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SYNTHESIS AND CHARACTERIZATION OF SOME NEW TRANSITION METAL COMPLEXES WITH 2,5-di(4-AMINO PHENAZONYL) HEXANE

Abbas Ali Salih Al-Hamdani
Department of Chemistry, College of Science for Women, University of Baghdad.

Abstract

A new tetradentate N_2O_2 type Schiff base ligand 2,5-di(4-amino phenazonyl)hexane L was synthesized from the condensation of 4-aminophenazone and 2,5-hexanedone. Monomeric complexes of this ligand, of general formulae [M(L)]X (M-X=Co(II)-$(OAc)_2$, Ni(II)-$(OAc)_2$, Cu(II)-$(OAc)_2$,VO(II)-SO_4,Zn(II)-SO_4,Mn(II)-Cl_2 or Fe(II)-Cl_2;OAc=acetate) are reported. The mode of bonding and overall geometry of the complexes were determined through I.R, UV-Vis, NMR spectral studies, magnetic moment measurements, elemental analysis, metal content and conductance measurement. These studies revealed tetrahedral geometries for the Co(II), Ni(II),Mn(II),Fe(II) and Zn(II) complexes, square pyramidal for VO(II) complex and square planar for Cu(II) complex. The study of complex formation via molar ratio in DMF solution was investigated and the results were compeer to those found in the solid complexes with a ratio of (M: L) as (1:1)

Keywork: 4-aminophenazone, 2,5-hexanedone, Schiff base complexes.

Introduction

Schiff bases from 2,5-hexanedione have often been used as chelating ligands in the field of coordination chemistry. Recently, liquid crystals researchers have made a significant revelation that the introduction of a lateral polar carbonyl group will enhance the molecular polarizabilty as well as stabilize the liquid crystalline compounds (1).

Diketone compounds take a role in creating various fragrances and compounds to form complexes with many transition metal ions. These compounds are readily soluble in inorganic solvents. Transition metal complexes with tetradentate Schiff base ligands have been extensively investigated as catalysts for a number of organic redox reaction and electrochemical reduction processes (2). Cyclic voltammetry has been a useful tool to investigate the mechanisms of catalysis by Schiff base metal complexes as well as to study the structure reactivity relationships in these compounds (3-5).

Phenazone derivatives are reported to exhibit analgesic and anti-inflammatory effects (6,7), antiviral(8) antibacterial(9)activities. Furthermore, they have been used as hair color additives (10)and to potentiate the local anesthetic effect of lignocaine.(11)

In the present paper, Co(II), Ni(II), VO(II), Mn(II), Fe(II), Zn(II) and Cu(II) complexes with Schiff base derived from 4–amino phenazone and 2,5-hexanedione are reported. These compounds have been characterized in the basis of analysis of the Schiff bases liquid and solid complexes. ^{1}HNMR, ^{13}CNMR, elemental analysis (C.H.N and M) whereas: M= Co,Ni,V,Mn,Fe,Zn and Cu, magnetic measurements, UV-Visible, FTIR Spectra, Conductivity Measurement and Molar Ratio.

Experimental

All the chemicals such as the metal salts [$Co(OAc)_2$. $4H_2O$, $VOSO_4$,$ZnSO_4$, $MnCl_2.4H_2O$, $FeCl_2$, $Ni(OAc)_2$ $6H_2$ $Cu(OAc)_2$. H_2O] and solvents dimetylformamide, Ethanol, Dimethylsulfoxide, diethyl ether and methanol were obtained from Merk and 2,5-hexandione and 4 –amino phenazone were obtained from Fluke and used without further purification. Conductivity measure- ments of 10^{-3}M solutions of the complexes were recorded in DMF at 25C° using Hand-Held Meter LF 330. The electronic spectra of the complexes in UV-Vis region were recorded in DMF solution using Shimadzu Model 160 UV-Visible Spectrophotometer. IR-spectra CsI discs in the range (4000-250)cm^{-1} were obtained using a Shimadzu, FTIR-8400 S Fourier Transform Infrared Spectrophotometer. Atomic

Absorption Data were obtained via using (Shimadzu A.A-160) Atomic absorption/ flame Emission Spectrophotometer. Magnetic properties were recorded via using (Balance Magnetic Susceptibility Model MSR-MKi). Furthermore, Melting Points were measured via using (Gallen Kamp Melting Point).

