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and Scientific Research

University of Babylon

College of science for women

Department of Chemistry

Synthesis, Characterization of Some New Metal Ions Complexes of Triazene Derivatives and Evaluation of their Biological Activity and Corrosion Inhibition"

A Thesis

Submitted to the Council of the College of Science for Women/
University of Babylon as a Partial Fulfilment of the
Requirements for the Degree of Master of Science in Chemistry

By

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2023 A.D **1444 A.H**

بسم الله الرحمن الرحيم

قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا ۖ إِنَّكَ أَنتَ الْعَلِيمُ الْحَكِيمُ 

صدق الله العظيم

الآية ٣٢ من سورة البقرة المباركة

Supervisor Certification

I certify g

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Date: / /2023

Recommendation of Head of Chemistry Department

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Date: / / 2023

Dedication

To the masters of the universe, Muhammad and the pure family of Muhammad

(Peace be upon them)

To whose name I proudly bear,

To a Literary and my dream

To patience and optimism

To my support and strength

For those I don't know and those who don't know me

To those who were my sanctuary and refuge to my happiness and sadness

Haneen

Acknowledgments

Praise be to **Allah**, Lord of the worlds. Praise be to **Allah**, who helped me and gave me the strength, patience, and endurance to complete this thesis.

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Haneen

Abstract:

Preparing new triazene compounds derived from 6-aminopenicylic acid, characterizing these ligands, and preparing new complexes with a number of metal ions (zinc, copper, and cadmium).

Where the first step included the reaction of the amine(5-amino-2-methylphenol and 4-aminoantipyrine and para- Nitro aniline,) with 6-aminopenicillin compound to produce the corresponding triazene compound.

Which in turn entered into the reaction of the formation of complex compounds in the second step with a salt of divalent metal ions chlorides, gave octahedral ,hybridization sp^3d^2 complexes with a molar ratio(1:2) M:L. The prepared compounds were identified using FTIR and ^{1}HNMR spectroscopy, UV-vis, mass spectrometry, magnetic susceptibility, thermal analyses, as well as atomic absorption spectrometry.

In addition to studying some physical properties of the prepared compounds, The effectiveness of the prepared ligands and complexes in protecting carbon iron from corrosion was studied in the acidic medium of 0.1 M hydrochloric acid, and the compounds gave good results in protection, as the protection for the ligands reached 73%, while the prepared complexes gave a higher protection rate of 86% for the cadmium complex and 90% for the zinc complex. As well as studying the effectiveness of the prepared compounds in the inhibition of bacteria of the type GM positive and gave a positive result in the inhibition of both ligands and complexes.

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List of Abbreviations

Shorten	Full name
λ max	Maximum Wavelength
6APA	6-Aminopenicillanic Acid
DMSO	Dimethyl Sulfoxide
Oct	Octahedral
β-lactam	Beta Lactam
C.T	Charge Transfer
M.P	Melting Point
^{1}HNMR	Proton-Nuclear Magnetic Resonance
FT-IR	Fourier Transform Infrared
UV–Vis	Ultraviolet-Visible Spectroscopy

nm	Nanometer

Chapter one
Introduction

1.1. Heterocyclic chemistry

The development of heterocyclic chemistry coincided with the advancement of organic chemistry in the 1800s [1]. Fried-lander discovered indigo dye in 1906, [2] Heterocyclic compound is the class of cyclic organic compounds those having at least one hetero atom (atom other than carbon) in the cyclic ring system. [3] the most common heteroatoms are nitrogen (N), oxygen (O) and Sulphur (S) [4] elucidating petroleum's biological origin. Chargaff's principles, published in 1951, elucidated the significance of heterocyclic chemicals pyrimidines and purines in the genetic code [5] Heterocyclic chemistry is the largest and most diverse family of organic molecules, and it is one of the most challenging and fascinating fields of organic chemistry [6] For a long time, the chemistry of heterocyclic compounds has been an intriguing subject of study due to its increasing applicability in various sectors such as medical and selective therapeutics [7] Heteroatoms are a very common fraction of various active medications. Various compounds such as hormones, alkaloids antibiotic, essential amino acids, hemoglobin, vitamins, dyestuffs and pigments have heterocyclic structure. [8], heterocyclic compounds may be classified into two categories:

- Aliphatic heterocyclic compounds called saturated
- Aromatic heterocyclic compounds which may be saturated or unsaturated [9].

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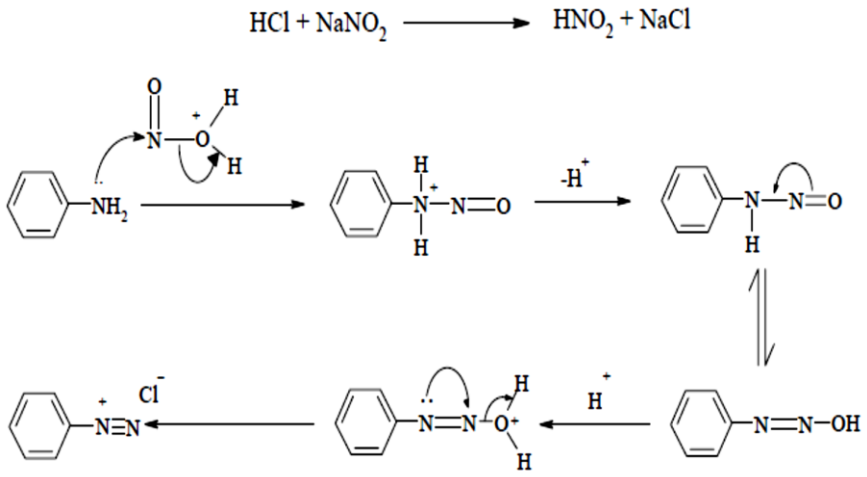
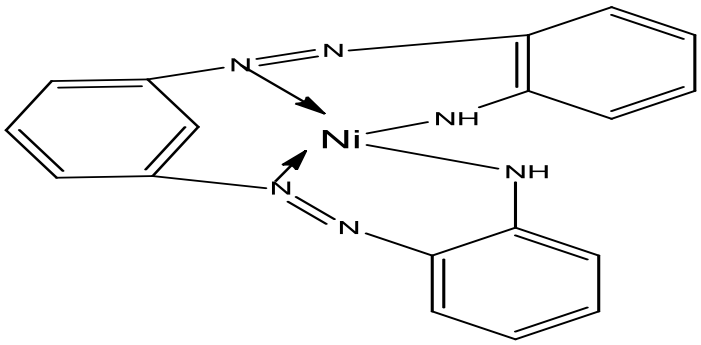
1.2. Dizaniume Salt

Dizaniume salts are a group of organic compounds that have a functional group in them RN2X, where R can be any organic molecule such as an alkyl or aryl, and X is any inorganic moiety such as halogen. [10] Dizaniume salts have been developed as important intermediates in the organic synthesis of dyes. [11] Dizaniume salts are used to manufacture azo dyes [12] ,A zo compounds are among the most important synthetic dyes. It contains the azo group Ar-N = N-Ar. It accounts for about 70% of all pigments and is the most important class of organic compounds, attracting the attention of researchers because of its wide-ranging applications [13]. azo imidazole compounds are usually applied in methods of coloring cotton, wool, silk, rubber, plastic, printing and some drugs, including the inhibition of microbial growth [13] Azo compounds are created through diazotization and coupling, which entails reacting aromatic amines with $NaNO_2$/HCl to make a dizaniume salt,[14] then coupling with electron-rich aromatics more stable, **scheme (1-1)** [15] show the equation of prepare it . dizaniume salts, a lot of study has been done. The salts allow groups such as OH, halogens, CN, H, etc. to be added to compounds), Dizaniume salts are among the most versatile compounds in organic chemistry[16]



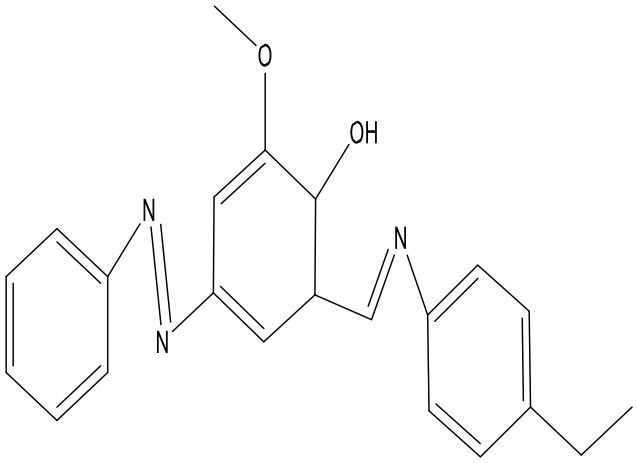
Scheme (1-1) Mechanism of diazotization of aromatic amine

Anitha ,et.al.,(2015) [17], prepared a series of (Cu II and Ni II) complexes with novel bis azo dye 2,2 benzene-1,3-diyl di (E)diazene-2,1- diyldi aniline derived from m-phenylene diamine and aniline ,**Scheme (1-2)** show as azo complex. Stoichiometric ratio of the complexes has been found to be 1:1 (M: L). the shape of the complex was a square planar geometry the proved the shape were characterized by, mass spectroscopy , IR, UV–vis, 1H and 13C NMR spectroscopy, Atomic Absorption ,C.H.N.S



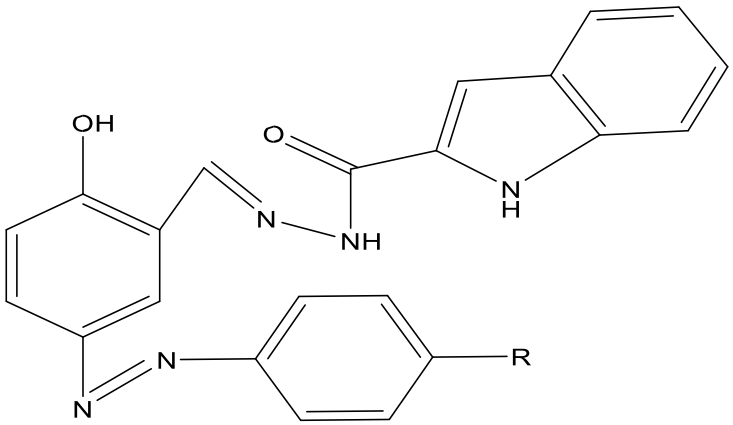
Scheme (1-2): Structure of Ni II metal chelate of bis azo dye 2,2[benzene-1,3-diyl di (E)diazene-2,1- di yl] di aniline ligand

Sarigul, M., Sari, et al., (2016) [18] prepared azo- azo methine. **Scheme (1-3)** shows the synthesis of azomethine compounds, using 4-ethylaniline and reacting it with 2-hydroxy-3methoxy- 5- (E) -phenyl di azenyl] benzal dehyde to give the final compound. the proved the shape were characterized by, mass spectroscopy , IR, UV–vis, 1H and 13C NMR spectroscopy



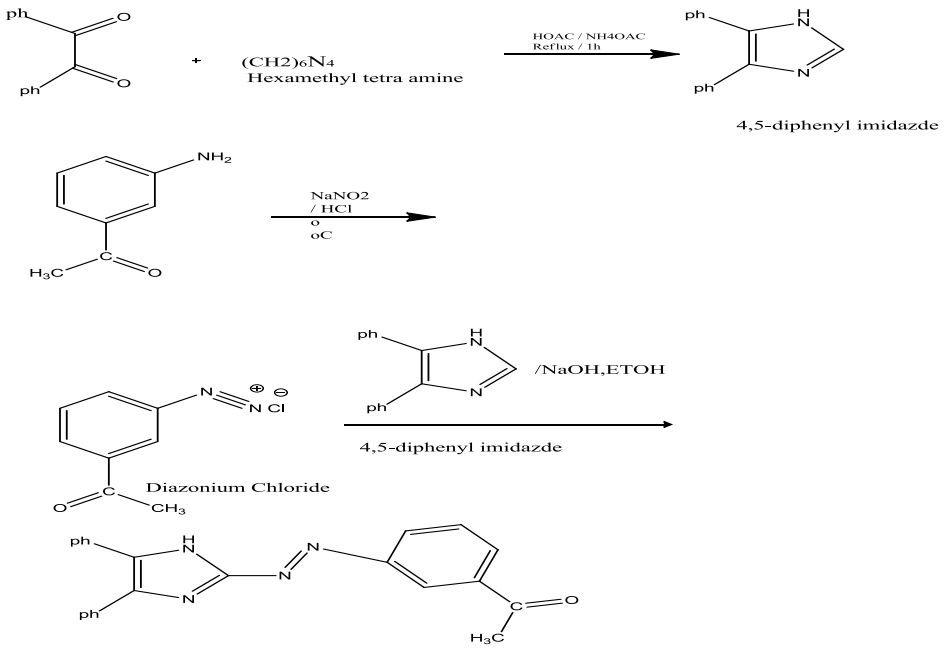
Scheme (1-3) Synthesis of Azo-azo methine Compounds

Yang, X, et., al., (2020) [19] synthesis of azo-azo methine by using azo methine to react with an azo-dye compound to give the final compound. the proved the shape were characterized by, mass spectroscopy , IR, UV–vis, 1H and 13C NMR spectroscopy **Scheme (1-4)** shows the synthesis



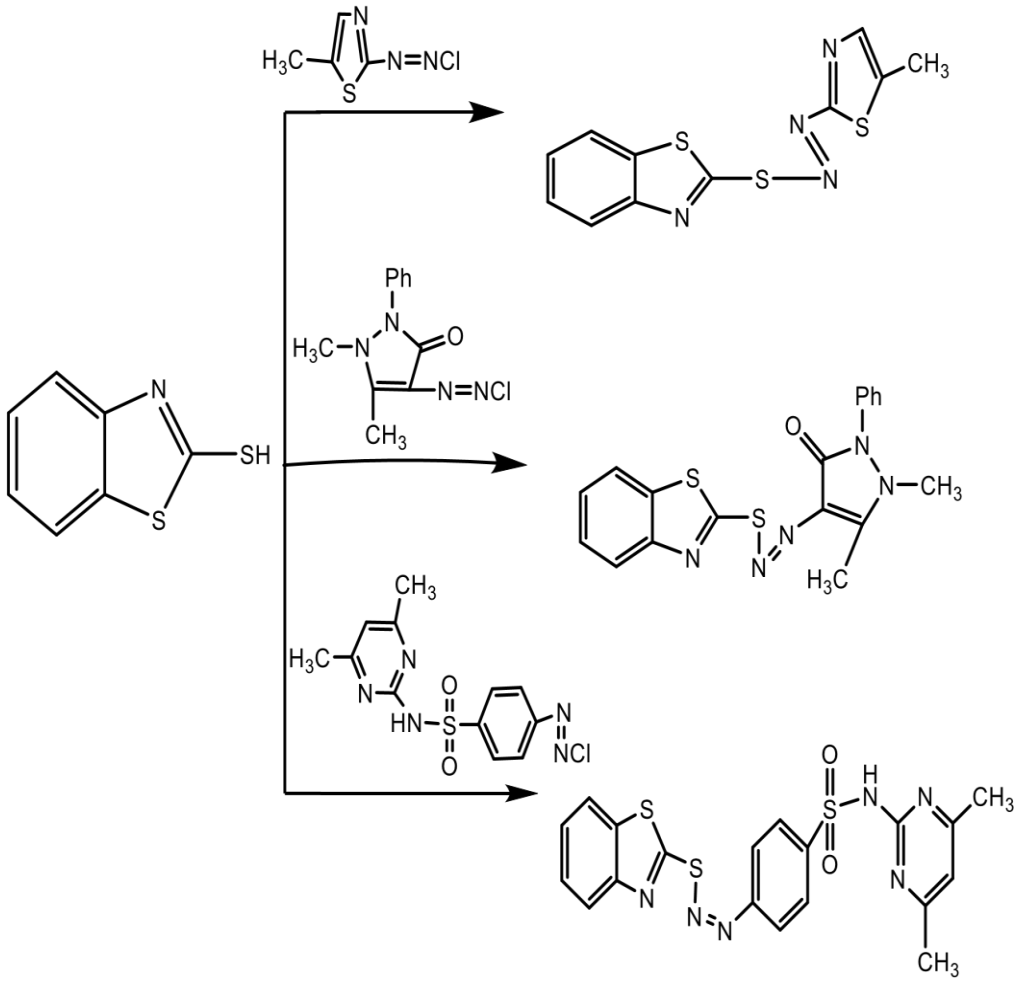
Scheme (1-4) the Synthesis of Azo-azomethine Compounds

Alaa Farag.,et.,.al (2015) [20] studied, prepared and identified one of the new azo compounds (APAI-3) (3- Acetyl phenyl)azo - 4,5-diphenyl imidazole using dizaniume Chloride salt, **scheme (1-5)** shows the synthases of ligand , and the shape was identified through infrared, mass ,^{1}HNMR.



Scheme (1-5) synthases of (3- Acetyl phenyl) azo - 4,5-diphenyl imidazole (3-APAI)azo dyes

M. Niluvanji Matada et. al., (2020) [21] have used 1, 3-benzothiazole-2-thiol with various amines by diazo-coupling method and structures are established. **Scheme (1-6)** shows the synthesis of azo dye

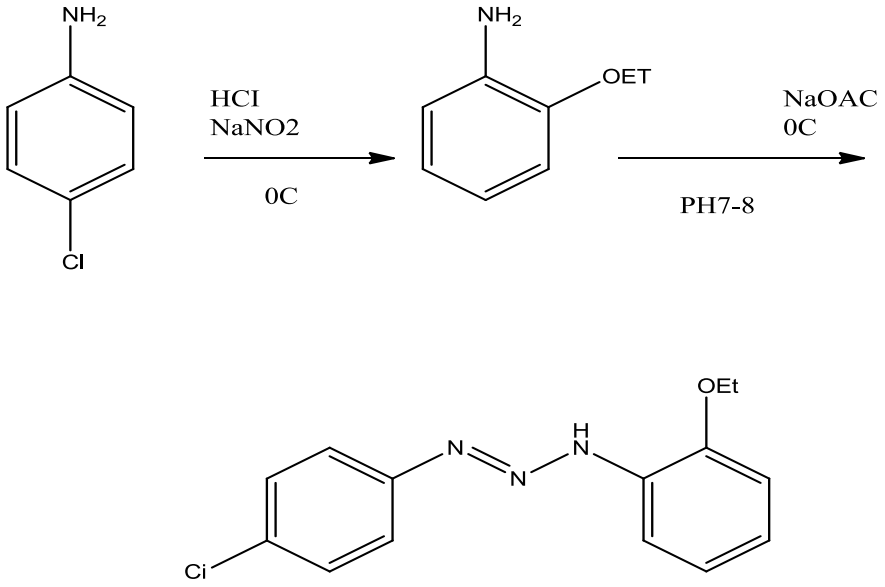


Scheme (1-6) the Synthesis of Azo Dye

1.3. Triazene

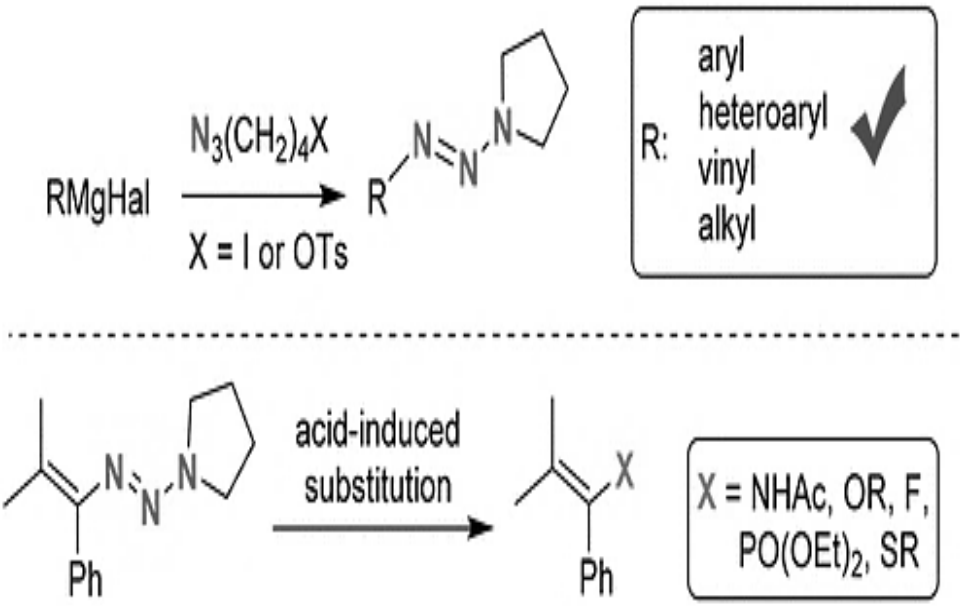
Triazene is an intriguing class of chemicals that have a wide range of applications in the synthesis of various products,[22] some of which have pharmacological benefits[23] triazene moiety, are in clinical usage for cancer treatment due to their low toxicity and strong pharmacokinetic characteristics[24]. Triazene are substances that are organic and have the functional group N(R) N=N. (where R is H, alkyl, aryl it produces by The N-coupling reaction between dizaniume salts and primary or secondary amines. The first triazene was synthesized in 1859The triazenyl group, which confers chemical, physical, and anticancer characteristics as well as the ability to form hydrogen bonds, is the active,[25]component of triazene compounds[26]. . Compounds containing triazene, Because of their potential reactivity in connection to their coordination modes, the research of transition metal complexes. 1,3-diaryl triazenide ligands has increased significantly in recent years[27] One- and double-chained triazenes are well-known ligands. Aside from their ability to coordinate in various ways with transition metals [28], they are also capable of assembling novel supramolecular aggregates due to their exceptional ability to achieve intermolecular,

Fatima, et al., (2019) [30] synthesized the triazene compound (4-chlorophenyl)-3-(2-ethoxyphenyl) as a large basic group **scheme (1-7)** showing how to prepare these compounds, which is triazine. synthesis has been demonstrated FT-IR, 1 HNMR, 13 CNMR, and X-ray crystallography diagram metal-ligand, and ligand-ligand interactions [29]



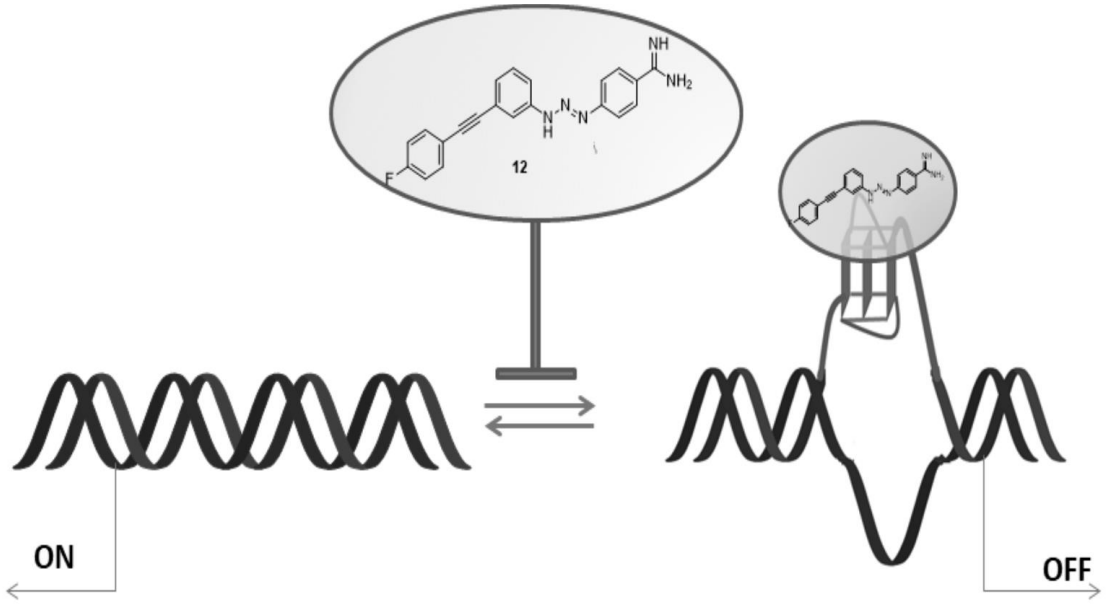
Scheme (1-7) Synthesis of -(4-Chlorophenyl)-3-(2-ethoxyphenyl)triazene

Abdusalom A.et.,al., (2014) [31] prepared linear three-substituted triazines. By reacting Grignard reagents with 1-azido-4-iodobutane or 4-azidobutyl-4-methylbenzenesulfonate. These organic azides were able to selectively form triazenes intramolecular helical step. And he used the new method to prepare aryl, aryl, phenyl, and alkyl triazine. The synthetic usefulness of vinyl triazenes by the proved the shape were characterized by, mass spectroscopy , IR, UV–vis, 1H and 13C NMR spectroscopy**. Scheme (1-8) shows** this method.



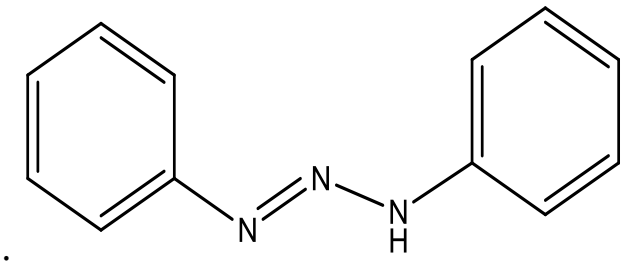
Scheme (1-8) new method to prepare aryl, aryl, phenyl, and alkyl triazene.

Ana P. Francisco, et.,al., (2019) [32] prepared a compound 4- nitro-substituted 1,3-diaryltriazenes and studied the effect of triazene as anti-cancer drugs and their effect on DNAG- A new triazene complex (triazene were developed as n-quaternary bonds with good anti-cancer properties, One example of such compounds is compound 12, the proved the shape were characterized by, mass spectroscopy , IR, UV–vis, 1H and 13C NMR spectroscopy shown in **scheme (1-9)**. It reduces the affinity of DNA double-strand binding.



