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Synthesis and characterization of Phenyl bis-hydrazone complexes with Pd (II), Mn (II), Ni (II) and Fe(III) ions.

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الخلاصة:-

تم تحضير ليكاند جديد من فنيل-ثنائي-هايدرازون(V) من خلال التفاعل بين فنيل-آيزاتين هايدرازون و سالسيل-الديهايد، و تم تشخيص 'اليكاند مستخدماَ دراسات أطياف (IR)، (^{1}H-n.m.r) ، (^{13}C-n.m.r) و قياسات التوصيلية، في حين شخصت المعقدات لـ [Pd(II) ، Ni(II)، Mn(II)، Fe(III) مع فنيل-ثنائي هايدرازون باستخدام قياسات التوصيلية المولارية و الحساسية المغناطيسية و دراسات اطياف IR و Uv-Vis.

حيث تشير القياسات الطيفية الى ان الليكاند ثلاثي السن من خلال ذرة الاوكسجين الفينولين، نيتروجين-ايزوميثاين، اوكسجين-الكاربونيل في جزء الايزانين. و اعتمادا على النتائج اعلاه فقد تم اقتراح الشكل الثماني السطوح لجميع المعقدات المذكورة.

Abstract:-

A new ligand of phenyl bis-hydrazone (V) was been synthesized as a result of a reaction between phenyl-isatin hydrazone and salicyladehyde. The yellow crystals of (V) was been studied using IR, ^{1}H.n.m.r ^{13}C-n.m.r, UV-Vis spectrum and molar conductivity measurements. The complexes of Palladium (II), Nickel (II), Manganese (II) and Iron (III) with phenyl bis-hydrazone have been synthesized and characterized on based on molar conductivity, magnetic susceptibility data, UV-Vis and IR spectral studies. The spectral data referred to that the ligand acts as monobasis tridentate, coordinating through phenolate oxygen, azomethine nitrogen, and carbonyl oxygen of isatin moiety. On the basis on the above results an octahedral geometry has been proposed for the mentioned complexes.

Keyword: Phenyl- bis hydrazone, complexes.

Introduction

Isatin (1H-indole-2, 3-dione) was first obtained by Erdman and Laurent in 1841 as product from oxidation of indigo by nitric and chronic acid[1].

The synthetic versatity of isatin has led to extensive use of this compound in organic synthesis. The synthetic versatity of isatin has stemmed from the interest in the biological and pharmaceutical properties of its derivatives. [1]

The isatin derivatives are fully detailed in the supplementary researches, Schiff bases of isatin were reported to possess antibacterial, antifungal, antiviral, anti HIV, antiprotozoal and anthelminic activities. [2]

The discovery of the anticancer activity of cis-dichlorodiammine platinum (II) (Cisplatin) and subsequently its use as drug in the treatment of several human tumors, estimated many research group to synthesize new platinum group metal complexes and test them for their anti-tumor activity. [3]

The study of three different Schiff base derived from isatin and thiosemicarbazide, were used to study of antigungal activities of thiosemicarbazones and their corresponding metal chleates, which explained that the substitution dependent with the chemical nature of the segment attached to the thione(C=S) carbon atom having the greeting effect. [4]

The synthesis of transition metal complexes with Schiff base hydrazone bases of nitrogen and oxygen donor has stimulated interest due to their vast variety of biological activities ranging from pharmological, anti tumor, fungicide bactericide antifalmentory and anti-viral activities. [5]

A significant rising in the design of metal compounds as drug and diagnostic agent is curr observed in the area of scientific inquiry appropriately termed medical inorganic chemistry, based on these arguments, different copper compounds with diverse ligands have been isolated and potential therapeutic agent, among them are oxindoles which are endogenous compounds found in mammalian body fluids and tissues, ubiquitously displace the central nervous system, that have shown an extensive range of biological effects, including antifungal, anticonvulsant, antiviral and anti proliferate activity. [6]

Besides hydrazone are azomethines characterized by the presence of triatomic group >C=N-N< and form an interesting class of compounds which find extensive application in various field. [7]

In this present work the efforts were been made to synthesize of a new ligand of phenyl-bishydrazone and their related complexes with Pd(II), Mn(II), Ni(II) and Fe(III). Our interest aim is synthesize of a ligand which binding with the central metal throng oxygen and nitrogen atoms which plays important role in biological and medical fields.

Experimental

a- All chemical are AR grade

b- Instruments:

1- Melting point and decomposed degree were measured employing Electrothermal 9100 (UK).

2- IR spectra were recorded as KBr dises in range (4000-400) cm^{-1} using Bio-Red MERLIN, FT-IR spectroscopy mod Ts 3000(KBr) and a Py-Unicam-300 infrared spectrophotometer in the range (4000-200) cm^{-1} (KBr).

3- The ^{1}H.n.m.r and ^{13}C.n.m.r were taken on a Bruker Ultra shield 300 MHZ with DMSO in Al-al- Bayt Central labs. (Jordan).

4- Uv-Vis spectra were recorded on a Data stream- CE 3000 series

5- Magnetic susceptibilities of the complexes were determined at 25 C^{o} using Bruker magnet BB6.

