Synthesis and characterization of new ligand of Dithiocarbamate derived from "2-Aminopyridine" with some metal ions

Safaa A.R. Ahmed- College of Applied Science - University of Samarra

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Keywords: Dithiocarbamate, 2-Aminopyridine, Complexes, benzoyl chloride.

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Abstract

This study included synthesis and characterization of new ligand of Dithiocarbamate, this ligand is:

KL = Potassium 2-Aminopyridine Dithiocarbamate

The preparation process included two interactive steps as follows : **step1**: involved the preparation of amines from the reaction of the primary amyloid compound (2-aminoperidine) with benzoyl chloride. The second step was to prepare the lycand from the reaction of the first step product with carbon disulfide with potassium hydroxide as a basic medium.

Step 2 : ligand reaction with metal ions (Co^{II}, Ni^{II}, Cu^{II}, Cd^{II}, Hg^{II}) For the preparation of ligand - derived complexes, the prepared complexes were characterized by infrared spectra, UV-Vis spectra , mass spectra,^{1}H,^{13}C- NMR spectra and molar conductivity And magnetic susceptibility. The propose geometrical shapes of the (Co^{II}, Ni^{II}, Cu^{II}) complexes were octahedral , while the geometrical shape of the complexes (Cd^{II}, Hg^{II}) was a tetrahedral.

تحضير وتشخيص ليكاند جديد لثنائي ثايوكارباميت ومعقداته المشتقة من 2-أمينوبيريدين مع بعض الايونات الفلزية

صفاء عبد الرحمن احمد السامرائي - جامعة سامراء – كلية العلوم التطبيقية

الخلاصة

تَضمن هذا البحث تحضير وتشخيص ليكاند جديد لثنائي ثايوكاربايت والمتمثل بما يلي:

KL=Potassium 2-Amino predin Dithiocarbamate

اشتملت طريقة التحضير على خطوتين تفاعليتين وكما يلي

الخطوة الأولى: تضمنت تحضير الأمايد من تفاعل المركب الأميني الأولي (2-أمينوبيريدين) مع كلوريد البنزوايل. اما الخطوة الثانية: فتضمنت تحضير الليكاند من تفاعل ناتج الخطوة الاولى مع ثنائي كبريتيد الكاربون بوجود هيدروكسيد البوتاسيوم كوسط قاعدي.

الخطوة الثانية : تفاعل الليكاند المحضر مع الايونات الفلزية (Co^{II}, Ni^{II}, Cu^{II}, Cd^{II} ,Hg^{II}) لتحضير المعقدات المشتقة من الليكاند المحضر ، تم تشخيص المعقدات المحضرة بوساطة أطياف الأشعة تحت الحمراء ، وأطياف الأشعة فوق البنفسجية –المرئية ، وطيف الكتلة ، وطيف الرنين النووي المغناطيسي ، والتوصيلية المولارية ، والحساسية المغناطيسية وتم اقتراح الأشكال الفراغية لمعقدات (Co^{II}, Ni^{II}, Cu^{II})وهي أشكال ثمانية السطوح، بينما كان الشكل الهندسي لمعقدات (Cd^{II} ,Hg^{II}) هو رباعي السطوح .

1 - 1Introduction

The importance of chemical consistency has become great and the consistency applications of compounds in the scientific world are enormous(1). In addition to the increasing bio-commercial importance of dithiocarbamate compounds and their complexities with transient elements(2), researchers have been interested in studying their chemistry and identifying their properties. (3) Since many donor atoms such as sulfur, oxygen, nitrogen and phosphorus have been mentioned and studied by many researchers in this field, especially since it has been present in dithiocarbamate as early as the date of (4), bicarbonate thiocarbamate can be defined as compounds formed as a result of the primary or secondary amino reaction with carbon dipered sulfide with a suitable basal medium and solvent(5). Two-thiocarbamate ligands are important compounds that play an important role in organic and inorganic chemistry, (6) because they have the ability to form stable compounds with transition metals and in different oxidation states, resulting in their widespread use in conformational chemistry. Lycandates can be followed by two-year-old thiocarbamate (8),double-clawed (9), or double-grained (10). Dioxin thiocarbamate has received increasing interest in recent years because of the important applications of these compounds in the fields of industry, agriculture, pharmaceuticals and in various pharmaceutical fields such as fungi, bacteria, insects and algae pesticides (10-13)

2- Experimental part

2.1. Chemical substances

All the materials used were of a high degree of purity and equipped by international companies, which were equipped with companies (ALPHA, Fluka, CDH, BDH, GCC)

2.2. Devices used

(Shimadzu-Uv-1800 series) and infrared (Testscan Shimadzu FTIR 8300 series) within the range of 400-4000 using potassium bromide tablets, NMR device using 1H.NMR, Bruker Ultra Shild 400MHz, JPSELECTA, Sa conductivity meter CD-2005 using a solvent (DMSO), 10-3 at laboratory temperature, magnetic susceptibility (MSB-MKI) and mass spectrometer (GC-Mass QP-2013) Digimelt Fusion Measuring Device (SMP10)

