Synthesis and Characterization of Some Metal Complexes of [2-chloro-N-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylcarbamothioyl)acetamide] (L)

تحضير وتشخيص بعض المعقدات الفلزية مع -(5,1- داي مثيل-3-اوكسو-2-فنيل-3,2-داي هايدرو-1- بايرازول-4-يل 2-كلورو-Nكاربامو ثايويل)استمايد

Basima M. Sarhan*
Enass J. Waheed**
Nada J. Kadhim***
*Department of Chemistry, College of Education for Pure Sciences,
Ibn-AL-Haitham, University of Baghdad
** College of Pharmacy, University of Karbala.

Abstract

A new ligand [2-chloro-N- (1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro -1H-pyrazol- 4-ylcarbamothioyl)acetamide](L) was synthesized by reacting the Chloro acetyl isothiocyanate with 4-aminoantipyrine,The ligand was characterized by(C HNS) elemental microanalysis and the spectral measurements including Uv-Vis ,IR ,^{1}H and^{13}C NMR spectra, some transition metals complex of this ligand were prepared and characterized by Uv-Vis, FT-IR spectra, conductivity measurements, magnetic susceptibility and atomic absorption. From the obtained results the molecular formula of all prepared complexes were $[M(L)_2(H_2O)_2]Cl_2$ (M^{+2} =Mn, Co, Ni, Cu, Zn, Cd and Hg),the proposed geometrical structure for all complexes were octahedral.

Key Word : 4-Aminoantipyrine, Cloro acetyl isothiocyanate, complexes.

الخلاصة

حضر الليكاند الجديد
-(5,1- داي مثيل-3-اوكسو-2-فنيل-3,2-داي هايدرو-1- بايرازول-4-يل كاربامو ثايويل)استمايد2N-كلورو-
وذلك من مفاعله (كلورواستيل ايزوثايوسيانات) مع 4-امينو أنتي بايرين وشخص بوساطة التحليل الدقيق للعناصر(C.H.N.S.)والدراسات الطيفة وتتضمن الأشعة فوق البنفسجية- المرئية والأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي ^{13}C NMR , كما حضرت وشخصت معقدات أملاح بعض ايونات العناصر الانتقالية الثنائية التكافؤ (Hg, Cd, Zn, Cu, Ni, Co, Mn)مع الليكاند (L) وشخصت المعقدات المحضرة باستعمال الأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية والتوصيلية المولارية والحساسية المغناطيسية والامتصاص الذري واستنتج من الدراسات والتشخيصات إن المعقدات لها شكل ثماني السطوح حول الايون الفلزي مع اللكياند (L) ثنائي السن.

الكلمات المفتاحية: 4-امينو انتيبايرين, كلورواستيل ايزوثايوسيانات, معقدات.

Introduction

In recent years, there has been increasing interest in synthesis of heterocyclic compounds that have biological and commercial importance. Antipyrine compounds play an important role in modern organic synthesis, not only because they constitute a particularly useful class of heterocyclic compounds, but also because they are of great biological interest. One of the most important derivatives of antipyrine is 4-aminoantipyrine, It is very important in the field of Medicinal and Agricultural chemistry. It is also used as a hemolytic inhibitors, polorographic titration, conductometric and potentiometric determination of lanthanides. 4-aminoantipyrine have large scale of applications in biological, clinical, analgesics, antifungal, antibacterial, anticancereous and pharmacological areas[1,2]. synthesis a new series of transition metal complexes of Mn(II), Cu(II) from the Schiff base ligand derived from 4-aminoantipyrine, furfural and o-phenylene diamine [3]. synthesis Mn (II), Co (II), Ni (II), Cu (II), Zn(II), Cd (II), Hg(II) and Pb(II) complexes of Schiff base ligand containing 4-aminoantipyrine in a good yield and characterized using IR,^{1}HNMR,UV-Vis.,mass spectra, magnetic susceptibility and molar conductivity [4]. A new ligand synthesis by the reaction of 4-aminoantipyrine with 4-dimethylaminobenzaldehyde ,the complexes of Co(II), Zn(II) Cd(II) and Hg(II) with this ligand have been prepared and characterized by elemental analysis, FTIR and Uv-Vis spectra [5]. Anew research using a phosphonium-1-indenylide (PHIN) ligand with 4,7-dimethyl-1-C_9H_4PMePh and synthesis of a new PHIN complexes of rhodium and iridium [6] , The aim of this work is to prepare and characterize a new ligand

[2-chloro-N-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylcarbamothioyl acetamide](L), and it's metal complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions.

Experimental

Chemicals

All reagents were analar or chemical pure grade by BDH, Merck and Fluka. All metal chloride salts and solvents were purchased from Merk and Fluka com., and used without purification.

Instruments

^{1}H and ^{13}C NMRwere recorded using Ultra Shield 300 MH_z Switzerland and at University of Al al-Bayt, Jordan. Melting point was recorded by using Stuart- melting point apparatus. FT-IR spectra were recorded as KBr disc using 3800 Shimadzu in the range of (4000-400) cm^{-1}. Electronic spectra were obtained using Uv-160 Shimadzu spectrophotometer at 25℃ for 10^{-3}M solution DMSO with 1.000 ± 0.001 cm matched quartz cell. Molar Conductivity was measured at 25℃ for 10^{-3}M solution of DMSO by using Philips PW. Digital. micro elemental analysis(C HNS) were performed using Acrlo Erba 1106 elemental analyzer. Magnetic susceptibility measurements were obtained by balance magnetic susceptibility model MSB-MKI. Metal contents of the complexes were determined by atomic absorption technique by using Shimadzu (AA680G).