6- The Conductivity of the ligand and complexes were made on Jenway conductivity meter 4200(0. 93) cell constant (U.K)

7- A Py-UNICM SP9 atomic absorption spectrophotometer was used to measuring atomic absorption spectra of the complexes.

Synthesis of Phenyl Monohydrazone:-

A quantity of isatin(2.942 gm, 20 m.mole) was dissolved in 40 ml of methanol and was added to a 10 ml of methanolic solution of phenyl hydrazone (2. 162 gm, 20 m. Mole)the resulting mixture was refluxed for 3 hours on a hot plate magnetic stirrer and an yellow colored compound separated out on cooling. It was filtered m dried in vaccum and further purified by recrystallization from methanol m.p 268 ^{o}C.

Synthesis of the phenyl-bishydrazone:-

To a solution of phenyl monohydrazone (1.19 gm, 5 m.mole) in hot methanol (40) ml, a (0.61 gm, 5 m.mole) of salicylaldehyde in methanol (10) ml solution was added. The resulting mixture was refluxed on hot magnetic stirrer for 4 hrs. The orange colored crystals separated out was filtered, washed with methanol and dried in vaccum. The ligand was further purified by recrystallization from methanol. m.p (214-216) ^{o}C.

Synthesis of metal complexes:-

Palladium (II) complex:-

In order to synthesizing of Pd(II) complex, a (0.176 gm, 0.5 m.mole) of a ligand (ν) was dissolved in methanol (25)ml then a solution of (0.04275 gm , 0.25 m.mole) of Pd(II)chloride in methanol(25ml) was added to above solution in small portion and the refluxing was continued for 3 hrs. The resulting solution was concentrated and allowed to cool. The dark-Red product separated, was filtered, washed successively with methanol either and finally dried in vaccum d.c 268 ^{o}, Table (1)

Iron (III) complex:-

Ferric chloride (0.040gm, 0.25 m.mole) was dissolved in methanol (25ml) and it was added gradually to a hot magnetically stirred solution of the ligand (ν) (0.176 gm, 0.5 m.mole) in methanol (25ml). The mixture was refluxing for 3 hrs. A yellow crystals complex was filtered, washed with methanol and dried in vaccum., d.c 216 ^{o}. Table (1).

Mn (II) complex:

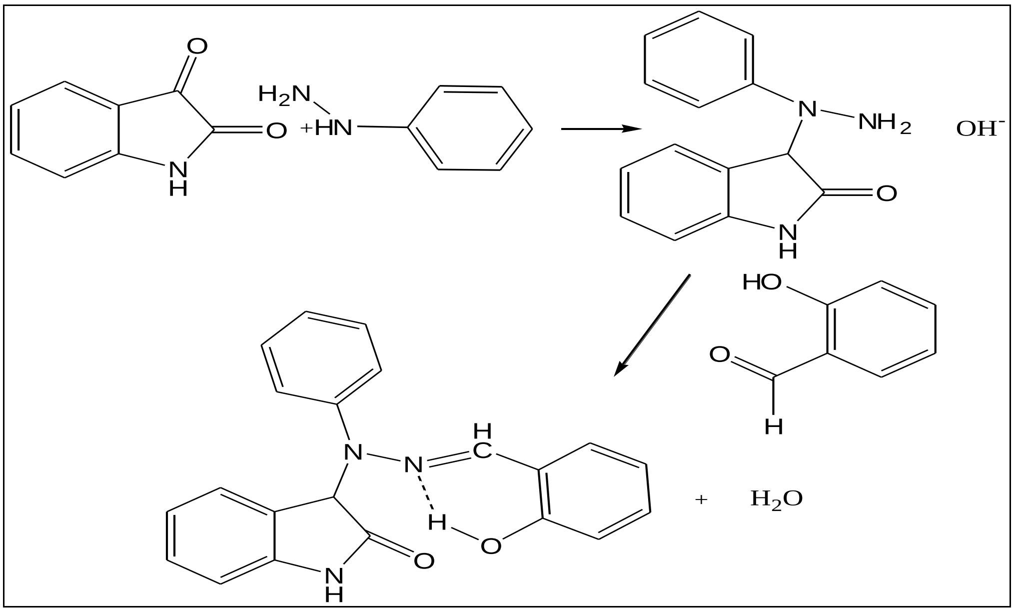
A (0.046 gm, 0.25 m.mole) solution of $MnCl_2.4H_2O$ in methanol (25ml) was added gradually to hoted solution of ligand (ν) (0.176 gm , 0.5 m.mole) in (25) ml of methanol, the mixture was refluxed for 3 hrs., the yellow-green crystals were separated, washed with methanol, dried in vaccum. Yield 82.29% d.c 253 ^{o}. Table (1).

Ni (II) complex

To a solution of (0/176 gm, 0.5 m.mole) of ligand (ν) in methanol (25), a (0.046 gm, 0.25 m.mole) of $NiCl_2$. $4H_2Cl_2$ in (25ml) of methanol was added, the resulting mixture was refluxed for 3 hrs. Then green-yellow crystals were allowed to separate, filtered, dried in vaccum, d.c 223 ^{o} Table (1).