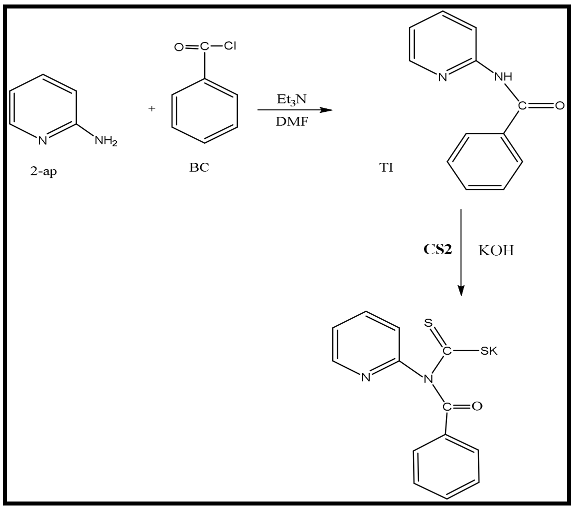
3 – 1 Preparation of ligands and complex

3-1-1 Preparation of amides [HL] (14)

(100ml) was dissolved (0.000g, 0.006mmole) of 2-aminopyridine in 10ml of DMF. Then add (0.7ml ,0.006mmole) of benzoyl chloride gradually with continuous stirring and then add (2ml)) From triethylamine to the reaction mixture. The mixture was then added for a period of 2-3 hours at a temperature of 90-110 ° C. The mixture was left for one night to settle. A white sediment was detected and isolated. Thin layer chromatography technique.

3-2-2 ligand preparation [KL] (15)

(0.336g, 0.006mmole) of potassium hydroxide. Gradually the acidic function was measured at each addition. The mixture was then cooled to an ice bath and added to the reaction solution (0.006mmole) of the carbon disulfide and then left to stir for one hour after it was disposed of From the solvent where it was observed that the product of light brown washed the precipitate several times in ether and then dried and calculated the percentage of the output and the degree of fusion and the process of the reaction was followed through the technique of chromatography thin layer.



Form (1-3) Preparation of ligand Diethyocarbamate

3-3-3 Preparation of Ni(II) complex For the ligand [KL]

In the bottom flask capacity (100ml) put (0.188 g, 2mmole) of ligand [KL] , Dissolve in (20 ml) methanol with little heating to complete the dissolving process , Add to it gradually with continuous stirring (0.09504g, 1mole) of dissolved $NiCl_2.6H_2O$ in (10ml) Methanol Leave the mixture for the reverse escalation process (1-2) hours, so it is a greenish deposit greenish , Leave the solution to the normal evaporation so that it will be a green precipitate and the output weight.

3-3-4 Preparation of ligand[KL] complexes with metal ions Hg(II), Ni(II), Cu(II), Co (II) , Cd(II) .

These complexes were introduced in the same manner as in the same paragraph (2-3-3) and in the same quantities of ligand [KL] with the metal salt used to prepare the complex.

4 - Results and discussion

4 – 1 Molecular conductivity

The molar conductivity of the prepared complexes was measured at a concentration of 10^{-3} molar in a DMSO solvent at the laboratory temperature to determine the ionic formulas of the complexes which gave values within range (59.2-70.1) indicating their ionic electrical nature (1: 2) (17,18)

4 – 2 Magnetic sensitivity measurements

The cobalt complex showed effective magnetic torque (B.M 4.92), This value is expected for the octahedral surfaces (19) , The nickel complex showed an effective magnetic resonance (2.74 B.M) , This falls within the range of eight high-pitched surfaces and approximates the theoretical BM (eff = 2.83μ) that is due to the presence of two individual electrons(20) , The magnetic measurements of the copper complexes show values lower than the values of the magnetic moments in the high beam state of the metal ion (21) , The copper complex showed an effective magnetic resonance (1.78 B.M), which falls within the range of octahedral -pitched deformed surfaces (22).

The complexes of Cd^{II} and Hg^{II} are electromagnetic compounds (Diamagnetic) Due to the absence of individual electrons in orbital (d) because it is full of electrons ($4d^{10}$-$5d^{10}$) respectively, so that the geometry of these complexes can not be determined by magnetic properties (23) .

Table (1-1) Molecular conductivity data and magnetic susceptibility of prepared complexes

Complexes	**M.C** **$\mu s.cm^{-1}$**	**μ_{eff} (B.M)**	**Proposed Composition**
$K_2[Co(L)_2 Cl_2]H_2O$	**59.2**	**4.92**	Octahedral
$K_2[Ni(L)_2 Cl_2]H_2O$	**70.1**	**2.74**	Octahedral
$K [Cu(L)_2 (H_2O) Cl_2]$	**59.2**	**1.78**	Octahedral
$K_2[Cd(L)_2 Cl_2]H_2O$	**68.1**	**-----**	Tetrahedral
$K_2[Hg(L)_2 Cl_2]H_2O$	**69.7**	**-----**	Tetrahedral

4 – 3 Precise analysis of elements

The complexes is prepared by precise quantitative analysis of elements (C.H.N) , The measurement of the chlorine content and the measurement of the ratio of the metal to the atomic absorption technology. The results were included in table (1-1) . When comparing the values obtained in practice with those calculated values theoretically, there was a great convergence between them, which confirms the validity of the chemical formulas proposed for the complexes .

