# AL-TAHADY UNIVERSITY
# FACULTY OF SCIENCE
# CHEMISTRY DEPARTMENT

M.Sc Thesis Entitled:
# Preparation and Spectroscopic Studies of some Oxo-metal Complexes of Imines Ligand

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# Faculty of Science
# Department Of Chemistry

## Title Of Thesis

**Preparation and Spectroscopic Studies of some Oxo-metal complexes of Imines ligand**

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بِسْمِ اللهِ الرَّحْمٰنِ الرَّحِيمِ

وَقُلِ اعْمَلُواْ فَسَيَرَى اللّهُ عَمَلَكُمْ وَرَسُولُهُ وَالْمُؤْمِنُونَ وَسَتُرَدُّونَ
إِلَى عَالِمِ الْغَيْبِ وَالشَّهَادَةِ فَيُنَبِّئُكُم بِمَا كُنتُمْ تَعْمَلُونَ

[التوبة : 105]

صَدَقَ اللهُ الْعَظِيمُ

# Dedication

I heartily would like to dedicate this work to; the candles of my life "my parents". The persons whom I share my life for better and worse "my brothers and sisters ". The woman whom I love and respect alit "my honey wife" the light of my eyes "my two babies", and all intellectual people.

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# ABSTRACT

Neutral tetra dentate $N_2O_2$ type complexes of VO(II), ZrO(II), MoO$_2$(II), and UO$_2$(II) have been synthesized using a Schiff base formed by the condensation of o-aminobenzoicacid, o-amino phenol. Benzidin and 1,4-phenylenediamine with Benzil, saliasldehyde, and 2-methlycyclo-pentane-1,3-dione in alcohol medium. All the complexes were characterized on the basis of their micro analytical data, elemental analysis, IR, UV–Vis and Mass spectroscopy. The infrared spectrum of the complexes under investigation confirmed the site of chelation, hence, the complexes showed strong absorptions due to $v(C=N)$ and $v(C—O)$. The above absorptions have been shifted to lower frequencies on complexation confirming the chelation positions. Magnetic susceptibility and UV–Vis spectral data suggest that all the complexes are octahedral except the ZrO(II) and VO(II) complexes, which are of square pyramidal geometry respectively. The monomeric and neutral nature of the UO$_2$(II) complexes was confirmed by the analysis. On the other hand the VO(II), ZrO(II) and MoO$_2$(II) species showed the mononuclear and polynuclear metal complexes. Due to the complexity of the oxo-metal complexes under investigation further study have to be involved to confirm the suggested structures. The study may involve the $^1$H, $^{13}$C NMR, thermal analysis and X-ray crystallography.

# *Acknowledgment*

# Chapter(I)

# Introduction

# 1. Introduction

## 1.1. Introduction to Schiff base:

Schiff base ligands and their metal complexes have been extensively studied over past few decades. Of the various classes of Schiff base which can be prepared by condensation of different types of amines and carbonyl compounds salicylaldimines, potential O, N-donors derived from salicylaldehydes and primary amines, are very popular due to diverse chelating ability. Copper (II)- salicylaldimine complexes play important roles in both synthetic and structural research because of their preparative accessibility and structural diversity. In addition to the varied magnetic property and catalytic activity, the metal-Schiff base complexes can also serve as efficient models for the metal containing sites in metallo-proteins and –enzymes[1].

Schiff bases derived from an amine and an aldehyade are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively. Schiff base complexes are important for designing metal complexes related to synthetic and natural oxygen carriers. The complexes make these compounds effective and stereo specific catalysts for oxidation, reduction and hydrolysis and they show biological activity, and other transformations of organic and inorganic chemistry. It is well known that some drugs have higher activity when administered as metal complexes than as free ligands[2].

The Schiff bases are of interest because they have long been known to show photochromism and thermochromism in the solid state. Photochromism is produced by an intra molecular proton transfer associated with a change in the $\pi$-electron configuration. The presence of ortho hydroxyl group, for instance, has been regarded as one of the importance

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elements which favors for the existence of intermolecular hydrogen bonding (O-H...N and O...H-N) and also the tautomerism which accounts for the formation of either enol-imino or keto-amino tautomer [3].

The family of Schiff bases derived from diamines (especially ethylene diamine), phenolic aldehyades and salen has proved to be the source of versatile ligands for many transition metals, including vanadium (IV). Salen complexes of transition metals have been used in solution as biomimetic catalysts for oxygen atom transfer, and as catalysts for enantioselective epoxidation, aziridinations, mediating organic redox reactions and other oxidative processes [4].



W= -CH$_2$-CH$_2$-                x= H,MeO,Br,NO$_2$

W= -CH$_2$-CH$_2$-CH$_2$-         x= H,MeO,Br,NO$_2$

W= -C$_6$H$_4$-                    x= H,MeO,Br
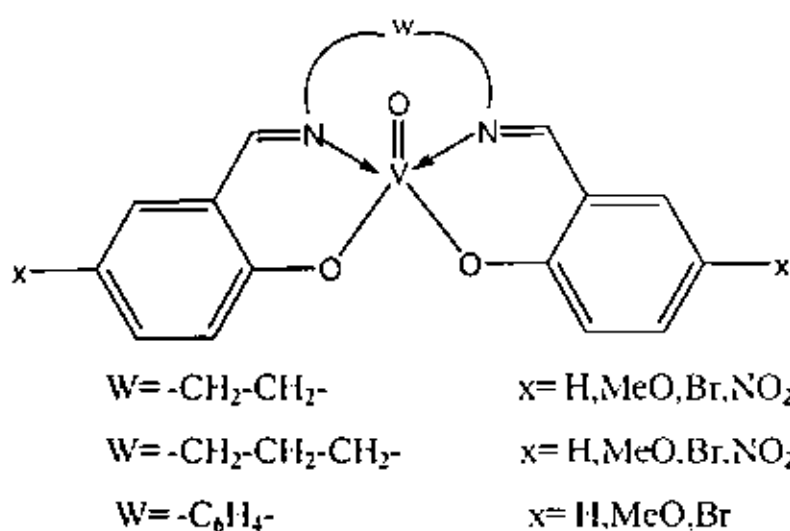
Vanadium complexes are very interesting as model compounds for the clarification of several biochemical processes However, the metal or the ligand may become oxidized. The electrochemical methods also provide highly valuable information regarding catalytic processes since catalytic conversions are frequently accompanied by the change in the structure of the complex and the oxidation state of the metal; however, the electrochemical approaches for these purposes have not been fully explored. Knowledge of

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the electronic and steric effects that control the redox chemistry of these metal complexes may prove to be critical in the design of new catalysts. [4].

Recently investigation of porphyrin has been of increasing interest. In particular, focus was directed to the synthesis and study of well-designed porphyrin derivatives which could act as molecular switches, as well as materials for non-linear optics and solar cells. In these fields, investigation of photo-induced electron and energy transfer of unsymmetrical porphyrin are essential for understanding the mechanism and evaluating the progress. Therefore, unsymmetrical porphyrin, especially tetraphenyl porphyrin derivatives substituted with an expanded $\pi$ conjugated system at the meso-position, are of potential interest. There are a few reports about porphyrin Schiff bases, which are ligands produced by the reaction of porphyrin and aldehydes. In the present study, a novel series of porphyrin Schiff bases was synthesized by a simple Schiff base condensation in refluxing toluene between 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (ATTP) and styryl aldehydes or $p$-halobenzaldehydes. The styryl group was firstly used to expand the $\pi$ system of porphyrin macrocycle at one of the meso-phenyl groups [5].

## 1.2. Literature survey:

Ligands derived from substituted salicylaldimine have played an important part in revealing the preferred coordination geometries of metal complexes. Of particular interest have been those involving copper (II) since they reveal surprising molecular diversity not only in coordination geometry but in more subtle changes in the ligands. Thus complexes with four, five and six donors or with marked tetrahedral «distortions» are accompanied by bond length changes and deviations from expected ligand geometry[6].

Salicylaldehyde and o-amino benzoic acid compounds are capable to form complexes with transition metal ions in the form of Schiff bases. The complexes of Cr(III), Fe(III), Co(II) and Ni(II) ions with a Schiff base derived from 4–dimethylamino benzaldehyde and primary amines have been prepared and investigated using different chemical techniques, such as; elemental analysis, molar conductance measurements, infrared and electronic spectra. The obtained chemical analysis data showed the formation of 1:1 [M: L] ratio and a square planar geometry was suggested for Co (II) and Ni (II) complexes and an octahedral structure for Cr (III) and Fe (III) complexes[7].

There has been considerable current interest in the chemistry of ruthenium, primarily because of the fascinating electron-transfer, photochemical and catalytic properties exhibited by the complexes of this metal. As the coordination environment around the central metal ion directs properties of the complexes, complexation of ruthenium by ligands of different types has been of significant importance. Ruthenium Schiff base complexes, particularly those containing oxygen and nitrogen as donor atoms were found to be very efficient catalysts in the oxidation of alcohols using N-methylmorpholine-N-oxide as co-oxidant[8].

Schiff base complexes of transition-metal ions continue to be of wide interest with respect to studies of long-range magnetic interactions through extended bridging ligands both in inorganic and biological materials. Also, it has been studied and shown that two paramagnetic centers could interact through molecular bridging even if these centers were relatively far away (>11Å) from each other provided that the metal atoms and the bridging ligand have the proper symmetry. The terephthalato dianion being a potential ambient ligand seems to be appropriate bridging unit to design such magnetic systems with a separation >11 Å between the two magnetic centers[9].

It is the purpose of this review to consider the coordination chemistry of tetra imine Schiff base macrocycles which result from [2+2] condensation reactions of heterocyclic dicarbonyl containing species with 1, n-diamines. Serious exploitation of tetra imine Schiff base macrocycles as binucleating ligands commenced in 1970 with Robson's work on the template synthesis of transition metal complexes of macrocycles derived from the condensation of 2,6-diformyl-4-methylphenol with 1,3-diaxninopropane . The subsequent exploitation of such phenol-containing systems has been extensive and the subject of review. It was not possible to isolate metal-free macrocycles from the phenolic systems. that metal-free macrocycles were available from the condensations of 3, 4-di-bromothiophene-2,5-dicarbaldehyde with a range of primary diamines. The intense colour and amorphous nature of these materials led to the suggestion that they were likely to be polymers rather than discrete tetra imine Schiff base macrocycles[10].

Schiff-base ligands derived from salicylaldehyde and chiral amines have been widely applied in enantioselective cyclopropanation of styrenes, asymmetric aziridination of olefins, enantioselective epoxidation,

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enantioselective ring opening of epoxides, borohydride reduction of aromatic ketones, and asymmetric oxidation of methyl phenyl sulfide, enantioselective oxidation of silyl enol and trimethylsilylcyanation of benzaldehydes. In particular the Merck Company has successfully developed a process for the industrial manufacture of antibacterial drug Cilastatin using chiral copper (II) Schiff-base complexes derived from salicylaldehyde and chiral amine. However, so far there have been few reports about the synthesis and application of Schiff-base ligands derived from 2-hydroxyacetophenone and chiral amines [11].
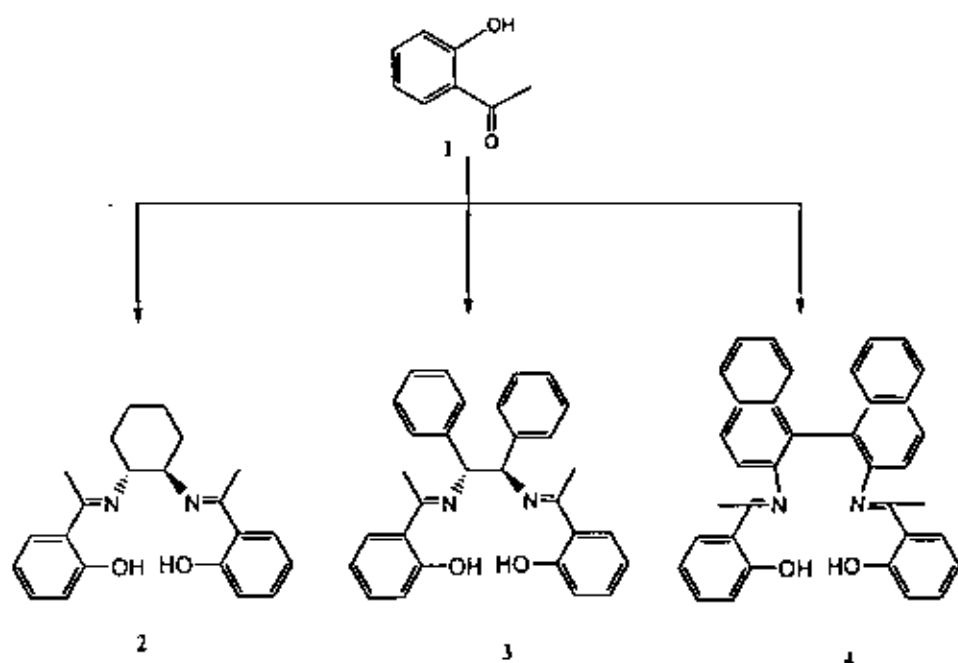


In order to investigate the electronic, steric and geometric effect of a methyl group on an imine carbon on asymmetric catalytic reactions, 2-hydroxyacetophenone (1) was chosen to synthesize Schiff-base ligands 2, 3, 4 by the condensation with chiral diamines such as 1,2-diaminocyclohexane, 1,2-diphenylethylenediamine and 2,2'-diamino-1,1'-binaphthalene [11].

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Recent interest in the synthesis and characterization of unsymmetrical tetradentate Schiff base complexes has been prompted by the belief that systematic investigation of these complexes may shed light on the nature of complexes of biological interest. In these compounds, the metal is in an unsymmetrical ligand environment. Many hydrazine derivatives have been reported to inhibit the numerous reactions catalyzed by pyridoxal 5-phosphate as coenzyme. The aminooxidase enzyme requires such a coenzyme besides copper(II) ions for catalytic activity. At this point, it seems necessary to investigate the reaction of derivative of hydrazine with divalent metal ions, especially Cu(II), to gain information concerning the coordination chemistry of these molecules in the highly unsymmetrical environment[12].

Enantiopure epoxides are highly valuable chiral synthons useful for the synthesis of various biologically active molecules. For the preparation of chiral epoxides, the transition metal-catalyzed enantioselective epoxidation of different organic substrates is of the utmost importance and has been widely studied over the past decades. The generally good catalytic activities of several molybdenum (VI)-oxo complexes in oxidation reactions make this type of complexes in principle promising candidates for asymmetric catalysis by using chiral ligands. 2-Pyridyl alcohols and phosphino alcohols have been reported to induce of $20 - 40\%$ for functionalized olefins when coordinated to dioxo or peroxo molybdenum (VI) fragments[13].

In principle, the central transition metal atoms of different soft and hard Lewis acidity usually need to be satisfied in the most suitable fashion. Hence heterodentate ligands have the greatest possibility to form polynuclear complexes according to many available reports for the preparation of model copper complexes containing mimic copper

metalloproteins such as hemocyanine and tyrosinase. In order to elucidate the factors that determine the function and activation of metalloproteins, several studies have focused on understanding the correlation between the active site of metalloproteins with their metallocenters. A number of dinuclear complexes from various type ligand systems have been prepared and examined in terms of their oxygen uptake or redox processes of oxygen. In addition, dinucleating macrocycles have been synthesized by combining chelating acyclic subunits or by functionalizing a macrocyclic structure by attaching side chains. It has been reported that the derivatized macrocyclic systems exhibited the characteristics of mono- and dinuclear complexes such as catalysis and molecular recognition. Furthermore, various mononuclear metal complexes from Schiff base ligands modified with benzo-15-crown-5 have been shown to possess enzyme-like activities[14].

Schiff bases from 2-hydroxy-1-naphthaldehyde have often been used as chelating ligands in the field of coordination chemistry. Recently, liquid crystals researchers have made a significant revelation that the introduction of a lateral polar hydroxyl group will enhance the molecular polarizability as well as stabilize the liquid crystalline compounds. One of the typical examples is the study on the effect of a lateral hydroxyl group on mesomorphism of azobenzene derivatives. Transition metal complexes with tetradentate Schiff-base ligands have been extensively investigated as catalysts for a number of organic redox reactions and electrochemical reduction processes. Cyclic voltammetry has been a useful tool to investigate the mechanisms of catalysis by Schiff-base metal complexes as well as to study the structure-reactivity relationships in these compounds[15].

Schiff base ligands which are able to form binuclear transition metal complexes have been of interest for many years, partly because of the

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relation between structures and magnetic exchange effects in homo- and hetero-binuclear metal complexes and partly because of the use of such complexes to mimic aspects of bimetallic bio sites in various proteins and enzymes. The complexes thus play an important role in developing the coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures. Although a large number of unsymmetric doubly-bridged binuclear copper (II) complexes have been extensively studied, relatively few structures of unsymmetric doubly bridged binuclear nickel(II) complexes have been reported [16].

It is well known that the preparation of new ligands is perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity. Changes in the electronic, steric, and geometric properties of the ligand alter the orbitals at the metal center and thus affect its properties. In asymmetric catalyst systems, small changes in the donating ability of the ligand or the size of its substituents can have a dramatic effect a catalyst's efficiency and enantioselectivity. The nitro group is a strong electron withdrawing group and, due to its steric effects, has played an important role in affecting the reactivities and enantioselectivities in asymmetric cyclopropanation and allylic alkylation reactions. have investigated the actions of various chiral benzaldehyde Schiff base ligands in the asymmetric azirination of olefin. To the best of our knowledge, however, nitrobenzaldehyde Schiff base ligands have never been applied in an asymmetric catalytic system, although some of them have been mentioned in recent publications [17].

a-c

2a-c

2a R=o-NO$_2$
2b R=m-NO$_2$
2c R=p-NO$_2$
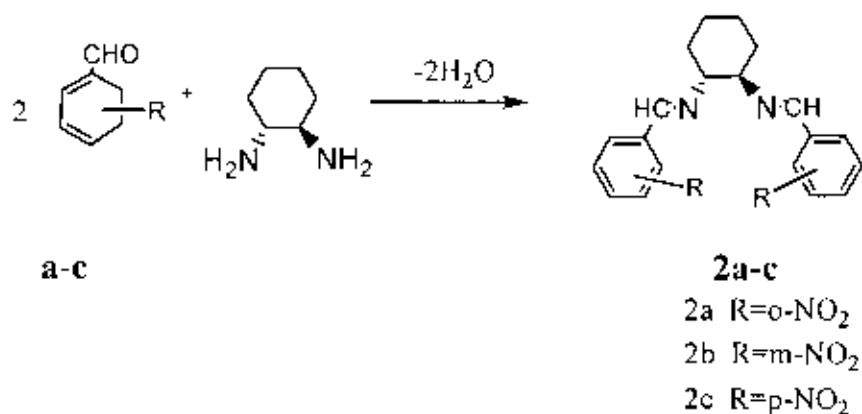
Thus, in order to investigate their catalytic properties, *ortho*, *meta*, and *para*-NO$_2$ substituted benzaldehydes **1a-c** were used to prepare the Schiff base ligands **2a-c** by reaction with chiral 1,2-diaminecyclohexane[17].

The numerous molybdenum (VI) Schiff base complexes have been extensively investigated for over twenty years. Owing to their importance in the domains of stereochemistry, structural and analytical chemistry and as model systems for the interaction of organic substrates with catalytic oxide surfaces, some of them are also interesting due to their ability to oxidize thiols, hydrazines, polyketones and tertiary phosphines. Their oxygen atom transfer properties play a significant role in investigating the functioning mechanism of molybdenum oxotransferase. Although a number of literature reports deal with the mononuclear dioxomolybdenum(VI) complexes of bi-, tri- or tetradentate Schiff base ligands, complexes containing monodentately coordinated Schiff base derivatives as zwitterionic ligands are extremely rare[18].

Molybdenum as a trace element plays an important role in metabolic processes. Complexes of molybdenum (V) and molybdenum (VI) with cysteine, histidine and organic sulphur compounds are of interest as models for molybdenum-containing enzymes. These enzymes are known to catalyse

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a number of important biological oxotransfer reactions where the valence of molybdenum alternates between molybdenum (VI) and molybdenum (IV) states in reactions with substrates and subsequent reactivation. N-alkylphenothiazines (NAP) are versatile anticholinergic, antihistamine and antiemetic compounds. The study of metal–phenothiazine complexes has gained much importance in recent years due to their potential pharmacological activities. The possible use of metal–phenothiazine complexes as fungicides and considerable increase in their fungicidal activity by complexation of phenothiazines with copper (II), dioxouranium (VI), yttrium (III) and lanthanides (III) have been reported [19].

Molybdenum has been found to be a very important element in biological systems. Apart from the nitrogenases in where a molybdenum atom can be a component of the multinuclear active sites, there are a number of mononuclear molybdenum enzymes that are often referred to as oxomolybdenum enzymes. The latter can be divided into two groups: Enzymes from the first group catalyze the oxidative hydroxylation of aldehyades and aromatic heterocycles in reactions that necessarily involve the cleavage of a C-H bond. Mononuclear enzymes from the second group catalyze proper oxygen atom transfer reactions to or from a n available electron lone pair of substrates. In order to mimic the biological systems, a number of dioxomolybdenum complexes have been synthesized and characterized the oxygen atom transfer ability of dioxomolybdenum complexes to some substrates is related to the liability of (Mo=O) bonding [20].

Vanadium is a physiologically important trace element that is found in both anionic and cationic forms with oxidation states ranging from −1 to +5 (I–V). The cationic form of vanadium complexes with oxidation state +4

(IV) have been shown to function as modulators of cellular redox potential, regulate cellular phosphorylation events, and exert pleiotropic effects in multiple biological systems. Besides the ability of the vanadium metal to assume various oxidation states, its coordination chemistry also plays a key role in its interactions with various biomolecules. In particular, organometallic complexes of vanadium(IV) linked to *bis*(cycopentadienyl) moieties or vanadocenes exhibit antitumor properties both *in vitro* and *in vivo*. In a systematic effort aimed at identifying new cytotoxic agents with potent activity against cancer cells, them synthesized 15 oxovanadium compounds and examined their cytotoxicity against a panel of 14 human cancer cell lines. The oxovanadium co mpounds included *mono* and *bis* ancillary ligands of phen and bipy substituted with dimethyl, chloro, and nitro groups and acph [VO(Br, OH-acph)$_2$]. The *mono*-chelated [VO(Me$_2$-phen), and *bis*-chelated-1,10-phenantroline [VO(Me$_2$-phen)$_2$, complexes were the most potent oxovanadium compounds and killed target cancer cells at low micromolar concentrations. Notably, the presence of two phenanthroline rings and their dimethyl substitution were essential for the anticancer activity of both [VO(Me$_2$-phen)$_2$] and [VO(Me$_2$-phen)] because unsubstituted *bis*-chelated and *mono*-chelated phen oxovanadium(IV)complexes [VO(phen), , or VO(phen)$_2$, were less active. Addition of a chloro or nitro group to the phen complexes did not significantly improve the cytotoxic activity of the unsubstituted oxovanadium(IV) complexes. Irrespective of the ligands, *bis*-chelated phenanthroline containing compounds showed better activity than the *mono*-chelated phenanthroline containing complexes. The marked differences in the cytotoxic activity of oxovanadium(IV) complexes containing different heterocyclic ancillary ligands suggest that the cytotoxic activity of these

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compounds is determined by the identity of the five-member bidentate ligands, as well as the nature of the substitutents on the heterocyclic aromatic rings[21].