Results and Discussion:-

Phenyl bis hydrazone (V) was synthesized according to the following scheme:



The ligand has been characterized by IR, Uv, 1H-n.m.r , ^{13}C-n.m.r spectra and molar conductivity, The infrared spectrum of the ligand (ν) Fig(1) and Table(2) exhibits the characteristics bands at 3200 and 1685 cm^{-1} which assigned to ν(NH) of indole ring and ν(C=O) respectively[8], while the bands at 3131 cm^{-1} due to ν(N-H) group in ligand (V) spectrum and disappearance of band around(1250-1270) cm^{-1} indicated of the absence of ν(C=N) in it and the vibration characteristics at 3300 and 3525 cm^{-1} of ν(NH_2) which was appeared at a spectrum of ligand (IV) and disappearance it in spectrum of ligand (V).[9,10] The appearance of a sharp peak at 1617 cm^{-1} may be due to ν(C=C) aromatic ring.[11] The ^{1}H.n.m.r of the ligand (V) showed a set of signals.

The peak which arises around σ (6.914- 7.271) ppm which due to (2H, metaprotons) and σ (7.247-7.415) ppm which assigned to (2H, para protons).[12, 13] The signal which ranged between σ (2.45-2.5) ppm may be due to (1H, CH) and a peak which appeared around σ (3.38-3.44) ppm which due to (1H, NH) [14]. Other peaks at σ (11, 12.75) ppm are due to (NH and OH) respectively [15]. The ^{13}C.n.m.r was been studied according to system in Fig (3). The major band showed in Fig (4).

The appearance of sets of band at σ [(39.120, 39.397, 39.676, 40.232, 40.510, 40.786)] ppm may due to DMSU solvent [11]. The peak which arised at σ (142.970, 140.276) ppm which due to aromatic (C_1- NH) ring and σ

(163.647) ppm which due to (C_8-C=O), while σ (110.972, 114.536, 115.415, 128.963 129.545, 129.545, 129.93] (aromatic carbons) [9, 16, 17]. Another bands were listed in Table (2). The study of UV-Vis spectra of ligand (V) exhibited the transition bands at 25000 cm^{-1} and 38535 cm^{-1} which assigned to ($\pi-\pi^*$ *and* $n-\pi^*$) transitions respectively[18] Fig(5).

The molar conductivity was carried out using 10^{-3} M solution in DMSO at a room temperature the results exhibited a non-conductance ligand. Table (1)

The metal complexes were studied using IR, UV-Vis, molar conductivity and magnetic susceptibility, The IR spectral data of the complexes are presented in Table(2) and Fig(6). The weak band at (3444-3440)cm^{-1} which due to ν(OH) of salicylidine moiety[7] disappeared in the complex spectra indicating the formation of metal bond, consequently the phenolic ν(C-O) frequently increased by ~80 cm^{-1} confirming the coordination of the phenolate oxygen [19]. The ν(C=N) ketamine is shifted to lower frequently by about 25 cm^{-1} in complexes indicating the involvement of the azomethine nitrogen in chleation with metal ion. The band corresponding to ν(C=O) is shifted to lower frequency by ~ 40 cm^{-1} in the spectra of the complexes indicating the binding via carbonyl oxygen.

However, the characteristic ring ν(NH) at 3131 cm^{-1} are main almost unaffected. The far infrared spectra of the Pd (II) complex showed characteristic bands which are not observed in the ligand spectrum. The band which appeared at 409 cm^{-1} may due to ν(pd-N) while the band which appeared at 514 cm^{-1} may due to ν(Pd-O) [20].

The electronic spectra of complexes Fig (7) and Table (1) showed a major transition bands. The transition band for pd (II) complex d^8 system exhibited bands at 19342 cm^{-1} (ν_2) and 26178 cm^{-1} (ν_3) and calculated transitions equal to 15000 cm^{-1} which are related to ${}^3A_2g \xrightarrow{\nu_3} {}^3T_2g$, ${}^3A_2g \xrightarrow{\nu_2} {}^1Eg$ and ${}^3A_2g \xrightarrow{\nu_1} {}^3T_1g$ respectively these transition are indication of an octahedral geometry. [21]

Another transition peaks are listed in Table (1) which they indicated that the complexes have octahedral geometrical shapes. The magnetic study explained that the manganese (II) complexes are high-spin type with (B.M = 4.8) [22]. In high spin iron (III) complexes the ^6S free ion ground term is the term arising from d^5 and it does not split in a crystal field (B.M = 5.81). [23]

The pd(II) and Ni(II) complexes are related to d^8 system which have ^3F term symbol they have (B.M= 2.12 and 3.05) respectively [24,25].

They study of the molar conductivity showed that the ligand and its related complexes are non-conductance (except iron(III) complex is ionic), using 10^{-3} M solution in DMSO at room temperature. The atomic absorption study of Ni(II) complex exhibited that the ratio between L/M is approximately 2/1 Table(4).. According to the mentioned studies an octahedral geometry was been suggested for all of the synthesized complexes Fig. (8, 9) .