Table (1-2) Data for accurate analysis of elements for ligand and prepared complex

Comp No.	Complexes	Found (Cal.) %						
		M.wt gm/mol	C	H	N	S	Cl	M

1	L	312	54.16 (53.93)	3.57 (3.22)	9. 02 (9.31)	20.65 (20.26)	—	—
2	$K_2[Co(L)_2\ Cl_2].H_2O$	772	40.41 (40.29)	2.61 (2.39)	7.25 (7.21)	16.60 (16.52)	9.18 (8.71)	7.63 (7.38)
3	$K_2[Ni(L)_2\ Cl_2].H_2O$	771.7	41.11 (40.93)	2.68 (2.26)	7.41 (7.15)	16.55 (16.36)	9.27 (9.12)	7.59 (7.28)
4	$K_2\ [Cu(L)_2Cl_2].\ H_2O$	776.5	40.17 (39.90)	2.59 (2.33)	7.21 (7.81)	16.50 (16.17)	9.12 (8.89)	7.21 (7.06)
5	$K_2[Cd(L)_2\ Cl_2].H_2O$	825.4	37.80 (37.66)	2.44 (2.29)	7.21 (7.08)	16.50 (16.18)	9.12 (8.81)	13.61 (13.51)
6	$K_2[Hg(L)_2\ Cl_2].H_2O$	913.6	34.15 (33.95)	2.20 (2.11)	6.13 (6.86)	14.02 (13.89)	7.75 (7. 48)	21.94 (21.36)

4 -4 Infrared measurements

The infrared spectra showed a distinctive packet of the main beams of the ligand , The spectra of the complex have been somewhat similar, but different from the ligand spectrum , Similarity in spectra of complexes can be attributed to the same effects in ligands vibrations , changes were observed in the main packages. These changes included a change in the site first and in the second intensity before and after the consistency , These changes are a clear indication of the process of harmonization and the formation of new complexities . The most important characteristic of the ligand is the record for the dithiocarbamate is the disappearance of NH_2 absorption bundles due to the reaction of the primary secretary with benzoyl chloride and carbon sulphide with a basal state (24) .

The most important vibrations related to the diagnosis of ligand and prepared complexes are shown in Figs. (3-3), (4.3) and Table (3-3).

1- Packet packing for the package C====N

The daggers of this group in the ligand appeared at 1620 cm^{-1} Which is due to matrices of the **C====N** bond associated with sulfate in dithiocarbamate ligand , where the vibrations of this signal appear between the double finger C=N and the singles C-N in the complex prepared on the site (1620-1616 cm^{-1}) this is consistent with literature (25) . The t-shirt Patch is not changed **C====N** in the ligand, the complexes at the site and the intensity and shape indicate that the process of consistency between metal ion and nitrogen .

2 - Absorption packages of group C = O

The ligand dithiocarbamate has demonstrated a strong intensity package at 1701 cm^{-1} these are attributable to the carbonyl group (amide thiocarbamate) , and in prepared complexes containing copper, nickel and cobalt it appeared at (1666, 1681 and 1685 cm^{-1}) respectively , With a change in shape and intensity indicating coherence between metallic ions and carbonyl (17,26) . In the cadmium and mercury complexes, the beam remained intact at (1701 cm^{-1}) an indication of the lack of consistency between metal ion and carbonyl group.

3 - absorption packs of the two groups C-S and C=S

The IR spectra of the record showed a suction package at position (975 cm^{-1}) these belong to the C-S group , In the metal complex, it has suffered a change in location, shape and severity (914 -946cm^{-1}) The change of this package shows the consistency of metal ion with the sulfur atom by the C-S group and this is stated in the literature (27) . The IR spectra also showed a set vibration of C = S at position (1022cm^{-1}) for the recorded ligand which did not suffer from any deviation in the complex prepared in shape, severity and location(28) . The infrared spectra showed weak absorption peaks in the region of (428 – 443 cm^{-1}) (509 – 555 cm^{-1}) which belong to the M-S and M-O nodes in the complex, respectively (17,29,30)

Table (1-3) irradiated IR values and prepared complexes

Comp.	C-S	C=S	CH Ar	C=O	C N	M-O	M-S
L	975	1022	3065	1701	1620	…….	…….
$K_2[Co(L)_2Cl_2]H_2O$	999	1022	3066	1666	1620	532	432
K_2 $[Ni(L)_2Cl_2]H_2O$	999	1022	3055	1685	1620	520	432
$K_2[Cu(L)_2Cl]$. H2O	999	1022	3028	1681	1616	555	439
K_2 $[Hg(L)_2Cl_2]$ H_2O	979	1022	3065	1701	1616	516	443
$K_2[Cd(L)_2Cl_2]$ H_2O	946	1022	3066	1701	1620	509	428

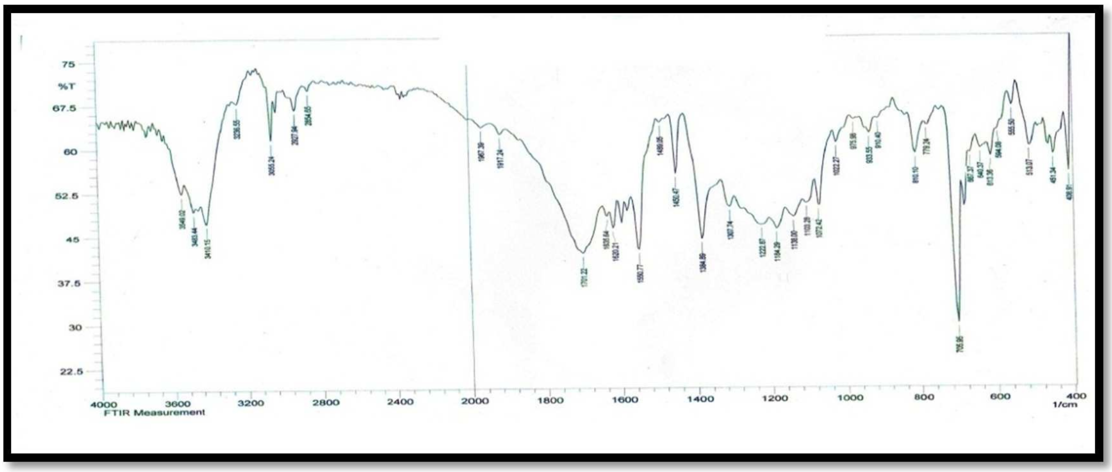


Figure (1-2) Infrared Spectrum of ligand [KL]