During the last years, a great deal of work has been devoted to the development of new compounds or ligands to increase the natural rate of elimination of uranium from the human body and to reduce the fixation within target organs (kidney, bone). The principle of chelating agent efficiency is that the agent combines with the metal to form a stable complex that can be easily excreted and thus reduces the radiation doses delivered to sensitive cells or organs and the risk of delayed radiation effects, such as cancer. Soluble uranyl ion ($UO_2^{2+}$) or uranium (VI) is known to be a kidney poison. It also accumulates in bone where a high dose of radiation of some uranium isotopes ($^{234}U$, $^{233}U$) can induce bone cancer. Although numerous studies have been carried out since the 1940s, ligands that efficiently and stably bind $UO_2^{2+}$ at pH corresponding to biological barriers, promote its excretion, and reduce significantly deposits in kidneys and bones remain to be discovered. Some promising ligands were synthesized and tested such as 5-LI(Me-3,2-HOPO) (hydroxypyridinoate function), which shows significant decrease in the kidney, or 5-LICAM(S) (catecholate function), which induces significant decrease in the bone: a combination of two ligands is recommended. Because their toxicity is not well defined, the only used and recommended treatment, up to now, is intravenous administration of bicarbonate. Bis-phosphonates are known to reduce the rate of bone turnover, that is, the rate of removal and replacement of bone tissue. Because phosphonates are hardly biodegradable, chemical speciation based on numerous chemical equilibrium data are of great importance for such applications as environmental fields, waste management, agriculture, scale

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inhibition, magnetic resonance imaging, behavior of radiopharmaceuticals in blood plasma, or decorporation [22].

Schiff base complexes of uranium have aroused interest on account of their stability, high coordination numbers and usefulness in selective chemical separations. Uranyl complexes of ligands with O and N donors have been extensively reviewed and quite a few complexes of hydrazone Schiff bases have been reported. As part of systematic studies on the coordination chemistry of the early actinide elements [23].

Actinide complexes are of considerable interest due to their importance in the environmental migration of the high-level nuclear wastes. Experimental and theoretical studies of geologically relevant actinide complexes are central to the understanding of the migration of actinides and sorption complexes formed by actinides in geochemical and biological environments. It is well known that the migrating actinide in the natural ground water can be sorbed onto geological interfaces, plants and bacteria and the sorption process plays a major role in the distribution and migration of actinides in the environment. Under most environmental conditions, U will be present as the Trans dioxo (uranyl) cation, $UO_2$ [24].

## 1.3. Biological activity:

The synthetic versatility of isatin (salicylaldehydes and β-hydrazone) has led to the extensive use of this compound in organic synthesis, which stemmed from the interest in the biological and pharmacological properties of its derivatives. It is also known that mono- and bishydrazones find wide application in medicine as active physiological preparations, due to their antibacterial, tuberculostatic, fungicidal properties, as well as activities against certain types of cancersand microorganisms. Benzylidene derivatives have also found wide application, not only because of their strong activity against some micoorganisms. but also because they can act as free radical scavengers. Many coordinaton compounds of transition metals with Schiff bases show greater activity than the ligands alone [25].

Generally, the chelating ligands are poly functional molecules which can encage heavy metals in an organic sphere. Many types of Schiff base ligands are known and the properties of their metal chelates have been investigated. Acyclic ligands containing nitrogen, oxygen and sulphur donor atoms in their structures can act as effective chelating agents for transition and non-transition metal ions. The importance of the coordination compounds in biological structures, the increasing proportion of the application and utilization of these compounds as agents has given rise to intensification into the investigations of the complexes, especially "vic-dioxime compounds" [26].

Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups and it is multiplied many fold when the ligands have biological importance [27].

Selectivity of metal complexation by ligands is a chemical feature that has long been valued by chemists and one which has many important technological applications. Examples include metal ore processing, analytical and environmental applications, and pharmaceuticals. The standard approach in the design of metal ion selective complexing agents relies on two basic tenets: (1) the construction of a ligand cavity of appropriate size consisting of convergent donor groups; and (2) a match of the metal ion and ligand electronic properties summarized by the principle of hard and soft acids and bases. Both of these considerations essentially treat the metal ion as a hard sphere whose properties are defined by a fixed charge and radius. Metal oxo cations such as $VO^{2+}$, $TcO^{3+}$, and $UO_2^{2+}$ have pronounced three-dimensional anisotropy that in principle allows for a kind of molecular recognition approach in their selective complexation. The coordination chemistry and ligand preparation for these metal ions have usually treated the metal oxo group as an occupied coordination site of the metal [28].

Schiff base of 4-aminoantipyrine and its complexes have a variety of applications in biological, clinical, analytical and pharmacological areas. Studies of a new kind of chemotherapeutic Schiff bases are now attracting the attention of biochemists. Earlier work reported that some drugs showed increased activity, when administered as metal complexes rather than as organic compounds. Deoxyribonucleic acid (DNA) is the primary target molecule for most anticancer and antiviral therapies according to cell biologists. Investigations on the interaction of DNA with small molecules are important in the design of new types of pharmaceutical molecules. Since the chemical nuclease activity of transition metal complexes was discovered in the 1980s, studying the interaction model and the mechanism of transition

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metal complexes with DNA, and exploring the application of metal complexes in antineoplastic medication, molecular biology and bioengineering have become hotspots in recent years. Some kind of metal complexes interacted with DNA could induce the breakage of DNA strands by appropriate methods. In the case of cancer genes, after DNA strands are cleaved, the DNA double strands break. The replication ability of cancer gene is destroyed. Copper complex could cleave DNA in the presence of ascorbate or hydroquinone. It was suggested that the reductive capability of reductants had a critical influence on DNA cleavage. The coordinating property of 4-aminoantipyrine ligand has been modified to give a flexible ligand system, formed by condensation with a variety of reagents like aldehydes, ketones thiosemicarbazides and carbazides, etc [29].

# Chapter (II)

# Experimental

## 2. Experimental

### 2.1. Materials and reagents

All materials and reagents used in this study were laboratory pure chemical. They include, Benzil, Salicylaldehyde, 2-methlycyclopentane-1, 3-dione, 1,4-phenylenediamine, Benzidin, o-aminobenzoicacid and o-amino phenol. The solvent used are ethanol, acetone, dimethylformamide (DMF), chloroform ($CHCl_3$), distilled water and diethyl ether (40 -60C°). The metal used are Ammonium-Meta-vanadate [$NH_4VO_3$], Sodium Molebdate dihydrate [$Na_2MoO_4.2H_2O$], Zirconium oxiy chloride Octahydrate [$ZrOCL_2.8H_2O$], and Uranyl Nitrate hexahydrate [$UO_2(NO_3)_2.6H_2O$].

| Materials and reagents | M.Wt | The company |
|---|---|---|
| Benzil | 210.23 | Aldrsch |
| Salicylaldehyde | 122.12 | Riedel-Dehaenag |
| 2-methlycyclopentane-1, 3-dione | 112.13 | Sigma Chemical CO. Steinheim, Germany |
| Benzidin | 184.24 | FlukaAG,chem..Fabrik CH-9470 Buchs. |
| 1,4-phenylenediamine | 108.14 | Aldrsch |
| o-aminobenzoicacid | 137.14 | Meark |
| o-amino phenol | 109.13 | Riedel-Dehaenag |
| Ethanol | 46.07 | Carblo erba regenti |
| Chloroform | 119.38 | Ricdel-dehaen |
| Dimethylformamide | 73.09 | Carblo erba regenti |
| Zirconium oxiy chloride.octahedrite $ZrOCL_2.8H_2O$ | 322.25 | Koch-Liht Laboratories LTD England |
| Uranyl Nitrate. hexahedrite $UO_2(NO_3)_2.6H_2O$ | 502.20 | Koch-Liht Laboratories LTD England |
| Ammonium meta vanadate $NH_4VO_3$ | 116.96 | Riedel-Dehaenag |
| Sodium molybdate $Na_2MoO_4.2H_2O$ | 241.96 | Riedel-Dehaenag |

## 2.2. The synthesis of the Schiff base ligands

An ethanolic solution (20ml) of amine was refluxed with ketone or Aldehyde for about 12hrs. The reaction molar ratio was 1:2 or 1:1 (amine to ketone or aldehyde). The volume of the solution was reduced to one third. The precipitate which formed was filtered, washed, recrystallized from ethanol and dried in vacuum. This method was based on the previous methods reported for the preparation Schiff base ligands [31].

For example:

Synthesis of $(L^1 = C_{40}H_{28}N_2O_2)$ ligand

An ethanolic solution of Benzidin (1.84g, 0.01mol) in (20ml) alcohol was refluxed with Benzil (4.2g, 0.02mol) for about 12hrs. The volume of the solution was reduced to one third. The precipitate which formed was filtered, washed, recrystallized from ethanol and dried in vacuum, other ligands prepared by the same method.

## 2.3. The synthesis of metal Complexes:

The metal complexes of the Schiff bases, $L^1$ to $H_2L^6$, were prepared by the addition of a hot solution (60 C°) of the appropriate metal ion $M^{+2}$ (M= $VO^{+2}$, $ZrO^{+2}$, $UO_2^{+2}$, $MoO_2^{+2}$) (1 m mol) in an ethanol-water mixture (1:1, 25ml) to hot solution (60C°) of two equivalents of Schiff bases in the same solvent. The resulting mixture was stirred under reflux for 1 h whereupon the complexes precipitated. were collected by filtration, washed with a 1:1 ethanol-water mixture and diethyl ether and dried in vacuum [32].

For example:

Synthesis of $(VO\ L^1)_2$ .$5H_2O$ complexes

The metal complex $(VO\ L^1)_2$ .$5H_2O$ was prepared by the addition of a hot solution (60C°) of the appropriate Ammonium-Meta-vanadat (0.12g,0.001 mol) in an ethanol-water mixture (1:1, 25ml), to hot solution (60 C°) of the Schiff base $H_2L^1$(0.56g,0.001 mol) in 25ml of the same

solvent. The resulting mixture was stirred under reflux for 1 h, whereupon the complex precipitated. They was collected by filtration, washed with a 1:1 ethanol-water mixture and diethyl ether and dried in vacuum. other complexes prepared by the same method.

## 2.4. The studies on ligands and its metal Complexes

## 2.4.1. Physical techniques measurements and spectroscopic

### 2.4.1.1. Elemental analysis

All the Schiff base ligands and their complexes under investigation, were subjected to (C, H and N) elemental analysis which performed at Micro Analytical Center Faculty of Science-Cairo University (Egypt) and laboratories of RASCO company Libya.

### 2.4.1.2. Mass spectra

Mass spectra were recorded with a Shimad 24 GCMS-QP 1000EX, at micro analytical center University of Cairo.

### 2.4.1.3. Melting point

The melting point of ligands and their complexes were measured in capillary tubes Philip Haris, Shenston-England, serial NO.B/A-211, at chemistry department. Faculty of Science, Al-Tahadi University (Siret).

### 2.4.1.4. Magnetic moment measurements

The magnetic moment measurements of complexes under investigation were measured by using a magnetic susceptibility balance Sherwood Scientific England, at Micro Analytical Center, Cairo University, and Giza-Egypt.

### 2.4.1.5 Infrared spectra

The IR spectra of the Schiff base ligands and their complexes under investigation were recorded using a BRUKER IFS-25 FT-IR spectrophotometer using KBr at the region 400-4000cm$^{-1}$ at Advanced Laboratory for Chemical Analysis, Al Fateh University Tripoli.

### 2.4.1.6 Electronic spectra

In $10^{-3}$ M solution of Schiff base ligands and their complexes were prepared by dissolving the required accurate weight of the compound in 25 cm$^3$ of DMF or CHCl$_3$. The spectra of the obtained solutions were scanned within the visible and ultraviolet (200-900nm) using measured using a 640S UV-vis spectrophotometer using 1cm matched silica cells, at Chemistry Department, Faculty of science, University of Garyounis (UOG).

# Chapter (III)

# Results and discussion

# 3. Results and discussion

## 3.1. The studies of the Schiff base ligands and their complexes

The Schiff base ligands under investigation were formed from the condensation of amine and some carbonyl molecules. The condensation of Benzidin and Benzil gave $L^1 - [C_{40}H_{28}N_2O_2]$, o-aminophenol and Salicylaldehyde gave $H_2L^2 - [C_{13}H_{11}NO_2]$, p-amino aniline and Benzil gave $L^3 = [C_{34}H_{24}N_2O_2]$, p-amino aniline and Salicylaldehyde gave $H_2L^4 - [C_{20}H_{16}N_2O_2]$, o-aminobenzoic acid and 2-methlycyclopentane-1,3-dione gave $H_2L^5 - [C_{20}H_{16}N_2O_4]$ and finally, o-aminobenzoic acid and Salicylaldehyde gave $H_2L^6 - [C_{14}H_{11}NO_3]$. The complexes were prepared by the reaction of suitable ligands with metal salt. The compounds were subjected to elemental analysis, magnetic susceptibility, Infrared, Mass spectroscopy and Electronic spectroscopy to confirm their structures

### 3.1.1 The elemental analysis of the compounds

Elemental analysis namely, C%, H%, and N% results of the ligands and their complexes are given in Table. (1). The results are in good agreements for the compounds and correlated well with the calculated ones.

### 3.1.2. The infrared spectra of the compounds

The infrared spectra data are given in Table. (2) and Fig. 1-22. The assignments of the infrared bands of the Schiff base and their complexes are in good agreement with the previously reported results[13, 21, 32, 34-40].

The ligands showed the following characteristic bands. The bands ranging at 3350-3396 cm$^{-1}$ are attributed to the OH group. A bands ranging at 1588-1631 cm$^{-1}$ are due to C=N vibration. Meanwhile, the bands ranging at 1662-1683 cm$^{-1}$ are assigned to the C=O stretching frequency. The C—O stretching absorption bands are ranging at range 1211-1366 cm$^{-1}$.

The IR spectrum of Schiff base ligand ($L^1$) derived from Benzidin and Benzil, showed medium broad band at 3377 cm$^{-1}$, which is attributed to OH group. The intense band at 1286 cm$^{-1}$ is assigned to C—O stretching mode. The band at 1619 cm$^{-1}$ is assigned to C=N azomethine group stretching. Finally, the weak medium band at 1671 cm$^{-1}$ is attributed to C=O group.

The Infrared spectra of Schiff base ligand ($H_2L^2$) derived from o-aminophenol and Salicylaldehyde, showed a strong absorption band at 1631 cm$^{-1}$ which is assigned to the C=N azomethine group. The intense band at 1274 cm$^{-1}$ is assigned to C—O stretching mode. The weak band at 3380 cm$^{-1}$ is due to hydrogen bonding of OH group.

The Infrared spectra of Schiff base ligand ($L^3$) derived from p-amino aniline and Benzil , The imine Structure of this Ligand is clearly indicated by the intense and sharp band at 1593 cm$^{-1}$ which is assigned to the C=N group. Moreover two bands at 1662 cm$^{-1}$ and 1211cm$^{-1}$ are assigned to the bands of C=O and C—O respectively.

The IR spectrum of Schiff base ligand ($H_2L^4$) derived from p-amino aniline and Salicylaldehyde, is exhibited a weak absorption of OH near 3396 cm$^{-1}$ which due to the hydrogen bands. The band at 1280 cm$^{-1}$ in IR spectrum of the ligand is attributed to the phenolic C—O stretching vibration according to the assignment. Finally, the ligand showed absorption bond at 1609 cm$^{-1}$ which is assigned to the C=N azomethine group.

The infrared spectrum of Schiff base ligand ($H_2L^5$) derived from o-amino Benzoic acid, showed a medium absorption band at 1588 cm$^{-1}$ which is assigned to the C=N azomethine group. The intense band at 1285 cm$^{-1}$ present in IR spectrum of the Schiff base ligand is assigned to C—O stretching mode. The band at 1683 cm$^{-1}$ is attributed to the carbonyl group.

The ligand exhibited a weak band at the region 3363 cm$^{-1}$ which assigned to the OH group.

The Infrared spectrum of Schiff base ligand ($H_2L^6$) derived from o-amino Benzoic acid and Salicylaldehyde, imine structure of this ligand is clearly indicated by the intense and sharp strong band of C=N which is located at 1624 cm$^{-1}$. The intense band at 1366 cm$^{-1}$ present in IR spectrum of the Schiff base ligand is assigned to C—O stretching mode. Finally, the ligand showed medium absorption band at 3350 cm$^{-1}$ which is assigned to the OH group.

The IR spectra of the complexes showed the following characteristic features. On complexation the C=N bands at 1585-1622 cm$^{-1}$ are shifted to lower frequencies as expected, in contrast, some other complexes their bands are shifted to a higher frequencies in accordance with previously reported behavior [34]. The bands ranging at 1200-1396 cm$^{-1}$ are assigned to C—O stretching. The bands ranging at 3225 - 3454 cm$^{-1}$ are attributed to O-H stretching. The C=O stretching absorptions are seen at 1652-1671cm$^{-1}$. An observation of new bands ranging at 486-708 cm$^{-1}$ and 414 - 548 cm$^{-1}$ those are assigned to M—O and M—N stretching which are not observed in the spectra of the ligands. Finally M=O stretching frequencies are ranging at 926, 895-1000, 891-932 and 905-925 cm$^{-1}$ which are assigned for zirconyl, vandyl, molybdyl and uranyl respectively.

The infrared spectrum of $ZrO(H_2L^2)_2.3H_2O$ Complex showed a strong band at 1606 cm$^{-1}$ which is assigned to the azomethine group C=N again this band is shifted to lower frequency by 25 cm$^{-1}$ in comparison with free ligand. This indicates that the chelating has been occurred through the nitrogen of azomethine group. The complex exhibited broad band at 3425 cm$^{-1}$ which is assigned to OH stretching vibration. The complex is exhibited a band at 1258 cm$^{-1}$ which is due to the C—O stretching vibration, this vibration was shifted to higher frequency in comparison to the free ligand.

This shift is due to the new evolvement in the chelating to the Zr(II) ion. The new bands at 604 and 548 cm$^{-1}$ regions are attributed to Zr—O and Zr—N stretching vibration respectively. Finally, Zr=O band is appeared at 926 cm$^{-1}$.

The IR spectrum of VO $(H_2L^2)_2.2H_2O$ complex exhibited a strong band at 1606 cm$^{-1}$ which has been assigned to C=N group. The same band was observed at 1631cm$^{-1}$ for the free ligand. The complex is exhibited a band at 3404 cm$^{-1}$ which attributed to the OH group of the water molecules associated with complex formation. The C—O stretching absorption is observed at 1234cm$^{-1}$ and it shifted to a lower frequency in complex. The complex showed new bands which are not observed in the free ligand spectra. The new bands are observed at 662cm$^{-1}$ and 475cm$^{-1}$ and they are attributed to the present of M—O and M—N vibrations respectively. Finally, V=O band is observed at 985 cm$^{-1}$.

The infrared spectrum of Mo $(L^3)_2.2H_2O$ complex exhibited new strong absorption at 1585 cm$^{-1}$ which is assigned to C=N band. This band is shifted to lower frequency compared to that of the free Schiff base ligand. The C—O frequencies at 1211 cm$^{-1}$ is shifted to lower value as result of coordination. The shifts in the above bands confirmed the chelation site between the metal and the ligand. The spectra of he complex showed sharp band at 3370 cm$^{-1}$ which suggested that the water is coordinated to the central metal ion. The spectra of complex showed a weak band at 1652 cm$^{-1}$ which is attributed to C=O group, again this band is shifted to lower frequency. The new bands are observed at 600cm$^{-1}$ and 480 cm$^{-1}$ and they are attributed to the present of M—O and M—N vibrations respectively. Finally, Mo=O band is observed at 932 cm$^{-1}$.

The infrared spectrum of UO$_2$ $(H_2L^2)_2.3H_2O$ complex Showed a peak at 1606 cm$^{-1}$ which is assigned to the C=N stretching frequency. This band is shifted to lower frequency by 25 cm$^{-1}$ compared to the free ligand which

indicated that chelating take place through the nitrogen atom of azomethine group. The spectra of complex exhibited a band at 1295 $cm^{-1}$ which is attributed to the C—O vibration. This vibration is shifted to higher frequency which is suggesting the formation of C—O—M band. The broad band at 3384 $cm^{-1}$ is attributed to the presence of OH group of water molecules. The coordination mode of ligand is further supported by the appearance of new bands at 576 and 480 $cm^{-1}$ which are indicating the formation of M—O and M—N bands respectively. Finally, U=O band is observed at 905 $cm^{-1}$.

### 3.1.3 Electronic spectra and magnetic measurements of ligands and their complexes.

The electronic spectra of the ligands and their complexes are given in Table. (3).The electronic spectra are measured in $10^{-3}M$ DMF or Chloroform. The ligands spectra showed bands in 38022-49571$cm^{-1}$ region which are attributed to $\pi \_ \pi^*$ transition. These transitions are shifted to the lower frequencies on coordination to the metals.

The electronic spectra of the complexes in $10^{-3}$ M DMF or chloroform showed the d-d transition at 430-845nm region. The complexes showed several bands at 290-368nm region which are assigned to the $\pi \_ \pi^*$ transition of the aromatic ring or azomethine. The magnetic moment values, $\mu_{eff}$ measured for all complexes at room temperature 298 K. The recorded data of the magnetic moment are given in Table. 3. For example, the electronic spectra of the vanadyl complex $(VOL^1)_2.5H_2O$ exhibits bands at 11834 $cm^{-1}$ and 22471 $cm^{-1}$ which are assigned to $^2B_2 \rightarrow$ $^1A_1$ and $^2B_{2(P)} \rightarrow$ E transition respectively. The band at 27173 $cm^{-1}$ is assigned to the $\pi \_ \pi^*$ transition of the aromatic ring or azomethine group which are inconformity with the previously reported results. These transitions, as well as the measured value of magnetic moment 1.2 B.M of

the above complex suggest the square pyramidal stereochemistry of the compound[30, 41].

The electronic absorption spectra of the $VO(H_2L^2)_2.2H_2O$ complex exhibited three bands at 13157 cm$^{-1}$, 20833 cm$^{-1}$ and 31250 cm$^{-1}$ which are assigned to $^2B_2 \rightarrow {}^1A_1$, $^2B_{2(P)} \rightarrow E$ and $\pi \rightarrow \pi^*$ transitions respectively. These transitions as well as the measured value of magnetic moment 1.65 B.M support the square pyramidal stereochemistry of the compound.

The electronic spectra of the vanadyl complex $(VOH_2L^4)_2.2H_2O$ is showed a bands at 13351cm$^{-1}$ and 23255cm$^{-1}$ which are assigned to $^2B_2 \rightarrow {}^1A_1$ and $^2B_{2(P)} \rightarrow E$ transition respectively. The band at 32786 cm$^{-1}$ is assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic ring or azomethine group which agreeable with the reported results. These transitions, as well as the measured value of magnetic moment 0.8 B.M suggest the square pyramidal stereochemistry of the compound.

The electronic absorption spectra of the $(VOH_2L^5)_2.6H_2O$ complex is exhibited three bands at 12738 cm$^{-1}$, 19607 cm$^{-1}$ and 34482 cm$^{-1}$ which are assigned $^2B_2 \rightarrow {}^1A_1$, $^2B_{2(P)} \rightarrow E$ and $\pi \rightarrow \pi^*$ transitions respectively. This transition as well as the measured value of magnetic moment 1.76 B.M suggested the square pyramidal stereochemistry of the compound. In contrast, and based upon the magnetic moment values the zirconyl complexes are diamagnetic and exhibited a square pyramidal structures, the uranyl and molebdyl complexes are diamagnetic and appeared to possessed an octahedral structures

## 3.1.4 The mass spectra of the Schiff base ligands

The mass spectroscopy technique is proven to be very useful in structural identification based on the fragmentation pattern of the mother molecule. The ligands fragmentation patterns are given in Schemes1-6 and Fig. 23-28. The compound peaks are in good agreements with their

empirical formula as indicated from elemental analyses measurements. The other peaks represent the fragments of the ligands.

The mass spectrum of $(L^1)$ showed the following fragmentation scheme the molecular ion peak at m/z 568 is corresponding to the molecular weight of $(C_{40}H_{28}N_2O_2)$. The peak at m/z 463 which is the base peak is assigned to $(C_{33}H_{24}N_2O)^+$ fragment. A peak at m/z 255 is due to $(C_{19}H_{15}N)^+$ fragment. A peak at m/z 179 is assigned to $(C_{13}H_{11}N)^+$ fragment. A peak at m/z 152 is due to $(C_{12}H_{10})^+$ fragment.