Table (1) : The Physical properties of synthesized compounds

Compounds	Molecular weight	Color	Yield %	UV-Vis cm^{-1} in DMSO	Transition	Molar conductance $ohm^{-1}.cm^2\ mol^{-1}$	Magnetic Moment B.M
$C_{21}H_{16}N_3O_2$(V)	342	Orange	76.2	25000 35535	$\pi - \pi^*$ $n - \pi^*$	2.08	---
$(C_{21}H_{14}N_3O_2)_2$ Pd	786.4	Dark-red	79.29	15000 19342 26178	${}^3A_2g \rightarrow {}^3T_1g\ (\nu_1)$ ${}^3A_2g \rightarrow {}^1Eg\ (\nu_2)$ ${}^3A_2g \rightarrow {}^3T_2g\ (\nu_3)$	2.04	2.12
$(C_{21}H_{14}N_3O_2)_2$ Fe	735.85	Yellow	81	17421	${}^6A_1g \rightarrow {}^4T_1g\ (\nu_1)$	54.5	5.81
				18450	${}^6A_1g \rightarrow {}^6T_2g\ (\nu_2)$		
				19607	${}^6A_1g \rightarrow {}^6T_2g\ (\nu_2)$		
				24813	${}^6A_1g \rightarrow {}^4Eg\ (\nu_3)$ ${}^6A_1g \rightarrow {}^4A_1g\ (\nu_3)$		
$(C_{21}H_{14}N_3O_2)_2$ Mn	734.94	Yellow-green	82.29	17421	${}^6A_1g \rightarrow {}^4T_1g\ (\nu_1)$	2.08	4.8
				18450	${}^6A_1g \rightarrow {}^4T_2g\ (\nu_2)$		
				24813	${}^6A_1g \rightarrow {}^4Eg\ (\nu_3)$ Or ${}^6A_1g \rightarrow {}^4A_1g\ (\nu_3)$ ${}^6A_1g \rightarrow {}^4T_2g\ (\nu_3)$		
$(C_{21}H1_4N_3O_2)_2$ Ni	738.71	Yellow-green	86	14166	${}^3A_2g \rightarrow {}^3T_1g\ (\nu_1)$	2.04	3.05
				19607	${}^3A_2g \rightarrow {}^1Eg\ (\nu_2)$		
				25000	${}^3A_2g \rightarrow {}^3T_2g\ (\nu_3)$		

Table (2): IR spectra band in cm^{-1} of the synthesized compounds

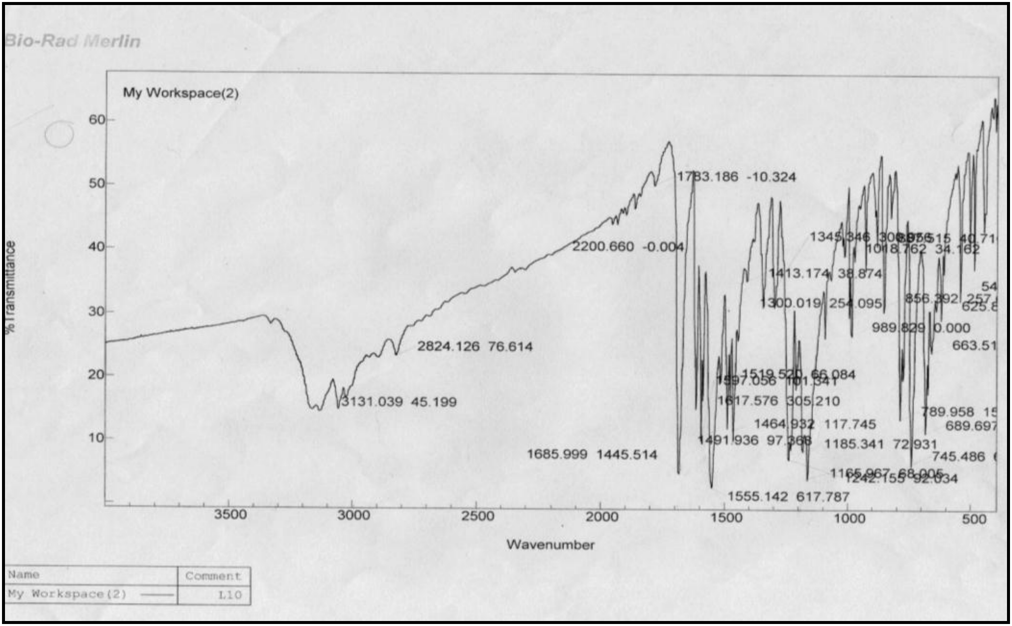
Compounds	**Tentative assignment**								
	ν(OH)	**Indole ring ν (NH)**	**ν (C=O)**	**ν (C=N) ketimine**	**ν (C=N) aldimine**	**ν (C-O)**	**ν (N-N)**	**ν (M-N)**	**ν (M-O)**
(IV)	3300	3280	1723	1600	1590	1282	995	--	--
(V)	3350 (V.W)	3200	1700	1617	1597	1266	989	--	--
Pd(II) complex	--	3150	1660	1660	1594	1345	1087	409	514
Fe(III) Complex	--	3165	1683	1683	1597	1345	1091	411	516
Mn(II)Complex	--	3230	1680	1680	1596	1345	1093	414	512
Ni(II) complex	--	3230	1683	1683	1598	1345	1095	416	517

Table (3) : The ^{13}C.n.m.r data of ligand (V).

