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Preparation, Identification and analytical studies of some Metal Complexes with Schiff base ligand (*p*-NPHAC)

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Abstract

Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes containing a tetra dentate N_2O_2 ligand β-[(P-Nitro phenyl) azo]-2-(imino-4-antipyrinyl)-4-(2-imino- benzoic acid) pentane (*p*-NPHAC) have been preparation and characterization. The ligand was characterized on the basic of elemental analyses, FTIR, ^{1}HNMR and electronic spectra studies while that the complexes were characterized by molar conductance, magnetic Susceptibility measurements, elemental analyses, FTIR and electronic spectra. The data show that the complexes have composition of $[ML(H_2O)_2]Cl$ type. From analytical and spectral data of the complexes has been found to be (1:1) (metal:ligand). FTIR spectral data showed that the ligand behaves a tetra dentate moleculare with (N_2O_2) doner sequence to wards metal ions. Electronic spectra, magnetic susceptibility and FTIR spectral data of all the complexes suggest octahedral geometry around the central metal ion.

Key words: *Tetradentate, Transition metal complexes , Identification, analytical study.*

1. Introduction

Schiff bases are widely employed in synthetic organic and inorganic chemistry, they were reported to show diverse biological activity ,and have many applications as ligands in coordination chemistry of transition metals(1). Tetra dentate Schiff bases are well known for their coordination with various metal ions, forming stable compounds(2), metal complexes of Schiff base containing ligands with (N_2O_2) doners atoms play an important role in inorganic research and know to exhibit interesting electrochemical, electronic properties, biological activities as antibacterial, anticancer(3-6), and antifungal(7). A large number of acetyl acetone possess powerful antifungal, antimicrobial, and DNA cleavage studies(8,9), Some Studies on the metal chelates with Schiff base of acetyl acetone have been reported due to their excellent chelating capacity in modern coordination chemistry(10). In via of this importance will describe her in the preparation and identification of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes with new schiff base ligand.

2. Experimental

2.1. Materials and measurements

All chemical used in the present work isatin, P-Nitro aniline, 4- amino antipyrine, metal chlorides and solvents were supplied from BDH, Aldrich and used with out further purification.

The electro thermal melting point model 9300 was used to measure the melting points of the ligand and its complexes. Elemental analyses were carried out by measurement of Micro analytical unit of 1108 C.H.N Elemental analyzer. FTIR spectra were recorded using KBr discs in 4000-400 cm^{-1} range on FTIR Shimadzu Spectrophotometer model 8400. Uv-Vis spectra were recorded in ethanol on Shimadzu Spectrophotometer double beam model 1700 Uv-Vis spectrophotometer.

The ^{1}HNMR spectra were obtained in DMSO solution using (Bruker, Ultra Shield 3000 MKZ, Switzerland), spectrophotometer Magnetic Susceptibilities were measured as powder samples using Faraday method, a Balance Magnetic MSB- MKI was employed for this purpose. The diamagnetic corrections were made by Pascal's constants(11). Molar conductance measurements were determined in DMF by using an Alpha Digital conductivity meter model 800. Physical characterization of the ligand and its metal chelate complexes was listed in table .1.

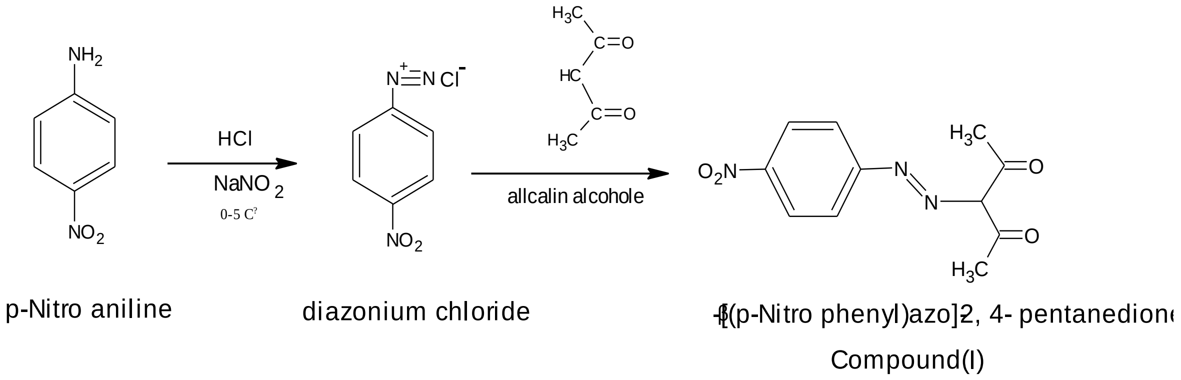
2.2. Preparation of New Schiff base ligand (*p*-NPHAC)

