Diala , Jour , Volume , 32 , 2009

Synthesis and Characterization of Novel Bidentate Ligand type NO and Its Complexes with (Co^{II} , Ni^{II} ,Cu^{II} and Zn^{II}).

Leqaa khalid Abdulkarim
Department of chemistry, College of Education, Ibn Al-Haitham, University of Baghdad,
P.O. 4150, Adhamiyah , Baghdad ,Iraq .

Abstract

The [2-aminobenzothiazole]was reacted with [2,4,6 triyhydroxy-acetophenon monohydrate] to give a new ligand [2-N-2,4,6-trihydroxyacetophenonyliden benzothiazole] [H_3L]. This ligand was reacted with metal ions (Co^{II}, Ni^{II},Cu^{II} and Zn^{II}) in methanol as solvent with (1:2) metal : ligand ratio to give a series of new complexes with general formula [$M(H_2L)_2$],(where:M= Co^{II}, Ni^{II} ,$Cu^{II}$and, Zn^{II}).All compounds were characterized by spectroscopic methods (I.R , U.V – vis,HPLC) atomic absorption, along with chloride content and conductivity measurements. According to the data of these measurements we suggested a tetrahedral geometry for (Co^{II}, Ni^{II},Cu^{II}, and, Zn^{II}) complexes.

Introduction

Thiazoles are used for manufacturing biocides,fungicides ,pharmaceuticals,and days, they are a class of organic compound related to azoles with a common thiazole functional group[1].2-aminobenzothiazole represent an important class of hetrocyclic compounds that have many applications in our life [2-5].Some of these are employed as herbicides[6]. Hetrocyclic compounds such as thiazoles are considered to be a good coordinated Ligands[7,8]. In this paper reports the synthesis and characterization of a new [2-N-2,4,6-trihydroxyacetophenonyliden benzothiazole] ligand [H_3L] which derived from the reaction of [2-aminobenzothiazole] and [2,4,6-triyhydroxy- acetophenon monohydrate] and is their metal complexes with (Co^{II}, Ni^{II}, Cu^{II}, and, Zn^{II}).

Experimental

Reagents were purchased form Fluka and Redial – Dehenge chemical Co. I.R spectra were recorded as (KBr) discs using a Shimadzu 8300 FTIR spectrophotometer in the rang (4000 – 400)cm^{-1}. Electronic spectra of the prepared compounds were measured in the region (200–1100) nm for 10^{-3} M solution in (methanol) at 25^0C using a Shimadzu, 160 spectrophotometer with 1.000±0.001 cm matched quartz cell.Metal contents of the complexes were determined by atomic absorption (A.A) techniqus a Shimadzu AA 680 G atomic absorption spectrophotometer.The Chloried contents for complexes was detrmined by potentiometric titration method on (686-titro processor-665),Dosinat-metrom Swiss. The (HPLC)chromatograms the complexes were obtained by using a Shimadzu 2020. Electrical conductivity measurements of the complexes were recorded at 25^0C in 10^{-3} M solutions of the sample in (methanol) as asolvent using a pw 9526 digital conductivity meter.

Synthesis of ligand [H_3L] :

A solution of [2,4,6 Triyhydroxy-acetophenon monohydrate](0.55 g,1 mmol) in (5ml) methanol and (2-4) drops of glacial acetic acid was added to a solution of [2-aminobenzothiazole] (0.45g,1 mmol) dissolved in (5ml) methanol in (100ml) round bottom flask.The mixture was allowed to refluxed for 4hrs, with stirring at room temperature. During which time a yellow solid material was collected by filtration ,dried under vacuum for 24hrs , to give [H_3L] as a yellow solid , yield (0.7g ,77%) m.p (136 – 138^0C).

Synthesis of complexes:

Synthesis of [Co (H_2L)$_2$](1) :

In(50ml) round bottom flask (0.098g,0.41mmol)of[$CoCl_2.6H_2O$] was dissolved in (5ml) mthanol .Asolution of (0.25g,0.83mmol) of [H_3L] in (5ml)and KOH (0.046g,0.83mmol) was added to the above mixture.The reaction was allowed to reflux for (2hrs).The greenish-blue precipetate formed which was filtered ,washed with (1ml) ether and dried to (0.35g,71%) of the title compound,m.p(255^0C)dec. (Table-1).