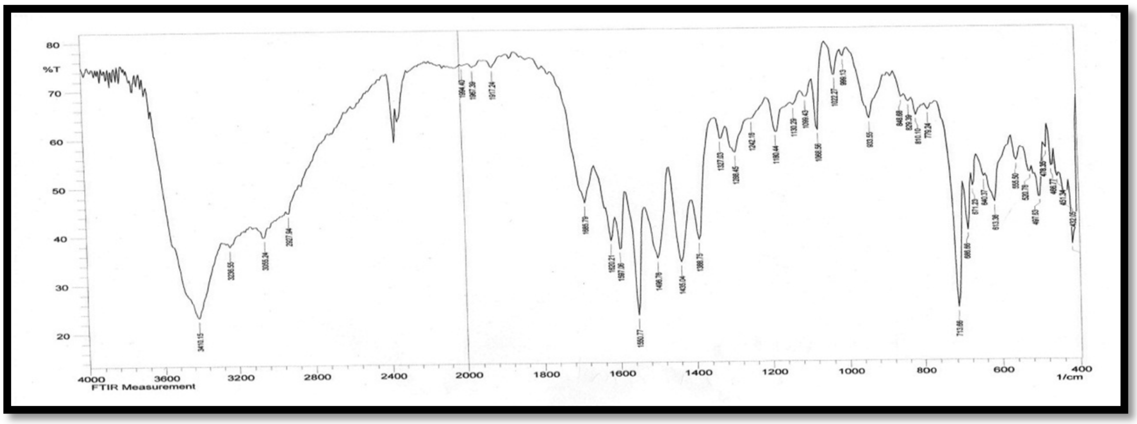


Figure (1-3) IR spectrum of the NiL complex

4-5 UV-Vis spectra of KL and its complexes

The electron is spectrum of ligand[KL] in the ethanol solvent was shown in figure (5-3) , the first two peaks at (225nm) (ε_{max}= 1379$M^{-1}.L.cm^{-1}$) (44444cm^{-1}) refer to electronic transfers π–π* for each of the aromatic rings found in the recorded ligand, The second summit at (270nm)(ε_{max}= 127$M^{-1}.L.cm^{-1}$) (37037cm^{-1}) go back to the electronic transition n–π* in the recorded ligand , which belong to atoms containing non-interactive electronic dichotomies (free) . These transitions suffered from a few displacements in the metal complexes illustrated in Figs. (3-3) to (4-3) as shown in table (4.3) (31).

1 - The e-spectra of the cobalt complex showed five peaks , Two peaks were given a sign of consistency first when (226nm) (ε_{max}= 700$M^{-1}.L.cm^{-1}$) (44248cm^{-1}) and second (278nm) (ε_{max}= 106$M^{-1}.L.cm^{-1}$) (35971cm^{-1}) which are linked to electronic transfers (L.F) , The other three peaks were shown respectively (415nm) (ε_{max}= 124$M^{-1}.L.cm^{-1}$) (24096cm^{-1}) ,(658nm)(ε_{max}= 658$M^{-1}.L.cm^{-1}$) (24cm^{-1}) ,(962nm)(ε_{max}= 962$M^{-1}.L.cm^{-1}$) (12cm^{-1}) respectively, to electronic transfers

${}^4T_1g(f) \longrightarrow {}^4T_1g(p)$, ${}^4T_1g(f) \longrightarrow {}^4A_2g(f)$, ${}^4T_1g(f) \longrightarrow {}^4T_2g(f)$, These are the characteristic transitions of the octahedral cobalt ion (32) .

2- The electronic spectrum of the nickel complex showed five peaks , two peaks were given a sign of consistency first when (231nm) (ε_{max}= 2753$M^{-1}.L.cm^{-1}$) (43290cm^{-1}) , and the second at (277nm) (ε_{max}= 322$M^{-1}.L.cm^{-1}$) (36101cm^{-1}) which are attributable to electronic transfers (L.F) , the other three peaks were shown respectively (408nm) (ε_{max}= 138$M^{-1}.L.cm^{-1}$) (24510cm^{-1}) and (752nm) (ε_{max}= 30$M^{-1}.L.cm^{-1}$) (13298cm^{-1}) and (968nm) (ε_{max}= 20$M^{-1}.L.cm^{-1}$) (10331cm^{-1}) respectively, to electronic transfers : ${}^3A_2g(f) \longrightarrow {}^3T_2g(f)$, ${}^3A_1g(f) \longrightarrow {}^3T_1g(f)$, ${}^3A_2g(f) \longrightarrow {}^4T_1g(p)$, These are the characteristic transitions of the octahedral nickel ion(33)

3 - The electronic spectrum of the copper complex showed a peak at (734nm)(ε_{max}= 40M^{-1}.L.cm^{-1}) (13624cm^{-1}) which are due to electronic transmission $^2Eg \rightarrow {}^2T_2g$ and two at (230nm) (ε_{max}= 2854M^{-1}.L.cm^{-1}) (43478cm^{-1}) and (278nm) (ε_{max}= 518M^{-1}.L.cm^{-1}) (35971cm^{-1}) respectively , which are due to the transition (L.F) These are the characteristic transitions of the octahedral distorted copper ion that indicate consistency (34) .

