

Synthesis and Characterization of 2-amino -5-phenyl-1,3,4-Oxadiazole Complexes with Selected Metal Ions.

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Abstract:-

The new bidentate ligand 2-amino-5-phenyl-1,3,4-oxadiazole (Apods) was prepared by the reaction of benzaldehyde semicarbazone with bromine and sodium acetate in acetic acid gave. The prepared ligand was identified by Microelemental Analysis, FT.IR, UV-Vis and ¹HNMR spectroscopic techniques. Treatment of the prepared ligand with the following selected metal ions (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) in aqueous ethanol with a 1:2 M:L ratio, yielded a series of complexes of the general formula [M(L)₂Cl₂]. The prepared complexes were characterized using flame atomic absorption, (C.H.N)Analysis, FT.IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements. Chloride ion content was also evaluated by Mohr method. From the obtained data the octahedral structure was suggested for all prepared complexes.

Introduction :-

1,3,4- oxadiazoles are known to exhibit diverse pharmacological activities like antimicrobial^(1,2), antihistaminic⁽³⁾, anticancerous⁽⁴⁾, anti-inflammatory and antihypertensive activities⁽⁵⁾.

1,3,4-oxadiazole derivatives are reported to show a broad spectrum of biological activities, which include antibacterial, anticonvulsant and antihypertensive^(6,7). This prompted use to synthesize and study anticonvulsant activity of compounds incorporating both these moieties, 1,3,4-oxadiazole and coumarin. This compounds were evaluated for their antiepileptic and neurotoxic properties according to the protocols of antiepileptic drug development⁽⁸⁾. In this work, we synthesized and characterized a new 1,3,4-oxadiazole derivative. The complexes of the ligand with some selected metal ions have also been studied and characterized physicochemically.

Experimental

a. Instrumentation

UV-Vis spectra were recorded on a (Shimadzu UV-160 A) Ultra Violet-Visible Spectrophotometer. I.R-spectra were taken on a (Shimadzu, FTIR-8400 S) Fourier Transform Infrared Spectrophotometer (4000-400)cm⁻¹ with samples prepared as KBr discs. Atomic Absorption were obtained by using a (Shimadzu A.A-160A) Atomic Absorption / Flame Emission Spectrophotometer. The ¹HNMR spectrum of 2-amino -5- phenyl -1,3,4-oxadiazole was obtained on (Brucker-300 MHz Ultra Shield) University of AL-al-Bayt-Jordan by using deuterated DMSO as a solvent and (TMS) as

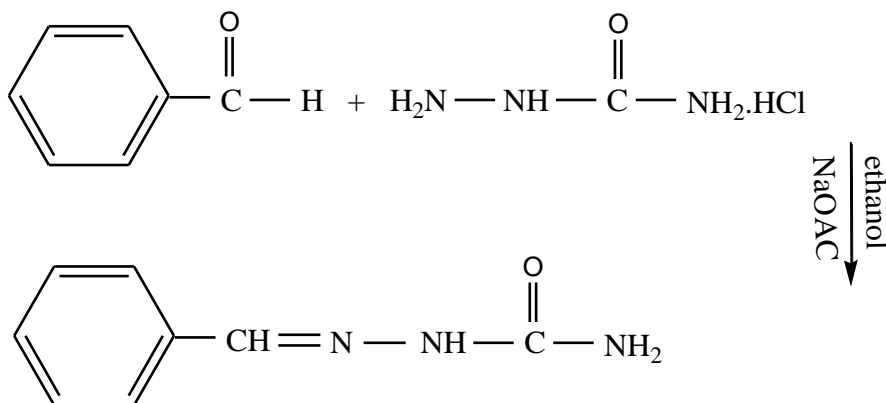
a reference. Microelemental analysis (C.H.N) were performed in AL-al- Bayt University, Jordan by using (Euro Vector EA 3000 A Elemental Analyser). Conductivities were measured for $10^{-3}M$ of complexes in DMF at $25^{\circ}C$ by using (Philips PW- Digital Conductimeter). Magnetic susceptibilities were performed by using (Brucker Magnet B.M.6) instrument at $25^{\circ}C$. Melting points were obtained by using (Melting Point Apparatus).

b. Materials:-

The following chemicals were used as received from suppliers; $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$ (Fluka); $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$ (Merck); benzaldehyde, semicarbazide hydrochloride, sodium acetate, glacial acetic acid (B.D.H). All chemicals were of analytical grade used as suppliers without further purification .