Scheme (1-9) Compound 12 as a G-Quadruplex ligand

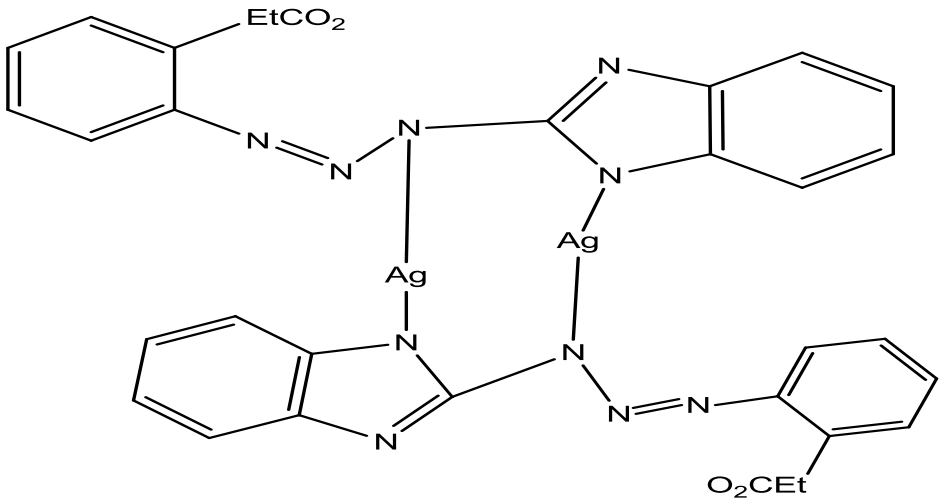
Patricia de Maria Silva Figueirêdo., et.,al., (2021) [33] synthesized new triazene **scheme (1-10)** compounds derived from 1,3-diaryltriazines and tested. And it was proven through measurements that it has biological, antifungal and antimicrobial properties through the experiment on three types of positive bacteria and proved to be inhibited. the proved the shape were characterized by, IR, UV–vis, 1H and 13C NMR spectroscopy



Scheme (1-10) 1, 3-diaryltriazines

Su-Ping Luo, Jia-Mei Le., et, al., (2018) [34] have studied the catalytic performance of a novel binuclear silver complex, [Ag2 (L) 2], formed

by the reaction of the triazinido ligand 1-[(2-carboxymethyl) benzene]-3-[(2-methoxy) benzene] triazene (HL) with $AgNO_3$. At room temperature,. Electrochemical investigations indicate that both the silver ion and the triazinido linker play a role in determining the catalytic activities of the electro catalytic system. show in the **scheme (1-11)** the proved the shape were characterized by, IR, UV–vis, 1H and 13C NMR spectroscopy, Atomic Absorption.



Scheme (1-11)1-[(2-carboxymethyl) benzene]-3-[(2-methoxy) benzene] triazene (HL)

1.4. Coordination chemistry

Coordination chemistry is one of the basic pillars of inorganic chemistry, which is both an interesting and experimentally difficult frontier in current chemical sciences.[34] Today's inorganic chemistry is dominated by coordination molecules, which has produced the creation of novel items with equally novel features applications in a multitude of industries, including pharmaceuticals, fungicides, and cosmetics polymers, pigments, paints, and photoconductors

[35],Coordination compounds are not a particularly novel notion in the area of medicine and drug development, because coordination chemistry has numerous interests and is involved in many fields [36] This field, which bridges the gap between medicine and inorganic chemistry, includes metal-based therapeutically significant chemicals, agents that isolate or mobilize metal, diagnostic tools containing metal, and the therapeutic recruitment of endogenous metal ions[37]. A regular biological process also necessitates hundreds of inorganic complexes and metals, which are found in our bodies and biological systems as various enzymes and protein Cofactor.[38] Many scientists define a "transition metal" as any element in the periodic table's d-block, which encompasses groups 3 through 12.[39]. As a result of the partially filled d shell, the transition elements have a variety of properties that are not shared by other elements. These are some examples [40] The presence of unpaired d electrons causes the production of numerous paramagnetic substances. [41] A few main-group element compounds are also paramagnetic (e.g. nitric oxide, oxygen [42]

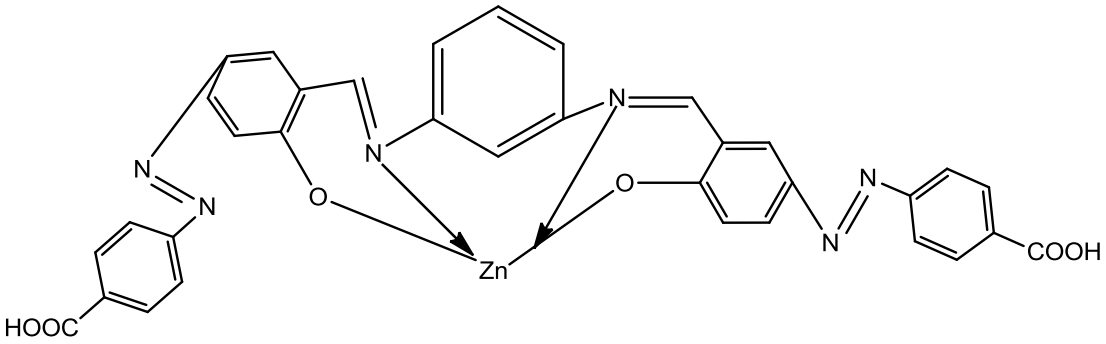
Most transition metals can be attached to a wide range of ligands, resulting in a diverse range of transition metal complexes. [43]

1.5. Zinc chemistry

The symbol Zn and the atomic number 30 .[44] .zinc is a slightly brittle metal with a shiny-greyish appearance once oxidation is removed. It is the first element in the periodic table's group 12 (IIB). In several ways, zinc and magnesium are chemically similar: both elements have just one normal oxidation state (+2), and the Zn^{2+} and Mg^{2+} ions are of comparable size. [45].

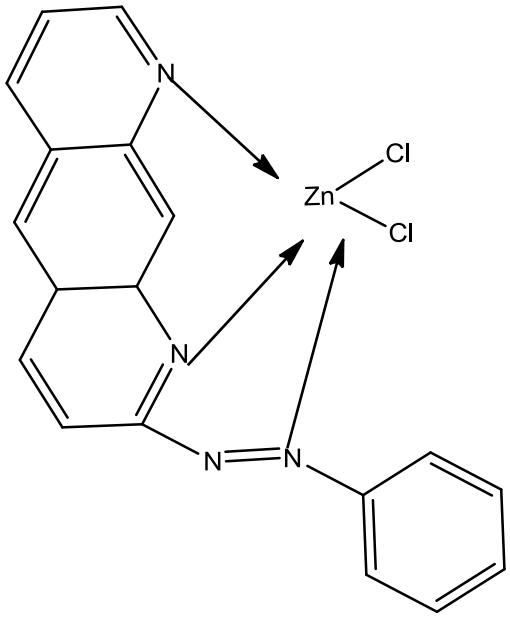
Because zinc is an effective Lewis acid, it can be used as a catalytic agent in hydroxylation and other enzymatic reactions [46] Zinc has long been recognized as a messenger capable of activating signaling pathways. [47] Their central roles in trace element biology, and implications in many human diseases, including cancers [48].

Ali Kakane jadifard., et., al., (2013) [49] prepared a new complex of zinc binary metal and proved the complex shape were characterized by elemental analysis, mass spectroscopy , IR, UV–vis., 1H and 13C NMR spectroscopy. And it was found through the methods that the complex shape is tetrahedral As shown in the **scheme (1-12)**



Scheme (1-12) zinc (II) complex of azo di benzoic acid Schiff base of zinc

Siuli Das .,et.,al (2021) [50] has prepared a new complex of zinc dimetallic with the ligand -tetrahydro-isoquinoline, indoline, 2-phenyl-2,3-dihydro-1H-benzoimidazole,2,3-dihydro-2-phenylquinazolin-4(1H)-one,and1,2,3,4-tetrahydro-2-phenylquinazoline, and he proved the shape of the complex through FT-IR, ^{1}HNMR, and it was reached through the techniques to its final form As shown in the **scheme (1-13)**

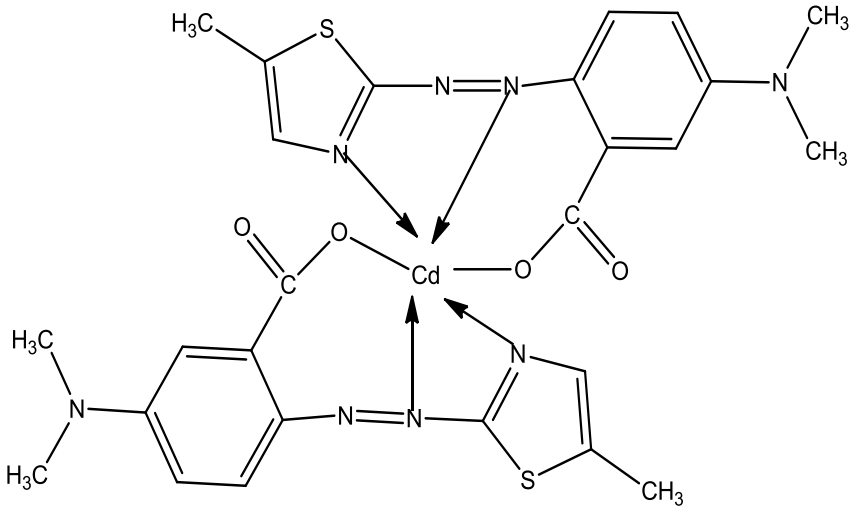


Scheme (1-13) zinc (II) complex of azo-anion radical ligand

1.6. Cadmium chemistry

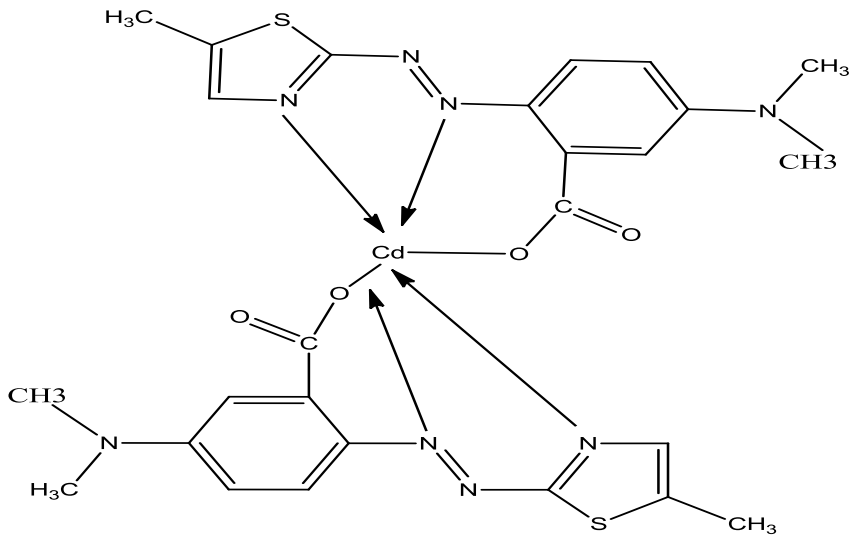
Cadmium is a silver-white metal that is ductile and malleable [51]. Its chemical symbol was discovered by the German pharmacist Friedrich Stormier [52] It is used as an anti-friction agent. It is also used in electrical industries and nuclear reactors. It is used in the manufacture of batteries and other industries.[53] This element can be estimated by thermal, electrical, optical method,. flame atomic .[54]

Sudad A. Jaber.,et.,al., (2021) [55] prepared the cadmium complex **scheme (1-14)** from the reaction of the azo ligand with cadmium(II) metal and characterized the complex using, UV-Vis, elemental analysis (C.H.N.S), measurement of electrical conductivity, magnetic susceptibility, TGA, XRD data and SEM spectra[53]



Scheme (1-14) Cadmium (II) Complex of Azo 2-[2\-(5-Bromo Thiazolyl) Azo]-5-Dimethyl Amino Benzoic Acid Ligand

Sudad A.Jaber . ..et al(2021) [56] prepared and identified the cadmium complex with the ligand. 2-[2\-(5-bromo thiazolyl) azo]-5-di-methyl amino benzoic acid (5-BrTAMB) and Cd(II) coordinate complex The complex was identified by microelement analyzers, atomic absorption, molar conductivity, FTIR, Uv-Vis . as show in the **scheme (1-15)**

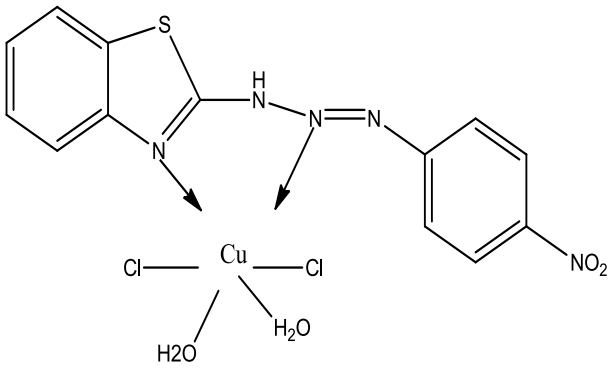


Scheme (1-15) Cadmium (II) complex of 2-[2\-(5-bromo thiazolyl) azo]-5-di-methyl amino benzoic acid (5-BrTAMB)

1.7. Copper chemistry

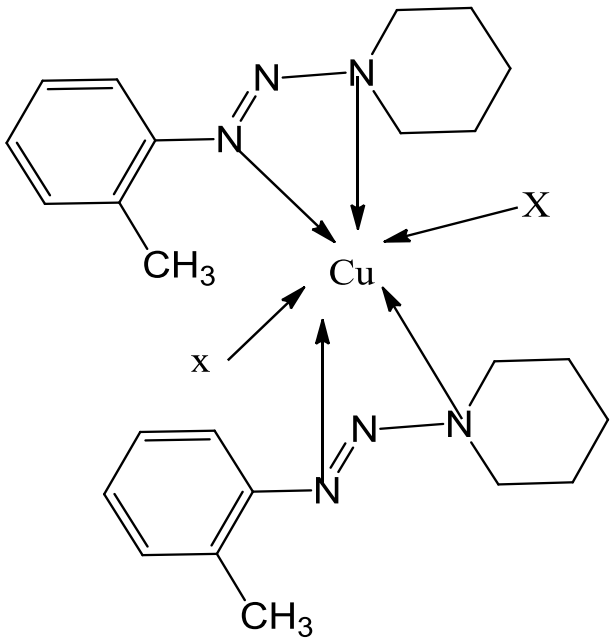
Metallic element with an atomic number of (29) and an atomic weight of (63.546) [57]. It is classified as a transitional element (71). From the periodic table, copper is a soft reddish metal with the IB (first transition series) group3is highly conductive and electrical, malleable and ductile Copper has an electron order of 10 d is outside the S shell even though the copper atom only has one electron in its orbital [58]

Mona. A. Alamri .,et., al (2022) [59] Triazene compound prepared by the diazotization of o-toluidine then reacting with piper dine to give the corresponding triazene compound (1-(o-tolyldiazenyl)piperidine). The complexes M[(2-CH3-C6H3-N=N)-N-C5H10)] $2X^{2-}$ of Cu(II) with triazene compound (1-(o-tolyl di azenyl)piper dine) has been synthesized by the reacting between copper bromide, hydrate n, and iron bromide in 1:2 mole ratio. It has been isolated in the solid state and characterized by (C.H.N) data, IR and 1H NMR spectroscopy. Six coordinate and octahedral complexes, as shown in the **scheme (1-16)**



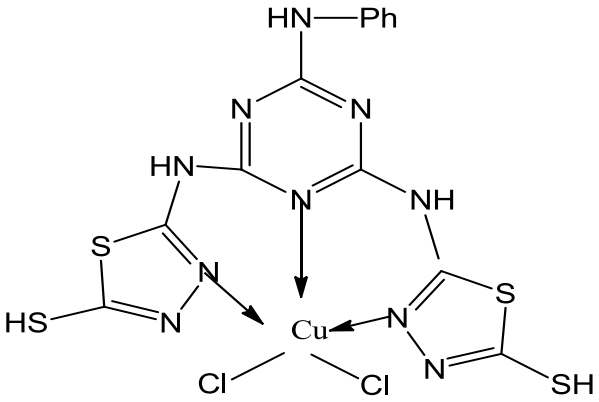
Scheme (1-16) copper (II) complex of triazene compound (1-(o-tolyldiazenyl)piper dine) ligand

Nuha H. Al-Saadawy ., et., al., (2016) [60] prepared a new complex of triazene Cu[(2-CH3-C_6H_3-N=N)-N-C_5H_{10})]$^2Br_2$ with copper(II) metal and confirmed the complex structure through FT-IR, C.N.S,^{1}H NMR , and it was reached Through the techniques that the complex shape is octahedral ,show in **scheme (1-17)**



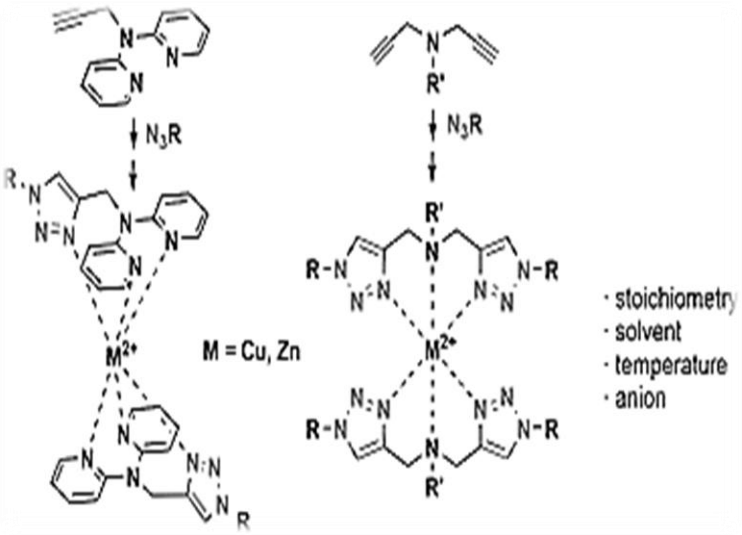
Scheme (1-17) copper(II) complex of M[(2-CH3-C_6H_3-N=N)-N-C_5H_{10})] $^2X^{2-}$ ligand

R. Shanmugakala .,et.,al.,(2012) [61] prepared the copper-triazine ligand4,6-bis(5-mercapto-1,3,4-thiadiazol-amine)2-phenylamino-1,3,5-triazine (BMTDT)with Cu form complex in the **scheme (1-18)** and characterized the complex throughFT-IR,Uv-visible, Atomic absorption ,conductivity .it was shape Square pyramidal



Scheme (1-18) ,copper(II) complex of 6-bis(5-mercapto-1,3,4-thiadiazol-amine)2-phenylamino-1,3,5-triazine (BMTDT)ligand

Natalija pantalone.,et., al., (2020) [(62)] prepared Cu complex by amide conjugation of L-phenylalanine methyl ester. The prepared Cu (II) complexes were studied in situ by NMR spectroscopy, and confirmed by DFT calculations of the electronic structure.in the **scheme (1-19)**



Scheme (1-19) Copper(II) complex of mono- and bis-1,2,3-triazole-substituted heterocyclic ligands

1.8. Anti-corrosion

considered one of the important organic compounds that have been widely spread recently due to the great development and expansion in industries [63], especially the oil and construction industries, which use anti-corrosion compounds widely [64] And organic compounds that are used to protect iron from corrosion must have certain atoms (heterocyclic atoms) in their composition, which give them effectiveness in protecting against corrosion. These atoms are nitrogen, sulfur and oxygen, which give the organic compound the ability to be adsorbed on the surface of iron and form an insulating layer for it from its surroundings. [65] The compounds prepared in this research have the characteristics that qualify them for use as anti-corrosion and metal protection, and this is what the research found, as these compounds gave good results in protection[66][67] The use of organic compounds with heterogeneous atoms in protecting metals from corrosion is a widely used method, and compounds containing nitrogen, oxygen, phosphorus and sulfur atoms are among the most used compounds in this aspect, where [68] Thamer and a group of researchers used compounds containing imidazo group (1, 2-a) pyrimidine linked to heterocyclic rings in the protection of iron in corrosion in the local medium and gave a protection efficiency of up to 92%. Wu and a group of researchers prepared three derivatives of hexagonal heterocyclic triazene, which contains a xanthite group, and studied their anti-corrosion properties on iron and copper. They found that these compounds interacted with metal contact surfaces and formed complex tribofilms.[69] Mahrous and a group of researchers studied the preparation of a group of triazene compounds and studied their use in

protecting iron from corrosion in the acidic medium of sulfuric acid 1 M H2SO4 at different concentrations and temperatures.[70] Singh and a group of researchers prepared the preparation of the triazine compound 1,3,5-tri-p-tolyl-1,3,5-triazene and studied the possibility of using it as an anti-corrosion of copper in the acidic medium of hydrochloric acid 0.5 M HCl, using different measurement methods, concentrations and degrees Different temperatures and the best percentage of protection was 76%.[71] Abdul Latif (13) and a group of researchers also prepared compounds containing triazine groups and studied these compounds and the possibility of using them to protect iron iron N80 from corrosion in a medium of 5% sulfamic, and the highest protection rate reached 88.5% and the concentration of the inhibitor was10-4 M.

There is a patent document No. 7859/2021 in which heterocyclic compounds were used to protect carbon steel 45 from corrosion in an acidic solution of 1 M HCl [72]

1.9. Penicillins

Penicillins are among the most important and oldest antibiotics, and their role is to stop the production of bacterial cell walls.[73]

The first of its substances to be discovered is penicillin G, which is derived from the particular broom fungus Penicillium notatum, and is structurally a beta-lactam[74]. It is not effective in the oral route due to its sensitivity to gastric secretions and acids. Its effect is limited (mostly on Gram-positive bacteria); It is inactivated by the bacterial enzyme penicillinase (beta-lactamase). Gram-negative bacteria, according to the Gram reaction, include small amounts of mucopeptides containing muramin acid. This layer of murein is in turn

surrounded by a double layer of phospholipids (or "phospholipids"). This layer explains the resistance of Gram negative bacteria[75] Penicillin is effective against many pathogenic bacteria. Such as pneumococci, streptococci, gonococci, meningococci, Clostridium tetani, which causes tetanus, and Treponema pallidum, which causes syphilis.[76] Some bacteria have the ability to synthesize enzymes that inactivate penicillin by opening the β-lactam ring of penicillin, the β-lactamase (or penicillinase).[77]

1.10. Antibiotic

The term antibiotic was coined in 1942 by Waxman[78] This term has been used to describe living microorganisms produced by another substance that are used to kill and inhibit the growth of other living organisms[79] They are small molecules and are produced by living organisms such as Aminoglycoside[80] And others are synthesized chemically, such as oxazolidinone[81] Antibiotics were classified into two groups, one that kills bacteria, such as penicillin, and another that inhibits its growth, such as erythromycin.[82]

There are several mechanisms for the action of these antibiotics [83]

- Antibodies that target cell protein synthesis, such as erythromycin[84]
- Anti-nucleic acid inhibitors such as Ciprofloxin [85]
- Antibiotics that target metabolism, such as trimethoprim[86]

Antibiotics that target cell wall processes such as penicillin [87]

- Study of the biological activity of Gram –positive bacteria
- The prepared compounds gave a high protection against corrosion

1.11. Aim of work:

- Preparation of new ligands containing beta-lactams in triazene and their composition

- Preparation of new complexes from the reaction of synthesis ligands With different metals

- Preparation of compounds containing biological activity

- Preparation of compounds containing inhibitory activity against corrosion

Chapter Two

Experiment

2.1. Chemical Reagents:

The used chemicals with their molecular formula, suppliers and degree of purity are shown in **table (2-1),(2-2).**

Table (2-1): Chemicals used, their molecular formula, suppliers and degree of purity

	Material	Molecular Formula	Company	Purity
1	Sodium Nitrite	$NaNO_2$	Fluke	99%
2	Sodium carbonate	Na_2CO_3	Fluke	98%
3	4-Nitro aniline	$C_6H_6N_2O_2$	Sigma-Aldrich	98%
4	6-Amino Pencillanic Acid	$C_6H_{12}O_3N_2S$	Sigma-Aldrich	99.98%
5	5-Amino -2-methyl phenol	C_7H_9NO	Sigma-Aldrich	98%
6	4-Amino antipyrine	$C_{11}H_{13}N_3O$	BDH	98%
7	Hydrochloric Acid	HCl	BDH	35-38%
8	Absolute Ethanol	C_2H_5OH	BDH	99.8%
9	Cadmium Chloride DiHydrate	$CdCl_2.2H_2O$	BDH	98%
10	Copper Chloride Di Hydrate	$CuCl_2.2H_2O$	BDH	98%
11	Zinc Chloride	$ZnCl_2$	BDH	98%

2.2. Instrument Analysis and Equipment:

2.2.1 ._Melting Points Apparatus

Melting points were determined using SMP30 melting point apparatus and are uncorrected; College of Science for Women, University of Babylon.

2.2.2._ Fourier Transform Infrared Spectra (FT-IR)

The FT-IR spectra were obtained as KBr discs using a FT-IR8400S spectrophotometer in the range 4000-400 cm^{-1}. Which, were recorded at the College of Science for Women University of Babylon

2.2.3._ Conductivity Measurements:

Electrical conductivity measurements of the complexes were made with absolute ethanol at 25 ºC using WTW Cond 7300 digital conductivity meter at College of Science for Women, , University of Babylon.

2.2.4. _UV-Visible Spectra Measurements:

UV-visible spectra of prepared ligand solutions and their complexes were recorded using PEAK/ INSTRUMENTS (C-7200) in ethanol absolute. At College of, Science for Women, University of Babylon.

2.2.5. _^{1}H NMR Spectra Measurements:

The nuclear magnetic resonance spectra were measured at University of Bsrah /Iraq using an instrument Germany Bruker ometer Operating at (400Hz) with (DMSO). spectra

2.2.6. _Flame Atomic Absorption Spectroscopy

The atomic absorption analysis was used to determine the metal contents by Nova350 Spectrophotometer, Ibn-sina / Ministry of Industry and Minerals / Baghdad

22.7. _Mass Spectrometric

LC-Mass measurement were carried out using a devise shamidaszu-model LC-Mass-8045-triple quadrupole, at Turkey, Department of chemistry, college of science, University Aksa ray

2.2.8 -Magnetic Moment Measurement:

Magnetic moments were determined at 25 °C with a magnetic susceptibility balance (Sherwood Scientific). At the College of Science, Al Mustansiriyah University.

2.2.9 –TG Differential Thermal Gravimeter (DTG)-60 Shimadzu (Japan)

The thermal analysis was measured for all the compounds. differential thermal gravimeter (DTG-160-FC-60A) was used. It is available at College of Science for Women, University of Babylon..