^{1}HNMR, ^{13}CNMR spectra were recorded via using Bruker 400 MHz Spectrophotometer Elemental Analysis for (C, H and N) was carried out on a Perkin-Elmer Automatic Equipment Model 240.B.

Synthesis of ligand:2,5-di(4-amino phenazonyl) hexane

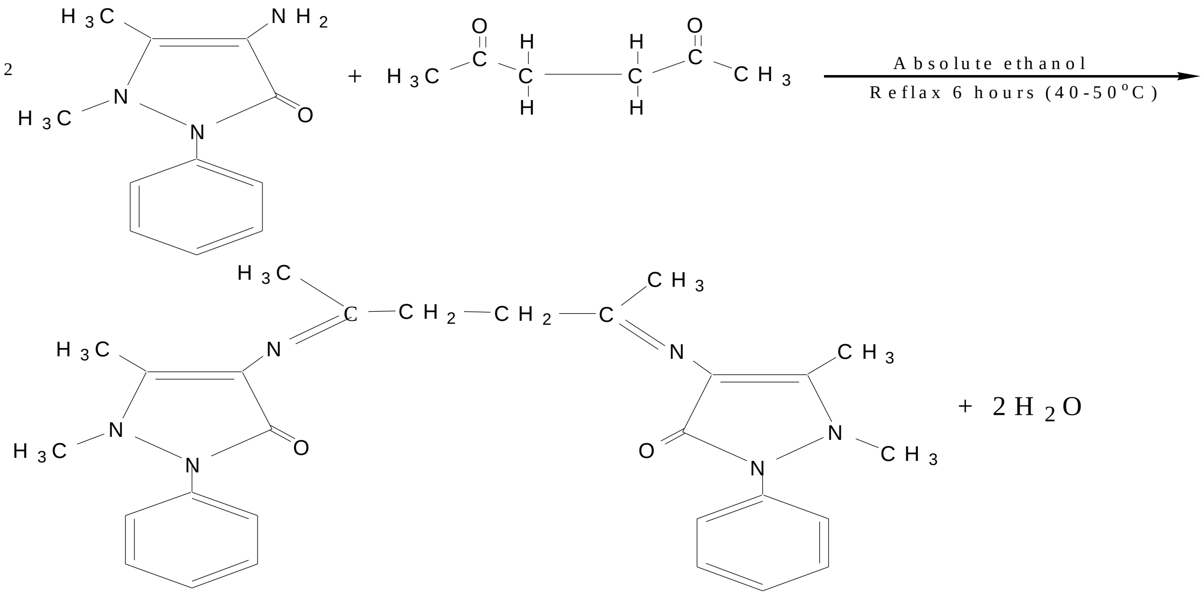
A solution of 4-amino phenazone (4.06 g. 20 mmole) in absolute ethanol (25 ml) was added to a solution of 2,5–hexandione (1.14g, 10mmol) in ethanol (15) ml.The reaction was Stirred and heated in water bath(40-50) ^{o}C for six hr. after the addition of excess of Ethanol (50ml). A colorless precipitated and washed with diethyl ether .Recrystallization has been carried out in methanol. The product was dried via anhydrous $CaCl_2$ in vacuum. The yield is (3.3g),83%,mp.198C^o.

Synthesis of VO(II),Mn(II),Fe(II)Co(II), Ni(II) Cu(II) and Zn(II) complexes:

A solution of metal salts [$VOSO_4$, $MnCl_2.4H_2O$,$FeCl_2$,$Co(OAc)_2$. $4H_2O$, $Ni(OAc)_2$ $6H_2$ $Cu(OAc)_2.H_2O$ and $ZnSO_4$,]in DMF (20mmol) was mixed with the Schiff base in DMF (20mmol, 5.628g) in a (1:1) molar ratio. The contents were refluxed in 100 ml of DMF in an oil bath for six to seven hr. The refluxed solution was poured into ice cold water. A colored solid product was separated and isolated by filtration. Then, was washed with ether. Recrystallization has been carried out in dimethyl sulfoxide and dimethyl formamide. The product was dried via anhydrous $CaCl_2$ in vacuum at room temperature. The yield was in the range (75-83)% for all the complexes with respect to the ligand. They decomposed at 288-300^{o}C.

