

***Synthesis and Characterisation of Novel
Bidentate Ligand N-Propyl Salicylamid and its
complexes with (Cr^(III), Co^(II),
Ni^(II), Cu^(II), Zn^(II), Cd^(II) and Hg^(II))***

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Abstract:

A methyl Salicylate was reacted with Propyl amine to produce the new bidentate ligand (N-Propyl Salicylamid) [H₂L]. Also complexes of the ligand H₂L in general formula [M (HL)₂], [M= Co^{II}, Zn^{II}, Cd^{II}, Hg^{II}] and [Et₃NH]_n [M'(HL)₂Cl₂], M'= Cr^{III}, n=1; M'=Ni^{II}, Cu^{II}, n=2 were prepared. All compounds have been characterised by spectroscopic methods [I.R., UV-Vis, atomic absorption, (¹H NMR and EI-mass for the ligand)] microanalysis (C.H.N) along with conductivity measurements. From the above data, the proposed molecular structure for Cr, Ni and Cu complexes is distorted octahedral, while Co, Zn, Cd and Hg complexes are forming tetrahedral geometry.

Introduction:

In the last few years there have been much interest in the preparation and characterisation of organic compounds with N,O donor atom such as NO bidentate ligands and their complexes with some metal ions (1,2) Great attention was given to synthesis complexes of Fe(II), Ni(II) and Cu(II) for some biological systems (3) and with Tc and Re for radiopharmaceuticals applications (4,5). Recently complex of N,O type ligand with Mn(II) and Mn(IV) is used as catalyst for polymerization of dipole molecules and for alkenes oxidation (6). This paper reports the synthesis and characterisation of new ligand derived

from the reaction of methyl Salicylate with Propyl amine and its complexes.

Experimental:

Reagents were purchased from Fluka and Rediel – Dehenge Chemical Co. I.R spectra were recorded as KBr,CsI disc using a Shimadzu 8300 FTIR in the range (4000-400) cm^{-1} . Electronic spectra of the prepared compounds were measured in the region (200-900) nm for 10^{-3}M solution in DMSO at 25°C using a Shimadzu-U.V -160 Aultra violet visible spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. Mass spectrum for the ligand was obtained by Electron-Impact (EI) on a Shimadzu GCMSOPA 1000 spectrometer and FAB on a TSQ spectrometer(Finnigau), at the University of free Berlin, Germany. ^1H NMR were acquired with Bruker 400 and jeol EX 400, EX 270 MHz spectrometer in DMSO d_6 , the sample is recorded at University of free Berlin, Germany. Elemental microanalysis(C.H.N) were performed by Elemental Analyzer perkin-Elmer 240B. while metal contents of the complexes were determined by atomic absorption types Shimadzu (A.A) 670 . Electrical molar conductivity measurements of the complexes were recorded at 25°C for 10^{-3}M solutions of the samples in DMSO using a PW 9529 digital conductivity meter (Philips).

Synthesis of the ligand (H_2L)

To (0.469g, 3mmole) of methyl Salicylate in (100) ml round bottom flask in ice path was added slowly with stirring (0.182g, 3mmole) of Propyl amine, during which time a thick oily liquid was formed which was dried under vacuum for (6) hrs to give a colourless thick precipitate which was cooled at $(4)^{\circ}\text{C}$ for (10) days to give white crystal (0.46g), yield 83%, m.p. $(48-50)^{\circ}\text{C}$.

