

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

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Abstract

The [2-aminobenzothiazole] was reacted with [2,4,6 trihydroxy-acetophenon monohydrate] to give a new ligand [2-N-2,4,6-trihydroxyacetophenonyliden benzothiazole] [H₃L]. 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(H₂L)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 dyes, they are a class of organic compound related to azoles with a common thiazole functional group [1]. 2-aminobenzothiazole represent an important class of heterocyclic compounds that have many applications in our life [2-5]. Some of these are employed as herbicides [6]. Heterocyclic 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 [H₃L] which derived from the reaction of [2-aminobenzothiazole] and [2,4,6-trihydroxy- acetophenon monohydrate] and is their metal complexes with (Co^{II}, Ni^{II}, Cu^{II}, and, Zn^{II}).

Experimental

Reagents were purchased from Fluka and Redial – Dehenge chemical Co. I.R spectra were recorded as (KBr) discs using a Shimadzu 8300 FTIR spectrophotometer in the range (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 25⁰C 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) technique using a Shimadzu AA 680 G atomic absorption spectrophotometer. The Chloride contents for complexes were determined by potentiometric titration method on (686-titro processor-665), Dosinat-metrom Swiss. The (HPLC) chromatograms of the complexes were obtained by using a Shimadzu 2020. Electrical conductivity measurements of the complexes were recorded at 25⁰C in 10⁻³ M solutions of the sample in (methanol) as a solvent using a pw 9526 digital conductivity meter.

Synthesis of ligand [H₃L] :

A solution of [2,4,6 Trihydroxy-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 [H₃L] as a yellow solid , yield (0.7g ,77%) m.p (136 – 138⁰C).

Synthesis of complexes:

Synthesis of [Co (H₂L)₂](1) :

In(50ml) round bottom flask (0.098g,0.41mmol)of[CoCl₂.6H₂O] was dissolved in (5ml) mthanol .Asolution of (0.25g,0.83mmol) of [H₃L] 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(255⁰C)dec. (Table-1).

Synthesis of [Ni (H₂L)₂] (2),[Cu(H₂L)₂] (3)and [Zn (H₂L)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 ₃ L*	300	136-138	yellow	-	-	-	0.7	77	-	-
[Co(H ₂ L) ₂]**	655	255	greenish- blue	CoCl ₂ .6H ₂ O	0.096	0.41	0.35	71	9.96 (10.35)	nil
[Ni(H ₂ L) ₂]	656	278	Green	NiCl ₂ .6H ₂ O	0.097	0.41	0.31	63	9.54 (10.27)	nil
[Cu(H ₂ L) ₂]	661.5	249	yellow	CuCl ₂ .2H ₂ O	0.069	0.41	0.29	59	10.98 (11.36)	nil
[Zn(H ₂ L) ₂]	663	263	Yellowish -white	ZnCl ₂ .2H ₂ O	0.07	0.41	0.29	59	10.98 (11.36)	nil

