Synthesis, Characterization and Stability Study of V(IV), Zr(IV), Rh(III), Pd(II), Cd(II) and Hg(II) Complexes with Pyrazol Derivative

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Abstract:

In this work lactone (1) was prepared from the reaction of p-nitro phenyl hydrazine with ethylacetoacetate, which upon treatment with benzoyl chloride afforded the lactame (2). The reaction of (2) with 2-amino phenol produced a new Schiff base (L) in good yield. Complexes of V(IV), Zr(IV), Rh(III), Pd(II), Cd(II) and Hg(II) with the new Schiff base (L) have been prepared. The compounds (1, 2) were characterized by FT-IR and UV spectroscopy, as well as characterizing ligand (L) by the same techniques with elemental analysis (C.H.N) and (^{1}H-NMR). The prepared complexes were identified and their structural geometries were suggested by using elemental analysis (C.H.N), flame atomic absorption technique, FT-IR and UV-Vis spectroscopy, in addition to magnetic susceptibility and conductivity measurements. Metal to ligand [M:L] ratio was obtained for all complexes in ethanol using molar ratio method, which gave comparable results with those obtained for the solid complexes. As well as the apparent stability constant of the complexes have been studied with the time and their color were stable for more than 4 hrs., furthermore the molar absorptivity have been calculated.

Key words: Stability Study, Pyrazol Derivative Schiff Base Complexes

Introduction:

Pyrazoline nucleus shows various biological and pharmacological activities such as antitumor, anticonvulsant, antiviral, divretic, antidiabetic, analgesic and anticancer [1-3]. The chemistry and antimicrobial activity of some substituted pyrazolone have been investigated in recent years and it was thought worldwide to synthesis novel pyrazolones from easily available starting materials and evaluations of their possible antimicrobial and anti-inflammatory activity [4]. Even the simplest pyrazolone derivatives like antipyrine and amidopyrine are widely used analgesic medicines [5]. In addition, pyrazolone and its derivatives can form a verity of Schiff bases and are reported to be superior reagents in biological, clinical and analytical applications [6, 7].

In continuation of our work on the metal complexes of Schiff bases, we report here the study of some new V(IV), Zr(IV), Rh(III), Pd(II), Cd(II) and Hg(II) complexes of Schiff bases derived from 5-methyl-2-(4-nitro phenyl)-4-(phenyl carbonyl)-2,4-dihydro-3*H*-pyrazol-3-one with benzoyl chloride, the reaction carried out in dioxan as solvent. The ligand (L) and its complexes have been fully characterized.

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Materials and Methods:

Physical Measurements and Analysis:

All starting materials and solvents were purchased from Aldrich and Fluka and have been used without further purification. Melting points were determined on electrothermal capillary apparatus and were uncorrected, elemental analysis (C.H.N) were carried out using Perkin-Elmer model 2400 instrument, FT-IR measurements were recorded on Shimadzu model FT-IR-8300 Shimadzu in the range (4000-200) cm^{-1}. ^{1}HNMR spectra were obtained with Bruker spectrophotometer model ultra shield at 300 MHz in DMSo-d_6.solution with the TMS as internal standard. Electronic spectra were obtained using UV-1650 Pc Shimadzu spectrophotometer at room temperature. Conductivity measurements were obtained using corning conductivity meter 220. These measurements were obtained in (DMF) as a solvent using concentration of 10^{-3} M at 25^{o}C. Magnetic susceptibility measurements were obtained at 25^{o}C on the solid state applying Faraday's Method using Bruker BM6 instrument.

(A) Synthesis of 3-Methyl-1-(2`,4`-Nitrophenyl)-2-Pyrazoline-5-One (1):

Mixture of p-nitro phenyl hydrazine (1.53g, 0.01mole) with ethyl aceto acetate (1.30g, 0.01mole) was refluxed for 6-7hrs in absolute ethanol 25ml, the solvent was removed and the solid product was collected and crystallized from absolute ethanol.

(B) Synthesis of 5-Methyl-2-(4-Nitro Phenyl)-4-(Phenyl Carbonyl)-2,4-Dihydro-3*H*-Pyrazol-3-One (2):

To solution of compound (1) (2.19g, 0.01mole) in 25 ml of 1,4-Dioxane as solvent, solution of benzoyl chloride (1.41g, 0.01 mole) with calcium hydroxide (0.75 g, 0.01mole) was added. The mixture was refluxed for 2hrs. The solid product was crystallized from absolute ethanol.