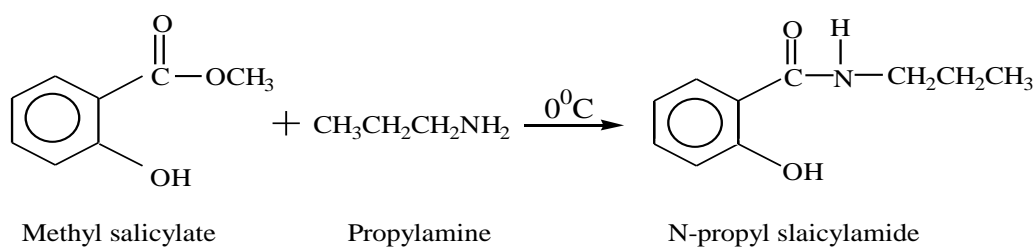
Synthesis of complexes

All complexes were prepared by adding dropwise a solution of the ligand (H_2L) (0.096g, 0.54 mmole) and triethyl amine Et_3N (0.054g, 0.54 mmole) in (5) ml methanol with stirring, to a solution of metal chloride salt $\text{MCl}_n \cdot \text{XH}_2\text{O}$ dissolved in (5)ml methanol, where: ($\text{M} = \text{Cr}^{\text{III}}$, $n=3$); [$\text{M} = \text{Co}^{\text{II}}$, Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} , Hg^{II} , $n=2$]; ($\text{X} = 6$ for Cr^{III} , Co^{II} ,

Ni^{II} and $X = 2$ for Cu^{II} , Zn^{II} , Cd^{II} , Hg^{II} . The reaction mixture was allowed to reflux for (2) hrs under inert atmosphere from nitrogen gas, let the coloury precipitate formed which was filtered, washed with (5) ml diethyl ether and dried at room temperature for (24) hrs. Table (1) shows the stated weight of metal chloride salt, % yield and some physical properties of the ligand and prepared complexes.

Results and discussion

Synthesis of the ligand : The $[\text{H}_2\text{L}]$ pro-ligand with molecular formula $\text{C}_{10}\text{H}_{13}\text{NO}_2$ was prepared by the reaction of methyl Salicylate with Propyl amine according to the general method shown in Scheme (1). The (I.R) spectrum of the ligand $[\text{H}_2\text{L}]$ (Fig .2a), displayed a band at $(3357)\text{cm}^{-1}$ is attributed to $\nu(\text{N-H})$ stretching frequency of amide group (7). A band at $(3550)\text{cm}^{-1}$ due to the $\nu(\text{O-H})$ stretching frequency. The three strong bands at $(1541, 1587 \text{ and } 1644)\text{cm}^{-1}$ are attributed to the $\nu(\text{C=O})$ stretching frequency of the amide group (8) . The (U.V-Vis) spectrum for ligand $[\text{H}_2\text{L}]$ (Fig. 3a) exhibits a high intense absorption peak at $(302\text{ nm}, 33112\text{ cm}^{-1}, \epsilon_{\text{max}} = 2499\text{ M}^{-1} \cdot \text{cm}^{-1})$ which assigned to overlap of $(\pi \rightarrow \pi^*)$ and $(n \rightarrow \pi^*)$ electronic transitions (9). The EI (+) mass spectrum of the ligand $[\text{H}_2\text{L}]$ (Fig .4) Shows the parent ion peak at $(m/z=179)$ which corresponds to (M^+) , and the fragments at $(140), (86), (58)$ and (43) assigne to $[\text{M}-(\text{CH}=\text{CH}-\text{CH})]^+$, $[\text{M}-(\text{C}_6\text{H}_4\text{OH})]^+$, $[\text{M}-(\text{C}_6\text{H}_4\text{OH}-\text{CO})]^+$ and $[\text{M}-(\text{C}_6\text{H}_4\text{OH}-\text{CO}-\text{NH})]^+$ respectively (10). $^1\text{H NMR}$ spectrum (Fig .5) of the ligand $[\text{H}_2\text{L}]$ in $\text{DMSO}-d_6$ displayed signals at the chemical shifts $(0.85), (1.51), (3.26), (3.79),$ (at range $6.81-7.84$) and (8.76) ppm which are attributed to protons of groups : $\text{CH}_3, \text{CH}_2, \text{CH}_2, \text{NH},$ aromatic C_6H_4 and OH respectively. In fact the chemical shifts values and the mass spectrum data are a strong evidence for the structure of the ligand $[\text{H}_2\text{L}]$.



