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Synthesis and Characterization of Some Transition Metal Complexes with a New2-(1,2-dihydroxyethyl-1-(2-mercaptophenyl)-5-(2 mercaptophenylimino)-2,5-dihydro-1H-pyrrol-3,4- diol.

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Abstract

2-(1,2-dihydroxy ethyl -1- (2-mercaptophenyl)-5-(2-mercaptophenyl imino)-2,5-dihydro-1H-pyrrol-3,4-diol(H_2L`)a lactam derivative of L-ascorbic acid was prepared by reaction of 5,6-O-isopropylidene L-ascorbic acid with 2-amino thiophenol in a mole ratio of (1:2) respectinely. A series of new metal complexes of this ligand ($H_2L$`) were prepared by a reaction with the chlorides of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II). The new ligand and its metal complexes were characterized by C.H.N.,^{1}H and ^{13}C NMR, IR as well as UV-Visible spectra and mass spectra of Ni(II) and Zn(II) complexes was also done. Atomic absorption of the metal percentage, electrical conductivity and magnetic measurements at room temperature was carried out. From these analysis showed that the ligand H_2L` ($C_{18}H_{18}O_4N_2S_2$) is coordinated to the metal ions through the nitrogen atom of the azomethine group and the two sulphur atoms of thiol groups as a tridentate ligand or through the two sulphur atoms of thiol groups as a bidentate ligand an octahedral geometries, except the (Hg) complex which shows a tetrahedral. Theoretical calculations of the electronic structure of the new ligand HL and its metal complexes were carried out applying the semi-emiprical computation methods PM3 and PM6 which confirmed the suggested structures of all complexes.

Keywords: Synthesis, Complexes, Transition Metals, Ascorbic Acid.

تحضير وتشخيص معقدات بعض العناصر الأنتقالية مع مشتق جديد(5,6-O- داي هيدروكسي اثيل -1- (2-مركبتوفنيل) -O- (2-مركبتو فنيل ايمين)-2,5-داي هيدرو-1H - بايرول 3,4 - دايول.

ندى علي النجار[1]، فالح حسن موسى [2]، مثنى عبد الجبار شنشل[3]*
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الخلاصة

حضرالمشتق (5,6-O- داي هيدروكسي اثيل -1- (2-مركبتوفنيل) -O- (2-مركبتو فنيل ايمين)-2,5-داي هيدرو-1H - بايرول 3,4 - دايول) من تفاعل 5,6-O-ايزوبروبيليدين -L- حامض الاسكوربيك مع 2-امينو ثايوفينول بنسبة مولية (1:2) على التوالي. حضرت سلسلة معقدات جديدة لليكاندH_2L`من تفاعلة

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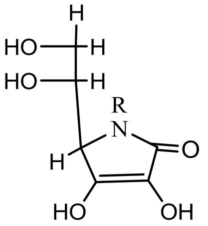
المباشرمع كلوريدات بعض العناصر والتي تشمل ايون الكروم الثلاثي وايونات المنغنيز، الكوبلت، النيكل، النحاس، الزنك، الكادميوم والزئبق الثنائية التكافؤ. شخص تركيب الليكاند الجديد H_2L` ومعقداته باستخدام تقنية التحليل الدقيق للعناصر (كربون، هيدروجين، نتروجين،كبريت) ،الرنين النووي المغناطيسي ^1Hو ^{13}Cو اطياف الاشعة تحت الحمراء والاشعة فوق البنفسجية– المرئية بالاضافة الى طيف الكتلة لمعقدي Ni(II) و Zn(II) كذلك تم التحليل الكمي للفلز باستخدام تقنية الامتصاص الذري وقياسات التوصيلية والصفات المغناطيسيه في درجة حرارة الغرفة. بينت نتائج من التحاليل السابقة بأن الليكاند $H_2L(C_{18}H_{18}O_4N_2S_2)$` يسلك سلوك ثلاثي السن ويتناسق مع الايون الفلزي من خلال ذرة النتروجين لمجموعة الازوميثين وذرتي الكبريت لمجموعتي الثايول أو ثنائي السن ويتناسق من خلال ذرتي الكبريت لمجموعتي الثايول .ووفقا للنتائج المستحصلة فقد أقترح الشكل ثماني السطوح لجميع المعقدات المحضرة ماعدا معقد الزئبق في شكل رباعي السطوح. اجريت الدراسة النظرية لليكاند الجديد H_2L` ومعقداته بطريقة الشبة التجريبية Semi–empirical PM_6 و PM_3 والتي اثبتت صحةالأشكال الهندسية المقترحة لجميع المعقدات المحضرة .

Introduction

It is well documented that L-ascorbic acid can react with amine, amino acids or proteins [1-3], a process which is of considerable interest in food chemistry and medicine. Ascorbic acid is basically a tetranolactone replacement of the ring oxygen atom with nitrogen atom in the tetranolactone to form lactam derivatives [4] scheme-1.



Scheme 1-lactam derivatives of L-ascorbic acid.

This reaction undergoes ring-opining of lactone with amines to give the enol-keto amides. The latter undergoes intramolecular ring closure to give the lactams or tetramates. A verity of lactams derivatives were synthesized which were explained via the intermediates in organic synthesis and biologically active molecules [5-8].

Major work and applications were done on L-ascorbic acid metal complexes and less attention was paid on metal complexes of lactam derivatives of L-ascorbic acid. In the present work we describe the synthesis of a new derivative of L-ascorbic acid, which is used as a complexation ligand (H_2L`) with some ions Cr(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II).

Experimental

Materials:

L- ascorbic acid (Asc.)(99.5%) was supplied from Merck (Germany) and O-aminothiophenol (99%) from Fluka (Germany). Metal salts ($CrCl_3.6H_2O$, $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2.2H_2O$ and $HgCl_2$) were obtained from BDH and Merck in high purity. The solvent were distilled before use.

Apparatus:

The following instruments were used for the analytical measurements; elemental microanalyses (Euro Vectro-3000A and Element arvariomicrocube Elemental Analyzer), the Infrared (IR) spectra in the range (4000-400) cm^{-1} using KBr disc for the ligand and in the range (4000-200)cm^{-1} using CsI discs for the complexes; (Shimadzu, FT-IR prestige-21), electronic spectra (UV-Visible and near I.R region, 200-1100 nm in methanol solution (10^{-3}M) using (Shimadzu-UV-160A*)* Spectrophotometer with 1 cm matched quartz cells. Proton and carbon-13 nuclear magnetic resonance spectra were measured with Bruker, Ultrasheild 300MHz and DPx-400 Bruker NMR instruments. Mass spectra were recorded on **(**Micromass ZQ "Waters") instrument**.** The metal contents of the complexes were determined by atomic absorption technique (A.A) using (GBC933Plus) Atomic Absorption Spectrophotometer. The magnetic moments ($\mu_{eff.}$) for the prepared complexes at room temperature were measured applying Faraday's method with (Johnson Mattey Catalytic Systems Division) instrument. Electrical conductivity measurements of the complexes in MeOH (ca 10^{-3}M) were made at room temperature using Lassco Digital Conductivity Meter. Gaussian03, package was applied for the optimized geometry calculations applying the semiempirical PM3 and PM6 methods.

Preparation of 2-(1,2-dihydroxyethyl-1-(2-mercaptophenyl)-5-(2-ercaptophenylimino)-2,5-dihydro-1H-pyrrol-3,4- diol. (ligand H_2L`):

An ethanolic solution of 2-aminothiophenol (0.25gm, 0.002 mol.) was added drop wise to (0.22gm, 0.001 mol.) of 5,6-O-IAsc.synthesized according to Solomon[9]. The solution mixture was further stirred at room temperature for 24h. The color of solution turned yellow. Then the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in a mixture of ethanol: water (3:7v/v), then cooled down. The crystals were collected by filtering, washed with cold water and dried in vacuum. The ligand H_2L`as fine yellow needles was obtained with yield % 77.92%, m.p83-85 ^{0}C and gave a single spot on thin layer chromatograph (chloroform: ethanol 4:4, v:v) with relative mobility $R_{f\,=}$ 0.2.