The ligand was prepared as follows:

1. Preparation of the diazo dye *(NPAP)*.

The diazo dye *(NPAP)* was prepared using the following method:- diazoinum chloride solution was prepared by dissolving (1.38 gm, 0.01 mol) of *p*-Nitro aniline in (50ml) of distilled water containing (3ml) hydrochloric acid. The resulting mixture was stirred and cooled to 0C°, then a solution of (0.69, 10mmol) sodium nitrite in (20ml) of water was added dropwise.

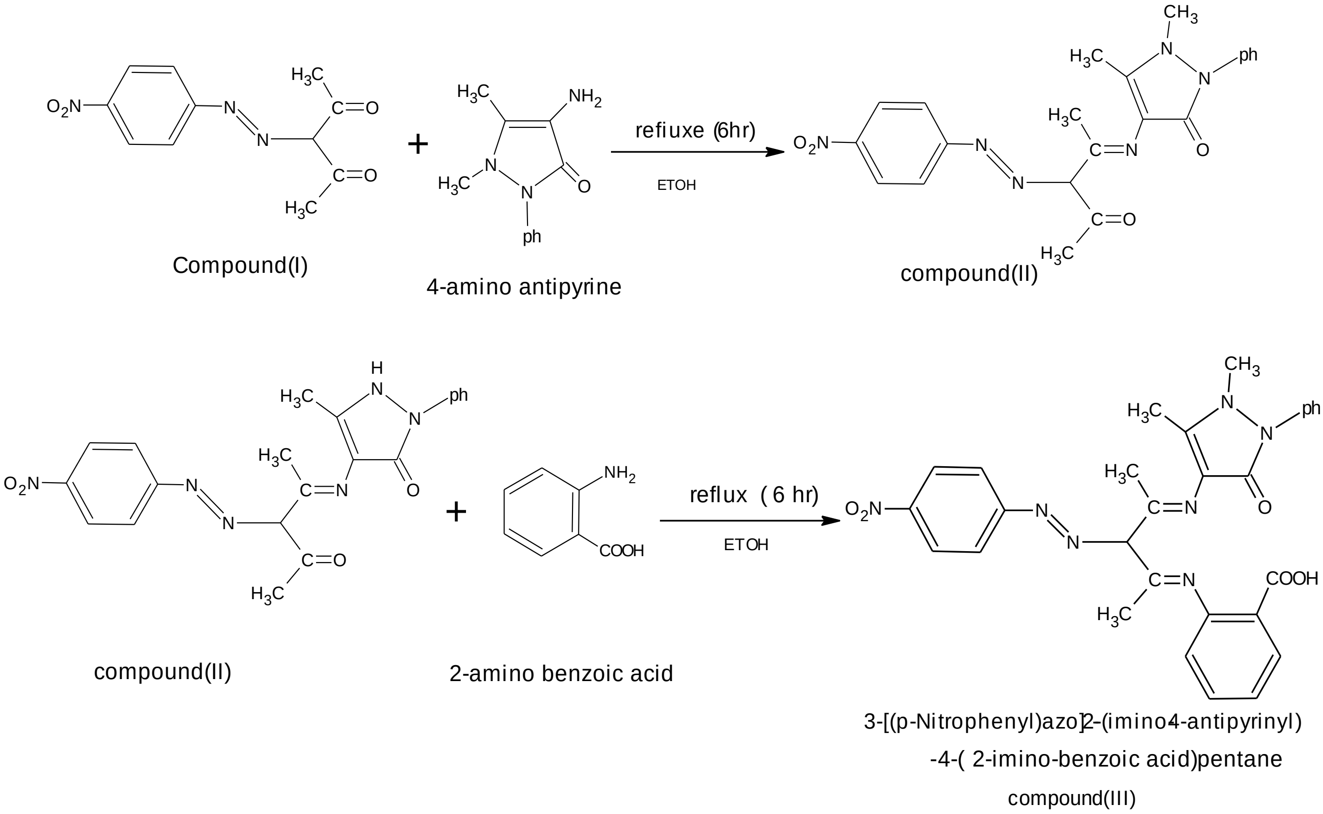
The diazonium chloride solution was consecutively coupled with an alkaline solution of (0.1gm, 10mmol) acetyl acetone, in (150) ml of ethanol. The mixture was stirred for (3hr) at 0-5 C°. The formed precipitate was filtered off, washed several times with water and air dried.
The red product was purified by recrystallization twice from hot ethanol, then dried oven at 100 C° for (2hr), The ligand illustrated in Scheme. 1.