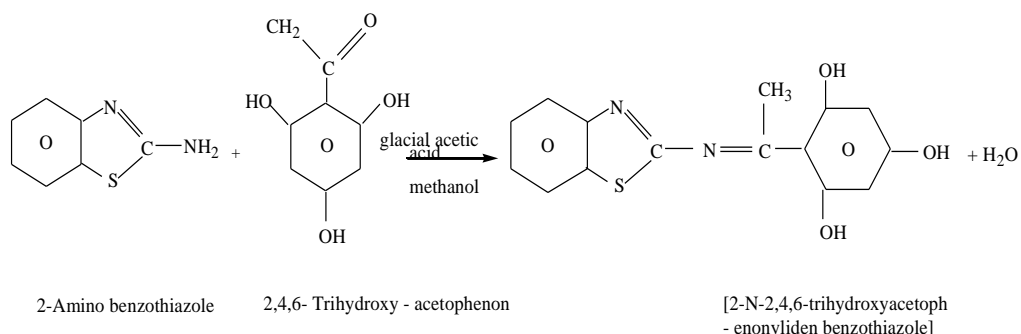
* $H_3L=C_{15}H_{12}N_2O_3S$

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

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 ν (O-H) stretching frequency for the hydroxyl groups, on the other hand, a band at 1622 cm^{-1} due to ν (C=N) stretching frequency for the imine groups[9], and a band at 748 cm^{-1} assigned to ν (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}) ($\epsilon_{max} = 2049$ 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 [H₃L] with [MCl₂.X H₂O] [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) spectra for all complexes revealed bands at rang (3533–3289) cm⁻¹ were attributed to ν (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 ν (C=N) stretching for the imine groups [12]. These results showed that the bands of ν (C=N) were shifted to higher 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 ν (C–S) stretching at 748 cm⁻¹ for the free ligand did not change values that's mean the sulfur 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 ν (M–N) and ν (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 range (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 (⁴A₂ → ⁴T_{1(F)}). The weak peak in spectrum of complex (2) at (403) nm was assigned to (d-d) electronic transition type (³T₁ → ³T_{1(P)}). The spectrum of complex (3) exhibited weak at (669) nm which can be attributed to (d-d) transition type (²B₂ → 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 complex (4) indicate no (d-d) electronic transition happened (d¹⁰-system) in visible region, that is a good 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 and 5.894 min 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 298 K° (table-3) indicated non electrolytic nature [18-19]. The (A.A) measurements and chloride content results for the complexes [Co(H₂L)₂], [Ni(H₂L)₂], [Cu(H₂L)₂] and [Zn(H₂L)₂], (table-1) are in a good agreement with the calculated values.

References

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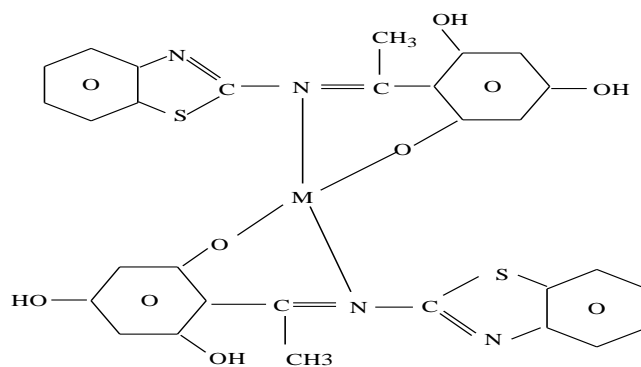


Figure (1) The suggested structure for the complexes

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

Compound	ν (o-H) phenol	ν (C = N)	ν (C-N)	ν (C-S)	ν (M - N)	ν (M - O)	Other bands
[H ₃ L]	3319 3452 3529	1622	1537	748	-	-	ν (C - H)aliph2987 ν (C - H)arom 3006
[Co(H ₂ L) ₂]	3307 3461 3533	1632	1529	749	613	419	ν (C - H)aliph 2929 ν (C - H)arom 3030
[Ni(H ₂ L) ₂]	3527 3456 3296	1635	1527	749	609	418	ν (C - H)aliph 2964 ν (C - H)arom 3066
[Cu(H ₂ L) ₂]	3519 3455 3289	1630	1530	750	616	414	ν (C - H)aliph 2933 ν (C - H)arom 3047
[Zn(H ₂ L) ₂]	3533 3460 3292	1636	1525	749	615	420	ν (C - H)aliph 2918 ν (C - H)arom 3052

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

Compound	$\lambda \text{ nm}$	Wave number Cm^{-1}	ϵ_{max} Molar Cm^{-1}	Assignment	HPLC Min	Λ ($\Omega^1.\text{cm}^2.\text{Mole}^{-1}$)
[H ₃ L]	300	33333	2049	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
[Co(H ₂ L) ₂]	300 343 833	33333 29154 12004	2215 1981 14	Ligand field C.T $^4A_2 \rightarrow ^4T_{1(F)}$	11.462	4.13
[Ni H ₂ L) 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 ₂ L) ₂]	277 368 669	36101 27173 14947	1285 1766 8	Ligand field C.T $^2B_2 \rightarrow ^2E$	-	7.3
[Zn H ₂ L) ₂]	299 342	33444 29239	1954 1955	Ligand field C.T	-	6.7