Preparation of Benzaldehyde Semicarbazone

This compound was synthesized according to the general method⁽⁹⁾ in (100 mL) round bottom flask, (1g) of respective benzaldehyde was dissolved in (10 mL) ethanol, then (1g) of semicarbazide hydrochloride and (1.5g) of fused sodium acetate were added to alcoholic solution. The solution was refluxed, with constant stirring for about 40 minutes. After the reaction period the material was allowed to cool at room temperature and then poured in water. The separated solid was filtered and recrystallized from glacial acetic acid. The reaction is shown in scheme (1).

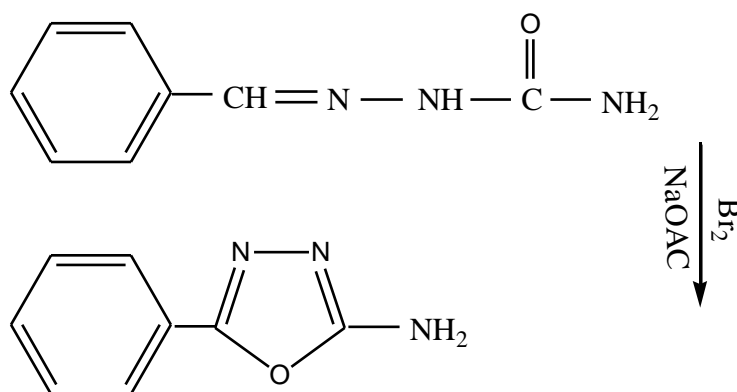


Scheme(1):- Preparation of Benzaldehyde Semicarbazone.

Preparation of 2-Amino -5-Phenyl-1,3,4-Oxadiazole (Ligand)

The ligand was prepared according to the general method⁽¹⁰⁾. Bromine (0.6mL) in acetic acid (5mL) was added to a stirred slurry of benzaldehyde semicarbazone (2g) and anhydrous sodium acetate (4g) in acetic acid (5mL) contained in a (150 mL) flat bottom flask. Due to exothermic reaction, the mixture became warm and rapidly

became colorless. This mixture was poured in water. The solid which was separated, filtered and dried. All the amino oxadiazoles were recrystallized from the mixture of alcohol and glacial acetic acid. The reaction is shown in scheme(2).



Scheme(2):- Prerparation of 2-Amino -5-Phenyl-1,3,4-Oxadiazole.

Preparation of Metal Complexes (general procedure)

An aqueous solution of the metal salts containing 0.30g, 0.37g, 0.36g, 0.26g and 0.21g (1m mole) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 respectively was added gradually to ethanolic solution of 2-amino-5-phenyl-1,3,4-oxadiazole (0.5 g, 2m mol) by using stichiometric amount (1:2) metal : ligand molar ratio. The mixture was refluxed with constant stirring for about 1 hour. The mixture was cooled at room temperature dark precipitate was formed, filtered and recrystillized from glacial acetic acid.

Result and Discussion:-

The synthesized ligand was characterized by FT.IR, UV-Vis, ^1H NMR spectra and (C.H.N) analysis. The ^1H NMR spectrum of ligand in DMSO (Fig-1) shows multiplet signals at ($\delta = 7.40-7.94$ ppm) referring to aromatic proton for benzene ring⁽¹¹⁾. On the other hand⁽¹²⁾, the signal at ($\delta = 3.38$ ppm) is assigned to (NH_2) and the signal peak at ($\delta = 2.5$ ppm) referred to DMSO- d_6 .