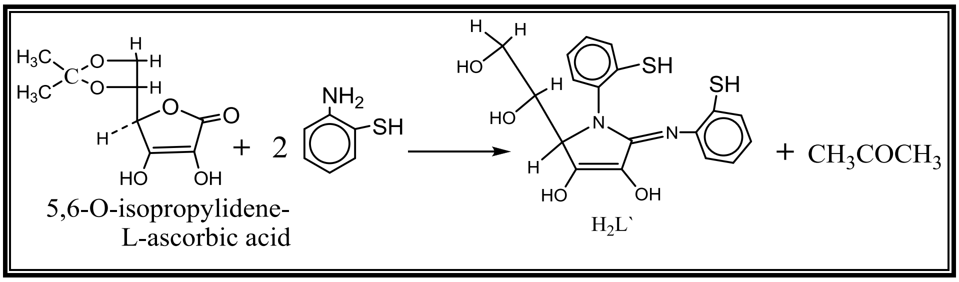
Preparation of metal complexes:

To a stirred solution of H_2L` (0.40gm., 0.001 mol.) in ethanol alcohol, a solution of metal chloride ($CrCl_3.6H_2O$ = 0.27gm.; $MnCl_2.4H_2O$ = 0.20 gm.; $CoCl_2.6H_2O$ = 0.24gm.; $NiCl_2.6H_2O$ = 0.24gm.; $CuCl_2.2H_2O$ = 0.28gm.; $ZnCl_2$ = 0.14gm.; $CdCl_2.2H_2O$ = 0.23gm. and $HgCl_2$ = 0.16gm.) in (0.001mol.) was added with continuous stirring. A precipitate was formed. The mixture was further stirred at room temperature for 1 hour. The product was collected by filtration and washed with ethanol and vacuum dried except Cr(III), Mn(II) and Zn(II) complexes, which were precipitated by addition of diethyl ether to the cold mixture. The precipitates were filtered off, washed with a mixture of (diethyl ether: ethanol 2:1 v/v) and dried.

Results and Discussion:

Synthesis, Physical Properties and Elemental Analysis of ligand H_2L` and It's Metal Complexes:

The new ligand (H_2L`) was prepared as a lactam derivative of L-Asc. By reaction of 5,6-O-isopropylidene L-Asc. With amine (2-aminothiophenol) in a mole ratio (1:2) respectively. The reaction is illustrated in scheme-2.



Scheme 2- Reaction of 5,6-O-isopropylidene L-ascorbic acid and 2-aminothiophenol.

The ligand (H_2L`) was characterized by elemental analyses and spectral data. It was found to be air sensitive; the yellow color turns dark, which could be due to the $H_2L$`oxidation. This ligand was soluble in ethanol, acetone, chloroform and dimethylsulphoxid but insoluble in water. The general physical properties of ligand H_2L` are presented in table-1.

The synthesis and coordinating behavior of this ligand H_2L`with metal ions (Cr(III), Mn(II) Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)) have been synthesis and studied . The analytical data of the ligand $H_2L$`metal complexes suggest their 1:1 (metal: ligand) stoichiometry. Most of the complexes have high decomposition points showing stability. They were all soluble in DMF and DMSO but sparingly soluble in ethanol, insoluble in water, acetone and chloroform, and stable towards light, air and moisture. The formula structures of the metal complexes of this work may be suggested as, [Trichloro [2-(1,2-dihydroxy ethyl)-1,-(2- mercaptophenyl)-5-(2-mercapto phenyl imino)-2,5-dihydro-1H-pyroll-3,4-diol]chromium(III)] hexahydrate[$Cr(H_2L`)Cl_3].6H_2O$ and [Dichloro[2-(1,2-dihydroxyethyl)-1,-(2-mercapto phenyl)-5-(2-mercapto phenyl imino)-2,5-dihydro-1H pyroll-3,4-diol]-n, aqua-metal(II)$]_X$ hydrate $[M(H_2L`)Cl_2.(H_2O)_n]xH_2O$.

Where; M=	*Mn(II),*	*Co(II),*	*Ni(II),*	*Cu(II),*	*Zn(II),*	*Cd(II),*	*Hg(II)*
n=	*1,*	*1,*	*1,*	*2,*	*1,*	*1,*	*0*
x =	*2,*	*2,*	*1,*	*1,*	*2,*	*1,*	*0*

Physical properties, elemental analyses and metal percentage of the complexes are described in table-1.

Table 1-Some physical properties and analytical data for the ligand $H_2L`$and its metal complexes.

Comp. No. ***Molecular formula***	***Color***	***Decomp. Temp. ^0C***	***Yield %***	***Elemental Analysis % Found (calculated)%***				***M% found (calculated)***
				C	***H***	***N***	***S***	
$H_2L`$ $C_{18}H_{18}O_4N_2S_2$	Yellow	83-85* ***melting point***	63.44	56.81 (55.38)	4.32 (4.60)	6.95 (7.18)	15.28 (16.41)	
$[Cr(H_2L`)Cl_3].6H_2O$ $C_{18}H_{30}O_{10}N_2S_2Cl_3Cr$	Dark green	190	85.52	32.95 (32.90)	4.46 (4.57)	5.02 4.27	11.32 9.75	6.67 (7.92)
$[Mn(H_2L`)Cl_2(H_2O)]2H_2O$ $C_{18}H_{24}O_7N_2S_2Cl_2Mn$	White	260	32.48	37.43 (37.90)	3.78 (4.22)	3.83 (4.9)	12.11 (11.20)	9.55 (9.63)
$[Co(H_2L`)Cl_2(H_2O)]2H_2O$ $C_{18}H_{24}O_7N_2S_2Cl_2Co$	Black	265	38.46	37.92 (37.64)	3.58 (4.18)	5.52 (4.88)	12.62 (11.15)	9.56 (10.27)
$[Ni(H_2L`)Cl_2(H_2O)].H_2O$ $C_{18}H_{22}O_6N_2S_2Cl_2Ni$	Parrotia Green	255	82.05	38.75 (38.87)	3.35 (3.96)	6.20 5.83	10.00 (11.52)	10.72 (10.56)
$[Cu(H_2L`)Cl_2(H_2O)].H_2O$ $C_{18}H_{22}O_6N_2S_2Cl_2Cu$	Black	118	30.23	38.26 (38.53)	2.99 (3.92)	5.02 4.99	12.90 11.42	10.66 (11.34)
$[Zn(H_2L`)Cl_2(H_2O)]2H_2O$ $C_{18}H_{24}O_7N_2S_2Cl_2Zn$	White	130	30.92	37.74 (37.22)	3.65 (4.14)	3.54 (4.84)	10.26 (11.03)	11.14 (11.27)
$[Cd(H_2L`)Cl_2(H_2O)].H_2O$ $C_{18}H_{22}O_6N_2S_2Cl_2Cd$	Cream	265	35.88	35.93 (35.44)	3.93 (3.61)	3.36 (4.59)	9.88 (10.50)	18.34 (18.45)
$Hg(H_2L`)Cl_2$ $C_{18}H_{18}O_4N_2S_2Cl_2Hg$	Yellow	90	36.46	34.33 (34.94)	3.22 (2,91)	3.78 (4.53)	9.59 (10.36)	32.41 (32.48)

Spectroscopy studies:

1.Infrared (I.R) Spectra

The prominent infrared absorption along with the assignments of the ligand ($H_2L`$) and metal complexes are presented in table-2.