Preparation of ligand(L)

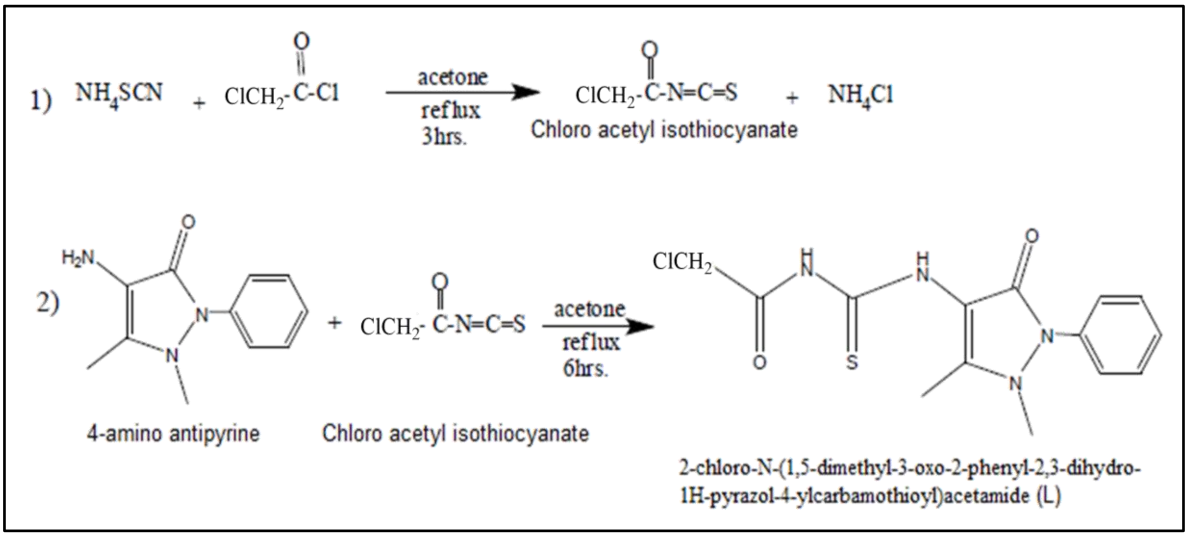
The ligand was prepared by two steps (Scheme-1)

(A)- Preparation of the (Chloro acetyl isothiocyanate)[7]

Mixture of Chloro acetyl chloride(2 ml,1mmol) and ammonium thiocyanate (2g, 1mmol) in (25 ml) of acetone was stirred under refluxed for 3 hrs and then filtered, the filtrate was used for further reaction.

(B)- Preparation of [2-chloro-N-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylcarbamothioyl)acetamide] (L)

(5.33g, 1mmol) of 4-aminoantipyrine in (20 mL) acetone was rapidly added to Chloro acetyl isothiocyanate and maintaining reflux. After refluxing for 6 hrs, the resulting solid was collected, washed with acetone and recrystallization from ethanol, yield (75%), (m.p =210-212)˚C**,** C% found (50.1) calc.(49.63), H% found (4.75) calc.(4.46), N% found (16.32) calc.(16.54), S% found (10.1) calc.(9.46).



Scheme-:Synthesis of ligand (L)

Synthesis of ligand complexes

Synthesis of the $[Cd(L)_2(H_2O)_2]Cl_2$ complex

A solution of (0.20g, 1mmol) $CdCl_2.2H_2O$ in (10mL) ethanol was added to solution of (0.60g, 2 mmol) (L) in (10ml) ethanol. The mixture was stirred for 6 hrs at room temperature, the brown solid was collected by filtration, washed with (1:1) mixture of water: ethanol and dried in an oven (50˚C).

Synthesis of $[Mn(L)_2(H_2O)_2]Cl_2$, $[Co(L)_2(H_2O)_2]Cl_2$, $[Ni(L)_2(H_2O)_2]Cl_2$, $[Cu(L)_2(H_2O)_2]Cl_2$, $[Zn(L)_2(H_2O)_2]Cl_2$, $[Hg(L)_2(H_2O)_2]Cl_2$ complexes.

A similar method to that mentioned for preparation of $[Cd(L)_2(H_2O)_2]Cl_2$ complex was used to prepare the complexes of [Mn^{+2},Co^{+2},Ni^{+2}, $Cu^{+2,}$ Zn^{+2}, and Hg^{+2}] ions with (L), table (1) showed some physical properties of the prepared complexes.

Results and Discussion

Ligand (L)

The Uv-Vis spectrum of the free ligand (L). Fig.(1) exhibits a high intense absorption peak at (33670)cm^{-1} which may be attributed to electronic transition type $\pi \longrightarrow \pi^*$[8].The data of electronic spectrum of the free ligand (L) were listed in table (2).

The FT-IR spectrum of the free ligand (L) ,Fig.(3) showed bands at(1635) cm^{-1},(1600)cm^{-1} and (1367)cm^{-1} due to υC=O(in ring) , υC=O(amidic) and υC=S respectively. While another absorption band at (3140)cm^{-1} could be explained as υ N-H [9-11].The FT-IR spectral data of the free ligand were listed in table(3).

The ^{1}H-NMR spectrum of free ligand (L),Fig.(5) which was recorded in DMSO-d_6 solvent showed the following signals: singlet at δ(1.2) ppm refers to (3H, CH_3), singlet at δ(1.90) ppm refers to (3H,CH_3N),singlet at δ(2.69) ppm refers to DMSO, singlet at δ(3.45) ppm refers to (2H,ClCH_2),singlet at δ(3.92) ppm refers to (1H, NH sec. amine), the multiplet signals δ(6.21-8.43) ppm were attributed to aromatic protons, singlet at δ(9.80) ppm refers to (1H,NH sec. amide).