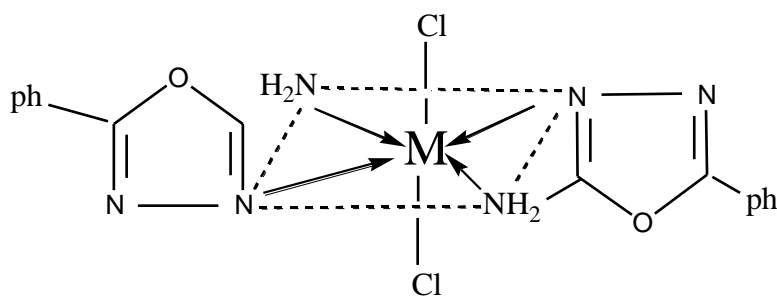
The solid complexes were prepared by reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions in a (M:L) of (1:2). The (C.H.N) and chloride analysis with metal contents of these complexes were in good agreements with the calculated values (Table-1) includes the physical properties and elemental analysis. The observed molar conductance in DMF(10^{-3}M) fall in the range of ($15.6-44.5 \text{ S.cm}^2 \cdot \text{Mol}^{-1}$). These values of the molar conductance are well within the expected range for non-electrolytes⁽¹³⁾, therefore, the two (Cl) ions were considered to be coordination with the metal ion, the data were recorded in (Table-2).

The effective magnetic moments (Table-2) of the complexes lie in the range (1.63-4.68) B.M. This value refers to a paramagnetic (high spin) which has been reported for most octahedral geometry⁽¹⁴⁾.

The UV-Vis spectra data for the free ligand and all metal complexes are listed in (Table-2). The UV-Vis spectrum of the ligand (Fig-2) shows two peaks at 252 nm and 319 nm assigned to ($\pi-\pi^*$) and ($n-\pi^*$) electronic transitions^(15,16). The electronic spectrum of Mn^{II} complex gave absorption peak at 260 nm related to charge transfer (C.T). Other peak at 382 nm was assigned to ${}^6A_{1g} \rightarrow {}^4T_{2g(D)}$ ⁽¹⁷⁾. The spectrum of Co^{II} complex (Fig-3) showed peak at 305 nm due to charge transfer. Other three peaks at 609 nm, 673 nm and 827 nm were found to be caused by (d-d) electronic transition type ${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$, ${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$ and ${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$ respectively⁽¹⁸⁾. The spectrum of Ni^{II} complex appeared absorption peak at 293 nm was related to charge transfer, then other three peaks at 430 nm, 620 nm and 803 nm were assigned to electronic transition type ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$, ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$ and ${}^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$ respectively⁽¹⁹⁾. The spectrum of Cu^{II} complex gave absorption peak at 300 nm due to charge transfer. The peak at 450 nm was caused by electronic transition ${}^2E_g \rightarrow {}^2T_{2g}$. The spectrum of Zn^{II} complex (Fig-4) showed absorption peak at 311 nm due to charge transfer. The absence of absorption peaks in the visible region indicated no (d-d) electronic transition happened, this is a good result for octahedral complex.⁽²⁰⁾

In order to study the binding mode of the new ligand with the metal ions, a comparison was made for the FT.IR spectra of the free ligand and those of the prepared complexes and the data was tabulated in (Table-3). The IR spectrum of the ligand (Fig-5) exhibited two bands at 3429 cm^{-1} and 3221 cm^{-1} indicated to the stretching mode of $\nu(\text{NH}_2)$ ^(21,22), on complexation (Fig-6) a shift with change in shape were observed from these bands, while increasing in intensity were noticed. The significant may be a result of coordination with metal ion. Very strong band in the ligand spectrum was observed at 1585 cm^{-1} ascribed to the $\nu(\text{C}=\text{N})$ stretching⁽²³⁾, suffered a great change to higher frequency was also observed on complexation (Fig-7) with metal ion. The characteristic band in the ligand spectrum at 1423 cm^{-1} which was assigned to the ($-\text{C}=\text{N}-\text{N}=\text{C}-$) stretching⁽²⁴⁾, suffered a great change in the intensity and in position, splitting to higher frequency was also observed on complexation with metal ion. This may suggest the participation of the nitrogen in this complexation. Two new stretching bands were noticed around $(416-496)\text{ cm}^{-1}$ which were assignable to the $\nu(\text{M}-\text{N})$ of the primary amine and ($\text{C}=\text{N}$) group^(25,26).