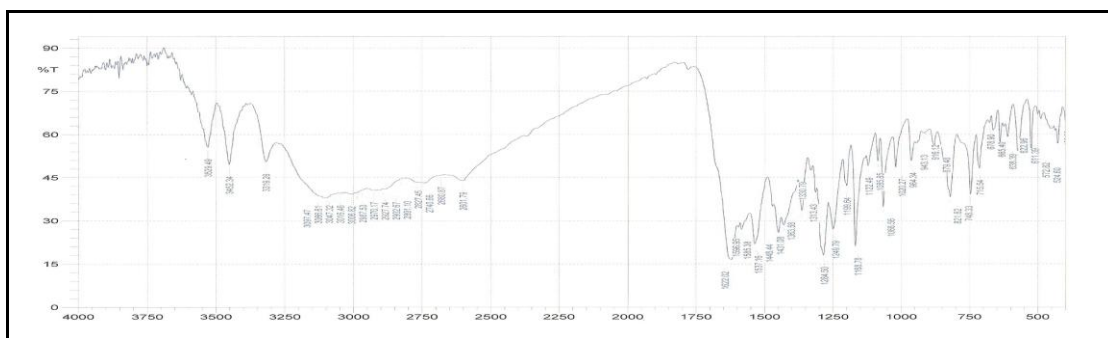


Fig.(2)The(I.R)spectrum of ligand [H₃L]

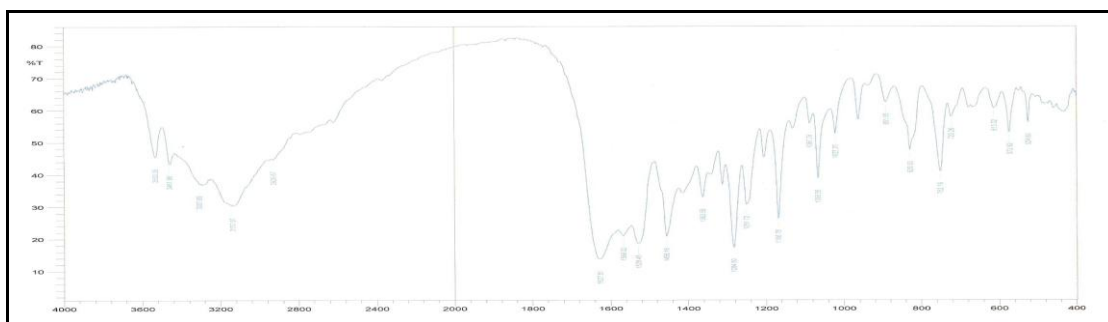


Fig.(2.a)The(I.R)spectrum of [Co(H₂L)₂]

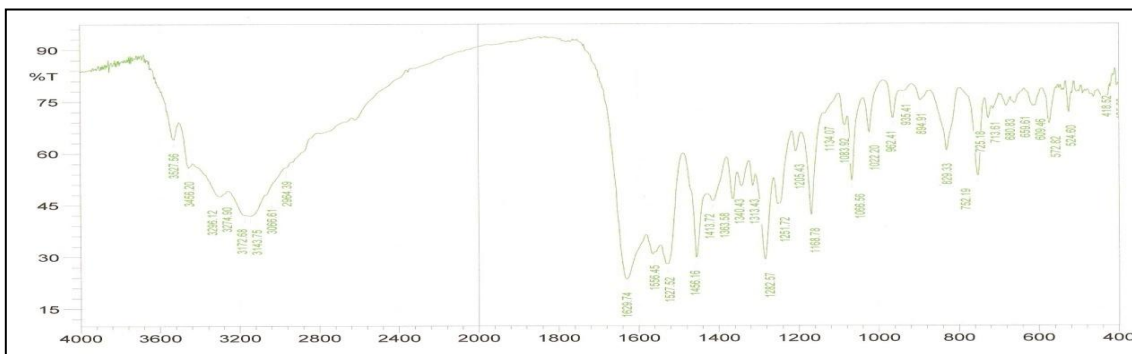


Fig.(2.b)The(I.R)spectrum of [Ni H₂L)₂]

