

The preparation and characterization of some metal complexes with tridentate ONO ligand derived from phenyl hydrazine

*Mahmoud S. Muter**

*Hikmat A. Mohamad***

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Abstract:

The phenyl hydrazine was react readily with acetic acid chloride in [1:2] ratio in alkyl of ethanolic solution, and reflux for five hours to produce a new ligand of (N-Carboxymethyl-N-phenyl-hydrazino)-acetic acid [H₂L].

This ligand used to synthesize complexes with Cu(II), Co(II), Cr(III) and Pd(II), the structures of some compounds were studied and by Elemental analyses (C H N), IR, UV-Visible and ¹³C ¹H-NMR spectra, as well as molar conductance measurements, magnetic susceptibility data, and melting point. According to These studies the suggested structure was spin-paired octahedral for the prepared complexes, except the structure of palladium complex was square planar around Pd(II) ion.

Key words: complexes of hydrazine derivatives

Introduction:

Hydrazine derivatives with alkanolic[1] and aromatic carboxylic acid[2], play very important role in biological activities, like anticancer[3], anti-inflammatory[4], anti-infective [5], antituberculosis[6].

Depending on the synthesis and biological evaluation of ethyl 2-benzo [1,2,3 triazole] acetate[7], and oxadiazole derivatives[1,8] such [5-(4-phenylpiperazin-1-ylmethyl)-1,3,4-oxadiazole-2-ylsulfanyl]-acetic acid[6], some hydrazine derivatives can be used to prepared new ligand containing ON donor atoms that have interesting class of compounds, which find an extensive applications in various fields[9,10].

The oxygen and nitrogen may be involved in coordination providing a useful model for bioinorganic processes[11,12]. These compounds are also of interest due to their pharmaceutical applications and biological activities[9,10,13]. In the

present work we reported the synthesis and characterization of some complexes with (N-carboxymethyl-N-phenyl-hydrazino)- acetic acid [H₂L].

Materials and Methods:

1. Materials:

Analar or equivalent grade chemicals commercially available from BDH, Merck and Aldrich etc, were used for synthesis.

2. Instruments:

1. Melting or decomposition points were measured using Electrothermal 9100 (U.K).
2. IR spectra were recorder as KBr discs in the range of (4000-400)cm⁻¹ using Shimadzu 8300 FTIR spectrophotometer.
3. Elemental analyses (C, H, N) were carried out using Heraeus instrument (Vario EL). AL al. Bayt University. Jordan.

*Department of Basic Science, College of Dentistry, University of Anbar, Iraq.

**Education of Science College, Department of Chemistry, University of Salahaddin, Erbil.

4. ^1H , and ^{13}C NMR were recorded on a DXP-400 MHz Bruker spectrophotometer (England). AL al. Bayt University. Jordan.
5. UV-Vis spectra were recorded on data steam - (3000) series. Anbar University.
6. Moler conductivity of the complexes of $(10^{-3})\text{M}$ was determined using Jenway conductivity meter 4200(0.93) cell constant (U.K).
7. The magnetic susceptibilities of the complexes were determined at 25°C using Bruker magnet BM_6 .

3. Synthesis:

3.1. preparation of (N-Carboxymethyl-N-phenyl-hydrazino)-acetic acid [H_2L]

A solution of KOH (0.12 gm, 2.1 mmol) in ethanol, was added to a solution of phenyl hydrazine (1 gm, 9.24mmol) in hot ethanol (25ml). The resulting mixture was refluxed on a water-bath for (30) minutes. A quantity of (1.74 gm, 18.48 mmol) of acetic acid chloride (ClCH_2COOH) was added to the above solution and the refluxing was continued for 5 hours [6].

The resulting solution was concentrated and allowed to cool. The separated readish brown product was filtered, further purified by recrystallization from ethanol, dried under vacuum. Yield (0.76 gm) (63.07%), m.p(108°C).

3.2. Preparation of $\text{K}_2[\text{Cu}(\text{L})_2]$ complex

The solution of copper(II) dichloride Hexahydrate (0.27 gm, 1.1 mmol) in methanol was added slowly with stirred to a solution of ligand [H_2L] (0.5 gm, 2.05 mmol) and potassium hydroxide (0.24 gm, 4.2

mmol) in (50 ml) methanol. The resulting mixture was refluxed for 4 hours on a water-bath and deep green coloured compound separated out on cooling. It was filtered, dried in vacuum. Yield(65%) and m.p(140°C).