The mass spectrum of $(H_2L^2)$ showed the following fragmentation scheme 2. The molecular ion peak at m/z 213 is related to the molecular weight of $(C_{13}H_{11}NO_2)$. The peak at m/z 212 which is the base peak and is assigned to $(C_{13}H_{10}NO_2)^+$ fragment. A peak at m/z 181 is due to $(C_{12}H_{11}N)^+$ fragment. A peak at m/z 120 is attributed to $(C_7H_6NO)^+$ fragment. A peak at m/z 94 is assigned to $(C_6H_6O)^+$ fragment. A peak at m/z 77 is assigned to $(C_6H_5)^+$ fragment.

The mass spectrum of $(L^3)$ showed the following fragmentation scheme 3. The molecular ion peak at m/z 492 is related to the molecular weight of $(C_{34}H_{24}N_2O_2)$. The peak at m/z 387 which is the base peak and is assigned to $(C_{27}H_{19}N_2O)^+$ fragment. A peak at m/z 179 is due to $(C_{14}H_{12})^-$ fragment. A peak at m/z 76 is assigned to $(C_6H_5)^+$ fragment.

The mass spectrum of $(H_2L^4)$ showed the following fragmentation scheme 4. The molecular ion peak at m/z 316 is related to the molecular weight of $(C_{20}H_{16}N_2O_2)$ and also it is the base peak. The peak at m/z 212 is assigned to $(C_{13}H_{10}N_2O)^+$ fragment. A peak at m/z 197 is due to $(C_{13}H_{10}NO)^+$ fragment. A peak at m/z 76 is assigned to $(C_6H_5)^+$ fragment.

The mass spectrum of $(H_2L^5)$ showed the following fragmentation scheme 5. The molecular ion peak at m/z 350 is related to the molecular weight of $(C_{20}H_{18}N_2O_4)$. The peak at m/z 306 which is the base peak is assigned to $(C_{19}H_{18}N_2O_2)^+$ fragment. A peak at m/z 261 is due to $(C_{18}H_{18}$

$N_2)^+$ fragment . A peak at m/z 184 is assigned to $(C_{12}H_{13}N_2)^+$ fragment A peak at m/z 77 is due to $(C_6H_5)^+$ fragment.

The mass spectrum of $(H_2L^6)$ showed the following fragmentation scheme 6. The molecular ion peak at m/z 241 is related to the molecular weight of $(C_{14}H_{11}NO_3)$. The peak at m/z 223 which is assigned to $(C_{14}H_{10}NO_2)^+$ fragment. A peak at m/z 195 which is the base peak is assigned to $(C_{13}H_{11}NO)^+$ fragment . A peak at m/z 120 is due to $(C7H6NO)^+$ fragment A peak at m/z 77 is assigned to $(C_6H_5)^+$ fragment. Unfortunately, the mass spectra of the complexes are not recorded due to the technical problems.

**Table. (1)** *Elemental analysis, Color and M.P of compounds under investigation.*

| Compounds | M.w$_t$ | color | m.p C° | Found (cale.) | | |
|---|---|---|---|---|---|---|
| | | | | C% | H% | N% |
| L$^1$.2H$_2$O | 605.67 | Olive green | 230 | 78.79 (79.45) | 4.98 (5.33) | 5.31 (4.63) |
| H$_2$L$^2$ | 213.23 | bright red | 185 | 72.64 (73.22) | 5.34 (5.19) | 6.64 (6.56) |
| L$^3$.H$_2$O | 511.29 | bright golden | 133 | 78.51 (79.96) | 5.29 (5.13) | 6.11 (5.49) |
| H$_2$L$^4$ | 316.35 | orange | 208 | 74.91 (75.93) | 5.19 (5.09) | 8.94 (8.85) |
| H$_2$L$^5$ | 348.35 | Yellow | 240 | 68.36 (69.15) | 6.00 (5.18) | 7.90 (8.06) |
| H$_2$L$^6$ | 241.24 | orange | 205 | 69.65 (69.70) | 4.77 (4.59) | 5.92 (5.80) |
| (VOL$^1$)$_2$.5H$_2$O | 1361.28 | Pale Green | >250 | 70.03 (70.58) | 4.89 (4.62) | 5.35 (4.12) |
| UO$_2$(L$^1$)$_2$.9H$_2$O | 1569.4 | Golden | >250 | 60.79 (61.22) | 5.54 (4.75) | 4.01 (3.57) |
| VO (H$_2$L$^2$)$_2$.2H$_2$O | 527.42 | Brown | >250 | 58.35 (59.21) | 3.66 (4.59) | 6.22 (5.31) |
| ZrO(H$_2$L$^2$)$_2$.3H$_2$O | 585.72 | Dark Yellow | >250 | 53.08 (53.32) | 3.52 (4.47) | 4.95 (4.78) |
| UO$_2$(H$_2$L$^2$)$_2$.3H$_2$O | 748.53 | Dark Red | >250 | 41.51 (41.72) | 3.02 (3.50) | 4.09 (3.74) |
| MoO$_2$(L$^3$)$_2$.2H$_2$O | 1149.00 | Pale Brown | >250 | 71.8 (71.06) | 5.22 (4.56) | 6.4 (4.88) |
| UO$_2$ (H$_2$L$^3$)$_2$.8H$_2$O | 1399.28 | Dark Brown | >250 | 58.13 (58.37) | 3.97 (4.61) | 4.30 (4.00) |
| (MoO$_3$)$_4$ (H$_2$L$^4$)$_2$ | 1204.43 | Dark Yellow | >250 | 41.72 (39.89) | 3.02 (2.34) | 4.92 (4.65) |

| Compounds | M.w₁ | color | m.p C° | Found (calc.) | | |
|---|---|---|---|---|---|---|
| | | | | C% | H% | N% |
| $(VOH_2L^4)_2 .2H_2O$ | 798.59 | Dark Brown | >250 | 60.15 (60.16) | 4.01 (4.04) | 7.01 (7.02) |
| $(ZrO)_3 (H_2L^3Cl.H_2O)_2.9H_2O$ | 1219.42 | Yellowish Brown | >250 | 39.07 (39.40) | 4.21 (4.13) | 4.69 (4.59) |
| $UO_2 (H_2L^4)_2$ | 900.72 | Brown | >250 | 53.22 (53.34) | 4.04 (3.36) | 6.80 (6.22) |
| $(MoO_2H_2L^5)_2.16H_2O$ | 620.41 | Pale Yellow | >250 | 38.21 (38.72) | 3.79 (5.20) | 4.60 (4.52) |
| $(VOH_2L^5)_2.6H_2O$ | 469.33 | Pale Green | >250 | 50.66 (51.18) | 4.69 (4.72) | 7.10 (5.97) |
| $UO_2 (H_2L^5)_2.8H_2O$ | 1112.87 | Dark Yellow | >250 | 43.84 (43.17) | 3.78 (4.53) | 4.96 (5.03) |
| $MoO_2(H_2L^6)_2.12H_2O$ | 824 | Pale Yellow | >250 | 38.77 (40.70) | 3.31 (5.38) | 3.25 (3.40) |
| $UO_2(H_2L^6)_2.4H_2O$ | 822.55 | Orange | >250 | 40.62 (40.88) | 2.71 (3.43) | 4.68 (3.41) |

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**Table (2)** *Infrared bands assignments (cm⁻¹) of compounds under investigation*

| The compounds | ν(C=N) cm⁻¹ | ν(C=O) cm⁻¹ | ν(OH) cm⁻¹ | ν(C–O) cm⁻¹ | ν(M-O) cm⁻¹ | ν(M-N) cm⁻¹ | ν(M=O) cm⁻¹ |
|---|---|---|---|---|---|---|---|
| L¹.2H₂O | 1619 | 1671 | 3377 | 1286 | — | — | — |
| H₂L² | 1631 | — | 3380 | 1274 | — | — | — |
| L³.H₂O | 1593 | 1662 | — | 1211 | — | — | — |
| H₂L⁴ | 1609 | — | 3396 | 1280 | — | — | — |
| H₂L⁵ | 1588 | 1683 | 3363 | 1285 | — | — | — |
| H₂L⁶ | 1624 | — | 3350 | 1366 | — | — | — |
| (VOL¹)₂.5H₂O | 1622 | 1671 | 3225 | 1289 | 708 | 490 | 1000 |
| UO₂(L¹)₂.9H₂O | 1608 | — | 3414 | 1292 | 630 | 485 | 921 |
| VO (H₂L²)₂.2H₂O | 1606 | — | 3404 | 1234 | 662 | 475 | 985 |
| ZrO(H₂L²)₂.3H₂O | 1606 | — | 3425 | 1258 | 604 | 548 | 926 |
| UO₂(H₂L²)₂.3H₂O | 1606 | — | 3384 | 1295 | 576 | 480 | 905 |
| MoO₂(L³)₂.2H₂O | 1585 | 1652 | 3370 | 1200 | 600 | 480 | 932 |
| UO₂ (H₂L³)₂.8H₂O | 1590 | 1665 | 3380 | 1211 | 639 | 458 | 925 |
| (MoO₃)₄ (H₂L⁴)₂ | 1612 | — | 3404 | 1283 | 514 | 414 | — |
| (VOH₂L⁴)₂ .2H₂O | 1612 | — | 3238 | 1283 | 514 | 485 | — |
| (ZrO)₃ (H₂L⁴Cl.H₂O)₂.9H₂O | 1609 | — | 3370 | 1280 | 545 | 480 | — |
| UO₂ (H₂L⁴)₂ | 1619 | — | 3380 | 1283 | 542 | 480 | — |
| (MoO₂H₂L⁵)₂.16H₂O | 1597 | — | 3454 | 1294 | 571 | 435 | 981 |
| (VOH₂L⁵)₂.6H₂O | 1594 | — | 3418 | 1292 | 486 | 428 | 895 |
| UO₂ (H₂L⁵)₂.8H₂O | 1594 | — | 3420 | — | 600 | 515 | 921 |
| MoO₂(H₂L⁶)₂.12H₂O | 1591 | 1655 | 3434 | 1376 | 580 | 440 | 903 930 |
| UO₂(H₂L⁶)₂.4H₂O | 1594 | — | 3370 | 1396 | 582 | 453 | 917 |

**Table.** (3) *Electronic Spectra an magnetic moment of compounds under*

*Investigation*

| The compounds | nm $\lambda$ | $\varepsilon$ Lmol$^{-1}$cm$^{-1}$ | v cm$^{-1}$ | $\mu_{eff}$ B.M | Transitions | Geometry |
|---|---|---|---|---|---|---|
| L$^1$.2H$_2$O | 263 | 0.533 | 38022 | ― | $\pi \to \pi^*$ | ― |
| H$_2$L$^2$ | 257 | 0.678 | 38910 | ― | $\pi \to \pi^*$ | ― |
| L$^3$.H$_2$O | 201 | 2.502 | 49571 | ― | $\pi \to \pi^*$ | ― |
| H$_2$L$^4$ | 207 | 2.030 | 48309 | ― | $\pi \to \pi^*$ | ― |
| H$_2$L$^5$ | 210 | 1.067 | 47619 | ― | $\pi \to \pi^*$ | ― |
| H$_2$L$^6$ | 251 | 3.068 | 30211 | ― | $\pi \to \pi^*$ | ― |
| (VOL$^1$)$_2$.5H$_2$O | 845 445 368 | 2.294 1.345 0.864 | 11834 22471 27173 | 1.2 | $^2B_2 \to {}^1A_1$ $^2B_{2(P)} \to E$ $\pi \to \pi^*$ | Square pyramidal |
| VO (H$_2$L$^2$)$_2$.2H$_2$O | 760 480 320 | 2.461 2.274 0.361 | 13157 20833 31250 | 1.65 | $^2B_2 \to {}^1A_1$ $^2B_{2(P)} \to E$ $\pi \to \pi^*$ | Square pyramidal |
| (VOH$_2$L$^4$)$_2$.2H$_2$O | 749 430 305 | 1.056 2.292 0.930 | 13351 23255 32786 | 0.8 | $^2B_2 \to {}^1A_1$ $^2B_{2(P)} \to E$ $\pi \to \pi^*$ | Square pyramidal |
| (VOH$_2$L$^5$)$_2$.6H$_2$O | 785 510 290 | 2.249 2.063 0.963 | 12738 19607 34482 | 1.76 | $^2B_2 \to {}^1A_1$ $^2B_{2(P)} \to E$ $\pi \to \pi^*$ | Square pyramidal |
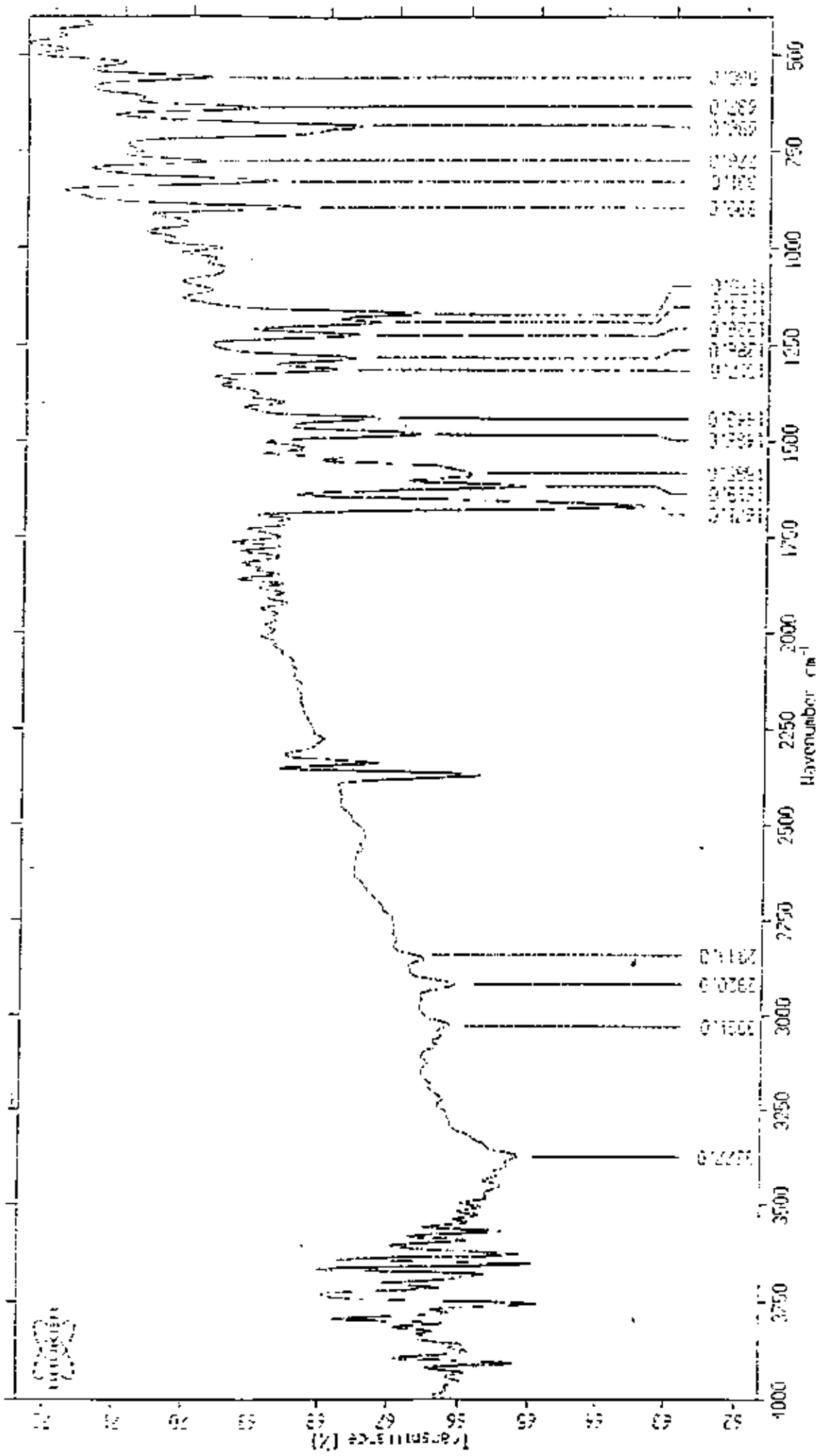
Fig (1) The IR spectrum of $(L^1)$ ligand

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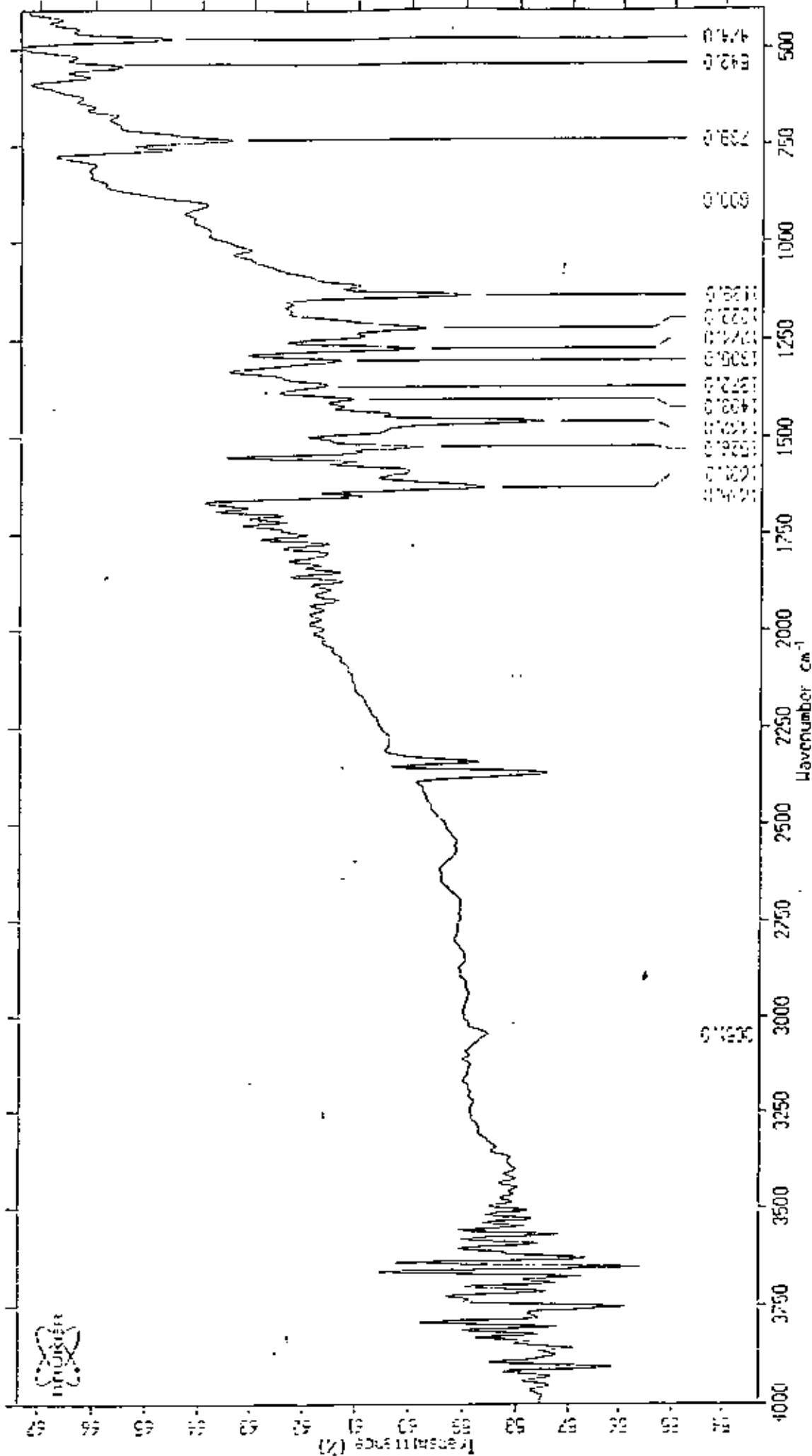
Fig.(2) The IR spectrum of $(H_2L^2)$ ligand