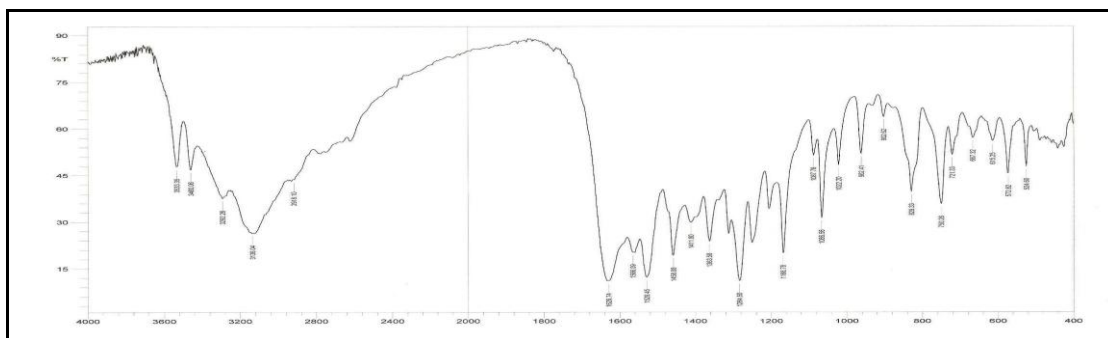


Fig.(2.C)The(I.R)spectrum of [Zn H₂L)₂]

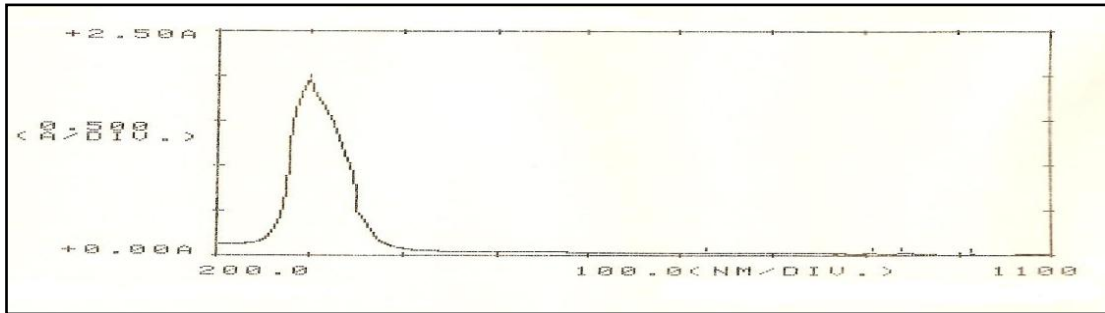


Fig.(3)The(UV - Vis) spectrum of ligand[H₃L]

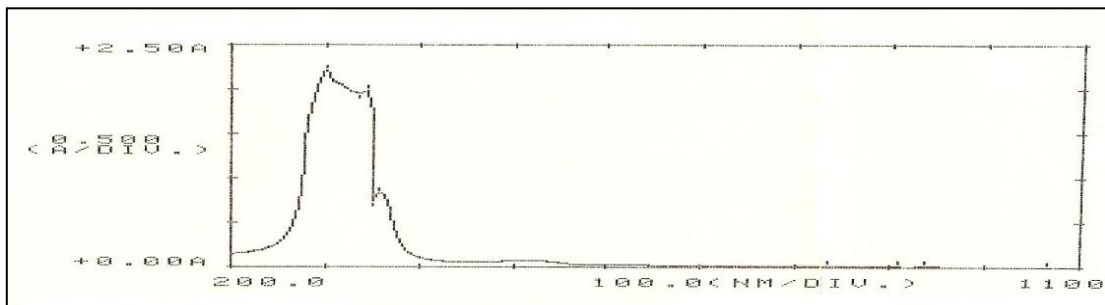


Fig.(3.a)The(UV - Vis) spectrum of [Co H₂L)₂]