Scheme (1): The Synthesis route of the ligand H₂L

Synthesis of complexes: the reaction of ligand [H₂L] with MCl_n.XH₂O, [Where M= Cr^(III), n=3 ;(M=Co^(II), Ni^(II) Cu^(II), Zn^(II), Cd^(II) Hg^(II) n=2) ; (X=6 ; for Cr^(III), Co^(II) and Ni^(II)) and X=2 for Cu^(II), Zn^(II), Cd^(II) and Hg^(II)], were carried out in methanol under reflux. These complexes are stable in solution and electrolyte (Table -3) The analytical and physical data (Table-1) and spectral data (Table -2 and 3) are compatible with the suggest structure (Fig.1). The I.R. spectra for all complexes (Table -2) in general formula [M(HL)₂], [Et₃NH]_n [M' (HL)₂Cl₂], (M=Co^(II), Zn^(II), Cd^(II), Hg^(II)), n=0), (M'=Cr^(III), n=1 ; (M'= Ni^(II), Cu^(II), n=2) gave a different spectra in comparison with that of free ligand [H₂L]. In general the I.R spectra of all complexes show a band at range (3552-3425) cm⁻¹ assigned to ν(N-H) stretching frequency of the amide group which was shifted to higher frequency, these shifting indicates the coordination between nitrogen atom of [H₂L] ligand and metal ion(11). The two bands at the range (1676-1580) cm⁻¹ which attributed to the ν(C=O) stretching frequency of the amide group were shifted to lower frequency in comparison with that of free ligand, these shifting can be related to the delocalization of metal ion electronic density into π - orbital of the ligand and formation of π – back bond (d π -p π) (12). Moreover the I.R spectra of the complexes (Fig.2a) show new bands, the first at range (680-511) cm⁻¹ and the second band at range (640-453) cm⁻¹ due to ν (M-N) vibration (13,14), the third band at range (570-432) cm⁻¹ and the fourth band at the range (453-410) cm⁻¹ due to ν(M-O) vibration ,while the two new bands at (2925,2780) cm⁻¹ assigned to the vibration of ammonium salt [Et₃NH]⁺ (15). The electronic spectra of the free ligand [H₂L] and their complexes are summarized in (Table - 3). The (U.V-Vis.) spectra of complexes display two absorption peaks, the first at the range (270-303) nm and the second at range (321-351) nm, assigned to the ligand field(16) which were shifted to higher or lower frequency when it compared with spectrum of the free ligand . The electronic spectra of complexes Cr,Co,Ni,Cu and Zn exhibit a new absorption peaks at 345 nm, 361 nm, 351 nm, 365nm and 351 nm respectively which are attributed to charge transfer spectra (M → L) (17).

The new peak at 355 nm in the U.V-Vis spectrum of [Et3NH][Cr(HL)2Cl2] is assigned to electronic transition type (${}^4A_{2g} \rightarrow {}^4T_{1g(p)}$), suggesting distorted octahedral geometry about $Cr^{(III)}$ (18). The peak at 796 nm in the spectrum of [Co(HL)2] is attributed to (${}^4A_2 \rightarrow {}^4T_{1(p)}$) transition which is a good evidence for tetrahedral geometry about $Co^{(II)}$ (19). The U.V-Vis spectrum of [Et3NH]2[Ni(HL)2Cl2] (Fig.3b) shows a new peak at 373 nm which attributed to (d-d) electronic transition type (${}^3A_{2g} \rightarrow {}^3T_{1g(p)}$) suggesting distorted octahedral geometry about $Ni^{(II)}$ (20). The electronic spectrum of [Et3NH]2 [Cu(HL)2Cl2] shows a new absorption peak at 706 nm attributed to electronic transition type (${}^2B_{2g} \rightarrow {}^2B_{1g}$), in fact this result is in a good agreement with previous work of $Cu^{(II)}$ complexes of distorted octahedral geometry because of Jahn –Teller effect (21). The U.V-Vis spectra of $Zn^{(II)}$, $Cd^{(II)}$ and $Hg^{(II)}$ complexes show no absorption peak in the range (370-1000) nm which is indicate no (d-d) electronic transition happened (d^{10} -system) in the visible region. That is a good result for $Zn^{(II)}$, $Cd^{(II)}$ and $Hg^{(II)}$ tetrahedral complexes (18,22). The molar conductance of the complexes in DMSO solvent in (10^{-3} M) at 298 k (Table- 3) indicated electrolytic nature with (1:1) and (2:1) ratio for $Cr^{(III)}$ and ($Ni^{(II)}$, $Cu^{(II)}$) complexes respectively, while indicating non electrolytic nature for $Co^{(II)}$, $Zn^{(II)}$, $Cd^{(II)}$ and $Hg^{(II)}$ complexes (23,24).