According to the results obtained and spectral analysis concluded that the ligand (Apodz) acted as bidentate ligand in all these complexes, the metal ions are hexacoordinate with most probable octahedral structure has been suggested to these complexes.



Table(1): Physical Properties and Elemental Analysis of the Ligand and It's Complexes

Compounds	Color	M.P° C	Yield %	Analysis Calc (Found)				
				Cl%	M%	C%	H%	N%
Ligand(Apodz)	Yellow	202	72	-	-	59.62 59.31	4.34 3.95	26.08 25.73
[Mn(Apodz) ₂ Cl ₂]	Orange	262	68	18.83 (17.89)	14.58 (13.50)	50.92 (50.11)	3.71 (3.04)	22.28 (21.56)
[Co(Apodz) ₂ Cl ₂]	Redish Brown	285	75	18.63 (18.11)	15.48 (14.32)	50.39 (49.81)	3.67 (2.97)	22.04 (21.88)
[Ni(Apodz) ₂ Cl ₂]	Green	276	82	18.68 (17.91)	15.26 (15.01)	50.52 (50.22)	3.68 (3.11)	22.10 (21.74)
[Cu(Apodz) ₂ Cl ₂]	Yellowish Green	280	85	18.39 (17.52)	16.58 (15.91)	49.74 (49.33)	3.62 (3.22)	21.76 (20.91)
[Zn(Apodz) ₂ Cl ₂]	Pruple White	291	71	18.34 (17.73)	16.79 (15.26)	49.61 (48.88)	3.61 (3.05)	21.70 (20.75)

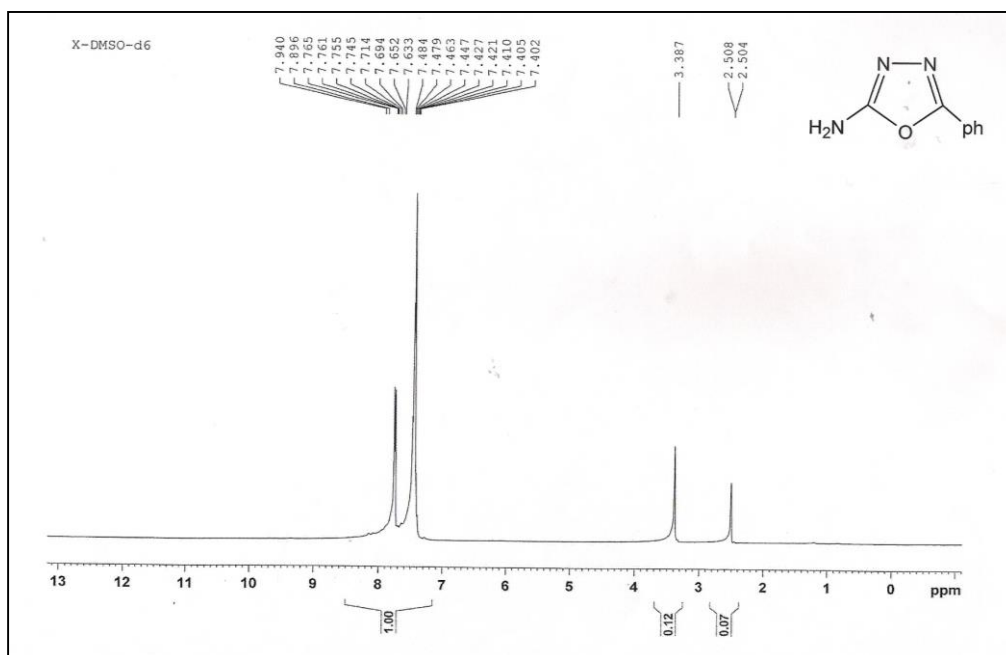
Table(2): UV-Vis, Magnetic Susceptibility and Conductance Measurements Data