Fig.(3) The IR spectrum of $(L^3)$ ligand
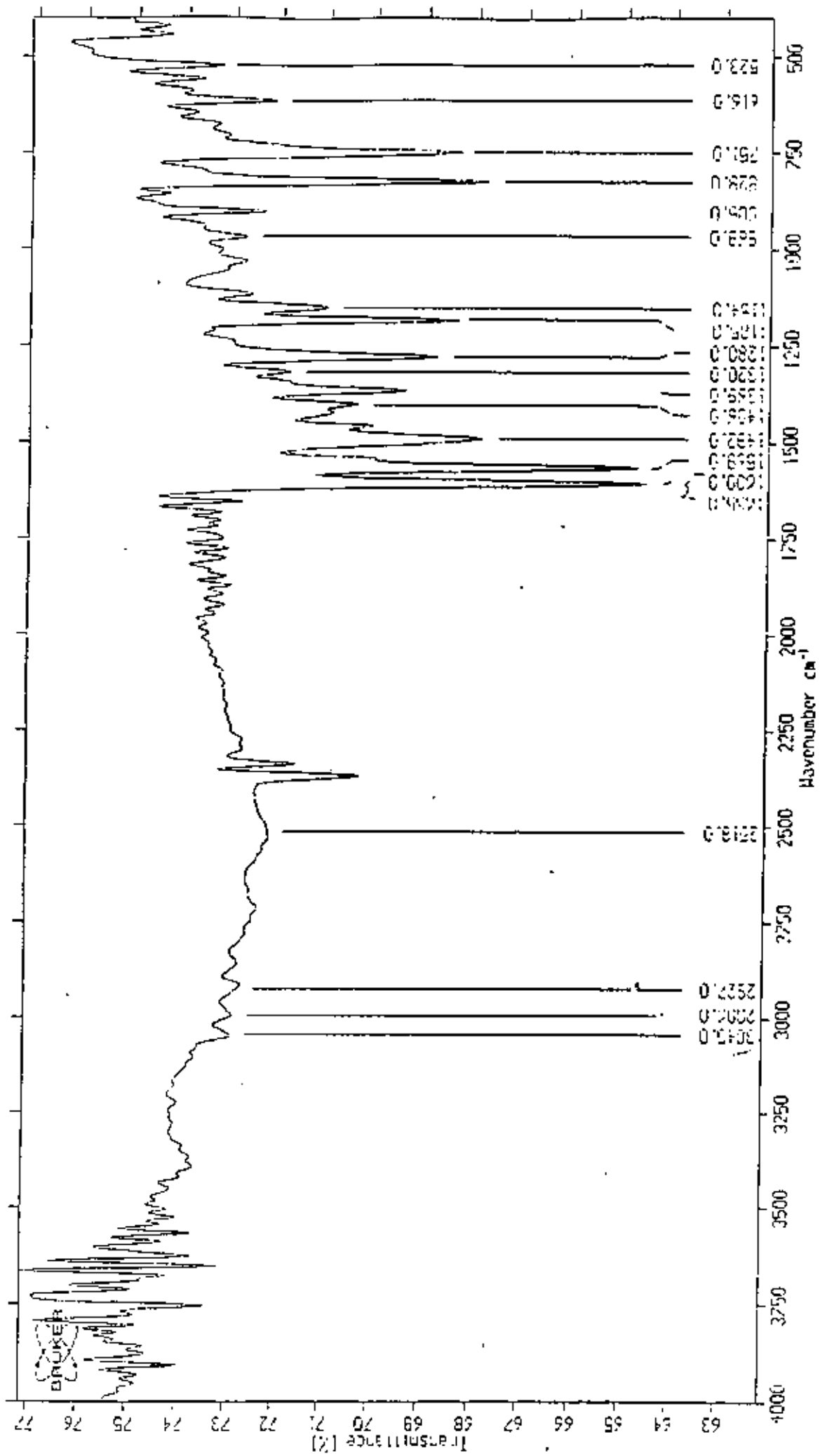
Fig.(4) The IR spectrum of $(H_2L^4)$ ligand
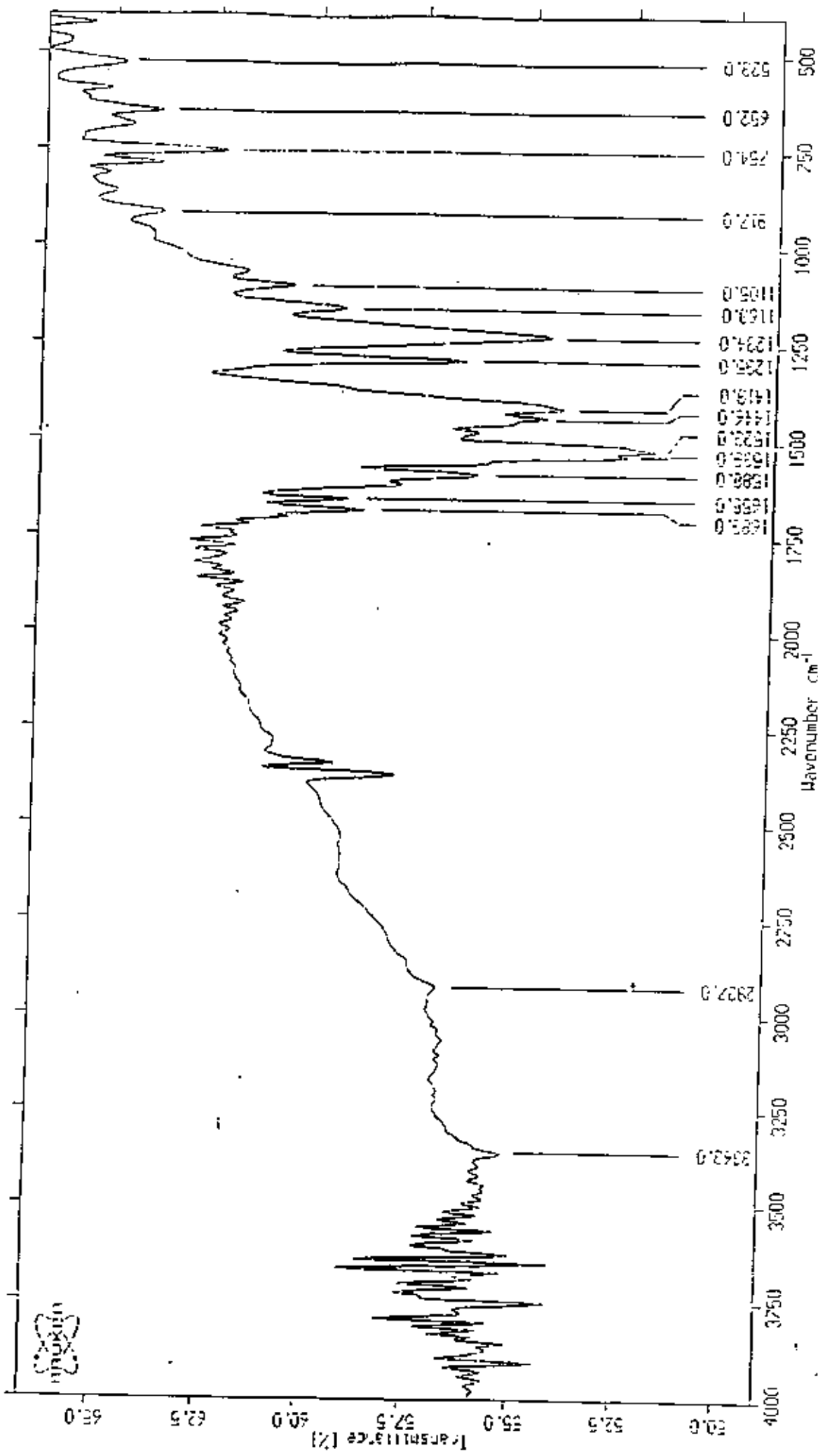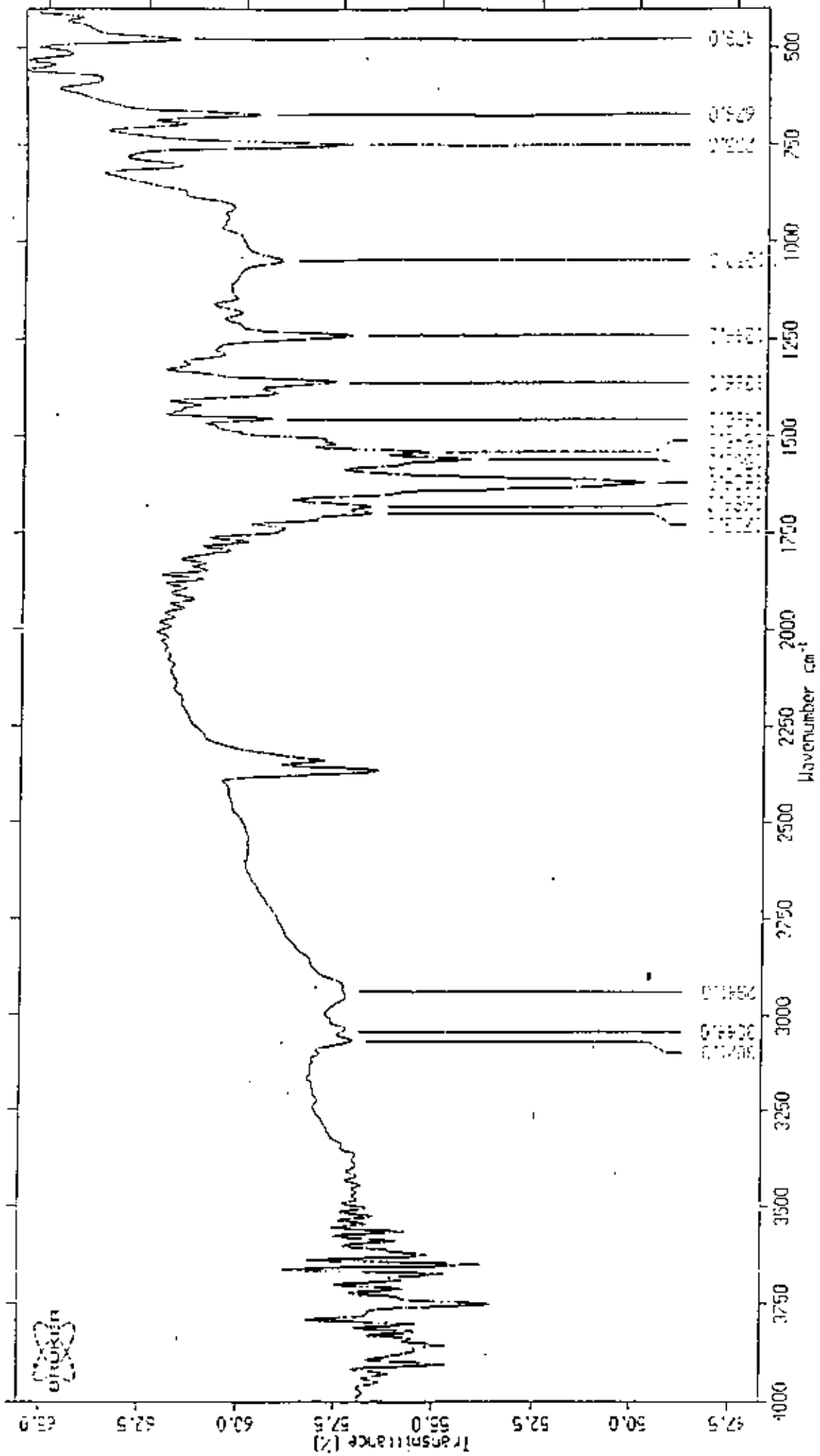
Fig.(5) The IR spectrum of $(H_2L^5)$ ligand

Fig.(6) The IR spectrum of $(H_2L^6)$ ligand

Fig.(7) The IR spectrum of $(VOL')_2.5H_2O$ Complex

Fig.(8) The IR spectrum of $(UO_2L^l)_2.9H_2O$ Complex

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Fig.(9) The IR spectrum of VO(H₂L²)₂2H₂O Complex

Fig.(10) The IR spectrum of $ZrO(H_2L^2)_2.3H_2O$ Complex
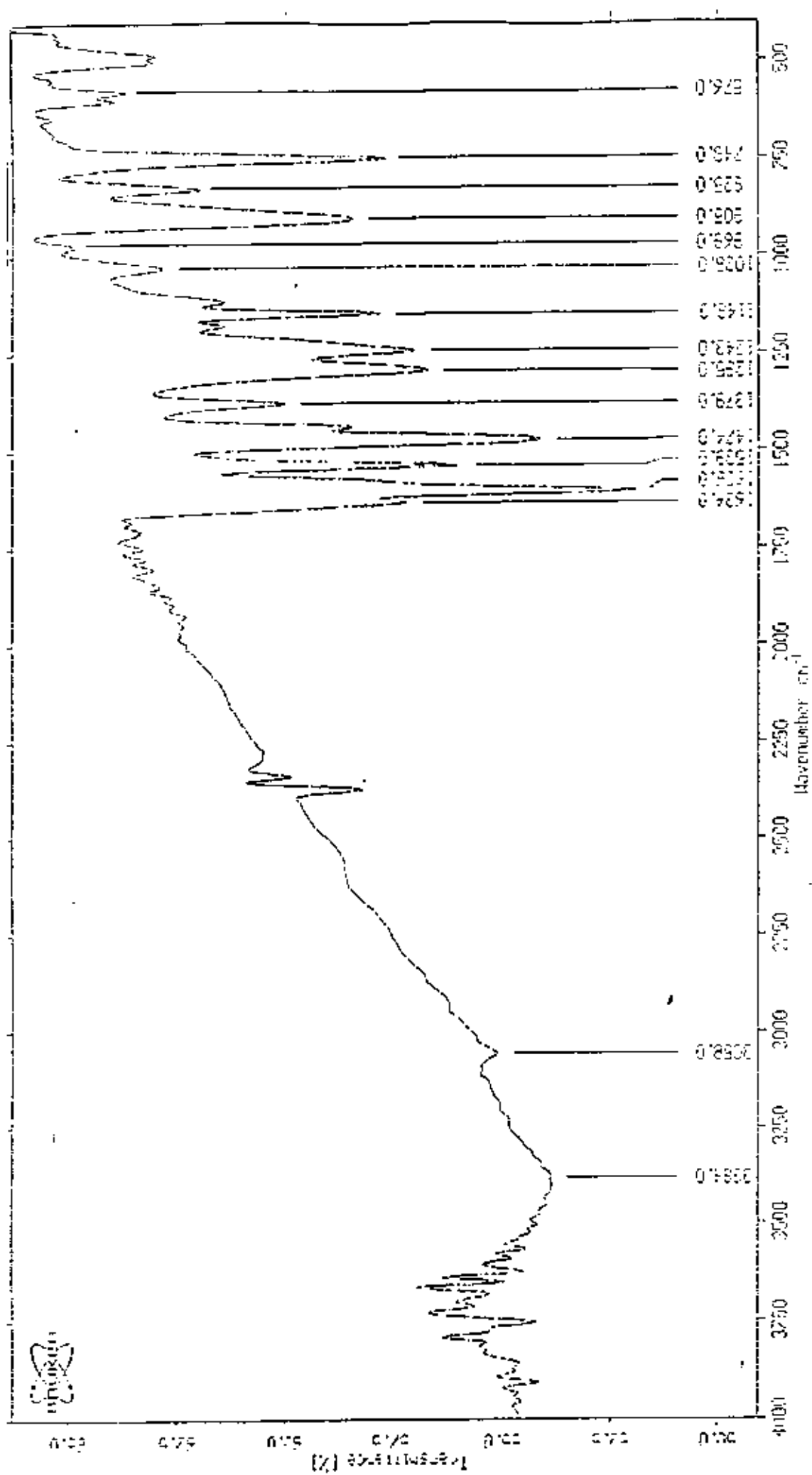
Fig.(11) The IR spectrum of $UO_2(H_2L^2)_2 \cdot 3H_2O$ Complex

Fig.(12) The IR spectrum of $MoO_2(L^1)_2 \cdot 2H_2O$ Complex
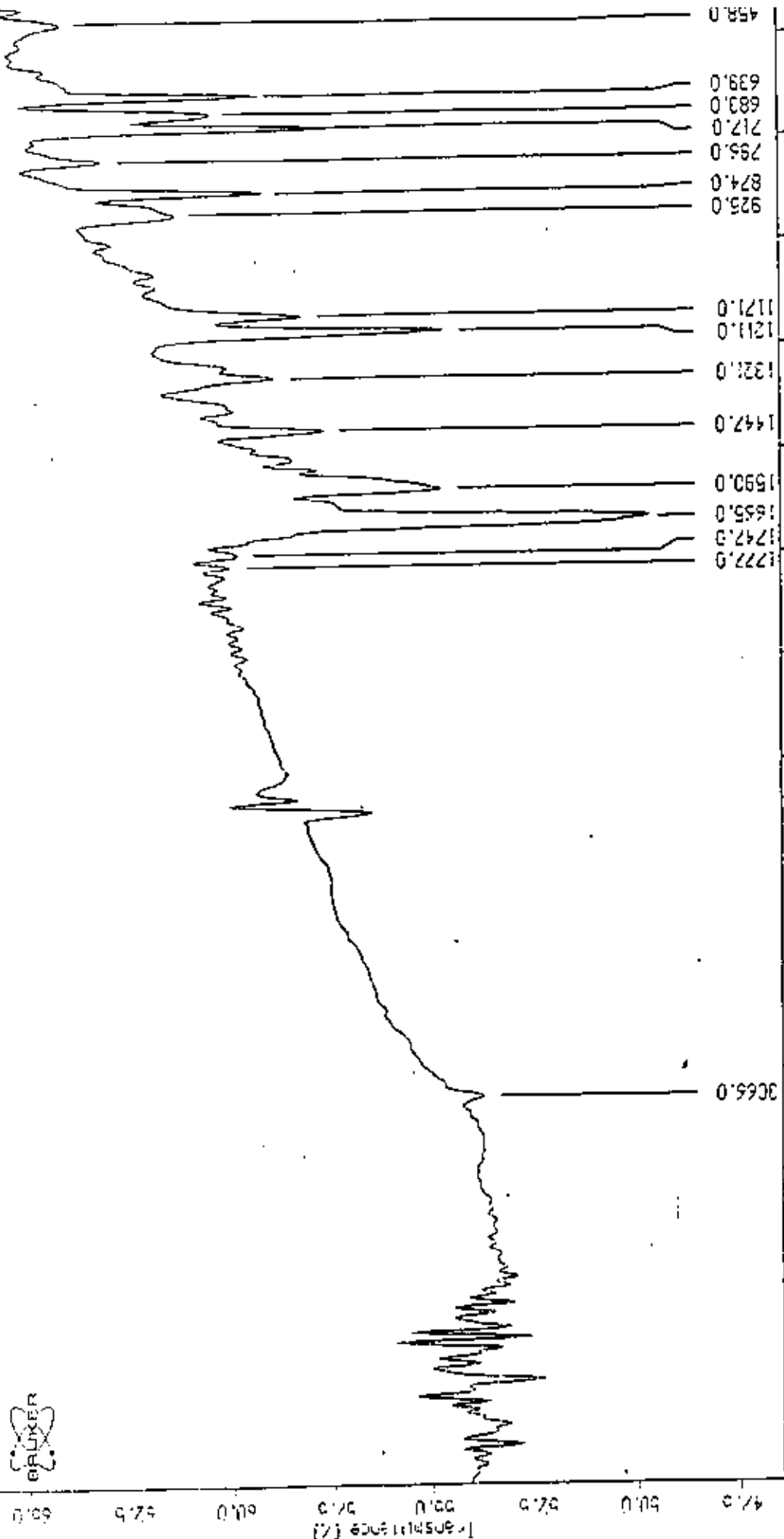
Fig.(13) The IR spectrum of $UO_2(L^3)_2 \cdot 8H_2O$ Complex