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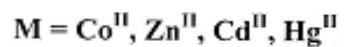
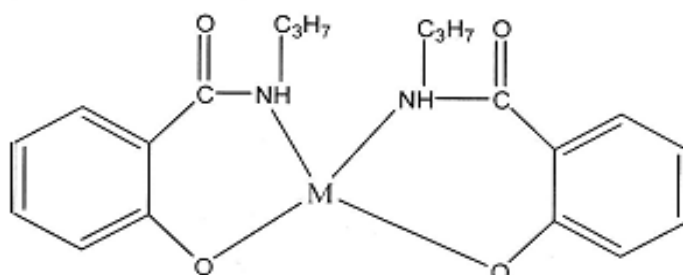
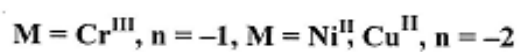
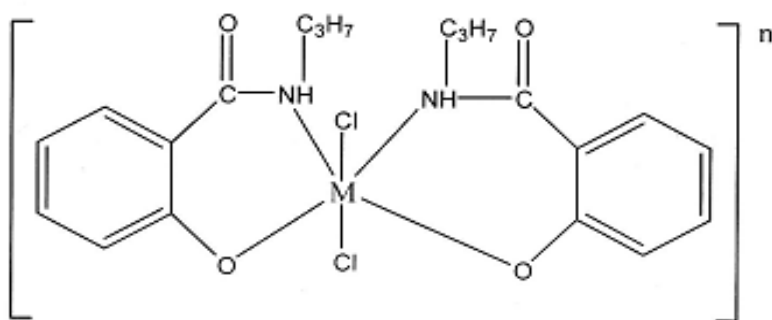


Fig. (1): the suggested structure for the complexes

Table (1): Analytical and physical data of the ligand and it's complexes and weight of metal chloride salt

Compound	M.W	Colour	Mp °C	Yield %	Found% , (Calcu.) %				Metal Chloride salt	Weight of metal chloride	
					C	H	N	Metal		g	mmole
[H ₂ L] *	179	White	50	83	67.01 (67.03)	7.20 (7.26)	7.80 (7.82)				
[(E ₀)NH][(HL) ₂ CrCl ₂] **	580	Dark green	202	80	53.76 (53.79)	6.86 (6.89)	7.21 (7.24)	8.12 (8.79)	CrCl ₂ .6H ₂ O	0.072	0.27
[(HL) ₂ Co]	414	Pale brown	200	83	57.95 (57.97)	5.77 (5.79)	6.74 (6.76)	13.31 (14.11)	CoCl ₂ .6H ₂ O	0.063	0.27
[(E ₀)NH] ₂ [(HL) ₂ NiCl ₂]	689	Pale green	217	80	55.70 (55.73)	8.10 (8.12)	6.06 (6.09)	9.05 (8.41)	NiCl ₂ .6H ₂ O	0.064	0.27
[(E ₀)NH] ₂ [(HL) ₂ CuCl ₂]	693 5	Yellowish green	212	81	55.30 (55.33)	8.04 (8.06)	6.02 (6.05)	8.62 (9.07)	CuCl ₂ .2H ₂ O	0.046	0.27
[(HL) ₂ Zn]	421	White	200	83	57.08 (57.10)	5.68 (5.70)	6.62 (6.65)	14.91 (15.43)	ZnCl ₂ .2H ₂ O	0.046	0.27
[(HL) ₂ Cd]	468	Yellowish White	182	83	51.26 (51.28)	5.10 (5.12)	5.96 (5.98)	24.62 (23.93)	CdCl ₂ .2H ₂ O	0.059	0.27
[(HL) ₂ Hg]	556	White	130	81	43.14 (43.16)	4.29 (4.31)	5.00 (5.03)	35.76 (35.97)	HgCl ₂ .2H ₂ O	0.082	0.27