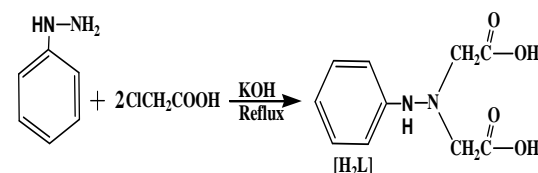
3.3. Preparation of $\text{K}_2[\text{Co}(\text{L})_2]$, $\text{K}[\text{Cr}(\text{L})_2]$ and $\text{K}[\text{pd}(\text{L})\text{Cl}]$ complexes

A similar method to that mentioned in preparation of $\text{K}_2[\text{Cu}(\text{L})_2]$ complex was used to prepare the complexes of Co^{II} , Cr^{III} and Pd^{II} ions with [H_2L] by used (0.26gm, 1.09mmol), (0.25gm, 0.93mmol) and (0.19gm, 1.07mmol) of $[\text{CoCl}_2 \cdot 6\text{H}_2\text{O}]$, $[\text{CrCl}_3 \cdot 6\text{H}_2\text{O}]$ and $[\text{PdCl}_2]$ respectively.

Results and Discussion:

Synthesis and characterization of [H_2L]

The new ligand (N-Carboxymethyl-N-phenyl-hydrazino)-acetic acid [H_2L] was synthesized according to the general method shown in Scheme (1).



Scheme (1) Synthesis route of the [H_2L] ligand

The ligand was characterized by elemental analysis, Table (1) in which the results were in a good agreement with the calculated values, as well as spectroscopic methods (IR), (UV-Vis), (^1H , ^{13}C) NMR.

The prepared ligand was Readish-brown crystals and soluble in different solvent (methanol, ethanol, DMF, DMSO and C_6H_6).

Table (1) Micro analysis and some physical properties for the ligand [H₂L]

Compound	M.Wt	Yield (%)	M.P °C	Colour	Micro analysis found (calc) %		
					C	H	N
[H ₂ L]	22.4	63	107–109	Reddish-brown	(4.46) 4.18	(5.35) 5.42	(0.89) 1.00
K ₂ [Cu(L) ₂]	585.5	65	140	Deep green	(40.9) 40.88	(3.41) 3.33	(9.56) 10.76
K ₂ [Co(L) ₂]	581	80	122	Deep-purple	(41.30) 40.10	(3.44) 3.31	(9.63) 10.30
K[Cr(L) ₂]	535	71	177	Yellowish-green	(44.8) 44.6	3.73 3.07	10.46 10.29
K[Pd(L)Cl]	402.8	66	214	Deep brown	(29.79) 26.37	(2.48) 2.44	(6.95) 6.55

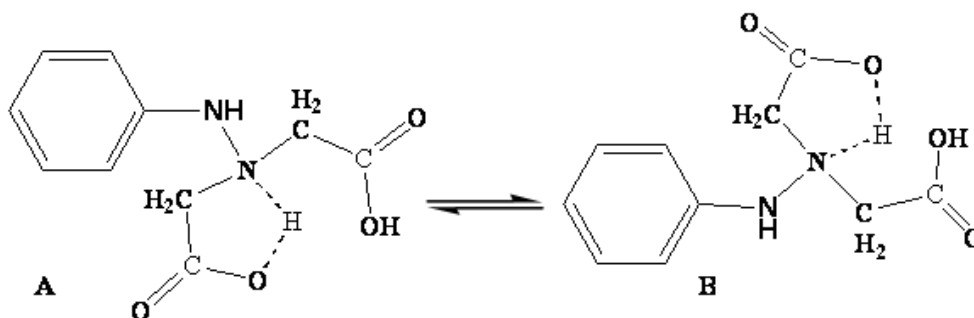
(Calc). Calculated.

1. Infrared spectra

Important infrared bands of the ligand [H₂L] and its complexes together with their assignments are collected in Table (2).

IR spectra of the free ligand, Fig (1), showed a broad band at (3241)cm⁻¹, which is due to hydrogen bonding of OH group. The interaction with ν(N-H) stretching[9], Scheme (2-

A and B). The bands appeared at 1312 and 1243cm⁻¹ are due to hydrazinic ν(N-N) and carboxymethyl imine ν(C-N) stretching of ligand [H₂L][1]. Another bands observed at (3029), (2912), (1677) and (1497)cm⁻¹ assigned to ν(C-H)_{Arom}, ν(C-H)_{Aliph}, ν(C=O) and δ(N-H) respectively[10,11].