2.3.1 -Preparation of Ligands:-

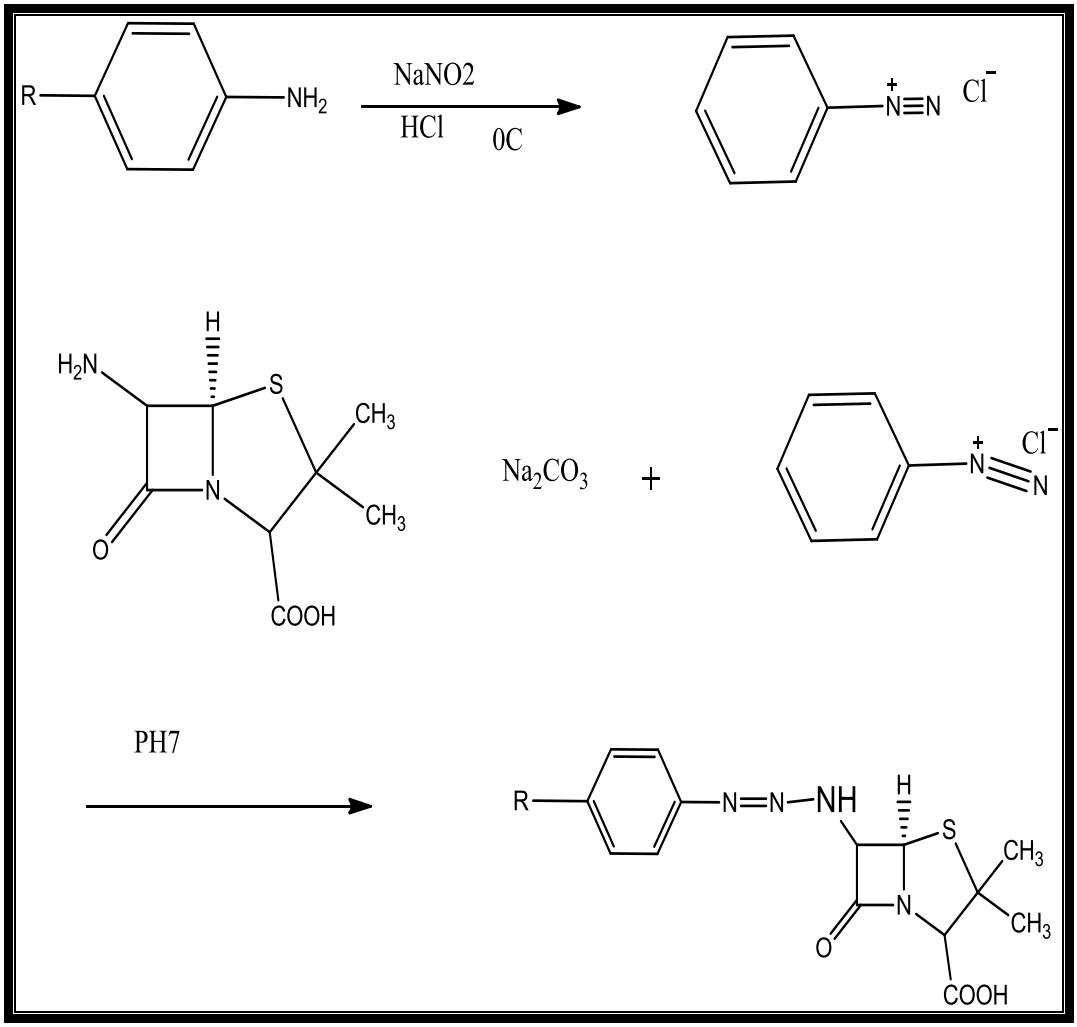
The synthesis of these ligands goes in there steps as shown below:

1- Dizaniume salts was prepared from a mixing of 3 ml HCl, 7ml distilled water, and 4-amino-antipyrine(1 mol; 2 g) to prepare (L1). p-nitro aniline (1 mol, 1.3 g) was used to prepare (L2) and 5- amino-2-methyl phenol(1mol, 1.2g) to prepare (L3). The mixture was cooled in an ice bath at 0–5 °C. A $NaNO_2$ solution (0.6 g dissolved in 1.2 mL D.W) was added to the aromatic amines dropwise with constant stirring, until the dizaniume salts were formed, then left for 15 minutes to complete the reaction.

2- Preparation of sodium carbonate solution (3 g, dissolved in 6 ml, DW) and added to 6-aminopenicillin (2 mol,2 g) while maintaining the temperature and adjusting the pH at PH6.8-7

3- Triazene compounds were prepared by adding the solutions in step No. (1) to the mixture in step No. (2) slowly with continuous stirring for half an hour. The solutions were filtrated and recrystallized using pure ethanol.

Schemes (2-1) shows the steps for preparing the three ligands.



Scheme (2-1) General equations for preparation

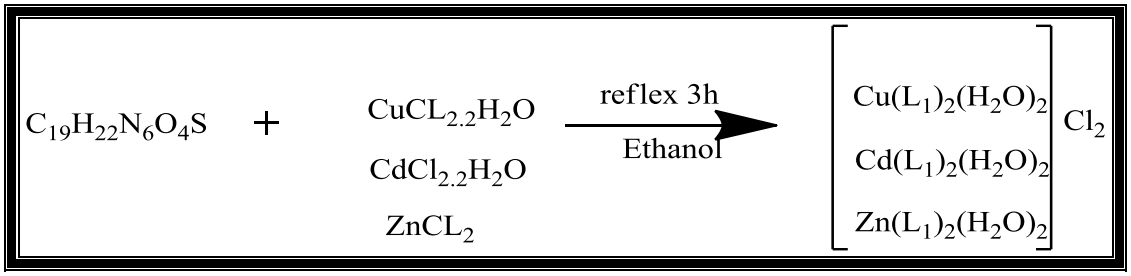
2.3.2 -Preparation of Complexes

1. 1- The complexes with L_1 have been prepared from mixing solution of L_1(2mol, 0.5 g) with (1 mol, 0.12 g) $CdCl_2.2H_2O$, (1 mol, 0.1 g) $ZnCl_2$, (1 mol, 0.08 g,) $CuCl_2.2H_2O$. **Scheme (2-2)** shows the preparing complexes for L1.

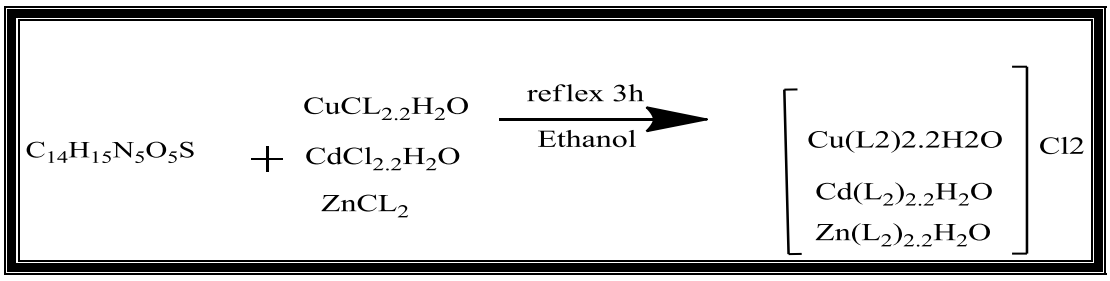
2. The (L2) complexes were prepared from mixing (2mol , 0.5 g) L2, with (1mol, 0.14 g) $CdCl_2.2H_2O$, (1 mol, 0.081 g) ZnCl2 , $CuCl_2.2H_2O$ (1 mol, 0.116 g,)**. Scheme (2-3)** shows preparing complexes for L_2.

3. The complexes of (L3) ligand prepared by mixing (2mol , 0.5 g)L3 with $CdCl_2.2H_2O$ (1 mol, 0.15 g), $ZnCl_2$ (1 mol, 0.1 g) , $CuCl_2.2H_2O$ (1 mol, 0.12 g,) **Scheme (2-4)** shows preparing complex for L_3.

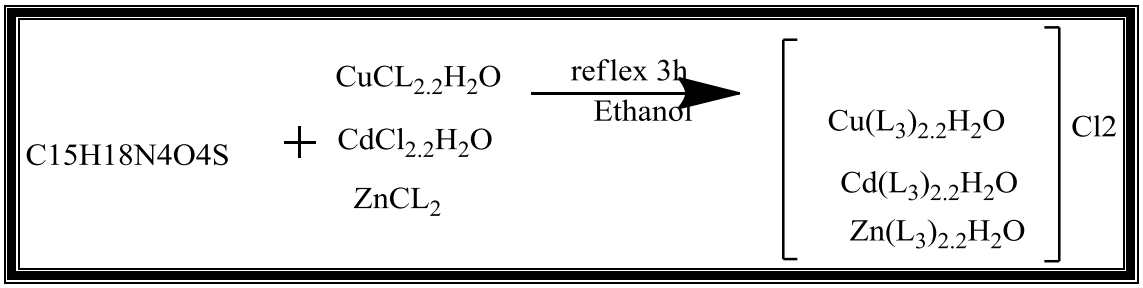
4. The mixture of complexes from (steps 1, 2 and 3) was dissolved in 15 ml of absolute ethanol, then it was reflexed for 3 hours until a precipitate was formed. The solution was filtered and dried.



Scheme (2-2) shows the synthesis of L_1 complexes



Scheme (2-3) show prepared of complexes forL2



Scheme (2-4) show prepared of complexes for L3

2.4.1 -Description of corrosion system.

1. The Corrosion Cell

Corrosion cell made of Pyrex with (250ml) capacity Consists of two vessels, Internal and external. **Fig. (2-3)** shows the corrosion cell and the three electrodes. Three electrodes and thermostat replaced in an internal vessel.

The three electrodes can be explained as follows:

A. A reference Electrode was used to determine the working electrode potential according to the potential of a reference electrode. The potential of reference electrode is well known and accurate. It is combined of two tubes; the inner tube contains Hg/Hg_2Cl_2 sat.KCl, The reference electrode stand at a distance 2 mm from the working electrode.

B. The Auxiliary Electrode consists of high purity platinum metal; and has a length of (10 cm).

C. The Working Electrode is the subject under study, where its potential should be measured. This electrode was formed from 20 cm length metallic wire and connected to the mounted specimen.

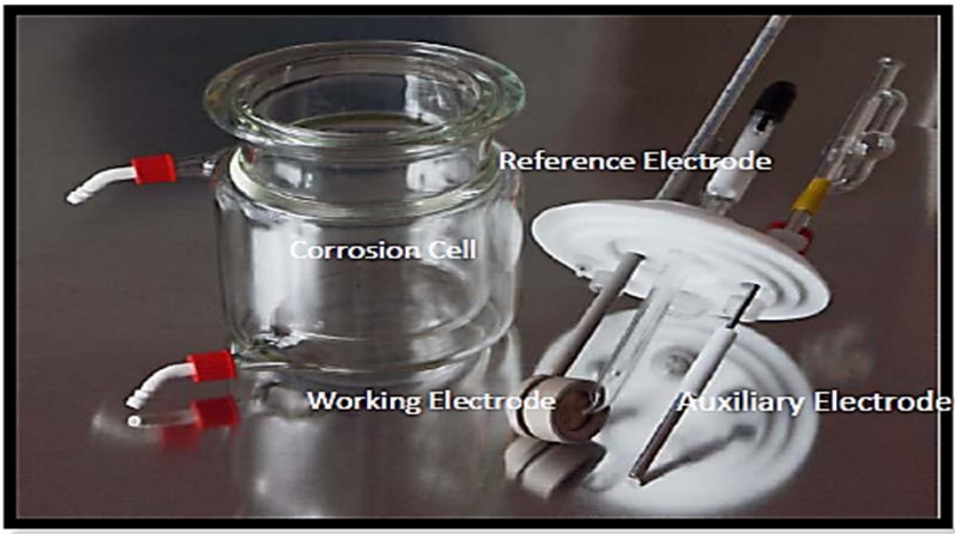


Fig . (2-3) set up the corrosion cell and three electrodes.

2.2.13-Biological Activities

Method of testing

Muller Hinton agar was made by dissolving 37 g of agar in 1 liter of distilled water, sterilizing it, and then distributing it in petri dishes. The bacterial species were cultured for 24 hours at 37°C on nutrient broth, then 0.1 ml of bacterial suspension was applied to the agar in each dish, left for half an hour, and a disc for each concentration was left in the dish next the control (Ethanol) sample. A ruler was used to determine the diameter of the inhibitory zone**.** types of bacteria were used, Gram-positive *Staphylococcus bacteria, Streptococcus bacteria and Gram-negative bacteria, E.coli bacteria.,klebsiella*

Chapter Three Results and Discussion

Ligands synthesis:

The current work includes the preparation of triazene ligands that were derived from the interaction of amines (4-amino anti pyrene ,p-nitro aniline, 5-amino -2-methyl phenol) with a compound containing a beta-lactam ring. Which is 6-amino pencillanic acid , and this reaction was carried out under certain conditions of Ph and low temperatures. The ligands were reacted with binary transition metal salts to obtain the complexes. **Table(3-1)** shows the physical properties of the prepared ligands and their complexes that were identified using different techniques, including: FT-IR , Uv-visible , Mass, ^{1}HNMR , atomic absorption , magnetic susceptibility , conductivity and TG .

Table (3-1) The Physical properties of compounds petties of compound

Compound	Color	Yield %	M .P C	M. Wt.
L1	Greenish	70	101-102	430
$[Cu(L_1)_2(H_2O)_2]Cl_2$	light-green	60	110-110.9	959
$[Cd\ (L1)_2(H_2O)_2]Cl_2$	Yellowish green	80	130-131	1008
$[Zn(L_1)_2(H_2O)_2]Cl_2$	Yellowish green	70	124-124.2	961

L2	Greenish yellow	70	90-100.2	365
$[Cu(L_2)_2(H_2O)_2]Cl_2$	Greenish yellow	90	134-134.9	899
$[Cd\ (L_2)_2(H_2O)_2]Cl_2$	Greenish yellow	50	124-124.5	948
$[Zn\ (L_2)_2(H_2O)_2]Cl_2$	Greenish yellow	80	120-121	897
L3	Red-Orange	60	113-114	350
$[Cu(L_3)_2(H_2O)_2]Cl_2$	Red	75	122-122.9	865
$[Cd\ (L_3)_2(H_2O)_2]Cl_2$	Orange	70	148-149	914
$[Zn\ (L_3)_2(H_2O)_2]Cl_2$	Orange	80	130-131	870

3.1. Solubility

The solubility of the prepared compounds was tested in different solvents and the results are listed in **Table (3-2)**. It was observed that the best solubility was in the organic solvent, ethanol, DMSO, and slightly soluble in distilled water.

Table (3-2) Shows the Solubility of the Prepared Compounds

Compound	absolute ethanol	DMSO	Distilled water
L_1	+	+	÷
$[Cu\ (L_1)_2\ (H_2O)_2]\ Cl_2$	+	+	÷
$[Cd\ (L_1)_2(\ H_2O)_2]Cl_2$	+	+	÷

$[Zn(L_1)2\ (H_2O)_2]Cl_2$	+	+	÷
L_2	+	+	÷
$[Cu\ (L2)_2\ (H_2O)_2]Cl_2$	+	+	÷
$[Cd\ (L2)_2\ (H_2O)_2]Cl_2$	+	+	÷
$[Zn(L2)_2(\ H_2O)_2]Cl_2$	+	+	÷
L_3	+	+	÷
$[Cu\ (L_3)_2\ (H_2O)_2]Cl_2$	+	+	÷
$[Cd\ (L_3)_2\ (H_2O)_2]Cl_2$	+	+	÷
$[Zn(L_3)_2\ (H_2O)_2]Cl_2$	+	+	÷

Where: + Soluble, ÷Slightly soluble,

3.2. ^{1}HNMR Spectroscopy for L1, L2, L3

Nuclear magnetic resonance (^{1}HNMR) spectra were used to determine the type of hydrogen in organic compounds. The ^{1}HNMR spectra of the prepared ligands were measured, and a group of bands appeared. These bands include CH_3 (0.9-1.7 ppm,) [88] , DMSO (2.5- 3.5ppm) [89], NH(2.3 ppm) [90], N=CH (2.5ppm), aromatic protons (7.5-8 ppm,)[91] -OH(9.5-10ppm). **Figures (3-1), (3-2) (3-3)** show ^{1}HNMR spectra for the prepared ligands

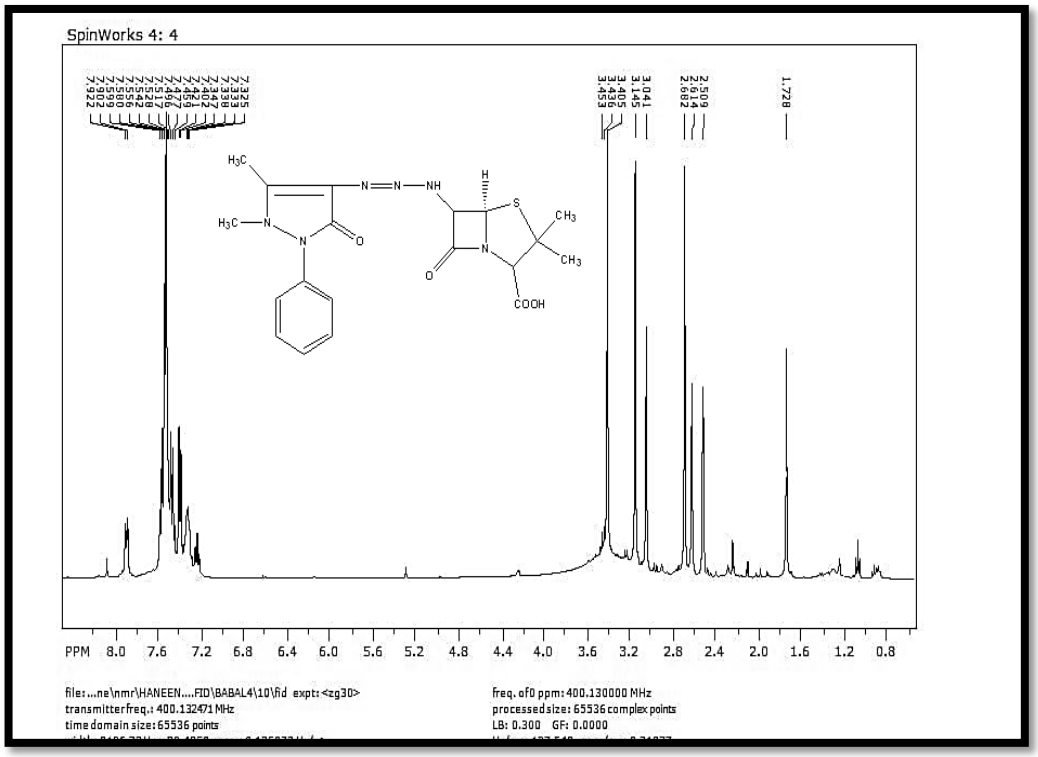


Fig. (3-1) ^{1}HNMR Spectrum for L_1

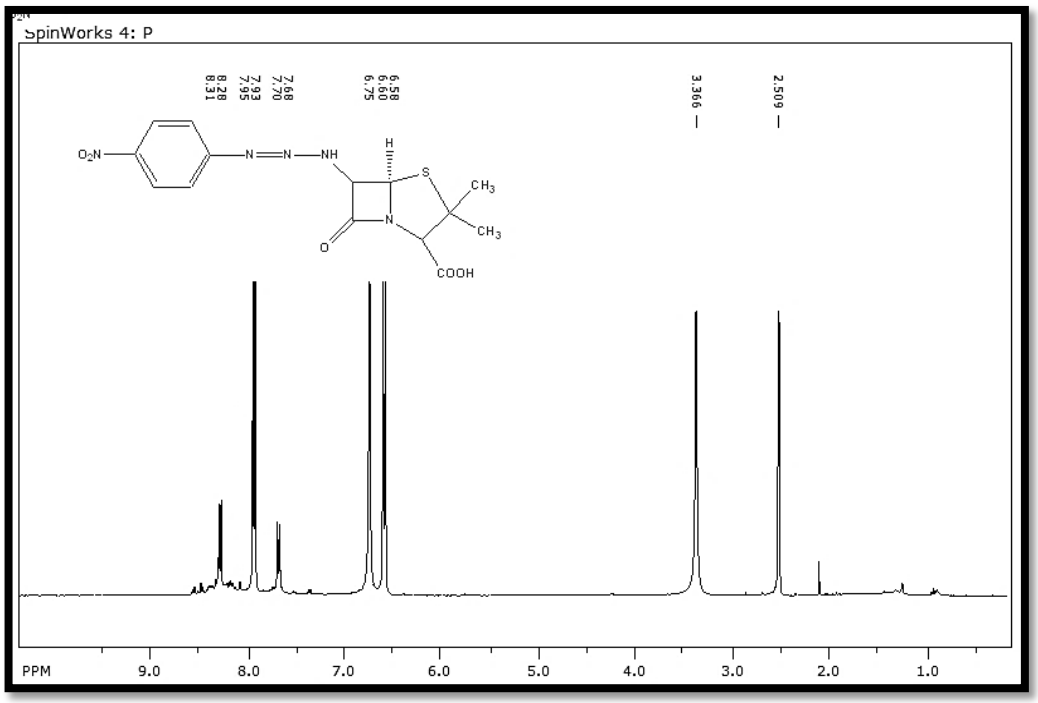


Fig. (3-2) ^{1}HNMR Spectrum for L_2

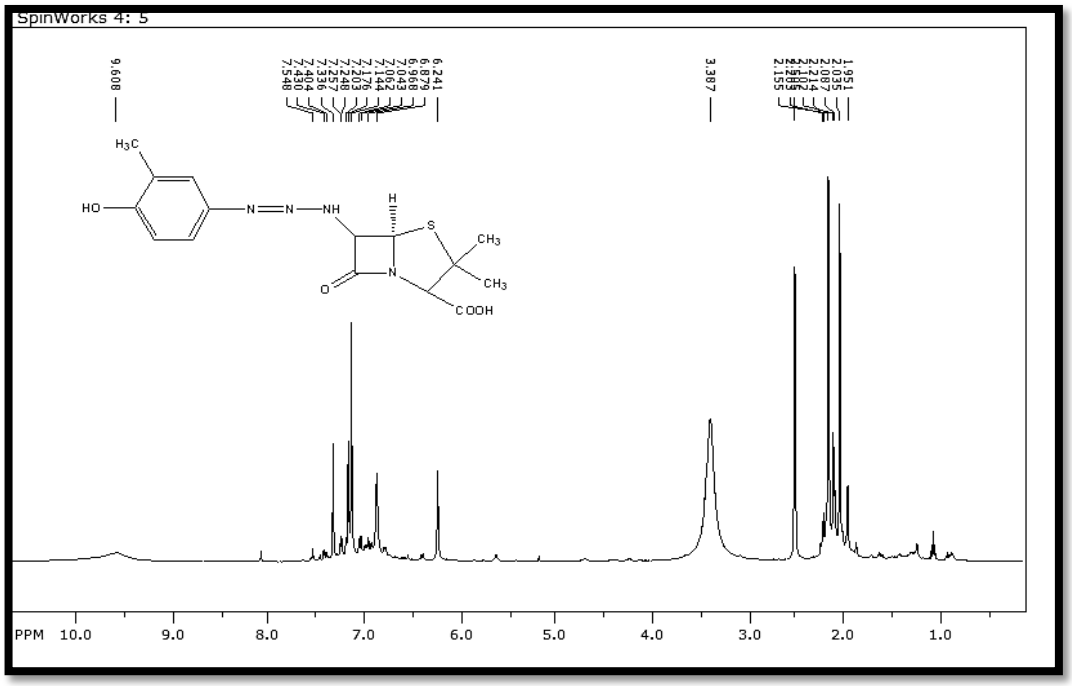


Fig. (3-3) ^{1}HNMR Spectrum for L3

3.3.1 Mass spectroscopy for L1.

In the mass spectrum of the ligand (L1), a peak appeared at (431) which is attributed to the parent molecular ion. **Figure (3-4)** shows the mass spectrum for (L1. The spectrum recorded other peaks that correspond to the fragments of the ligand molecule.

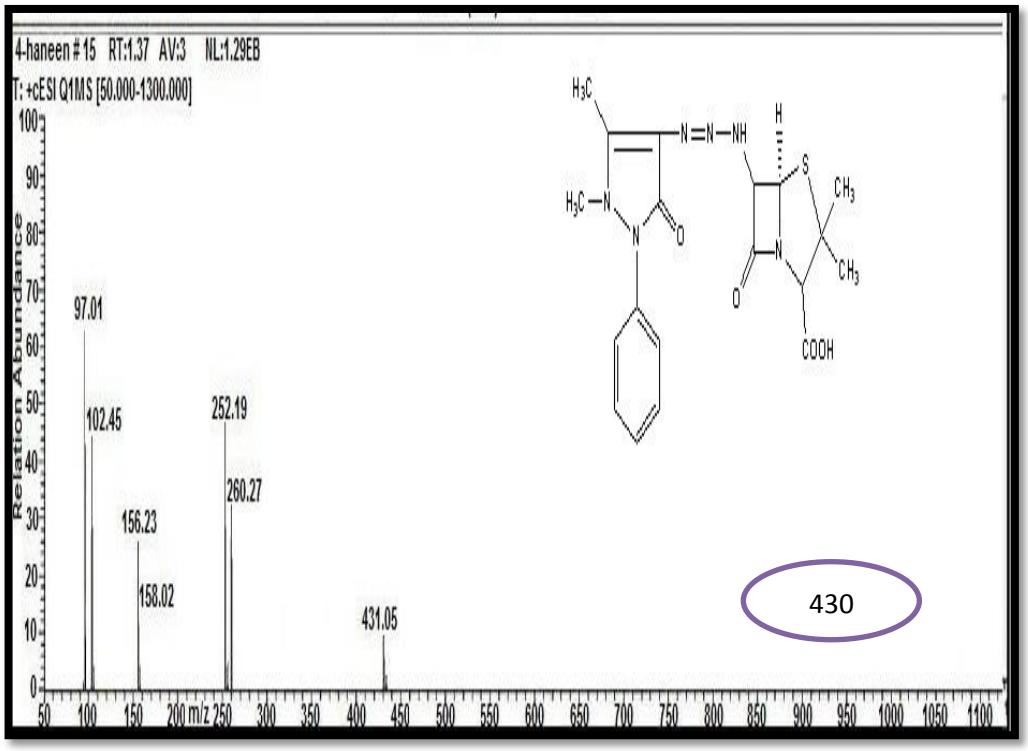


Fig. (3-4) Mass spectroscopy for L1

3.3.2 Mass Spectroscopy for L2

In the mass spectrum of the ligand (L2), a peak appeared at (367) which is attributed to the ($M+2H^+$). **Figure (3-5)** shows the mass spectrum for (L2). The spectrum recorded other peaks that correspond to the fragments of the ligand molecule.

