

Syntheses, Characterization and Antimicrobial Studies of a New Ligand (3-Hydrazino-5-phenyl-4H-1,2,4-triazole-4-amine) and Its Complexes with Some Transition Metal

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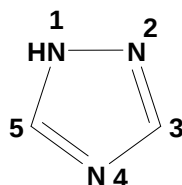
Abstract

A new ligand of (3-Hydrazino-5-phenyl-4H-1,2,4-triazole-4-amine) (L) and its complexes with Cr (III), Fe (III), Co (III), Ni (II) and Cu (II) were synthesized. These compounds were identified by elemental analysis, Molar conductivity, as well as spectroscopic methods (IR, ^1H NMR and Mass). It showed that the ligand coordinates through Nitrogen atoms of NH_2 groups for all the complexes as shown in figure (1). This was supported by the appearance of a band corresponding to the metal–nitrogen stretching vibration at $502\text{--}555\text{ cm}^{-1}$ in the complexes. The complexes of Cr (III), Fe (III) and Co (III) suggested an octahedral geometrics, while Ni (II) and Cu (II) tetrahedral geometry. All complexes and their parent organic moiety have been screened for antibacterial activities (*E-coli* and *staph aurens*) by using spread method and measurement of inhibition zone. This study showed inhibition zone against (*E-coli* and *staph aurens*).

Key words: triazol, Schiff base, Metal complexes, antibacterial studies.

Introduction

Triazole derivatives have been reported to have pharmacological, insecticidal, fungicidal, and herbicidal activities (Serdar *et al.*, 2007). The largest and most diverse group of heterocyclic amines is that represented by five membered ring systems containing more than one bridgehead nitrogen. 1, 2, 4-triazole is a symmetrical type of triazole, it is a basic unit to prepare several derivatives with a wide range of applications (Cansiz *et al.*, 2004; El-Sayed., 2006; Gumrukcuoglu *et al.*, 2006; Bekircan *et al.*, 2006; Serdar *et al.*, 2007; Al masirad *et al.*, 2007).



Materials and Apparatuses

Preparation of the Ligand

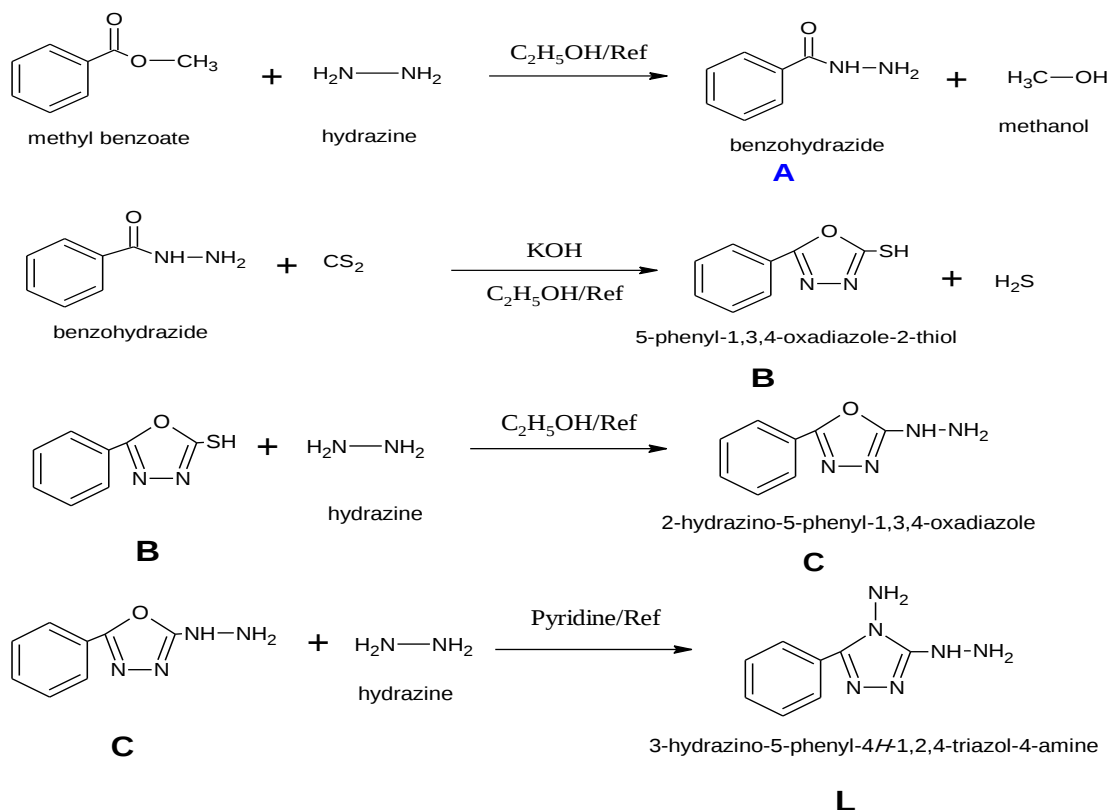
The novel ligand (3-Hydrazino-5-phenyl-4H-1,2,4-triazole-4-amine) (Scheme 1) was prepared as follows:- A mixture of methyl benzoate (0.1 mole ,13.6 gm) and hydrazine hydrate (0.2 mole , 6.2 ml) dissolved in ethanol (50 ml) (Arks *et al.*, 2005) was refluxed using water bath for 3 hrs, The resultant mixture [A] was concentrated