Results and Discussion

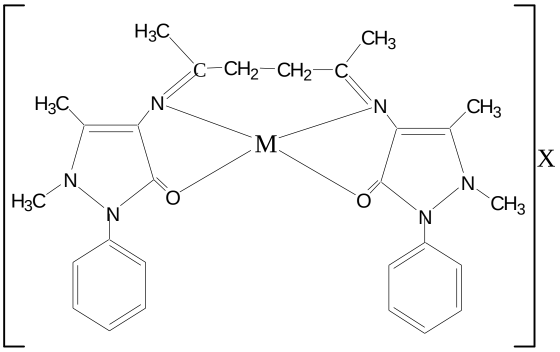
The new Schiff base was synthesized by the condensation reaction of 4–amino phenazone and 2,5-hexandion as described in Scheme (1).



Scheme (1): Preparation of the Schiff Base (L).

Micro analytical, molar conductance and magnetic susceptibility data of the ligand and its complexes are given in Table (1). The stoichiometries of the ligand and its complexes were confirmed by their elemental analyses. The molar conductivity measurements for the complexes were recorded via using DMF in 10^{-3}M solutions, which were in the range (169-178) ohm^{-1}.cm^2 mol^{-1}. The results indicated to their electrolytic (1:2) behavior.$^{(12,13)}$ The Metal-ligand Molar Ratio was found to be

(1:1) according to Elemental Analysis (Fig.(1)).



(M-X=Co(II)-(OAc)$_2$, Ni(II)-(OAc)$_2$, Cu(II)-(OAc)$_2$,VO(II)-SO$_4$,Zn(II)-SO$_4$,Mn(II)-Cl$_2$ or Fe(II)-Cl$_2$;OAc=acetate).

Fig.(1): Suggested structure as a tetrahedral for Co(II), Ni(II), Mn(II), Fe(II) and Zn(II) complexes square-planar for Cu(II) complex and square pyramidal for VO(II) complex.

The transition metal salts reactions with Schiff base are clarified in the following equations.

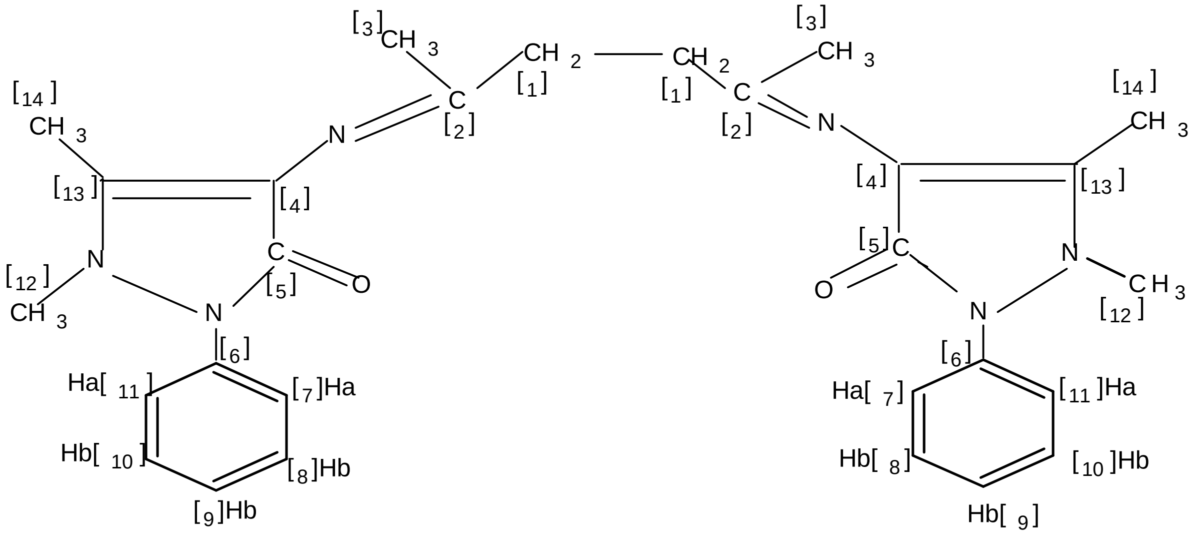
$L+MX.YH_2O \rightarrow [ML]X.H_2O$ where
M,X,Y=VO,SO_4,-; Mn,Cl_2,4;Fe,Cl_2,-;
Co,$(OAc)_2$, 4; Ni,$(OAc)_2$,6; Cu,$(OAc)_2$,-;and
Zn,SO_4,-.