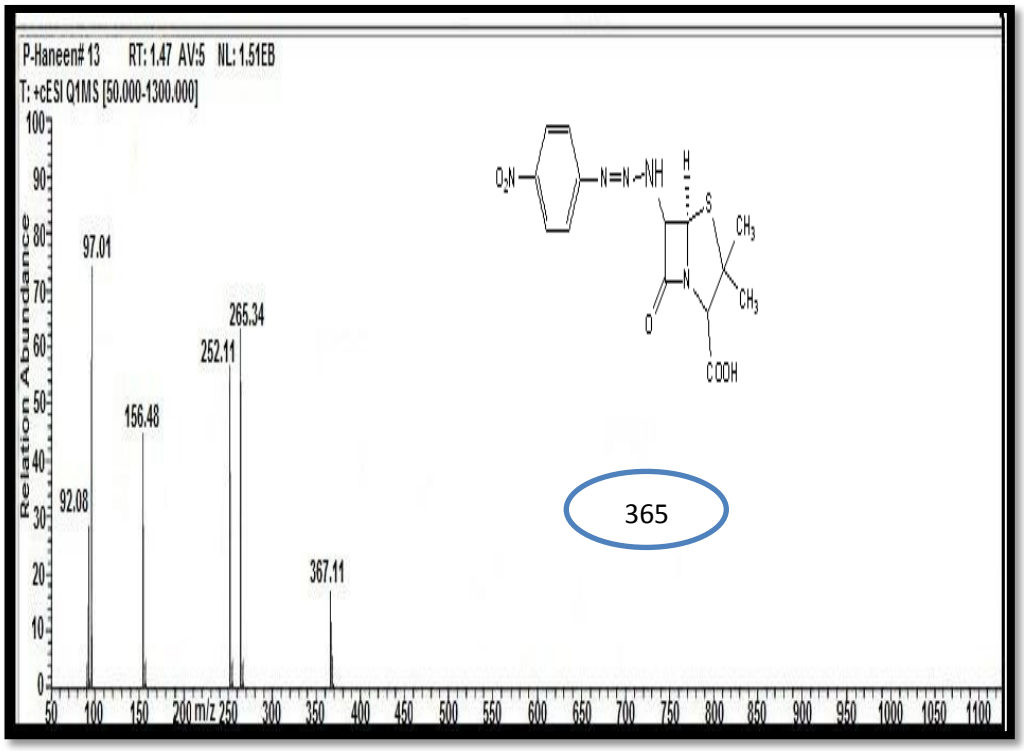


Fig. (3-5) Mass spectroscopy for L2

3.3.3 Mass spectroscopy for L3

In the mass spectrum of the ligand (L3), a peak appeared at (348.77) which is attributed to the parent molecular ion. **Figure (3-6)** shows the mass spectrum For (L3), which corresponds to the proposed molecular formula. The spectrum recorded other peaks that correspond to the fragments of the ligand molecule. These

peaks are listed in **Table (3-5).**

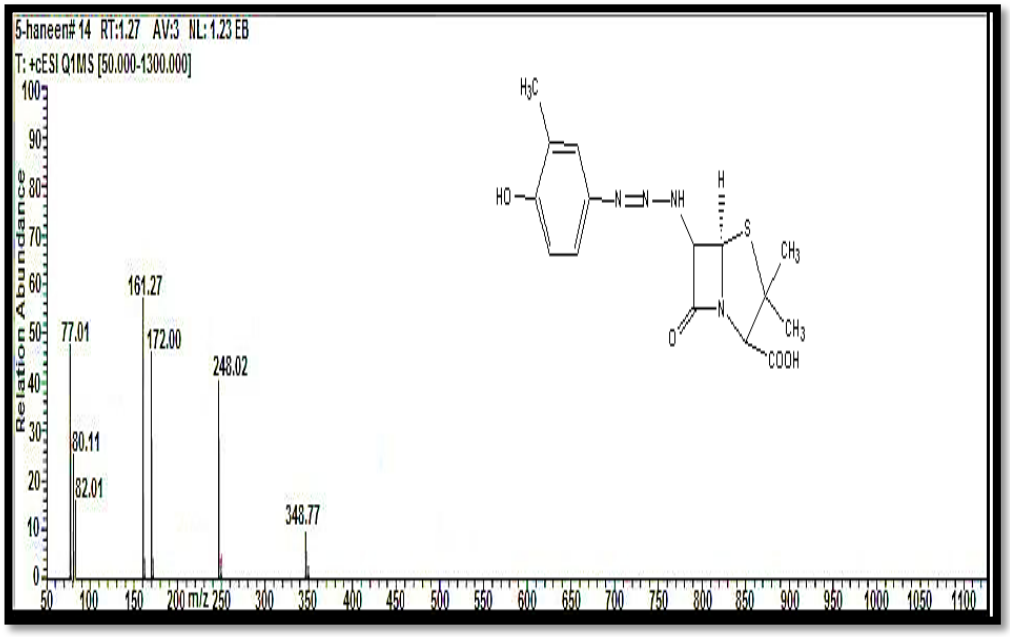


Fig. (3-6) the mass spectroscopy of the L3

3.4.1.1 FT-IR Spectra of ligand L1

Strong bands can be seen in the FT-IR spectra of the synthesized ligand, L1. In general, depending on the nature of the groups attached to it, the azo group absorption band emerges in the area (1403) cm^{-1} [92] the bands at 1541cm^{-1} for the C-C (aromatic) [93]. For the synthesized ligands, the B-lactam carbonyl group (C=O) appeared at 1673cm^{-1}[94]. The other significant distinctive peak strong bands between (3500 - 2500) cm^{-1}[95] for NH stretching, are shown in Fig .(3-7).

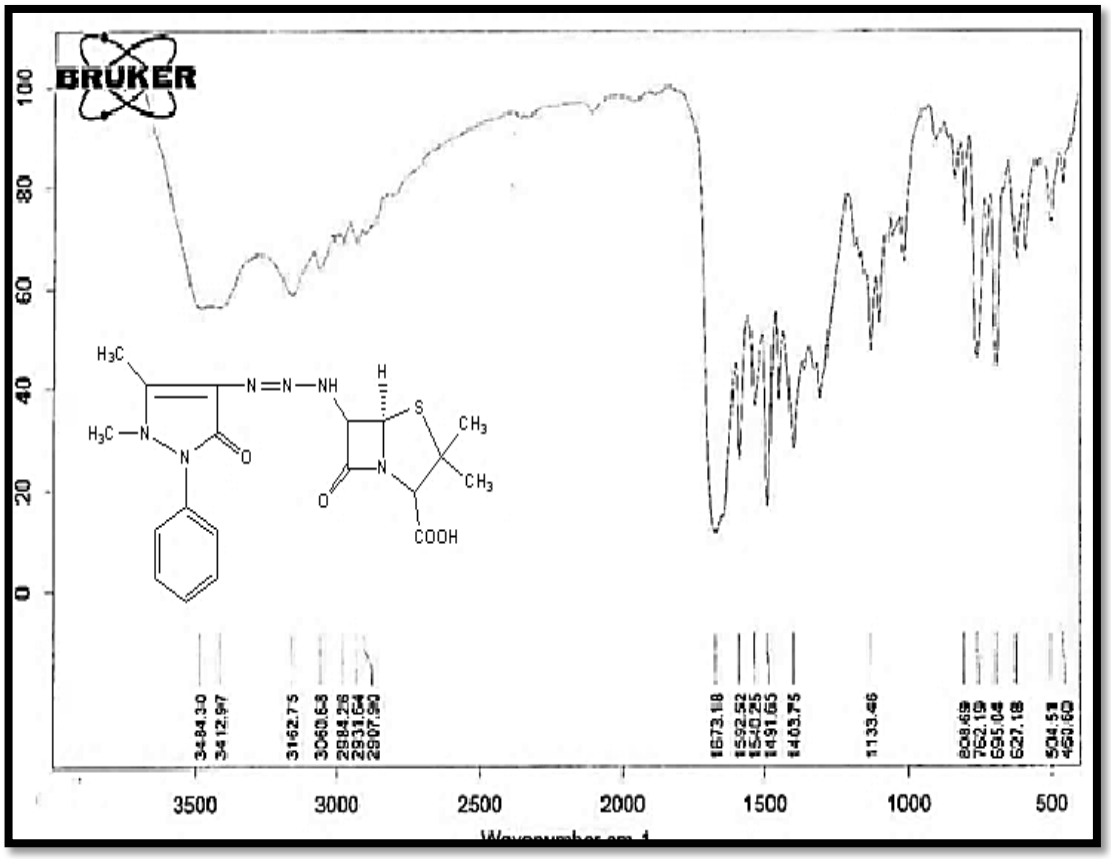


Fig (3-7) FT-IR for L1

3.4.1.2 FT-IR Spectra of complexes for L1

The azid group (N = N-N) appeared in the region (1405-1458) cm^{-1} (96) in coordination complexes, also through the carbonyl group present in the beta-lactam, where it appeared in the region, (1629-1701) cm^{-1} (97) This indicates the occurrence of a displacement, and through this displacement, this indicates the occurrence of metal ion bonding through them.Other significant peaks observed in the FT-IR spectra are mapped in **Fig. (3-8) (3-9). (3-10),** and in **Table (3-6)**

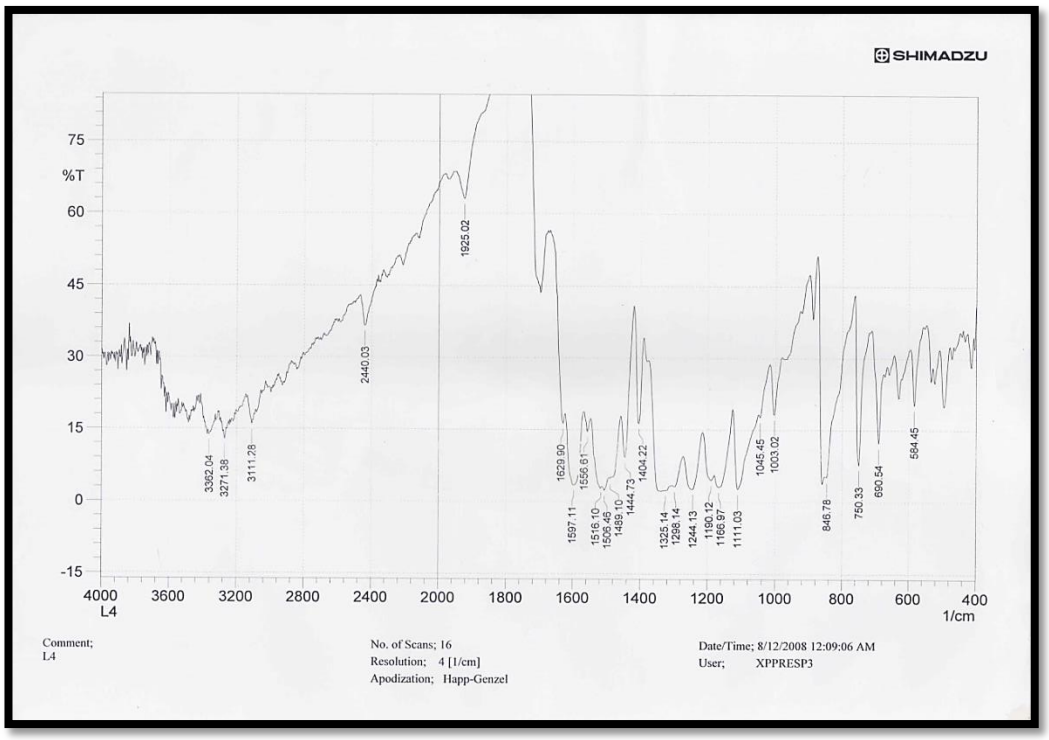


Fig. (3-8)FT-IR for [Zn $(L_1)2(H2O)_2]Cl_2$complex

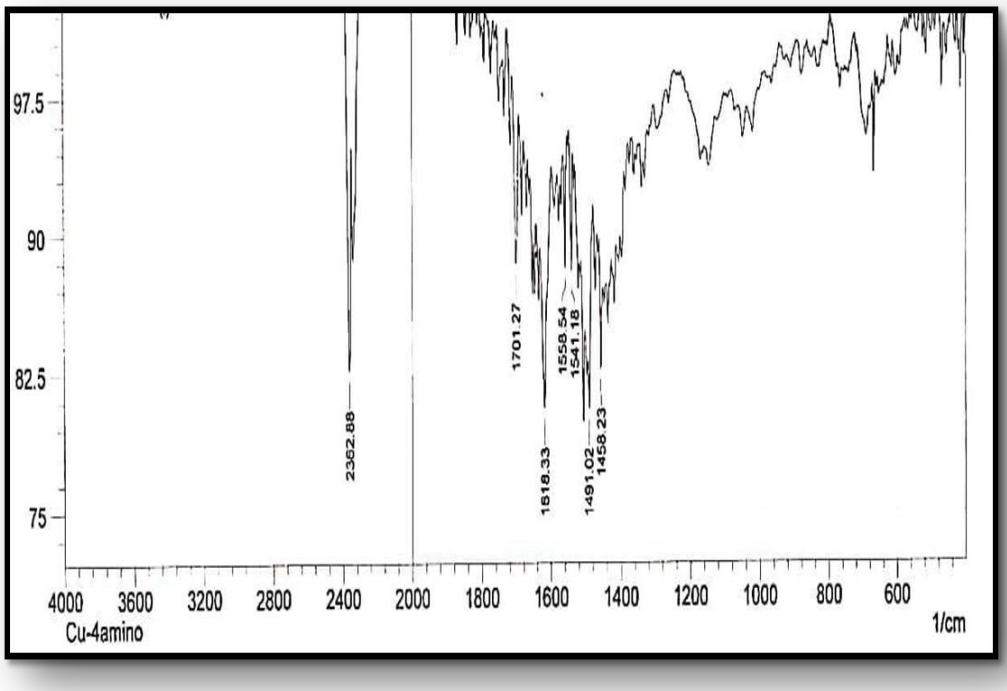


Fig. (3-9) FT-IR for $[Cu\ (L_1)_2(H_2O)_2]Cl_2$complex

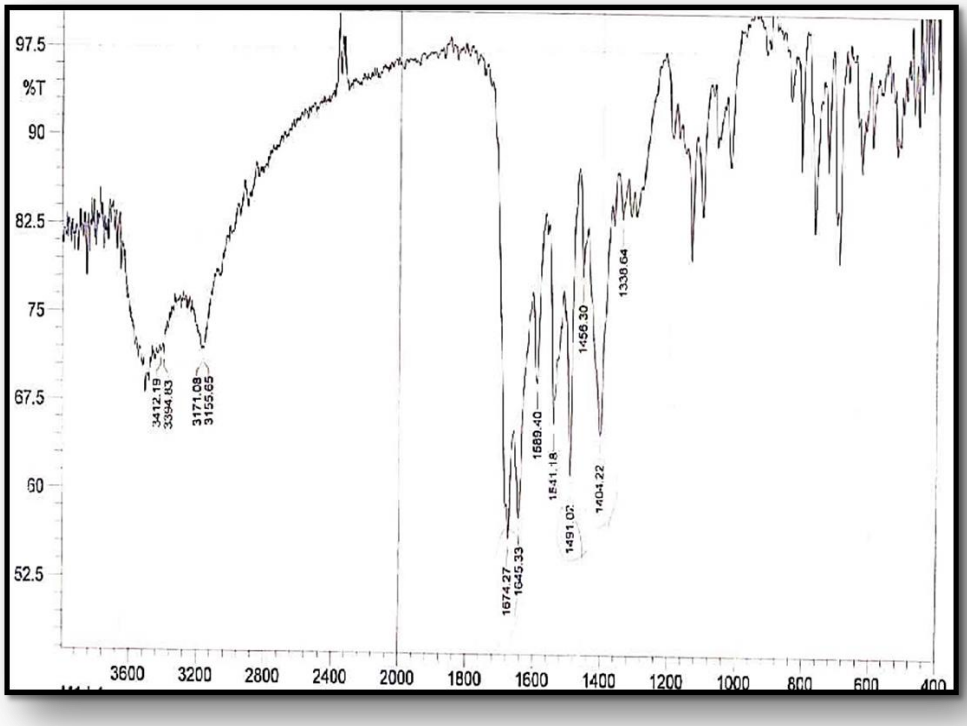


Fig. (3-10) FT-IR for [Cd $(L_1)_2(H_2O)_2]Cl_2$complex

Table (3-6) FT-IR peak of L1and complexes

Compound	C=O l act	O-H	N=N -N	C=C	C=O car	C-HAR	M-N	M-O
Ll	1673	3454	1403	1540	1592	3152	622	504
$[Cd(L_1)_2(H_2O)_2]Cl_2$	1675	3412	1405	1589	1645	3171	600	550
$[Cu(L_1)_2(H_2O)_2]Cl_2$	1701	3416	1458	1558	1599	3167	640	540
$[Zn(L_1)_2(H2O)_2]Cl_2$	1629	3326	1405	1597	1654	3111	690	584

3.4.2.1. FT-IR Spectra of Ligands L2

The FT-IR spectra of the L2 compound ligand shows strong bands. In general, the band of the azid group (N-N = N) vibrations appears in the region of 1508 cm-1 [98] depending on the nature of the bonding groups, and the β-lactam carbonyl group (C = O) of the covalent bonds appears in the region of 1633 cm^{-1}. [99] The other significant characteristic peaks in the FT-IR spectra [are mapped in **Table (3-7)** and shown in

Fig. (3-11)

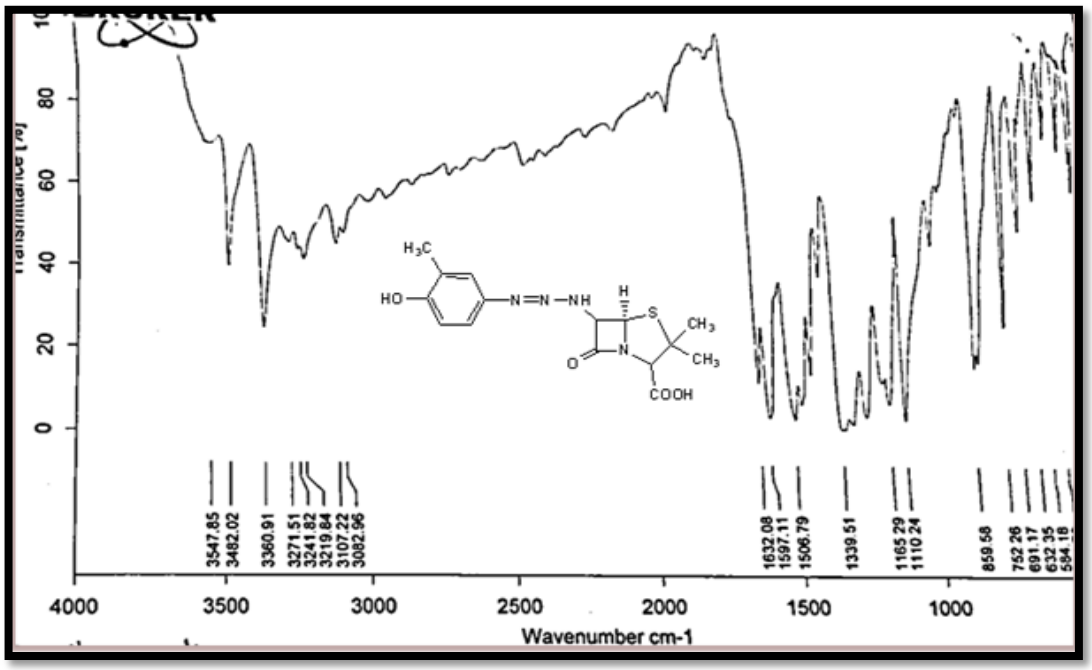


Fig. (3-11) FT-IR for the L2

3.4.2.2 The FTIR Spectra of Complexes of L2

The azid group (N = N-N) appeared in the region (1424-1446) $cm^{-1(100)}$ in coordination complexes, also through the carbonyl group present in the beta-lactam, where it appeared in the region (1597-1627) $cm^{-1\ (101)}$ .This indicates the occurrence of a displacement, and through this displacement, this indicates the occurrence of metal ion bonding through them. Other significant peaks observed in the FT-IR spectra are mapped in **Fig (3-12) (3-13). (3-14),** in the **Table (3-7)**

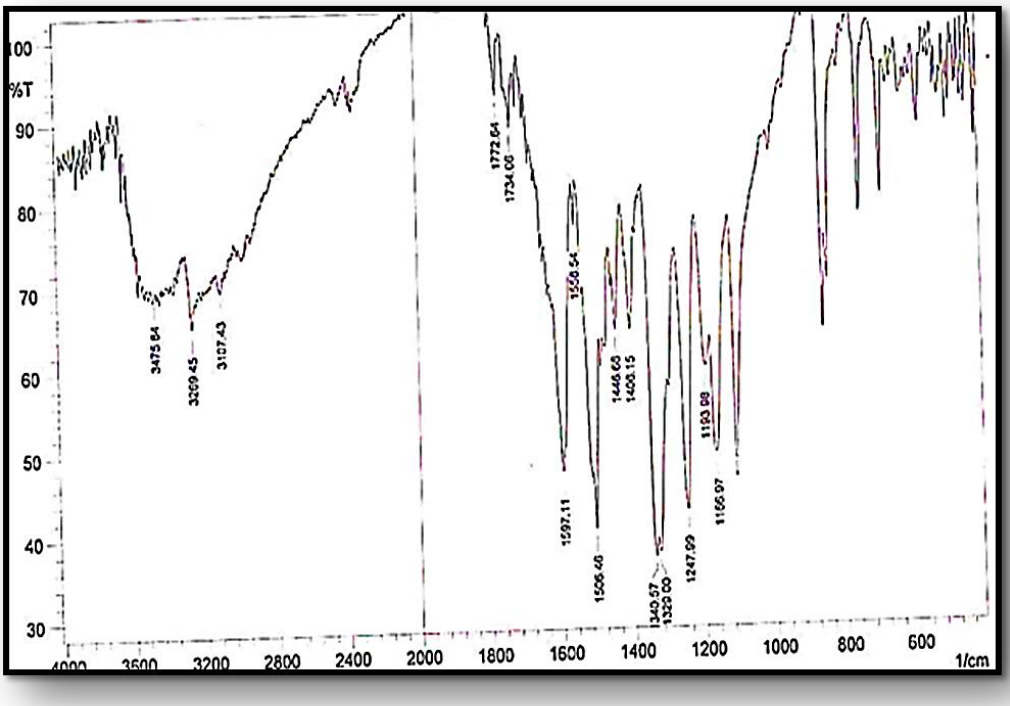


Fig. (3-12)FT-IR for $[Zn\ (L_2)_2(H2O)_2]Cl_2$ complex

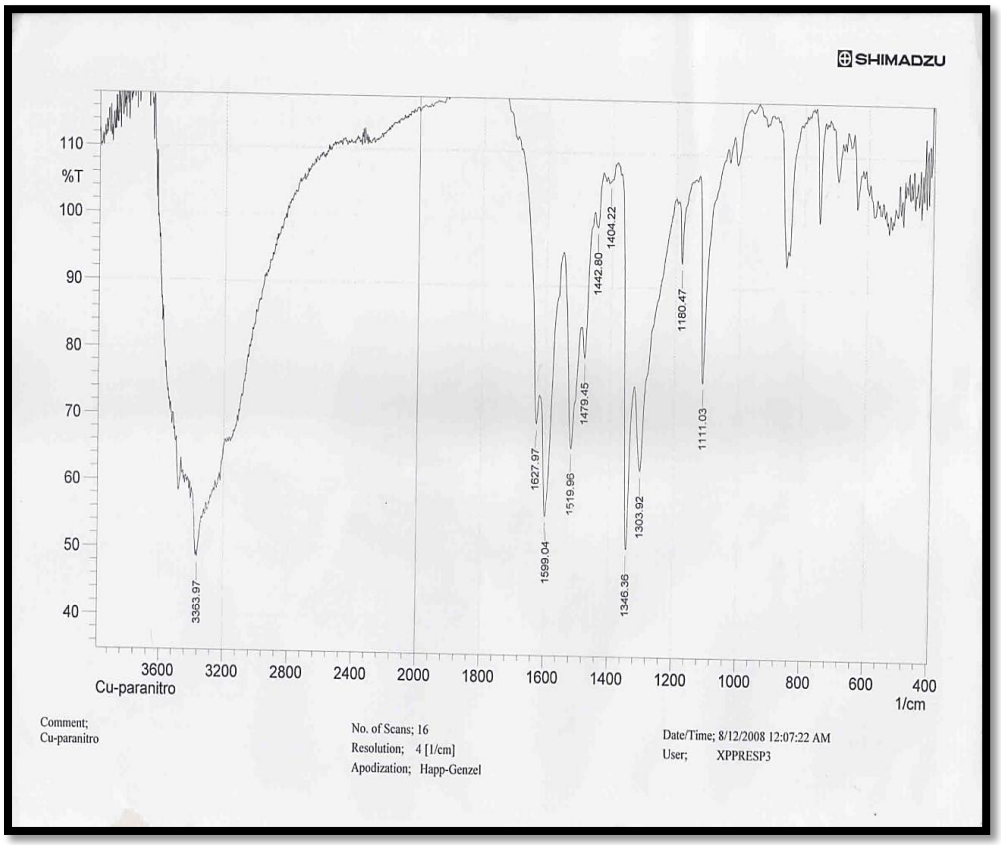


Fig. (3-13) FT-IR for $[Cu(L_2)_2(H_2O)_2]Cl_2$ complex

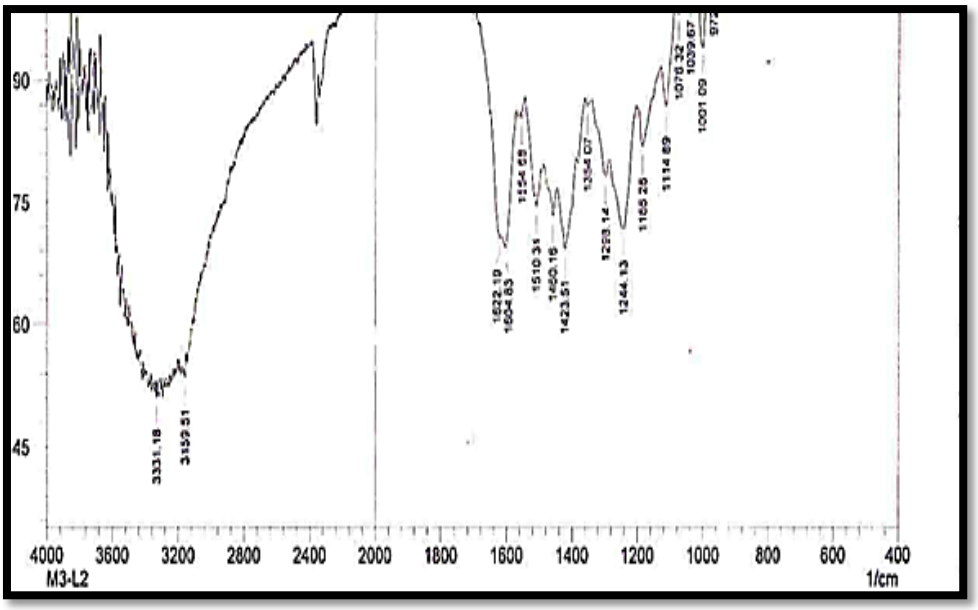


Fig. (3-14)FT-IR for $[Cd(L_2)_2(H_2O)_2]Cl_2$ complex Table (3-7) FT-IR of $L_2$and there complexes