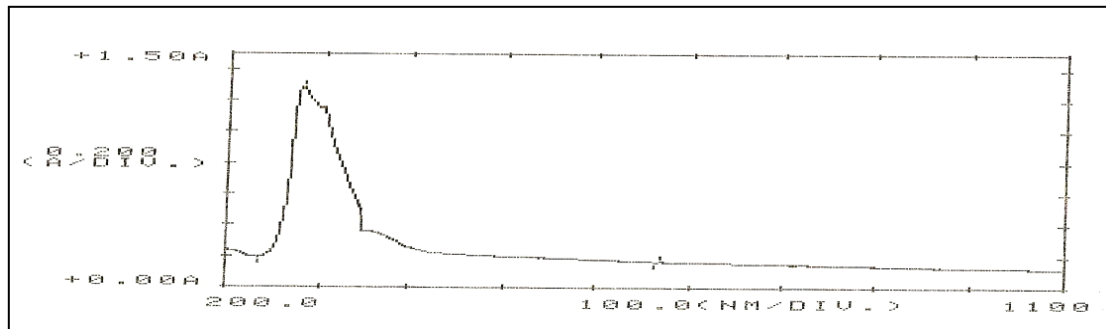


Fig.(3.b)The(UV - Vis) spectrum of [Cu H₂L)₂]

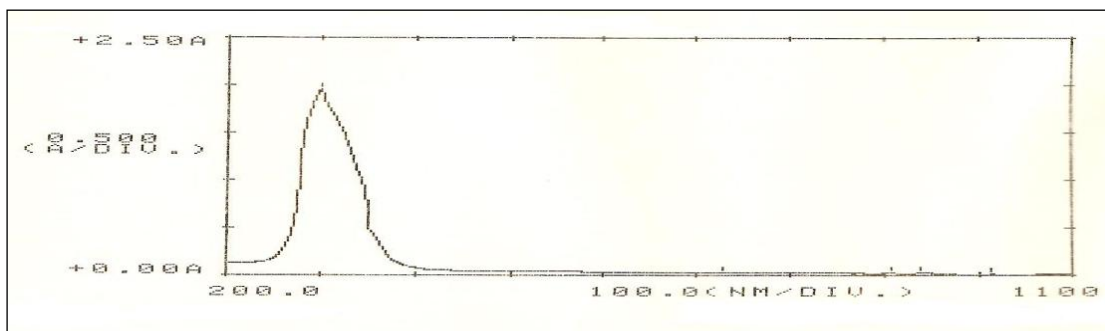


Fig.(3.C)The(UV - Vis) spectrum of [Zn H₂L)₂]