Compounds	λ_{\max} (nm)	ABS	Wave number (cm^{-1})	ϵ_{\max} ($\text{L.mol}^{-1}.\text{cm}^{-1}$)	Λ_m ($\text{S.cm}^2.\text{mol}^{-1}$) in DMF(10^{-3}M)	μ_{eff} (B.M)
Ligand(Apodz)	252 319	0.566 2.397	39682 31348	566 2397	-	-
[Mn(Apodz) ₂ Cl ₂]	260 382	0.821 1.762	38461 26178	821 1762	35.5	4.68
[Co(Apodz) ₂ Cl ₂]	305 609 673 827	1.832 0.227 0.334 0.019	32786 16420 14858 12091	1832 227 334 19	38.9	3.50
[Ni(Apodz) ₂ Cl ₂]	293 430 620 803	1.816 0.122 0.073 0.017	34129 23255 16129 12453	1816 122 73 17	44.5	2.97
[Cu(Apodz) ₂ Cl ₂]	300 450	1.918 0.341	33333 22222	1918 341	38.5	1.63
[Zn(Apodz) ₂ Cl ₂]	311	1.827	32154	1827	15.6	Dia

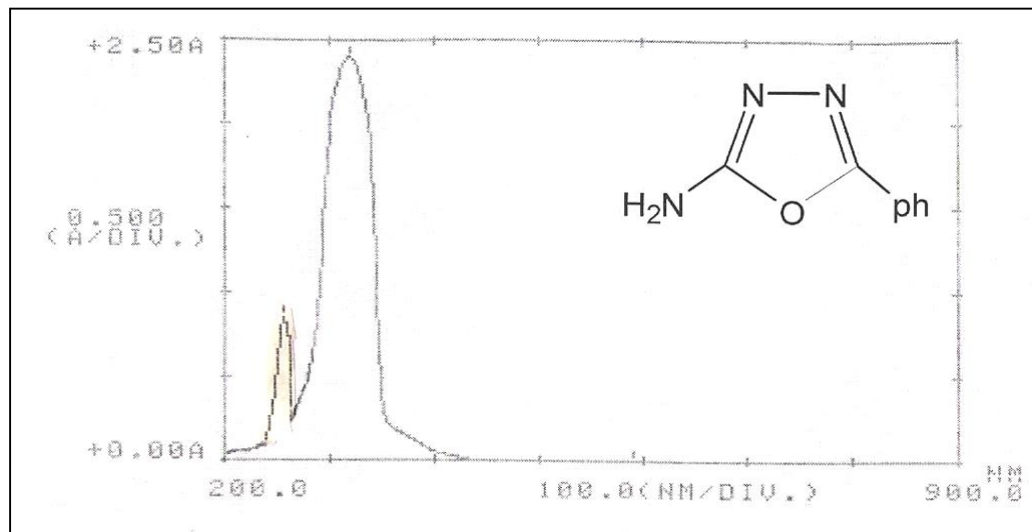
Table(3): The Main Frequencies of the Ligand and It's Complexes(cm^{-1})

Compounds	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{N})$	$\nu(-\text{C}=\text{N}-\text{N}=\text{C}-)$	$\nu(\text{M}-\text{N})$
Ligand(Apodz)	3429 s. 3221 s.	1585 v.s.	1423 V.S.	-
[Mn(Apodz) ₂ Cl ₂]	3309 br. 3124 br.	1651 s.	1475 sh. 1440 sh.	486 w. 430 w.
[Co(Apodz) ₂ Cl ₂]	3348 br. 3155 br.	1681 s.	1485 sh. 1425 s.	478 w. 416 w.
[Ni(Apodz) ₂ Cl ₂]	3379 br. 3286 br.	1666 s.	1489 s. 1450 sh.	496 w. 416 w.
[Cu(Apodz) ₂ Cl ₂]	3271 br. 3163 br.	1635 s.	1480 s. 1435 sh.	490 w. 470 w.
[Zn(Apodz) ₂ Cl ₂]	3291 br. 3116 br.	1651 v.s.	1489 sh. 1443 sh.	480 w. 462 w.