49
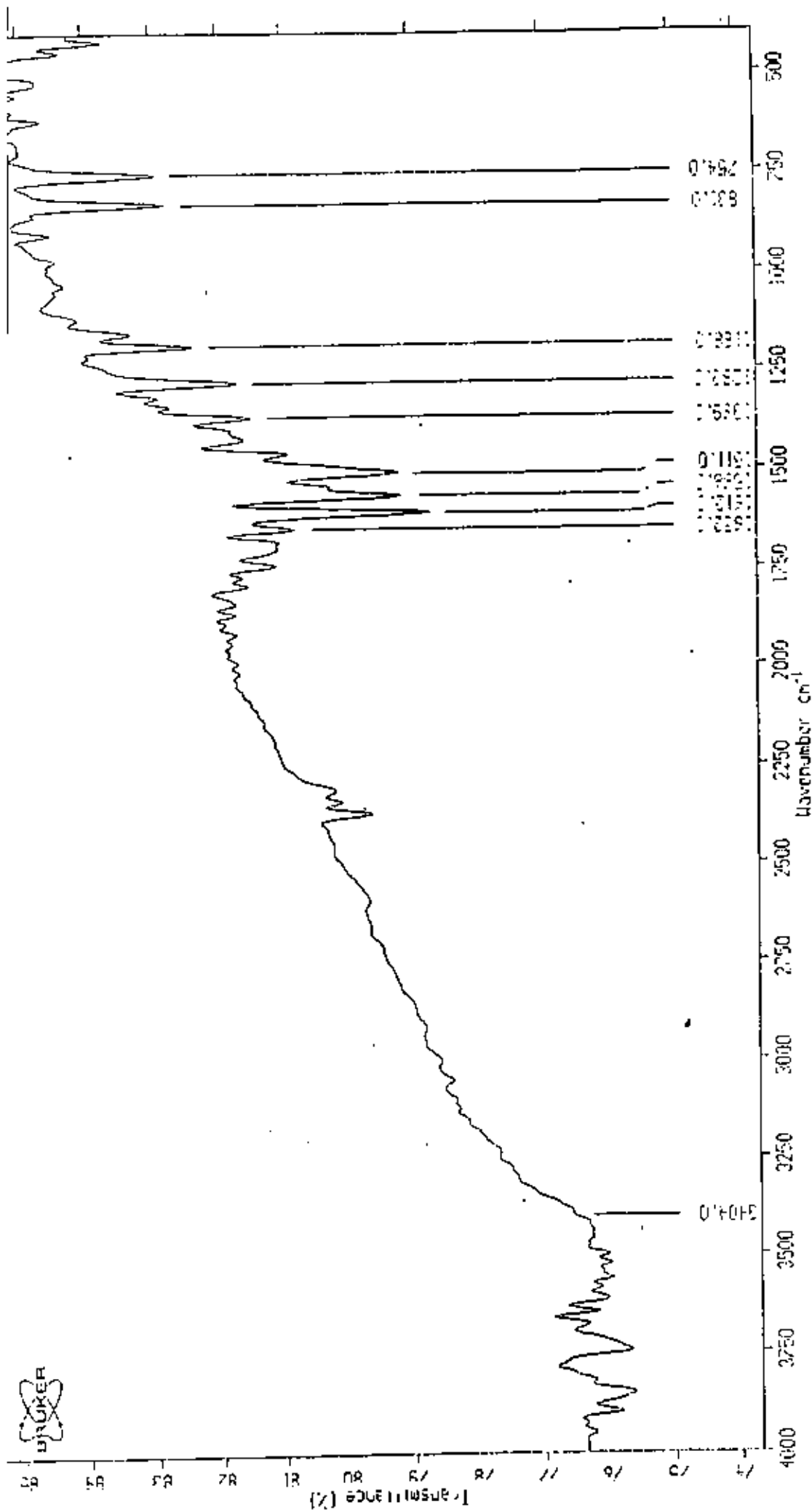
Fig.(14) The IR spectrum of $(MoO_3)_4(H_2L^4)_2$ Complex
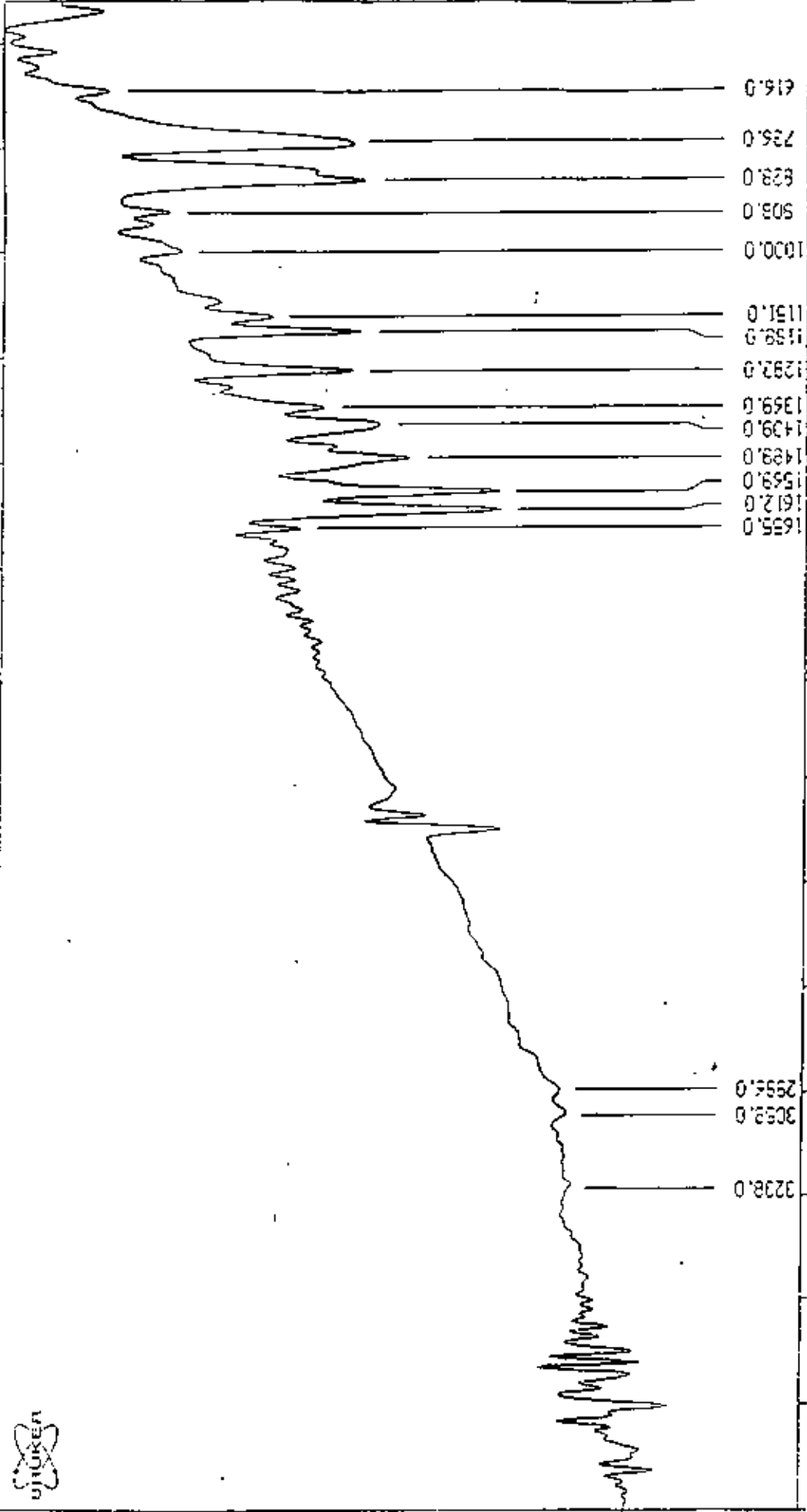
Fig.(15) The IR spectrum of $(VO (H_2L^4)_2.2H_2O$ Complex
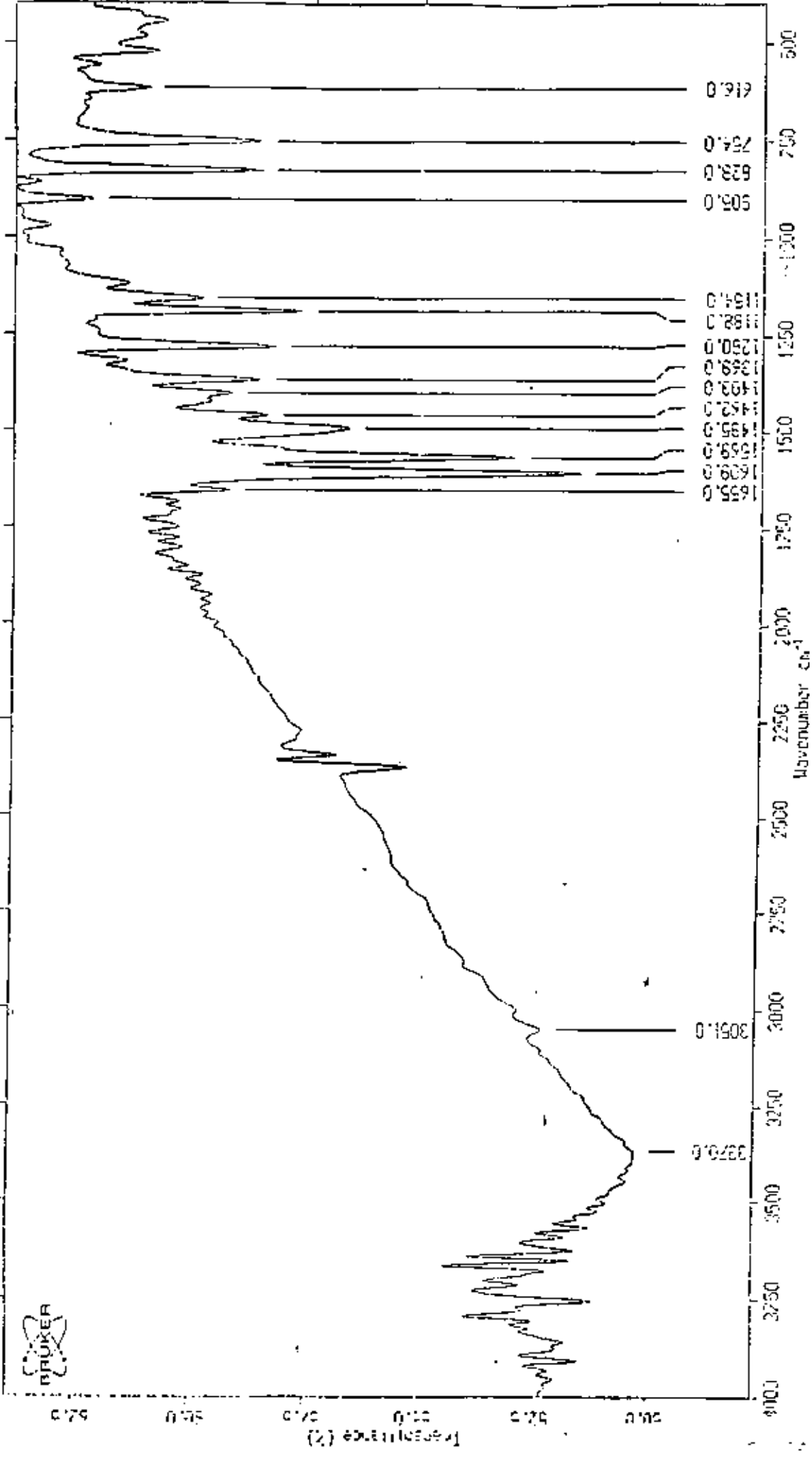
Fig.(16) The IR spectrum of $(ZrO)_3(H_2L^1.Cl.H_2O)_2.9H_2O$ Complex
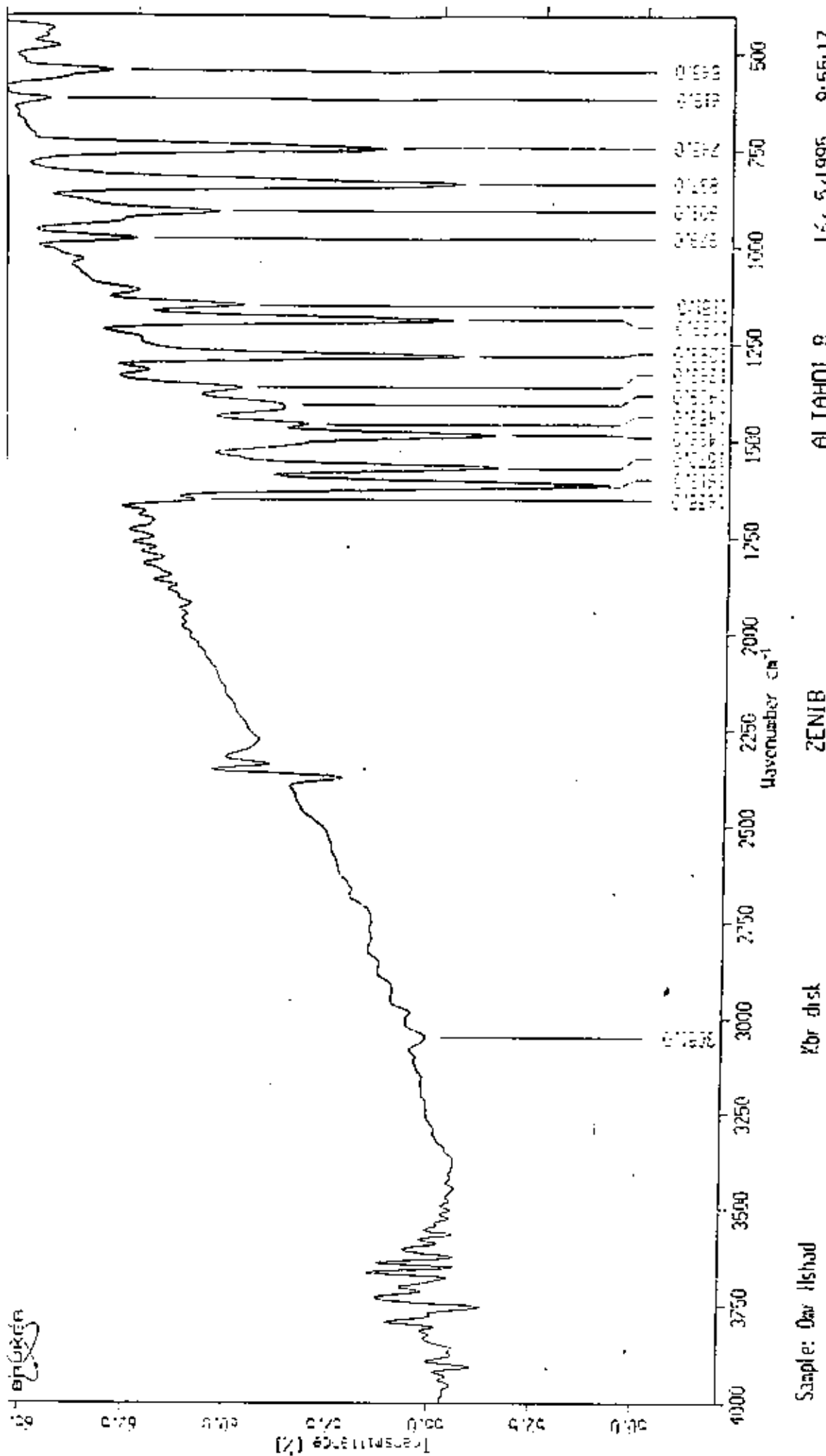
Fig. (17) The IR spectrum of $(UO_2 (H_2L^3)_2$ Complex
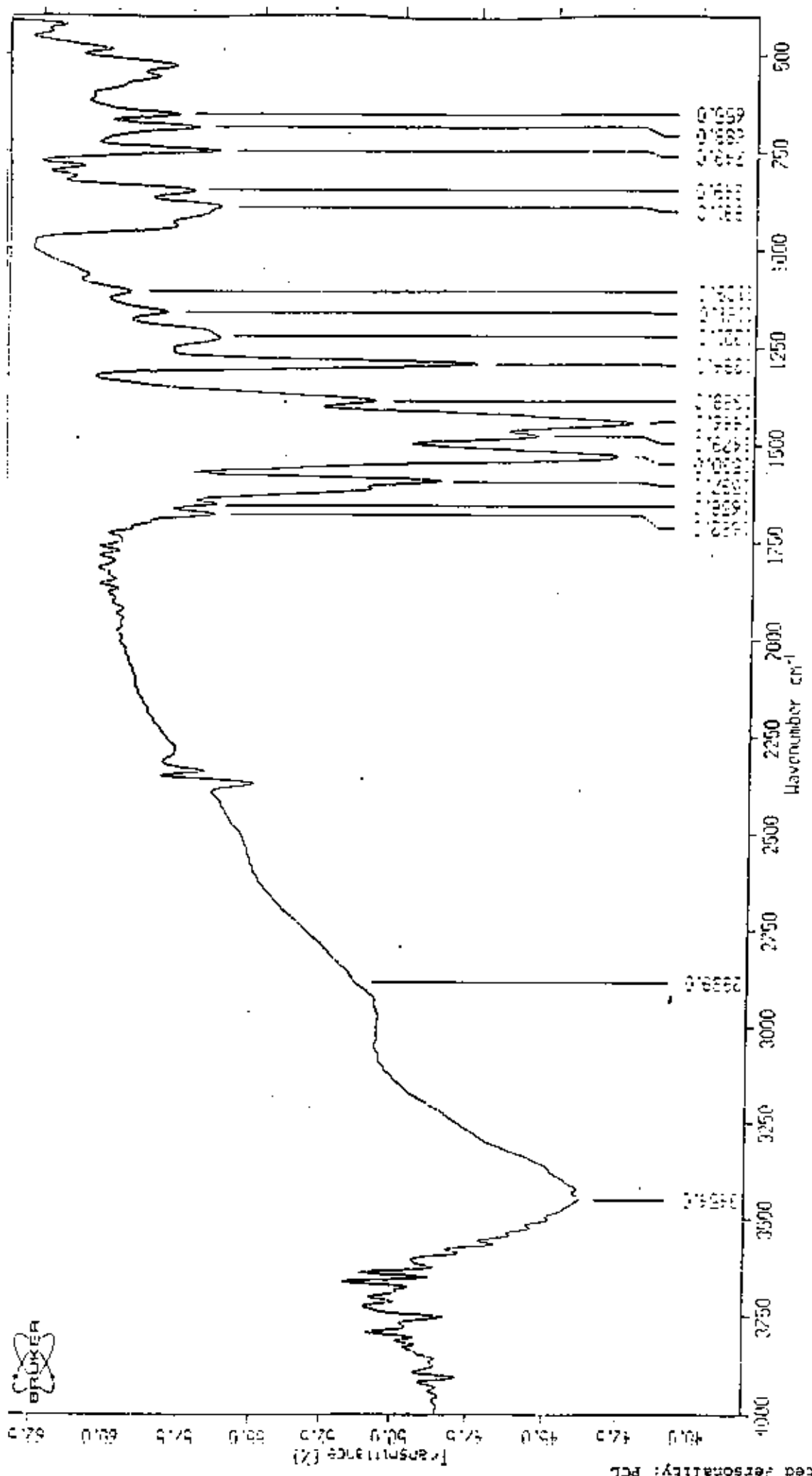
Fig.(18) The IR spectrum of $(MoO_2 \cdot H_2L^5)_2 \cdot 16H_2O$ Complex

54
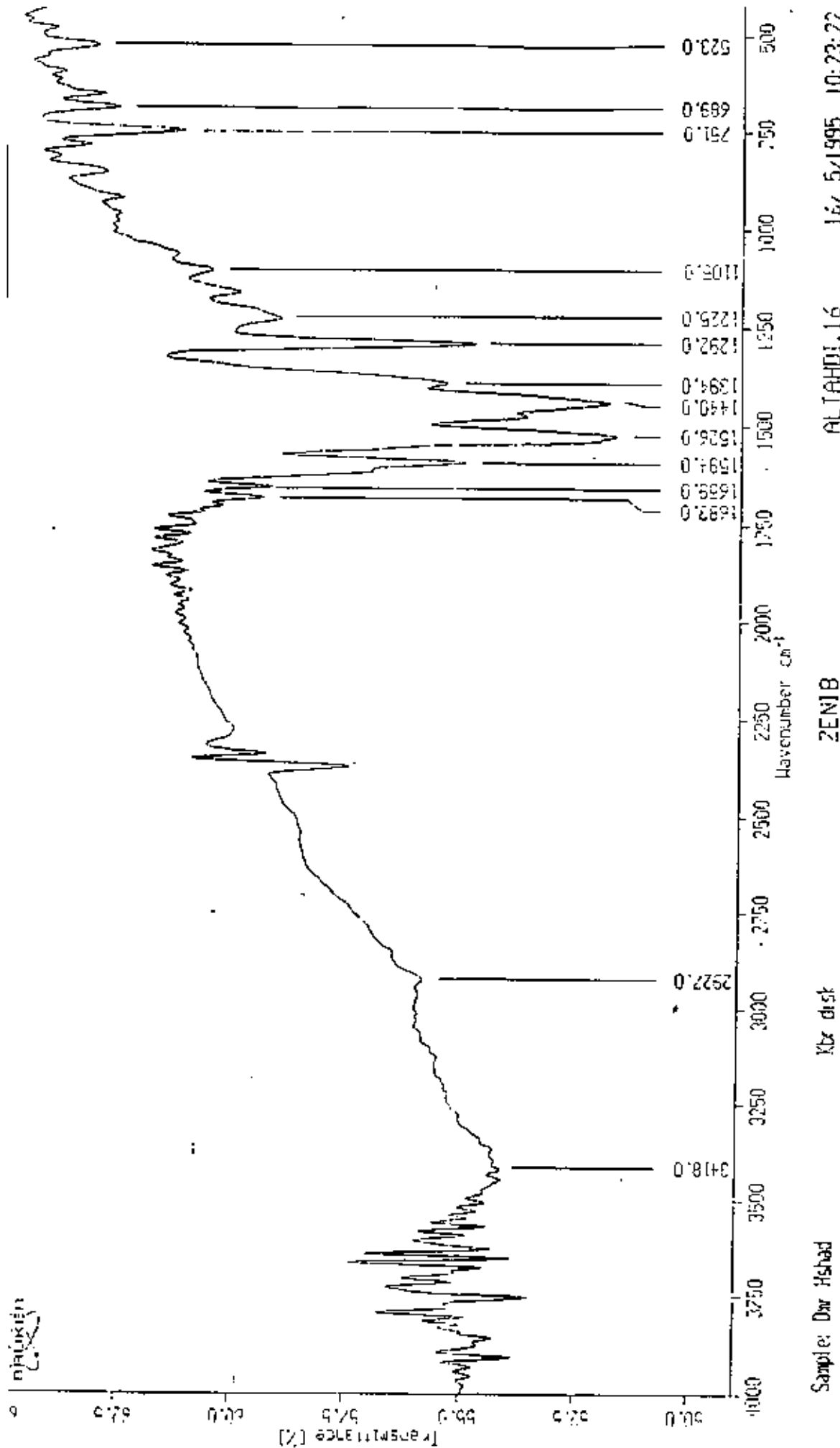
Fig. (19) The IR spectrum of $(VO\ H_2L^5)_2.6H_2O$ Complex
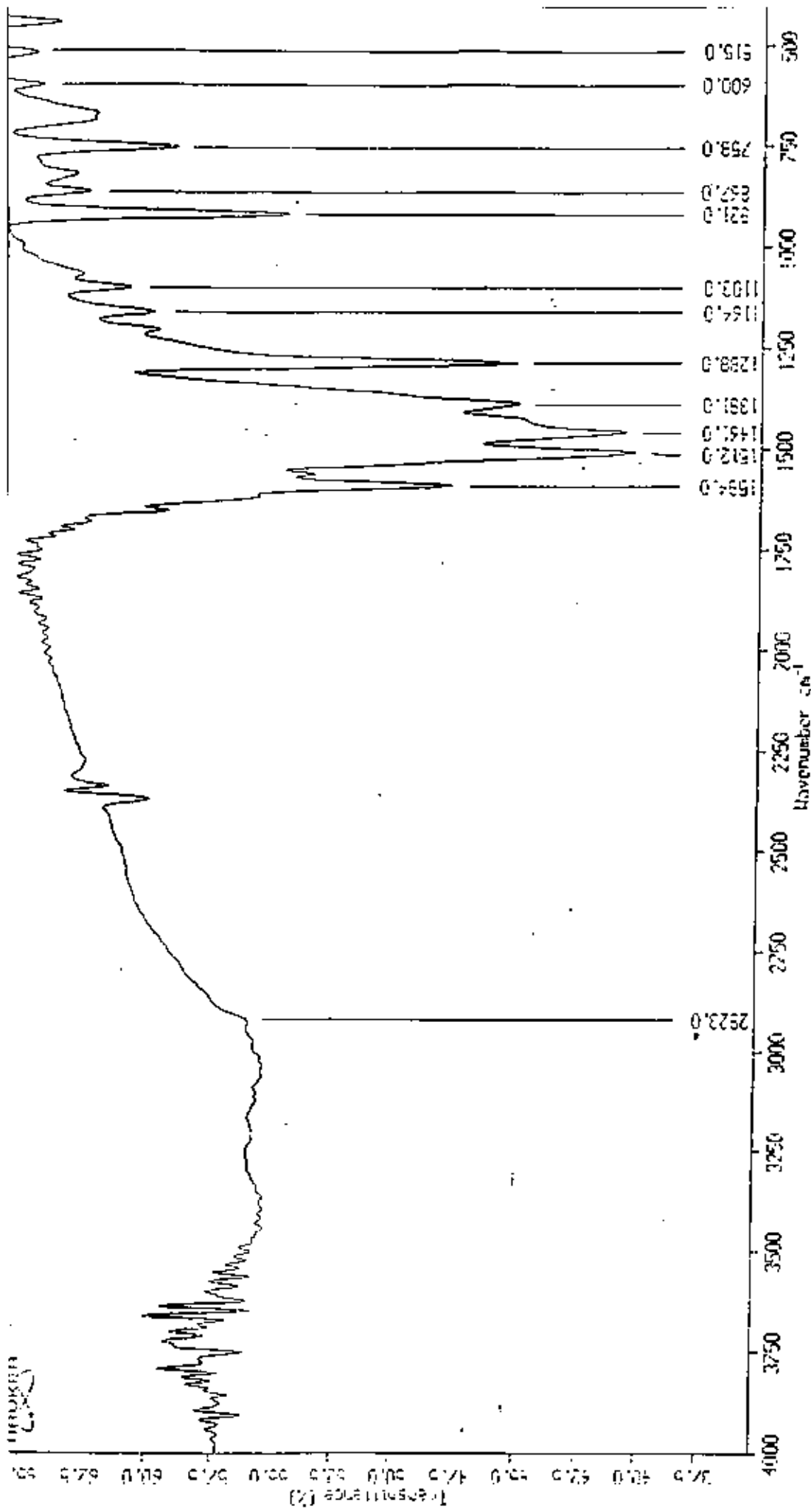
Fig.(20) The IR spectrum of $UO_2(H_2L^5)_2.8H_2O$ Complex

56
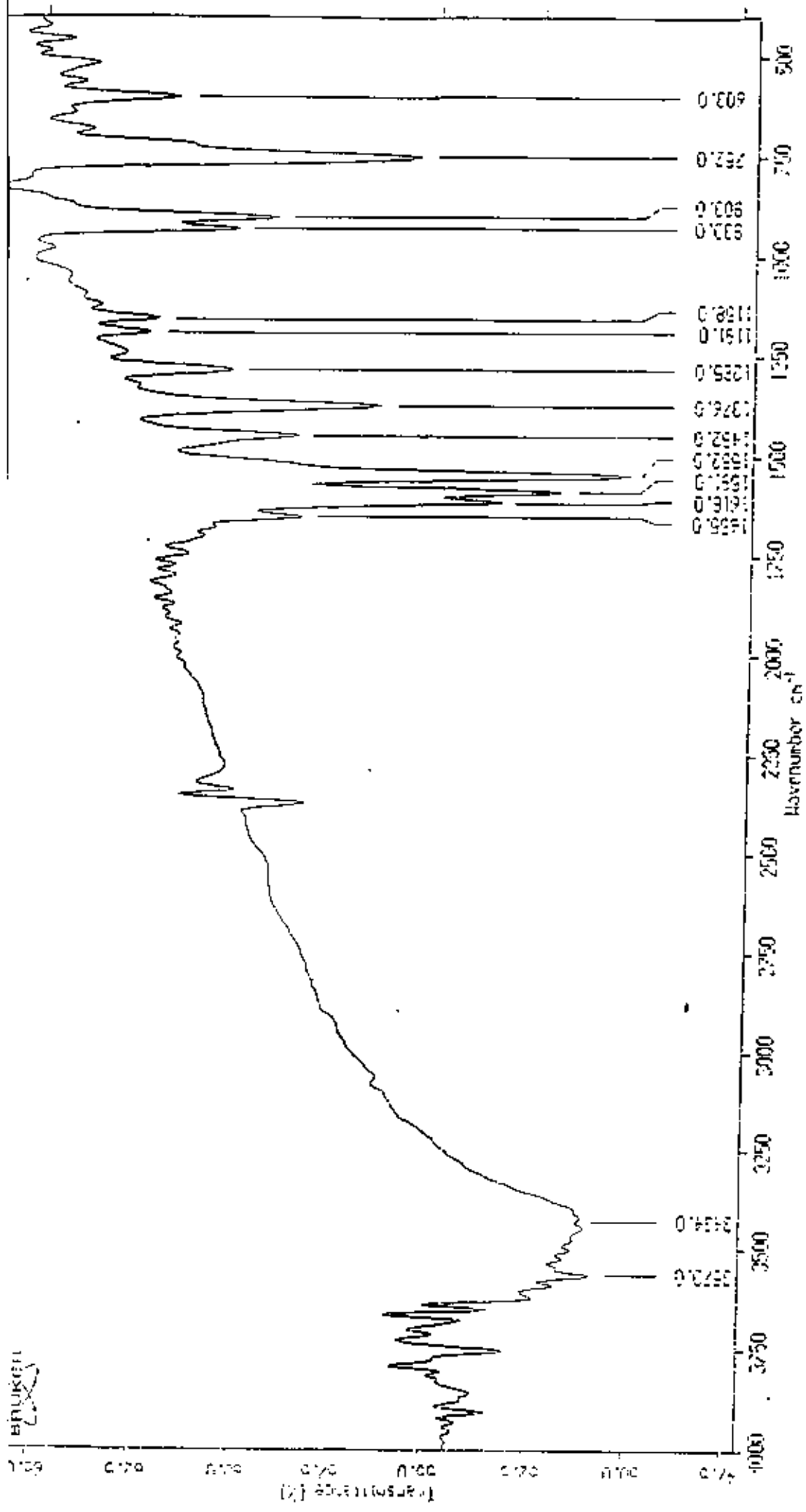
Fig.(21) The IR spectrum of $MoO_2 (H_2L^6)_2.12H_2O$ Complex
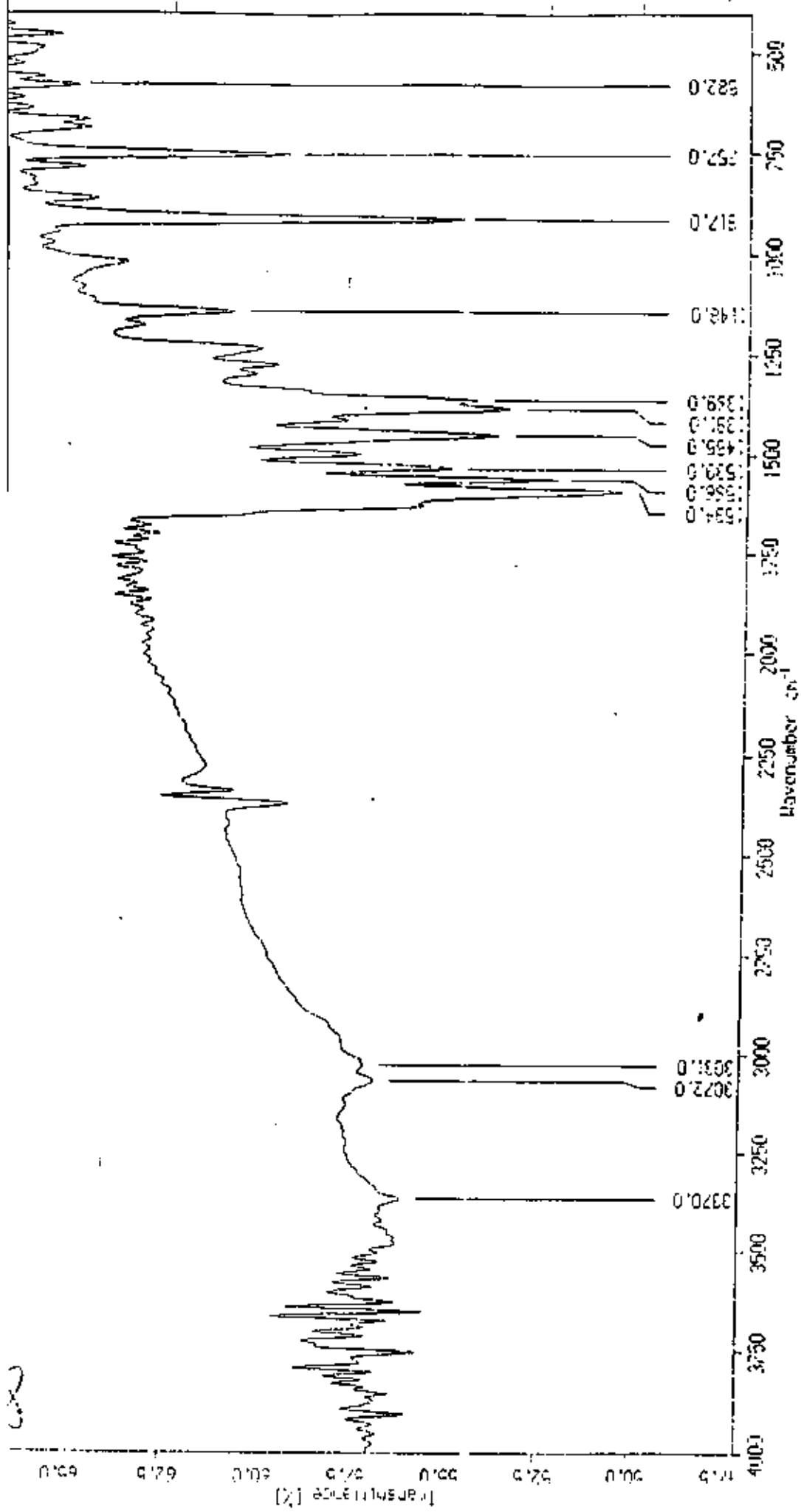
Fig.(22) The IR spectrum of $UO_2 (H_2L^6)_2.4H_2O$ Complex

58

Comment: Gamal Ouf
CAIRO_SC.X41  Date 09/18/10  Time 09:15:45  TIC

48076.