The infrared spectrum of the free Ligand $H_2L`$ table-2, figure-1, showed a strong band at (1612.49)cm^{-1} assignable to (C=N) stretching vibration[10-12]. This band was shifted towards lower frequencies in all metal complexes figure-2 the infrared spectrum of Ni(II) complex, except the Hg(II) complex figure-3 which was found at (1612.35) cm^{-1} in the same position in the free ligand. This may be attributed to the coordination of azomethine nitrogen atom to all metal ions except Hg(II) ion[13]. A broad band of medium intensity was observed at (2607) cm^{-1}in the free ligand was attributed to the stretching mode of the thiol group [10-12]. This band was also shifted towards lower frequencies and appeared as a single band between (2582.5-2545.12) cm^{-1} in Co(II),Ni(II),Zn(II) and Cd(II) complexes or as a doublet at (2600-2563.21),(2576.90-2505.33) cm^{-1} in Cr(III),Mn(II),Cu(II) and Hg(II) complexes. This confirms the coordination of sulfur atom with metal ions without deprotonating of thiol group. The splitting of this band is due to the fact that two thiol group were coordinated to the metal ions.

On the other hand, the free ligand also showed two strong bands appeared at (3379 .29 and 3302.13)cm^{-1}and two medium intensity bands at (3213.41 and 3062.96) cm^{-1}, which assigned to stretching vibration of hydroxyl groups O(6)-H, O(5)-H, O(3)-H and O(2)-H respectively as in the free ascorbic acid[14]. This indicates the removal of isopropylidene group [15]. These four strong bands were shifted toward higher frequencies in all metal complexes indicative of the non-participation of the ligand OH group in metal ligand bonding [16].

All metal complexes showed broad absorption band in the rang (3600.01-3425.21) cm^{-1} due to the (OH) stretching vibration of lattice water [13]. While the presence of coordinated water was detected by the appearance of bands at the range (536.21-470.63) cm^{-1} assigned to $M\text{-}OH_2$[17] except the Cr(III) and Hg(II) complexes which were showed absence to the bands related to the lattice and coordination water.

Other weak bands in the range (493.78-439.77), (447-405.05) and (396-280.73) cm^{-1} attributed to υ_{M-N}, υ_{M-S} and υ_{M-Cl} bands respectively [13], table-2. While the υ_{M-Cl} stretching vibration modes was difficult to locate in Mn(II), Zn(II) and Cd(II) complexes because it lies in a range out of the instruments scale.

All these differences indicate the coordination of ligand ($H_2L`$) to metal ions through the nitrogen atom of azomethine group and sulfur atoms of thiol groups, while in Hg(II) complex, the ligand coordinates with metal ions through the two sulfur atom of the thiol groups.

Table 2-Main characterized vibration frequencies of ligand $H_2L`$and its metal complexes

compound	υ_{OH}	$\upsilon_{C=N}$	υ_{S-H}	***Lattic H_2O $\upsilon_{OH}\delta_{OH}$***	***Coordinated water***	υ_{M-N}	υ_{M-S}	υ_{M-Cl}	υ_{M-O}
$H_2L`$	3379.29 3302.13 3213.41 3062.96	1612.49	2607	-	-	-	-	-	-
$[Cr(H_2L`)Cl_3].6H_2O$	3456.44 3329.14 3294.12 3078.94	1603.63	2594.08 2532.35	-	-	462.92	428.20	307.74 280.73	-
$[Mn(H_2L`)Cl_2(H_2O)]2H_2O$	3457.29 3194.12	1604.77	2563.21 2532.35	3546.02 (1671.23)	3546.02 806.25 pr	474.49	432.05	-	532.35
$[Co(H_2L`)Cl_2(H_2O)]2H_2O$	3410.15 3370.63 3317.82 3155.54 3116.97	1604.77	2545.12	3570-3425 1640.77	3570.63 570.07 pw	493.78	440	327.16	470.63
$[Ni(H_2L`)Cl_2(H_2O)].H_2O$	3282.84 3248.13 3213.41 3120.82 3062.96	1593.20	2582.50	3447 1689.04	3447 829.39pr	474.49	447.49	396.46 315.45	505.35
$[Cu(H_2L`)Cl_2(H_2O)].H_2O$	3451.34 3344.82 3280.04 3184.25	1604.77	2600.04 2576.90	3600-3451 1640.17	3451 709.8pr 578.64 pw	451.34	432.05	360 320 283	536.21
$[Zn(H_2L`)Cl_2(H_2O)]2H_2O$	3448.72 3417.86 3344.45 3309.85	1600.5	2557.61	3587.60	3522.02 875.68pr 675.09pw	489.92	424.34		520.78
$[Cd(H_2L`)Cl_2(H_2O)].H_2O$	3390.29 3311.01 3240.41 3132.40	1589.34	2576.90	3593.40 1681.93	3518.16 821.68pr 675.09pw	439.77	405.05	-	520.78
$[Hg(H_2L`)Cl_2]$	3417.86 3305.99 3263.56 3182.55	1616.35	2627.05 2505.33	-	-	-	435.91	357.01 330.01	-

υ= stretching vibration Pr=rocking vibration, Pw=wagging vibration, δ=bending vibration.

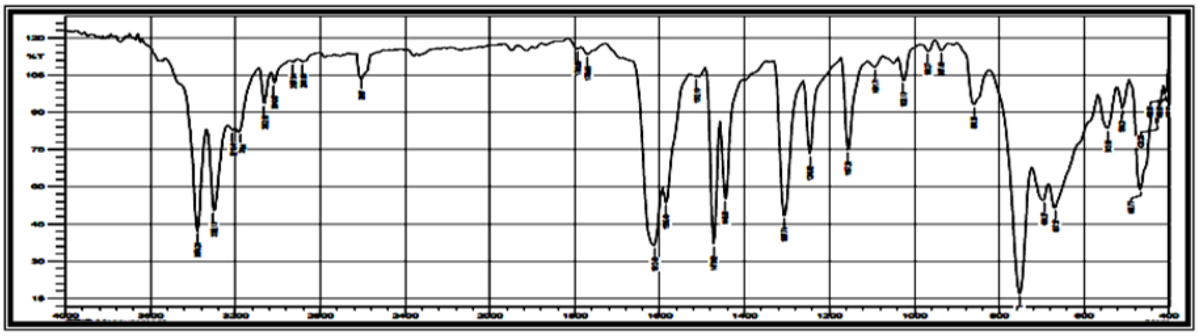


Figure 1-Infrared spectrum of ligand H_2L

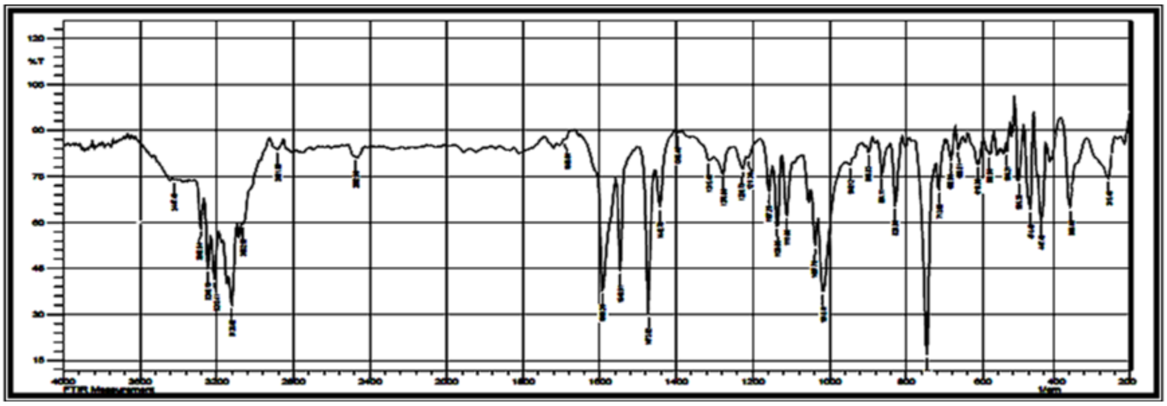


Figure 2-Infrared spectrum of $[Ni(H_2L`)Cl_2(H_2O)].H_2O$ complex.