Synthesis of [Ni (H_2L)$_2$] (2),[Cu(H_2L)$_2$] (3)and [Zn (H_2L)$_2$](4) Complexes:-

The method used to prepare the complexes (2),(3)and(4) was similar to that mentioned in preparation of cobalt complex(1).(Table-1) stated weight of starting materials, % yield and some physical properties of the ligand and prepared complexes.

Table (1): some physical properties of the ligand and its complexes and their reactants quantities.

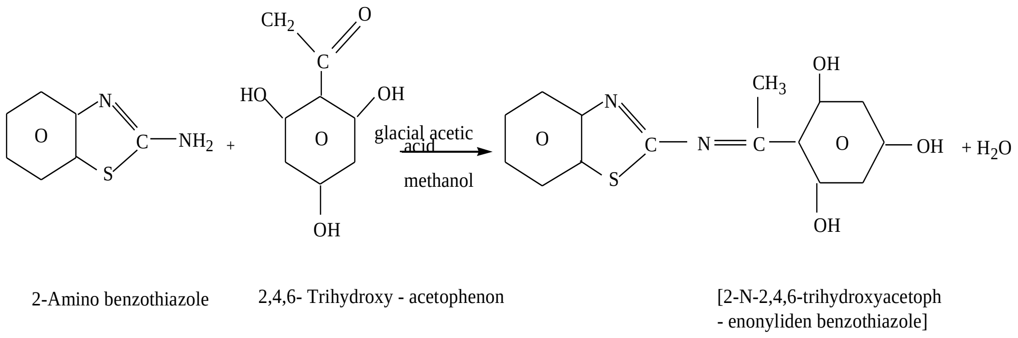
Compound	M.Wt g. mol^{-1}	M.p^{0}C (dec)	Color	Metal chloride salt	Weight of metal Chloride		Weight of product (g)	Yield %	Metal content found (calcd.) %	chloride content
					g	mmole				
H_3L*	300	136-138	yellow	-	-	-	0.7	77	-	-
[Co(H_2L)$_2$**	655	255	greenish-blue	$CoCl_2.6H_2O$	0.096	0.41	0.35	71	9.96 (10.35)	nil
[Ni(H_2L)$_2$]	656	278	Green	$NiCl_2.6H_2O$	0.097	0.41	0.31	63	9.54 (10.27)	nil
[Cu(H_2L)$_2$]	661.5	249	yellow	$CuCl_2.2H_2O$	0.069	0.41	0.29	59	10.98 (11.36)	nil
[Zn(H_2L)$_2$]	663	263	Yellowish-white	$ZnCl_2.2H_2O$	0.07	0.41	0.29	59	10.98 (11.36)	nil

* $H_3L=C_{15}H_{12}N_2O_3S$
** $H_2L=C_{15}H_{11}N_2O_3S$

Result and Discussion

Synthesis of Ligand

The pro–ligand[H_3L] was prepared according to the general method shown in scheme (1). The (I.R) spectrum for [H_3L] ligand Fig. (2), displayed three bands at 3529,3452 and 3319 cm $^{-1}$ due to υ (O–H) stretching frequency for the hydroxyl groups ,on the other hand,a band at 1622 cm $^{-1}$ due to υ (C=N) stretching frequency for the imine groups[9],and aband at 748 cm^{-1} assigned to υ (C –S) stretching frequency[10].(U.V-Vis) spectrum. Fig (3), shows one peak with a high intense absorption peak at (300) nm (33333 cm^{-1}) (ε_{max} = 2049 molar $^{-1}$.cm^{-1}) which assigned to an overlap of ($\pi \rightarrow \pi^*$), ($n \rightarrow \pi^*$) electronic transitions[11].