S=74  B=59  Bp=463  Di=15970.  RT=3.66  CT=189

463

255

179

368

S List >  S=74  R=59  Pos=4  Tot=4
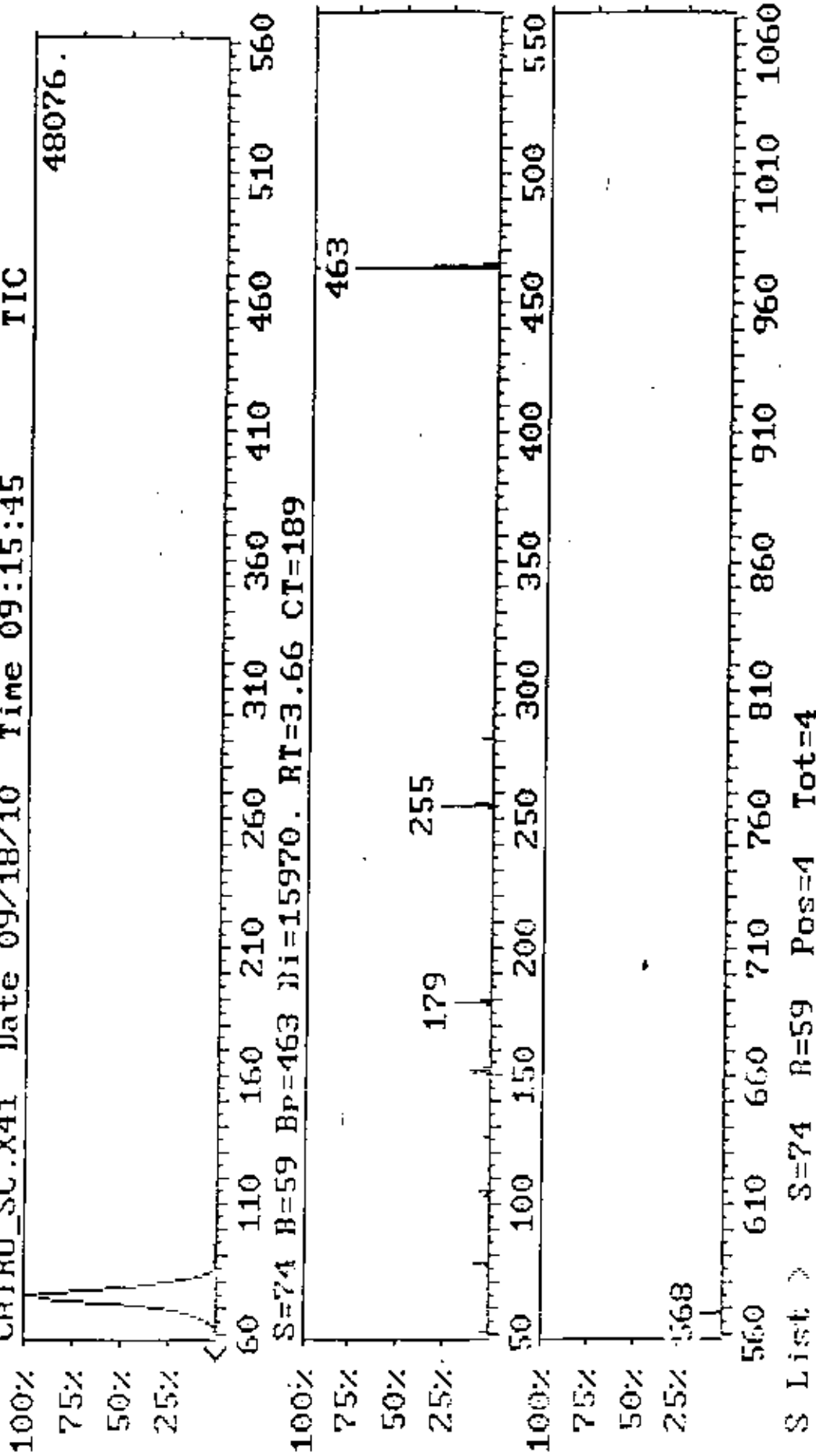
Fig.(23) The Mass spectra of (L¹) ligand

- 59

Fig.(24) The Mass spectra of $(H_2L^2)$ ligand

Comment
CAIRO SC.X44   Date 09/18/10   Time 09:34:57     TIC

82070.

100%
75%
50%
25%

20   70   120   170   220   270   320   370   420   470   520

S=51  B=43  Bp=387  Bi=13140.  RT=2.51  CT=154

100%
75%
50%
25%

76

179

*2

50   70   90   110   130   150   170   190   210   230   250   270   290

100%
75%
50%
25%

387

492

300   320   340   360   380   400   420   440   460   480   500   520   510

S List >   S=51   B=43   Pos=11   Tot=11
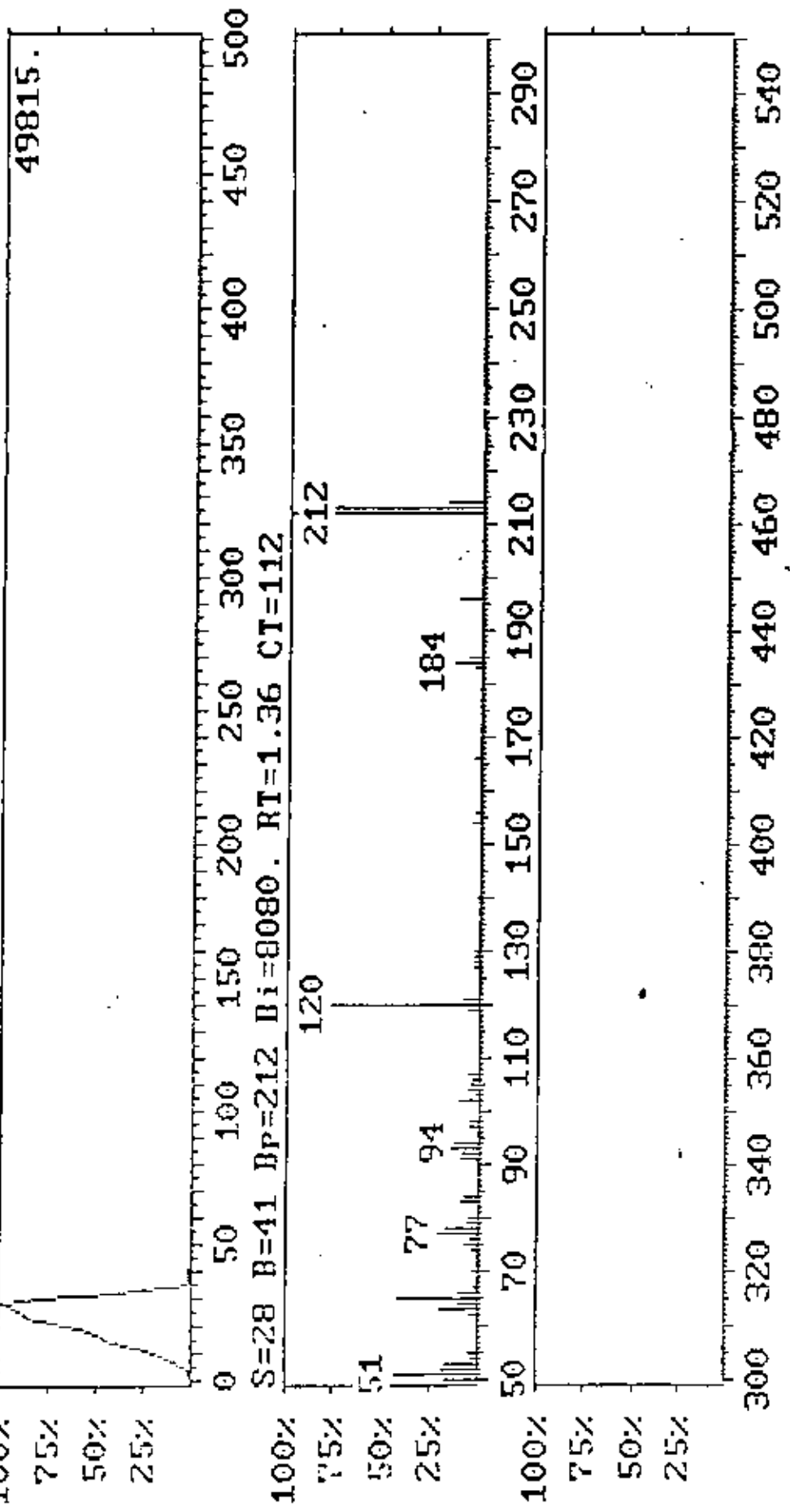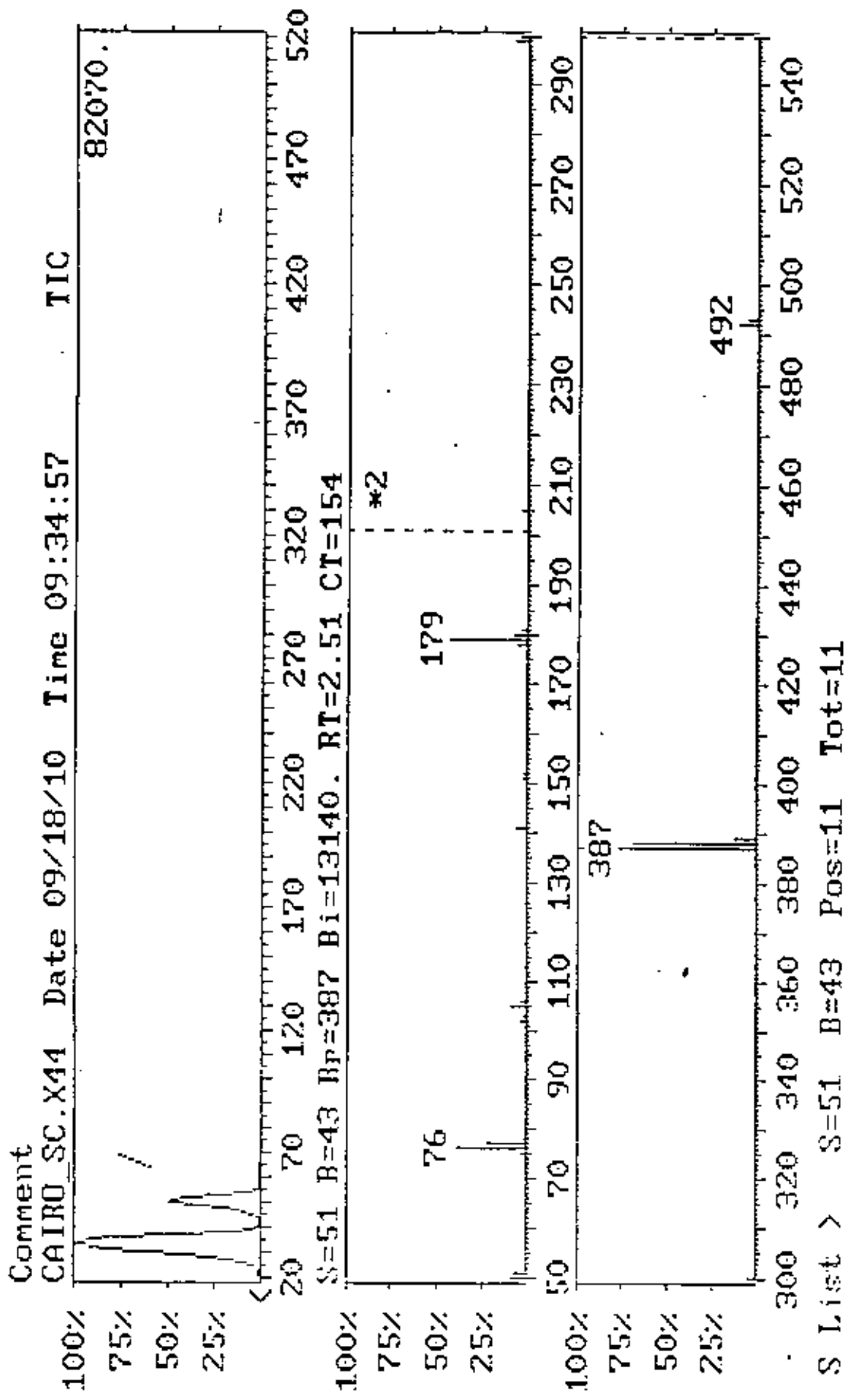
Fig.(25) Mass spectrum of $(L^3)$ ligand

Comment
CAIRO SC.X46   Date 09/18/10   Time 09:46:05   TIC

6054.

100%
75%
50%
25%

20   70   120   170   220   270   320   370   420   470   520

S=35  B=20  Bp=316  Bi=1610.  RT=1.71  CT=154

100%
75%
50%
25%

197

212

159

65   76

50   70   90   110   130   150   170   190   210

100%
75%
50%
25%

316

220   240   260   280   300   320   340   360   380
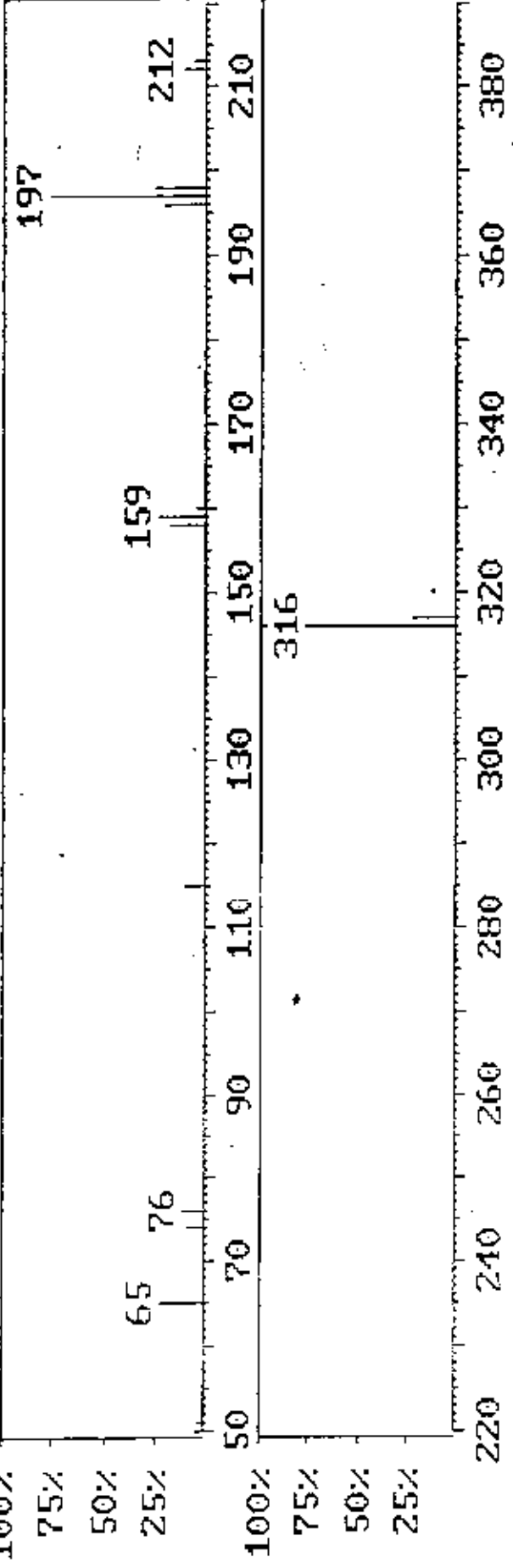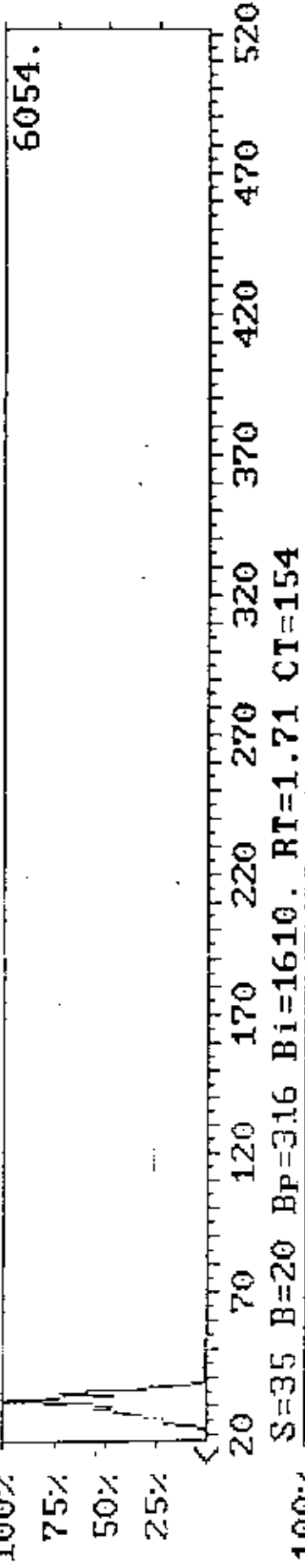
S List >   S=35   B=20   Pos=3   Tot=3

Fig.(26) The Mass spectra of $(H_2L^4)$ ligand

62

Comment
CAIRO_SC.X48   Date 09/18/10   Time 10:00:07   TIC

47437.
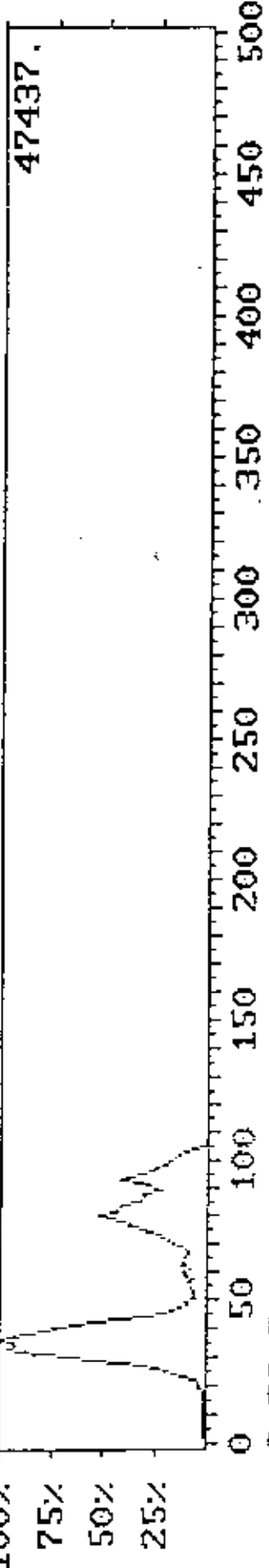
S=79 B=12 Bp=306 Bi=1330. RT=3.91 CT=248

77
143
184
261
306
350
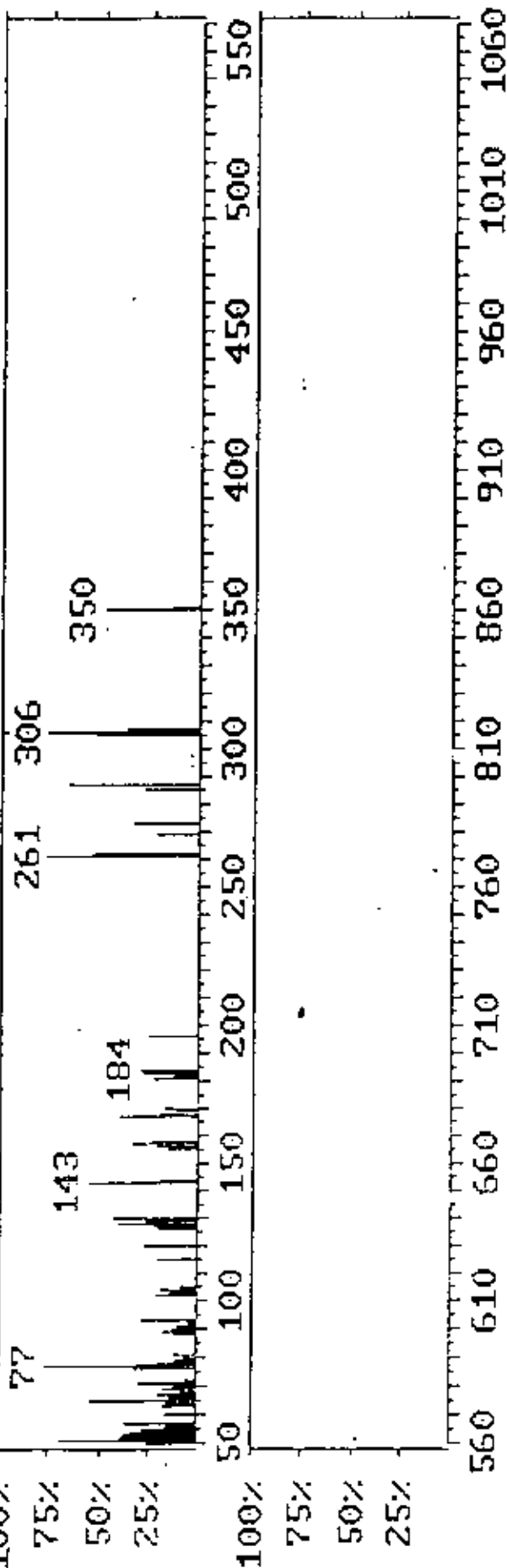
S=79 B=12 Pos=7 Tot=7

S List >

Fig.(27) The Mass spectra of $(H_2L^5)$ ligand .