^{13}C NMR spectrum of the free ligand (L),Fig.(6)showed chemical shift at δ(12.50) ppm refers (CH_3) for (CH_3CO) group, signal at δ(37.25) ppm for (CH_3N), signals at δ(40.00) ppm for DMSO, signals at δ(50.64) ppm for (ClCH_2), signal at δ(101.62) ppm refers to (**C**=C-CH_3), The chemical shifts at range δ(104.08-129.12) ppm due to aromatic carbons, signal at δ(135.00) ppm for (=C-N), signal at δ(150.00) ppm for (=C-N, aromatic carbons), while the signals at Fig. (6) showed the following signals at δ(161.25) ppm , δ(168.75) ppm and δ(172.50) ppm were attributed to ((C=O), antipyrine ring), (CONH) and (C=S)[12,13].

Complexes of the ligand(L)

The solid complexes soluble in some common solvent such as dimethyl formamide, dimethyl sulphoxideand relatively thermally stable. The molar conductivity values of all complexes in DMSO solvent in 10^{-3} M at 25˚C (table-1) indicated electrolyte nature with 1:2 ratio [14].The atomic absorption measurements for all complexes gave approximated values when its comparison with theoretical values, Table (1) includes the physical properties for the ligand and its complexes.

Magnetic moment

The values of measured magnetic susceptibility and effective magnetic moment (µeff) for the Mn(II), Co(II), Ni(II), Cu(II)complexes are shown in table(1), Mn(II), Co(II), Ni(II) and Cu(II) complexes exhibit µeff. (5.93, 4.82, 3.03, 1.72) B.M respectively ,which can be a normal values for high spin octahedral complexes.[15]

Electronic spectra for complexes

-$[Mn(L)_2(H_2O)_2]Cl_2$

The Brown complex of Mn(II) shows band at(37174)cm^{-1} due to ligand field and other bands at (14064)cm^{-1} and (10752)cm^{-1} which are caused by the electronic transfer $^6A_1g \longrightarrow {}^4T_2g_{(G)}$ and $^6A_1g \longrightarrow {}^4T_1g_{(G)}$ respectively, suggesting octahedral geometry around Mn(II) ion [16].

-$[Co(L)_2(H_2O)_2]Cl_2$

The spectrum of the deep violet complex gave four bands at (33670)cm^{-1}, (27777)cm^{-1}, (14705)cm^{-1} and (12019)cm^{-1} attributed to (L.F),C.T mixed with $^4T_1g_{(F)} \longrightarrow {}^4T_1g_{(P)}$, $^4T_1g_{(F)} \longrightarrow {}^4A_2g$ and $^4T_1g_{(F)} \longrightarrow {}^4T_2g_{(F)}$ respectively and the rachinter electronic repulsion parameter (B^-) was found to be (428)cm^{-1}, from the relation $\beta = B^- / B^0$, was found to be equal (0.84),these parameter are accepted to Co(II) octahedral complex[17].

-$[Ni(L)_2(H_2O)_2]Cl_2$

The spectrum of Green complex of Ni(II) has revealed the following electronic transfer(L.F),C.T mixed with $^3A_2g \longrightarrow {}^3T_1g_{(P)}$,$^3A_2g \longrightarrow {}^3T_1g_{(F)}$, and $^3A_2g \longrightarrow {}^3T_2g_{(F)}$, transition at (38910)$cm^{-1}$, (27472)$cm^{-1}$, (22222)$cm^{-1}$ and (12562)cm^{-1} respectively, the(B^-) value is found to be (800)cm^{-1},while β was equal to (0.76) these are the characteristics for octahedral complexes of Ni(II)[18].

-[$Cu (L)_2(H_2O)_2]Cl_2$

The spectrum of Brown complex of Cu(II) shows two bands at (34129)cm^{-1}, (11792)cm^{-1} caused to (C.T), $^2Eg \longrightarrow {}^2T_2g$ transition respectively ,which was a good agreement for distorted octahedral complex for Cu(II) ion[19,20].

- **$[Zn(L)_2(H_2O)_2]Cl_2$, $[Cd(L)_2(H_2O)_2]Cl_2$** and **$[Hg(L)_2(H_2O)_2]Cl_2$**, Fig.(2)

Show only charge transfer of (M→L) in range (38910-27472) cm^{-1}[21,22]. All transition with their assignments are summarized in Table (2).

FT-IR Spectra

These spectra exhibited marked difference between bands Fig. (4) belonging to the stretching vibration of υ(C=O amide) in the range between (1629-1621) cm^{-1}shifted higher frequencies by (29-21)cm^{-1} suggesting of the possibility of the coordination of ligand through the oxygen atom at the carbonyl group[23] while the band caused by υ(C=S) appeared between (1436-1413)cm^{-1} shifted to higher frequencies by (69-46)cm^{-1} which indicates to the coordination of ligand through the sulfur atom at the thion group to the central ion[24]. The stretching vibration band υ(C=O in ring), υ(N-H) either show no change or very little in their frequencies (1637-1635)cm^{-1},(3153-3143)cm^{-1}respectively there for indicating do not coordinate to the metal ion. Metal-oxygen and metal-sulfur bonds were confirmed by the presence of the stretching tremor of υ(M-O) and υ(M-S) around (504-453)cm^{-1} and (445-421)cm^{-1} respectively the spectra of complexes showed the appearance of bands in the range(916-823)cm^{-1} attributed to ρ(OH),these bands confirm the coordination of the water with metal[23],Table (3) describes the important bands and assignment for all prepared complexes.

The Suggested structures for complexes on the basis of molar conductivity, magnetic moment, spectroscopic studies (FT-IR,Uv-Vis and atomic absorption) and (^{1}H,^{13}C-NMR for ligand (L)only)for the ligand and all prepared complexes, we suggested that the ligand (L) behaves as bidentate on coordination with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions via oxygen atom of (C=O) amido group and sulfer atom of (C=S) group, suggesting octahedral geometry around metal ions for all prepared complexes.