Table(1-4) UV-Visibility values for ligand and prepared complexes

Compounds	**λ(nm)**	**υ⁻ (cm^{-1})**	**ε_{max} L.mol^{-1}.cm^{-1}**	**Transition**
L	**225**	**44444**	**1379**	**π→π***
	270	**37037**	**127**	**n→π***
$K_2[Co(L)_2Cl_2].H_2O$	**226**	**36765**	**986**	**L.F**
	278	**32787**	**1013**	**L.F**
	415	**28902**	**2360**	**$^4T_1g(F)\rightarrow{}^4T_1g$ (p)**
	658	**22936**	**1164**	**$^4T_1g(F)\rightarrow{}^4A_2g$ (F)**
	952	**15198**	**72**	**$^4T_1g(F)\rightarrow{}^4T_2g$ (F)**
$K_2[Ni(L)_2Cl_2].H_2O$	**231**	**43290**	**2753**	**L.F**
	277	**36101**	**322**	**L.F**
	408	**24510**	**138**	**$^3A_2g(F)\rightarrow{}^3T_1g$ (P)**
	752	**13298**	**30**	**$^3A_2g(F)\rightarrow{}^3T_1g$ (F)**
	968	**10331**	**20**	**$^3A_2g(F)\rightarrow{}^3T_2g$ (F)**
$K_2[Cu(L)_2Cl_2].H_2O$	**230**	**43478**	**2854**	**L.F**
	278	**35971**	**518**	**L.F**
	734	**13624**	**40**	**$^2Eg\rightarrow{}^2T_2g$**

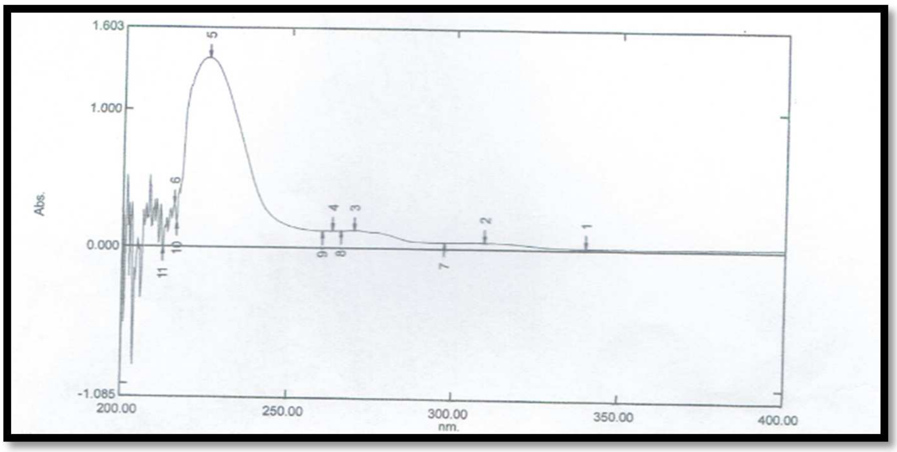


Figure (1-4) The electronic spectrum of the record ligand

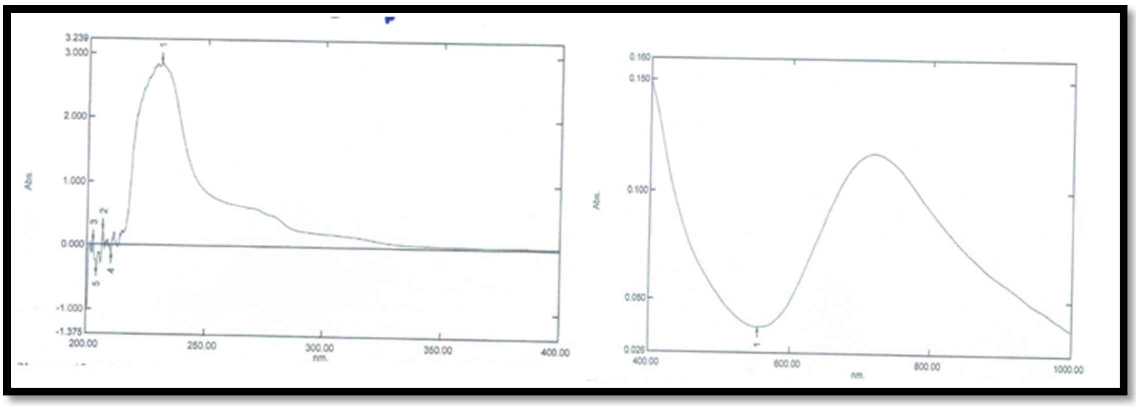


Figure (1-5) of the electronic spectrum of the complex $K[Cu(L)_2Cl].H_2O$

4-6 ^{1}H-NMR for the ligand(KL)and the prepared complexes

Show spectrum ^{1}H.NMR for the record ligand (KL) soluble in solvent (DMSO) –d^6 as in Figure (1-6) the following signals:

1 - Single signal at the site (ppm 2.4) is due to DMSO solvent.