* H₂L=C₁₀H₁₃NO₂

** HL=C₁₀H₁₂NO₂

Table (2): I.R spectral data of the ligand and it's complexes

Compound	ν (N-H)	ν (O-H)	ν (C=O)	ν (C-N)	ν (M-N)	ν (M-O)	Additional peaks
H ₂ L	3357	3550	1644 1587 1541	1359 1338	-	-	ν (C=C)1532
[(Et) ₃ NH][(HL) ₂ CrCl ₂]	3425	-	1620 1610	1340	511 478	465 453	ν (C=C) 1580,1530 ν (C-H) 1145, (C-C) 1058 ν (N-H ⁺) 2925
[(HL) ₂ Co]	3552	-	1638 1626	1332	545 453	432 410	ν (C=C) 1541,1590 ν (C-H) 1148, ν (C-C) 1081
[(Et) ₃ NH] ₂ [(HL) ₂ NiCl ₂]	3425	-	1639 1618	1338	661 570	462 451	ν (C=C) 1541,159 ν (C-H) 1145, ν (C-C) 1045 ν (N-H ⁺) 2925,2890
[(Et) ₃ NH] ₂ [(HL) ₂ CuCl ₂]	3529	-	1637 1604	1357	640 430	445 430	ν (C=C) 1541,1498 ν (C-H) 1159, ν (C-C) 1037 ν (N-H ⁺) 2962,2813
[(HL) ₂ Zn]	3425	-	1676 1647	1340	640 545	460 445	ν (C=C) 1548 ν (C-H) 1157, ν (C-C) 1087
[(HL) ₂ Cd]	3425	-	1647 1610	1358	640 590	490 410	ν (C=C) 1541,1471 ν (C-H) 1159, ν (C-C) 1095
[(HL) ₂ Hg]	3425	-	1596 1580	1350	680 640	570 440	ν (C=C) 1555,1508 ν (C-H) 1155, ν (C-C) 1027

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Table (3) : Electronic spectral data , and conductance measurement of the ligand[H₂L] and it's complexes in DMSO solvent

Compound	λ nm	Wave number Cm^{-1}	ϵ_{max} Molar ¹ Cm^{-1}	Assignment	M.C* ($\text{ohm}^{-1}.\text{cm}^2.\text{mole}^{-1}$)	Propose structure
H ₂ L	302	33112	2499	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	
[(Et) ₃ NH][(HL) ₂ CrCl ₂]	270.5	36968	2099	Ligand field	34	octahedral
	325	30769	1438	Ligand field charge transfer		
	345	28985	1635			
	355	28169	1069	$^4A_{2g} \rightarrow ^4T_{1g(p)}$		
[(HL) ₂ Co]	299	33444	2108	Ligand field	15	tetrahedral
	321	31152	940			
	361	27548	1101	Ligand field charge transfer		
	796	12562	17	$^4A_2 \rightarrow ^4T_{1(p)}$		
[(Et) ₃ NH] ₂ [(HL) ₂ NiCl ₂]	299	33444	2293	Ligand field charge transfer	72	octahedral
	351	28490	1099			
	373	26809	1431	$^3A_{2g} \rightarrow ^3T_{1g(p)}$		
[(Et) ₃ NH] ₂ [(HL) ₂ CuCl ₂]	303	33003	2631	Ligand field charge transfer	76	octahedral
	365	27397	112			
	706	14164	150	$^2B_{2g} \rightarrow ^2B_{1g}$		
[(HL) ₂ Zn]	284.5	35211	2515	Ligand field	18	tetrahedral
	351	28490	1099	Charge transfer		
[(HL) ₂ Cd]	291	34364	2032	Ligand field	4	tetrahedral
[(HL) ₂ Hg]	284	35211	2017	Ligand field	8	tetrahedral