Scheme (2- A, B) structure of ligand [H₂L]

In the spectra of [H₂L] complexes, the broad band due to hydrogen bonded OH of the ligand disappeared from the region (3241)cm⁻¹, and showed weak bands at (3440, 3401, 3420 and 3429)cm⁻¹ attributed to the ν(N-H) stretching of the complexes [Cu(L)₂], [Co(L)₂], [Cr(L)₂] and [Pd(L)] respectively, indicating the deprotonation and formation of metal oxygen bond. Consequently the ν(C=O) stretching was increased to higher frequency, whilst the ν(C-O) stretching was decreased to lower

frequency confirming the coordination of oxygen atom[14].

The free ligand exhibits a weak absorption bands at 1595cm⁻¹ and 1420cm⁻¹ due to ν_{asym}(COOH) and ν_{sym}(COOH) respectively. While in the complexes these bands shifted to lower frequency and appeared in the range (1582-1546)cm⁻¹ assigned to ν_{asym}(COO⁻) and one in the (1359-1353)cm⁻¹ assigned to ν_{sym}(COO⁻). This result indicates that carboxylic group is monodentate coordinate [15]. On the other hand, the hydrazinic ν(N-N) in the free ligand were shifted to

higher frequency, while the carboxymethyl imine $\nu(\text{C-N})$ shifted to lower frequency for their complexes. This may be due to the increase in the

repulsion between the lone pairs of electrons on the nitrogen atoms due to the complexation *via* the hydrazinic nitrogen[16].

Table (2) IR data (wave number ν) cm^{-1} of the ligand and it's complexes

Comp.	$\nu(\text{N-H})$	$\nu(\text{C-H})_{\text{Arom}}$	$\nu(\text{C-H})_{\text{Aliph}}$	$\nu(\text{C=O})$	$\nu(\text{C=C})$	$\nu(\text{N-N})$	$\nu(\text{C-N})$	Additional peaks
[H ₂ L]	3241(br)	3029	2912	1677	1600	1312	1243	1497 $\delta(\text{N-H})$ 1186 $\nu(\text{C-O})$
K ₂ [Cu(L) ₂]	3440	3050	2887	1687	1598	1317	1211	1495 $\delta(\text{N-H})$ 1176 $\nu(\text{C-O})$ 501 $\nu(\text{M-O})$ 440 $\nu(\text{M-N})$
K ₂ [Co(L) ₂]	3401	3041	2846	1688	1604	1320	1221	1498 $\delta(\text{N-H})$ 1166 $\nu(\text{C-O})$ 512 $\nu(\text{M-O})$ 422 $\nu(\text{M-N})$
K[Cr(L) ₂]	3420	3054	2874	1678	1594	1332	1200	1490 $\delta(\text{N-H})$ 1155 $\delta(\text{C-O})$ 513 $\nu(\text{M-O})$ 438 $\nu(\text{M-N})$
K[Pd(L)Cl]	3429	3059	2900	1680	1597	1319	1225	1493 $\delta(\text{N-H})$ 1156 $\nu(\text{C-O})$ 542 $\nu(\text{M-O})$ 480 $\nu(\text{M-N})$

The IR spectra of complexes showed bands at the regions (542-501) and (480-422) cm^{-1} , due to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ stretching respectively[10], (were M=Pd, Cu, Co and Ni). The assignment of the bands are

summarized in Table (2). Thus from the IR spectra, it is a tridentate fashion through deprotonated of two hydroxyl oxygen and the nitrogen of hydrazine moiety, Scheme (2).