Scheme.1: Preparation of the ligand (NPAP)

2. Preparation of the New Schiff base ligand.

The New Schiff base ligand (*p*-NPHAC) was prepared by condensation of compound (I) and 4-amino antipyrine in equimolar (1:1) mole ratio, in absolute alcohol and few drops of glacial acetic acid were added to the red reaction mixture and refluxed for (6hr),the product compound(II) was recrystallized from ethanol, and dried over anhydrous $CaCl_2$. The purity of the preparation ligand was checked by TLC(methanol : Benzen) (1:4). The compound(II) was condensation with 2-amino benzoic acid and refluxed for (6hr) in absolute ethanol. It was recrystallized from ethanol, and dried over anhydrous $CaCl_2$. The reaction mixture gave one product compound (III), m.p(113-115C◦).



Scheme.2: Preparation of the ligand (*p*-NPHAC)

2.3. Preparation of metal complexes

The complexes were prepared by adding the appropriate amount of the metal salt(1mmol), namely ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2$ and $HgCl_2$) dissolved in the least amount of absolute alcohol to (0.553, 1mmol) of ligand (*p*-NPHAC) dissolved in (50ml) of ethanol. The reaction mixture was refluxed for (30 min) with constant stirring. The precipitated solid complexes were filtered, washed with (3ml) of hot ethanol to remove any traces of the unreacted starting materials. Finally, the complexes were dried under vacuum.

3. Results and discussion

3.1. Identificatio of ligand and its metal complexes

The ligand was brown powder, but the prepared complexes of this ligand vary in colour depending of metal ion. The experimental results of the elemental analyses of the prepared ligand and its metal complexes are good agreement with theoretical expectations. The elemental analyses of the complexes indicate that the (metal:ligand) ratios were (1:1)in the $[ML(H_2O)_2]Cl$, where M= Ni(II), Co(II), Cu(II), Zn(II), Cd(II), and Hg(II), The complexes were stable at room temperature and insoluble in water, but its soluble in common organic solvents. Physical and analytical data of the ligand and its complexes are listed in table.1

3.2. Microanalysis

The elemental analysis data the complexes as shown in table (1) exhibit the formation 1:1 [M:L] ratio . it was found that the theoretical values are in a good agreement with the found data. The purity of the Schiff base ligand were tested by TLC (methanol : Benzen) (1:4), and C, H and N elemental analyses.

3.3. IR spectra

The IR spectra of the Schiff base and its metal complexes are summarized in table (2) with some assignments of the important characteristic bands. The spectrum of free ligand show band in the region 3460 cm^{-1} assignable to acidic (-OH) group, absence of this band in all the complexes indicates the deprotonetion of acidic (-OH) group upon complexation(12).

Abroad band is observed in all the complexes in the range 3367-3439 cm^{-1} due to υ(OH) of the coordinated H_2O. This is supported by the appearance of an additional band in the rang 818-840 cm^{-1} for (O-H) vibration deformation. These bands were not observed in the spectra of the ligand(13). The band observed at 1662 cm^{-1} is characteristic of the keto group in apyrazolone ring. In the complexes, this band is shifted to higher frequency 1676-1683 cm^{-1}, indicating the coordination of carbonyl oxygen to the metal ions(14). The presence of bands at 515-550 cm^{-1} in the IR spectra of complexes are due to M-O stretching vibrations(15). The azomethine band at 1624 cm^{-1} was shifted to higher frequencies in the spectra of all the complexes, confirming the participation of the azomethine nitrogen atom in the coordination of the metal ions. In the spectra of these complexes, the new band which appear in the 420-470 cm^{-1} region are assigned to the υ(M-N)(16). The band in the spectrum of free ligand observed at 1600cm^{-1} due to (C=O) group, this band remains in the same region in the complexes. Its was found that the υ(N=N) stretching vibration in free ligand was at 1423 cm^{-1} which no shifted in complexes(17). Representative example for there is given in Fig (1). this band remains in the same region in the complexes.