(C) Synthesis of 4-{[2-(Hydroxy Phenyl) Imino](Phenyl)Methyl}-5-Methyl-2-(4-Nitro Phenyl)-2,4-Dihydro-3*H*-Pyrazol-3-One (L):

To general procedure stirring solution of (2) (3.23 g, 0.01 mole) in absolute ethanol 30 ml, 2-amino phenol (1.1 g, 0.01mole) was added with drops of glacial acetic acid. The mixture was refluxed for 4 hrs. The product obtained after the evaporation of the solvent was filtered and recrystallized from ethanol.

The compounds (1, 2 and L) were characterized using elemental analysis, ^{1}H-NMR for ligand and FT-IR. The physical properties of the prepared ligand are described at table 1.

Preparation of Schiff Base Complexes (C_1-C_6):

Ethanolic solution of each of the following metal ion salts ([(0.18, 0.178, 0.226, 0.179, 0.183, 0.271)g, 1mmole] [$VOSO_4.XH_2O$, $ZrOCl_2$, $RhCl_3.XH_2O$, $PdCl_2$, $CdCl_2$ and $HgCl_2$] was added to ethanolic solution of (0.414g, 1mmole) of (L) with stirring. The mixture was heated under reflux for 1 hr. during this time a precipitate was formed. The product was isolated by filtration, washed several time with hot ethanol then dried under vacuum. The physical data of the prepared complexes are shown at table 1.

Study of Complexes Formation in Solution :

Complexes of (L) with metal ions were studied in solution using ethanol as solvents in order to determin [M:L] ratio in the complex following molar ratio method [8]. Series of solutions were prepared having a constant concentration 10^{-3}M of the metal ion and (L). the [M:L] ratio was determined from the relationship between the absorption of the absorbed light and the molar ratio of [M:L]. The results of complexes formation in solution were listed at table 1.

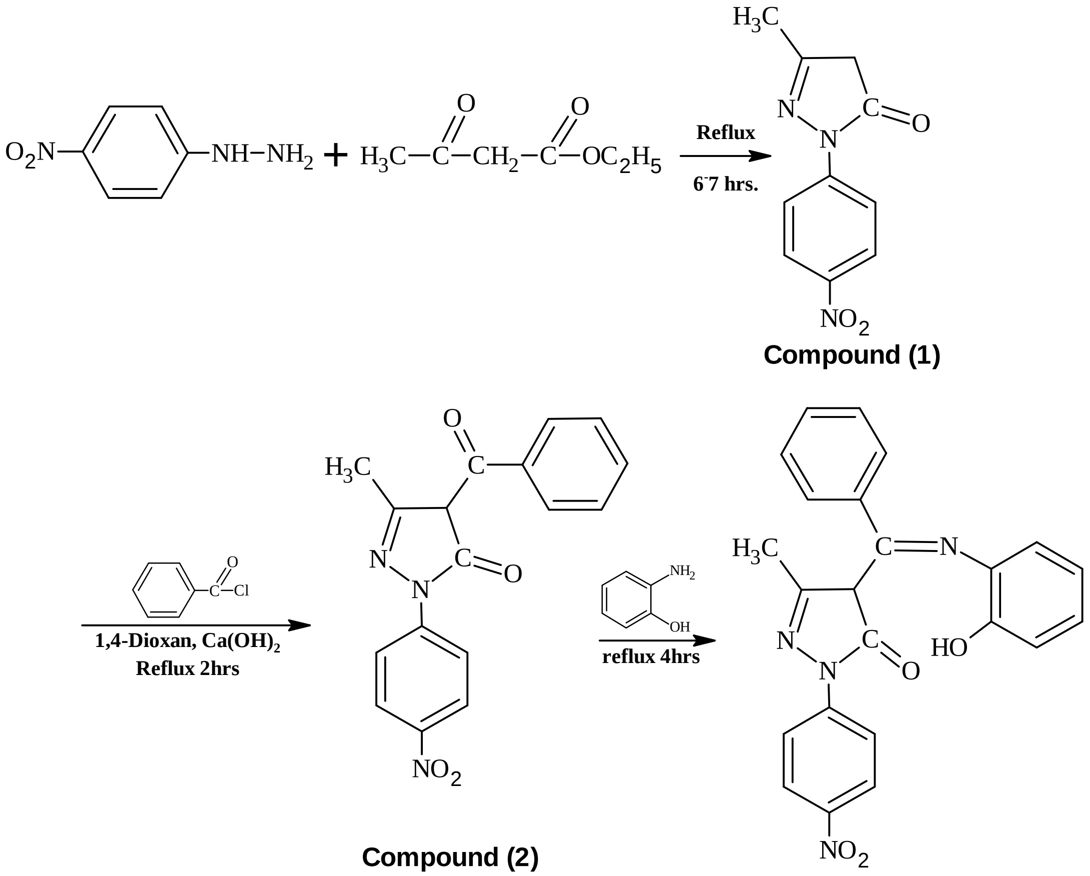
Stability Constant of Schiff Base Complexes :