Compound	C=O lact	O-H	N=N-N	C=C	C=O car	C-HAR	M-N	M-O
L2	1633	3481	1508	1630	1606	3107	632	584
$[Cd(L_2)_2(H_2O)_2]Cl_2$	1597	3475	1424	1620	1597	3107	610	590
$[Cu(L_2)_2(H_2O)_2]Cl_2$	1627	3363	1442	1602	1599	3167	660	550
$[Zn(L_2)2(H2O)_2]Cl_2$	1627	3485	1446	1605	1592	3107	680	580

3.4.3.1 FT-IR Spectra of L3

The FT-IR spectra of the synthesized ligand L3 exhibit strong bands. Generally, azid band appears at 1422cm^{-1} (102). For the synthesized ligand the carbonyl group band appears at 1606 cm^{-1} (103). The other important characteristic peaks in the FT-IR spectra were assigned in **table (3-8)** and shown in **Fig. (3-15)**

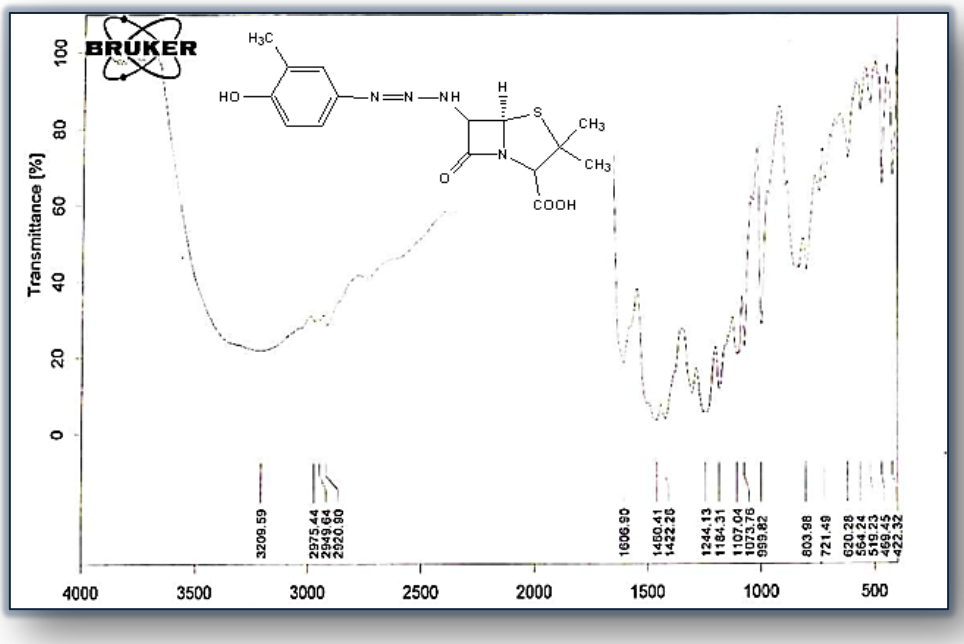


Figure (3-15) FT-IR for L3

3.4.3.2. The FTIR spectra for complexes of L3

The azid group (N = N-N) appeared in the region (1458-1489) cm^{-1}[104] in coordination complexes, also through the carbonyl group present in the beta-lactam, where it appeared in the region, (1622-1624) cm^{-1} [105] This indicates the occurrence of a displacement, and through this displacement, this indicates the occurrence of metal ion bonding through them . Other significant peaks observed in the FT-IR spectra are mapped in

Fig (3-16) (3-17). (3-18), in the **Table (3-8)**

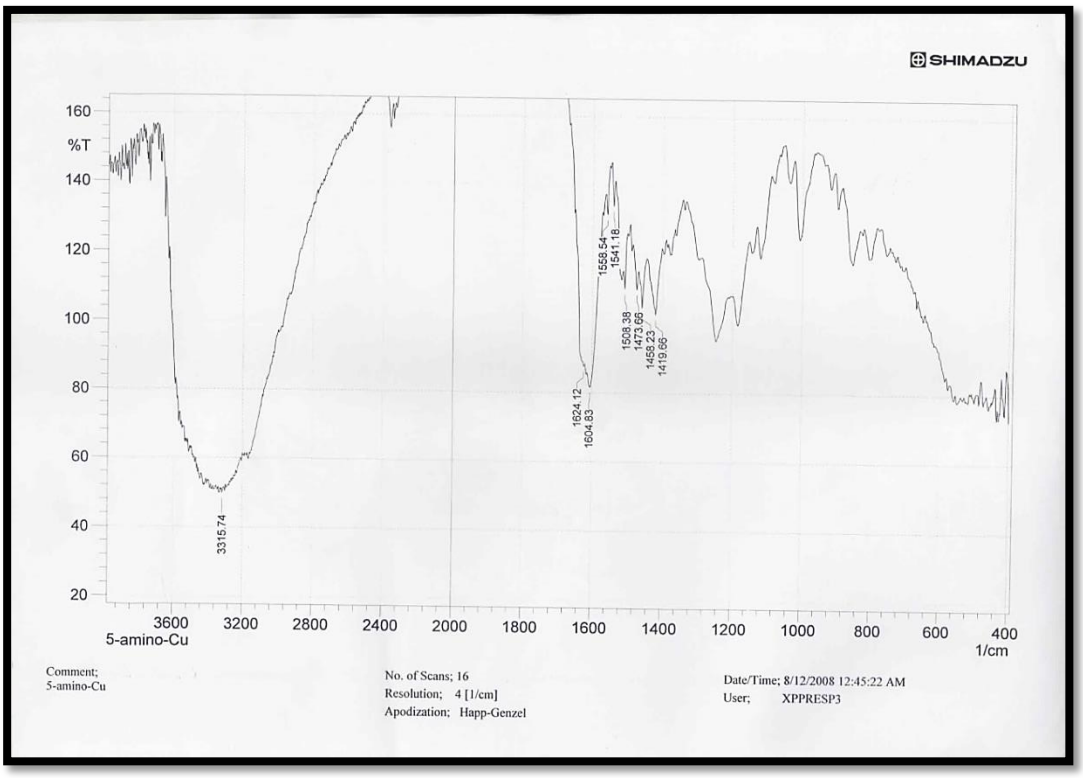


Fig. (3-16) FT-IR for[$Cu(L_3)_2(H_2O)_2]Cl_2$

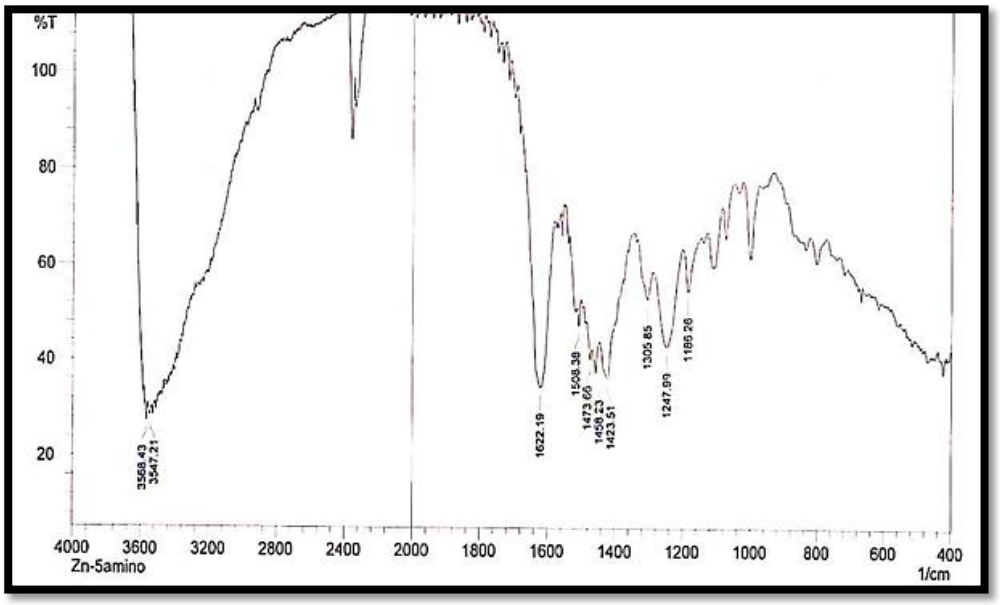


Fig. (3-17) FT-IR for [Zn $(L_2)2(H2O)_2]Cl_2$ complex

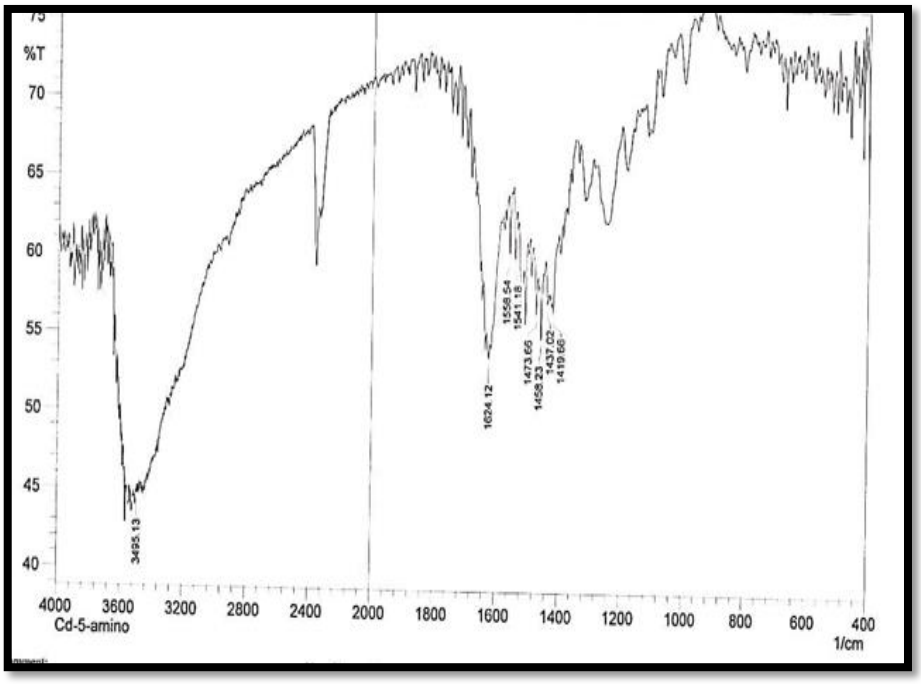


Fig. (3-18) FT-IR for [Cd $(L_3)_2(H_2O)_2$] Cl2 complex

Table (3-8) FT-IR peak of ligands and complexes

Compound	C=O l ac	O-H	N=N-N	C=C	C=O car	C-HAR	M-N	M-O
L3	1606	3209	1422	1558	1597	3209	620	564
$[Cd(L_3)_2(H_2O)_2]Cl_2$	1624	3495	1458	1541	1597	3107	660	510
$[Cu(L_3)_2(H_2O)_2]Cl_2$	1624	3367	1489	1541	1604	3167	680	590
$[Zn(L_3)_2(H_2O)_2]Cl_2$	1622	3331	1460	1590	1604	3159	610	550

3.5. UV-Visible Spectrum for ligand L1, L2, and L3 and there complexes

Electronic transitions occur due to the presence of double bonds. This leads to a transition of a kind(π-π *) [106] , and this transition appears in the peak shown in the **Fig .(3-19)-(3-31)**. Also, transitions n-π*[107] occur as a result of the presence of electronic doublets, and through the spectrum of Uv-visible , it was observed that there is a displacement in all complexes as a result of the bonding between the, as shown in the figure and shown in the **Tables below(3-9),(3-10),(3-11)**

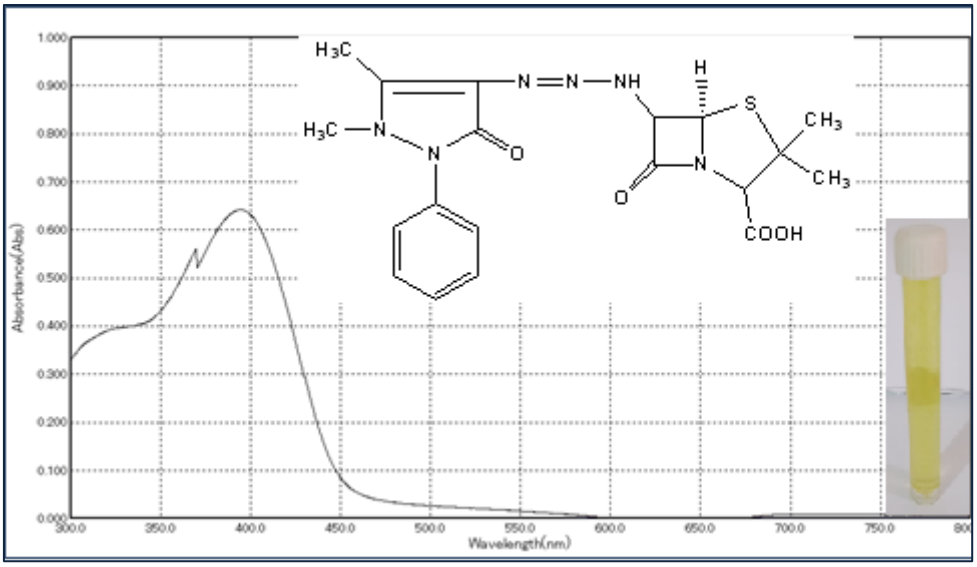


Fig. (3-19) Uv-visible Spectrum for (L1)

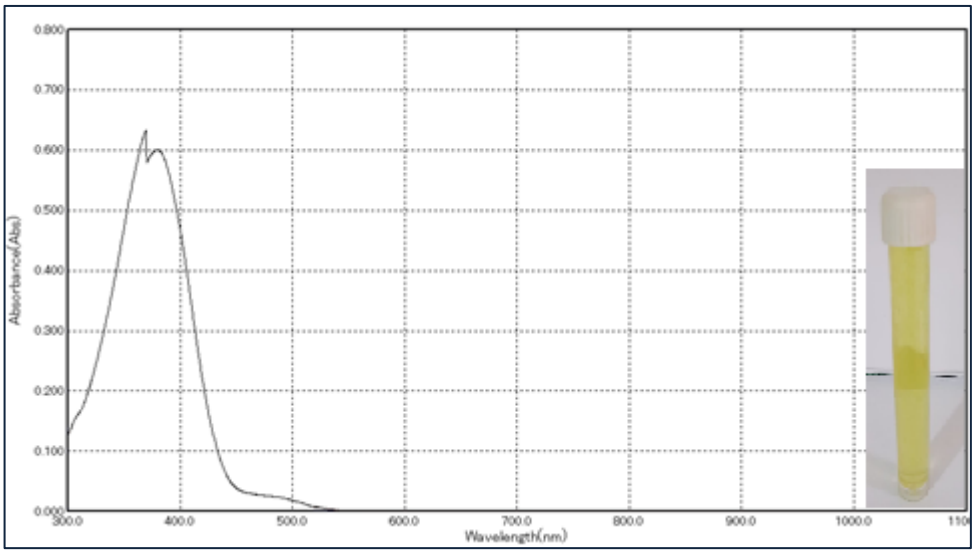


Fig . (3-20) Uv-visible Spectrum for [Cd $(L_1)_2(H_2O)_2]Cl_2$ complex

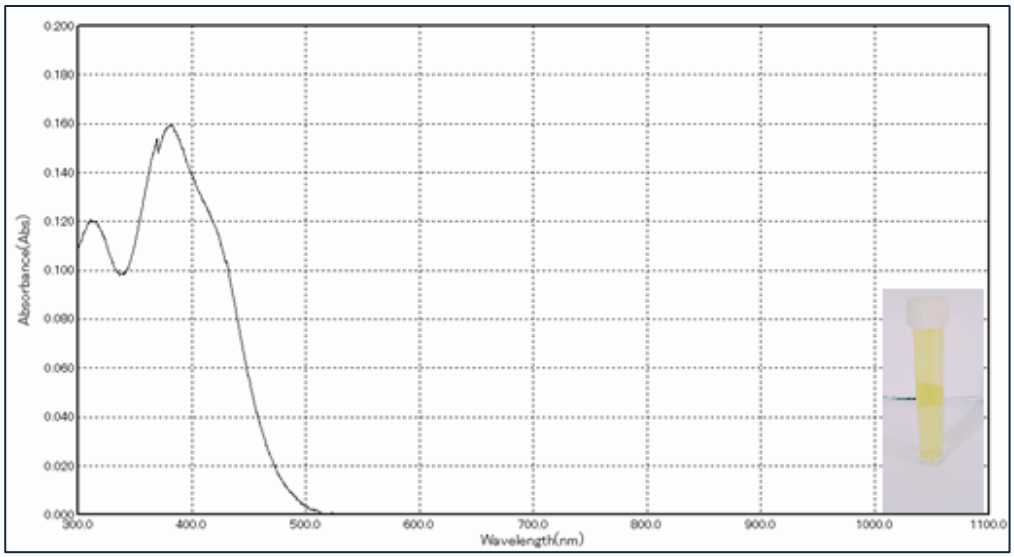


Fig (3-21) Uv-visible Spectrum for [Zn $(L_1)2(H2O)_2]Cl_2$ complex

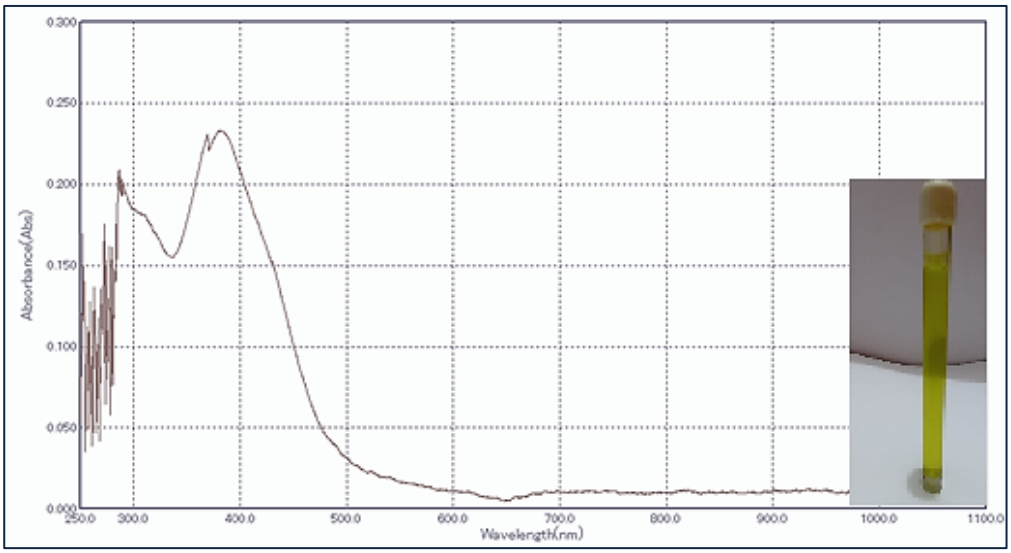


Fig . (3-22) Uv-visible Spectrum for [Cu $(L_1)_2(H_2O)_2]Cl_2$ complex

Table (3-9) Electronic transition of L1 and there complexes

Compound	Absorption Band n m λ	Assignment
L1	370 ,395	π-π*, n-π*
$[Cd(L_1)_2(H_2O)_2]Cl_2$	350,380,480	π-π*, n-π*,M→L
$[Zn(L_1)2(H2O)_2]Cl_2$	320,370,490	π-π*, n-π*, M→L
$[Cu(L_1)_2(H_2O)_2]Cl_2$	250,370,650	π-π*, n-π*, $B_1g \rightarrow {}^2B_2g$

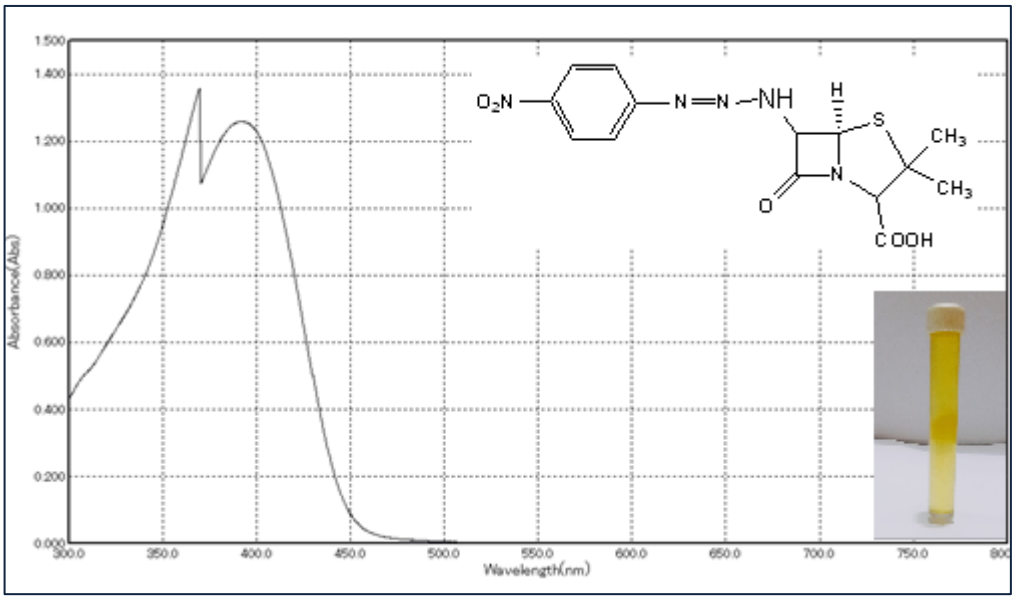


Fig. (3-23) Uv-visible Spectrum for L2

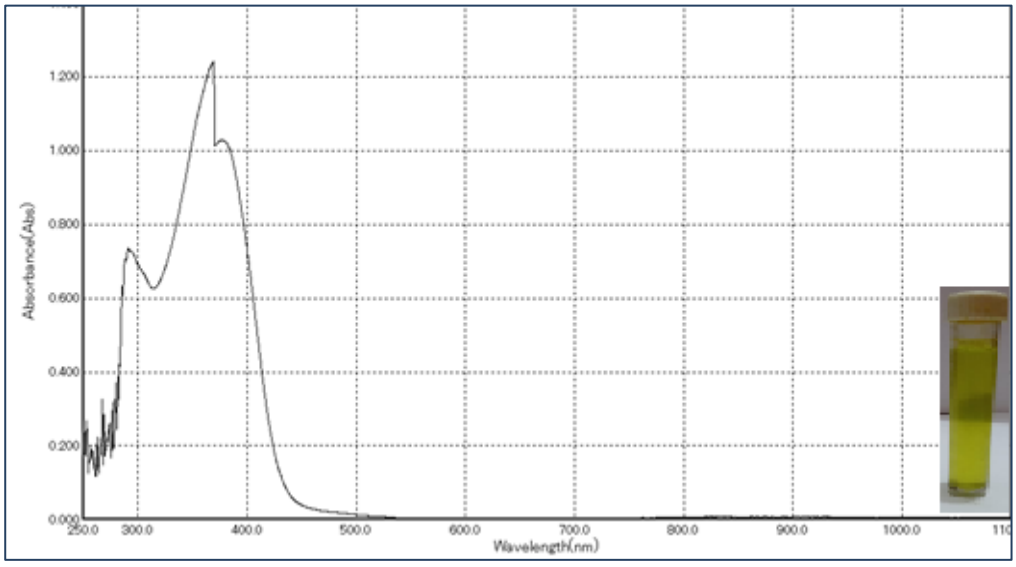


Fig. (3-24) Uv-visible for [Cu $(L_2)_2(H_2O)_2]Cl_2$ complex

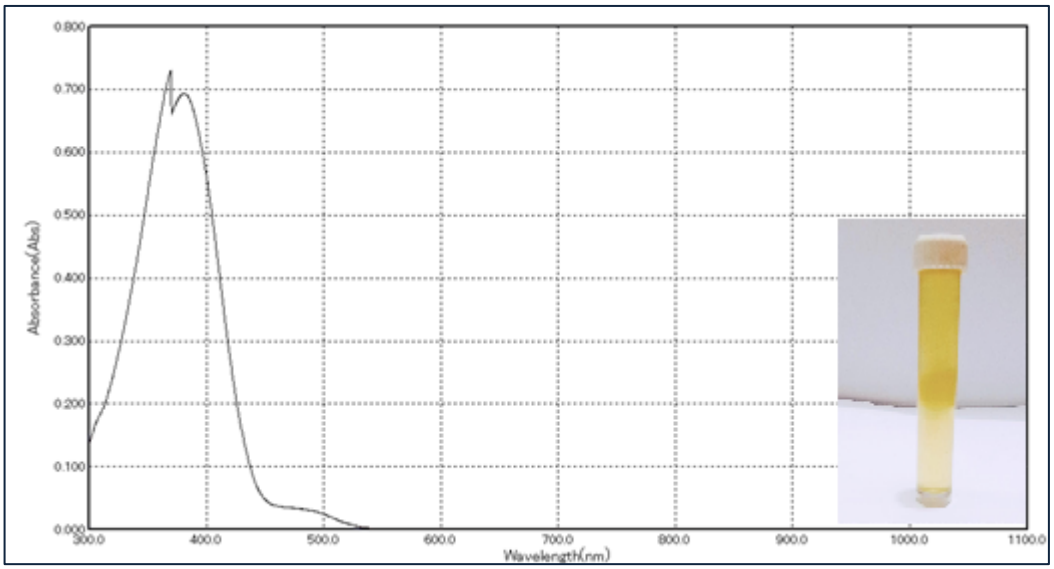


Fig. (3-25) Uv-visible for [Cd $(L_2)_2(H_2O)_2]Cl_2$ complex

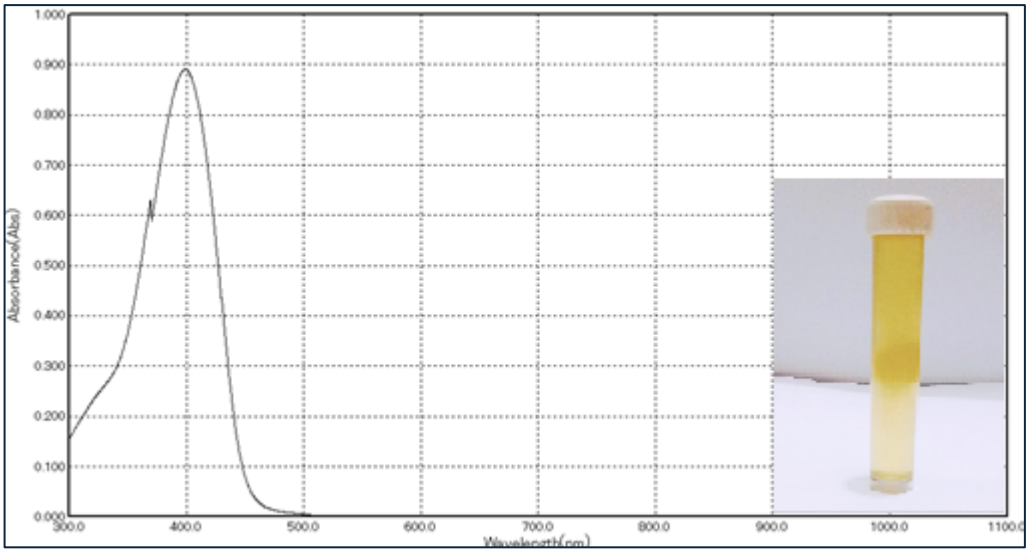


Fig. (3-26) Uv-visible for the [Zn $(L_2)2(H_2O)_2]Cl_2$ complex

Table (3-10) Electronic transition of L2 and there complexes

Compound	Absorption Band n m λ	Assignment
L2	370 ,3 90	π-π*, n-π*
$[Cd(L_2)_2(H_2O)_2]Cl_2$	350,380 ,450	π-π*, n-π*,M→L
$[Zn(L_2)2(H2O)_2]Cl_2$	370,400,480	π-π*, n-π*, M→L
$[Cu(L_2)_2(H_2O)_2]Cl_2$	350,3 80,800	π-π*, n-π, $B_1g \rightarrow {}^2B_2g$