Comment
CAIRD_SC.X47   Date 09/18/10   Time 09:52:04   TIC

129682.
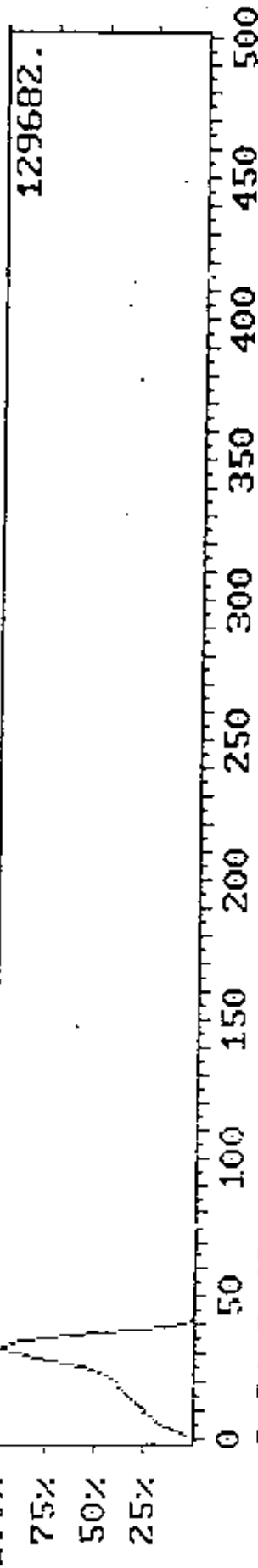
S=31  B=42  Br=195  Bi=11600.  RT=1.51  CT=137
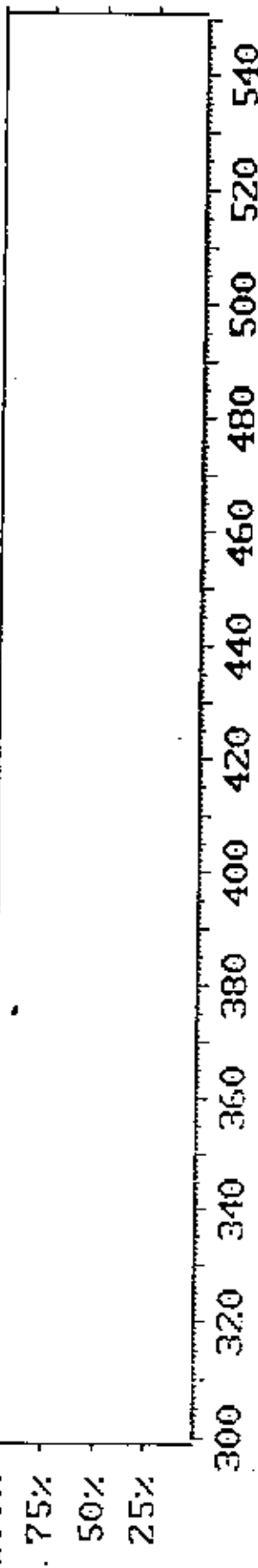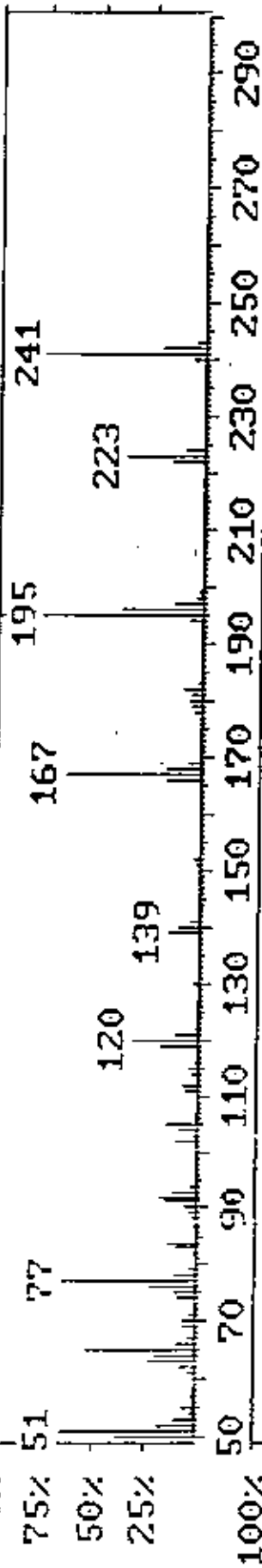
S List >   S=31  B=42   Pos=1   Tot=1

Fig.(28) The Mass spectra of $(H_2L^6)$ ligand

64

m/z=255 (27.9%)

m/z=179 (19.3%)

m/z=568 (10.5%)

m/z=152 (11.1%)

m/z=463 (100%)

Scheme 1

65

Scheme 2

66

m/z=76(39.3 %)

m/z=179(42.9 %)          m/z=492(5.6 %)          m/z=387(100%)

Scheme 3

m/z=76(10.6%)

m/z=197(91.9%)

m/z=316(100%)

m/z=212(11.8%)

Scheme 4

m/z=306(100%)

m/z=261(94.7%)

m/z=350(48.1%)

m/z=184(29.3%)

m/z=77(88.0%)

Scheme 5

m/z=195(100%)

m/z=223(37.2%)

m/z=241(95.3%)

m/z=77(64.5%)

m/z=120(31.3%)
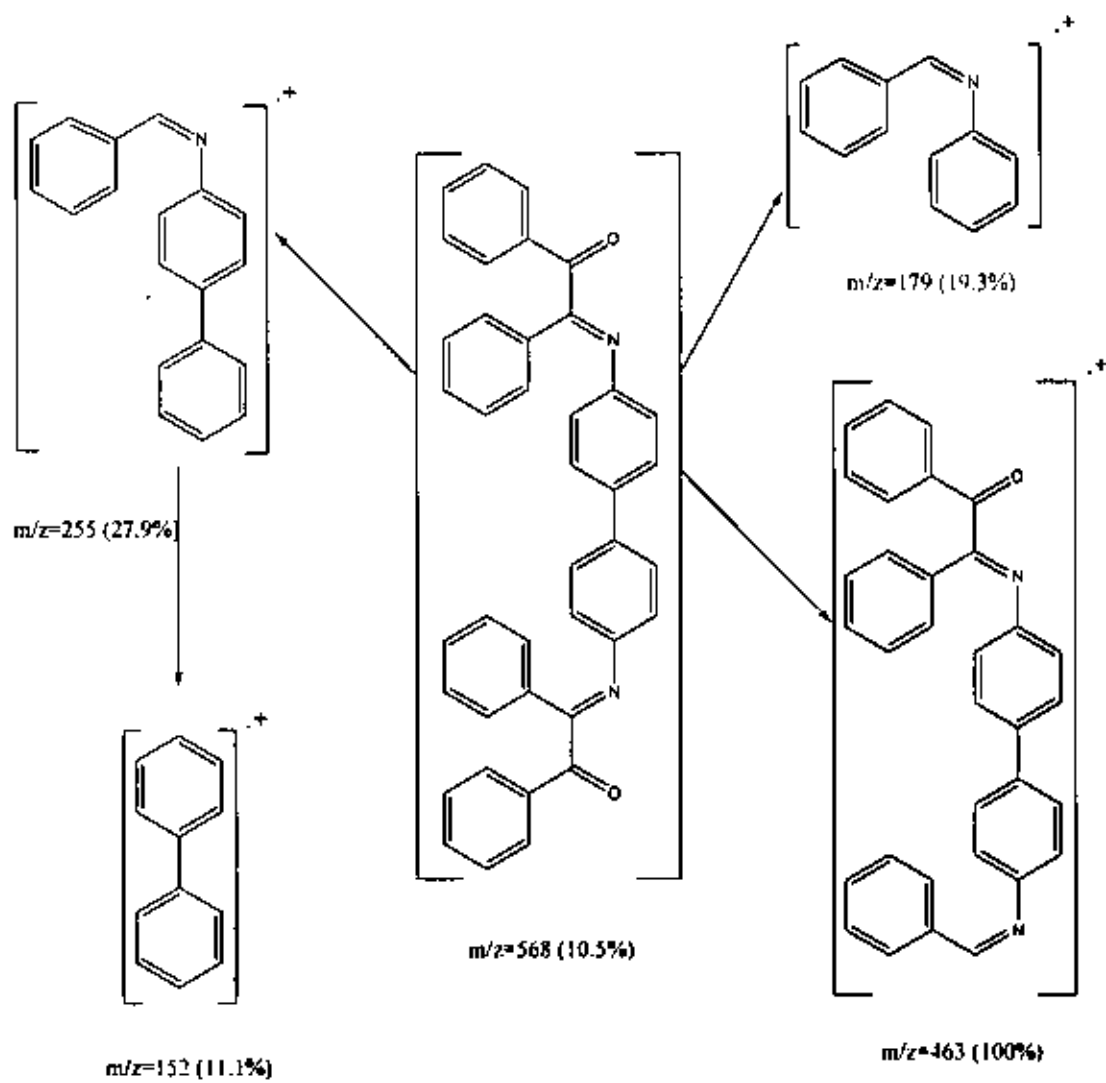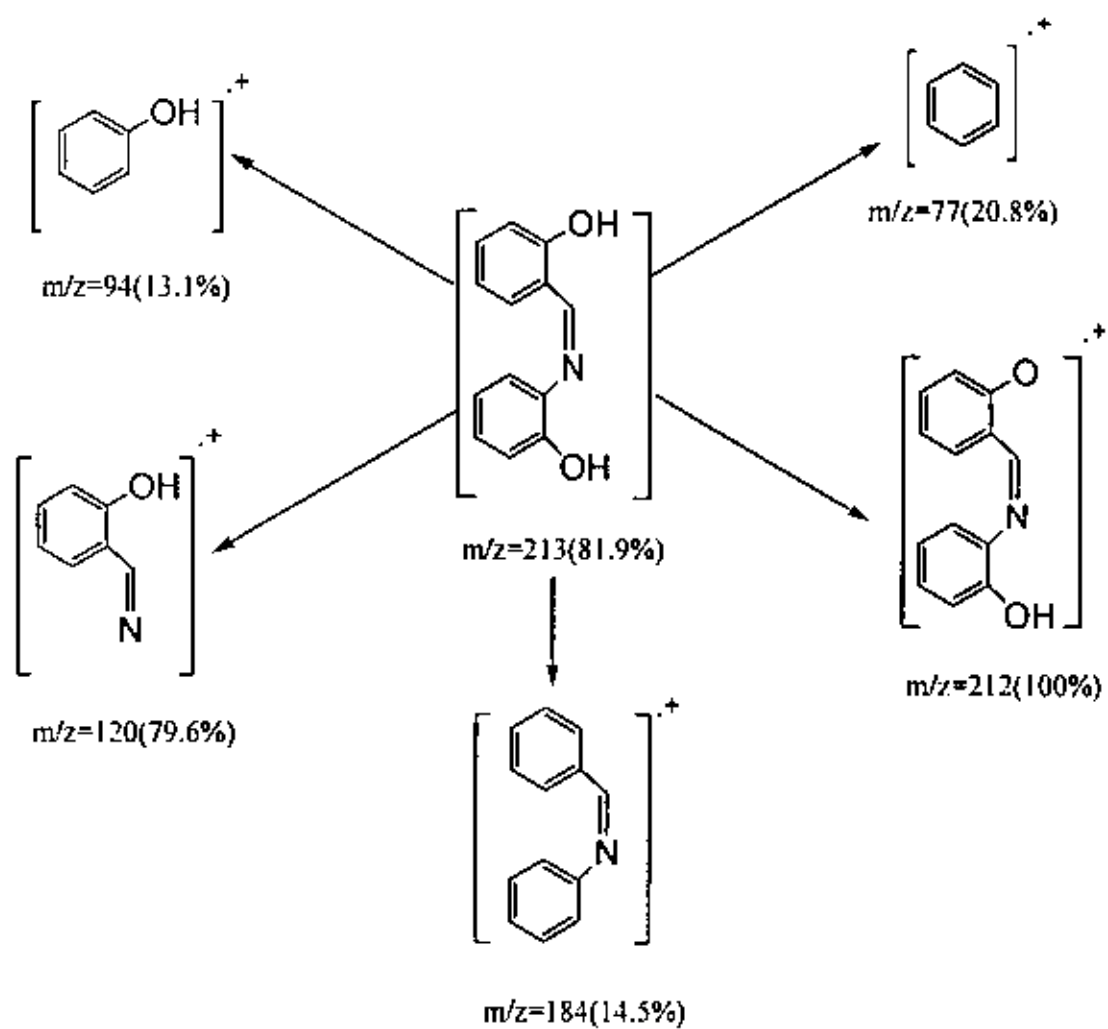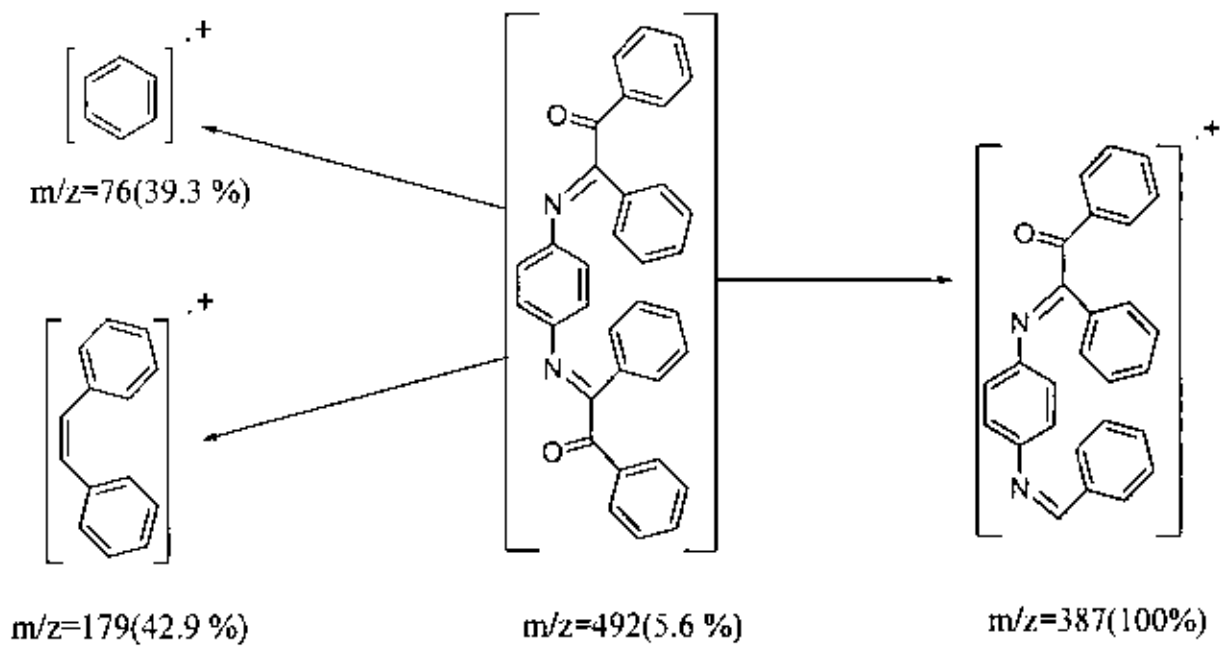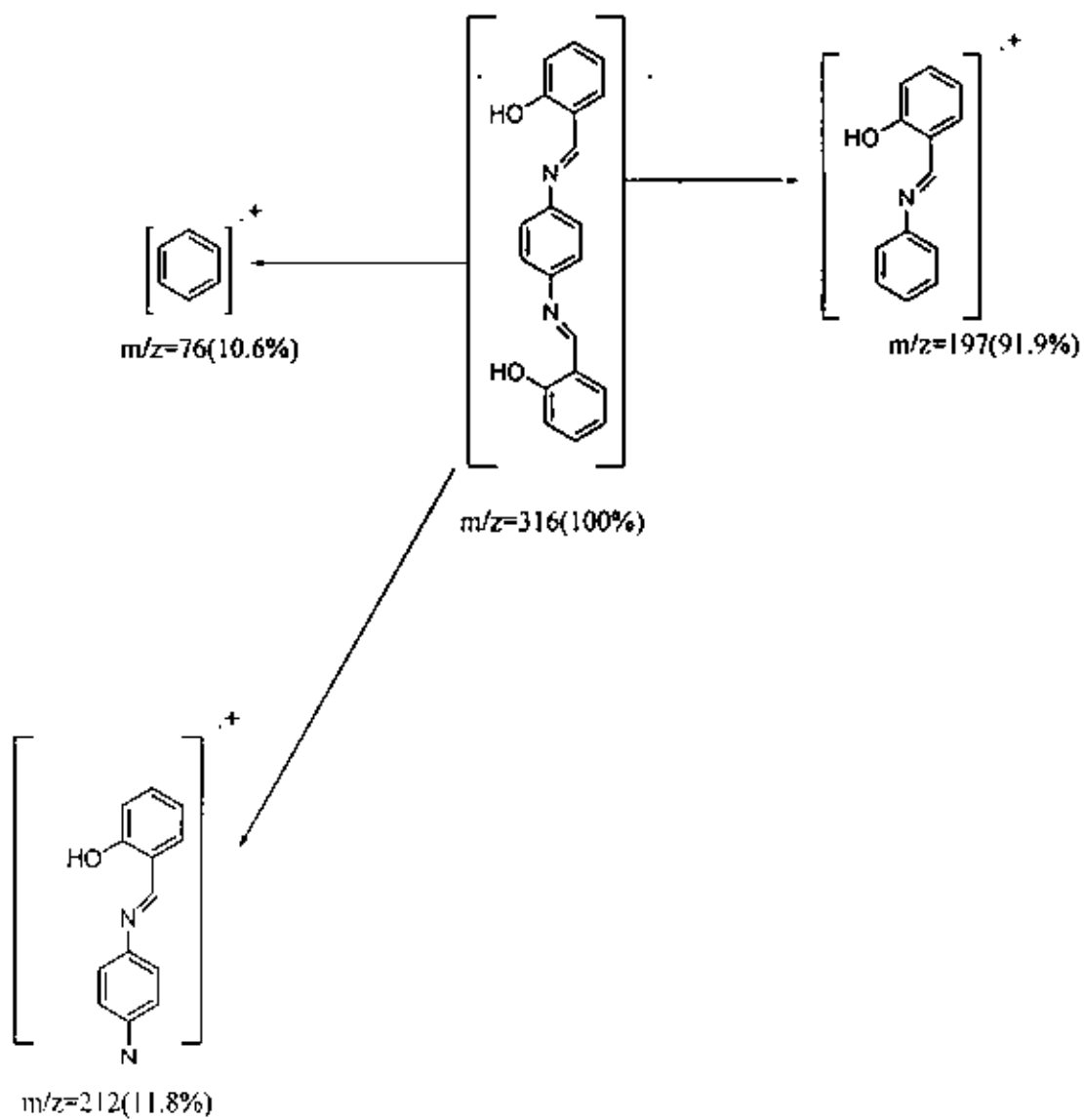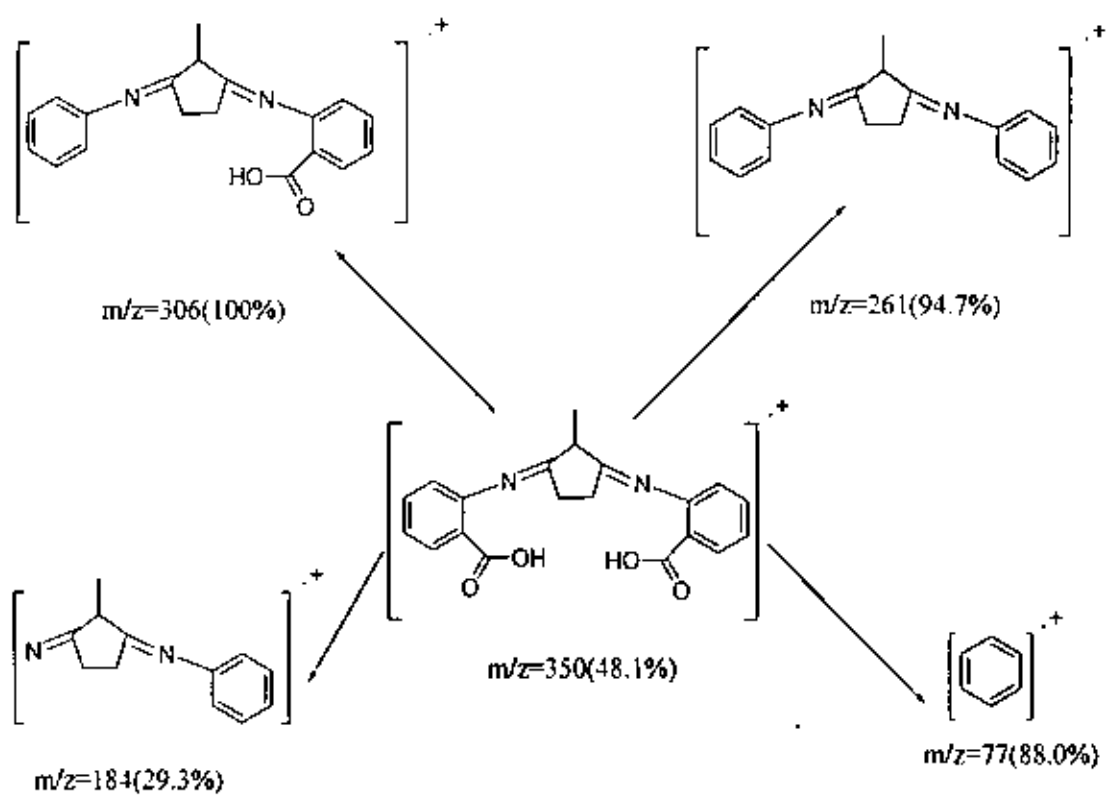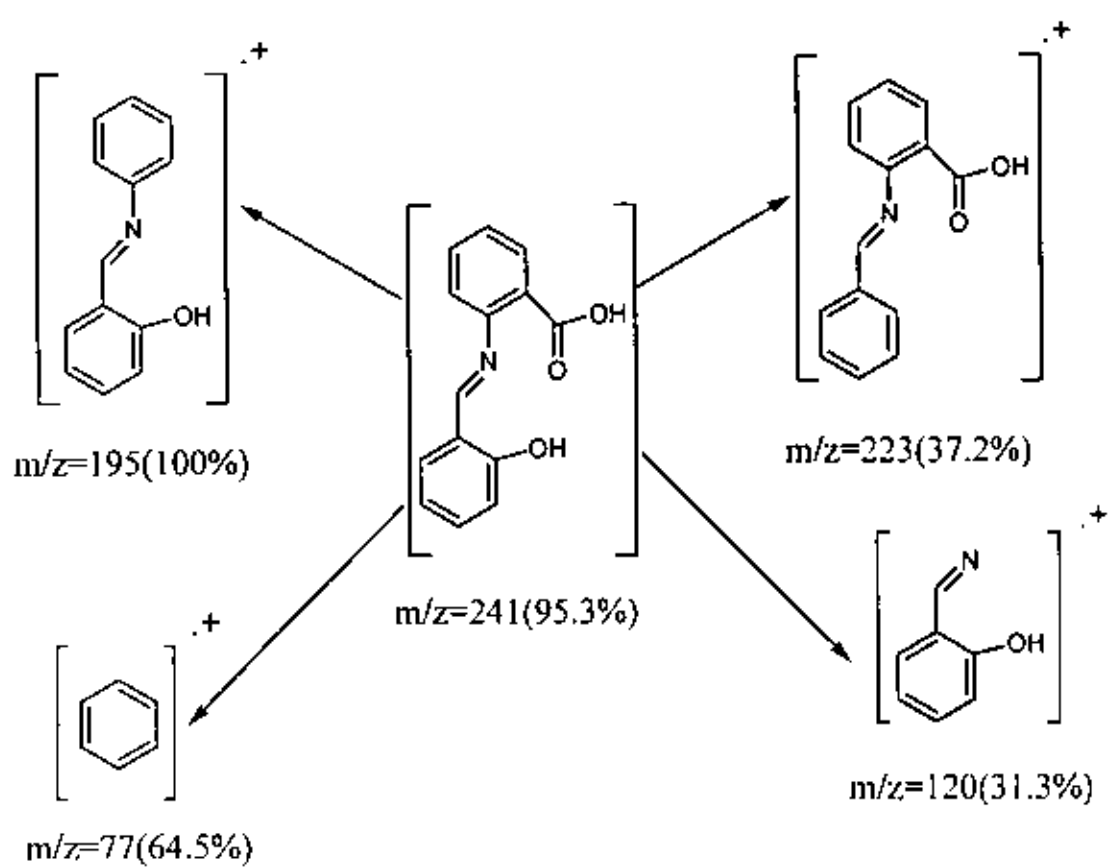
Scheme 6