References

1. Ahmed, A.F. and Khalid, M.E.; (2012) “Synthesis of novel azo disperse dyes derived from 4- aminoantipyrine and their applications to polyester fabrics”, American Journal of Organic Chemistry, 2(3): 52-57.
2. Rajasekar, K.; Balasubramaniya, S. and Durairaj, P. ;(2014) “Microwave assisted synthesis, spectral, antibacterial and antifungal activities of Cu(II) complex with 4-aminoantipyrine and oxalate ion”, World Journal of Pharmaceutical Research, 3(7): 844-849.
3. M. Suresh and V. Prakash; (2011) “Preparation characterization and antibacterial studies of chelates of Schiff's base derived from 4-aminoantipyrine vanillin and o-phenylene diamine” ,International Journal of Current Research,33(2): 68-75.
4. M. Mokhles, M. Mohamad, A. Hanan and A. Samia; (2014) “Synthesis, Characterization and Biological Activity of Some Complexes Containing Antipyrine Moiety”, Sop Transactions on Applied Chemistry,1:1-3.
5. M. Zainab; (2013) “Synthesis And Characterization Of Schiff-Base Ligand Derivative From 4-Aminoantipyrine And Its Transition Metal Complexes”, Journal of Kufa for Chemical Science, 2(8):70-78.
6. Kourosh Purdavaie,Michael C.Baird and Peter H,M,Budzeleaar.(2015) “Synthesis and structure of a new phosphonium-1-indenylide (PHIN)ligand ,4,7-dimethyl-1-C9H4PMePh2,and of new PHIN complexes of rhodium and iridium”,New.J.Chem,39,9429-9441.
7. Kabbani, A.T; Ramadan, H.; Hammuud, H.H. and Hanuom, A.M.G.; (2005) “Synthesis of some metal complexes of N-[(benzoyl amino)-thioxomethyl] amino acid (HL)”; Journalof the Universityof Chemical Technology and Metallurgy,40(4): 339-344.
8. Dyes, .R.J; (1996) “Application of absorption spectroscopy of organic compounds”, Prentice – Hall,Inc., Englewood cliffs,N,J.London.
9. Cary, F.A.(2005) “Organic Chemistry”, 6th Ed. the M.C Graw-Hill companies, Inc.,New York.
10. Silverstein, R.M. ; Bassler, G.C. and Morrill, T.C;(1981) “Spectroscopic identification of organic compounds”, 4th Ed., John Wiley and Sons, New York.
11. Marah,J.;(1991) “AdvancedOrganic Chemistry”; 4th Ed., J. Wiley and Sons, New York .
12. Seenaiah D., Venkatesh B.C., Padmaja A.and Padmavathi V. (2013)“Synthesis of some new oxazolinyl/thiazolinyl/imidazolinyl- benzoxazoles, benzothiazoles and benzimidazoles” ;Indian Journal of Chemistry , 52B : 942-948.
13. Kumar, K.; Satyanarayana, P.and Reddy, B.;(2013) “$NaHSO_4$-SiO_2-Promoted Solvent-Free Synthesis of Benzoxazoles, Benzimidazoles, and Benzothiazole Derivatives” ;Journal of Chemistry , 1 : 1-10.
14. Diebbar-Sid, S., Benali-Baitich, O. and Deloume, J.P.; (2001) “Synthetic and Structural Studies of Some Bivalent Transition Metal Complexes with Oxygen and Nitrogen Containing Schiff Base” ;J. mol. Struct., 569: 121.
15. Mulay,L., (1977) “ Magnetic Susceptibility”,John wiley and sons;New York;part1,vol(4).

16. Sarhan, B .M.; Abed, A.H. and Rumez, R.M. (2013) “Synthesis and characterization of some mixed ligand complexes of quinaldic acid andα -picoline with some metal salts”;AL-Mustansiriyah Journal of science,24(4): 65-74.
17. Lever, A.B.P.; (1968), 2nd “Inorganic electronic spectroscopy”, Elsevier publishing company Amsterdam, London, New York.
18. Drugo, R.S.; (1965) “Physical methods in inorganic chemistry”, Vann strand-Reinhold, New York.
19. Dichakjian, S. and Farrago, M.E. (1985) “Metal complexes of 2-amino-5-nitrothiazole”;Inorg.Chem.Acta,108: 247-259.
20. Walton, R.A.; (1966) “Some donor properties of 1,4-thioxane:complexes with transition metal halides”;Inorg.Chem.,5(4): 643-649.
21. Arjmamd, F.; Parveen, S. and Mohapatra, D.K. (2012) “Synthesis, characterization of Cu(II) and Zn(II) complexes of proline-glycine and proline-leucinetetrapeptides: in vitro DNA binding and cleavage studies”, Inorg.Chem.Acta,388(15): 1-10.
22. Naik, A.D.; Beck, J.; Dirtu, M.N. and Bebrone, C. (2011) “Zinc complexes with 1,2,4-triazole functionalized amino acid derivatives, synthesis, structure and β–lactamasessay”, Inorg.Chem.Acta,368: 21-28.
23. Nakamoto, K; (1996) “Infrared spectra of inorganic and coordination compounds”, 4th Ed., John Wily and Sons, New York.
24. Nawar, N.; El-swwah, I.I., Hosny, N.M. and Mostafa, M.M., (2011) “Novel mono-and binuclear complexes derived from N-benzoyl-N-glycylthiourea(BGH)with some transition metal ions”, Arabian Journal of chemistry,17(1):434–438.

Table (1): Some physical properties of the ligand (L) and its complexes.