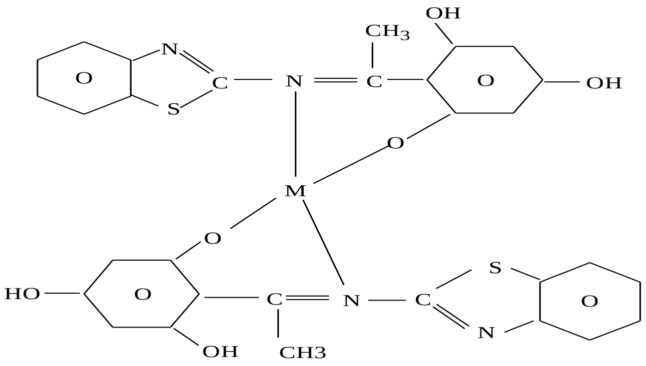
Scheme (1) Synthesis route of the ligand [H_3L]

Synthesis of complexes

The synthesis of the complexes was carried out by the reaction of the ligand [H_3L] with [$MCl_2.X\ H_2O$] [where M= (Co^{II}, Ni^{II},Cu^{II} and Zn^{II}) ,X=6 for Co^{II}, Ni^{II} and X=2 for Cu^{II} and Zn^{II}] in methanol under reflux. All complexes are stable in solution and electrolytes .The analytical and physical data (Table -1) and spectral data Table (2) and Table (3) are compatible with suggested structures Fig. (1). The (I.R) spectral data of the complexes are presented in (Table -2). In general the(I.R) spetra for all complexes revealed bands at rang (3533─3289) cm^{-1} were attributed to υ (O–H) stretching frequency . (I.R) spectra of the complexes (1), (2), (3) and (4) also displayed bands at 1632 cm^{-1},1635,1630 $cm^{-1}$and 1636 cm^{-1} respectively which assigned to υ (C=N) stretching for the imine groups[12].These results showed that the bands of υ (C=N) were shifted to highre frequencies in comparison with that of free ligand at 1622 cm^{-1}.These shifting can be attributed to delocalization of metal ion electronic density in to π-orbital of the ligand(π–system).Bands of υ(C–S) stretching at 748 cm^{-1} for the free ligand did not change values that's mean the sulfer atom did not coordinated with metal ion [13].The new bands at range(616–609)$cm^{-1}$and(414–420)cm^{-1} are shown in Fig. (2a,2b,2c)and table-2 are assigned to υ(M–N) and υ(M–O) stretching respectively .These bands indicate that the nitrogen of imine group and oxygen are involved in coordination with metal ion [14-15].The (U.V-Vis) spectra for all complexes shown in Fig.(3a,3b and 3c).The electronic spectral data for complexes are given in (table-3). The spectra show two intense peaks in the U.V region ,the first at reang(277-300)nm and the second at range (341-343) nm for all complexes. These two peaks were assigned to ligand field and charge transfer transition respectively[16].Complex (1) exhibited peak at (833) nm which can be attributed to (d-d) electronic transition type ($^4A_2\rightarrow{}^4T_{1\ (F)}$).The weak peak in spectrum of complex (2) at (403) nm was assigned to (d-d) electronic transition type ($^3T_1\rightarrow{}^3T_{1(P)}$).The spectrum of complexe(3) exhibited weak at (669)nm which can be attributed to (d-d) transition type ($^2B_2\rightarrow{}^2E$).The (d-d) electronic transition for the complexes (1),(2),(3) and (4) suggest tetrahedral configuration around Co^{II}, Ni^{II}, and Cu^{II} respectively [17].The absence of absorption peak in the range(360-1000) nm for the spectrum of complexe (4) indicate no (d-d) electronic transition happened (d^{10}-system) in visible region ,that is agood result for Zn^{II} tetrahedral complexes [16].The (HPLC) chromatograms for Co^{II} and Ni^{II} complexes (fig.4a,4b) (table-3) show one signal at t_R=11.462 and5.894min respectively, indicating the purity of the complexes and appear as a single species in solution.The molar conductances of the complexes in (methanol) solvent in 10^{-3}M at 298K° (table-3) indicated non electrolytic nature [18-19] The (A.A) measurments and chloride content results for the complexes [$Co(H_2L)_2$], [$Ni(H_2L)_2$],[$Cu(H_2L)_2$]and [$Zn\ (H_2L)_2$],(table-1) are in a good agreement with the calculated values .