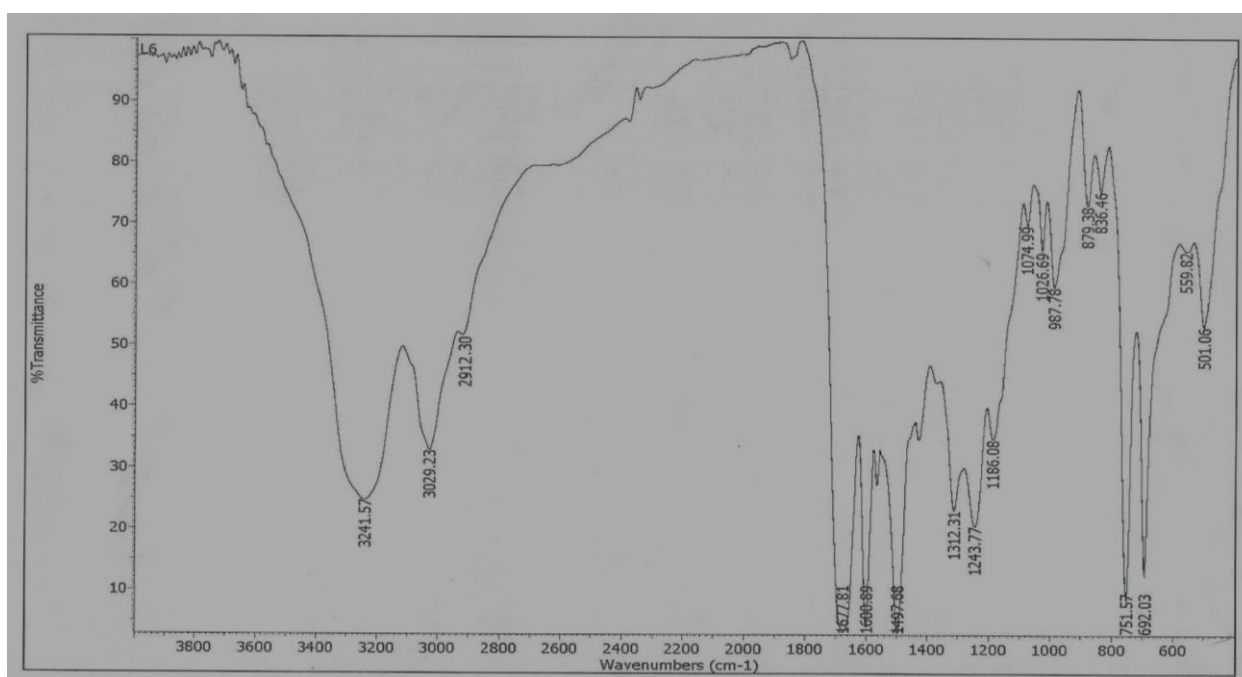


Fig (1) Infrared spectrum of [H₂L] ligand

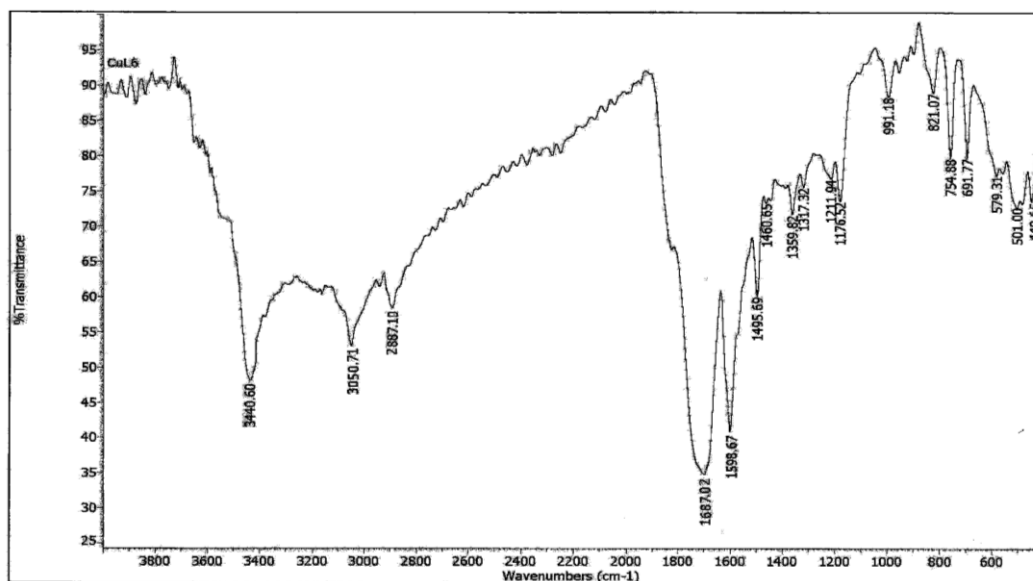


Fig (2) The IR spectrum of $K_2[Cu(L)_2]$ complex

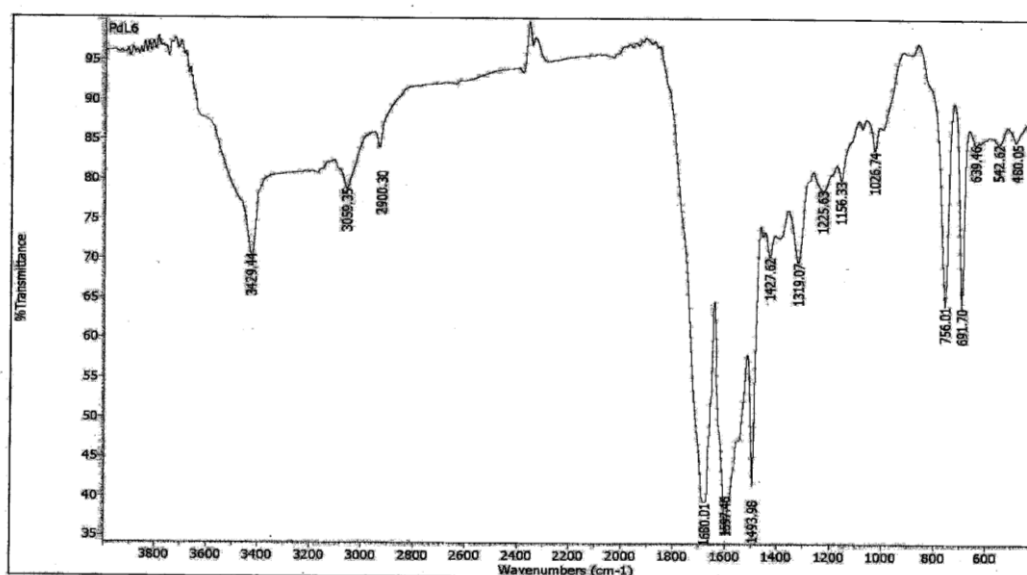


Fig (3) The IR spectrum of $K[Pd(L)Cl]$ complex

2. Electronic spectra, magnetic moments, conductivity measurements

The electronic spectrum of $[H_2L]$ Fig (4) exhibits an intense absorption band at 279nm assigned to $(\pi \rightarrow \pi^*)$, 357nm attributed to $(n \rightarrow \pi^*)$ and weak band at 620nm attributed to charge transfer transition. The spectra of the complexes of $[H_2L]$ displayed peaks in the (UV) region of the intraligand $(\pi \rightarrow \pi^*)$ transition, and shifted to higher by various extents in

comparison with that in free ligand, while the bands related to charge transfer transitions were observed in the spectra of the complexes, Table(3). The electronic spectra of the $Cu(II)$ and $Cr(III)$ complexes displayed bands at (598)nm and (612)nm may be attributed to spin allowed d-d transitions, type ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) respectively[17], suggesting an octahedral geometry around $Cu(II)$ and $Cr(III)$ ions.

The spectrum of the cobalt(II) complex, Fig (5) exhibited weak bands at 490nm and 588nm, arising from charge transfer and (${}^4A_{1g} \rightarrow {}^4T_{1g}$) d-d transition respectively. These observations are compatible with an octahedral geometry around the cobalt(II) ion[18]. The spectrum of Pd(II) complex shows a band at 417nm assigned to the ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition, suggesting a square planar structure, this is in accordance with the results reported by El-Sonbati, et. for palladium complex [19]. The elemental analysis of the complexes, Table (1) was in a good agreement with the calculated values. On the other hand the conductivity of the complexes determined in methanol $10^{-3}M$ at 25

