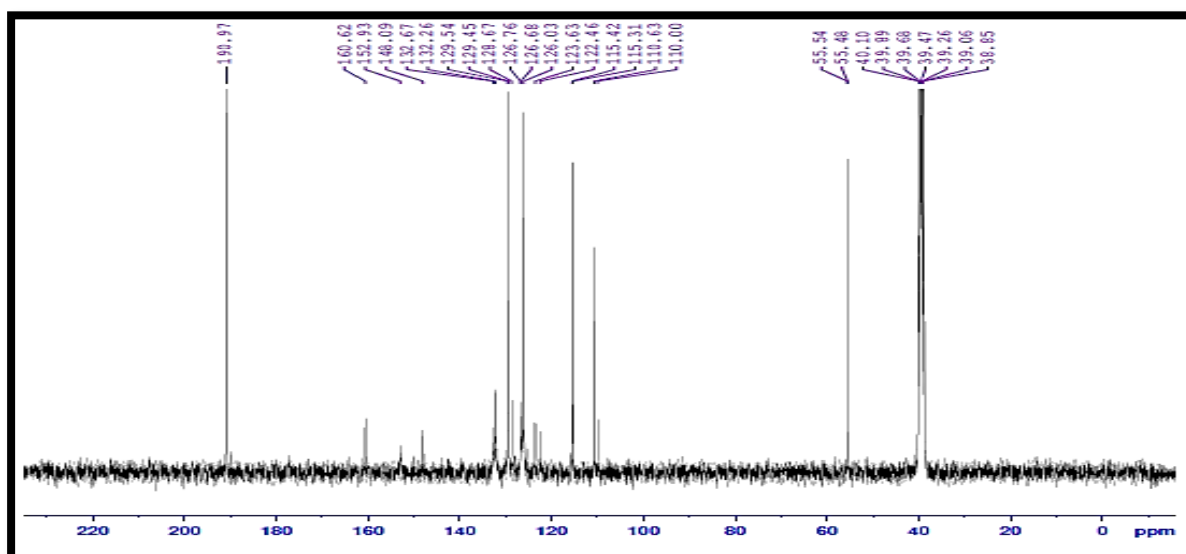


Figure 9-<sup>13</sup>C NMR Spectrum of ligand in DMSO-*d*<sub>6</sub>.

Table 7-<sup>13</sup>C NMR spectral data of ligand.

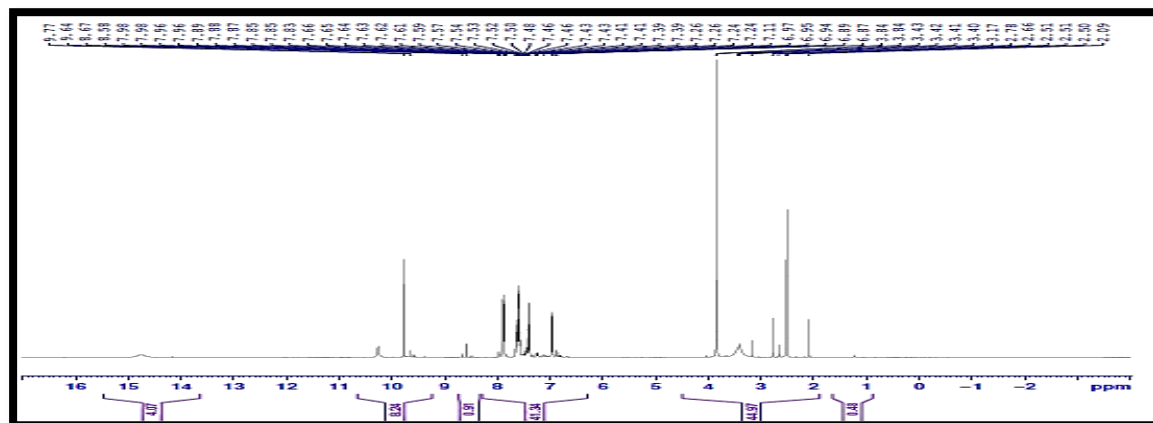
Assignment	Chemical shift (ppm)
$\delta$ O-CH <sub>3</sub>	56
$\delta$ C aromatic	110-132
$\delta$ N=C azomethine	153-160
$\delta$ C=S	190.9

**<sup>1</sup>HNMR spectra of complexes Sn(L)<sub>2</sub>, Cd(L)<sub>2</sub> and Zr(L)<sub>2</sub>(C<sub>1</sub>-C<sub>3</sub>).**