References

1. A.J.Arduengo,J.R.Goerlich and W.J.Marshall."A Stable Thiazol-2-ylidene and Its Dimer ".Liebigs Annalen 1997(2):365-374.
2. Ram,V.and Pandey,H.N.(1974).Chem.Pharm.Bull.22,2778.
3. Parmar,S.S.;Chaudhary,S.K.;Kumar,S.Spiro,H.R.(1977)J.Pharm.Sci(7):66,971
4. Mohan,J.(1983),.IndianJ.Chem.,22B270.
5. Maxwell,R.;Wasdahl,D.A.;Wolfson,A.C.;Stenberg, V.I.(1984) J.Med.Chem.,27,1967.
6. Abdul-Rahman,S.(2000),Engineering Journal e IslamicUniversity of Gaza.(1):13p35-95.
7. Rehab,A.M.;Ayad,H.jassim and Mouayed,Q.Al-Abachi(2003),National Journal of Chemistry,9,115-125.
8. Ahmed ,S.H;Modher,Y.M.and Salwa,A.Jabar(1999),IraqiJ.S.,40A,No.3,
9. G. Socrates " Infrared characteristic Group Frequencies " Wiley Inter science publication … (1980)
10. Kumer A,Singh G,Handa RN,Dubey SN,Squattrio PJ,Synthesis and characterization of complexes of Cobalt(II),Nickel(II),Copper(II)and Zinc(II) with Schiff Bases Derived from Cinnamaldehyde and4–Amino–3– ethyl– 5–mercapto – s–triazol and 4– Amino–5–mercapto–3–N–propyl–s– iazole.Indian Journal of Chemistry.1999;38A:613.
11. W. Kemp " organic spectroscopy " 2nd Edition , (1987) , 144
12. D. Hadzi, J. Chem. Soc., 1956,15,2725.
13. Sonmez,M.and Sekerci,M.(2000).Polish-J-Chem.,76,907-914.
14. K. Nakamoto "Infrared spectra of Inorganic and coordination compounds "4th. Ed. J. Wiely and son , New York , (1996)
15. J. Ferraro , " Low Frequency Vibrations of Inorganic and coordination compounds " plenum , New York (1971)
16. N.N. Green wood and A.Earnshow , " chemistry of the Elements " , J .wiley and Sons Inc . New York , (1998).
17. A.B. P.Lever , "Inorganic Electronic Spectroscopy " New York , (1968).
18. W.J. Geary , Coord .Rev. ,1971, 7,81.
19. S.F.A.Kette, "Coordination Compounds Thomas nelson and sons,Londone p.165,(1975).



$M=Co^{II},Ni^{II},Cu^{II}$ and Zn^{II}

Figure (1) The suggested structure for the complexes

Table (2) I.R spectral data of the ligand and their metal complexes

Compound	υ (o-H) phenol	υ (C = N)	υ (C-N)	υ (C-S)	υ (M – N)	υ (M – O)	Other bands
$[H_3L]$	3319 3452 3529	1622	1537	748	-	-	υ(C – H)aliph2987 υ (C – H)arom 3006
$[Co(H_2 L)_2]$	3307 3461 3533	1632	1529	74٩	613	419	υ(C – H)aliph 2929 υ (C – H)arom 3030
$[Ni(H_2L)_2]$	3527 3456 3296	1635	1527	74٩	609	418	υ(C – H)aliph 2964 υ (C – H)arom 3066
$[Cu(H_2L)_2]$	3519 3455 3289	1630	1530	7٥٠	616	414	υ(C – H)aliph 2933 υ (C – H)arom 3047
$[Zn(H_2L)_2]$	3533 3460 3292	1636	1525	74٩	615	420	υ(C – H)aliph 2918 υ (C – H)arom 3052

Table (3) Electronic spectral data and conductance measurement of ligand and its complexes

Compound	λ *nm*	**Wave number Cm^{-1}**	**ε_{max} Molar Cm^{-1}**	**Assignment**	**HPLC Min**	**Λ $(\Omega^{1}.cm^{2}.Mole^{-}m^{1})$**
[H_3L]	300	33333	2049	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
[Co($H_2L)_2$]	300 343 833	33333 29154 12004	2215 1981 14	Ligand field C.T $^4A_2 \rightarrow {}^4T1_{(F)}$	11.462	4.13
[Ni $H_2L)_2$]	300 341 403	33333 29325 24813	1520 1870 1784	Ligand field C.T $^3T_1 \rightarrow {}^3T_{1(P)}$	5.894	9.6
[Cu $H_2L)_2$]	277 368 669	36101 27173 14947	1285 1766 8	Ligand field C.T $^2B_2 \rightarrow {}^2E$	-	7.3
[Zn $H_2L)_2$]	299 342	33444 29239	1954 1955	Ligand field C.T	-	6.7