3.4. Magnetic Preparation and Electronic Spectra

The spectral data and the magnetic moment of prepared complexes are listed in Table.3. Fig.2. show the spectra of ligand and $[CuL(H_2O)_2]Cl$ complex.

1- Cobalt (II) Complex

The magnetic moment value of the Co(II) (d^7) complex is (5.57 B.M)(18). the electronic spectrum of this complex show bands at 15026 cm^{-1}, 17391, 26246 cm^{-1} which can be assigned to

$^4T_1g \rightarrow ^4T_2g(F)$, $^4T_1g \rightarrow ^4A_2g(F)$,and $^4T_1g \rightarrow ^4T_1g(P)$, respectively. The spectrum resemble those reported for octahedral complexes(19).

2- Nikel (II) Complex

The magnetic moment for the complex of Ni(II) (d^8) was found to be (3.34 B.M), which is with the range of octahedral Ni(II) complexes(24). The electronic spectrum of this complex show bands at 13071 cm^{-1}, and 14450 cm^{-1} which can be assigned to $^3A_2g \rightarrow ^3T_1g(F)$, and $^3A_2g \rightarrow ^3T_1g(F)$, respectively(20).

3- Copper (II) Complex

The magnetic moment value of the Cu(II) (d^9) complex (1.76 B.M), this value indicate within the expected for one electron, and d-d spectrum of this complex show band at 16051 cm^{-1} which may assigned to $^2Eg \rightarrow ^2T_2g$ transition in an approximately octahedral environment(21).

4- Zinc(II) Cadmium (II) and Mercury(II)

Metal complexes are diamagnetic consistent with the d^{10} configuration and the electronic spectra of these complexes exhibit high intense charge transfer transition which are assigned to (CT)(22).

3.5. ^{1}HNMR spectrum studies

^{1}HNMR spectrum of ligand showed clear signals involved singlet at δ =2.5ppm belong to the proton of solvent (DMSO), and multiplet signals at δ =(7.1-7.4) ppm which were assigned to aromatic protons of (*p*-Nitro aniline). Multiplet signals at δ =(7.12- 8.21) ppm and δ = (6.9-737)ppm which belong to aromatic protons of benzene ring of benzyl and antipyrine, respectively, more over HNMR spectrum of ligand showed singlet signal at δ =11.0 ppm belong to proton of benzoic acid derivative. Singlets at δ = (2.7-3.0) ppm belong to the proton of methyl (23)Fig.3

3.6. Conductivity measurement

Molar conductance data of the complexes were measured in the solvent DMF and the complexes were found to be electrolytic nature(24). Conductivity value of the chelate complexes are lie in the range (67 - 77) S. $cm^2.mol^{-1}$.

4. Conclusion

This paper report including flowing:

1. Preparation and identification of new tetra dentate Schiff base and its complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) metal ions.
2. All the complexes an stable and ionic.

3- Some of the complexes are paramagnetic and the other are diamagnetic.

4- All the proposed Geometry of the complexes are octahedral. According to these results the structural formulas of these complexes may be proposed in Fig.(4).

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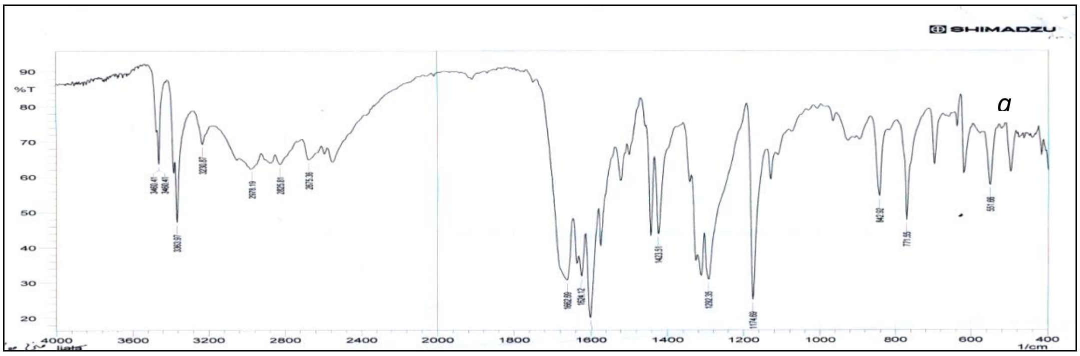