and white solid precipitate (Benzo hydrazide) which separated was filtered and recrystallised from ethanol.Yield: 95.58 %, m. p. 138-140°C.

A mixture of [A] (0.05mol, 6.8 gm), KOH (0.05 mol, 2.8 gm) in 100 ml ethanol and CS₂ (0.05 mol,3 ml) was refluxed on a water bath for 8 hrs, until the evolution of H₂S gas ceased (vogel. A., 1978). The excess CS₂ was removed under reduced pressure. The resultant mixture [B] was acidified with acetic acid and white solid (5-phenyl-1,3,4- oxadiazioie -2- thio) which separated was filtered and recrystallised from ethanol. Yield: 80 %, m. p. 220-222 °C.

A mixture of [B] (3gm , 0.02 mol) and hydrazine hydrate (0.02 mol, 2.5 ml) dissolved in ethanol (50 ml) was refluxed on a water bath for 3 hrs .The resultant mixture of [C] was concentrated and light brown solid (2-hydrazino-5- phenyl -1,3,4-oxadiazole) which separated was filtered and recrystallised from ethanol. Yield: 63.9 %, m. p. 189-192°C.

A mixture [C] (0.05 mol, 10 gm) and hydrazine hydrate (0.1 mol, 4 ml) dissolved in pyridine (20 ml) was refluxed on a water bath for 5 hrs..The resultant mixture [ligand] was concentrated and pale florid solid (3-hydrazino-5-phenyl-4H-1,2,4-trizole-4-amine) which separated was filtered and recrystallised from ethanol. Yield: 66.6 %, m. p. 202-204°C.



Scheme (1): Preparation of ligands

Preparation of complexes

The Cr(III), Co(III), Fe(III), Ni(II) and Cu(II) complexes were prepared by refluxing the respective hydrated metal chloride (1 mmol) in 15 ml ethanol with (50

ml) of an ethanolic solution of the ligand (1mmol, 0.3 gm) for 4 hrs. The resultant solids which separated were filtered, washed with ethanol and dried in air.

Apparatuses

Elemental C, H and N analysis were carried out on a Thermofinigan flash analyzer, the FTIR spectra in the range (200-4000) cm^{-1} were recorded as CsI discs using a Shimadzu FTIR spectrophotometer, molar conductance measurements were made in anhydrous DMSO at 25 °C using Inolabcond 720, The ^1H nuclear magnetic resonance spectra were recorded a Bruker DRX System AL500 (500 MHZ) spectrometer, relative to the internal standard tetramethylsilane (TMS), DOSO-d6 used as solvent. Melting points were determined in open capillary tubes using an electro thermal melting point /SMP3I apparatus. Mass spectra were recorded in the range (0-800) m/z on a 5973 network mass selective detector.