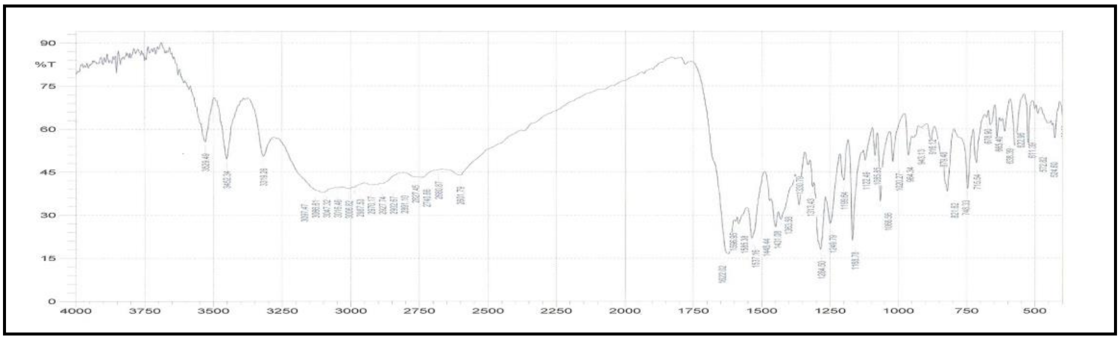


Fig.(2)The(I.R)spectrum of ligand [H_3L]

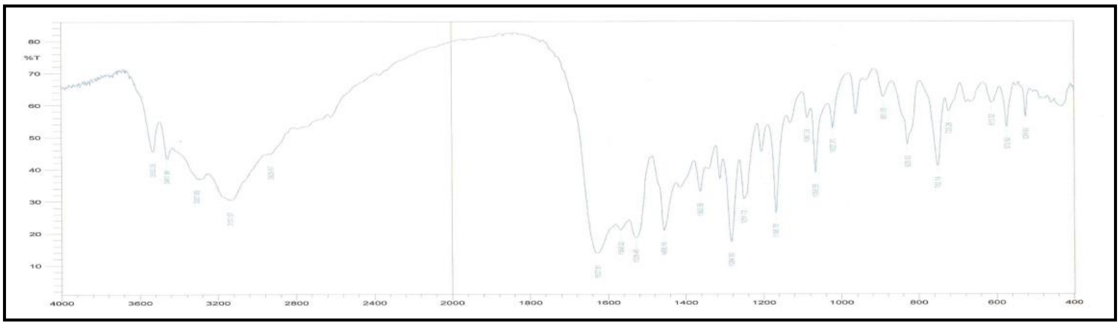


Fig.(2.a)The(I.R)spectrum of [$Co(H_2L)_2$]

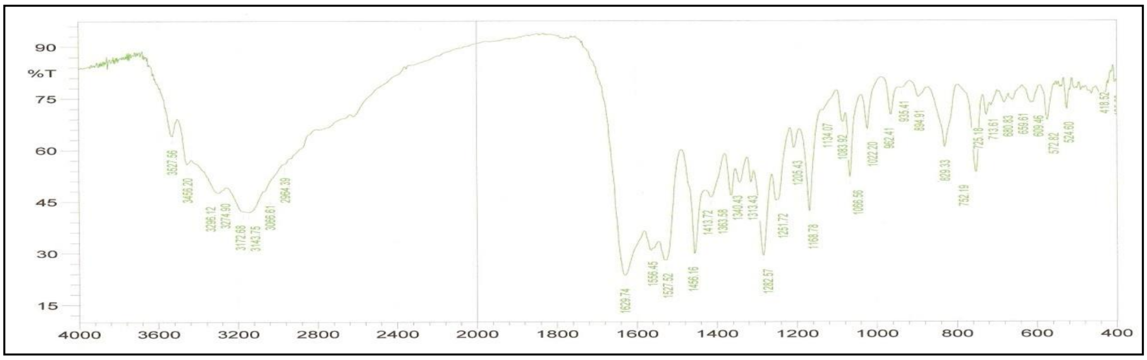


Fig.(2.b)The(I.R)spectrum of [Ni $H_2L)_2$]