$^{\circ}C$, Table (3). The molar conductivity of the complexes Cu(II) and Co(II) was (124) and (128) $S. cm^2. mole^{-1}$ respectively, indicating 1:2 electrolyte, while the conductivity of Cr(III) and Pd(II) complexes was (55.7) and (60.8) $S. cm^2. mole^{-1}$ respectively, indicating 1:1 electrolyte [20]. The magnetic susceptibility for complexes were measured at room temperature, Table (3), the magnetic moment of the complexes Cu(II), Co(II) and Cr(III) was typical for a high-spin octahedral structure[21], Fig- (6). The low magnetic moment values of Pd(II) complex as well as the other analytical data, indicate a square planar structure[19,22], Fig (7).

Table (3) Electronic spectral data of the ligand [H₂L] and its complexes

Comp.	λ_{nm}	ϵ_{max} molar ⁻¹ . cm ⁻¹	Assignment	molar conductivity S. cm ² . mol ⁻¹	Magnetic susceptibility B.M
[H ₂ L]	279 357 620	1982 960 191	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ Charge transfer	--	--
K ₂ [Cu(L) ₂]	330 365 598	1150 1040 60	$\pi \rightarrow \pi^*$ Charge transfer ${}^2B_{1g} \rightarrow {}^2B_{2g}$	124.6	1.32
K ₂ [Co(L) ₂]	226 384 490 588	1737 752 186 89	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ Charge transfer ${}^4A_{1g} \rightarrow {}^4T_{1g}$	128.2	1.42
K[Cr(L) ₂]	295 378 612	1100 880 26	$\pi \rightarrow \pi^*$ Charge transfer ${}^4A_{2g}^{(F)} \rightarrow {}^4T_{2g}^{(F)}$	55.7	3.77
K[Pd(L)Cl]	305 370 417	988 740 115	$\pi \rightarrow \pi^*$ Charge transfer ${}^1A_{1g} \rightarrow {}^1B_{1g}$	60.8	0.23