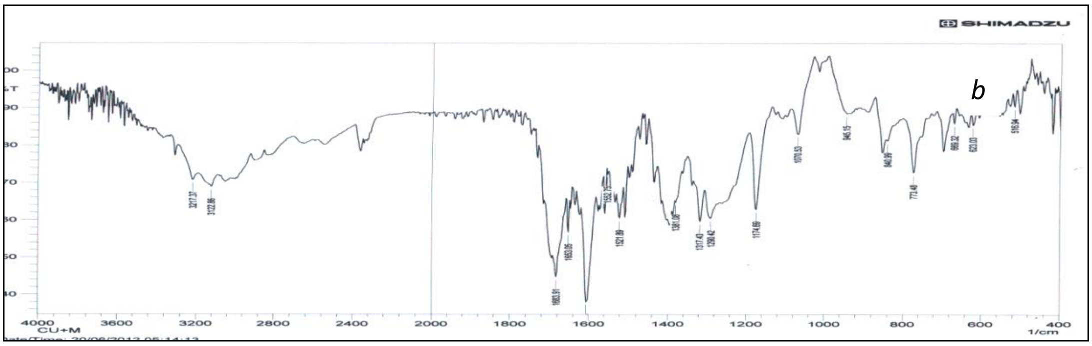

Fig.(1): IR spectra of : (a) the ligand (*P*-NPHAC) & (b) $[CuL(H_2O)_2]Cl$

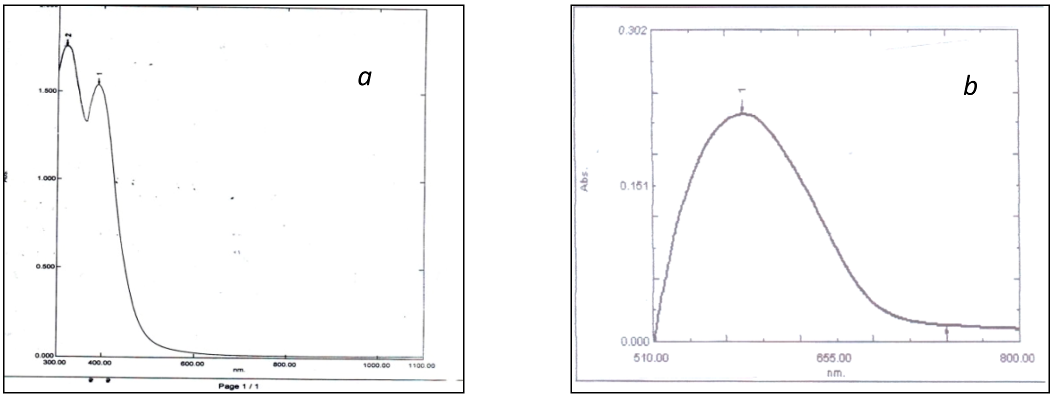

Fig.(2). Electronic spectrum of : (a) the ligand (*p*-NPHAC)&(b) $[CuL(H_2O)_2]Cl$