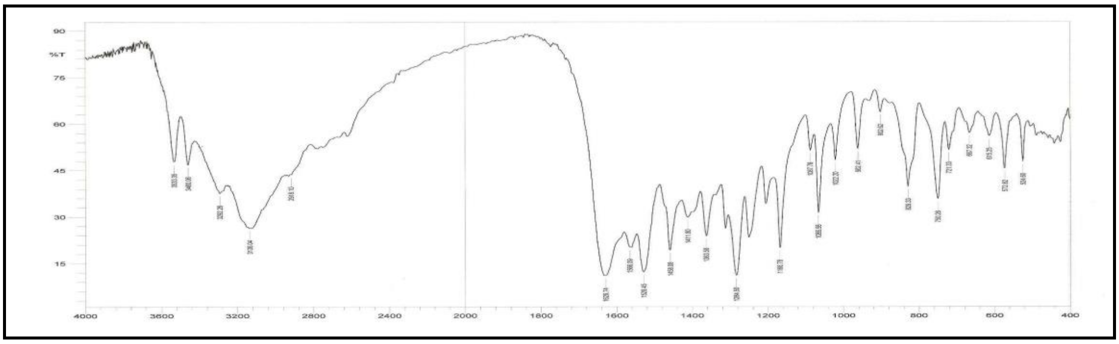


Fig.(2.C)The(I.R)spectrum of [Zn $H_2L)_2$]

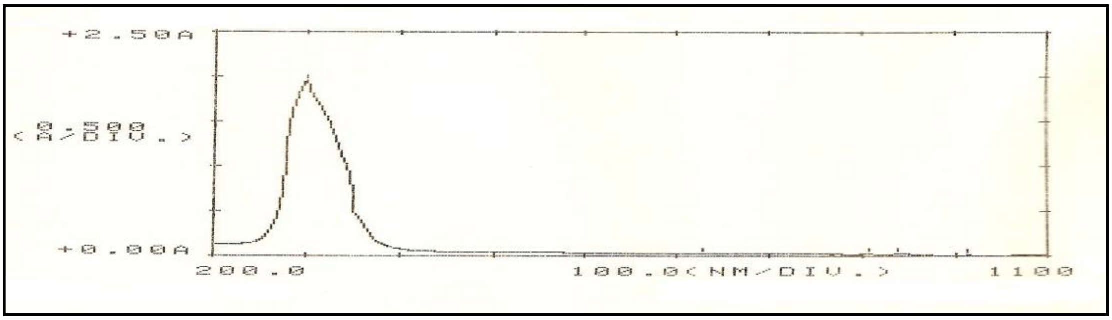


Fig.(3)The(UV - Vis) spectrum of ligand[H_3L]

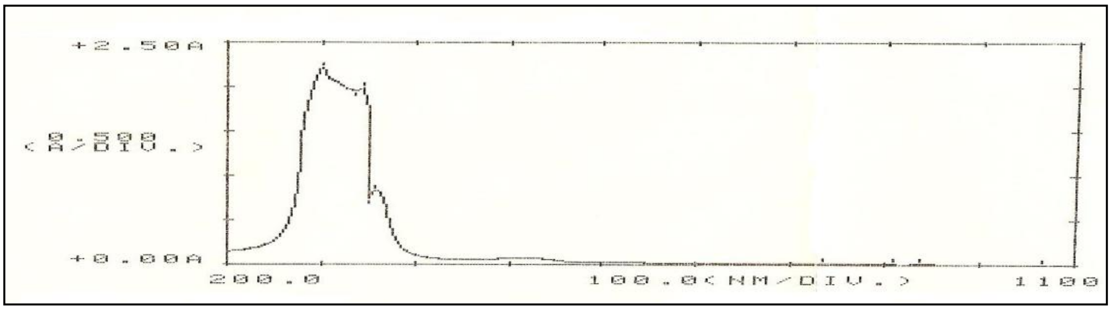


Fig.(3.a)The(UV - Vis) spectrum of [Co $H_2L)_2$]