2 - Multiple signals (e, f) are related to the proton ring protons which appeared between (7.39 - 7.41 ppm).

3 - The strong signal (h) between (7.45 - 7.91) ppm is due to the proton ring.

4 - The signals (b, c, d) between (7.37 - 7.39) ppm are due to the individual protons of the aromatic ring.

5 - The large (g, g ') and highly interrelated signals (7.44 - 7.45 ppm) are related to the aromatic ring protons [(36).]

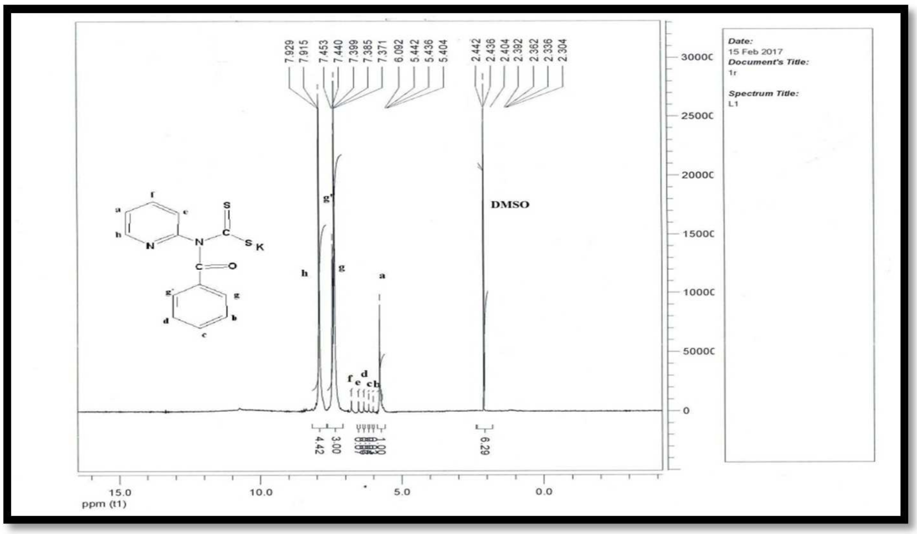


Figure (1-6) Spectrum ^{1}H.NMR for ligand record (L)

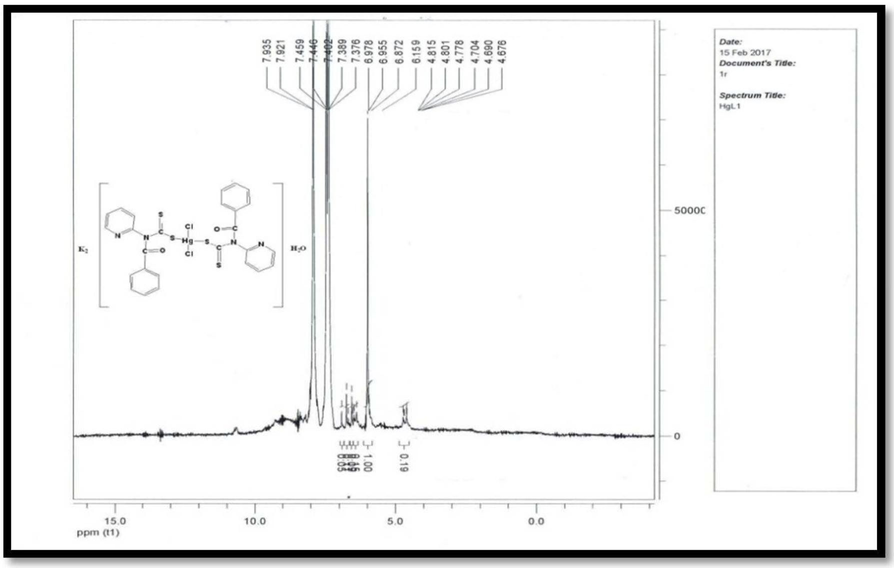


Figure (1-7) 1H.NMR spectra of the recorded complex $K_2[Hg(L)_2Cl_2]H_2O$

4 – 7 ^{13}C-NMR for the ligand(KL)and the prepared complexes

Show spectrum ^{13}C.NMR for the record ligand (KL) soluble in solvent (DMSO) –d^6 as in Figure (1-8) the following signals:

1 - The signal at the site (196.28) dates back to the carbon atom group CS_2.

2 - Signal at site (166.38) refers to the carbon atom related to nitrogen.

3 - A signal at the site (139.171) dates back to the carbon atom associated with the carbon monoxide carbon .

4 - The signal at the site (180.30) dates back to the carbonyl carbon atom.

5 - Single signals from (149.74 - 129.048) to the atoms of the aromatic ring (36 ,37) .