The conditional or apparent [8] stability constant of [1:1] or [1:2] [Metal:Ligand] complex were evaluated as follows:

Two sets of solution were prepared, **the first set** of solutions were formulated to contain stoichiometric amount 1ml of 10^{-3}M ligand to 1ml of 10^{-3}M of metal ion by placing into three series of 10ml volumetric flasks. The solution of the colored complexes was diluted to the mark with ethanol. **The second set** was formulated to contain fivefold excess 5 ml of 10^{-3}M ligand, by placing into three series of 10 ml volumetric flasks followed by addition of 1ml of 10^{-3}M of metal ion, the volumes were then completed to the mark with ethanol. The absorbance (As and Am) of the solutions were measured at (λ_{max}) of maximum absorption. The stability constant (K) and the molar absorptivity (ε_{max}) have been calculated were listed at table 4.

Results and Discussion:

Reaction between p_nitro phenyl hydrazine and ethylacetoacetate prepared the compound (1), which upon reacted with benzoyl chloride afforded the compound (2). The preparation of a new Schiff base (L) derivative produced from the reaction of compound (2) and 2-amino phenol to be used a ligand that provide three potential donor sites to form complexes with some metal ions. The ligand (L) and it's complexes have been characterized and their structures were determined as outlined below, scheme 1.



Compound (1)

Compound (2)

(L)

(A) Elemental Microanalysis Analysis :

The physical analytical data of free ligand (L) and its metal complexes are given at (table 1), in a satisfactory agreement with the calculated values. The suggested molecular which formulas supported by subsequent spectral and molar ratio and magnetic moment.

(B) ^{1}H-NMR Spectral :

The ^{1}H-NMR spectrum of the free ligand (L) recorded in DMSO. The proton NMR spectrum showed peaks at 2.48 ppm (s, 3*H*, pyrazolin-CH_3), 6.3-6.6 ppm (m, 1*H*, proton of pyrazolin ring), 7.46-7.96 ppm (m, 9*H*, phenyl), 8.2 ppm (m, 4*H*, phenyl-NO_2), 9.8 ppm (m, 1*H*, phenolic-OH).