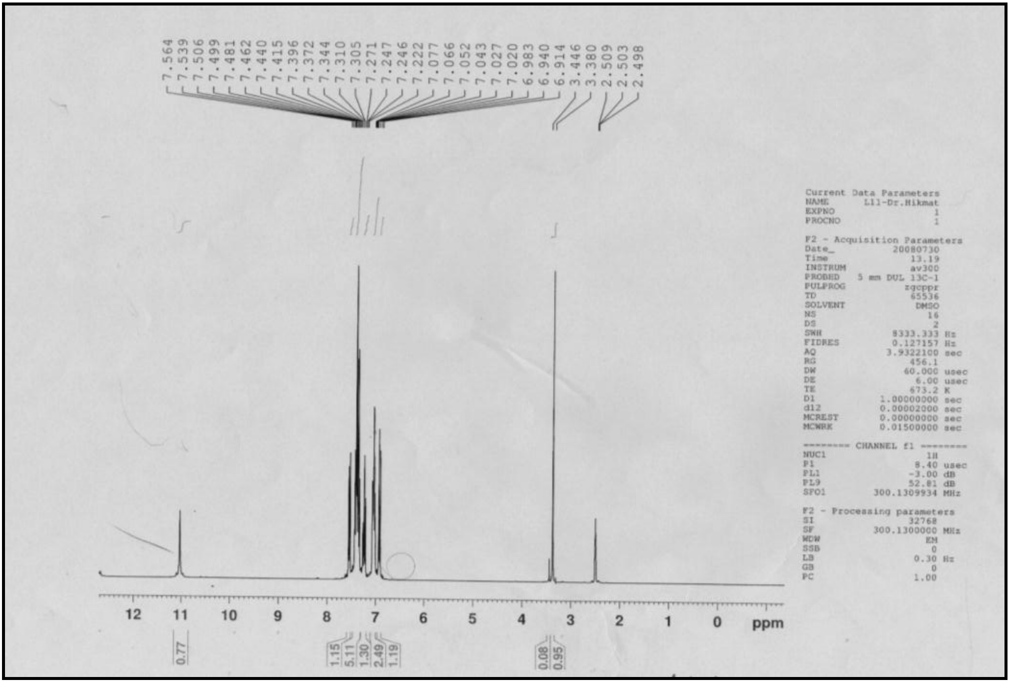
Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}
V	142.970	121.627	128.115	122.330	123.359	129.939	128.963	163.647	-	119.084	-	121.627	-	114.53	--
						m.Carbon of Aromatic ring 129.345 129.939								o.Carbon of Aromatic ring 110.972	
														p.Carbon of Aromatic ring 115.415	

Table(4): The atomic absorbtion data for phenyl bis-hydrazone (L)complexes

Standard curve of Cu(II)ion		Standard curve of Ni(II)ion		Standard curve of Fe(III) ion	
Conc.(ppm)	Abs.	Conc.(ppm)	Abs.	Conc.(ppm)	Abs.
2	44	5	12	5	10
4	98	10	24	10	20
6	124	15	36	15	31
8	162	20	45	20	34
[L-Cu]complex	73	[L-Ni]complex	9	[L-Fe]complex	7
r=0.9902 a=12 b=19 Conc.of Cu(II)3.21ppm in 10 ppm of [L-Cu]complex [L] = 10.00-3.21=6.70 ppm L/M = 6.70/3.21 ≅ 2.08		r=0.9978 a=1.5 b=2.22 Conc.of Ni(II) =3.40 ppm in 10 ppm of [L-Ni]complex ∴ [L] = 6.6 ppm ∴ L/M = 6.6/3.40=1.94 ≅ 2.0		r=0.9981 a=0.5 b=1.86 Conc.of Fe(III) =3.3 ppm in 10 ppm of [L-Fe]complex ∴ [L] = 6.7 ppm ∴ L/M = 6.7/3.3 ≅ 2.03	



Fig(1) The IR Spectra of Ligand(V).



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PROCNO                 1

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PULPROG           zgcppr
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH             8333.333 Hz
FIDRES          0.127157 Hz
AQ             3.9322100 sec
RG                 456.1
DW                60.000 usec
DE                  6.00 usec
TE                 673.2 K
D1            1.00000000 sec
d12           0.00002000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

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NUC1                  1H
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PL1                -3.00 dB
PL9                52.81 dB
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F2 - Processing parameters
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Fig(2): The ^{1}H.n.m.r Spectra of ligand (V) .