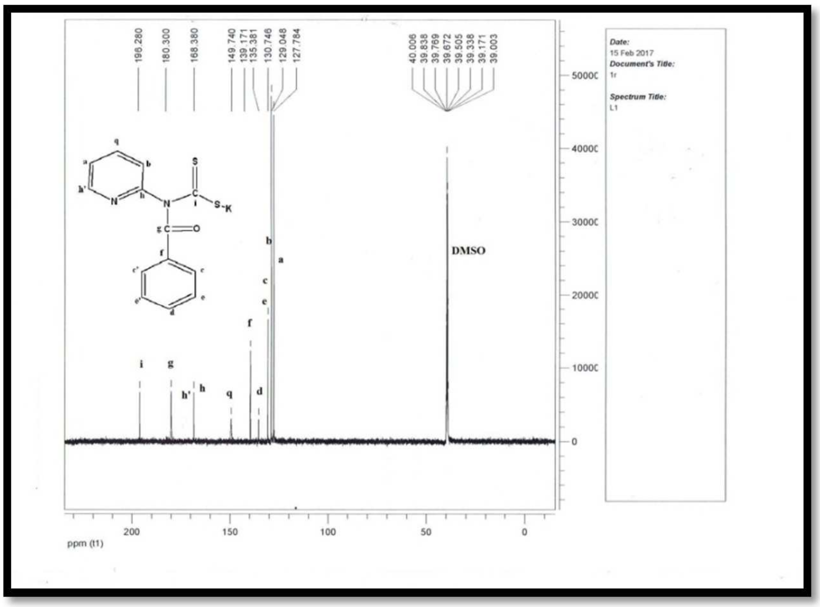


Figure (1-8) Spectrum ^{13}C.NMR for ligand record (L)

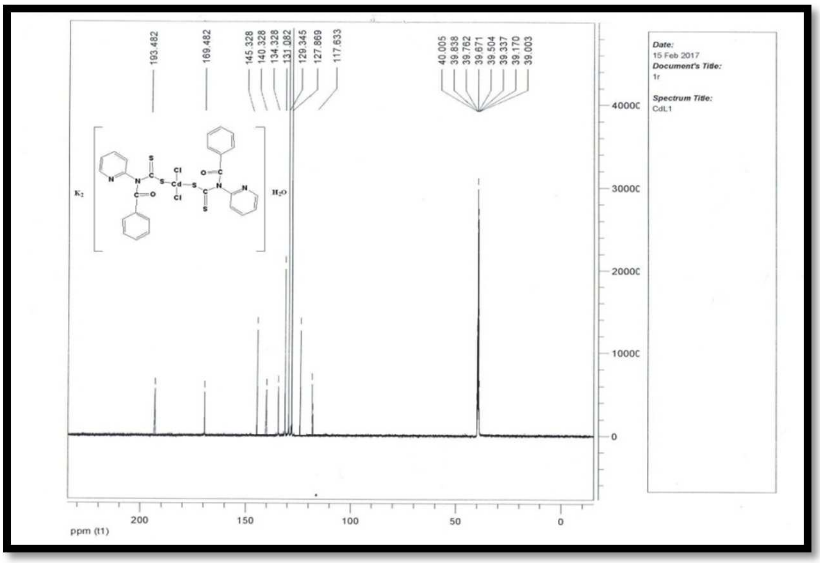


Figure (1-9) ^{13}C.NMR spectra of the recorded complex $K_2[Hg(L)_2Cl_2]H_2O$

4 – 8 Mass spectrometry

Determination of the molecular formula of the prepared compounds and the study of their thermal dissociation pathways is done by the use of mass spectrometry as a proof of the correct composition of the synthesized compound and the mass spectrometry is used to propose the disintegration of compounds and to study the mechanics of reactions(38). (L) at 341, indicating the validity of the recorded ligand composition by matching the molecular weight with the calculated theoretical value and by a simple difference as in Fig(1-10) Cluster spectrum of ligand. The mass spectrometry of the cobalt complex (M / Z)% at (773)showed the correctness of the complexity of the prepared complex by matching the molecular weight with the calculated theoretical value at (772) as shown in Figure (1-11). As for the cadmium complex, molecular ions were found at (914) compared to theoretical molecular weight (913.6) .

Table (1-5) shows the mass spectrum data

Comp	**Mol. Wt**	**Mass spectrometrym/z**
L	**312**	**312**
$K_2[Co(L)_2\ Cl_2]H_2O$	**831**	**829**
$K_2[Hg(L)_2\ Cl_2].H_2O$	**914**	**915**