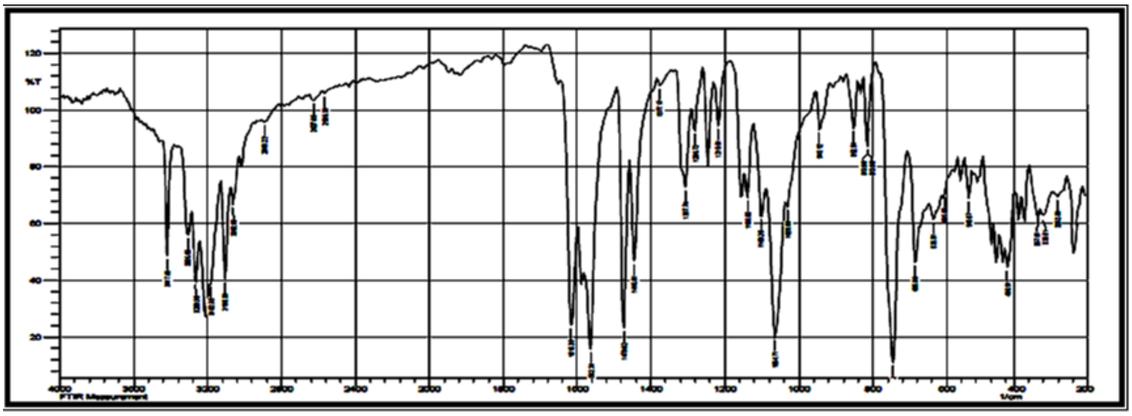


Figure 3-Infrared spectrum of $Hg(H_2L`)Cl_2$ complex.

2.The Proton Nuclear Magnetic Resonance (^1H-NMR) Spectra

Data of ^1H-NMR of ligand $H_2L`$ and metal complexes are presented in Table-3.The $^1H$-NMR spectrum of ligand $H_2L`$ figure-4, was characterized by the absence of any signals related to methyl protons of isopropylidene moiety and the presence of signal at 6.72 ppm gave doublet with signal at 6.43 ppm gave triplet which attributed to secondary and primary OH protons at C(5) and C(6) position[10,12] respectively, this indicating the cleavage of isopropylidene group[16]. The signals assigned to the protons on C(4), C(5) and C(6) respectively are not detected due to overlap with OH protons.

The spectrum also displayed a singlet two protons at 5.44 ppm which was attributed to OH protons at C(3) and C(2) position[7,16]. The S-H proton of 2-amino thiophenol[10] was observed at (3.34ppm) while, aromatic protons signals were observed as a multiples in the (6.99-7.11 ppm) region[10]

The ^1H-NMR spectra of metal complexes showed a singlet within the (3.34-3.61) ppm range which is assignable to SH proton. This signal is broadened suggesting that the S-atom of the 2-aminothiophenol unit is coordinated to the metal ions upon non-deprotonated [13, 19]. Many signals appeared in the region (7.07-6.87) ppm were assigned to phenyl ring protons[10,18] which remained almost in the same positions observed in the spectrum of the free ligand with some broadening due to the chelation with the metal ion. The proton signals due to the hydroxyl groups [8,19], were observed within the (6.13-5.37) ppm range, shift upfield which indicates the non-involvement of these groups in chelation. Some significant changes were observed in the spectra of these metal complexes, can be summarized below:

The spectrum of Mn (II) complex showed a broad singlet signal at (4.73)ppm can be assigned to coordinated or crystalline water (H_2O) protons in complex which was coupled with the signals OH protons in C(3)-OH and C(2)-OH position[20]. In spectrum of Co(II), Cd(II) and Hg(II) respectively, the signals of OH proton in C(3)-OH and C(2)-OH position are not detected due to overlap with OH protons in C(5) –OH and C(6) –OH [21]. The spectrum of Ni(II) metal complex showed that the SH signal proton and OH protons in the C(2) and C(3) position are not detected due to overlap with coordinated or crystalline water (H_2O) protons[21]and appeared as a broad singlet at (4.75)ppm .

In Cu(II) and Zn(II) spectra respectively. The (S-H) proton signal has been split into a doublet appeared at (3.35, 3.34) and (3.42, 3.42) ppm respectively which also refers to the presence of two SH groups coordinated to the same metal ion. The spectrum of Cu(II) complex also showed a broad singlet at (5.01 ppm) related to coordinated or crystalline water [21].

Table 3:^{1}H-NMR Signal position (δ) (ppm) of ligand H_2L\` and metal complexes.

Compound	***H aromatic***	***C(5)-OH***	***C(6) - OH***	***C(3) –OH and C(2) OH***	***SH***
H_2L\`	7.11-6.99	6.74, 6.72	6.45, 6.43 6.40	5.44 s	3.34 s
[Cr(H_2L\`)Cl_3].6H_2O	7.07-6.97	6.71,6.71	6.96, 6.40 6.39	5.37s	3.34
[Mn(H_2L\`)Cl_2(H_2O)].2H_2O	7.12-6.88	6.55 → 6.28		-	3.34
[Co(H_2L\`)Cl_2(H_2O)].2H_2O	7.12-6.89	6.50 br		-	3.42
[Ni(H_2L\`)Cl_2(H_2O)].H_2O	7.15-6.59	⟵ 4.75 br ⟶			
[Cu(H_2L\`)Cl_2(H_2O)].H_2O	7.34-6.89	6.80, 6.76	6.76 6.61 6.44	5.44 s	3.34 3.34 d
[Zn(H_2L\`)Cl_2(H_2O)].2H_2O	7.14-6.93	6.78 —— 6.40 br		5.45 s	3.42 3.42
[Cd(H_2L\`)Cl_2(H_2O)].H_2O	7.64-7.33	7.13 —— 6.50 br		-	3.36
[Hg(H_2L\`)Cl_2]	7.43-7.02	6.94 —— 6.75br		-	3.61

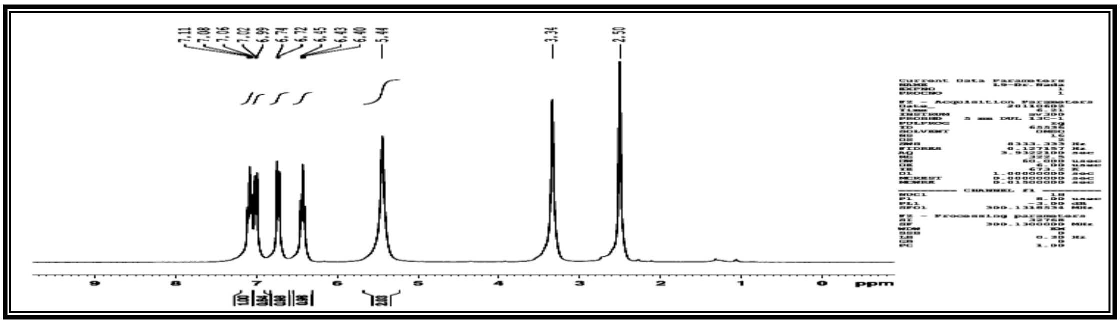


Figure 4-^{1}HNMR Spectrum of ligand H_2L\`

3.The ^{13}C-NMR Spectra

The ^{13}CNMR spectrum of the Ligand table-4, figure-5 was characterized by the absence of the signal related to carbonyl lactone [22] and aliphatic CH of isopropylidene moiety[22]at (~167)ppm and (~26)ppm respectively. Instead, a peak located at (150.196)ppm assignable to azomethin group[13]. Two signals were observed at (135.88 and 131.60)ppm were attributed to the (C-S) of 2-amino thiophenol moiety[10]. This clearly confirms the formation of H_2L\` by cleavage of isopropylidenemoiety[15]. The peaks observed at (60.60, 64.96, 72.60, 161.30 and 129.106)ppm were assigned to C-(6), C-(5), C-(4),C-(3) and C-(2) respectively[20]. While the peaks observed at (116.92, 116.52 and 115.25) ppm were due to aromatic carbon atoms [10]. The ^{13}CNMR spectra of H_2L\` metal complexes Table (4) showed appreciable chemical shifts downfield corresponding to azomethin and thiol carbons compared with free ligand, which support the coordination of nitrogen and sulfur atoms with the metal ions[23]. The peaks which were attributed to C-(6),C-(5),C-(4),C-(3) and C-(2)

appeared in the ranges (73.51-61.11) ppm C-(6),C-(5),(129.10-123.56) ppm C-(4) and (161.30-154-98) (C-(3)andC-(2)) [22]. The spectra also showed the signals related to aromatic carbon atoms [10] as are described in Table-4.