The <sup>1</sup>HNMR spectra data of L-complexes (Sn(L)<sub>2</sub>, Cd(L)<sub>2</sub> and Zr(L)<sub>2</sub>) in DMSO-*d*<sub>6</sub> are described in table 8 and the spectrum of the complex Sn(L)<sub>2</sub> is shown in figure.10. The spectra of the metal complexes exhibited chemical shifts at δ (9.78- 9.80) ppm assigned to azomethine proton, while that of the protons of methoxy group and phenolic group appeared at range δ = (3.82-3.88) ppm and δ =(4.5-10.3) ppm respectively. Chemical shifts of aromatic protons appeared at range δ =(6.97-7.9) ppm, while the chemical shifts of triazole ring protons appeared at δ= (8.6) ppm. The disappearance of signal due to -SH proton in the spectra of the complexes refers to deprotonation of the thiol group, which support the coordination of metal ions through the sulfur atom of the ligand [26-32].

**Table 8-** <sup>1</sup>HNMR spectral data in ppm of complexes Sn(L)<sub>2</sub>, Cd(L)<sub>2</sub> and Zr(L)<sub>2</sub> (C<sub>1</sub>-C<sub>3</sub>).

Assignment	Sn(L) <sub>2</sub> (C <sub>1</sub> )	Cd(L) <sub>2</sub> (C <sub>2</sub> )	Zr(L) <sub>2</sub> (C <sub>3</sub> )
δ O-CH <sub>3</sub>	3.85	3.82	3.88
δ O-H phenol	10.3	4.5	10.3
δ C-H aromatic	-7.96.97	6.87-7.9	6.99-7.9
δ N=CH	9.78	9.78	9.8
δ N-H	8.6	8.6	8.6
δ S-H	-	-	-

**Figure.10-** <sup>1</sup>HNMR Spectrum of Sn(L)<sub>2</sub> (C<sub>1</sub>)**<sup>13</sup>CNMR spectra of complexes Sn(L)<sub>2</sub>, Cd(L)<sub>2</sub> and Zr(L)<sub>2</sub> (C<sub>1</sub>-C<sub>3</sub>).**

The <sup>13</sup>CNMR spectra of these complexes are consistent with suggested structures. Chemical shifts and their assignments are described in table 9. In addition to the signal related to (N=C) which appeared at range δ = (155-163) ppm assigned to azomethine, the complexes exhibited chemical shifts assigned to aromatic carbon rings at range δ= (110-148) ppm. The spectra appeared a broad signal at lower fields at δ = (191-192) ppm were assigned to (C=S), while δ (O-CH<sub>3</sub>) appeared at δ = (56-57) ppm as shown in figure.11 for Cd(L)<sub>2</sub> complex . The considerable shift in the <sup>13</sup>C resonance of azomethine carbon atom indicates to the coordination of nitrogen atom of azomethine group with the central ion in metal complexes. Further, the low intensity and shifting of the <sup>13</sup>C resonance of triazole refers to the coordination of the central metal ion through sulfur atom of thion group. As a result the <sup>13</sup>CNMR spectral data as described above for the ligand and its metal complexes support the coordination of ligand through the azomethine nitrogen and thiotic sulfur atom [26-32].

**Table 9-** <sup>13</sup>CNMR spectral data in ppm of complexes Sn(L)<sub>2</sub>, Cd(L)<sub>2</sub> and Zr(L)<sub>2</sub>(C<sub>1</sub>-C<sub>3</sub>).

Assignments	Sn(L) <sub>2</sub> (C <sub>1</sub> )	Cd(L) <sub>2</sub> (C <sub>2</sub> )	Zr(L) <sub>2</sub> (C <sub>3</sub> )
δ O-CH <sub>3</sub>	56	56	57
δ C aromatic	110-148	110-148	110-148
δ N=C azomethine	155-162	155-163	153-163
δ C=S	191	192	191