*Molar Conductance

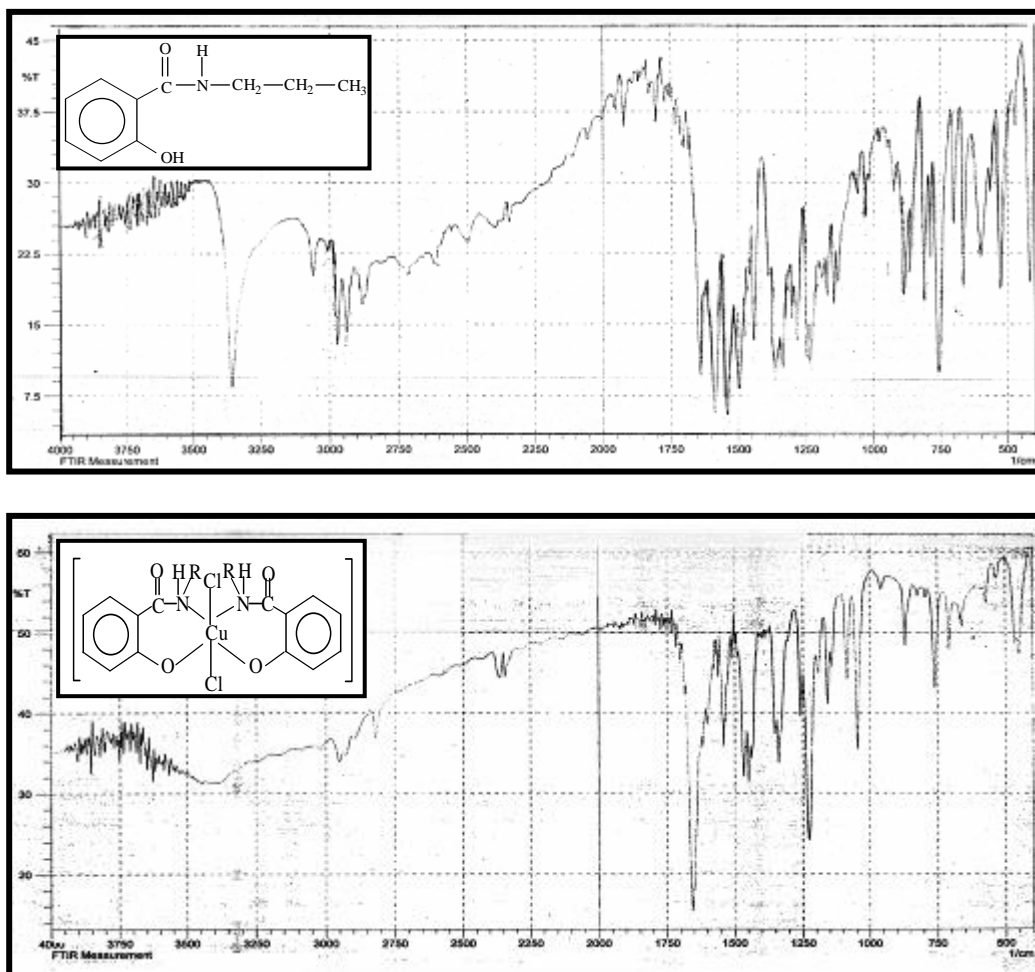


Fig .(2): The I.R. Spectrum of:
a- The ligand (H₂L)
b-The complex[(Et)₃NH]₂[(HL)₂CuCl₂]