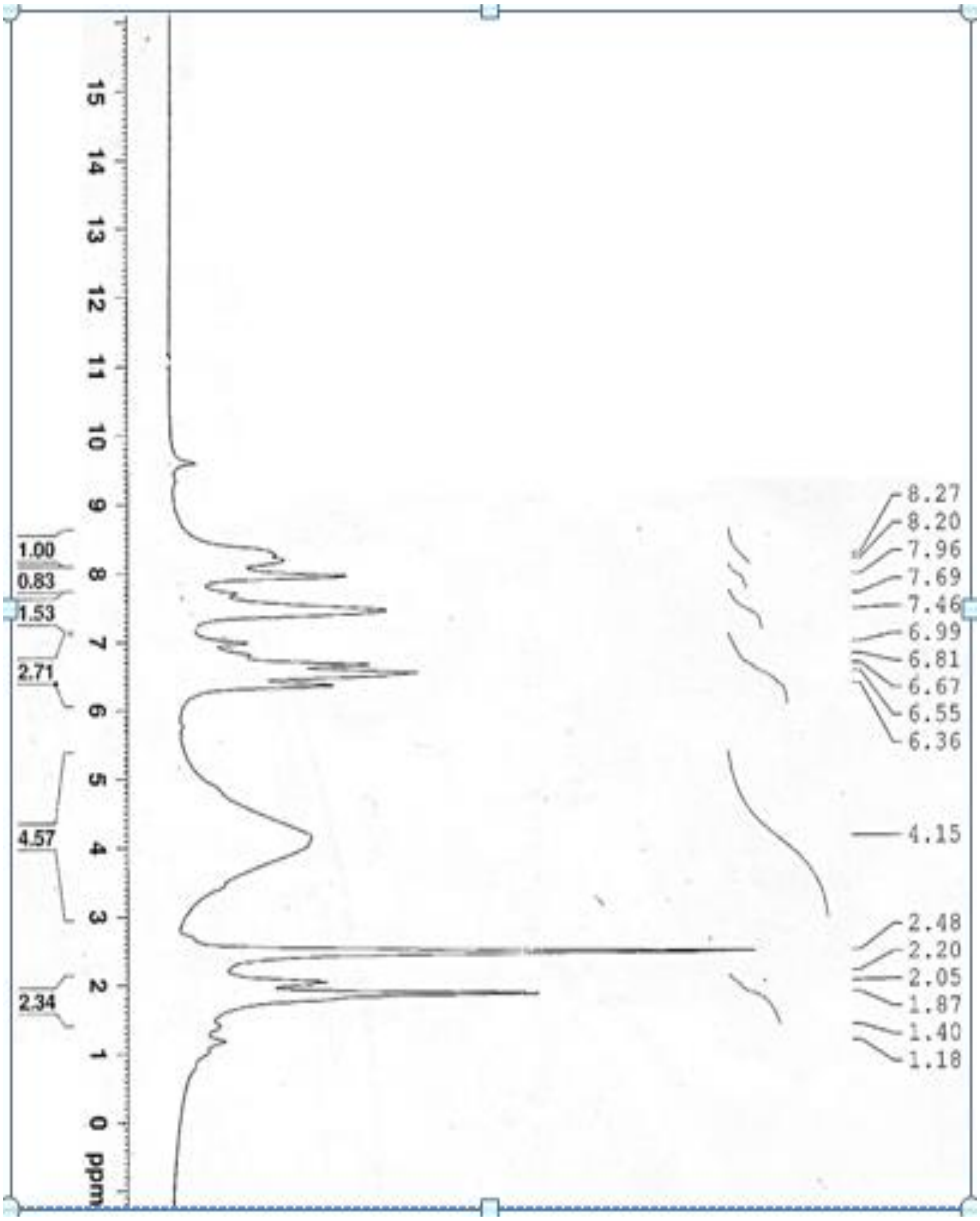


Figure 1: ^{1}H-NMR Spectrum of Ligand (L)

Table 1: The Physical Data for (L) and Schiff Base Complexes (C_1-C_6)

Compound No.	Color	M. p. °C	M.Wt g/mol	Yield%	%Elemental Analysis Found (Calc.)			Metal M% Found (Calc.)	M:L in (EtOH)	Suggest Formula
					C	H	N			
(1)	Brown	210	219	85	54.35 (54.79)	4.19 (4.10)	19.00 (19.17)	-	-	$C_{10}H_9N_3O_3$
(2)	Light Brown	184	323	83	63.32 (63.15)	4.16 (4.02)	13.25 (13.00)	-	-	$C_{17}H_{13}N_3O_4$
(L)	Orange	190	414	80	65.37 (66.66)	4.32 (4.34)	13.11 (13.52)	-	-	$C_{23}H_{18}N_4O_4$
C_1	Brown	217d*	893	73	60.83 (61.81)	3.23 (3.80)	11.99 (12.5)	5.22 (5.71)	1:2	$VO(C_{23}H_{17}N_4O_4)_2$
C_2	Deep Brown	230d*	933	70	58.98 (59.16)	3.42 (3.64)	11.98 (12.00)	9.38 (9.75)	1:2	$ZrO(C_{23}H_{17}N_4O_4)_2$
C_3	Dark Brown	195d*	964.5	75	56.99 (57.23)	3.33 (3.53)	11.43 (11.61)	10.20 (10.68)	1:2	$[Rh(C_{23}H_{17}N_4O_4)_2]Cl$
C_4	Brown	204d*	932	68	58.89 (59.22)	3.63 (3.86)	12.11 (12.01)	10.98 (11.37)	1:2	$Pd(C_{23}H_{17}N_4O_4)_2$
C_5	Brown	200d*	578.5	80	47.42 (47.70)	3.20 (3.28)	9.20 (9.68)	18.98 (19.36)	1:1	$[Cd(C_{23}H_{17}N_4O_4)(H_2O)]Cl$
C_6	Brown	210d*	667.5	77	40.88 (41.34)	2.68 (2.85)	7.99 (8.39)	29.56 (30.11)	1:1	$[Hg(C_{23}H_{17}N_4O_4)(H_2O)]Cl$

d* = decomposition

(C) Infrared Spectra :

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The IR spectra of the ligand showed a broad band in region 3422cm^{-1}, assignable to υ-OH group. The absence of this band in all metal complexes indicates the removal of proton of hydroxyl group of phenolic during the chelation. This is further support by shift of υC-O frequency from ∽1331 cm^{-1} (in ligand) to higher frequency 1398-1421 cm^{-1} (in complexes) [9]. Schiff base exhibit a strong intensity band at 1595 cm^{-1} due to υC=O. Moreover, a medium intensity band in ligand spectra at 1545 cm^{-1} is attributed to υC=N azomethine mode, the bands $\upsilon_{C=N}$ were shifted to lower frequencies in all complexes indicating that the nitrogen of azomethine group is involved in coordination [10].