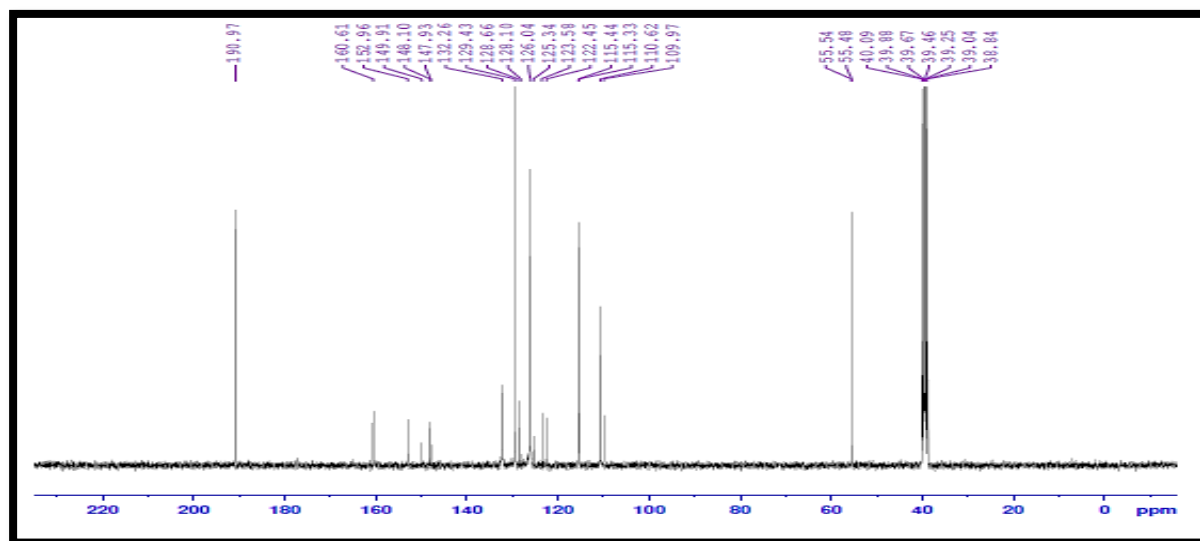


Figure.11-  $^{13}\text{C}$ NMR Spectrum of  $\text{Cd}(\text{L})_2$ .

### Electronic spectra, magnetic moments and conductivity measurements

The electronic spectra of the ligand and its complexes in general exhibited a high intensity bands appeared at  $\approx 220$  nm. It was assigned to ( $\pi \rightarrow \pi^*$ ) transition of the conjugated system. A low intensity band appeared in the near U.V. region at 308 nm was assigned to ( $n \rightarrow \pi^*$ ) transition which a signal to  $\text{C}=\text{N}$ , the intensity and positions of these bands depends on the structure of molecules. table10. The spectrum of complex  $\text{Sn}(\text{L})_2$  exhibited the presence of additional band attributed to a metal ligand ( $\text{M} \rightarrow \text{L}$ ) charge transfer. figures.12,13,14 and15 show the electronic spectra of the ligand and its complexes.

All complexes were diamagnetic, where the electron configurations of d-orbitals for ions are ( $d^{10}$  and  $d^0$ ) so that no d-d transition was observed in the visible region [33].

Conductivity measurements of these complexes were recorded as a solution in DMSO solvent. table10 shows the molar conductivity measurements of the complexes. All the prepared complexes were found to be non-electrolyte [34]

Table 10-Electronic spectra data and conductivity measurements of ligand and complexes ( $\text{C}_1$ - $\text{C}_3$ ).

Compound	UV bands (nm)		Charge transfer $\text{M} \rightarrow \text{L}$ (nm)	Conductivity measurement ( $\text{S.cm}^2 .\text{mol}^{-1}$ ), $10^{-3}\text{M}$
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$		
L	228	308	-	-
( $\text{C}_1$ ) [ $\text{Sn}(\text{L})_2\text{Cl}_2$ ]. $\text{H}_2\text{O}$ . $(0.5)\text{C}_2\text{H}_6\text{O}$	209,252	294	450	19.2
( $\text{C}_2$ ) [ $\text{Cd}(\text{L})_2\text{Cl}_2$ ]. $\text{H}_2\text{O}$	204,226,254	300	-	25.6
( $\text{C}_3$ ) [ $\text{ZrO}(\text{L})_2\text{Cl}_2$ ]. $2.5\text{H}_2\text{O}$	223,254	301	-	30.6

According to the above-mentioned data, the structures of three metal complexes can be suggested as illustrated in Scheme 3.

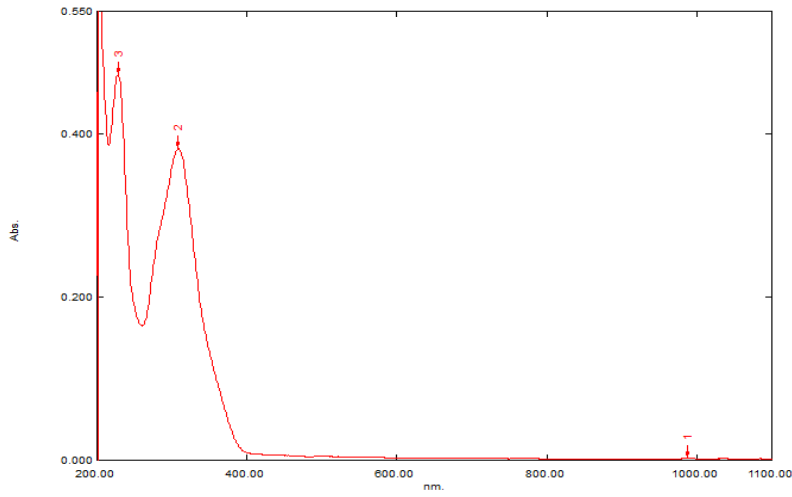


Figure.12-The Electronic Spectrum of the ligand L.