Table 4-^{13}CNMR Signals position (δ) (ppm) for ligand H_2L`and metal complexes.

Compound	*C=N*	*C-S*	*Ph*	*C6*	*C5*	*C4*	*C3*	*C2*
H_2L`	150.19	135.88 131.60	116.92 116.52 115.25	60.60	64.96	72.60	161.30	129.11
[Cr(H_2L`)Cl_3].6H_2O	152.22	138.13 135.88	118.36 117.48 115.23	68.13	69.03	73.51	156.20	123.56
[Mn(H_2L`)Cl_2(H_2O)]2H_2O	153.26	136.39 133.12	117.48 115.69	65.21	68.81	70.11	158.20	127.11
[Co(H_2L`)Cl_2(H_2O)].2H_2O	151.22	137.88 134.13	120.48 118.36 116.48 115.23	61.30	62.13	64.98	161.30	131.62
[Ni(H_2L`)Cl_2(H_2O)].H_2O	150.69	135.99 132.12	117.48 116.81 115.69	-	62.43	64.31	156.81	129.10
[Cu(H_2L`)Cl_2(H_2O)].H_2O	153.32	136.58 134.18	118.12 116.55 116.23	64.37	65.52	67.30	157.33	128.48
[Zn(H_2L`)Cl_2(H_2O)].2H_2O	151.62	135.98 134.13	120.48 118.36 116.48	67.62	69.23	71.50	155.22	127.56
[Cd(H_2L`)Cl_2(H_2O)].H_2O	152.14	137.88 135.13	117.46 116.44 115.03	61.14	-	68.98	154.98	123.56
[Hg(H_2L`)Cl_2]	152.02	136.80 134.14	118.36 116.48 115.23	61.11	62.13	64.48	161.30	130.31

*chemical shifts relative to DMSO -d^6 at (40.58- 39.32) ppm.

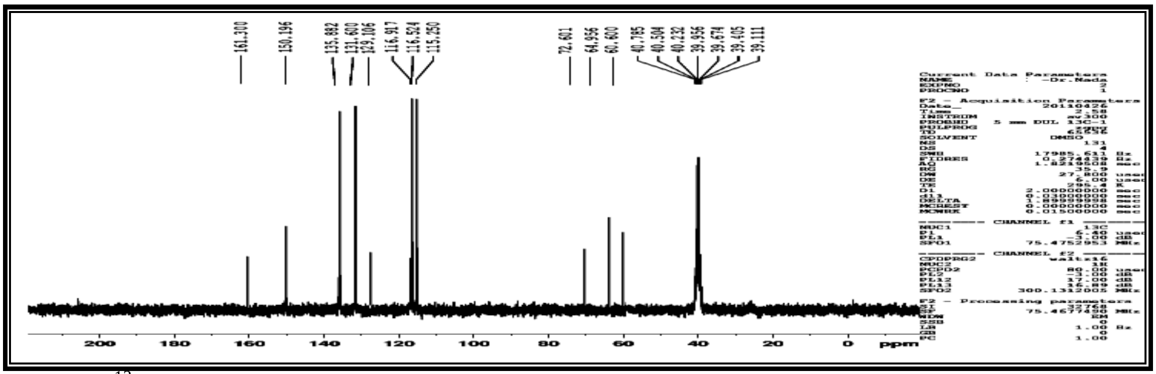


Figure 5- ^{13}CNMR Spectrum of ligand H_2L`

4.The Mass Spectra of the Ni(II) and Zn(II) Metal Complexes.

The mass spectra of the Ni(II) and Zn(II) metal complexes of ligand H_2L`, showed molecular ion peaks at $^{m}/_{Z}$= 554.03 and 579.05 with relative intensity 40% and 7.3% which correspond to [NiH_2L((H_2O)] and [ZnH_2L(H_2O)] stoichiometry respectively. The Fragments corresponding to the elimination of $C_2H_6O_2$, C_6H_7ONS, etc. from the molecular ion with their relative are shown in table-5, figure-6 and table-6, figure-7 for Ni(II) and Zn(II) respectively.

Table 5- Mass spectral data of [Ni(H_2L`)Cl_2(H_2O)].H_2O complex.

Fragment eliminated	***Fragment obtained***	***Molecular ion Peak m/z found(calc.)***	***Relative intensity %***
	$C_{18}H_{22}O_6N_2S_2Cl_2Ni$* Parent ion	554.03 (554.69)	4.0
-$C_2H_6O_3$	$C_{16}H_{16}O_3N_2S_2Cl_2Ni$	475.05 (475.69)	10.4
-C_6H_7ONS	$C_{10}H_{10}O_2NSCl_2Ni$	337.02 (336.69)	4.7
-$C_3H_2O_2$	$C_7H_8NSCl_2Ni$	269.02 (268.69)	1.9
-CH_4	C_6NSCl_2Ni	248.05 (247.69)	48.7
-C_4	C_2NSCl_2Ni	199.04 (199.09)	1.3
-NCl	C_2SNiCl	149.03 (150.19)	4.7
-C_2	NiSCl	124.01 126.19	96.3
-S	NiCl	93.05 94.19	22.0

*Parent ion

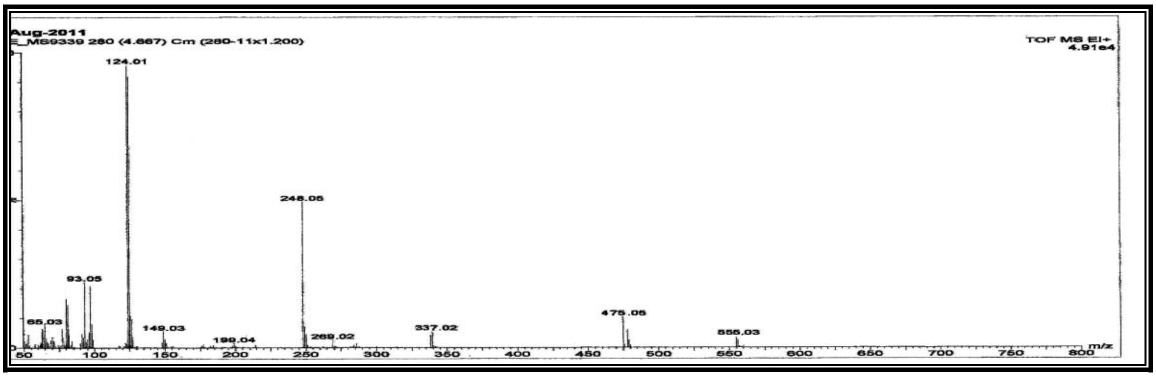


Figure 6-Mass spectrum of [Ni(H_2L`)Cl_2(H_2O)].H_2O complex**.**

Table 6-Mass spectral data of[Zn(H_2L`)Cl_2(H_2O)].2H_2O complex.