^{1}H and.^{13}C-NMR spectra analysis:

A new synthesized ligand gave a satisfactory spectral data and the molecular structure was assigned on the basis of ^{1}HNMR and ^{13}CNMR chemical shift. NMR spectra were determined in solution of ($CDCl_3$) with tetramethyl silane as an internal reference. The identification was using simple splitting patterns that were produced by the coupling of protons and carbons which they had a very different chemical shifts. according to the results obtained from the shift spectra, The molecular structure was illustrated as follows:

^{13}C-NMR ($CDCl_3$, ppm , 400MHz): δ12.5(C-1), δ153.2(C-2), δ10.62(C-3), δ105.9(C-4), δ162.2(C-5), δ129.3(C-6), δ129.5(C-7), δ67.93(C-8), δ77.29(C-9), δ77.57(C-10), δ127.6(C-11), δ134.6(C-12), δ124.3(C-13), δ109.6(C-14)

^{1}H-NMR ($CDCl_3$,ppm,400MHz): δ7.405-7.52 ppm (2^*.2H,m,a-H), δ7.3-7.36ppm (2^*.3H,m,b-H), δ5.83-5.93 ppm (2^*.2H,t,1-H), δ3.11-3.31 ppm(2^*.3H,s,12-H), δ2.04-2.14ppm (2^*.6H,s,3-H,14-H),$^{(14-16)}$



Infrared Spectra:

The characteristic stretching vibration modes concerning Schiff Base (L) and its metal complexes are described in Table (2).

The ligand (L) exhibited a strong high intensity bands appeared at (3035), (2920) and (1674) cm^{-1}, which were ascribed to the stretching mode of [νC-H aromatic, νC-H aliphatic and νC=O group respectively. Another strong bands appeared at 1620 and 1593 cm^{-1} were assigned to νC=N group.(17) as show in Table (2). Pertaining to the complexes, the Schiff base behaved as a tetradentate ligand, which were been coordinating with the metal via oxygen of carbonyl group and nitrogen of the azomethane group. The mentioned coordination was confirmed by shifting the bands (νC=O and νN=C) to lower frequencies about (24-40) cm^{-1} and (10-15, 11-14) cm^{-1} respectively.(18) as clarified in Table (2).These observations were further indicated by the appearance of (νM-N and ν(M-O) respectively, Table (2). In the other hand, Acetate anion bands for [F,D and E] complexes were observed at (1450, 1446, and 1440) cm^{-1} respectively which indicated to monodentate behavior of the mentioned anion.(19) The υ(V=O) bands appeared very strong 965 cm^{-1} (20).Abroad band was observed around (3450-3505)cm^{-1}in each of Mn(II), Co(II) ,Ni(II) and Cu(II) complexes spectra, which is assigned to νO-H. The results led to a suggestion for the presence of water molecules in the complexes. (21)

UV-Vis spectroscopic study:

The Electronic Spectra of the metal complexes were recorded in their solutions in 10^{-4}M DMF in the range (200-1100) nm. The spectrum of free Schiff base ligand (L) showed strong peaks at (39062 and 33783) cm^{-1} attributed to ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) respectively(22).