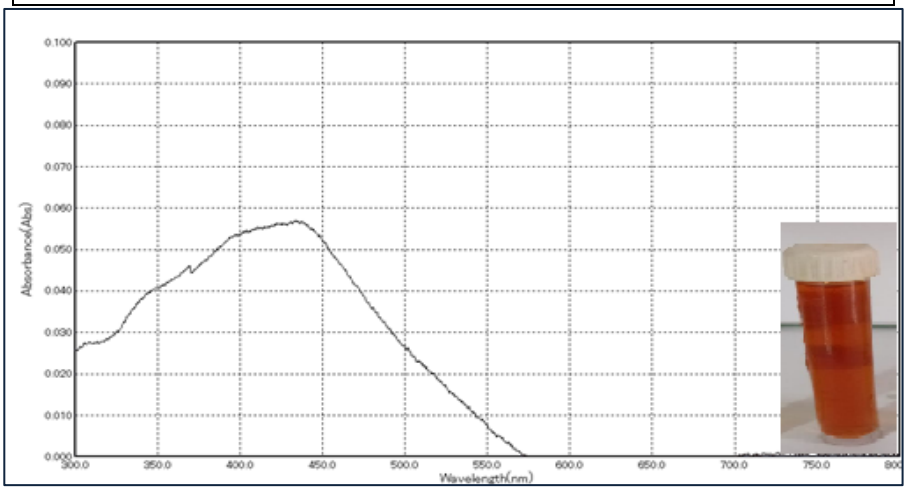


Fig. (3-27) Uv-visible of L3

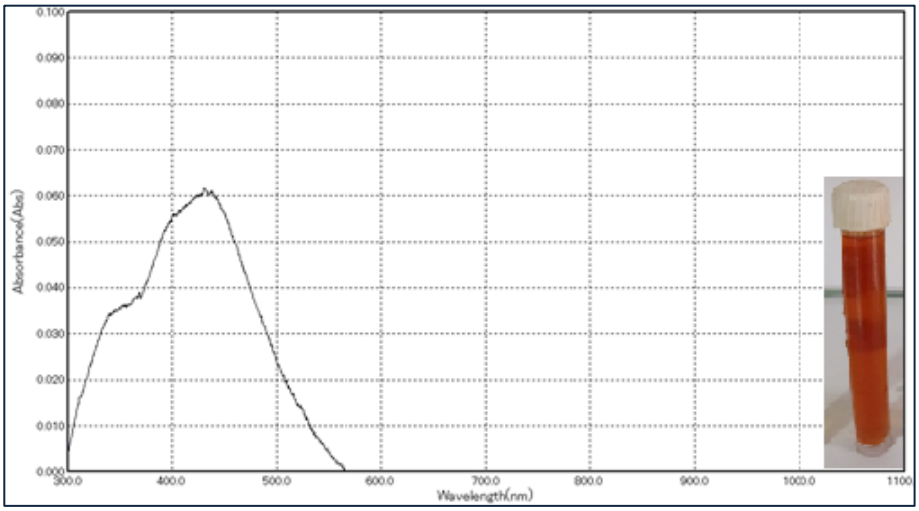


Fig. (3-28) Uv- visible for $[Zn\ (L_3)2(H2O)_2]Cl_2$ complex

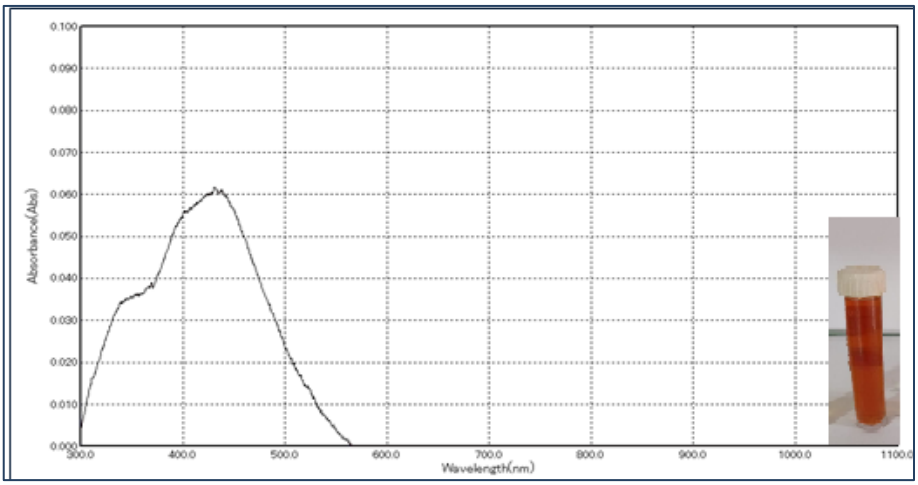


Fig. (3-30) Uv-visible for [Cd $(L_3)_2(H_2O)_2]Cl_2$ complex

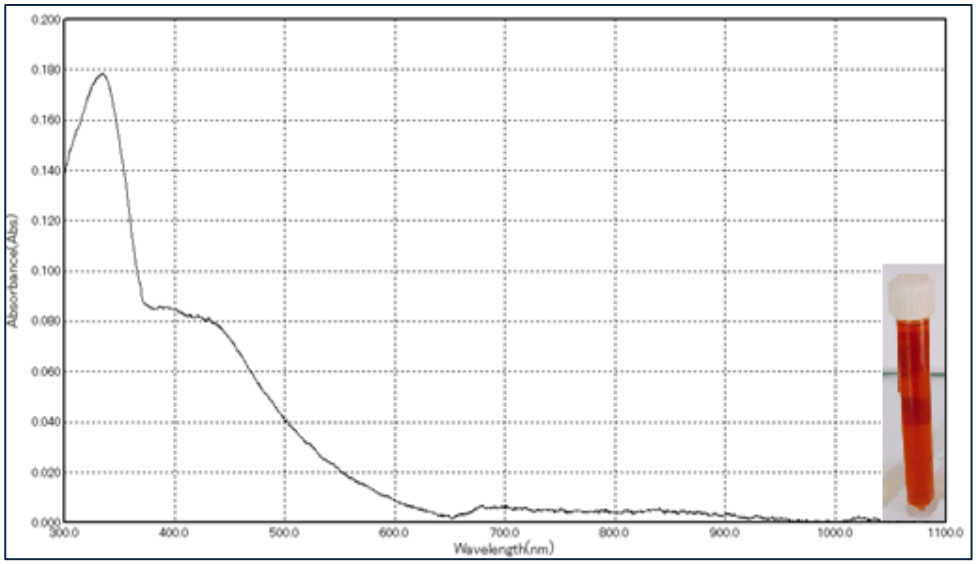


Fig. (3-31) Uv-visible for [Cu $(L_3)_2(H_2O)_2]Cl_2$ complex

Table (3-11) Uv-visible Electronic Transition of L3and there complexes

Compound	Absorption Band n m λ	Assignment
L3	380 ,445	π-π*, n-π*
$[Zn(L_3)2(H2O)_2]Cl_2$	370,440,	π-π*, n-π*
$[Cu(L_2)_2(H_2O)_2]Cl_2$	350, 450,650	π-π*, n-π*,$^2B_1g \rightarrow {}^2B_2g$
$[Cd(L_3)_2(H_2O)_2]Cl_2$	370,440	π-π*, n-π*

3.6.Thermal analysis(TG)

TGA experiments were used to investigate the thermal properties of complexes.. **Fig(32,33,34)** , in and **Tabe (3-12) (3-13) (3-14)**show the TG curves of complexes[(108)] .In Cd(II) complex of (L1,L2,L3), the decomposition takes place in two steps. The complexes showed stability to (38.55,36 ,61.50)°C respectively indicates the beginning of the decomposition of the organic compound which is attributed to the decomposition of the beta-lactam ring. Second step begins from (365,312.50 ,331.92)°C of (L1,L2,L3,) respectively indicates the end of the decomposition of the organic compound, leaving behind metal oxide as the end product[(109)]

Table (3-12) thermal analysis

Complexes	Steps of Degradation	Decomposition Tem C°	Mass % loss	Type of lost species
[Cd(L1)2(H2O)2]Cl2	1	38-106	9.7 %	CO_2,Cl ,N
	2	406-365	35%	$C_{14}H_{27}N_5O_2$,H_2O,CH_3

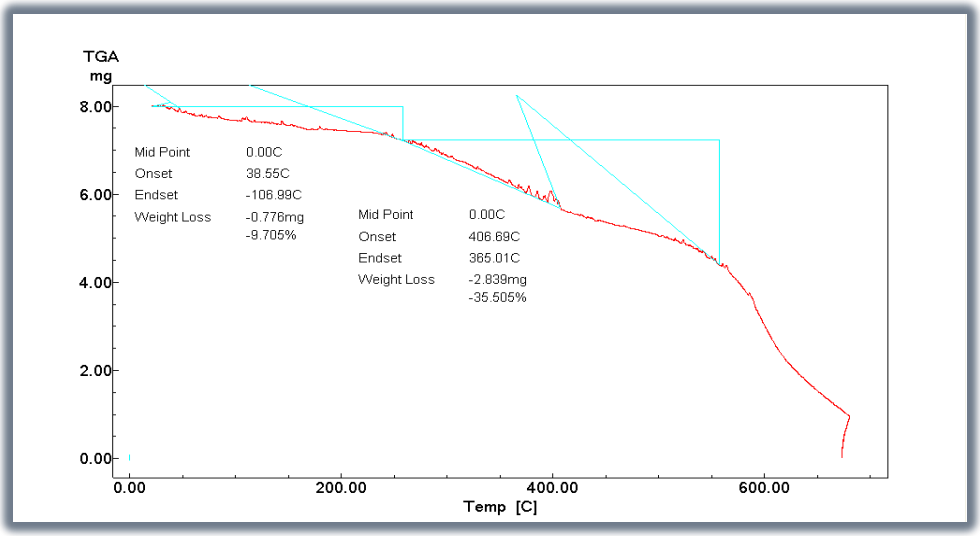


Fig. (3-32)TG curves of complex Cadmium L1

Table (3-13) thermal analysis

Complexes	Steps of Degradation	Decomposition Tem °C	Mass % loss	Type of lost species
$Cd(L_2)_2(H_2O)_2]Cl2]$	1	36-85	10.7	CO_2,Cl,N ,H_2
	2	310-312	23.051%	$C_{20}H_{30}N_4$,OS

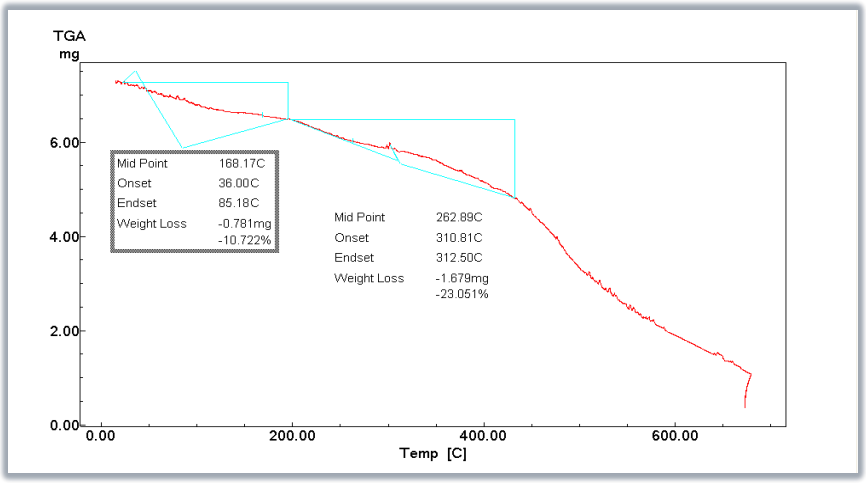


Fig. (3-33) TG for complex Cad mium L2

Table (3-14) thermal analysis

Complexes	Steps of Degradation	Decomposition Tem C°	Mass loss %	Type of lost species
$[Cd(L_3)_2(H_2O)_2]Cl_2$	1	61.5-1.25	8.5%	CO_2 ,Cl
	2	191-331	45%	$C_{13}H_{20}N_3O_2$

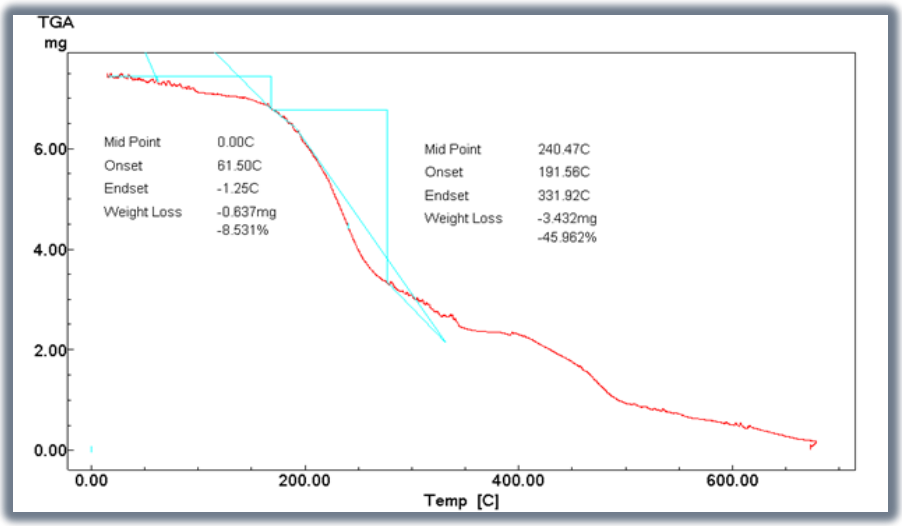


Fig. (3-34) TG for complex Cadmium L3

3.7. Atomic absorption

This technique is considered a quantitative technique as it relies on the principle of absorption spectroscopy to determine the concentration of the metal present in the complex depending on the extent to which it absorbs the radiation applied to it. The results have shown in the same case between practical and theoretical values, this indicates the correctness of the proposed formulas, as well as the correctness of the mixing ratios between metals and ligand .**Table (3-15)** shows theoretical and Practical Values for the ratio of metal to the ligand and the suggested formula of the prepared complexes

Table (3-15): Theoretical and Practical Values

complexes	Theoretical value %	Practical value
$[Cu(L_1)_2(H_2O)_2]Cl_2$	6.3	7.3
$[Zn\ (L_1)_2(H_2O)_2]Cl_2$	6.5	7.4
$[Cd\ (L_1)_2(H_2O)_2]Cl_2$	10.5	11.3
$[Cu(L_2)_2(H_2O)_2]Cl_2$	7.3	7.8
$[Zn\ (L_2)_2(H_2O)_2]Cl_2$	7.5	7.3
$[Cd\ (L_2)_2(H_2O)_2]Cl_2$	11.2	11.4
$[Cu(L_3)_2(H_2O)_2]Cl_2$	7.5	7.9
$[Zn\ (L_3)_2(H_2O)_2]Cl_2$	7.7	7.2
$[Cd\ (L_3)_2(H_2O)_2]Cl_2$	11.5	10.9

3.8. Conductivity

Absolute ethanol was used as a solvent for the complexes, which were prepared at a concentration of $1x10^{-3}$ M. To measure molar

conductivity, it has been found that all complexes are Conductive (the behavior of these complexes was conductive), molar

The conductivity value was restricted to between 80-93($Ohm^{-}.cm^{2}$; mol^{-1}), and these results in agreement with what was observed in the study .**Table (3-16)** shows molar

Conductivity for different types of electrolytes in different solvents (110)

and **Table (3-17)** shows the molar conductivity results for all complexes.

Table (3-16) molar conductivity for different types of electrolytes in different solvents

Solvent	non electrolyte	1:1	1:2	1:3	1:4
Water	0	120	240	360	480
DMSO	0-20	40-70	70-90	90-120	120-240
DMF	0-30	65-90	130-170	200-240	300
Ethanol	0-20	35-45	70-90	120	160
Methyl cyanide	0-30	120-160	220-300	340-420	500

Table (3-17) Molar conductivity values for complexes in Ethanol solvent

Complex	Molar conductivity
$[Cu(L_1)_2(H_2O)_2]Cl_2$	90
$[Cd\ (L_1)_2(H_2O)_2]Cl_2$	91
$[Zn\ (L_1)_2(H_2O)_2]Cl_2$	90

$[Cu(L_2)_2(H_2O)_2]Cl_2$	85
$[Cd\ (L_2)_2(H_2O)_2]Cl_2$	80
$[Zn\ (L_2)_2(H_2O)_2]Cl_2$	82
$[Cu(L_3)_2(H_2O)_2]Cl_2$	90
$[Cd\ (L_3)_2(H_2O)_2]Cl_2$	93
$[Zn\ (L_3)_2(H_2O)_2]Cl_2$	90

3.9. Magnetic Susceptibility for Coordination Complexes

Magnetic measurements have been widely used in the study of transition

metal complexes, as most transition metals possess single electrons and

show paramagnetic properties. In addition, the greater the number of lone

Electrons, the greater the magnetic moment of the ion ,as it gives information about the compound in terms of electronic structure and oxidative state of atoms. The transition metals produce the magnetic properties of the complexes as a result of the orbital motion and the Permian motion.

$\mu=\sqrt{4\ S\ (\ S+1)+L(\ L+1)}=B.M$

S=spin quantum number

L=orbital quantum number

$\mu=\sqrt{n\ (n+2)}=B.M$

(The number of unpaired electrons)=n

Bohr Magneton=B.M.

The value of the magnetic susceptibility of the prepared complexes was

measured at room temperature by using magnetic balance and the value

μ eff=2.828$\sqrt{}$XA .T= B.M

XA=XM+D

XM=X g x M .wt

Absolute temperature=T

Atomic sensitivity=XA

molarity sensitivity =XM

gram sensitivity =X g

Effective magnetic moment =μ eff

Correction factor for the compounds prepared in the study =D

The practical values for the effective magnetic moment obtained from the

above equations showed convergence with the theoretical value the results were included in **Table (3-18)**

Table (3-18) Magnetic susceptibility for coordination complexes

compound	Magnature	Xg *10^{-6}	µeff	Hyperdization
$[Cu(L_1)_2(H_2O)_2]Cl_2$	Paramagnetic	1.6	1.0	sp^3d^2
$[Cd\ (L_1)_2(H_2O)_2]Cl_2$	Diamagnetic	0	0	sp^3d^2

$[Zn\ (L_1)_2(H_2O)_2]Cl_2$	Diamagnetic	0	0	sp^3d^2
$[Cu(L_2)_2(H_2O)_2]Cl_2$	Paramagnetic	1	1.2	sp^3d^2
$[Cd\ (L_2)_2(H_2O)_2]Cl_2$	Diamagnetic	0	0	sp^3d^2
$[Zn\ (L_2)_2(H_2O)_2]Cl_2$	Diamagnetic	0	0	sp^3d^2
$[Cu(L_3)_2(H_2O)_2]Cl_2$	Paramagnetic	0.8	1.2	sp^3d^2
$[Cd\ (L_3)_2(H_2O)_2]Cl_2$	Diamagnetic	0	0	sp^3d^2
$[Zn\ (L_3)_2(H_2O)_2]Cl_2$	Diamagnetic	0	0	sp^3d^2

3.10. Polarization curves

The prepared ligands and complexes are of high protection quality, and this is due to the nature of these compounds and the presence of high electronic density in the groups of these compounds, especially the presence of heterogeneous atoms containing non-shared electronic pairs, which help them stick to the surface of the metal and form an insulating layer that protects it from the arrival of corrosion causes to the surface and thus Prevent corrosion.

Corrosion coefficients were estimated from the data generated in **Tables (3-19)** and **Fig. (3-35),(3-36),(3-37),(3-38)**. The corrosion current density (icorr) and corrosion potential (Ecorr) were obtained by extrapolating the cathodic and anodic taffer in the absence and presence of inhibitor molecules in HCl (0.1M) solution. The slopes of the anodic (ba) and cathodic (bc) tafels were also calculated from **the figure (35-38)**. **Table(3-19)** shows the data generated by corrosion potential Ecorr (Mv), corrosion current density icorr (A/cm2), cathodic and anodic Tafel slopes (mV/Dec), and protection efficiency PE%(17):

$$\%IE = \frac{(icorr)o - (icorr)}{(icorr)o} * 100$$

where (icorr) is the corrosion current density in the absence of inhibitors, (icorr) is the corrosion current density in the presence of inhibitors.

Table (3-19). Corrosion parameters for blank and compound in HCl solutions and different compound

Comp.	E corr.	I corr.	I corr / r	Anodic β	Cathodic β	Corr. rate,	IE%
Blank	-0.535	101.77	1.875E-4	0.103	0.057	0.920	-
L3	-0.695	27.30	5.460E-5	0.204	0.192	0.268	73
$[Cd(L_3)_2(H_2O)_2]Cl_2$	-0.669	13.90	2.979E-5	0.098	0.187	0.146	86
$[Zn(L_3)_2(H_2O)_2]Cl_2$	-0.652	10.28	2.456E-5	0.111	0.176	0.121	90

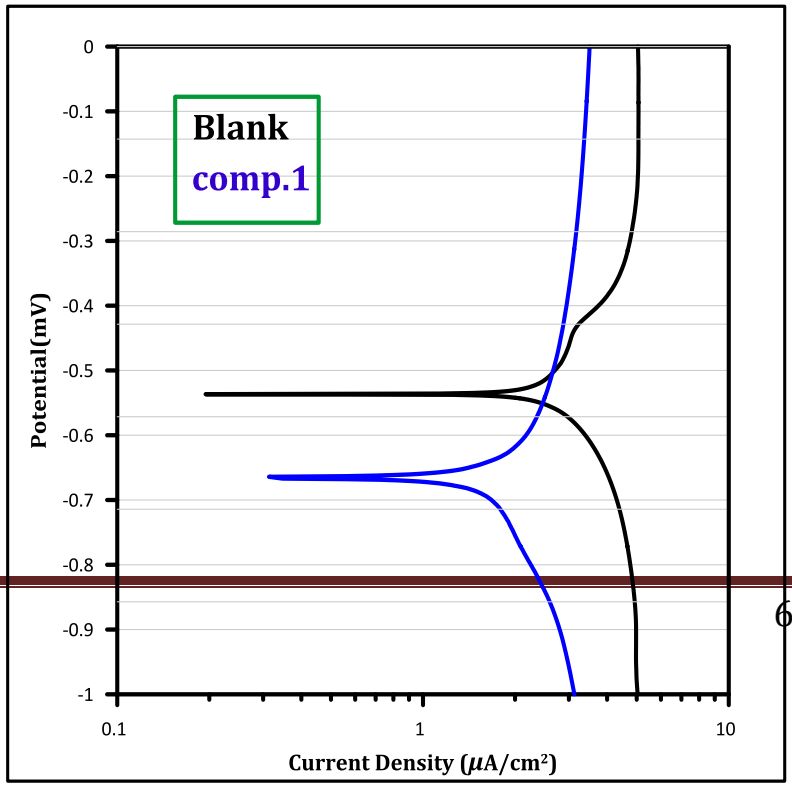


Fig. (3-35) Polarization curves for corrosion of blank HCl solution

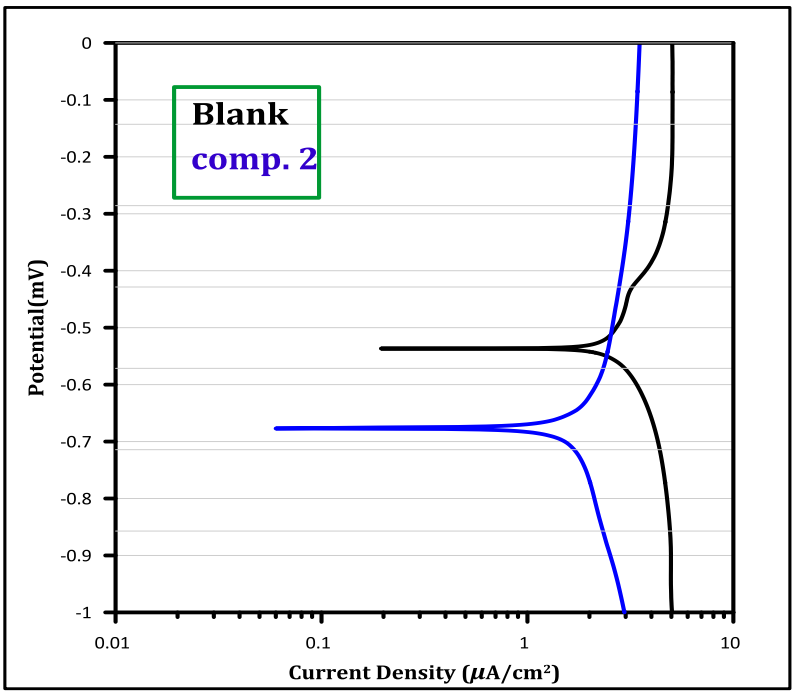


Fig. (3-36) Polarization curves for corrosion of blank HCl solution Comp.2.