Product	M.wt (gm/mol)	Color	m.p. °C	M% Calculation (Found)	Molar Cond. $Ohm^{-1}cm^{2}mol^{-1}$ in DMSO	μ_{eff} (B.M)
$C_{14}H_{15}N_4O_2SCl$ L	338.81	Brown	210-212	-	1.65	
$[Mn(L)_2(H_2O)_2]Cl_2$	839.56	Brown	234-236	7.00 (6.01)	76	5.93
$[Co(L)_2(H_2O)_2]Cl_2$	843.56	deep violet	231-233	7.51 (7.32)	77.15	4.82
$[Ni(L)_2(H_2O)_2]Cl_2$	843.33	Green	232-234	7.48 (8.11)	74	3.03
$[Cu(L)_2(H_2O)_2]Cl_2$	848.16	Brown	228-230	8.09 (8.60)	69.8	1.72
$[Zn(L)_2(H_2O)_2]Cl_2$	850	Brown	256-258	8.33 (8.15)	81	0
$[Cd(L)_2(H_2O)_2]Cl_2$	897.03	Brown	255-257	14.33 (14.51)	85	0
$[Hg(L)_2(H_2O)_2]Cl_2$	985.21	Brown	227-229	25.57 (26.11)	70	0

Table (2): The peaks electronic transitions and structure geometries of the ligand (L) and its complexes.

Compounds	λ(nm)	υ^{-}(cm^{-1})	ABC	ε_{max} molar^{-1} cm^{-1}	Transitions
Ligand (L)	297	33670	2.493	2493	$\pi \longrightarrow \pi^*$
$[Mn(L)_2(H_2O)_2]Cl_2$	296 711 930	37174 14064 10752	2.401 0.011 0.013	2401 11 13	L.F $^6A_1g \longrightarrow {}^4T_2g_{(G)}$ $^6A_1g \longrightarrow {}^4T_1g_{(G)}$
$[Co(L)_2(H_2O)_2]Cl_2$	297 360 680 832	33670 27777 14705 12019	2.120 0.332 0.030 0.011	2120 332 30 11	L.F C.T mixed with $^4T_1g_{(F)} \longrightarrow {}^4T_1g_{(P)}$ $^4T_1g_{(F)} \longrightarrow {}^4A_2g$ $^4T_1g_{(F)} \longrightarrow {}^4T_2g_{(F)}$
$[Ni(L)_2(H_2O)_2]Cl_2$	257 364 450 796	38910 27472 22222 12562	1.386 1.521 p0.282 0.082	1386 1521 282 82	L.F C.T mixed with $^3A_2g \longrightarrow {}^3T_1g_{(P)}$ $^3A_2g \longrightarrow {}^3T_1g_{(F)}$ $^3A_2g \longrightarrow {}^3T_2g_{(F)}$
$[Cu(L)_2(H_2O)_2]Cl_2$	293 848	34129 11792	2.062 0.019	2062 19	C.T $^2Eg \longrightarrow {}^2T_2g$
$[Zn(L)_2(H_2O)_2]Cl_2$	293	34129	2.013	2013	C.T
$[Cd(L)_2(H_2O)_2]Cl_2$	295	33898	2.112	2112	C.T
$[Hg(L)_2(H_2O)_2]Cl_2$	257 364	38910 27472	1.362 1.632	1362 1632	C.T C.T

C.T = Charge transfer

Table (3): The characteristic infrared band for free ligand (L) and its metal complexes in Cm^{-1}

Compound	υ^{-}(N-H)	υ^{-}(C=O) in Ring	υ^{-}(C=O) Amide	υ^{-} (C=S)	ρ (O-H) of water	υ^{-} (M-O)	υ^{-} (M-S)
Ligand (L)	3140 (s)	1635 (s)	1600(s)	1367(s)	-	-	-
$[Mn(L)_2(H_2O)_2]Cl_2$	3149(s)	1637(s)	1621(m)	1436(w)	854(s)	468(m)	423(w)
$[Co(L)_2(H_2O)_2]Cl_2$	3143(m)	1635(w)	1623(s)	1420(m)	823(m)	453(m)	423(w)
$[Ni(L)_2(H_2O)_2]Cl_2$	3147(m)	1635(s)	1623(m)	1413(m)	854(s)	503(m)	437(m)
$[Cu(L)_2(H_2O)_2]Cl_2$	3150(m)	1635(w)	1625(w)	1415(s)	916(s)	504(m)	445(w)
$[Zn(L)_2(H_2O)_2]Cl_2$	3151(m)	1635(s)	1629(w)	1413(s)	831(s)	470(s)	423(m)
$[Cd(L)_2(H_2O)_2]Cl_2$	3148(s)	1635(s)	1627(m)	1420(s)	882(m)	478(m)	421 (m)
$[Hg(L)_2(H_2O)_2]Cl_2$	3153(s)	1635(w)	1621(s)	1430(s)	868(s)	468(m)	423(w)

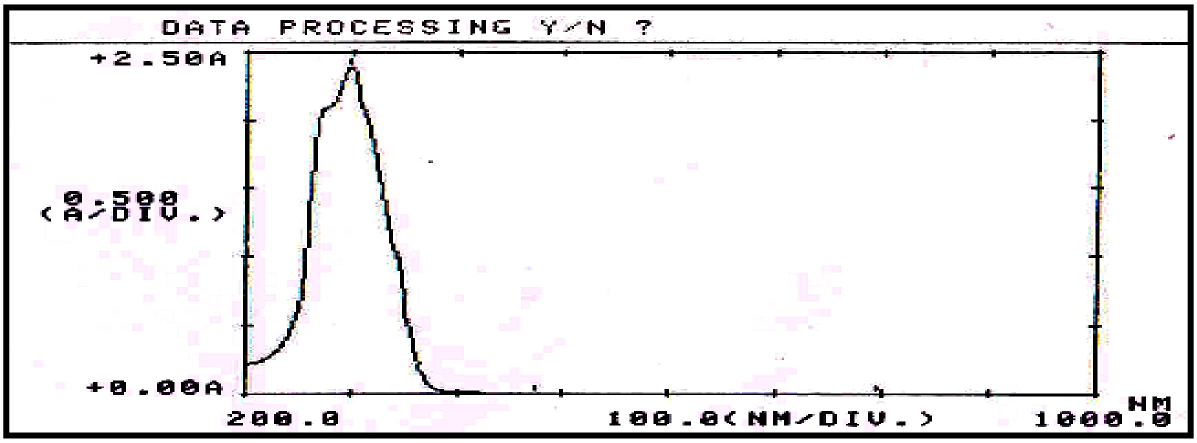


Fig. (1):U.V. spectrum of ligand (L)