Fragment eliminated	***Fragment obtained***	***Molecular ion Peak m/z found(calc.)***	***Relative intensity %***
	$C_{18}H_{24}O_7N_2S_2Cl_2Zn$* Parent ion	579.05 579.38	7.3
-$C_2H_{10}O_4$	$C_{16}H_{14}O_3N_2S_2Cl_2Zn$	478.05 (478.38)	8.7
-C_6H_7ONS	$C_{10}H_7O_2NSCl_2Zn$	399.09 (340.38)	2.0
-$C_4H_3O_2N$	$C_6H_4SCl_2Zn$	248.05 245.38	4.7
-C_2H_2Cl	$C_6H_4SCl_2Zn$	182.08 (183.88)	5.5
-C_2H_2S	C_2HZnCl	125.02 (125.88)	94.0
-C_2H-	ZnCl	100.02 100.88	76.4
-Cl	Zn	65.38 65.03	18.0

*Parent ion

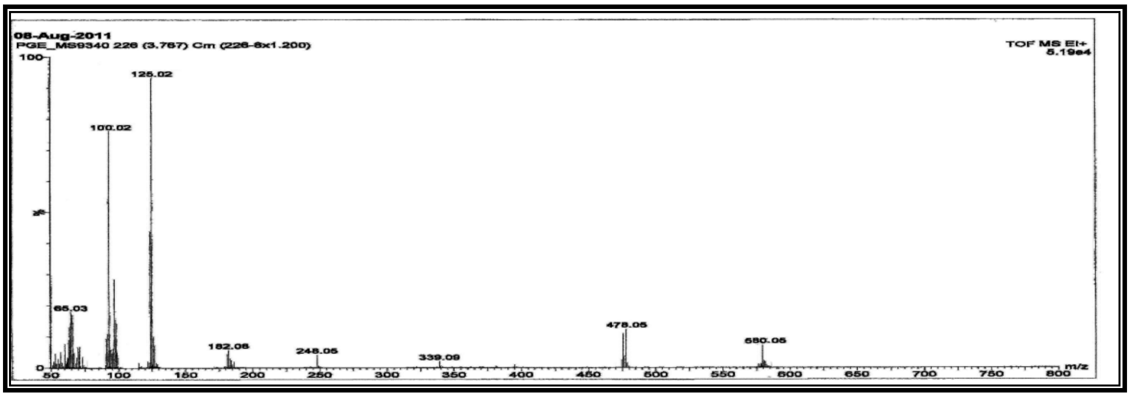


Figure 7-Mass spectrum of $[Zn(H_2L`)Cl_2(H_2O)].2H_2O$ complex.

5.Electronic Spectra, Magnetic Moments and Electrical Conductivity Measurements.

The electronic spectrum of ligand $H_2L`$ figure-8 consists of a high intensity band appearance in the U. V region at wave number (28777cm^{-1}, 347.5 nm(Ɛ 1797)).This band were attributed to intraligand $\pi \rightarrow \pi^*$ transitions [10]. The absorption peak related to the ligand and metal complexes and their assignments a listed in table-7.

The electronic spectra of ligand $H_2L`$ metal complexes exhibited bands in the region (32051-19048) cm^{-1} (312-525) nm and was attributed to intraligand $\pi \rightarrow \pi^*$ transition. These bands shift to lower energy relative to the free ligand due to complexation [24]. Bands observed in the visible and near i.r regions were referred to charge transfer and in the d-d,ligand field transition[24]. The ligand field parameters B`, 10Dq and β were obtained by applying the observed band energies on Tanabe Sugano diagram of the suitable d- system [24],Table-7.

The Mn(II) complex figure-9 , exhibited band related to the spin forbidden transition $^6S \rightarrow ^4G$ [24]while the Cr(III),Co(II),Ni(II) and Cu(II) complexes showed spin allowed transitions of ^4F states for Cr(III),(figure 10) and Co(II), ^3F state for Ni(II) and ^2D state for Cu(II) ,with the latter showing octahedral Jahan-Teller distortion[24].Since the chemistry of d^{10} configuration affords no crystal field stabilization energy, bands observed in the visible region of Zn(II),Cd(II) and Hg(II) complexes spectra were attributed to ligand to metal charge transfer transitions [24] . Magnetic moment [25]also measurement Table-8 (μ_{eff} B.M.) of Cr(III), Mn(II),Co(II),Ni(II) and Cu(II) refer to high spin paramagnetic octahedral geometry,while Zn(II),Cd(II) and Hg(II) were diamegnatic complexes .Molar conductance in dimethylsulfoxide at room temperature Table-7 showed that all complexes were nonionic nature[26].According to the above mentioned analytical and spectral results, the stereochemical structures of the metal complexes of this work may be suggested as illustrated in scheme-3.

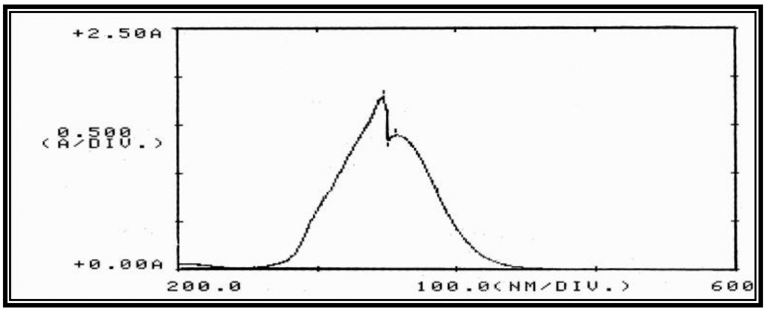


Figure 8-Electronic spectrum of ligand $H_2L`$.

Table 7- Electronic spectra, measurements of Racah parameter B`, nephelauxetic parameter β and molar Conductance in DMSO for ligand $H_2L$` and it's metal complexes.

Compounds	*Band position (Cm^{-1})*	*Assignments*	*Dq/B`*	*B`*	*B*	*10Dq Cm^{-1}*	*Conductivity $Cm^2.S.mol^{-1}$*
H_2L`	28777	$\pi \rightarrow \pi^*$	-	-	-	-	-
[Cr(H_2L`)Cl_3].$6H_2O$	$\upsilon_1$12658 $\upsilon_2$16667 $\upsilon_3$29875(cal) 31646	$^4A_2g \rightarrow {}^4T_2g$ $^4A_2g \rightarrow {}^4T_1g$(F) $^4A_2g \rightarrow {}^4T_1g$(P) (C.T)	1.32	871	0.91	11497	6.63
[Mn(H_2L`)Cl_2(H_2O)]$2H_2O$	$\upsilon_1$18966 31447	$^6A_1g \rightarrow {}^4T_1g$ (C.T)	-	-	-	-	-
[Co(H_2L`)Cl_2(H_2O)]$2H_2O$	$\upsilon_1$7284(cal) $\upsilon_2$13699 $\upsilon_3$19268 31348	$^4T_1g \rightarrow {}^4T_2g$(F) $^4T_1g \rightarrow {}^4A_2g$(F) $T_1g \rightarrow {}^4T_1g$(P) (C.T)	1.38	922	0.95	7376	9.23
[Ni(H_2L`)Cl_2(H_2O)].H_2O	$\upsilon_1$11682 $\upsilon_2$17094 $\upsilon_3$28015(cal) 31447	$^3A_2g \rightarrow {}^3T_2g$ $^3A_2g \rightarrow {}^3T_1g$(F) $^3A_2g \quad {}^3T_1g$(P) (C.T)	1.31	853	0.83	11169	8.23
[Cu(H_2L`)Cl_2(H_2O)] H_2O	$\upsilon_1$15873 18416 32051	$^2B_1g \rightarrow {}^2Eg$ (C.T)	-	-		-	2.93
[Zn(H_2L`)Cl_2(H_2O)]$2H_2O$	16393 30769	(I.L.C.T)	-	-		-	0.23
[Cd(H_2L`)Cl_2(H_2O)] H_2O	31746	(I..L.C.T)	-	-		-	1.53
[Hg(H_2L`)Cl_2]	17153 31250	(I.L.C.T)	-	-		-	0.93