For the cobalt complex, The measured Magnetic Moment was (4.56B.M) which is meant that the cobalt ion in its blue complex was paramagnetic with d^7 configuration in a distorted tetrahedral geometry (23).The Electronic Spectrum for this complex showed broad peak at (14840-17505)cm^{-1},the peak was to the transitions ${}^4A_2 \rightarrow {}^4T_1(P)$.(24)

[E] $[Ni(L)](OAc)_2.H_2O$ compound, the presence of the absorption peaks at (17300 and 11049)cm^{-1} which assign to the transition ${}^3T_1 \rightarrow {}^3T_{1}(p)$ and ${}^3T_1 \rightarrow {}^3A_2$.

These transitions were characterized to the tetrahedral geometry around the Ni^{+2} ions. The value of the magnetic moment was 2.8 B.M, which confirmed the structure. Dq value was 450 cm^{-1} (25,26).

[F] $[Cu(L)](OAc)_2$. H_2O, The solution spectrum of the dark green complex exhibited intensive peaks at (29850,27173 and 20533) cm^{-1}. The values of these peaks were in agreement with estimated values for highly distorted octahedral geometry.(27,28) an effective magnetic moment at room temperature was (2.04B.M) which agreed with square planar geometry around Cu(II)complex.(29). The green-yellow complex of Mn(II) showed strong bands at and the shoulder at 24213 cm^{-1}due to ${}^6A_{1\rightarrow}{}^4A_{1+}{}^4E_{(G)}$ finally the band at 15337 $cm^{-1}$${}^6A_{1\rightarrow}{}^4T_2$,these values are accepted for tetrahedral complex(30), the dark-green complex of iron(II) showed band at 31545cm^{-1} belong to (LMCT) and another band at 22174 cm^{-1}caused by the electronic transition ${}^5E \rightarrow {}^5T_2$(31). The oxovanadium(IV) complex, electronic spectrum of shows three absorption bands at 26455,21645 and 13262 cm^{-1} respectively, which is consistent with a five-coordinate, square-pyramidal and is assigned to ${}^2B_{2g} \rightarrow 2A_{1g}$, ${}^2B_{2g} \rightarrow 2B_{1g}$ and ${}^2B_{2g} \rightarrow 2E_g$ transitions.The spectrum of $[ZnL]SO_4$,gave as absorption above 20833 cm^{-1}, represents the internal ligand charge transfer.

Table (1)
The Physical properties, and Elemental Analyses for the ligand and its metal complexes.

Compounds	***F.Wt. g/mol***	***m.p (^OC)***	***Yield (%)***	***Elemental Analysis Calculated (Found) %*** ***C% H% N% M%***	***Ωo ohm^{-1} cm^2.mol^{-1}***	***μeff (BM)***
Ligand (**L**) colorless $C_{28}H_{32}N_6O_2$	484	198	83	69.4, 6.61, 17.2 , - (68), (6.05), (18.5), -	-	-
A-[VOL]SO_4 Pale-Green $C_{28}H_{32}N_6O_7SV$	665.348	305	78	50.5, 4.84, 12.63, 7.656 (49.53) (5.12) 11.97) (8.01)	173	1.71
B-[MnL]Cl_2 Green-yellow $C_{28}H_{34}N_6O_3Cl_2Mn$	653.188	316	69	51.487, 4.899, 12.866, 8.41 (52.09), (4.12), (11.68), (8.98)	169	4.65
C-[FeL]Cl_2 Dark-green $C_{28}H_{32}N_6O_2Cl_2Fe$	611.097	332	72	55.03, 5.236, 13.75, 9.138 (55.99), (4.65), (12.76), (10.11)	177	4.7
D-[CoL]$(OAc)_2$. H_2O blue $C_{32}H_{40}N_6O_7Co$	705.93	292	75	92.64, 5.66, 11.80, 8.34 (91.01), (6.1), (13.2), (8.05)	178	4.56
E-[NiL] $(OAc)_2$. H_2O blue $C_{32}H_{40}N_6O_7Ni$	705.69	280	83	92.67, 5.66, 11.03, 8.31 (93.15),(6.2),(11.8),(7.92)	172	2.8
F-[CuL]$(OAc)_2$. H_2O dark green $C_{32}H_{40}N_6O_7Cu$	710.5	300	78	92.04, 5.42, 11.88, 8.92 (93.2),(4.98),(13.4),(9.98)	169	2.04
F-[ZnL]SO_4 colorless $C_{28}H_{32}N_6O_6SZn$	645.798	288	88	52.07, 4.99, 13.013, 10.125 (53.01), (5.07), (12.89), (10.01)	170	Diamagnetic

Table (2)
The Characteristic infrared spectra bands for the ligand and its metal complexes.