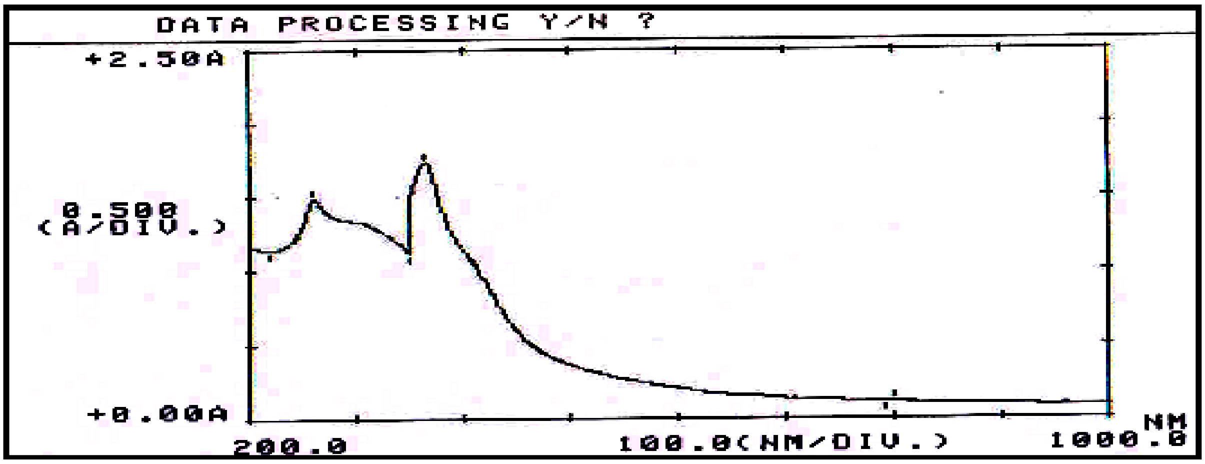


Fig. (2): U.V. spectrum of complex $[Hg(L)_2(H_2O)_2]Cl_2$

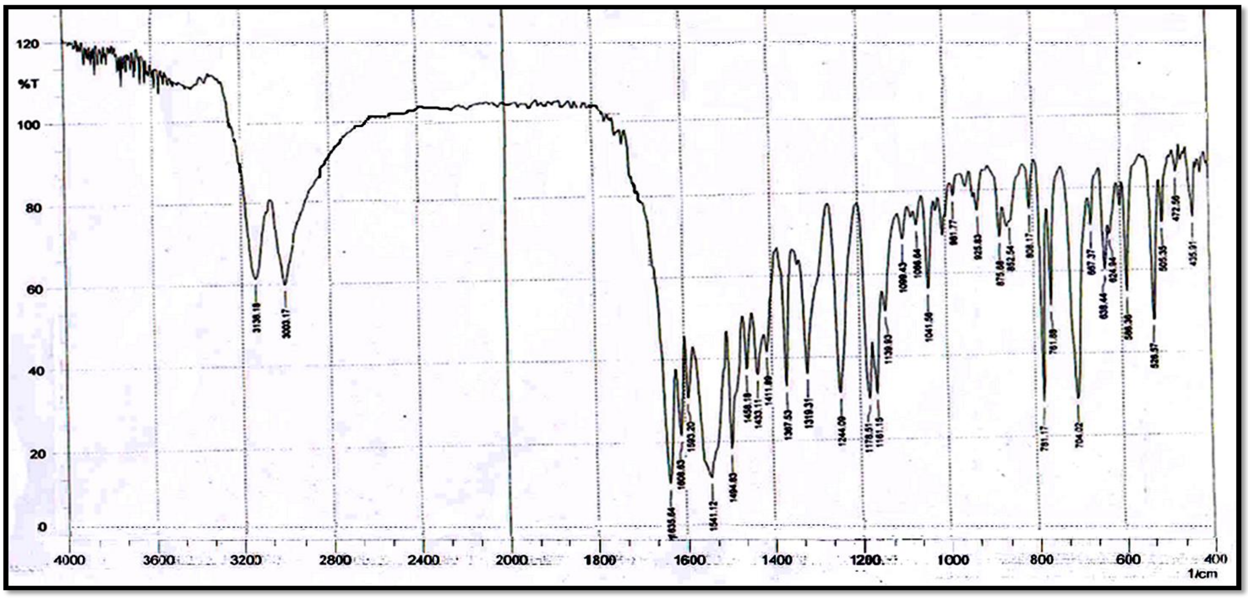


Fig. (3): Infrared spectrum of ligand (L)