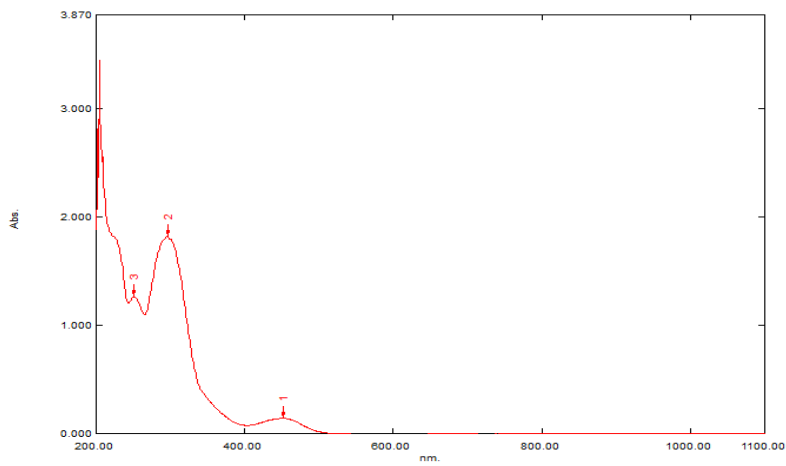


Figure.13-The Electronic Spectrum of the complex Sn(L)<sub>2</sub>(C<sub>1</sub>).