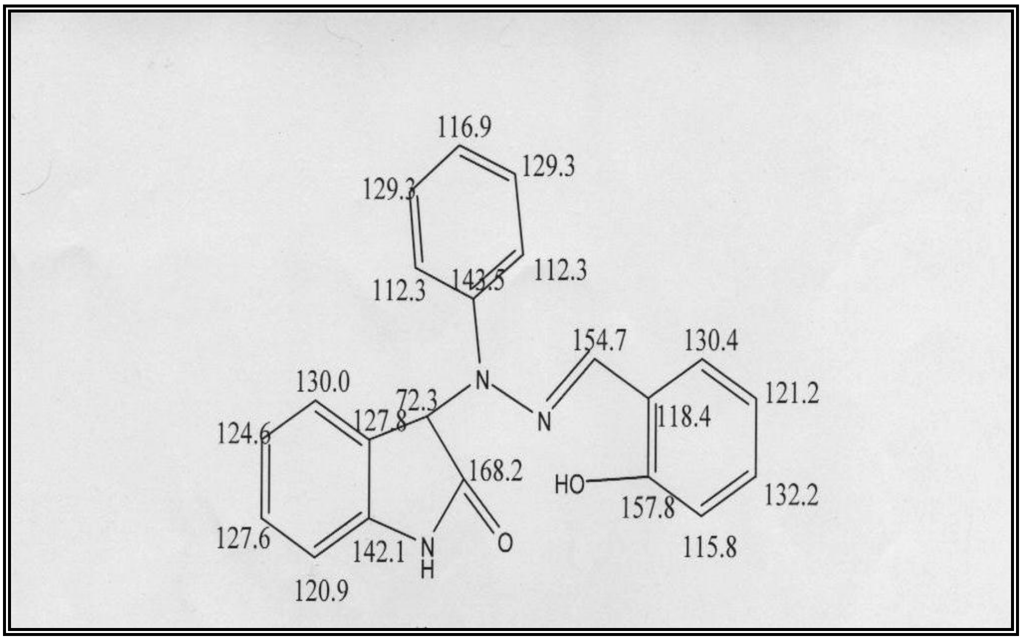
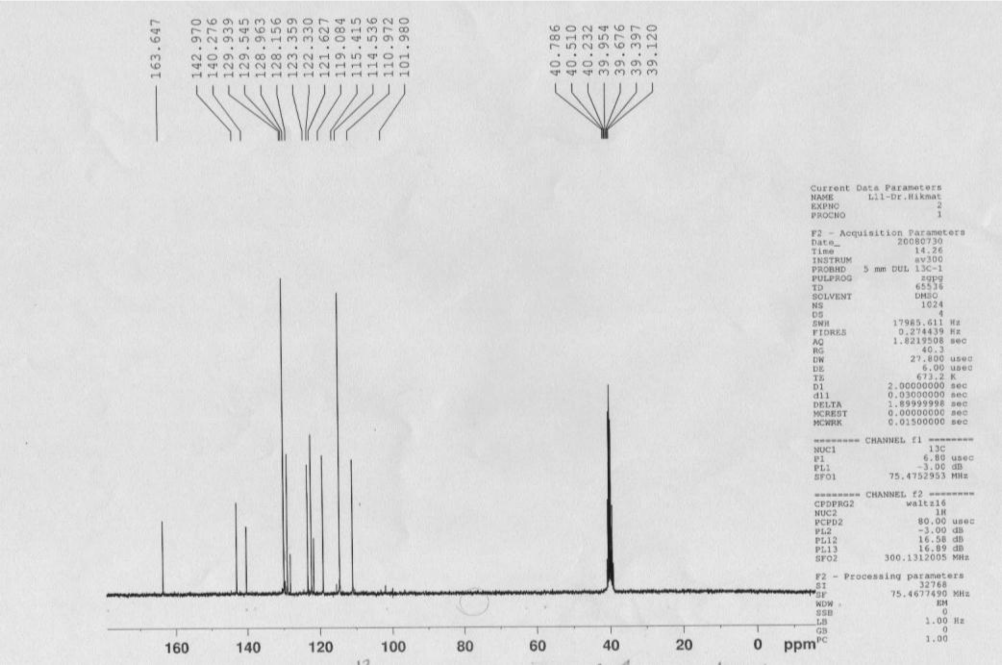


Fig (3): The ^{13}C.n.m.r system of compound (V).



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SOLVENT             DMSO
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DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                  40.3
DW                27.800 usec
DE                  6.00 usec
TE                 673.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
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P1                  6.80 usec
PL1                -3.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               16.58 dB
PL13               16.89 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
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SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00
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Fig (4): The ^{13}C.n.m.r of compound (III).