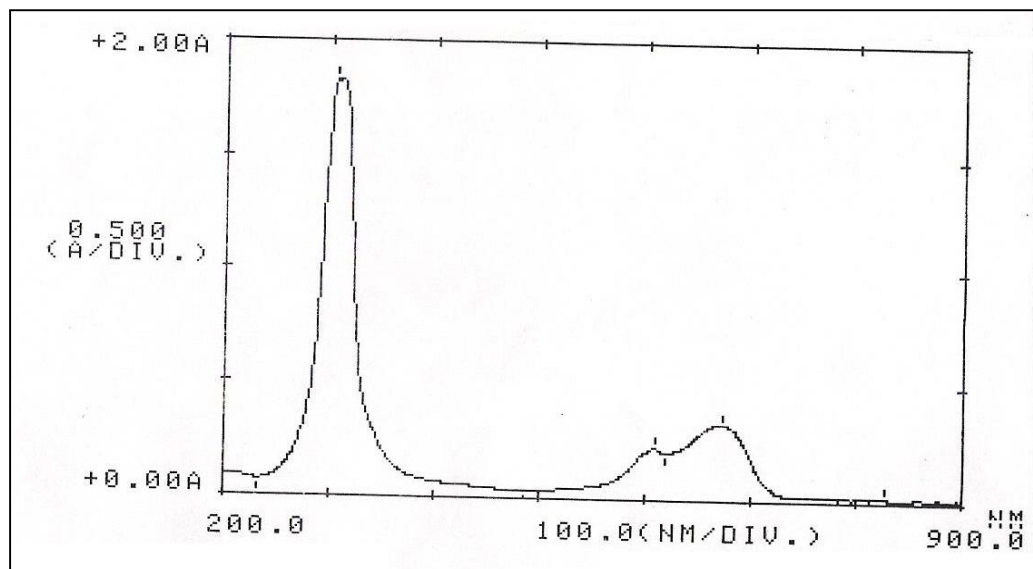
sh= sharp, sho= shoulder, v.s= very strong, s= strong, br= broad, w=weak.



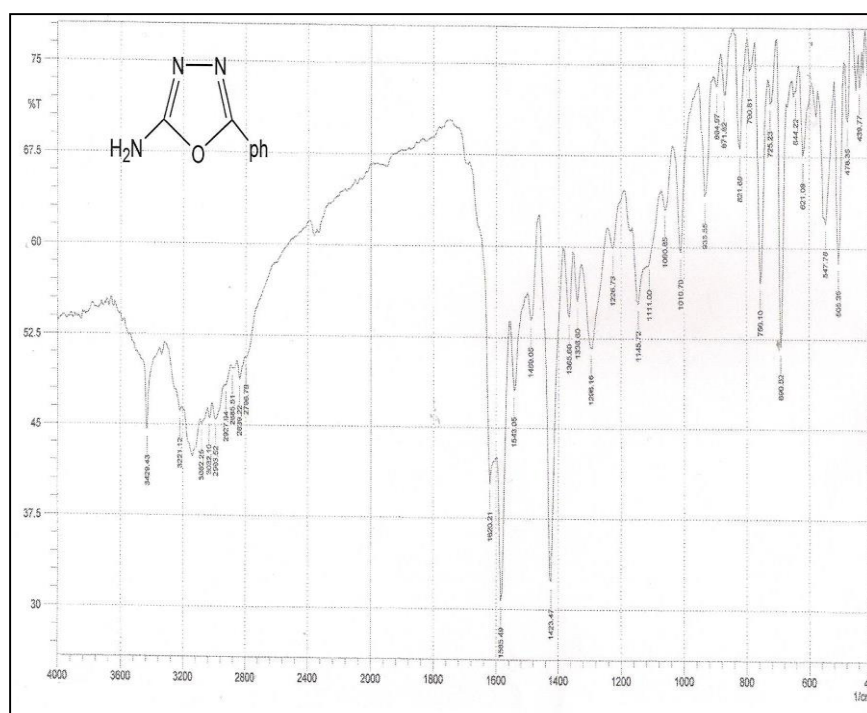
Fig(1):- ¹H NMR Spectrum of the Ligand(Apodz).