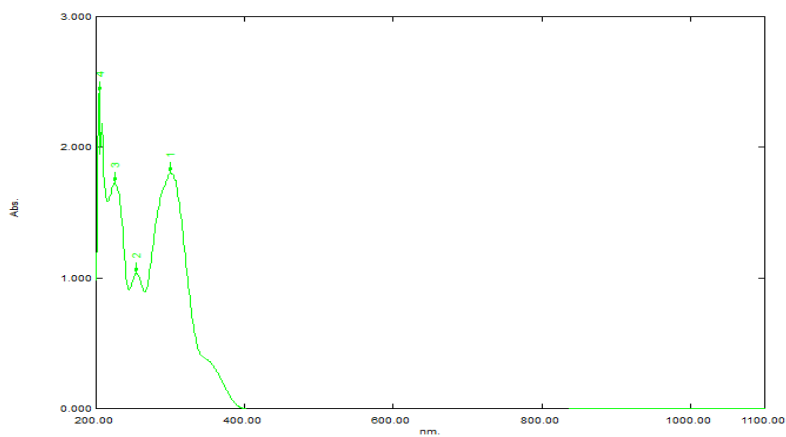
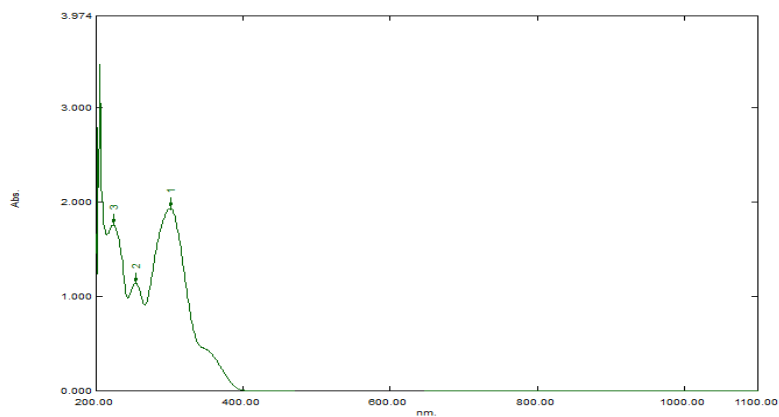
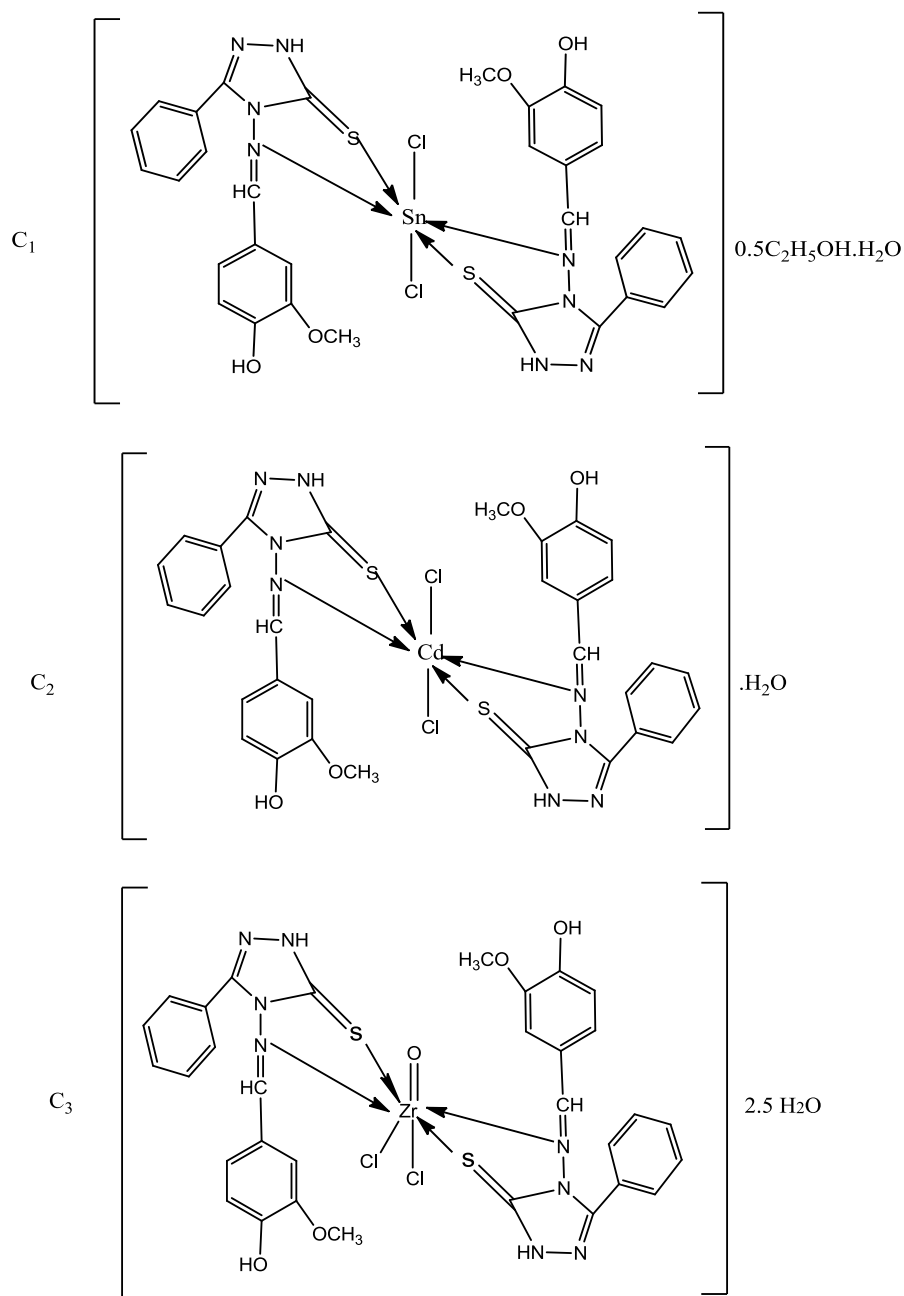


Figure.14-The Electronic Spectrum of the complex Cd(L)<sub>2</sub>(C<sub>2</sub>).



**Figure.15-**The Electronic Spectrum of the complex  $Zr(L)_2(C_3)$ .



**Scheme 3-**Suggested structures of the prepared complexes ( $C_1$ - $C_3$ ).

## Conclusion

The ligand [4-(((3-mercapto-5-phenyl-4H-1,2,4-triazole-4-yl)imino)methyl)-2-methoxy phenol] was successfully synthesized. This ligand was treated with different metal ion salts in [1:2] [M:L] ratio to afford the corresponding complexes. The ligand coordination to the metal ion occurred through azomethine and thiol groups leading to the formation of five membered chelate rings. The structures of prepared complexes were confirmed by analytical and spectroscopic methods. The (Sn(II) and Cd(II) complexes (C<sub>1</sub>,C<sub>2</sub>) exhibited octahedral geometry, while the Zr(IV)-complex (C<sub>3</sub>) has a pentagonal bipyramid structure.

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