Results and Discussion

The ligand and its complexes were checked by using elemental analyss. The results of C.H.N were shown in Table (1) The calculated values showed good agreement with the experimental values, Melting points, physical properties and molar conductance to all the compounds listed in Table (2).

Table (1): Elemental analysis data of the ligand

Ligand	Molecular Weight	Experimental			Theoretical		
		C%	H%	N%	C%	H%	N%
L	190	50.62	5.31	44.18	50.52	5.26	44.21

Table (2): Conductance, physical properties data of the ligand and its complexes

No	Compound	Molecular formula	Color	Λ $\text{Scm}^2 \text{mol}^{-1}$	Melting Point °c
1	Ligand	$\text{C}_8\text{H}_{10}\text{N}_6$	pale florid	-----	202-204
2	$[\text{Fe}(\text{L})_2\text{Cl}_2]\text{Cl}$	$\text{Fe}(\text{C}_{16}\text{H}_{20}\text{N}_{12})_2 \text{Cl}_3$	pale green	40.7	168-170
3	$[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$	$\text{Co}(\text{C}_{16}\text{H}_{20}\text{N}_{12})_2 \text{Cl}_3$	white	38	214-216
4	$[\text{Cr}(\text{L})_2\text{Cl}_2]\text{Cl}$	$\text{Cr}(\text{C}_{16}\text{H}_{20}\text{N}_{12})_2 \text{Cl}_3$	brown	37.6	218-220
5	$[\text{Cu}(\text{L})\text{Cl}_2]$	$\text{Cu}(\text{C}_8\text{H}_{10}\text{N}_6) \text{Cl}_2$	green	14	282-284 d*
6	$[\text{Ni}(\text{L})\text{Cl}_2]$	$\text{Ni}(\text{C}_8\text{H}_{10}\text{N}_6) \text{Cl}_2$	white	16	222-224

d*=decomposition

Infra-Red Spectroscopy

The FTIR spectrum for L shows a stretching absorption bands at 3101cm^{-1} , 1610 cm^{-1} , 1446 cm^{-1} and 1350 assigned to $\nu(\text{C-H})$ (Williams. H, *e al.*, 1973). Aromatic, C=N of the ring trizole, asymmetrical C-N-C and symmetrical C-N-C

stretching respectively. These bands shifted to lower wavelength in the spectra of complexes in comparison with ligand. The change of the spectra provides evidences of formation metal complex. The IR data of ligand and its complexes are shown in Table (3) and figure (2-4). The Table listed the stretching frequency (ν) for some of the characteristics groups exhibited by the ligand and its complexes.

Table (3): Characteristic absorption bands of ligand and its complexe.

No	Compound	ν C-H Aromatic Cm^{-1}	C=Nu Cm^{-1}	ν C-N-C asy Cm^{-1}	ν C-N-C sy Cm^{-1}	ν M-N Cm^{-1}	ν M-Cl Cm^{-1}
L	$\text{C}_8\text{H}_{10}\text{N}_6$	3101	1610	1446	1350		
1	$[\text{Fe}(\text{L})_2\text{Cl}_2]\text{Cl}$	3055	1610	1444	1386	542	318
2	$[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$	3149	1610	1448	1352	555	383
3	$[\text{Cr}(\text{L})_2\text{Cl}_2]\text{Cl}$	3112	1604	1444	1373	503	360
4	$[\text{Ni}(\text{L})\text{Cl}_2]$	3143	1610	1448	1352	555	329
5	$[\text{Cu}(\text{L})\text{Cl}_2]$	3122	1637	1492	1319	502	360

Nuclear Magnetic Resonance (^1H -NMR Spectra)

The data of proton NMR of the ligand (3-Hydrazino-5- phenyl- 4H-1,2,4-triazole-4-amine) displayed good solubility in DMSO. The proton nuclear magnetic resonance spectral data gave additional support for the composition of the ligand. The spectrum also exhibits -NH peaks at 5.4 ppm. Another peaks exhibit at 5.9 ppm due -NH₂. The aromatic ring exhibit peaks at (7.52-8.03) ppm and of peaks the proton NMR of the ligand which shown in figure (5).