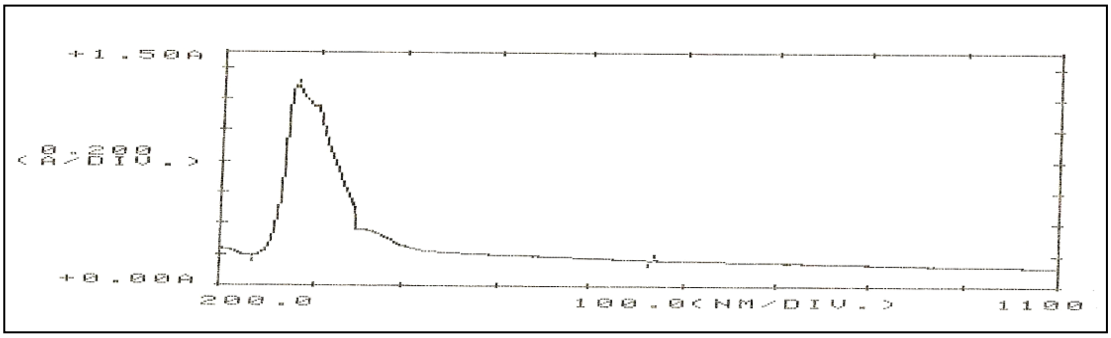


Fig.(3.b)The(UV - Vis) spectrum of [Cu $H_2L)_2$]

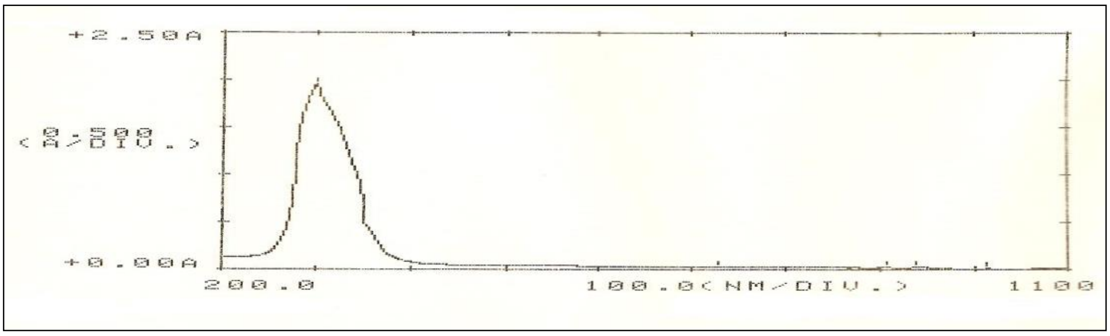


Fig.(3.C)The(UV - Vis) spectrum of [Zn $H_2L)_2$]

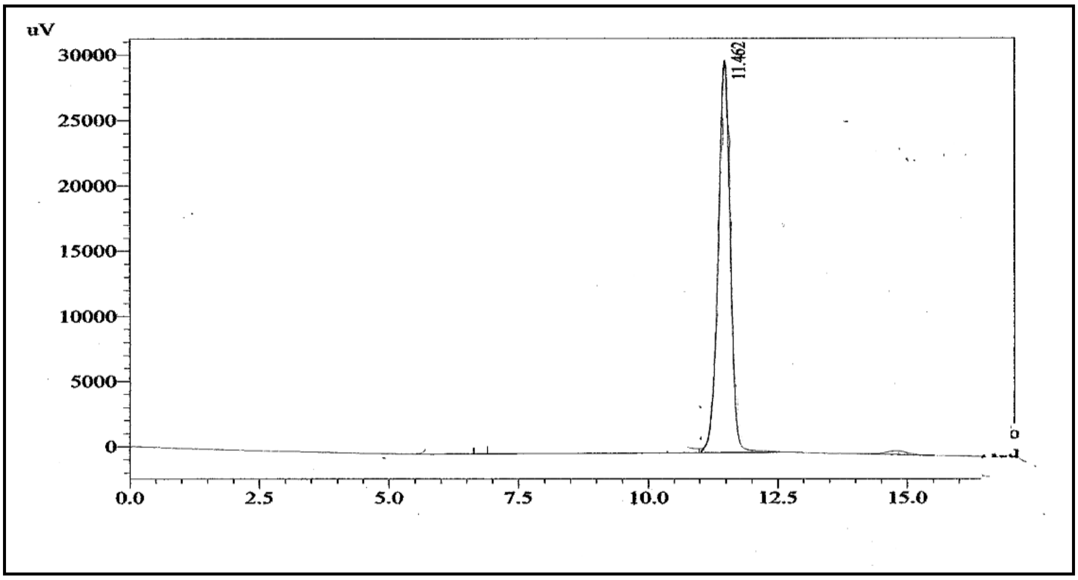


Fig (4a) .The HPLC chromatogram of the [Co $(H_2L)_2$]