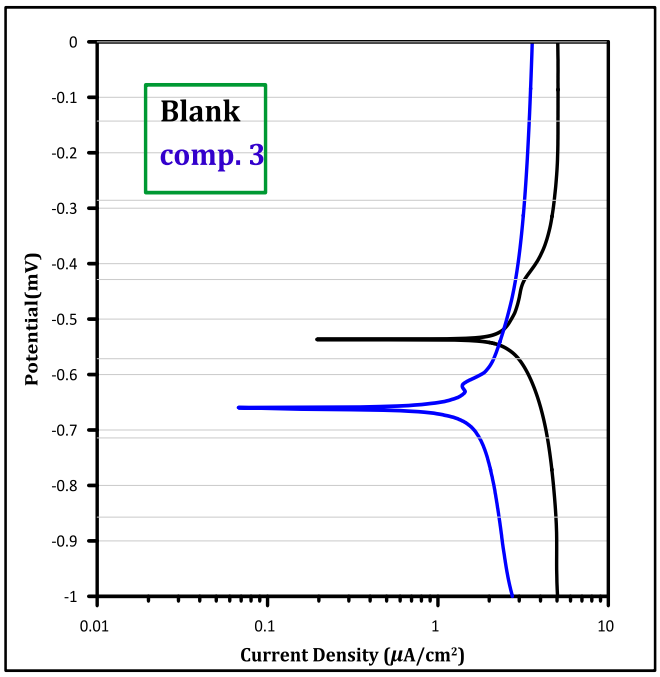


Fig. (3-37) Polarization curves for corrosion of blank HCl solution Comp.3.

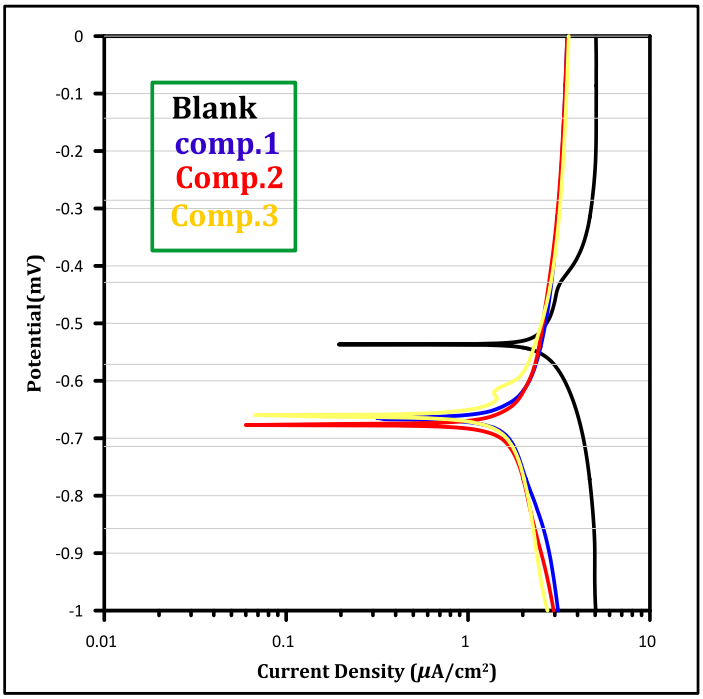


Fig. (3-38) Polarization curves for corrosion of blank HCl solution Comp.1, 2, and 3

3.11. Biological Action of Ligands and Complexes

The bioactivity of the ligands and its complexes was examined for diverse bacteria utilizing an inhibitory strategy The compounds exhibit inhibition diameter to the types of complexes that exhibit inhibition diameter against bacteria; the results show that the complexes have higher activity than the ligand under similar conditions **Figure (3-39)-(3-45)** Shows the effect of compounds on bacteria

Fig.(3-39*)* *Streptococcus bacteria*

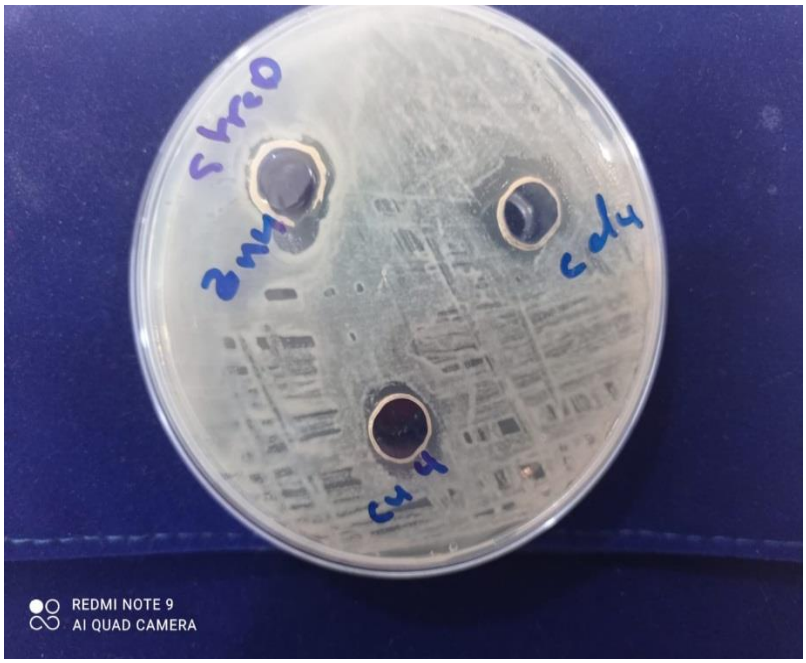


Fig.(3-40) ***Streptococcus bacteria***

Fig.(3-41) ***Streptococcus bacteria***

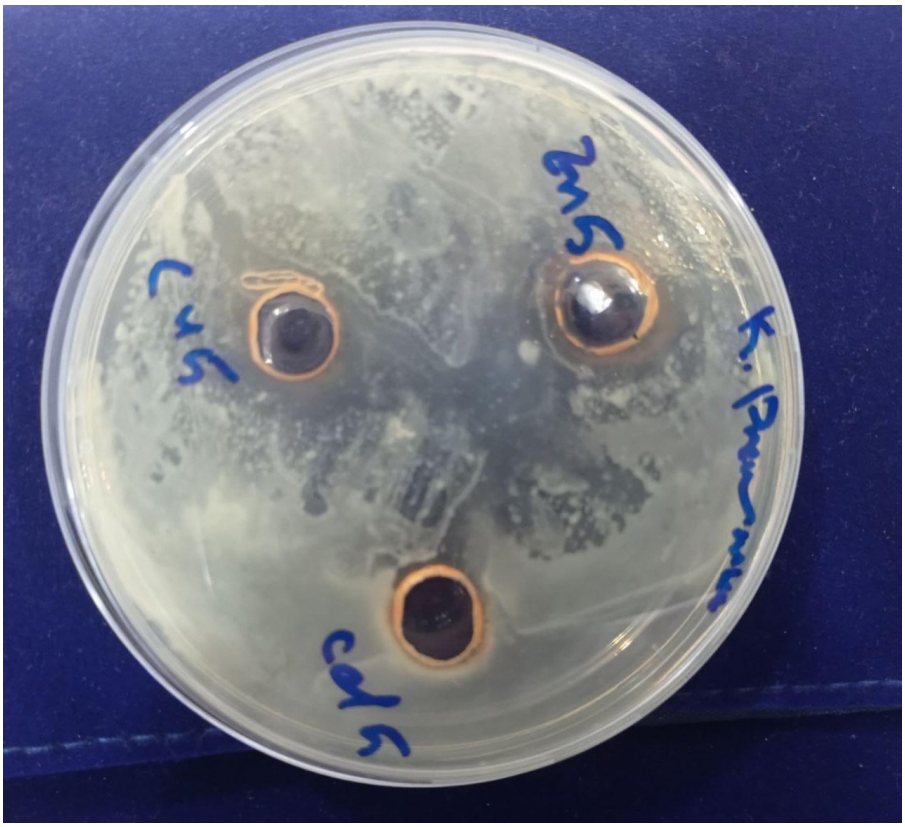


Fig.(3-42) ***Streptococcus bacteria***

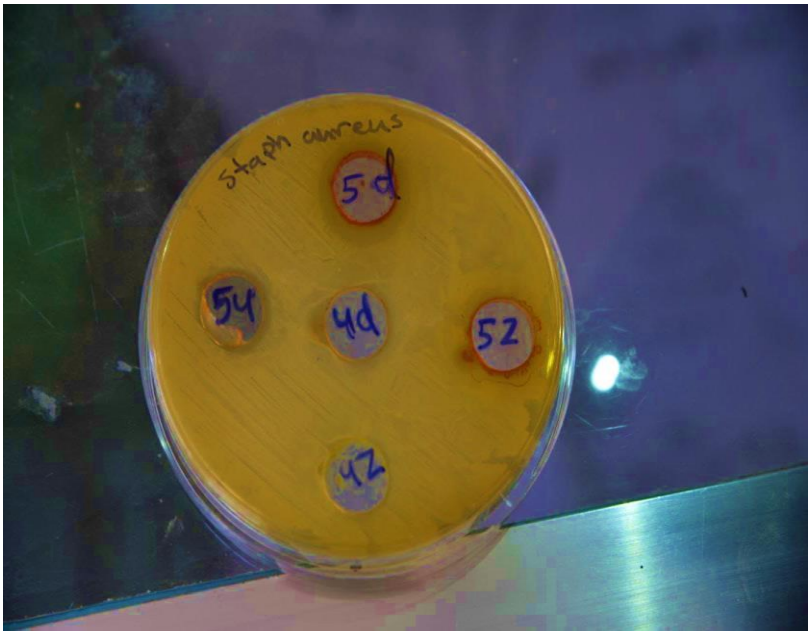


Fig. (3-43) ***Staphylococcus bacteria***

Fig.(3-44) ***Staphylococcus bacteria***

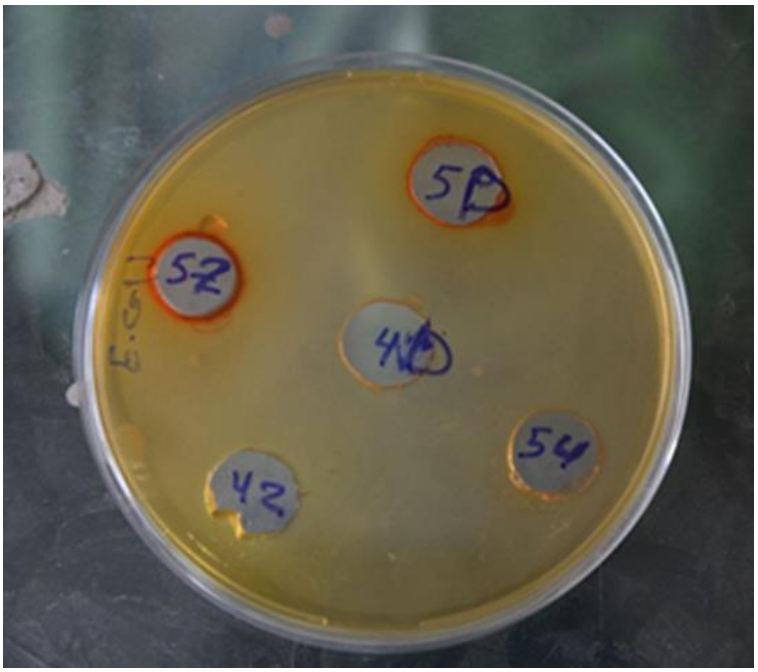


Fig.(3-45) ***E.coli bacteria***

Table (3-20) Biological activity for the ligand and complexes

	Klebsiella	**E.coli**	**Staphylococcus**	**streptococcus**
6-APA	0	0	10	11
$[Cu(L_1)_2(H_2O)_2]Cl_2$	0	0	50	15
$[Cd\ (L_1)_2(H_2O)_2]Cl_2$	0	0	20	20
$[Zn\ (L_1)_2(H_2O)_2]Cl_2$	0	0	55	22
$[Cu(L_2)_2(H_2O)_2]Cl_2$	0	0	20	23
$[Cd\ (L_2)_2(H_2O)_2]Cl_2$	0	0	22	30
$[Zn\ (L_2)_2(H_2O)_2]Cl_2$	0	0	30	30
$[Cu(L_3)_2(H_2O)_2]Cl_2$	0	0	20	25
$[Cd\ (L_3)_2(H_2O)_2]Cl_2$	0	0	15	40
$[Zn\ (L_3)_2(H_2O)_2]Cl_2$	0	0	22	25
L1	0	0	20	20
L2	0	0	10	15
L3	0	0	22	10

3.12. Conclusions:

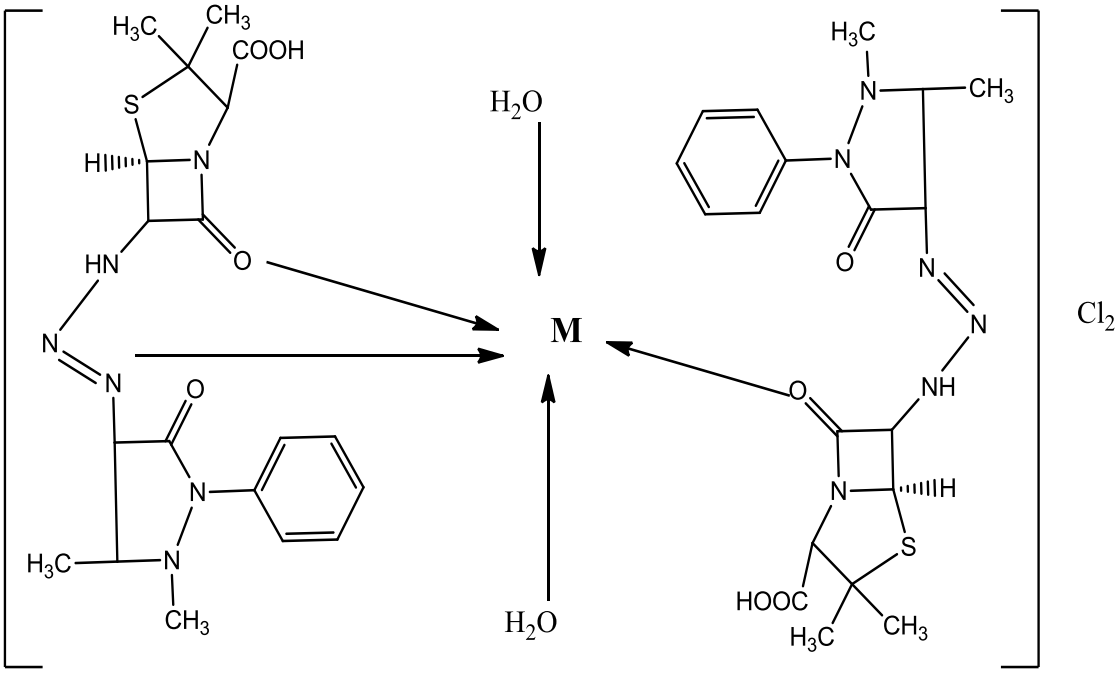
1- The reaction between amine and 6- amino pencillanic acid in 1:1mole product a triazene ligand .from (Mass spectroscoby,^{1}HNMR ,FT-IR,UV) Through these techniques, the shape of the ligand was proven Through these techniques, the shape of the ligand was proven, of the two-stranded ligand with the metal salt was formed, and its molar ratio was1:2. The prepared ligand corresponded to Cu, Cd, Zn can be proven it by(FT-IR,UV-Visible, molar conductance, magnetic susceptibility ,Atomic Absorption) The complex shape was proposed and found to be octahedral by these techniques . Scheme (3-1) Suggested forms of complexes for L1, L2, L3.

3- The preparation method is economically inexpensive and widely used in the preparation of inorganic complexes.

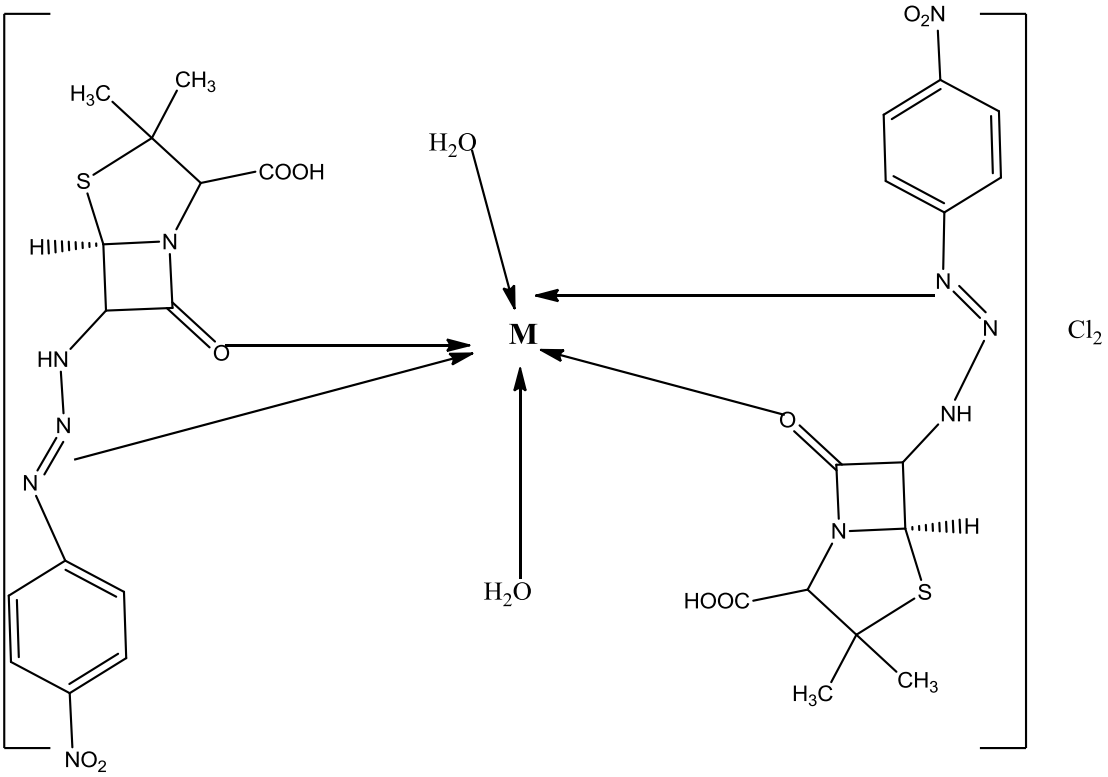
4- The prepared complexes are stable towards thermal and chemical factors.

5- The prepared compounds gave a high protection against corrosion of up to 90%, and this is considered important in protecting the metal equipment from corrosion and thus preserving it and reducing maintenance costs and safety from the risks of collapsing this equipment.

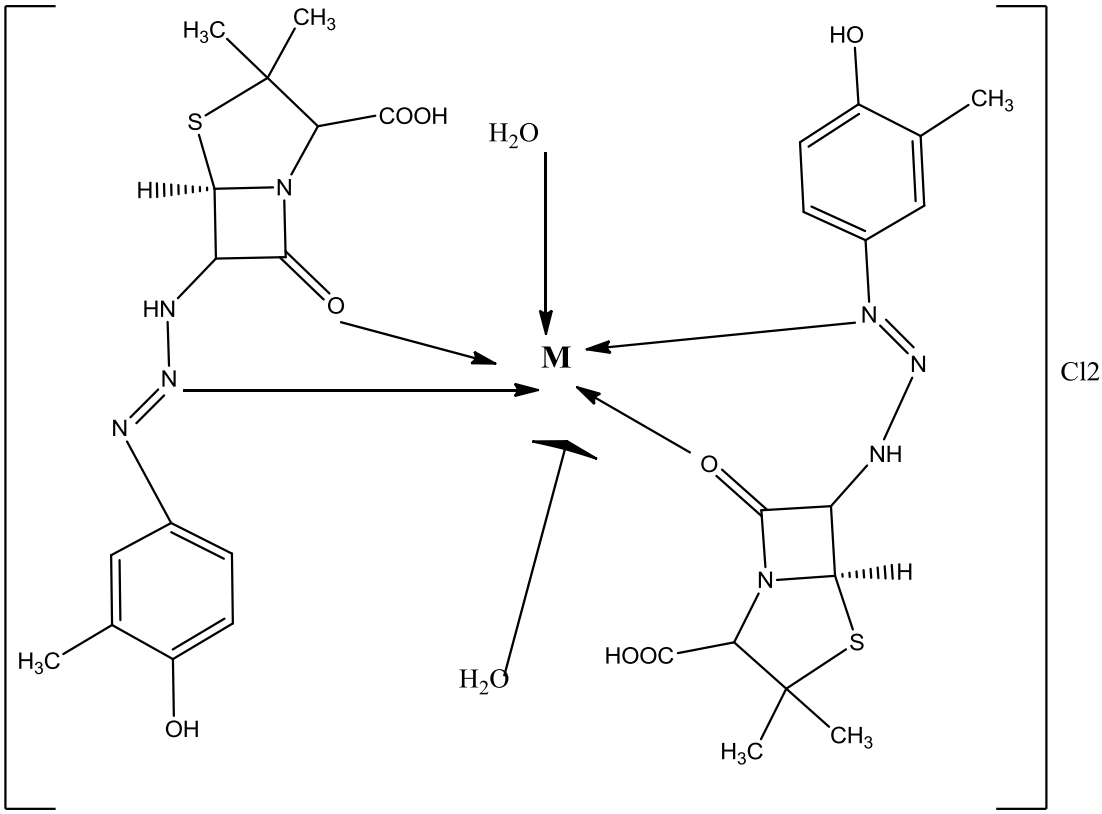
6- The prepared compounds contain the penicillin group, and this group is considered one of the important groups because of its pharmacological properties.



Complex for L 1



Complex For L2



Complex For L 3

Scheme (3-1) Suggested forms of complexes for L1, L2, L3

Suggestion for Future Work:-

- Synthesis of new triazene derivatives using different amines
- Synthesis of new sets of complexes for all ligands using other sets of metal ions
- Can be used DMSO instead of ethanol in dissolving
- Assessment of the anticancer action of made composites
- Conducting further biological studies on the prepared compounds, in vivo studying of interaction with various biological systems

Reference:

1. *Grundmann, C., & Grünanger, P. (2012). The nitrile oxides: versatile tools of theoretical and preparative chemistry (Vol. 13). Springer Science & Business Media.*

2. *Bhardwaj, N., Pathania, A., & Kumar, P. (2021). Naturally available nitrogen-containing fused heterocyclics as prospective lead molecules in medicinal chemistry. Current Traditional Medicine, 7(1), 5-27.*

3. Palaniappan, S. P. (2022). Pharmacological Role of Heterocyclic Compounds in the Treatment of Alzheimer's Disease: A Review.

4. Liu, F., Wang, Z., Zhang, H., Jin, L., Chu, X., Gu, B., ... & Yang, W. (2019). Nitrogen, oxygen and sulfur co-doped hierarchical porous carbons toward high-performance supercapacitors by direct pyrolysis of kraft lignin. *Carbon*, *149*, 105-116.

5. *Morey, P. B. (2015). Ultrasonic insight into substituted thiazoles and its biological activity. Research Journal of Chemical Sciences ____ ISSN, 2231, 606X.*

6. *Nasiriani, T., Javanbakht, S., Nazeri, M. T., Farhid, H., Khodkari, V., & Shaabani, A. (2022). Isocyanide-Based Multicomponent Reactions in Water: Advanced Green Tools*

for the Synthesis of Heterocyclic Compounds. Topics in Current Chemistry, 380(6), 50

7. *Zhang, L., Peng, X. M., Damu, G. L., Geng, R. X., & Zhou, C. H. (2014). Comprehensive review in current developments of imidazole-based medicinal chemistry. Medicinal research reviews, 34(2), 340-437.*

8. Mohammadnia, M., Aghdastinat, H., Kamalzadeh, S., & Nabaei, E. (2022). Preparation and Characterization of 2, 7-Diaminophenazine Supported on Nanocellulose as Novel Recyclable Nanocatalyst for Synthesis of Isoxazolo [4, 3-e] indazole Derivatives and Theoretical Study on the Mechanism using a DFT Method. *Polycyclic Aromatic Compounds*, 1-17.

9. Holmberg-Douglas, N., Choi, Y., Aquila, B., Huynh, H., & Nicewicz, D. A. (2021). B-Functionalization of saturated aza-heterocycles enabled by organic photoredox catalysis. *ACS catalysis*, *11*(5), 3153-3158..