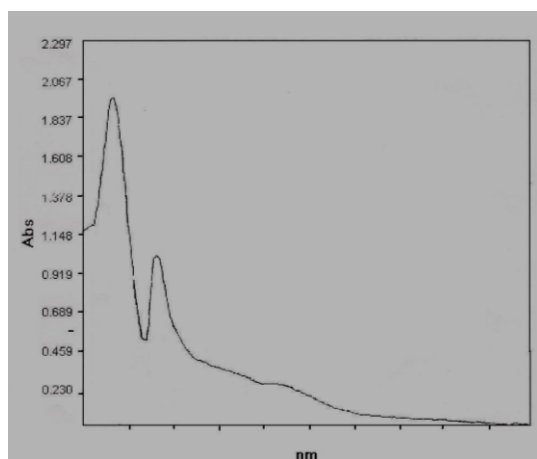


Fig (4) UV-Vis spectrum of [H₂L]

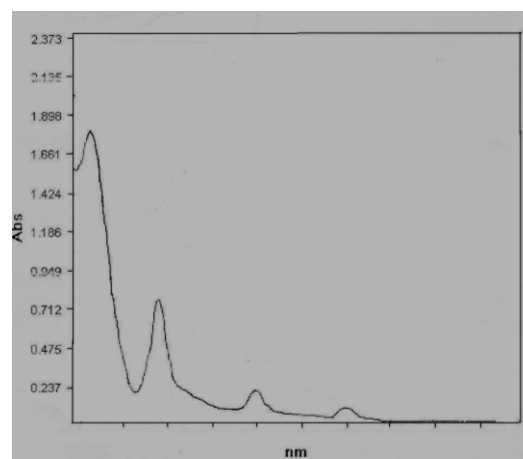


Fig (5) UV-Vis spectrum K₂[Co(L)₂]

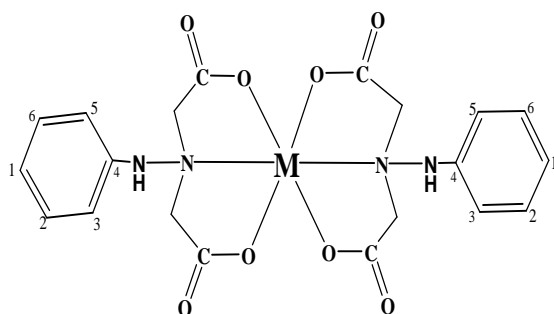


Fig (4) The proposed geometrical structure of $[M(L)_2]$ complex (where: $M=Cu, Co,$ and Cr)

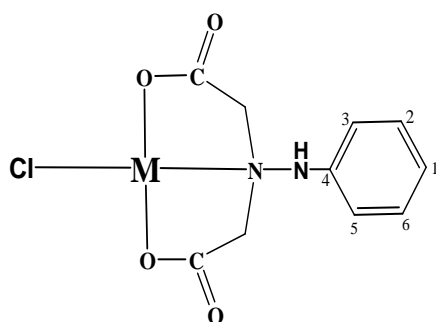


Fig (5) The proposed geometrical structure of $K[Pd(L)Cl]$ complex
3. 1H ^{13}C NMR spectra

The 1H NMR spectra recorded at 400 MHz by using a $DMSO-d_6$ solvent, are shown in Fig (8) and Table (4). The 1H NMR spectrum for the ligand $[H_2L]$ showed signal at 7.79ppm (2H, $2 \times OH$) due to the equivalent protons of (OH) groups, this lower chemical shift of OH refers to the hydrogen bond [10]. The signal at 7.73ppm (1H, NH) due to proton of $\delta(NH)$, While the band at 2.5 ppm (S, 4H) is due to $\delta(CH_2)$ [23]. 1H NMR for ligand showed signals for protons of aromatic group between 7.35-6.13 ppm (m, 5H).

^{13}C NMR spectrum of the $[H_2L]$ was carried out in $DMSO-d_6$,

Table (4), Fig (9). The spectrum showed a chemical shift at 169.4 ppm assigned to carbon atoms of $\delta(COOH)$ groups[24]. The chemical shift of the phenyl group appeared in the aromatic region at (129.5-112.5) ppm, whilst the carbon atoms of $\delta(CH_2)$ groups are equivalent and appeared as single at 56.9 ppm.

Table (4) The chemical shift in ppm for 1H ^{13}C NMR data of $[H_2L]$ measured in $DMSO-d_6$.