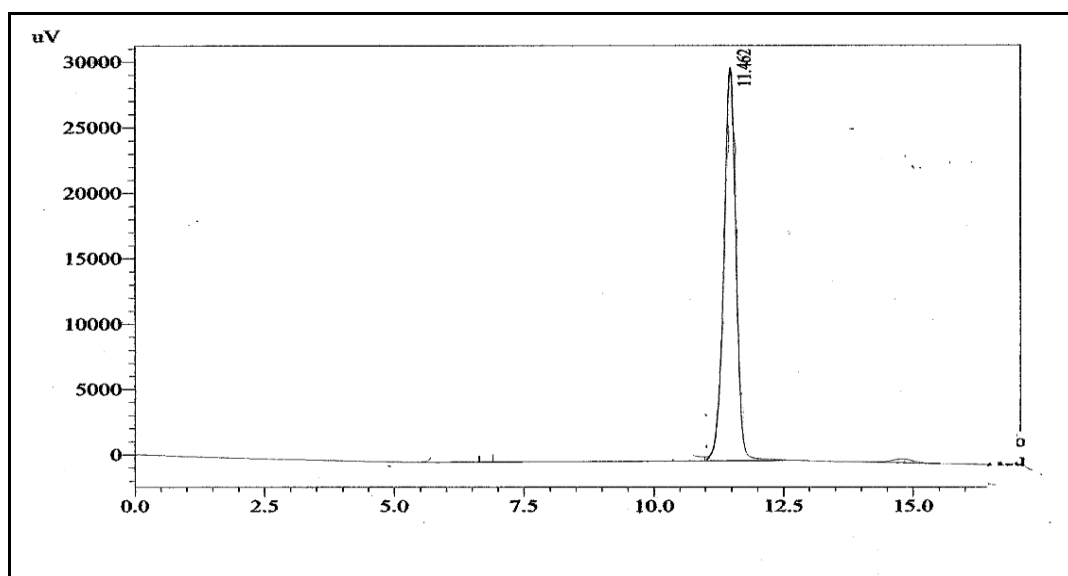


Fig (4a) .The HPLC chromatogram of the $[\text{Co}(\text{H}_2\text{L})_2]$

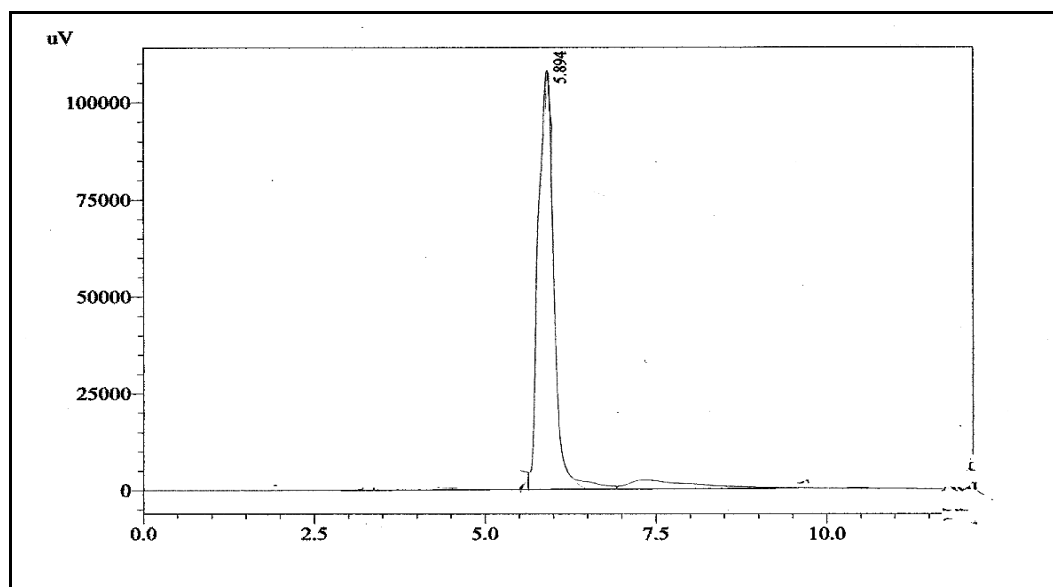


Fig (4b) .The HPLC chromatogram of the $[\text{Ni}(\text{H}_2\text{L})_2]$

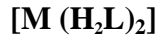
تحضير وتشخيص ليكاند ثنائي السن جديد نوع NO
ومعقداته مع
(Co^(II), Ni^(II), Cu^(II) and Zn^(II))

لقاء خالد عبدالكريم

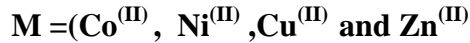
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كلية التربية ابن الهيثم قسم الكيمياء
العراق - بغداد - الاعظمية P.O.4150

الخلاصة:

تضمن البحث تحضير الليكاند ثنائي السن الجديد
[2-N-2,4,6-trihydroxyacetophenonylidene-benzothiazole] [H₃L]
وذلك من مفاعلة 2-aminobenzothiazole مع 2,4,6 trihydroxy-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 :



حيث



شخصت جميع المركبات المحضرة بوساطة الأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية و 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.