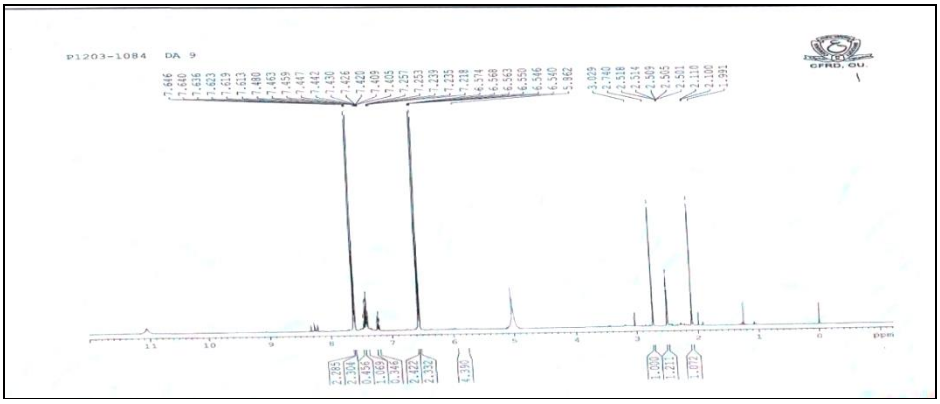

Fig.(3). ^{1}HNMR Spectrum of*: the ligand (p-NPHAC)*

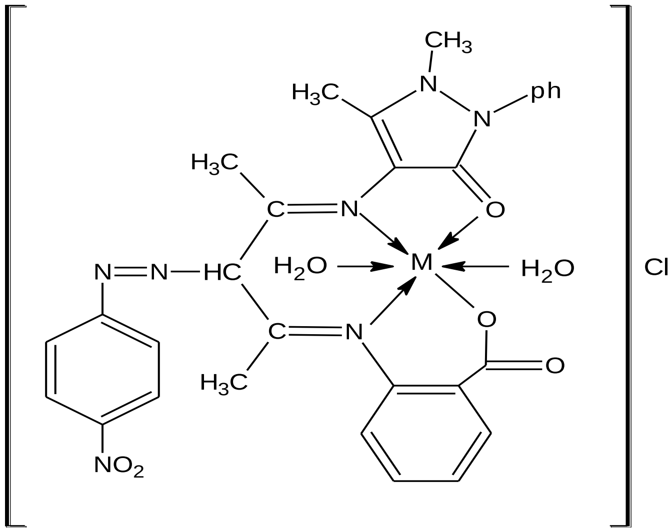

Fig. 4: The proposed structural formula of the metal chelate complexes M=Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II).

Table.1: Physical data and analysis of ligand and its complexes.

No.	***Compound***	***Colour***	***M.P ºC***	***Yield %***	***Formula***	***Found,(Calc.)%***			
						C	***H***	***N***	***M***
1	**L=(*p*NPHAC)**	**Brown**	**113-115**	**73**	**[$C_{29}H_{27}N_7O_5$]**	**62.0 (62.9)**	**4.6 (4.9)**	**17.2 (17.7)**	**----**
2	**[CoL(H_2O)$_2$] Cl**	**Green**	**177-178**	**68**	**[$C_{29}H_{26}N_7O_5(H_4O_2)$ Co]Cl**	**51.9 (51.0)**	**3.4 (3.8)**	**14.8 (14.3)**	**8.2 (8.6)**
3	**[NiL(H_2O)$_2$] Cl**	**Pale Green**	**169-171**	**69**	**[$C_{29}H_{26}N_7O_5(H_4O_2)$ Ni]Cl**	**51.2 (50.9)**	**3.2 (3.8)**	**14.3 (14.3)**	**7.4 (8.6)**
4	**[CuL(H_2O)$_2$] Cl**	**Dark green**	**185-186**	**75**	**[$C_{29}H_{26}N_7O_5(H_4O_2)$ Cu]Cl**	**50.1 (50.6)**	**3.0 (3.7)**	**14.0 (14.2)**	**9.7 (9.1)**
5	**[ZnL(H_2O)$_2$] Cl**	**Brown**	**180-183**	**81**	**[$C_{29}H_{26}N_7O_5(H_4O_2)$ Zn]Cl**	**50.2 (50.4)**	**3.6 (3.7)**	**14.0 (14.2)**	**9.4 (9.6)**
6	**[CdL(H_2O)$_2$] Cl**	**Brown**	**195-197**	**72**	**[$C_{29}H_{26}N_7O_5(H_4O_2)$ Cd]Cl**	**47.6 (47.3)**	**3.4 (3.6)**	**12.9 (13.3)**	**9.8 (9.0)**
7	**[HgL(H_2O)$_2$] Cl**	**Brown**	**<205 d**	**62**	**[$C_{29}H_{26}N_7O_5(H_4O_2)$ Hg]Cl**	**43.7 (42.2)**	**3.7 (3.1)**	**11.3 (11.9)**	**24.8 (24.2)**