Fund.Group	1H NMR (δ , ppm)	^{13}C NMR(δ_s , ppm)
OH	7.79	-
NH	7.73	
(C_2)H, (C_6)H	7.35, 7.25	129.5, 129
(C_3)H, (C_5)H	6.75, 6.6	112.9, 112.7
(C_1)H, C_4	7.10	119.2, 112.5
CH_2	2.5	56.9
$C=O$	-	169.4

Conclusion:

We have explored the syntheses and coordination chemistry of some complexes, obtained from reaction of tridentate ligand, derived from phenyl hydrazine $[H_2L]$, Scheme (1), with metal ions (Cu^{II} , Co^{II} , Cr^{III}) in [2:1] ratio respectively, and with Pd^{II} in [1:1] ratio. The mode of bonding and overall structure of the complexes, were determined by physico-chemical and spectroscopy methods. The results revealed that the ligand coordinate with center ion through oxygen atoms of hydroxyl groups and hydrazinic nitrogen as ONO donor atoms. According to the above results, its concluded that the geometry about Cu^{II} , Co^{II} , Cr^{III} is octahedral, Fig (4), and about Pd^{II} is square planar, Fig (5).

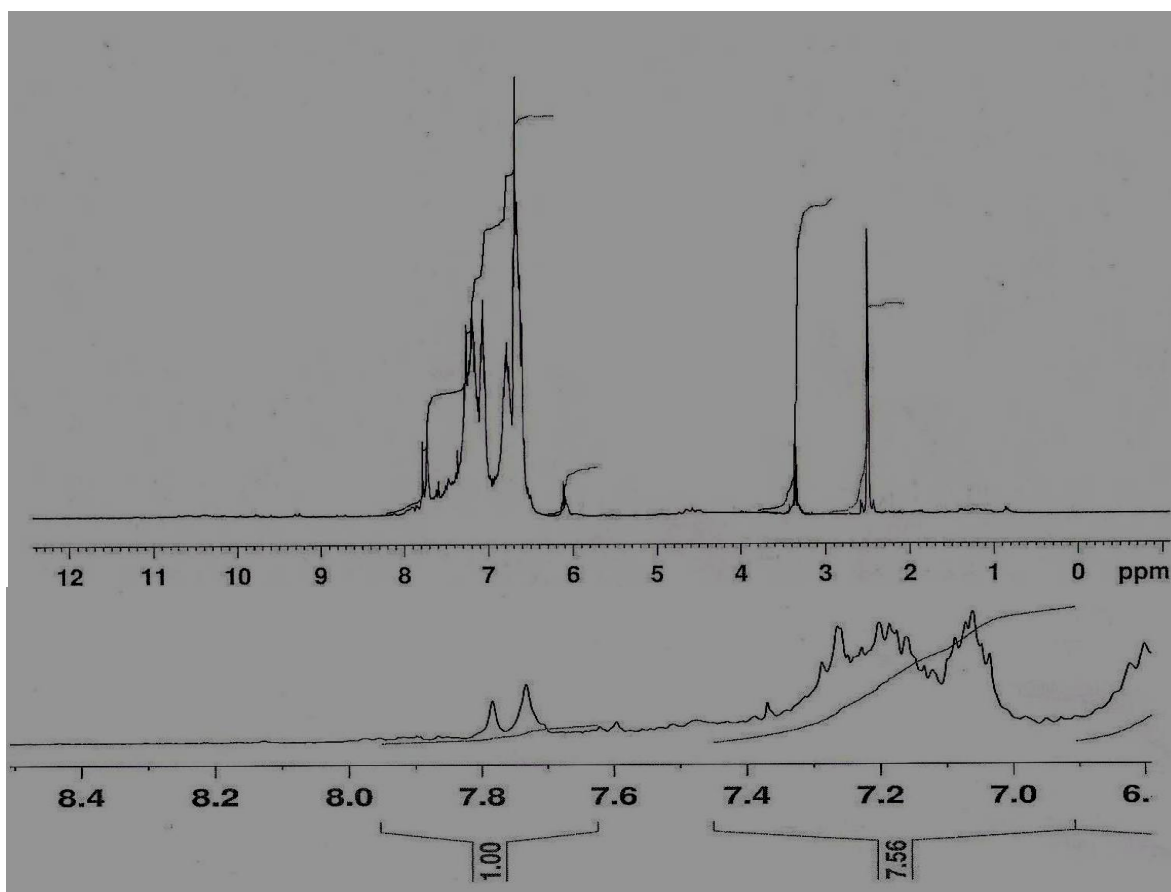


Fig (8) The ^1H NMR spectra for ligand $[\text{H}_2\text{L}]$