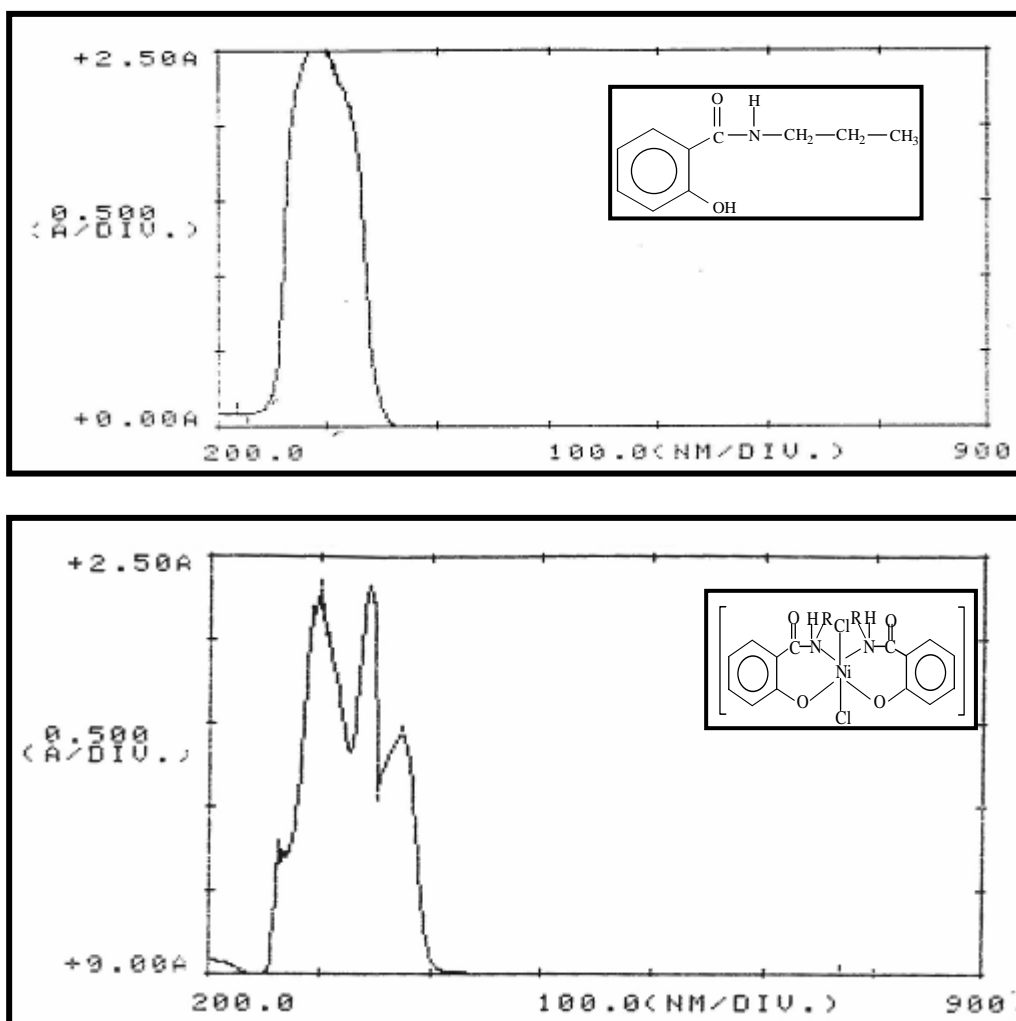


Fig.(3): The electronic Spectrum of:
a-The ligand (H₂L)
b-The complex[[(Et)₃NH]₂[(HL)₂NiCl₂]