Compounds	***Water υO-H***	***υC-H arom*** ***υC-H alph***	***υC=O***	***υC=N***	***υN-N*** ***υAr-N***	***υM-N*** ***υM-O***	***υM-OAc*** ***υM-SO_4*** ***υM-Cl***
(**L**)	-	3035	1674	1620	1034	-	-
		2920		1593	1321	-	
[VOL]SO_4	-	3050 2940	1650	1600 1580	1030 1322	512 486	1080
[MnL]Cl_2	3484	3048 2927	1648	1602 1579	1039 1324	498 450	405
[FeL]Cl_2	-	3030 2930	1646	1604 1581	1033 1321	495 442	392
[CoL]$(OAc)_2$. H_2O	3450	3040 2920	1634	1605 1579	1031 1320	510 480	1446
[NiL]$(OAc)_2$.H_2O	3470	3045 2915	1639	1609 1580	1035 1322	519 460	1440
[CuL]$(OAc)_2$. H_2O	4505	3038 2924	1642	1610 1582	1035 1320	495 439	1450
[ZnL]SO_4	-	3049 2930	1645	1609 1583	1032 1324	495 442	1100

Table (3)
Electronic Spectra in (DMF) Solvent for The Ligand and its Metal complexes.

Compounds	*λnm*	*ABS*	*νCm^{-1}*	*Transition*	*Suggested Structure*
(**L**)	256	1.65	39062.5	$\pi\rightarrow\pi^*$	-
	296	2.24	33783.7	$n\rightarrow\pi^*$	
$[VOL]SO_4$	240	1.12	41666	Ligand field	Square pyramidal
	310	1.26	32258	Ligand field	
	378	2.13	26455	$^2B_{2g}\rightarrow 2A_{1g}$	
	462	0.24	21645	$^2B_{2g}\rightarrow 2B_{1g}$	
	754	0.41	13262	$^2B_{2g}\rightarrow 2E_g$	
$[MnL]Cl_2$	274	1.36	36496	Ligand field	Tetrahedral
	321	2.23	31152	LMCT	
	413	0.07	24213	$^6A_1\rightarrow{}^4A_1+{}^4E_{(G)}$	
	652	0.04	15337	$^6A_1\rightarrow{}^4T_2$	
$[FeL]Cl_2$	275	1.12	36363	Ligand field	Tetrahedral
	317	1.97	31545	LMCT	
	451	0.08	22172	$^5E\rightarrow{}^5T_2$	
$[CoL](OAc)_2.\ H_2O$	263	1.05	38022.8	Ligand field	Tetrahedral
	285	1.60	35087.79	Ligand field	
	340	2.12	29411.76	LMCT	
	610	0.25	16393	$^4A_2\rightarrow{}^4T_1(P)$	
$[NiL](OAc)_2.H_2O$	310	1.78	32258	Ligand field	Tetrahedral
	407	1.9	24570	LMCT	
	578	0.095	17300	$^3T_1\rightarrow{}^3T_1$	
	905	0.05	11049	$^3T_1\rightarrow{}^3A_2$	
$[CuL](OAc)_2.\ H_2O$	262	1.65	38167	Ligand field	Square Planar
	315	2.34	31746	LMCT	
	335	0.5	29850	$^2B_{1g}\rightarrow{}^2A_{1g}$	
	368	0.19	27173	$^2B_{1g}\rightarrow{}^2B_{2g}$	
	487	0.02	20533	$^2B_{1g}\rightarrow{}^2E_g$	
$[ZnL]SO_4$	260	1.09	38461.5	Ligand field	Square Planar
	387	1.64	25839.8	Ligand field	
	480	1.97	20833.3	LMCT	