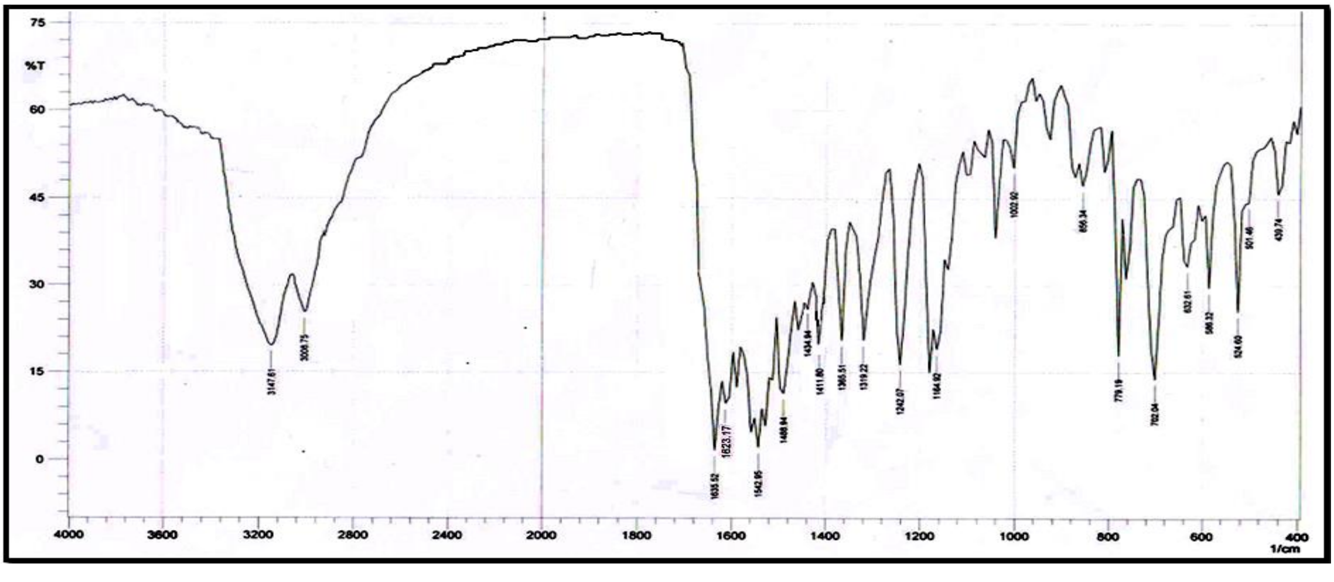
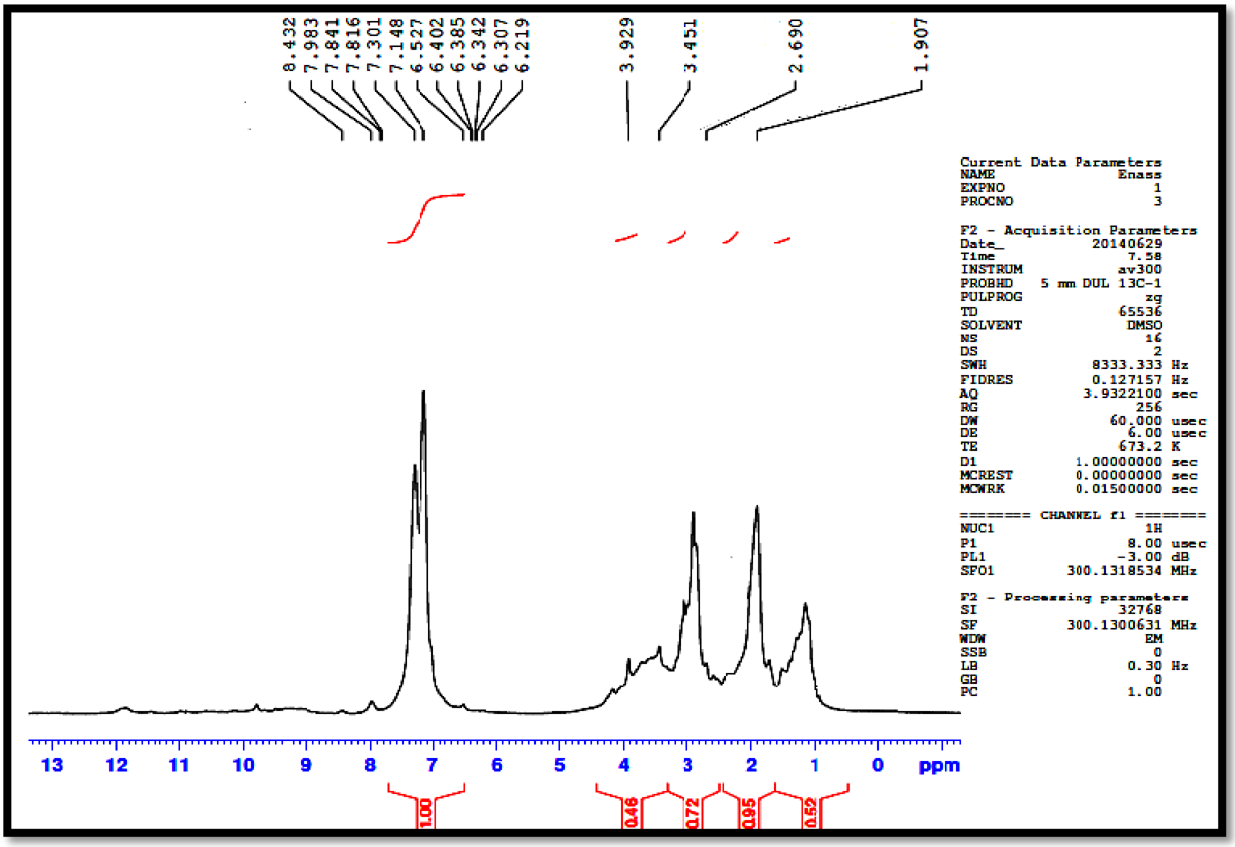