The spectra bands of V(IV) and Zr(IV) complexes were characterized for the carbonyl group in pyrazolone ring, which did not suffer a shift. Thus, it is suggested that the oxygen atom of the carbonyl group is not coordinated to the metal ion [11], while the other bands of Rh(III), Pd(II), Cd(II) and Hg(II) complexes, which belong to $\upsilon_{C=O}$ were shifted to lower frequencies in comparison with ligand (L) that indicated coordination of ligand with metal ions through oxygen atom [12, 13]. These observations were further indicated by the appearance of υM-O and υM-N respectively [14, 15], as well as the spectra of V(IV) and Zr(IV) complexes additional band observed at 923 and 1112 cm^{-1} due to υV=O and Zr=O modes respectively [16, 17], (table 2).

Table 2: IR Frequences (Cm^{-1}) of the Compounds

Compounds No.	υ_{C-O}	$\upsilon_{C=O}$	$\upsilon_{C=N}$	M-N	M-O	υ_{O-H}
(1)	-	1714	1591	-	-	-
(2)	-	1763	1510	-	-	-
L	1331	1595	1545	-	-	-
C$_1$	1400	1595	1500	509	619	-
C$_2$	1419	1593	1500	447	617	-
C$_3$	1408	1588	1512	503	602	-
C$_4$	1406	1581	1496	500	610	-
C$_5$	1398	1572	1500	491	576	3381
C$_6$	1421	1564	1502	489	534	3450

(D) Electronic Spectra, Magnetic Moment and Conductance Studies:

The UV spectrum of Schiff base (L) showed intense bands at 49019 cm^{-1} and at 31055 cm^{-1}, which belong to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively [18], table 3.

The electronic spectra of Schiff base and metal complexes were recorded for their solution in ethanol at 200-1100 nm, while the molar conductance was measurement in DMF as solvent.

[C$_1$]: The isolated oxovanadium complex show all expected three bands at (13698, 15873 and 24752) cm^{-1}, which are assigned to $^2B_2\rightarrow{}^2E$, $^2B_2\rightarrow{}^2B_1$ and $^2B_2\rightarrow{}^2A_1$ transitions respectively. Moreover, V(IV) complex showed magnetic moment 1.79 B.M indicating square-pyramidal geometry to the complex [16-19]. Conductivity measurement in DMF showed a non-conductive behavior of the complex, table 3.

[C$_2$]: Zr(IV) complex showed no absorption peak to rang 380-1000 nm that is indicated no d-d electronic transition happened (d^o-system) in visible region that is good result for Zr(IV) square-pyramidal complex [20].

[C3]: The solution spectrum of the dark brown complex gave band at 20408 cm^{-1} and a shoulder at 18181 cm^{-1}, these two bands correspond to those of octahedral Rh(III) complex [21, 22], and were assigned to $^1A_1g\rightarrow{}^3T_1g$ and $^1A_1g\rightarrow{}^1T_2g$ transitions respectively. The complex was found to be paramagnetic, (table 3). Conductivity measurement in DMF showed that the complex was to be ionic, (table 3).

[C4]: The brown Palladium complex exhibited a strong charge transfer bands that were extended to the visible region; so the ligand field bands could not establish easily. Nevertheless, absorption band as a weak shoulder at 18518 cm^{-1} due to $^3A_2g\rightarrow{}^3T_2g$ transition, which is equal to the value 10 Dq for octahedral configuration, and other band at 23255 cm^{-1} due to $^3A_2g\rightarrow{}^3T_1g$ transition. The positions of these bands are in a good agreement with that reported for octahedral geometry [21]. In addition the measured magnetic moment for this complex was found to be 2.43 B.M, this value refer to high spin d^8 complex, which is the only case in octahedral environment [22]. The conductance measurements indicate that the complex was non-conductive, (table 3).

[C$_5$] and [C$_6$]: The UV-Vis spectra of Cd(II) and Hg(II) complexes show no absorption peak at range 380-1000 nm that is indicates no d-d electronic transition happened d^{10}-system in visible region, which is a good result for Cd(II) and Hg(II) tetrahedral complexes [23]. The complexes were to be ionic, (table 3).