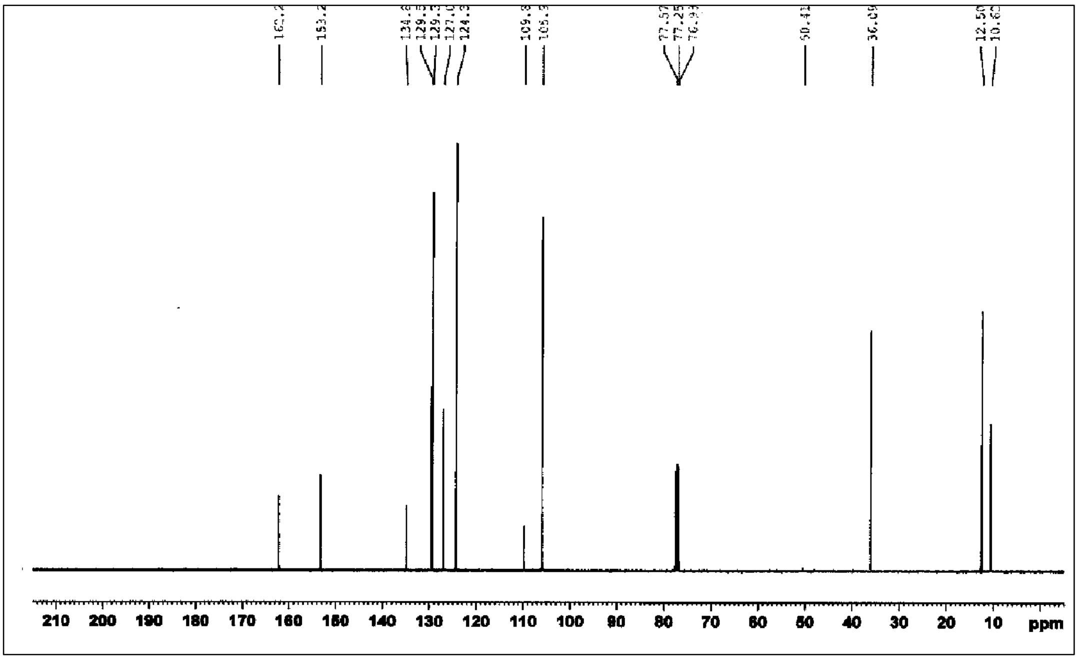


Fig. (1) : ^{13}C-NMR spectrum of the ligand (L).

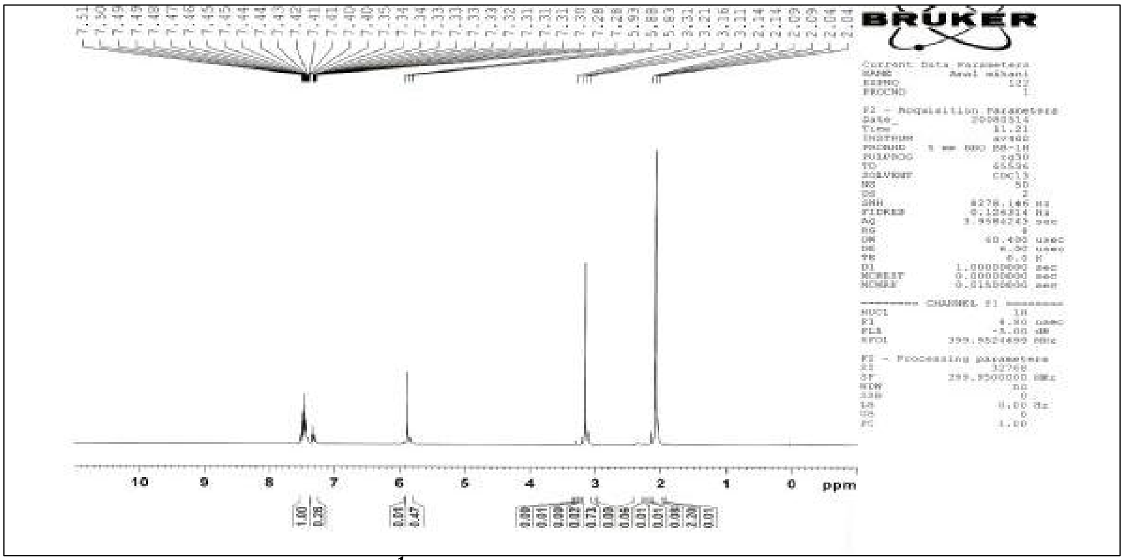


Fig. (2) : ^{1}H-NMR spectrum of the ligand (L).