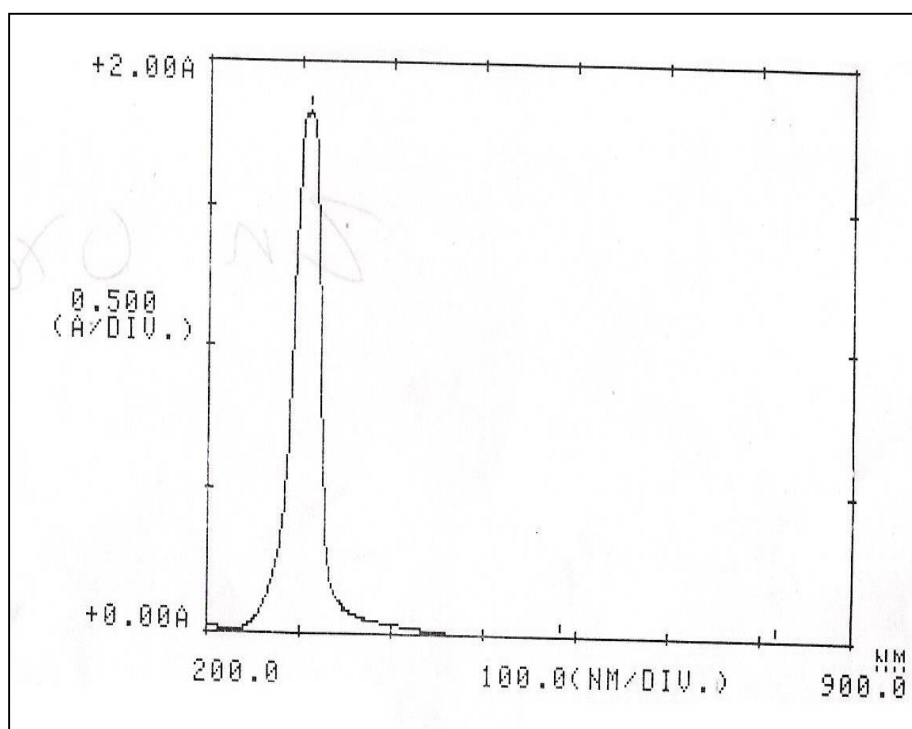
Fig(2):- UV-Vis Spectrum of the Ligand(Apodz)



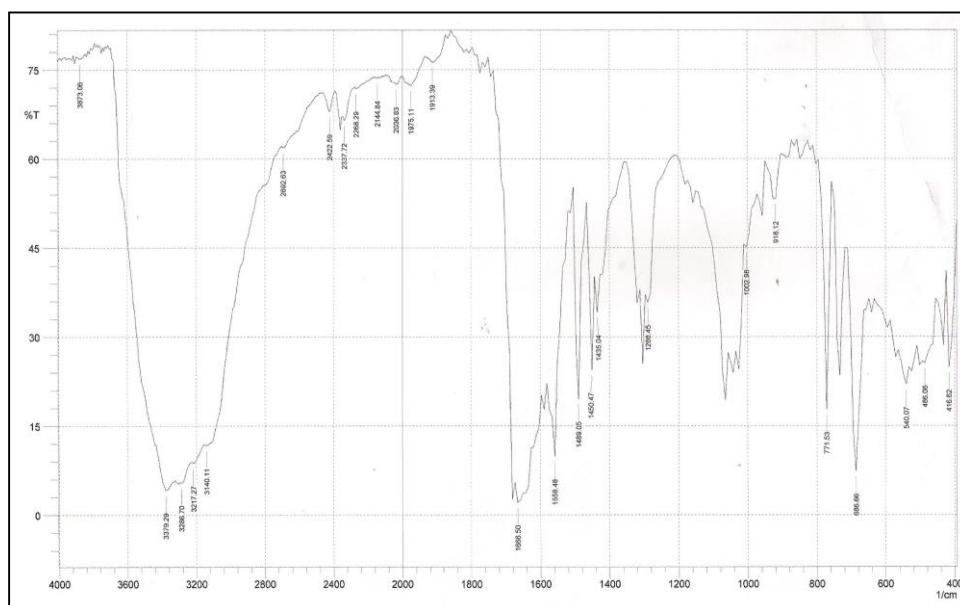
Fig(3):- UV-Vis Spectrum of the [Co(Apodz)₂Cl₂]