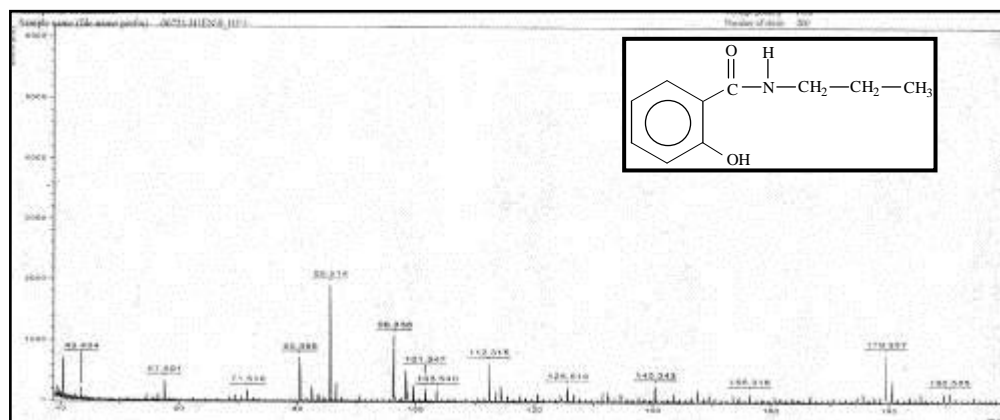


Fig .(4): The EI(+) mass Spectrum of the ligand (H₂L)

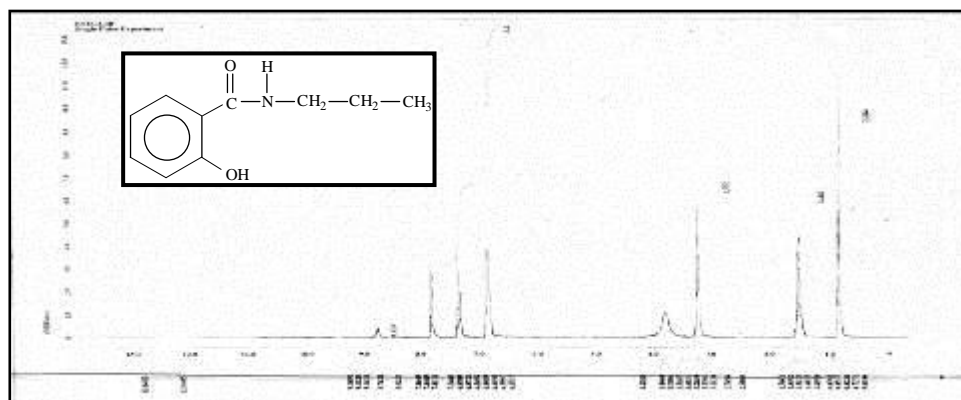


Fig .(5): The ¹H NMR Spectrum of the ligand (H₂L)

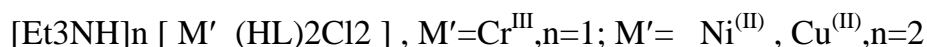
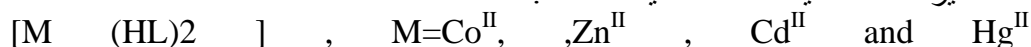
تحضير وتشخيص الليكاند ثنائي السن الجديد
N-Propyl Salicylamid
 ومعداته مع
 (Cr^(III) Co^(II), Ni^(II), Cu^(II), Zn^(II), Cd^(II) and Hg^(II))

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جامعة بغداد
 كلية التربية ابن الهيثم قسم الكيمياء
 العراق – بغداد - الاعظمية

الخلاصة

(N-Propyl Salicylamid) [H₂L] تضمن هذا البحث تحضير الليكاند ثنائي السن الجديد الحاوي على N,O كذرات مانحة ، وذلك من مفاعلة مثيل سالسليت وبروبيل امين كذلك تم تحضير معقدات الليكاند ذات الصيغة العامة :



شخصت جميع المركبات المحضرة بالطرائق الطيفية (الأشعة تحت الحمراء ، الأشعة فوق البنفسجية – المرئية ، مطيافية الامتصاص الذري للعناصر وطيف الرنين النووي المغناطيسي وطيف الكتلة بتقنية القصف الالكتروني EI لليكاند (H₂L) فقط) كذلك شخصت المركبات المحضرة بوساطة التحليل الكمي الدقيق للعناصر وقياس التوصيلية المولارية الكهربائية . من النتائج المحصول عليها فان الشكل الفراغي المقترح للمعدقات هو ثماني السطوح لمعدقات Co^(II), Zn^(II), Cd^(II) and Hg^(II) و رباعي السطوح لمعدقات Cr^(III) (Ni^(II)), (Cu^(II))