Table 3: Electronic spectra, conductance in (10^{-3}M) DMF and magnetic moment (B.M) for (L) and its metal complexes

Compound No.	λ_{Max} (nm)	ϵ_{Max} $L.mole^{-1}.cm^{-1}$	$\upsilon(cm^{-1})$	Assignment	Molar Cond. $ohm^{-1}.cm^2.mol^{-1}$	μeff. B.M	Suggested Structure
(L)	204 322	218.3 791	49019 31055	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-
C_1	206 315 730 630 408	279.5 120.2 135 292 349.5	48543 31746 13698 15873 24752	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $^2B_2 \xrightarrow{\upsilon_1} {}^2E$ $^2B_2 \xrightarrow{\upsilon_2} {}^2B_1$ $^2B_2 \xrightarrow{\upsilon_3} {}^2A_1$	20	1.79	Square-pyramidal
C_2	258 318	152.3 134.7	38759 31446	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	35	Diamagnetic	Square-pyramidal
C_3	238 327 550 490	921 798 469 649	42016 30581 18181 20408	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $^1A_1g \xrightarrow{\upsilon_1} {}^3T_1g$ $^1A_1g \xrightarrow{\upsilon_2} {}^1T_2g$	83	2.14	Octahedral
C_4	205 307 540 430	284.8 118.7 953 390.1	48780 32573 18518 23255	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $^3A_2g \xrightarrow{\upsilon_1} {}^3T_2g$ $^3A_2g \xrightarrow{\upsilon_2} {}^3T_1g$	30	2.43	Octahedral
C_5	205 320 351	271.3 102.2 776	48780 31250 28490	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ L→M (C.T)	70	Diamagnetic	Tetrahedral
C_6	210 325 360	254.3 115.6 720	476190 30769 27777	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ L→M (C.T)	80	Diamagnetic	Tetrahedral

Solution Study:

a) Molar Ratio:

The molar ratio method was followed to determine [M:L] ratio. The results of complex in ethanol as solvent suggest that the metal to ligand ratio were [1:1] for [C_5 and C_6], while [1:2] for [C_1, C_2, C_3 and C_4], which were comparable to those obtained from solid state study, (table 1).

b) Stability Constant of Schiff Base Complexes :

The apparent stability constant (K) and molar absorptivity (ϵ_{max}) for C_1, C_2, C_3 and C_4 complexes were calculated by using the following equations [8].

$$K = \frac{1-\alpha}{\alpha^2 C} \quad \text{where [1:1] of [M:L]}$$

$$K = \frac{1-\alpha}{4\alpha^3 C^2} \quad \text{where [1:2] of [M:L]}$$

$$A_m = \epsilon_{max}\, b\, c$$

The degree of dissociation (α) [24] of the complex was evaluated by calculating the average of the three measurements of the absorption of solution containing a stoichiometric amount of ligand and metal ions (A_s) and the average of three measurements of the absorption of solution containing the same amount of metal and five fold excess of ligand (A_m), where (A_s and A_m) of the solution were measured at λ_{max} of maximum absorption, (table 4).

The results at table 4 indicate that mole ratio of (1:2) of C_1, C_2, C_3 and C_4 were high stability constant, this probably due to the presence of the bulk aromatic groups and the higher oxidation state of the metal ions. Furthermore, the developed color for these complexes become stable after 1-4 hrs. (table 4).

Table 4: Stability constant and molar absorptivity of schiff base C_1, C_2, C_3, C_4 complexes at room temperature

Complex	A_s	A_m	α	K L-Mol^{-1}	ϵ_{max} L.mol^{-1}.cm^{-1}	λ_{max} nm
C_1	0.402	0.483	0.168	$4.37 * 10^7$	483	630
C_2	0.440	0.458	0.039	$4.05 * 10^9$	458	650
C_3	0.402	0.420	0.043	$3.01 * 10^9$	420	550
C_4	0.206	0.415	0.081	$4.28 * 10^8$	415	540

On the other side, the stability constant (κ_f) [25] of C_5 and C_6 complexes with d^{10} electronic levels calculated through the molar conductivity accounts for several concentration, table 5, in DMF as solvent. The calculation of dissociation constant (κ_d) of the conducting complexes in the same solvent using Cruze rearrangement of Ostwald dilution equation [8], (table 6).

$$\Lambda_m C = \kappa_d(\Lambda_o)\frac{1}{\Lambda_m} - \kappa_d \Lambda_o^2$$

The results at table 4 indicate that mole ratio of (1:2) for [C_1, C_2, C_3 and C_4] complexes yielded rather high stability constants in contrast to the other values obtained with (1:1) for [C_5 and C_6] complexes, table 6, for the previously mentioned reasons.