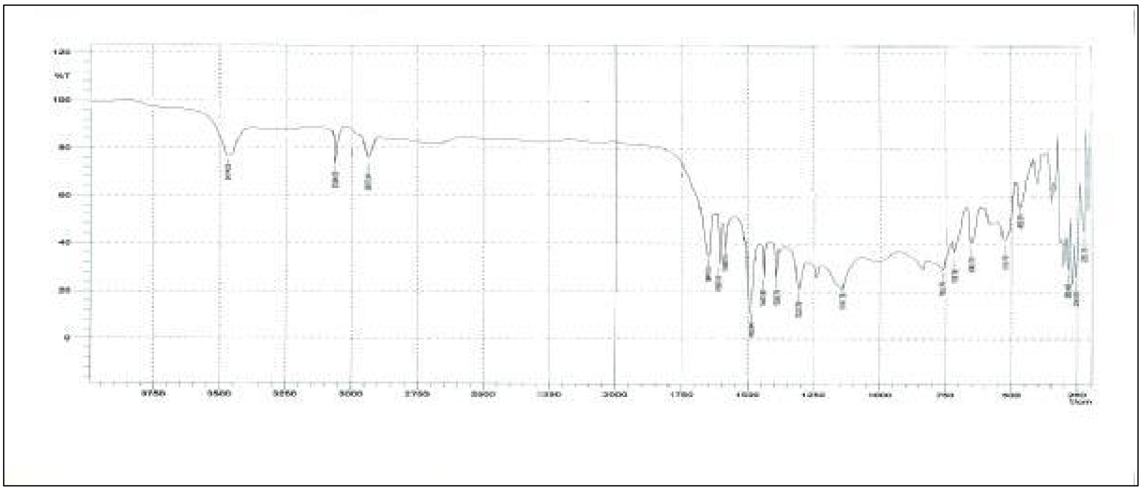


Fig. (3) : FT.IR spectrum for [NiL]$(OAc)_2.H_2O$ complex.

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الخلاصة

حضرت قاعدة شف الجديدة رباعية السن N_2O_2 مع 5,2-ثنائي (4-أمينوفينازويل)هكسان من تفاعل 4-امينو-2، 3-ثنائي مثيل-1-فنيل-3- بايروزولين-5-أون مع 2، 5-هكسان دايون حيث تم استخدام قاعدة شف (L) لتحضير عدد من المعقدات الجديدة مع ايونات العناصر الانتقالية الاتية:

VO(II),Mn(II),Fe(II),Co(II),Ni(II),Cu(II),Zn(II)

تم تحديد الشكل الهندسي المقترح لليكاند والمعقدات المحضرة من خلال تشخيصها بوساطة تحليل طيف الاشعة تحت الحمراء (FTIR) ، طيف الاشعة الرنين النووي المغناطيسي (^{1}HNMR) ، (^{13}CNMR) فضلاَ عن طيف الاشعة فوق البنفسجية والمرئية (UV-Vis). وتقنية الامتصاص الذري اللهبي للعناصر والتحليل الكمي الدقيق للعناصر (كاربون- هيدروجين، نتروجين) فضلاَ عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية.أظهرت الدراسة ان الشكل الهندسي رباعي السطوح لمعقدات الكوبلت والنيكل والمنغنيز والحديد والخارصين ثنائيات التكافؤ بينما اعطت شكل مربع مستوي لمعقد النحاس ثنائي التكافؤ بينما شكل هرم مربع القاعدة لمعقد الفناديل ، تم قياس النسبةالمولية للفلز مع الليكاند (L) في محلول ثنائي مثيل فورامايد وقد أعطت نتائج مطابقة مع التي تم الحصول عليها في الحالة الصلبة.بنسبة (1:1) من (الفلز:الليكاند).