L =ligand, d =Complex metal with decomposition

Table.2: Some IR frequencies in (cm^{-1}) of the ligand and its metal complexes

Ligand/complexes	*υ(OH)* *water*	*υ(C=O)*	*υ(C=N)*	*υ(N=N)*	*υ(H_2O)*	*υ(M-O)*	*υ(M-N)*
L= $C_{29}H_{27}N_7O_5$	**----**	**1662**	**1624**	**1423**	**---**	**---**	**---**
[CoL(H_2O)$_2$] Cl	**3439**	**1679**	**1638**	**1425**	**818**	**520**	**430**
[NiL(H_2O)$_2$] Cl	**3421**	**1676**	**1645**	**1423**	**820**	**536**	**460**
[CuL(H_2O)$_2$] Cl	**3439**	**1683**	**1653**	**1425**	**840**	**516**	**470**
[ZnL(H_2O)$_2$] Cl	**3420**	**1681**	**1648**	**1424**	**832**	**550**	**420**
[CdL(H_2O)$_2$] Cl	**3367**	**1677**	**1643**	**1421**	**826**	**520**	**427**
[HgL(H_2O)$_2$] Cl	**3425**	**1680**	**1641**	**1424**	**838**	**515**	**435**

Table.3 : Electronic spectra, conductivity and magnetic moment of complexes

Complexes	*Abs.B* *nm (cm^{-1})*	*Transition*	*Conductivity* *$S.mol^{-1}.\ cm^2$*	*μeff(B.M)*
L= Ligand	**313 (31948)** **389 (25706)**	**$\pi\rightarrow\pi^*$** **$n\rightarrow\pi^*$**	----	**---**
[CoL(H_2O)$_2$] Cl	**665 (15026)** **575 (17391)** **381 (26246)**	**$^4T_1g\rightarrow{}^4T_1g(F)$** **$^4T_1g\rightarrow{}^4A_2g(F)$** **$^4T_1g\rightarrow{}^4T_1g(P)$**	**69.14**	**5.57**
[NiL(H_2O)$_2$] Cl	**765 (13071)** **692 (14450)**	**$^3A_2g\rightarrow{}^3T_1g(F)$** **$^3A_2g\rightarrow{}^3T_1g(P)$**	**77.43**	**3.34**
[CuL(H_2O)$_2$] Cl	**623 (16051)**	**$^2Eg\rightarrow{}^2T_2g$**	**72.23**	**1.76**
[ZnL(H_2O)$_2$] Cl	**336 (29761)**	**CT**	**67.42**	**Dia**

[CdL(H_2O)$_2$] Cl	**327 (30581)**	**CT**	**76.13**	**Dia**
[HgL(H_2O)$_2$] Cl	**345 (28985)**	**CT**	**74.52**	**Dia**

تحضير، تشخيص ودراسة تحليلية لبعض المعقدات الفلزية مع ليكاند قاعدة شف

(*P*-NPHAC)

م. منى عباس هادي

قسم الكيمياء / كلية التربية للبنات / جامعة الكوفة

الخلاصة:-

تضمن البحث تحضير وتشخيص معقدات لايونات الكوبلت(II), النيكل(II) , النحاس(II) , الخارصين(II) , الكادميوم(II) والزئبق(II) المحتويه ليكاند رباعي المخلب (N_2O_2) β-[(P-Nitro phenyl) azo]-2-(imino-4-antipyrinyl)-4-(2-imino- benzoic acid) pentane (*p*-NPHAC) . شخصت الليكاند على أساس التحليل الدقيق للعناصر ، الأشعة تحت الحمراء، بروتون الرنين النووي المغناطيسي، والاطياف الالكترونية بينما درست وشخصت المعقدات بوساطة التوصيلية المولارية ، قياسات الحساسية المغناطيسية ، التحليل الدقيق للعناصر ، الأشعة تحت الحمراء والأطياف الالكترونية. أظهرت المعطيات بان المعقدات لها تركيب [ML(H_2O)$_2$]Cl. من البيانات التحليلية والطيفية للمعقدات وجد أن نسبة (فلز : ليكاند) (1:1) . بينت نتائج طيف الأشعة تحت الحمراء بان الليكاند يسلك جزيئة رباعية المخلب مع (N_2O_2) تترتب بالتعاقب نحو الايونات الفلزية. تم اقتراح الشكل ثماني السطوح حول الايون الفلزي لجميع المعقدات الفلزية بالاعتماد على نتائج الأطياف الالكترونية ، الحساسية المغناطيسية، والأشعة تحت الحمراء .