Mass spectra

The mass spectrum of the ligand exhibits a molecular ion peak [M⁰] at m/z 190, the ligand spectrum showed fragment at m/z (133, 103, 87 and 77) due to ($\text{C}_7\text{H}_7\text{N}_3$), ($\text{C}_7\text{H}_5\text{N}$), (CH_5N_5), and (C_6H_5) respectively as shown in Figure (6).

The mass spectrum to the complex $[\text{Cr}(\text{L})_2\text{Cl}_2]\text{Cl}$ shows a molecular ion peak at m/z [M⁰] 537 which is equivalent to molecular mass of the complex. This complex shows another a fragment ion peaks with loss of chlorine atom at m/z 501. The complex spectra shows fragment ion peak with loss two chlorine atom at m/z (466,430) due to $[\text{Cr}(\text{L})_2\text{Cl}]$ and $[\text{Cr}(\text{L})_2]$ respectively. The complex spectrum shows fragment ion peak at m/z (154) due to ($\text{C}_{12}\text{H}_{10}$).

The mass spectrum of the complex $[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$ shows a molecular ion peak at m/z [M⁰] 544, This complex spectrum shows another fragment ion peak with loss of chlorine atom at m/z 508. The complex spectrum shows fragment ion peaks with loss two chlorine atom at m/z (472,437) due to $[\text{Cr}(\text{L})_2\text{Cl}]$ and $[\text{Cr}(\text{L})_2]$ respectively the spectrum shows another peaks at m/z (318,171and 77) due to ($\text{C}_{16}\text{H}_{14}\text{N}_8$)⁺ . ($\text{C}_2\text{H}_4\text{N}_6\text{Co}$)⁺ . (C_5H_{10}).

The mass spectrum of the complex $[\text{NiLCl}_2]$ shows a molecular ion peak at m/z [M⁰] 318, This complex spectrum shows another fragment ion peaks with loss of

chlorine atom at m/z 283 and 248, the spectrum shows another peaks at m/z (133,115) due to $(C_7H_7N_3)^+$ $(CH_2N_3Ni)^+$. The mass spectra of the complexes shown in figure (7), (8), (9).

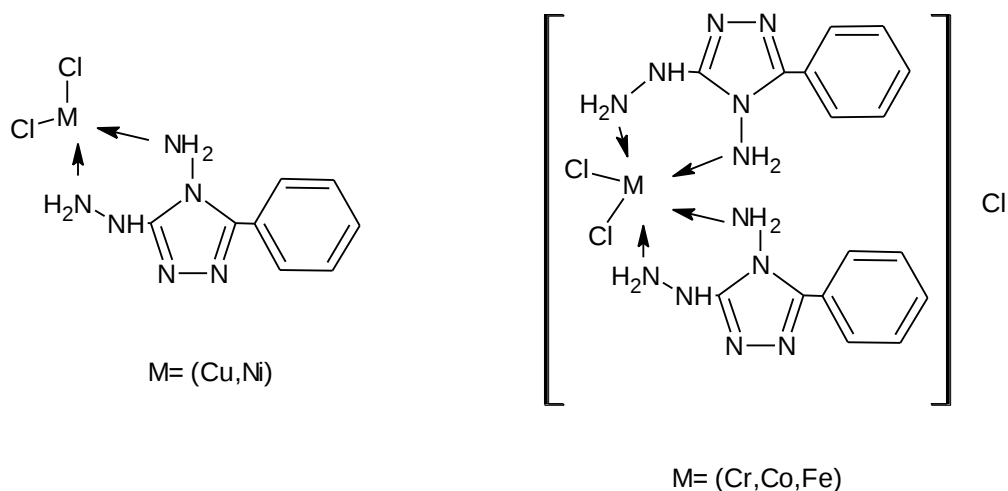


Figure (1): Suggested structural formula of the prepared metal complexes

Analytical and spectra data (1H NMR, IR and mass spectra) of all synthesized compounds were in full agreement with the proposed structure.