Table 5: The difference between molar conductivity Λ_m (ohm^{-1}.cm^{2}.mol^{-1}) and concentration (mol.lit^{-1}) in DMF as solvent

No.	Formula	Concentration (mol.lit^{-1})			
		10^{-3}	$0.5*10^{-3}$	$0.2*10^{-3}$	$0.1*10^{-3}$
C_5	$[Cd(C_{23}H_{17}N_4O_4)(H_2O)]Cl$	63	90	130	160
C_6	$[Hg(C_{23}H_{17}N_4O_4)(H_2O)]Cl$	60	30	120	150

Table 6: The Data of κ_f of Cd(II), Hg(II) Complexes in DMF as Solvent

No.	Formula	$1/\Lambda_o$	$-\kappa_d\Lambda_o^2$	κ_d	κ_f
C_5	$[Cd(C_{23}H_{17}N_4O_4)(H_2O)]Cl$	0.0013	-0.0055	$0.9*10^{-8}$	$1.07*10^{8}$
C_6	$[Hg(C_{23}H_{17}N_4O_4)(H_2O)]Cl$	0.0015	-0.01	$0.2*10^{-7}$	$4.5*10^{7}$

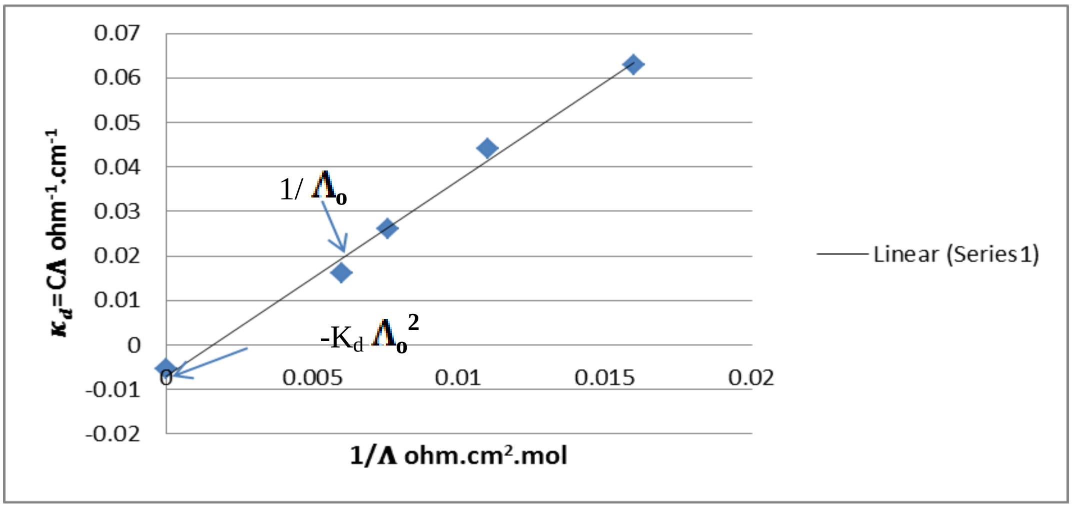


Fig.1: κ_d of $[Cd(C_{23}H_{17}N_4O_4)(H_2O)]Cl$

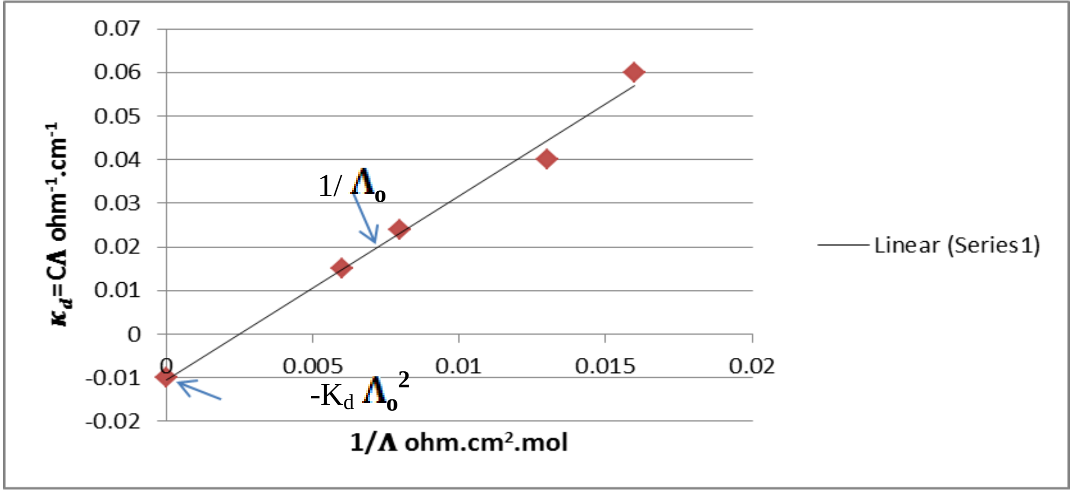
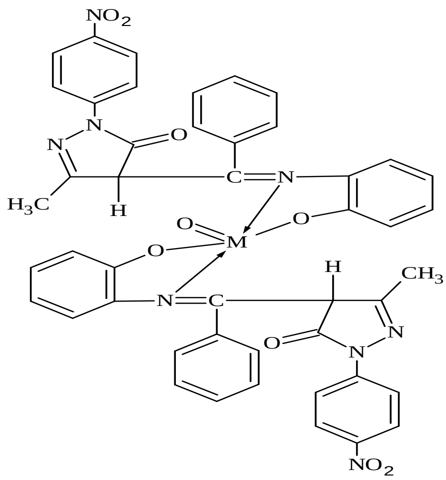