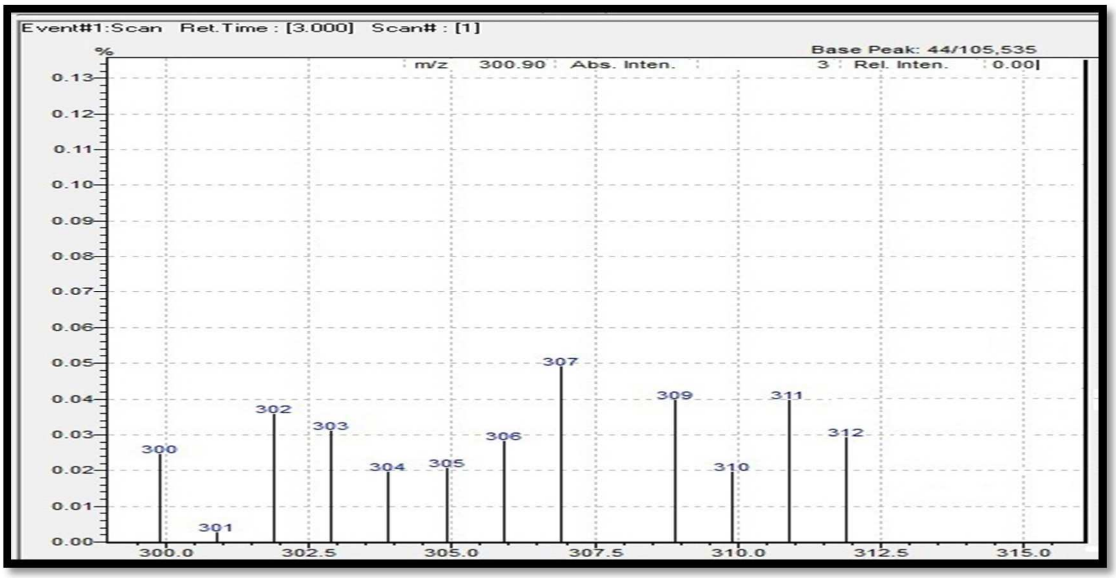


Figure (1-10) The mass spectrometry of the record ligand

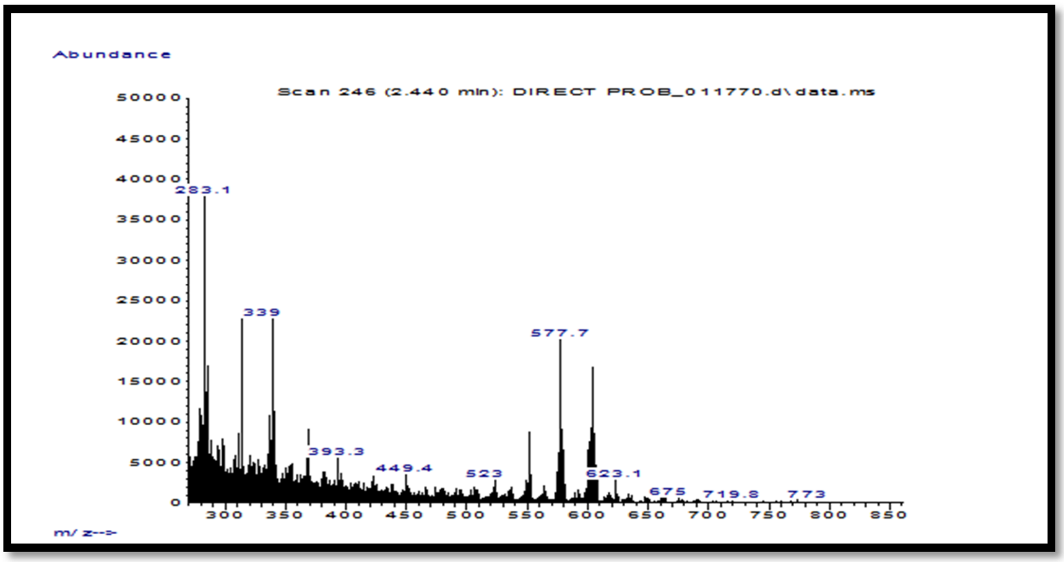


Figure (1-11) The mass spectrum of the complex $K_2[Co(L)_2 Cl_2].H_2O$

9 – 4 Proposed geometry of the complex

Based on the data of the ligand spectroscopy and the complexities prepared by the techniques of the precise analysis of elements (C.H.N), measurement of the ratio of the metal to atomic absorption technology, the measurement of chlorine content, the molar conductivity and the measurement of the magnetic sensitivity to find the effective magnetic torque, the infrared spectroscopy, the UV spectroscopy and the mass spectrometry of some complexities , It turns out that ligand is a bipolar consistency with both metal ions Co(II) Ni(II), Cu(II) Where it is consistent with metal ions by the oxygen atom (O) of the carbonyl group (C=O) , and by another atom (S) belonging to the group (C – S) , as for the complexes Cd(II), Hg(II) The ligand was associated with these two metal ions with a monochromatic association (C – S) it gave a tetrahedral shape(39) , The geometric shapes below illustrate this.

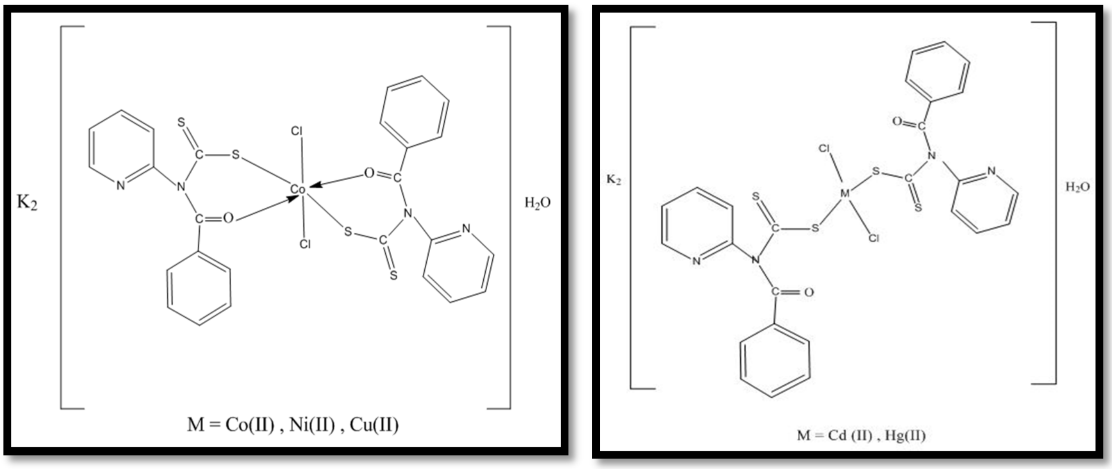


Figure (1-12) Prepared dithiocarbamate complexes

5- References

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