Biological activity

Testing the biological activity for ligands and their complexes by using spread method and measurement inhibition zone by using (DMSO) as a solvent showed an inhibition to the growth bacteria *E-coli* and *Staphylococcus*. The inhibition zon was measured by mm as showed in Table (4) Antibacterial activity of each compound was evaluated by measuring the zone of growth inhibition against the test organisms with zone reader (HiAntibiotic zone scale) (Andrews.j.,2001,Ahmad.I *et al.*,2001)

Table (4): Antibacterial screening data of the ligand and its metal complexes

Compound	<i>Escherichia coli</i>	<i>Staphylococcus Aurens</i>
	Inhibition zone(mm)	Inhibition zone(mm)
$L = C_8H_{10}N_6$	20+++	17++
$[Co(L)Cl_2] Cl$	14+	20+++
$[Cr(L)Cl_2] Cl$	12+	10+
$[Fe(L)Cl_2] Cl$	18++	12+
$[Cu(L)Cl_2]$	26++++	12+
$[Ni(L)Cl_2]$	15++	14+

**** (+ = Weak Inhibition, ++ =Medium Inhibition, +++ = Good Inhibition, ++++ =Very good Inhibition).**

Conclusion

The ligand (3-Hydrazino-5-phenyl-4H-1,2,4-triazole-4-amine) was successfully synthesized. The ligand was bonded to different transition metal salts to form the corresponded complexes. It may be concluded that the ligand coordinates through Nitrogen atoms of NH₂ groups as shown in figure (1). Observations suggest the octahedral geometry for the complexes of Cr (III), Co(III), Fe(III) and tetrahedral geometry the complexes of was proposed for Ni (II), Cu(II) . All complexes and their parent organic moiety have been screened for antibacterial (*E-coli and staphaurens*).

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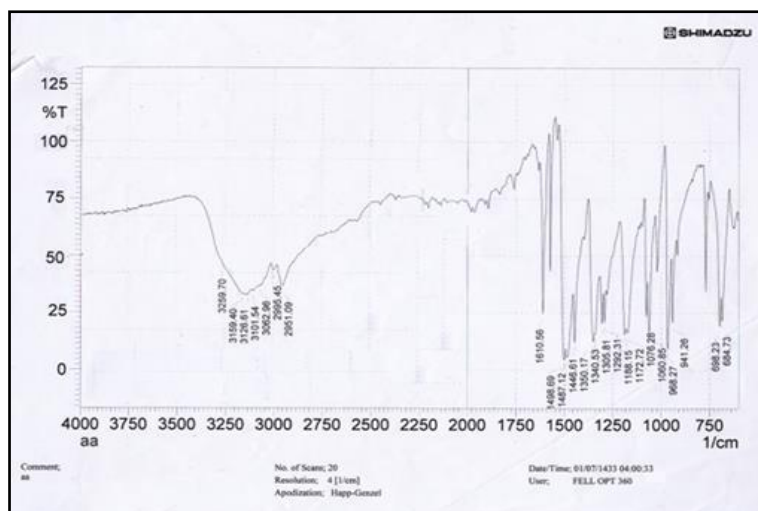


Figure (2): IR spectrum of Ligand ($C_8H_{10}N_6$)