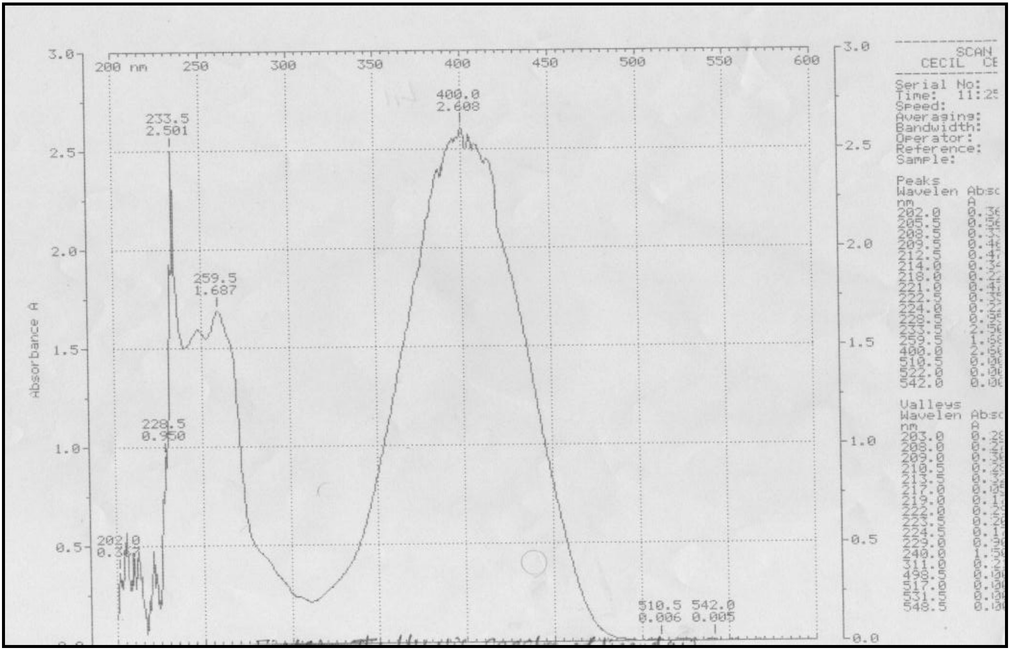


Fig (5): The UV-Vis spectra of ligand (V)

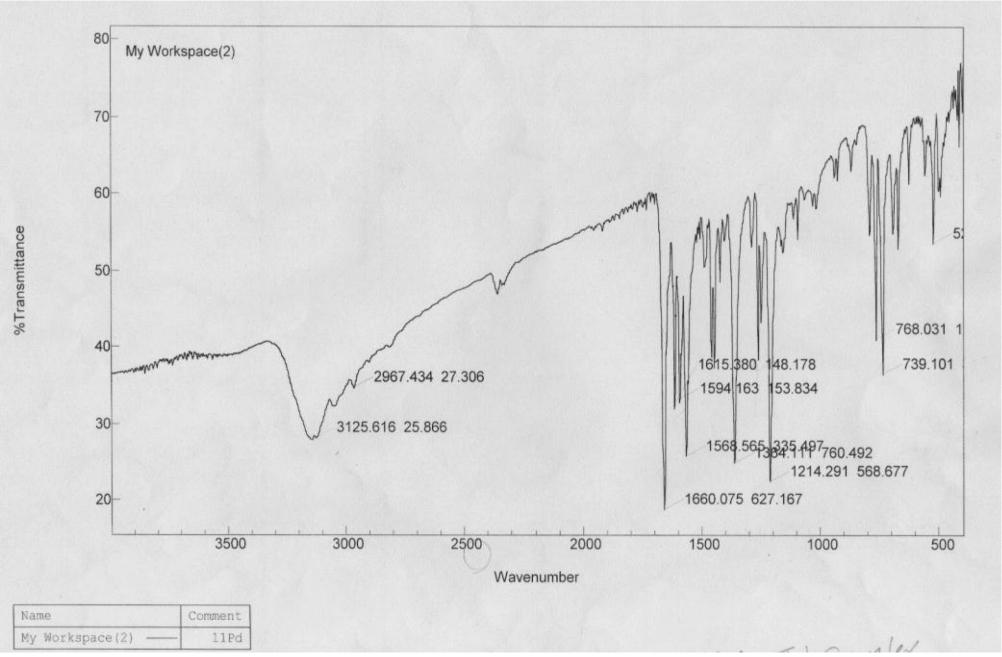
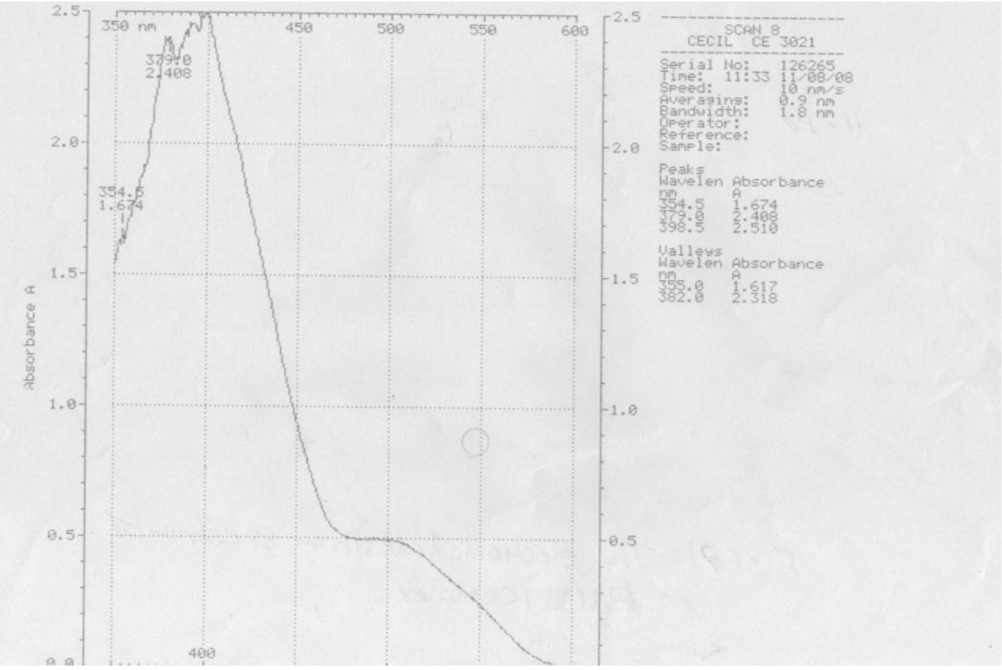