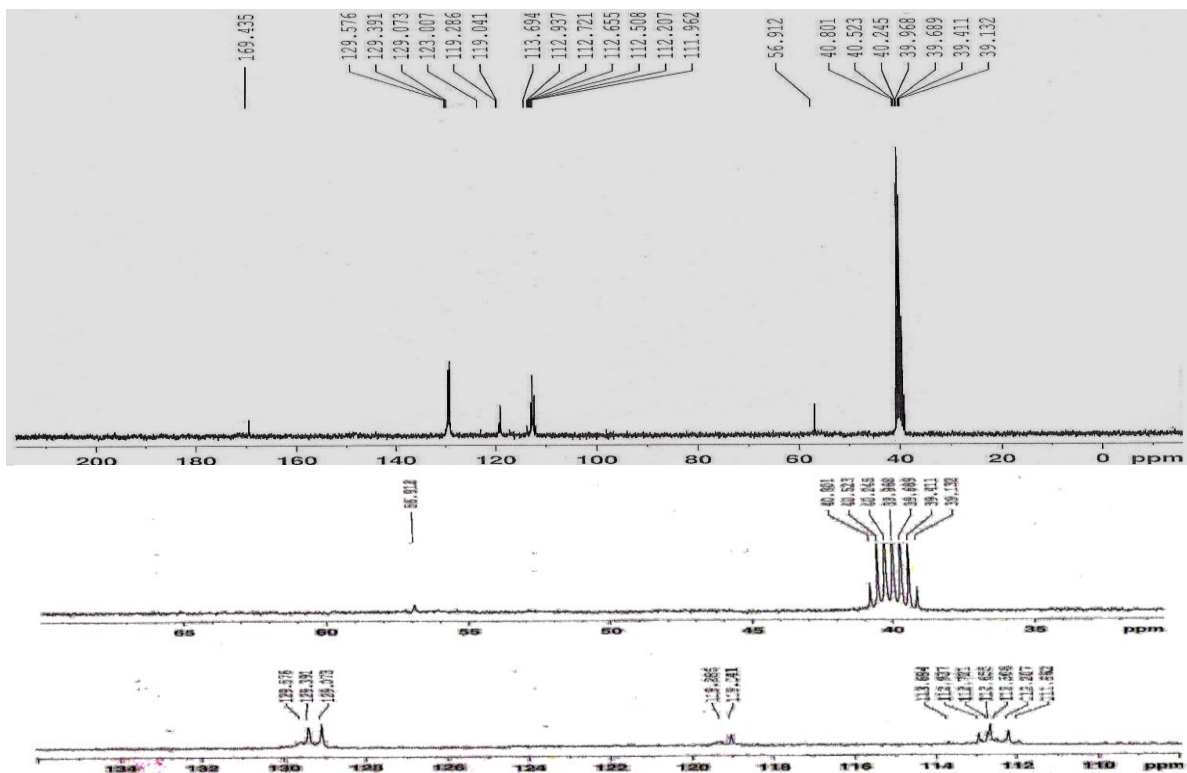


Fig (9) ^{13}C NMR spectra for ligand $[\text{H}_2\text{L}]$

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تحضير وتشخيص بعض المعقدات الفلزية مع ليكاند ثلاثي السن مشتق من هایدرازين الفينيل

حكمت علي محمد**

محمود صالح مطر*

*قسم العلوم الاساسيه/ كلية طب الاسنان/ جامعة الانبار
**قسم الكيمياء /كلية التربية / جامعة صلاح الدين- اربيل

الخلاصة:

تم مفاعلة هایدرازين الفينيل مع كلوريد حامض الخليك بنسبة (1 : 2) في محلول الايثانول القاعدي, حيث تم التصعيد الارجاعي لمدة خمس ساعات ليعطي ليكاند جديد متعدد السن (N- [H₂L] Carboxymethyl-N-phenyl-hydrazino)-acetic acid. استعمل هذا الليكاند لتحضير معقدات مع Cr(III), Co(II), Cu(II) و Pd(II). تم دراسة وتحديد بنى المركبات المحضرة بواسطة التحليل الدقيق للعناصر, اطياف كل من الاشعة تحت الحمراء, فوق البنفسجية والمرئية, الرنين النووي المغناطيسي, قياسات التوصيلية المولارية والحساسية المغناطيسية مع درجة الانصهار. اظهرت هذه الدراسات بأن للمعقدات المحضرة شكلا ثنائي السطوح باستثناء معقد البليديوم حيث الشكل المقترح هو مربع مستوي.