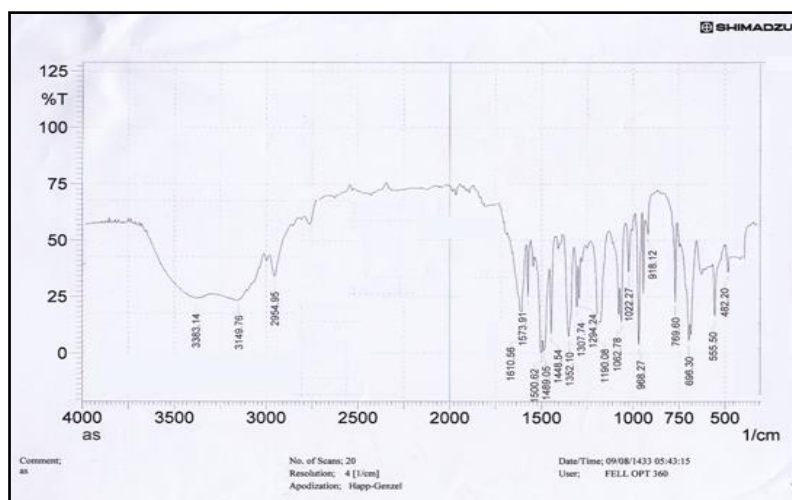


Figure (3): IR spectrum of $[Co(L)_2Cl_2]Cl$

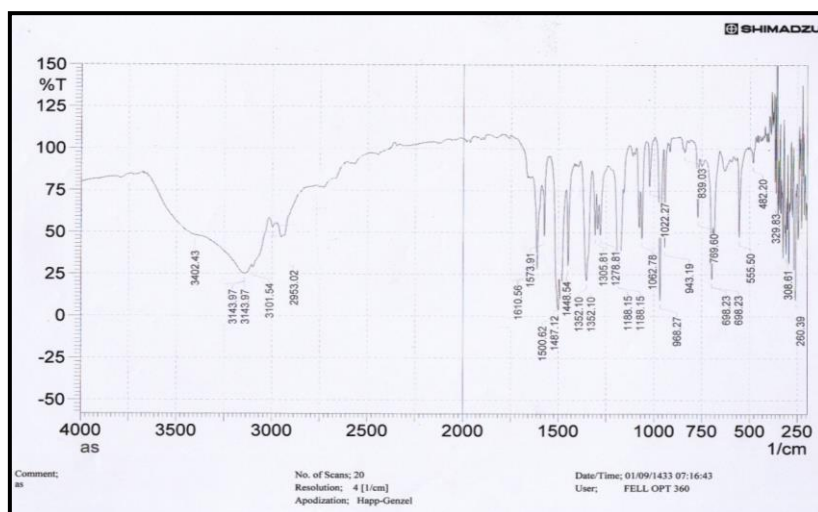


Figure (4): IR spectrum of $[Ni(L)Cl_2]$

Mass spectrum showing relative abundance (Y-axis, 0 to 3,200,000) versus m/z (X-axis, 40 to 220). The base peak is at m/z 121. Other significant peaks are labeled at m/z 41, 57, 65, 77, 87, 93, 103, 133, 152, 162, 177, and 190.

Mass spectrum of the sample showing relative intensity versus m/z. The base peak is at m/z 64. Other significant peaks are labeled at m/z 77, 96, 128, 154, 192, 224, 240, 256, 276, 350, 396, 430, 466, 501, and 537.