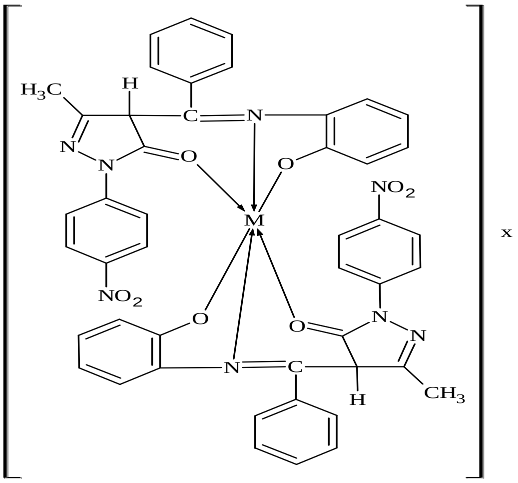
Fig.2: κ_d of $[Hg(C_{23}H_{17}N_4O_4)(H_2O)]Cl$

The suggested stereo chemistry structure of schiff base (L) and their metal complexes [C_1-C_6]

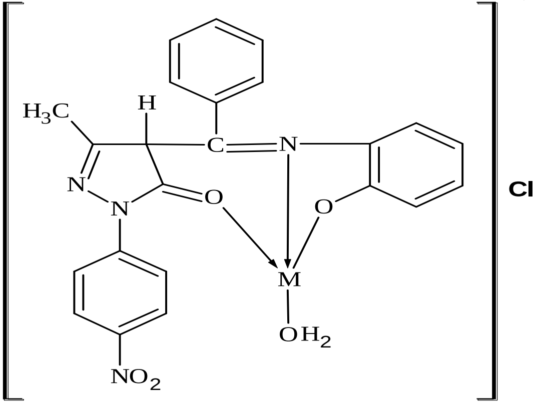
According to the results obtained from elemental, spectral analyses as well as magnetic moment and conductivity measurements, the suggested structure of the above mentioned compounds can be illustrated as follows:



Where M= V(IV) OR Zr(IV)



Where M= Rh(III), x= Cl OR M= Pd(II), x=O



Where M= Cd(II), Hg(II)

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تحضير وتشخيص ودراسة إستقرارية المعقدات V(IV) وZr(IV) وRh(III) وPd(II) وCd(II) وHg(II) مع مشتقات البايروزول

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الخلاصة:

حضر الليكاند (L)
4-{[2-(Hydroxy phenyl) Imino] (phenyl)Methyl}-5-Methyl-2-(4-Nitro phenyl)-2,4-Dihydro-3*H*-Pyrazol-3-one.
من تفاعل المركب (2) (المحضر من تفاعل مركب (1) مع كلوريد البنزويل مع المركب 2-أمينو فينول. شخص الليكاند (L) بوساطة أطياف الأشعة تحت الحمراء وفوق البنفسجية إضافة إلى التحليل الدقيق للعناصر (C.H.N) و(^{1}H.NMR). إستعمل الليكاند (L) لتحضير سلسلة من المعقدات من تفاعله مع أملاح كل من $VOSO_4.XH_2O$, $ZrOCl_2$, $RhCl_3.XH_2O$, $PdCl_2$, $CdCl_2$, $HgCl_2$.شخصت المعقدات المحضرة بوساطة الأشعة تحت الحمراء والأشعة فوق البنفسجية والتحليل الدقيق للعناصر (C.H.N) والإمتصاص الذري اللهبي إضافة إلى قياس الحساسية المغناطيسية والتوصيل الكهربائي. أظهرت النتائج أم المعقدات الناتجة ذات
الصيغة $MO(C_{23}H_{17}N_4O_4)_2$ حيث M=V(IV), Zr(IV)
والصيغة $[M(C_{23}H_{17}N_4O_4)_2]X$ حيث M=Rh(III), x=Cl أوx=O, M=Pd(II)
والصيغة $[M(C_{23}H_{17}N_4O_4)(H_2O)]Cl$ حيث M=Cd(II), Hg(II)
كما درست إستقرارية المعقدات وتم تحديد النسبة المولية لها والتي أكدت الصيغة المقترحة لها.