Fig. (4):Infrared spectrum of complex $[Ni (L)_2(H_2O)_2]Cl_2$



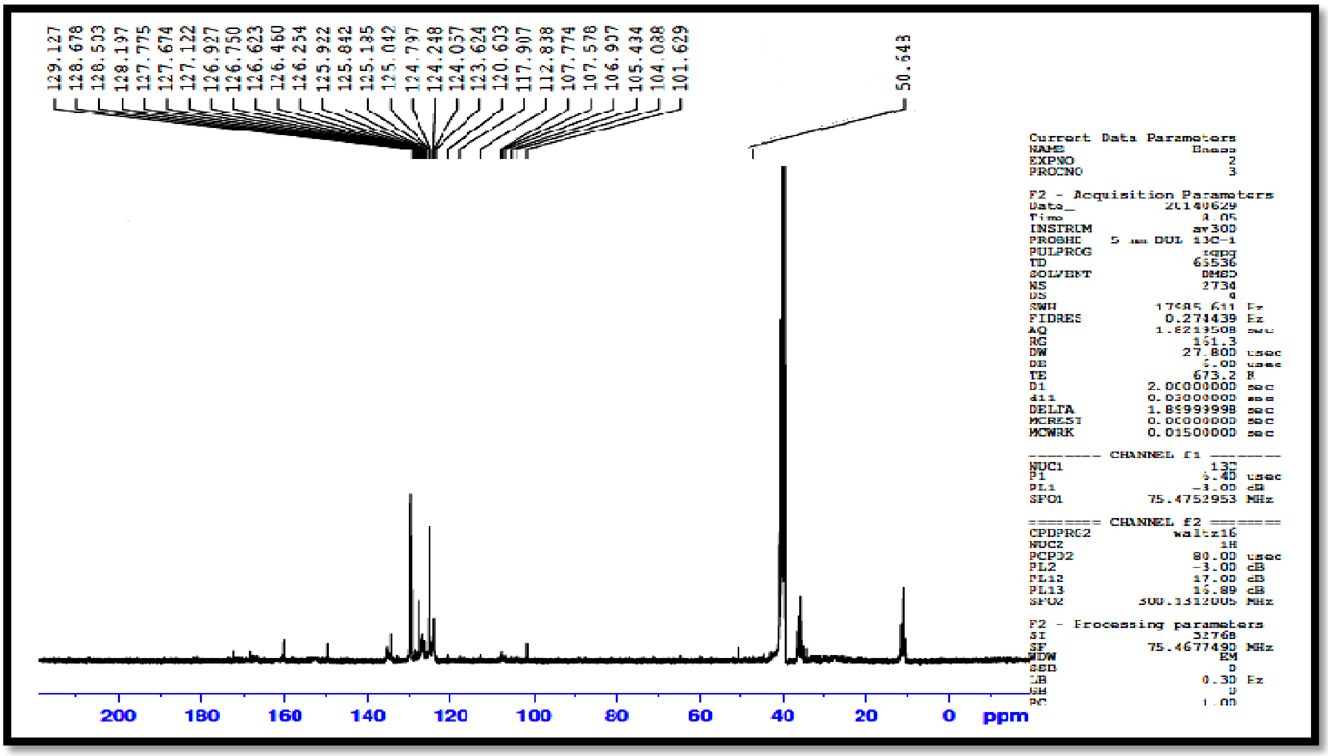
```
Current Data Parameters
NAME                Enass
EXPNO                   1
PROCNO                  3

F2 - Acquisition Parameters
Date_            20140629
Time                 7.58
INSTRUM             av300
PROBHD    5 mm DUL 13C-1
PULPROG                zg
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH              8333.333 Hz
FIDRES           0.127157 Hz
AQ              3.9322100 sec
RG                    256
DW                 60.000 usec
DE                   6.00 usec
TE                  673.2 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.00 usec
PL1                 -3.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300631 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

Fig. (5):^{1}H NMR spectrum of ligand (L)



```
Current Data Parameters
NAME                Enass
EXPNO                   2
PROCNO                  3

F2 - Acquisition Parameters
Date_            20140629
Time                 8.05
INSTRUM             av300
PROBHD    5 mm DUL 13C-1
PULPROG              zgpg
TD                  65536
SOLVENT              DMSO
NS                   2734
DS                      4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                  161.3
DW                 27.800 usec
DE                   6.00 usec
TE                  673.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   6.40 usec
PL1                 -3.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -3.00 dB
PL12                17.00 dB
PL13                16.89 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

Fig. (6):^{13}C NMR spectrum of ligand (L)

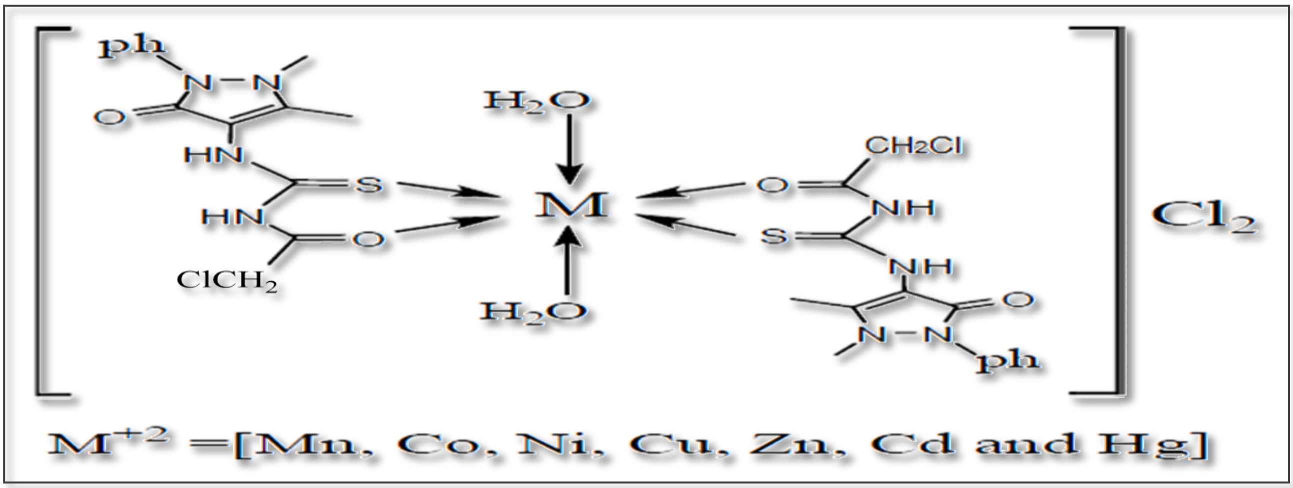


Fig. (7):The proposed chemical structure formula of the complexes