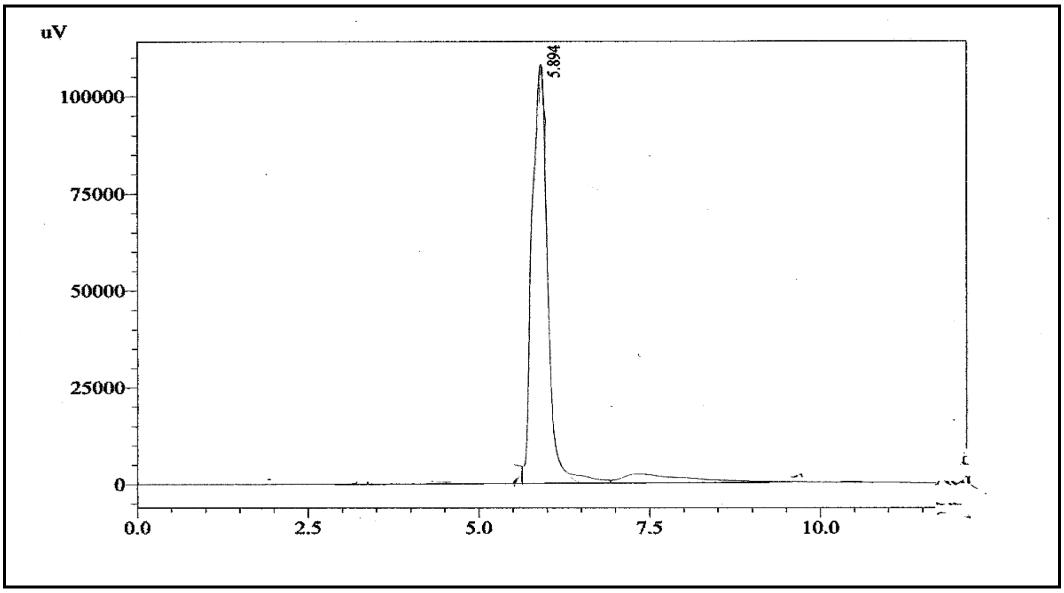


Fig (4b) .The HPLC chromatogram of the [Ni $(H_2L)_2$]

تحضير وتشخيص ليكاند ثنائي السن جديد نوع NO ومعقداته مع $(Co^{(II)}, Ni^{(II)},Cu^{(II)}$ and $Zn^{(II}$)

لقاء خالد عبدالكريم

جامعة بغداد
كلية التربية ابن الهيثم قسم الكيمياء
العراق – بغداد - الاعظمية P.O.4150

الخلاصة:

تضمن البحث تحضير الليكاند ثنائي السن الجديد
[2-N-2,4,6-trihydroxyacetophenonylidene-benzothiazole] $[H_3L]$
وذلك من مفاعلة **2-aminobenzothiazole** مع **2,4,6 triyhydroxy-acetophenon monohydrate** ثم مفاعلة الليكاند مع ايونات **$(Co^{(II)}, Ni^{(II)},Cu^{(II)}$ and $Zn^{(II)}$)** بوجود **KOH** باستخدام الميثانول وسطا للتفاعل وبنسبة(1:2) تكونت سلسلة من المعقدات الجديدة ذات الصيغة العامة :

$[M (H_2L)_2]$

حيث

$M =(Co^{(II)}, Ni^{(II)} ,Cu^{(II)}$ and $Zn^{(II)}$

شخصت جميع المركبات المحضرة بوساطة الأشعة تحت الحمراء والأشعة فوق البنفسجية – المرئيةو**HPLC** ومطيافية الامتصاص الذري للعناصر ومحتوى الكلور ودرجات الانصهار , مع قياس التوصيلية المولارية الكهربائية من معطيات التحليل فان الشكل الفراغي لجميع المعقدات هو رباعي السطوح.