I.L.C.T: Internal Ligand Charge Transfer

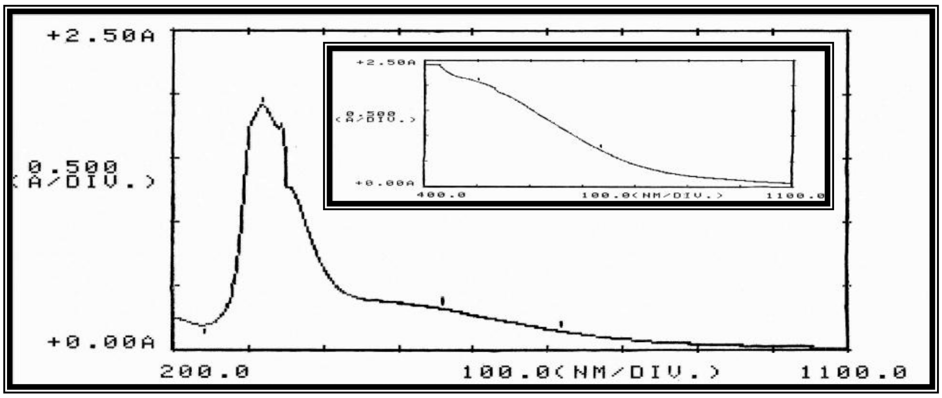


Figure 9-Electronic spectrum of [Mn(H_2L`)Cl_2(H_2O)].$2H_2O$

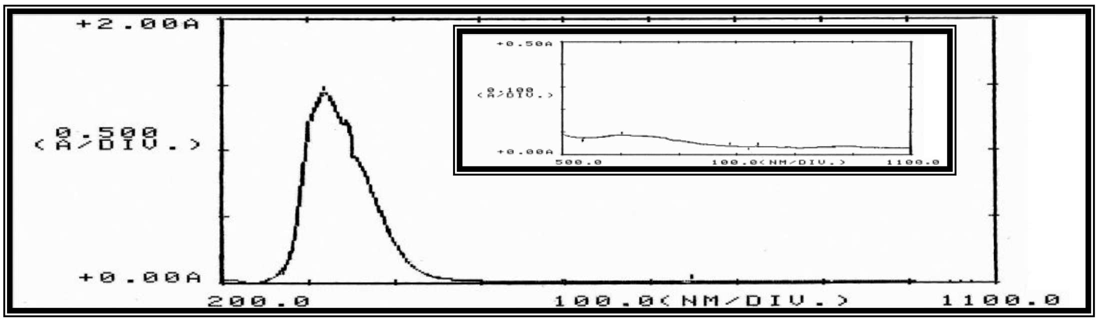
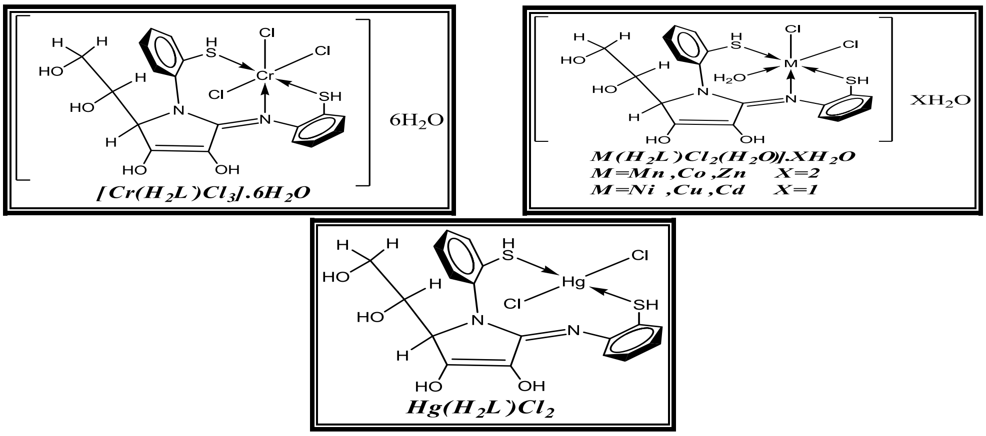


Figure 10-Electronic spectrum of [Cr(H_2L`)Cl_3].$6H_2O$ complex.

Table 8- Data of magnetic moment (μ_{eff}=B.M.) of solid at 298K and suggested stereochemical structure of complexes.

Complex	*Gram Suscept Xg x 10^{-6}*	*Diamagnetic Correction D x 10^{-6}c.g.s*	*Paramagnetic Atomic sucept X A x 10^{-6}*	*μ_{eff} B.M.*	*Suggested structure*
$[Cr(H_2L`)Cl_3].6H_2O$	6.82	+233.01	4712.94	3.35	Octahedral
$[Mn(H_2L`)Cl_2(H_2O)]2H_2O$	20.79	+173.61	12021.83	5.35	Octahedral
$[Co(H_2L`)Cl_2(H_2O)]2H_2O$	4.83	+173.61	8341.78	4.46	Octahedral
$[Ni(H_2L`)Cl_2(H_2O)].H_2O$	7.35	+160.61	4247.15	3.18	Octahedral
$[Cu(H_2L`)Cl_2(H_2O)].H_2O$	27.80	+160.61	1718.94	2.02	Octahedral
$[Zn(H_2L`)Cl_2(H_2O)]2H_2O$	-	-	-	Diamagnetic	Octahedral
$[Cd(H_2L`)Cl_2(H_2O)]2H_2O$	-	-	-	Diamagnetic	Octahedral
$[Hg(H_2L`)Cl_2]$	-	-	-	Diamagnetic	tetrahedral



Scheme 3- Suggested sterochemical structures of the lactam derivative of L-ascorbic acid metal complexes.

Computational Studies

Geometrical optimization of ligand H_2L` and Cr(III), Mn(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal complexes were performed applying the PM6 semiempirical method[12]. Table-9 shows the calculated atomic charges and bond distances of these molecules.

The optimized geometry of H_2L` Figure-11, Table-9 showed the atomic charges of S1, S2 (sulphur atom of thiol groups in 2-aminothiophenol moiety) were -0.276 and -0.062 respectively while the atomic charge on azomethine group was -0.432 . The bond distance of C-S1 and C-S2 were 1.369 and 1.359Å respectively ,the bond distance of C=N was 1.296Å. Total energy of this ligand was -0.121 a.u. which coordinated with metal ions through S1 and S2 of its thiol groups and N atom of azomethine group as a tridentate ligand. The calculated optimized structures of the metal complexes Figures (12-19) showed that these complexes have a distorted octahedral geometry with two chloride ions occupying the axial positions. The coplanar four positions were occupied by three donor atoms of H_2L` moieties and one H_2O molecule or in the case of Cr(III) complex one Cl ion. While the computational results showed the Hg(II) complex was more stable in the tetrahedral geometry, where the co-planer four positions were occupied by three donor atoms of the ligands and one chloride ion. Upon complexation, the bond lengths C-S^1H and C-S^2H showed shortening, while C=N showed elongation, as compared to their values in free ligand H_2L`.That indicates a much tighter binding in all metal complexes except the bond length of C=N in Hg(II) complex which is virtually identical in uncomplexed ligand andconfirms no bond formation between the N atom of imine group and Hg(II)ion. Figures (12-19) showed the optimized structure of these complexes.

H_2L` acts as electron- donor while Cl and $H_2O$ withdraw charge from the central metal ions. Thus, it becomes obvious that the charge differences on the atoms that interact with metal ions are greater. These changes indicate that these ions receive part of their charges from the same atoms in $H_2L$` molecule. Therefore, a weak bonding was formed between coordinated sites of ligand and metal ions, while the copper accumulates much less charge than the other studies central ions studied. This is expected in terms of the size and lower electronegativity of Cu(II). Table-9 shows total energies of

H_2L` metal complexes from this data, the stability of these metal complexes are predicted as: **Cr > Cd > Zn >Cu > Co > Ni >Mn> Hg**
Indicating that Cr(III) complex is the most stable among the other metal complexes of H_2L`.

Table 9-Theoretical parameters of atomic charge , bond length and total energy values of ligand H_2L` and metal complexes.