Fig (6): The IR spectra of Pd (II) complex



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Speed:        10 nm/s
Averaging:    0.9 nm
Bandwidth:    1.8 nm
Operator:
Reference:
Sample:

Peaks
Wavelen Absorbance
nm      A
354.5   1.674
379.0   2.408
398.5   2.510

Valleys
Wavelen Absorbance
nm      A
355.0   1.617
382.0   2.318
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Fig (7): The electronic transition spectrum of Pd (II) complex

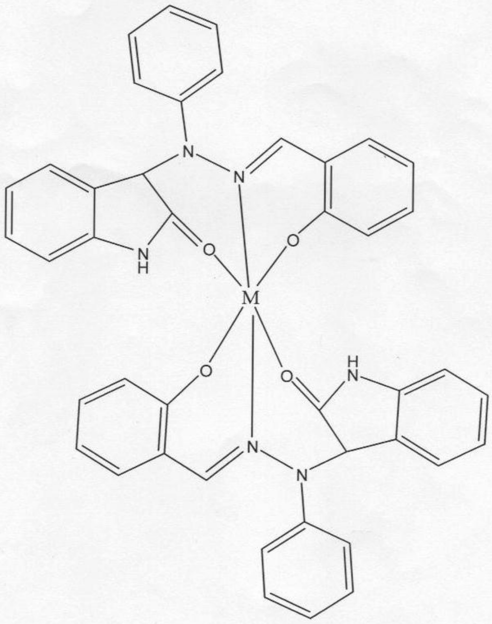

Fig (8): The Structure of metal complexes where M: Pd (II), Mn (II), and Ni (II).

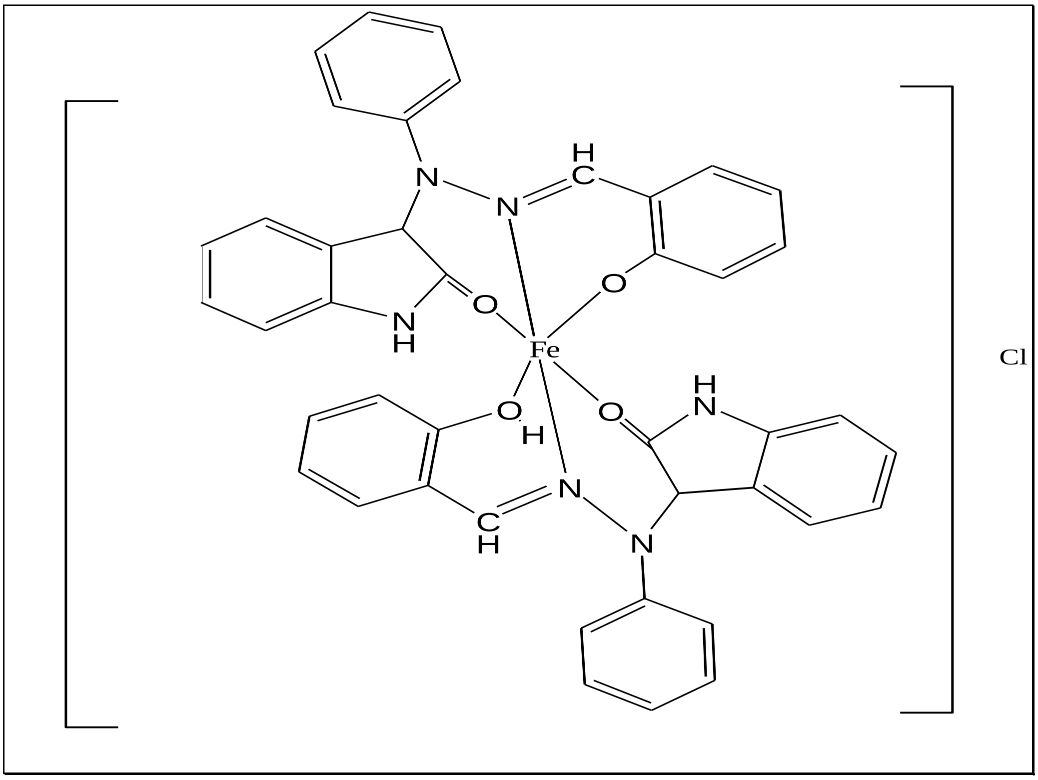

Fig (8): The Structure of Fe (III).complex.

Acknowledgment:-

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