.

10. *Gordon, P. F., & Gregory, P. (2012). Organic chemistry in colour. Springer*

Science & Business Media.

11. *Qiu, J., Tang, B., Ju, B., Xu, Y., & Zhang, S. (2017). Stable diazonium salts of weakly basic amines—Convenient reagents for synthesis of disperse azo dyes. Dyes and Pigments, 136, 63-69.*

12. *Venil, C. K., Velmurugan, P., Dufossé, L., Renuka Devi, P., & Veera Ravi, A. (2020). Fungal pigments: Potential coloring compounds for wide ranging applications in textile dyeing. Journal of fungi, 6(2), 68*

13. *Alkurdi, A. F., AlJahdali, M. S., & Alshehri, A. A. (2022). Synthesis, characterization, DFT calculation, and biological activity of pyrazole-based azo-metal (II) complexes. Results in Chemistry, 4, 100566.*

14. *R.H. Fayadh, A.A. Ali, F.M. Al-Jabri; Int. J. Engin. Techn. Res., 2(2015): 24-28.*

15. *Sandomierski, M., & Voelkel, A. (2021). Diazonium modification of inorganic and organic fillers for the design of robust composites: a review. Journal of Inorganic and Organometallic Polymers and Materials, 31, 1-21.*

16. *Anith, K.R. Reddy and Fasiulla; Arch. Appl. Sci. Res.,7(2015): 59-65*

17. *Sarigul, M., Sari, A., Kose, M., McKee, V., Elmastas, M., Demirtas, I., & Kurtoglu, M. (2016). New bio-active azo-azomethine-based Cu (II) complexes. Inorgan. Chim. Acta, 444, 166-175.*

18. *Yang, X., Zhu, F., Li, Y., Yan, M., Cui, Y., & Sun, G. (2020). Three Indole Derived Azo-Azomethine Dyes as Effective Chemosensors for F− Ion and Trace Water Detection. Bulletin of the Chemical Society of Japan, 93(7), 870-879.*

19. *Farag, M. R., Abou-Hadeed, A. H., Ghoniem, M. H., Alagawany, M., Laudadio, V., & Tufarelli, V. (2015). Chemical composition and mineral contents differentiation in hairs of some wild animal species. Pakistan Journal of Zoology, 47(4).*

20. *M. Niluvanji Matada et al.,(2020) „A new sulphur containing heterocycles having azo linkage: Synthesis, structural characterization and biological evaluation", J. King Saud Univ. - Sci., vol. 32, no. 8, pp. 3313–3320, 2020, doi: 10.1016/j.jksus.09.016*

21. *Zhang, F. G., Chen, Z., Tang, X., & Ma, J. A. (2021). Triazines: Syntheses and inverse electron-demand diels–alder reactions. Chemical Reviews, 121(23), 14555-14593*

22. *Jaiswal, S., & Verma, N. K. (2021). Benzothiazole Moiety with Sulphonamide as Anti-Inflammatory and Analgesic Activity: A Review.*

23. *Bilginer, S., Gonder, B., Gul, H. I., Kaya, R., Gulcin, I., Anil, B., & Supuran, C. T. (2020). Novel sulphonamides incorporating triazene moieties show powerful carbonic anhydrase I and II inhibitory properties. Journal of Enzyme Inhibition and Medicinal Chemistry, 35(1), 325-329.*

24. *Chen, J., Xie, X., Liu, J., Yu, Z., & Su, W. (2022). Revisiting aromatic diazotization and aryl diazonium salts in continuous flow: highlighted research during 2001–2021. Reaction Chemistry & Engineering, 7(6), 1247-1275.*

25. *Nath, D., & Banerjee, P. (2013). Green nanotechnology–a new hope for medical biology. Environmental toxicology and pharmacology, 36(3), 997-1014. -*

26. *Preusser, S., Schönherr, P. R., Görls, H., Krieck, S., Imhof, W., & Westerhausen, M. (2020). 2-Halo-and/or 4-ethoxycarbonyl-substituted asymmetric 1, 3-diaryltriazenes and 1, 3-diarylamidines as well as N-methylated congeners. Journal of Molecular Structure, 1205, 127622.*

27. *Valinia, F., Shojaei, N., & Ojaghloo, P. (2019). Novel 1-(4-chlorophenyl)-3-(2-ethoxyphenyl) triazene ligand: Synthesis, X-ray crystallographic studies, spectroscopic characterization and DFT calculations. Chemical Review and Letters, 2(2), 90-97.*

28. *Song, S., Wang, Y., He, W., Wang, K., Yan, M., Yan, Q., & Zhang, Q. (2020). Melamine N-oxide based self-assembled energetic materials with balanced energy & sensitivity and enhanced combustion behavior. Chemical Engineering Journal, 395, 125114.*

29. *Fatemeh Valinia; Nasrin Shojaei; Parisa Ojaghloo. "Novel 1-(4-chlorophenyl) -3-(2-ethoxyphenyl)tri-azene ligand: Synthesis, X-ray crystallographic studies, spectroscopic characterization and DFT calcu-lations". Chemical Review and Letters, 2, 2, 2019, 90-97. doi: 10.22034/crl.2018.85596, 49-55. doi: 10.22034/crl.2018.85119*

30. *Prieschl, D., Arrowsmith, M., Dietz, M., Rempel, A., Müller, M., & Braunschweig, H. (2020). Synthesis of polyheterocyclic 1, 1-diboryltriazenes by γ-nitrogen insertion of azides into activated B–B single bonds. Chemical Communications, 56(42), 5681-5684.*

31. Suleymanov, A. A., Scopelliti, R., Fadaei Tirani, F., & Severin, K. (2018). One-Pot Synthesis of Trisubstituted Triazenes from Grignard Reagents and Organic Azides. Organic letters, 20(11), 3323-3326.

32. *Figueirêdo, P. D. M. S., Sampaio Filho, J. C., Sodré, A. D. J. S., de Castro Júnior, J. R., Gonçalves, I. S., Blasques, R. V., ... & Villis, P. C. M. (2021). Assessment of the biological potential of diaryltriazene-derived triazene compounds. Scientific Reports, 11(1), 2541.*

33. *Luo, S. P., Lei, J. M., & Zhan, S. Z. (2018). Synthesis, characterization, luminescent, and catalytic performance of a dinuclear triazenido–silver complex. Journal of Coordination Chemistry, 71(8), 1193-1204.*

34. *Ashley, D. C., & Jakubikova, E. (2017). Ironing out the photochemical and spin-crossover behavior of Fe (II) coordination compounds with computational chemistry. Coordination Chemistry Reviews, 337, 97-111.*

35. *Mjos, K. D., & Orvig, C. (2014). Metallodrugs in medicinal inorganic chemistry. Chemical reviews, 114(8), 4540-4563*

36. *Shaibu, R. O. (2007). A bioinorganic study of some cobalt (II) Schiff base complexes of variously substituted hydroxybenzaldimines (Doctoral dissertation, Rhodes University).*

37. *Jomova, K., Makova, M., Alomar, S. Y., Alwasel, S. H., Nepovimova, E., Kuca, K., ... & Valko, M. (2022). Essential metals in health and disease. Chemico-Biological Interactions, 110173*

38. *McCusker, J. K. (2019). Electronic structure in the transition metal block and its implications for light harvesting. Science, 363(6426), 484-488.*

39. *Cox, P. A. (2010). Transition metal oxides: an introduction to their electronic structure and properties (Vol. 27). Oxford university press*

.

40. *Heinrich, T. A., da Silva, R. S., Miranda, K. M., Switzer, C. H., Wink, D. A., & Fukuto, J. M. (2013). Biological nitric oxide signalling: chemistry and terminology. British journal of pharmacology, 169(7), 1417-1429*

41. *Niewa, R. (2013). Alkaline-Earth Metal Nitrides of the Main-Group Elements: Crystal Structures and Properties of Inverse Perovskites. Zeitschrift für anorganische und allgemeine Chemie, 639(10), 1699-1715.*

42. *Crabtree, R. H. (2009). The organometallic chemistry of the transition metals. John Wiley & Sons*

43. *Anastassakis, K. (2022). Zinc (Zn). In Androgenetic Alopecia From A to Z: Vol. 2 Drugs, Herbs, Nutrition and Supplements (pp. 405-416). Cham: Springer International Publishing.*

44. *Yaghoobnejad Asl, H., & Manthiram, A. (2019). Mass Transfer of Divalent Ions in an Oxide Host: Comparison of Mg2+ and Zn2+ Diffusion in Hexagonal K x W3O9 Bronze. Chemistry of Materials, 31(7), 2296-2307*

45. *Jiang, L., Sun, Y., Chen, Y., & Nan, P. (2020). From DNA to nerve agents–the biomimetic catalysts for the hydrolysis of phosphate esters. ChemistrySelect, 5(30), 9492-9516*

46. *Yamasaki, S., Sakata-Sogawa, K., Hasegawa, A., Suzuki, T., Kabu, K., Sato, E., ... & Hirano, T. (2007). Zinc is a novel intracellular second messenger. The Journal of cell biology, 177(4), 637-645*

47. *48- Hu, J. (2021). Toward unzipping the ZIP metal transporters: structure, evolution, and implications on drug discovery against cancer. The FEBS Journal, 288(20), 5805-5825*

48. *Kakanejadifard, A., Esna-ashari, F., Hashemi, P., & Zabardasti, A. (2013). Synthesis and characterization of an azo dibenzoic acid Schiff base and its Ni (II), Pb (II), Zn (II) and Cd (II) complexes. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 106, 80-85..*

49. *Das, S., Mondal, R., Chakraborty, G., Guin, A. K., Das, A., & Paul, N. D. (2021). Zinc stabilized azo-anion radical in dehydrogenative synthesis of N-heterocycles. An exclusively ligand centered redox controlled approach. ACS Catalysis, 11(12), 7498-7512.-*

50. *Ullah, H., Rahaman, R., & Mahmud, S. (2017). Optical properties of cadmium oxide (CdO) thin films. Indonesian Journal of Electrical Engineering and Computer Scien Schütt, H. W. (1997). Eilhard Mitscherlich, prince of Prussian chemistry. Chemical Heritage Foundation. ce, 5(1), 81-84*

51. *Schütt, H. W. (1997). Eilhard Mitscherlich, prince of Prussian chemistry. Chemical Heritage Foundation*

52. *Martelli, A., Rousselet, E., Dycke, C., Bouron, A., & Moulis, J. M. (2006). Cadmium toxicity in animal cells by interference with essential metals. Biochimie, 88(11), 1807-1814.*

53. *- Citak, D., Tuzen, M., & Soylak, M. (2009). Simultaneous coprecipitation of lead, cobalt, copper, cadmium, iron and nickel in food samples with zirconium (IV) hydroxide prior to their flame atomic absorption spectrometric determination. Food and chemical toxicology, 47(9), 2302-2307.*

54. *55- Jaber, S. A., Kyhoiesh, H. A., & Jawad, S. H. (2021, March). Synthesis, characterization and biological activity studies of cadmium (II) complex derived from azo ligand 2-[2\-(5-bromo Thiazolyl) azo]-5-dimethyl amino benzoic acid. In Journal of Physics: Conference Series (Vol. 1818, No. 1, p. 012013). IOP Publishing*

55. *al-Nuaimi, A. THE GLOBAL ANTI-AGGRESSION CAMPAIGN Overview.*

56. *Gadekar, B. (2021). Synthesis, characterization and Microbiological activities of metal chelate of Fe (II) and Cu (II) with ligand 2-amino-1, 4-naphthoquinone (ANQ). REX-ISSN 2321-1067, 85.*

57. *Zhao, C., Qin, K. Z., Song, G. X., Li, G. M., & Li, Z. Z. (2019). Early Palaeozoic high-Mg basalt-andesite suite in the Duobaoshan Porphyry Cu deposit, NE China: Constraints on petrogenesis, mineralization, and tectonic setting. Gondwana Research, 71, 91-116*

58. *Alamri, M. A., Al-Jahdali, M., Al-Radadi, N. S., & Hussien, M. A. (2022). Characterization, theoretical investigation, and biological applications of Mn (II), Co (II), Ni (II), Cu (II), and Zn (II) complexes of a triazene ligand containing a*

benzothiazole ring. Applied Organometallic Chemistry, 36(1), e6466

59. *Al-Saadawy, N. H., & Faraj, H. R. (2016). Synthesis and characterization of a new triazene complexes for cu (ii), ni (ii), co (ii), zn (ii) and fe (ii). Journal of Computational Theoretical Nanoscience, 4(11), 3669-3675-*

60. *Shanmugakala, R., Tharmaraj, P., Sheela, C. D., & Anitha, C. (2012). Synthesis and studies on s-Triazine-based ligand and its metal complexes. International Journal of Inorganic Chemistry, 2012.*

61. *Pantalon Juraj, N., Krklec, M., Novosel, T., Perić, B., Vianello, R., Raić-Malić, S., & Kirin, S. I. (2020). Copper(ii) and zinc(ii) complexes of mono- and bis-1,2,3-triazole-substituted heterocyclic ligands. Dalton Transactions, 49(26), 9002-9015. doi:10.1039/D0DT01244K*

62. *Li, Y., & Ning, C. (2019). Latest research progress of marine microbiological corrosion and bio-fouling, and new approaches of marine anti-corrosion and anti-fouling. Bioactive materials, 4, 189-195*

63. *Guo, L., Obot, I. B., Zheng, X., Shen, X., Qiang, Y., Kaya, S., & Kaya, C. (2017). Theoretical insight into an empirical rule about organic corrosion inhibitors containing nitrogen, oxygen, and sulfur atoms. Applied surface science, 406, 301-306.*

64. *Rani, B. E., & Basu, B. B. J. (2012). Green inhibitors for corrosion protection of metals and alloys: an overview. International Journal of corrosion, 2012.-*

65. *M. E. Belghiti, S. Tighadouini, Y. Karazazi, A. Dafali, B. Hammouti, S. Radi and R. Solmaz, J. Mater. Environ. Sci., 7(1), 2017. 337-346.*

66. *Y. H. Yu, J. M. Yeh, S. J. Liou, C. L. Chen, D. J. Liaw and H. Y. Lu, Journal of Applied Polymer Science, 92(6), 2004. 3573-3582.*

67. *A. R. Thamer, N. A. Lami, and N. A Khudhair, Chemical Methodologies, 5(5), 2021, 285-295.*

68. *Y. Wu, Z. Hed, X. Zeng, T. Renc, E. de Vries and E.van der Heide, Tribological and anticorrosion behaviour of novel xanthate-containing triazine derivatives in water-glycol, Tribology International, 2017, 110, 113-124*

69. *M.H. Mahross, M. A. Taher, M. A. Mostfa, K. F. Chong and G.A.M. Ali, Experimental and quantum investigations of novel corrosion inhibitors based triazene derivatives for mild steel, Journal of Molecular Structure, 2021, 1242, 130831*

70. *P. Singh, A. Singh and M. A. Quraishi, Inhibition effect of 1,3,5-tri-p-tolyl-1,3,5-triazene on the corrosion of brass in 0.5 M HCl solution, Res Chem Intermed, 2014, 40, 595-604.*

71. *H. M. Abd El-Lateef, K. Shalabi, A. M. Arab and Y. M. Abdallah, Corrosion Mitigation Performance of N80 Steel in 5% Sulfamic Acid Medium by Applying Novel Tetrahydro-1,2,4-triazines Including Triazene Moieties: Electrochemical and Theoretical Approaches, ACS Omega, 2022, 7, 23380−23392*

72. *Hutchings, M. I., Truman, A. W., & Wilkinson, B. (2019). Antibiotics: past, present and future. Current opinion in microbiology, 51, 72-80.*

73. *Canto, E. S. M., Segundo, W. O. P. F., Cortez, A. C. A., Barbosa, F. R., Monteiro, J. S., & de Souza, J. V. B. (2022). Freshwater fungi in the Amazon as a potential source of antimicrobials. Freshwater Mycology, 261-275.*

74. *Exner, M., Bhattacharya, S., Christiansen, B., Gebel, J., Goroncy-Bermes, P., Hartemann, P., ... & Trautmann, M.*

(2017). Antibiotic resistance: What is so special about multidrug-resistant Gram-negative bacteria?. GMS hygiene and infection control, 12.

75. *Kayser, F. H., Bienz, K. A., Eckert, J., & Zinkernagel, R. M. (2005). Medical microbiology*

76. *Bush, K., & Bradford, P. A. (2016). ?-Lactams and ?-lactamase inhibitors: an overview. Cold Spring Harbor perspectives in medicine, 6(8), a0-*

77. *Jose, P. A., & Jebakumar, S. R. D. (2013). Non-streptomycete actinomycetes nourish the current microbial antibiotic drug discovery. Frontiers in microbiology, 4, 240.*

78. *Pal, K. K., & Gardener, B. M. (2006). Biological control of plant pathogens*

79. *Arroyo-Currás, N., Somerson, J., Vieira, P. A., Ploense, K. L., Kippin, T. E., & Plaxco, K. W. (2017). Real-time measurement of small molecules directly in awake, ambulatory animals. Proceedings of the National Academy of Sciences, 114(4), 645-650.*

80. *Foti, C., Piperno, A., Scala, A., & Giuffrè, O. (2021). Oxazolidinone antibiotics: chemical, biological and analytical aspects. Molecules, 26(14), 4280*

81. *Mancuso, G., Midiri, A., Gerace, E., & Biondo, C. (2021). Bacterial antibiotic resistance: The most critical pathogens. Pathogens, 10(10), 1310*

82. *Wenzel, M. (2020). Do we really understand how antibiotics work?. Future Microbiology, 15(14), 1307-1311.*

83. *Hemeg, H. A. (2017). Nanomaterials for alternative antibacterial therapy. International journal of nanomedicine, 12, 8211*

84. *O'Donnell, J. A., Lehman, J., Roderick, J. E., Martinez-Marin, D., Zelic, M., Doran, C., ... & Kelliher, M. A. (2018). Dendritic cell RIPK1 maintains immune homeostasis by preventing inflammation and autoimmunity. The Journal of Immunology, 200(2), 737-748.*

85. *Stokes, J. M., Lopatkin, A. J., Lobritz, M. A., & Collins, J. J. (2019). Bacterial metabolism and antibiotic efficacy. Cell metabolism, 30(2), 251-259.*

86. *Piepenbreier, H., Diehl, A., & Fritz, G. (2019). Minimal exposure of lipid II cycle intermediates triggers cell wall antibiotic resistance. Nature Communications, 10(1), 2733.*

87. *Kolganov, A. A., Gabrienko, A. A., Chernyshov, I. Y., Stepanov, A. G., & Pidko, E. A. (2020). The accuracy challenge of the DFT-based molecular assignment of 13 C MAS NMR*

88. *characterization of surface intermediates in zeolite catalysis. Physical Chemistry Chemical Physics, 22(41), 24004-24013*

89. *Ashutosh, N., Gupta, A. K., & Sharma, V. Interaction between Irrigants commonly used in Endodontic Practice and their Characterization using 1H NMR Spectra م.dmso 2*

90. *Al-Hamdany, W. J., Dabbagh, M. M., & A Shareef, O. (2012). Synthesis of Spiropyrrolidines via 1, 3 Anionic Cycloaddition. Rafidain Journal of Science, 23(5), 94-105*

91. *Yildiko, U., Ata, A. C., & Cakmak, ?. (2020). Synthesis, spectral characterization and DFT calculations of novel macro MADIX agent: mechanism of addition-fragmentation reaction of xanthate compound. SN Applied Sciences, 2(10), 1691.*

92. *Muhammad?Ali, M. A., Hamza Salman, H., & Jasim, E. K. H. L. A. S. Q. A. N. B. E. R. (2019). Antioxidant activity of some newly prepared symmetrically azo dyes derived from sulfa drugs. Asian J Pharm Clin Res, 12(2), 479-483.*

93. *Abraham, C. J. (2009). Catalytic, enantioselective bifunctional [4+ 2]-inverse electron demand hetero-Diels-Alder reactions of chiral ketene enolates and o-Benzoquinone derivatives. The Johns Hopkins University .*

94. *Gbenebor, O. P., Adeosun, S. O., Lawal, G. I., Jun, S., & Olaleye, S. A. (2017). Acetylation, crystalline and morphological properties of structural polysaccharide from shrimp exoskeleton. Engineering Science and Technology, an International Journal, 20(3), 1155-1165.-*

95. *La Nasa, J., Nodari, L., Nardella, F., Sabatini, F., Degano, I., Modugno, F., ... & Tomasin, P. (2020). Chemistry of modern paint media: The strained and collapsed painting by Alexis Harding. Microchemical Journal, 155, 104659.*

96. *Al-Adhami, H. J., & Al-Majidi, S. M. H. (2021). Design, Synthesis, and Antimicrobial and Antioxidant Activities of Some New Dihydrotetrazole, Dihydroquinazolin-4-one, and 1, 3-Benzothiazin-4-one Derivatives Based on 6-Amino-1, 3-dimethyluracil. Russian Journal of Organic Chemistry, 57, 448-454*

97. *Kyhoiesh, H. A. K., & Al-Adilee, K. J. (2021). Synthesis, spectral characterization, antimicrobial evaluation studies and cytotoxic activity of some transition metal complexes with tridentate (N, N, O) donor azo dye ligand. Results in Chemistry, 3, 100245.*

98. *Mukhopadhyay, D., Khan, N., Kamal, N., Varjani, S., Singh, S., Sindhu, R., ... & Bhargava, P. C. (2022). Degradation of ?-lactam antibiotic ampicillin using sustainable microbial peroxide producing cell system. Bioresource Technology, 361, 127605.*

99. *Chen, H., Chen, W., Lin, Y., Xie, Y., Liu, S. H., & Yin, J. (2021). Visible and near-infrared light activated azo dyes. Chinese Chemical Letters, 32(8), 2359-2368.*

100. *Ali, I., Said, M. H., & AlWazn, W. (2021). Preparation, Characterization, and Study of Complexes Containing Beta-lactam Group with Some Transitional Elements and their Biological Activity. Egyptian Journal of Chemistry, 64(10), 5703-5712.*

101. *Ahmed, F., Dewani, R., Pervez, M. K., Mahboob, S. J., & Soomro, S. A. (2016). Non-destructive FT-IR analysis of mono azo dyes. Bulg. Chem. Commun, 48(1), 71-77..*

102. *Farhan, M. M., Guma, M. A., Rabeea, M. A., Ahmad, I., & Patel, H. (2022). Synthesizes, Characterization, Molecular docking and in vitro Bioactivity study of new compounds containing Triple Beta Lactam Rings. Journal of Molecular Structure, 1269, 133781.*

103. *Biswas, N., & Umapathy, S. (2000). Structures, vibrational frequencies, and normal modes of substituted azo dyes: infrared, Raman, and density functional calculations. The Journal of Physical Chemistry A, 104(12), 2734-2745.*

104. *Anacona, J. R., Bravo, A., & Lopez, M. E. (2013). Cefoperazone metal complexes: synthesis and characterization. Journal of the Chilean Chemical Society, 58(1), 1520-1523.*

105. *Fogel, Y., Kastler, M., Wang, Z., Andrienko, D., Bodwell, G. J., & Müllen, K. (2007). Electron-deficient N-heteroaromatic linkers for the elaboration of large, soluble polycyclic 107-aromatic hydrocarbons and their use in the synthesis of some very large transition metal complexes. Journal of the American Chemical Society, 129(38), 11743-11749.*

106. *Kosower, E. M., & de Souza, J. R. (2006). n-ct-* Transitions: n* Transitions of the second kind. Chemical physics, 324(1), 3-7.*

107. *109-Ai, L., Hu, J., Ji, X., & Zhao, H. (2019). Structure confirmation and thermal kinetics of the inclusion of cis-jasmone in β-cyclodextrin. RSC advances, 9(45), 26224-26229.*

*AL-Hmedawi, H. H., & Al-Musawi, R. A. (2013). Synthesis and Characterization of some Transition Metal Complexes via Schiff Bases Derived from Dithiooxamide and Selective Aldehydes (Doctoral dissertation, M. Sc. Thesis, Kerba*la Univer

الخلاصة :

تحضير مركبات الترايازين كليكاند جديد مشتق من حامض ٦-امينو بنسلينك وتشخيص هذهاالليكاندات وتحضير معقدات جديدة مع عدد من الايونات الفلزية (االنحاس والخارصين والكاديميوم)، حيث تضمنت الخطوة الاولى مفاعلة الامين ٥-امينو-٢-مثيل فينول و ٤ - امينو انتي بايرين بارا- نايترو انيلين ، مع مركب ٦-امينو بنسلينك لينتج مركب الترايازين المقابل والذي بدوره ادخل في تفاعل تكوين مركبات معقدة في الخطوة الثانية مع ا ملاح كلوريدات لايونات فلزية ثنائية التكافوء. تم تشخيص المركبات المحضرة باستخدام مطيافية FTIRو HNMR١ وطيف الاشعه فوق البنفسجية والمرئية وطيف امتصاص الكتلة والحساسية المغناطيسية وكذلك طيف الامتصاص الذري. بالاضافة الى دراسة بعض الخصائص الفيزيائية للمركبات المحضرة. وتمت دراسة فعالية الليكاند المحضر والمعقدات في حماية الحديد الكاربوني من التاكل في الوسط الحامضي لحامض الهيدروكلوريك ٠,١ مولاري واعطت المركبات نتائج جيدة في الحماية، حيث كانت الحماية لليكاند تصل الى ٧٣% بينما اعطت المعقدات المحضرة نسبة حماية اعلى هي ٨٦% لمعقد الكاديميوم ٩٠% لمعقد الخارصين ، وكذلك دراسه فعالية المركبات المحضرة في تثبيط البكتريا من نوع غم موجب واعطى نتيجة اجابية في التثبيط لكل من الليكاندات والمعقدات .

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة بابل – كلية العلوم للبنات

قسم الكيمياء

تحضير وتشخيص بعض معقدات الايونات الفلزية لمشتقات ترايازين وتتقيم فعاليتها البايولوجية وتثبيطها للتاكل

رسالة مقدمة الى مجلس كلية العلوم للبنات –جامعة بابل

هي من متطلبات نيل درجة الماجستير في العلوم / الكيمياء

من قبل

حنين سعدي حسين

بكلوريوس علوم كيمياء .جامعة بابل (٢٠١٤)

اشراف

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