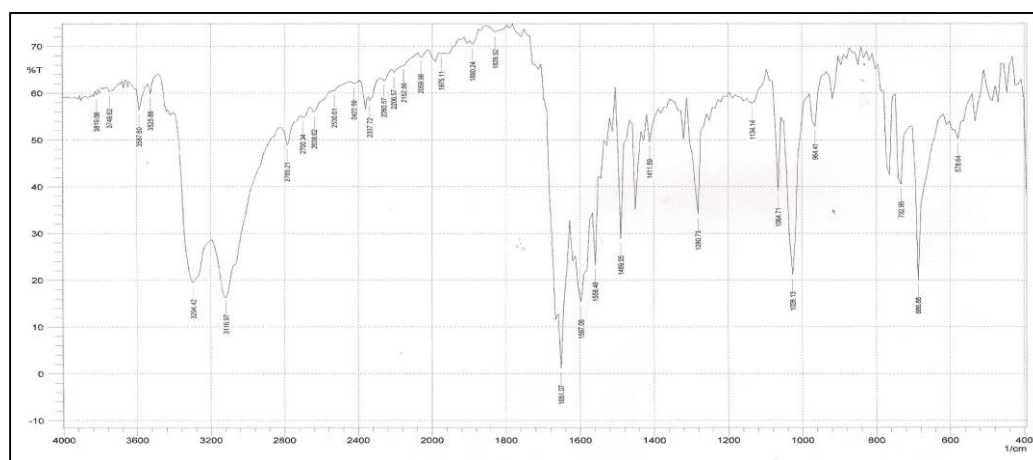
Fig(4):- UV-Vis Spectrum of the [Zn(Apodz)₂Cl₂]



Fig(5):- FT.IR Spectrum of the Ligand(Apodz)



Fig(6):- FT.IR Spectrum of the $[Ni(Apodz)_2Cl_2]$



Fig(7):- FT-IR Spectrum of the [Zn(Apodz)₂Cl₂]

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تحضير وتشخيص معقدات 2- امينو -5-فنيل 1، 3، 4- اوكسادايازول مع بعض
الأيونات الفلزية المنتخبة.

عامر جبار جراد ، زهراء عاصم الوتري
قسم الكيمياء ، كلية التربية – ابن الهيثم ، جامعة بغداد

الخلاصة:-

حضر الليكاند الجديد 2- امينو -5- فنيل – 1، 3، 4- اوكسادايازول من تفاعل بنز الديهايد سيمكاربازون مع البروم وخلات الصوديوم في وسط حامض الخليك. شخض الليكاند المحضر بوساطة أطياف الرنين النووي المغناطيسي للبروتون والأشعة تحت الحمراء وفوق البنفسجية – المرئية والتحليل الدقيق للعناصر (C.H.N) . تمت مفاعلة الليكاند مع بعض الأيونات الفلزية المنتخبة (Mn^{II} , Co^{II} , Ni^{II} , Cu^{II} and Zn^{II}) في وسط ايثانول- ماء وبنسبة فلز: ليكاند (2:1) وتم الحصول على سلسلة من المعقدات ذات الصيغة العامة $[M(L)_2Cl_2]$. شخضت هذه المعقدات باستخدام تقنية الامتصاص الذري أللهبي ، أطياف الأشعة تحت الحمراء وفوق البنفسجية – المرئية والتحليل الدقيق للعناصر (C.H.N) فضلاً عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية ، كما تم تقدير محتوى الكلور باستخدام طريقة مور. ومن النتائج المحصول عليها تم اقتراح الشكل ثماني السطوح للمعقدات المحضرة.