Compounds.	***Charge of metal***	***Charge of 1SH***	***Charge of 2SH***	***Charge imine group C=N***	***B.L. C=N***	***B.L. C-S^{1}H***	***B.L. CS^{2}H***	***Total energy a.u***
H_2L`		-0.276	0.062	-0.432	1.2968	1.77253	1.76250	-0.12127
[Cr(H_2L`)Cl_3].$6H_2O$	0.745	0.214	0.096	0.189	1.3136	1.75433	1.76502	-2.2538
[Mn(H_2L`)Cl_2(H_2O)]$2H_2O$	0.463	0.230	0.211	0.037	1.36819	1.75722	1.75203	-0.26522
[Co(H_2L`)Cl_2(H_2O)]$2H_2O$	0.194	0.221	0.210	0.320	1.32746	1.75519	1.75779	-0.30708
[Ni(H_2L`)Cl_2(H_2O)].H_2O	0.480	0.327	0.288	0.260	1.30299	1.75235	1.75501	-0.294925
[Cu(H_2L`)Cl_2(H_2O)].H_2O	1.272	-0.089	-0.877	-0500	1.30051	1.74943	1.76674	-0.3101785
[Zn(H_2L`)Cl_2(H_2O)]$2H_2O$	0.282	0.157	0.186	0.377	1.29033	1.75593	1.75434	-0.335419
[Cd(H_2L`)Cl_2(H_2O)].H_2O	0.896	-0.016	-0.020	-0.496	1.32009	1.76320	1.75618	-0.3551138
[Hg(H_2L`)Cl_2]	0.546	-0.002	-0.003	-0.334	1.29692	1.76320	1.76869	-0.179548

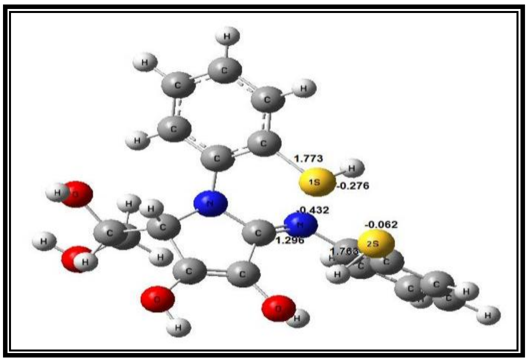


Figure 11-Optimized geometric structure of ligand H_2L`.

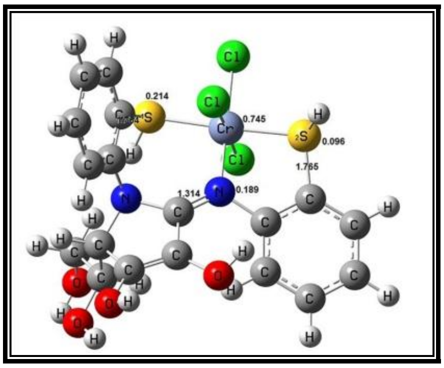


Figure 12-Optimized geometric structure of [Cr(H_2L`)Cl_3].$6H_2O$.

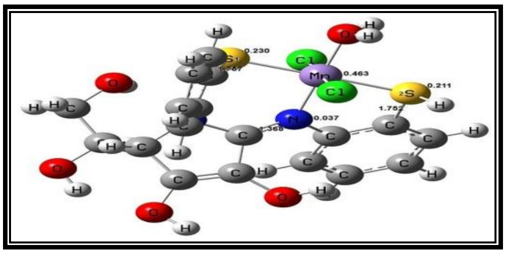


Figure 13-Optimized geometric structure of [Mn(H_2L`)Cl_2(H_2O)]$2H_2O$.

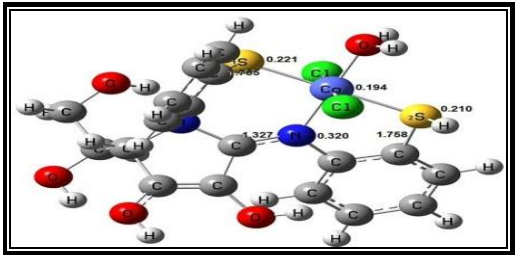


Figure 14-Optimized geometric structure of [Co(H_2L`)Cl_2(H_2O)]$2H_2O$

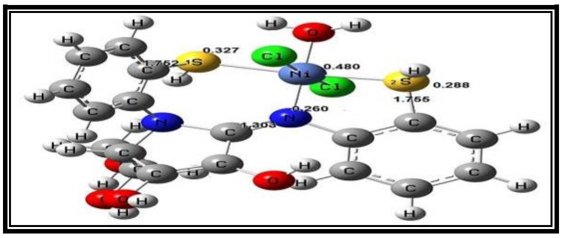


Figure 15-Optimized geometric structure of [Ni($H_2L`$)Cl_2(H_2O)].H_2O

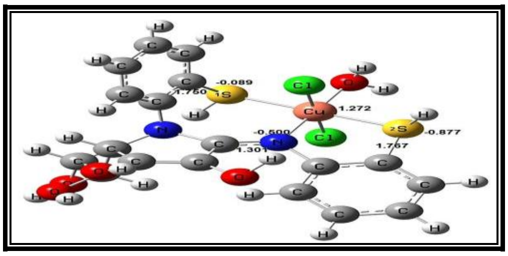


Figure 16-Optimized geometric structure of [Cu($H_2L`$)Cl_2(H_2O)].H_2O

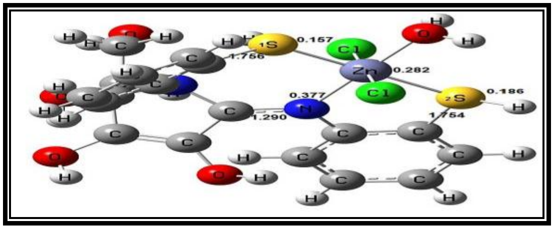


Figure 17-Optimized geometric structure of [Zn($H_2L`$)Cl_2(H_2O)].2H_2O

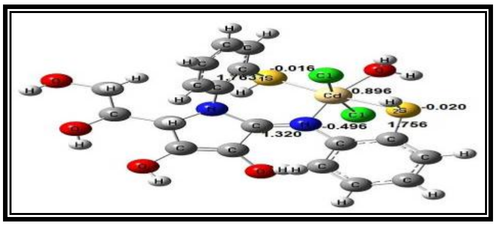


Figure 18-Optimized geometric structure of [Cd($H_2L`$)Cl_2(H_2O)].H_2O

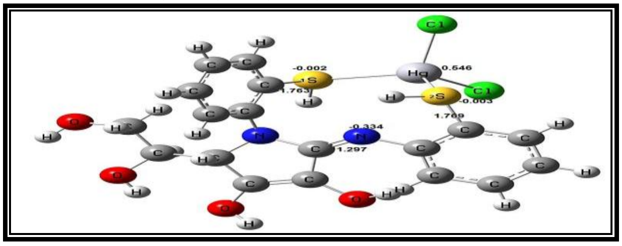


Figure 19- Optimized geometric structure of Hg($H_2L`$)Cl_2.

Conclusions

$H_2L`$ was synthesized as a lactam derivatives of L-ascorbic acid by reaction of 5,6-O-isopropylidene-L-ascorbic acid and 2-aminothiophenol . As part of a program directed toward the transformation of $H_2L`$ into metal complexes ,we reported the synthesis of Cr(III),Mn(II),Co(II),Ni(II),Cu(II),Zn(II),Cd(II) and Hg(II) metal complexes . Ligand $H_2L`$ acts as a neutral tridentate in its metal complexes and coordinate through nitrogen atom of azomethine group and sulphur atom of two thiol group in octahedral geometry except in complex which acts as a bidentate and coordinated through sulphur atom of two thiol group and the Hg(II) ion acquired tetrahedral geometry. Molecular structure studies were proposed for metal complexes and were in a good agreement with the spectroscopic and theoretical results.

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