Figure (7): Mass spectrum of $[\text{Cr}(\text{L})_2\text{Cl}_2]\text{Cl}$

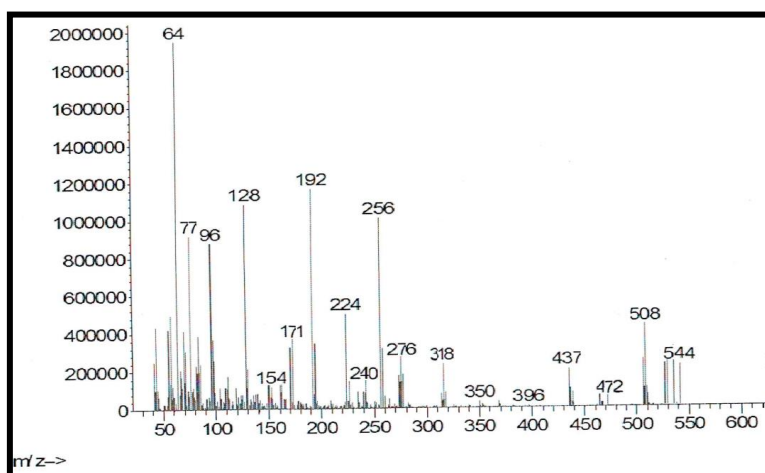


Figure (9): Mass spectrum of $[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$

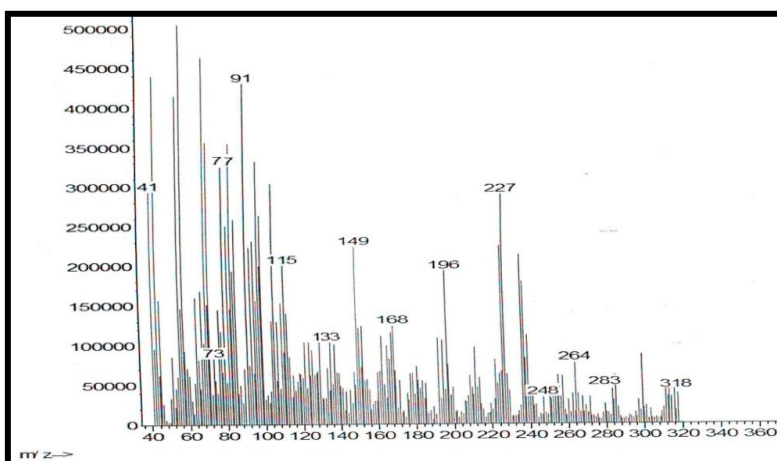


Figure (10): Mass spectrum of $[\text{Ni}(\text{L})\text{Cl}_2]$

تحضير وتشخيص ودراسة الفعالية الحيوية لليكاند (3-Hydrazino-5-phenyl-4H-1,2,4-triazole-4-amine) ومعقداته مع بعض العناصر الانتقالية

منتهى ياسين حيال

قسم الكيمياء، كلية العلوم، جامعة ذي قار

الخلاصة

تم تحضير بعض معقدات العناصر الانتقالية $\text{Cr}(\text{III})$, $\text{Fe}(\text{III})$, $\text{Co}(\text{III})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ مع اليكاند (3-Hydrazino-5-phenyl-4H-1,2,4-triazole-4-amine) وشخصت الصيغ التركيبية لليكاند ومعقداته باستخدام تقنية تحليل العناصر، التوصيل المولاري بالإضافة إلى استخدام أطياف الأشعة تحت الحمراء، أطياف الرنين النووي المغناطيسي وطيف الكتلة. ويحصل التناسق من خلال ذرت النيتروجين التابعة لمجاميع NH_2 وهذا الاستنتاج يؤكد من خلال تشخيص حزم امتصاص عند (502-555) عائدة إلى تناسق الذرة

المركزية مع ذرة النيتروجين (M- N) وكانت النتائج مطابقة لما هو متوقع عمليا. وتم تعيين الهيئة الفراغية لكل من معقدات النيكل الثنائي والنحاس الثنائي بأنها رباعي السطوح بينما أظهرت معقدات الحديد الثلاثي، الكوبلت الثلاثي والكروم الثلاثي شكل ثماني السطوح. وتم اختبار الفعالية البايولوجية لليكاند المحضر ومعقداته باستخدام طريقة الانتشار وذلك بقياس منطقة التثبيط وباستخدام مذيب ثنائي مثيل اوكسيد الكبريت (DMSO). وأعطت اختبارات الفعالية نتائج ايجابية حيث لوحظ ظهور تثبيط جيد ضد بكتريا *E-coli* و *Staphaurens*.