# APPENDIX

## Suggested geometrical structures for the Schiff base ligands and metal complexes under investigation
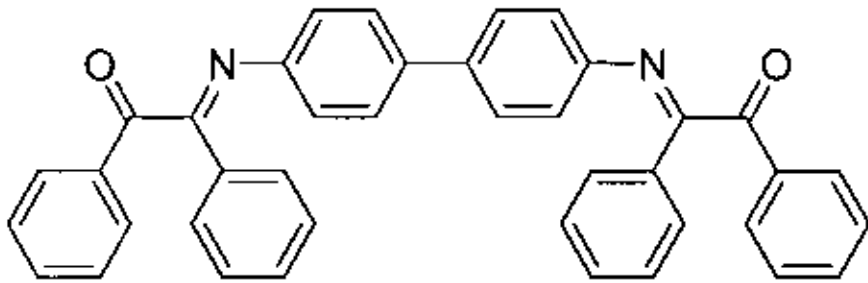
Structure of $(L^1)$ ligand
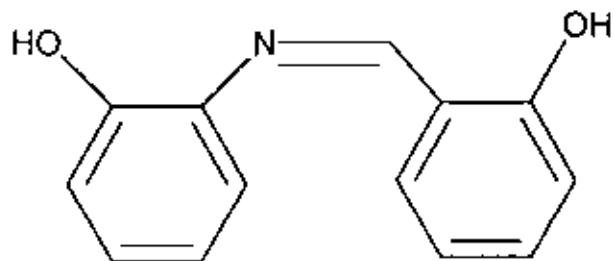


Structure of $(H_2L^2)$ ligand
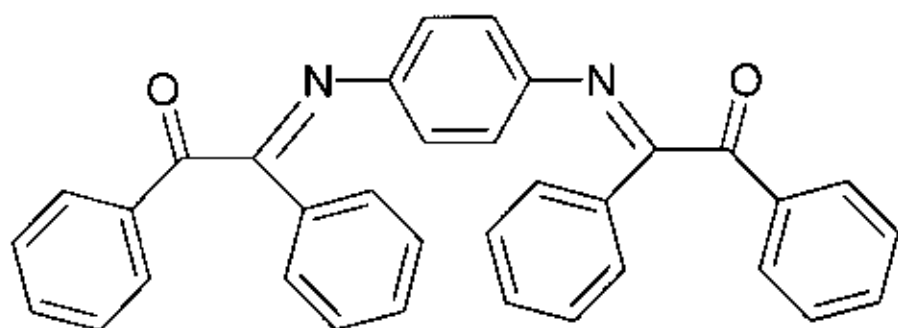
Structure of ($L^3$) ligand
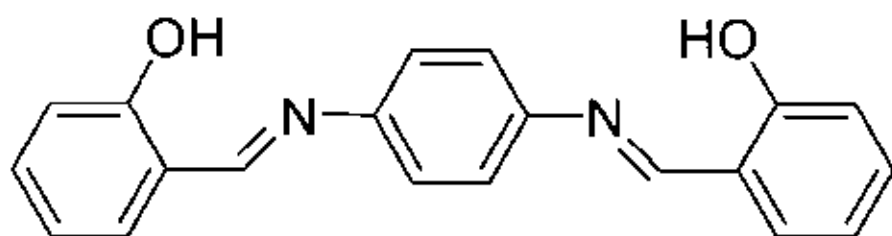


Structure of ($H_2L^4$) ligand
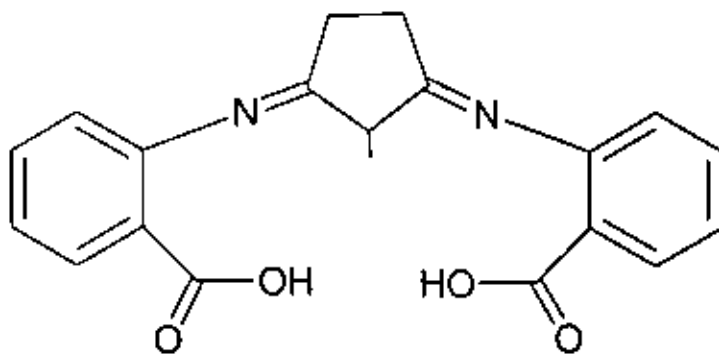
Structure of $(H_2L^5)$ ligand
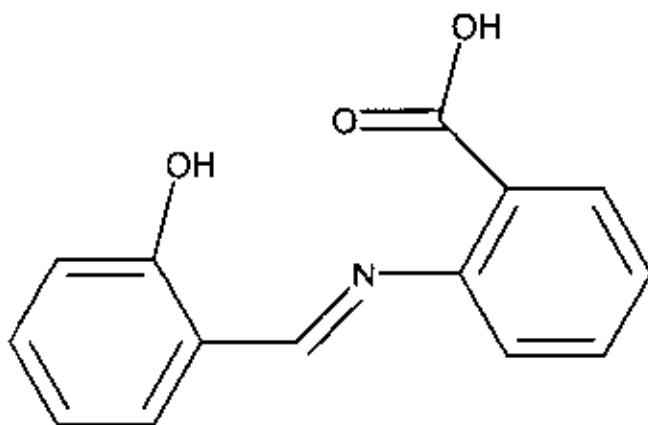


Structure of $(H_2L^6)$ ligand
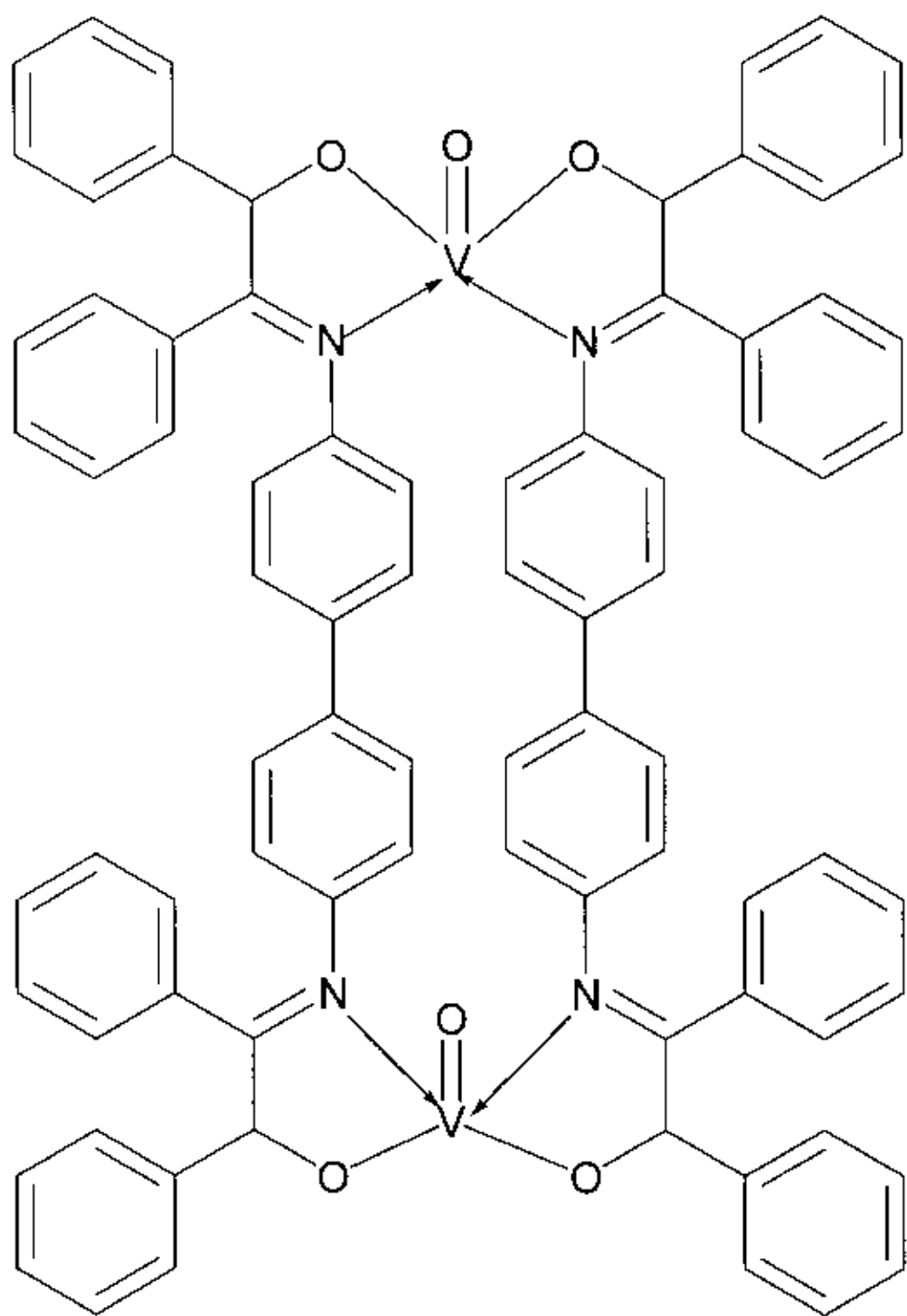
Structure of $(VOL^1)_2 \cdot 5H_2O$ Complex
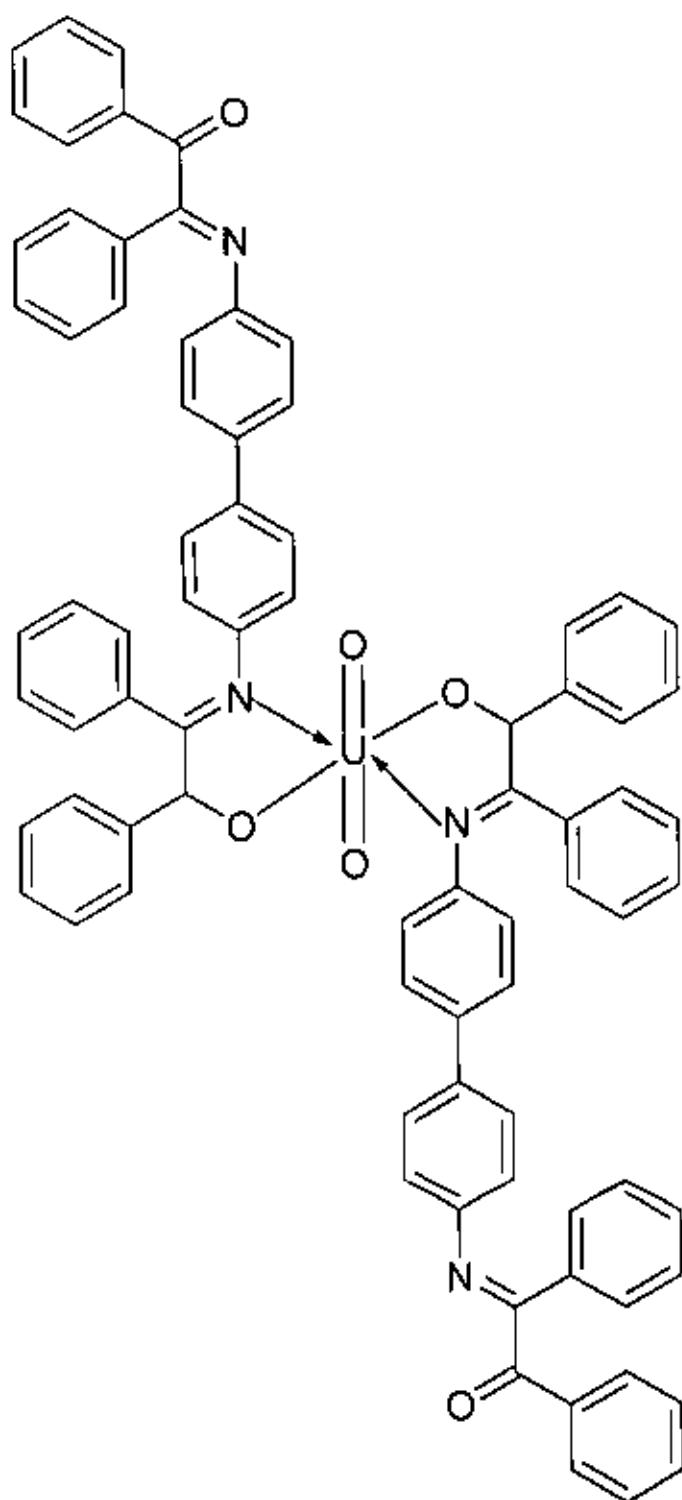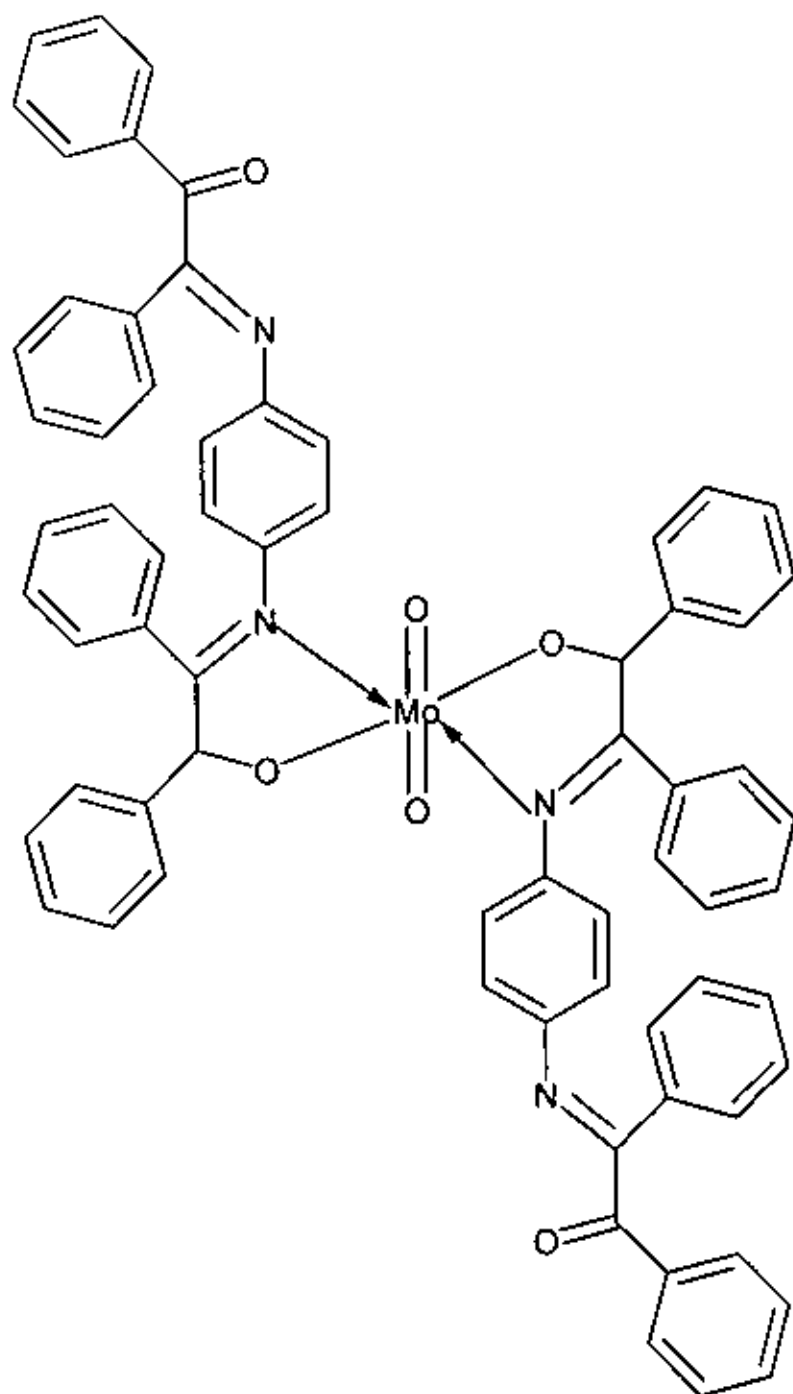
Structure of $UO_2(L^1)_2 \cdot 9H_2O$ Complex
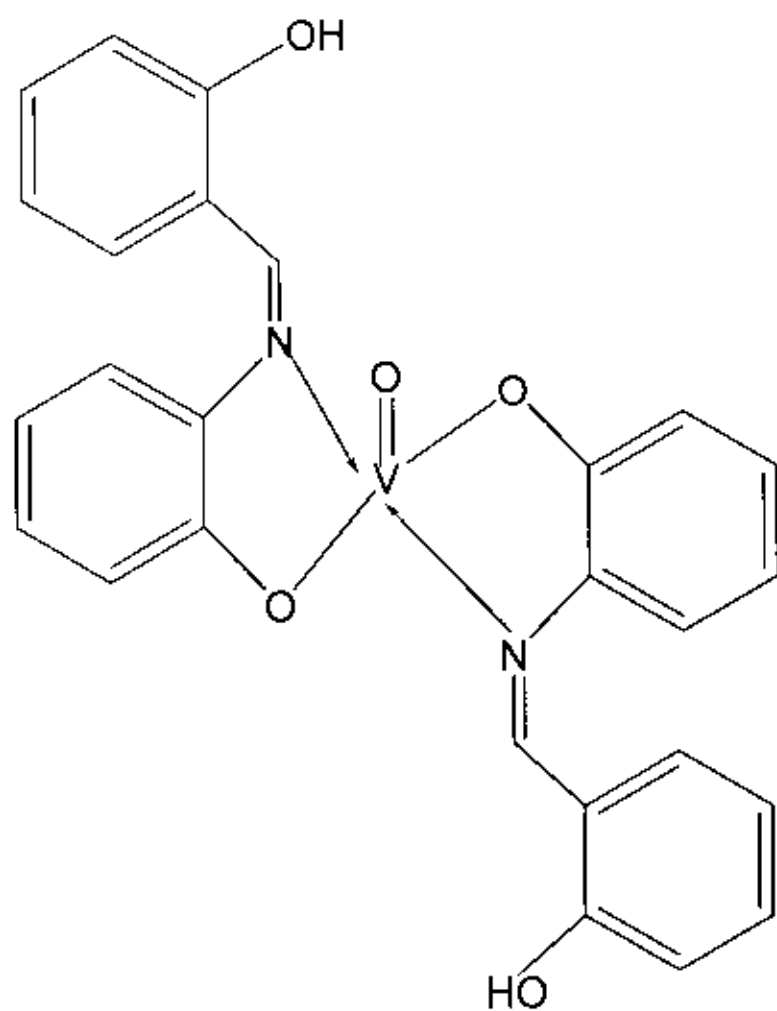
Structure of VO $(H_2L^2)_2 . 2H_2O$ Complex
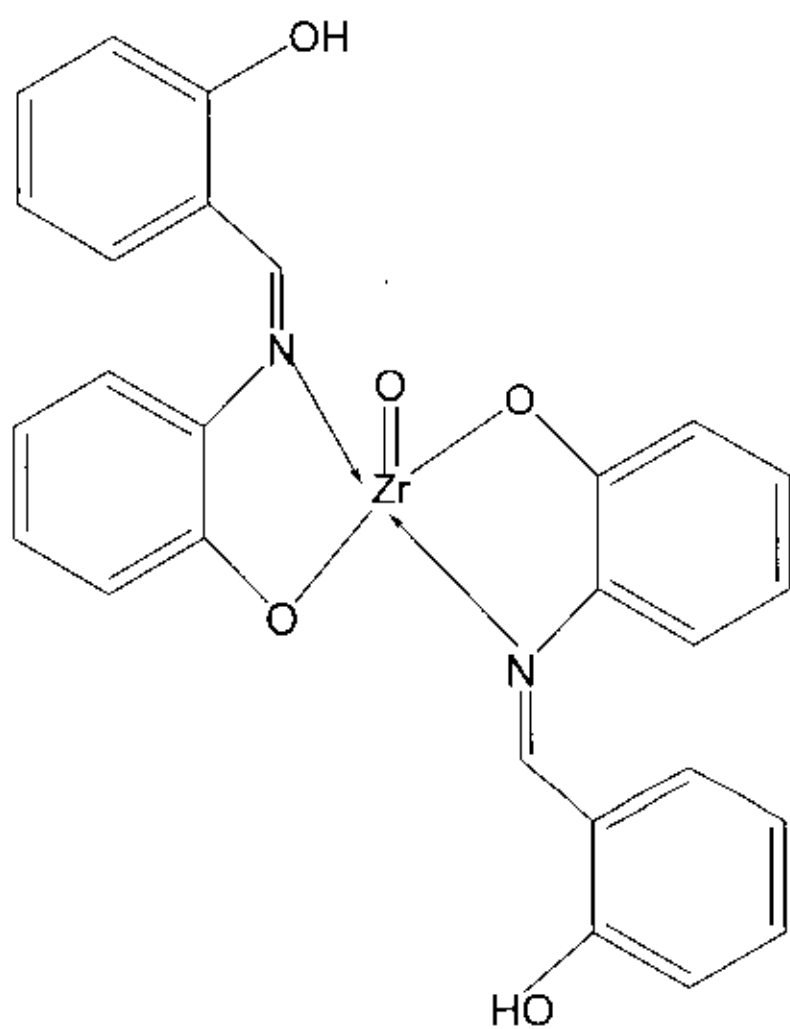
Structure of ZrO $(H_2L^2)_2.3H_2O$ Complex
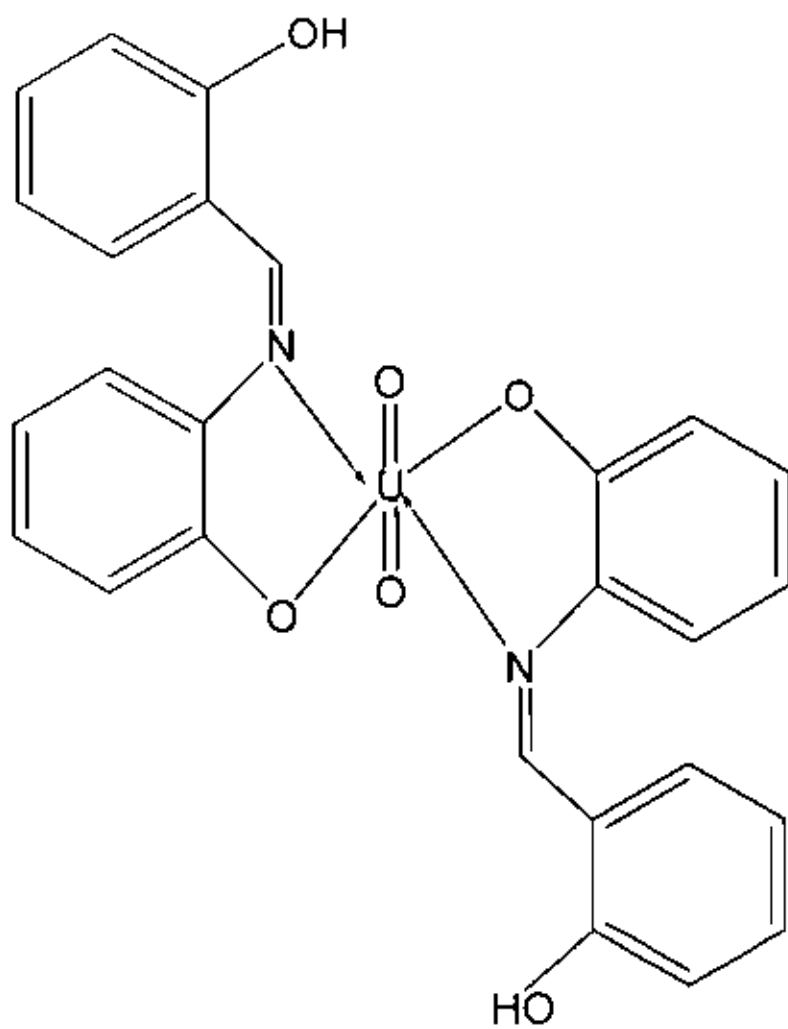
Structure of $UO_2(H_2L^2)_2 \cdot 3H_2O$ Complex

Structure of $MoO_2 (L^3)_2 .2H_2O$ Complex
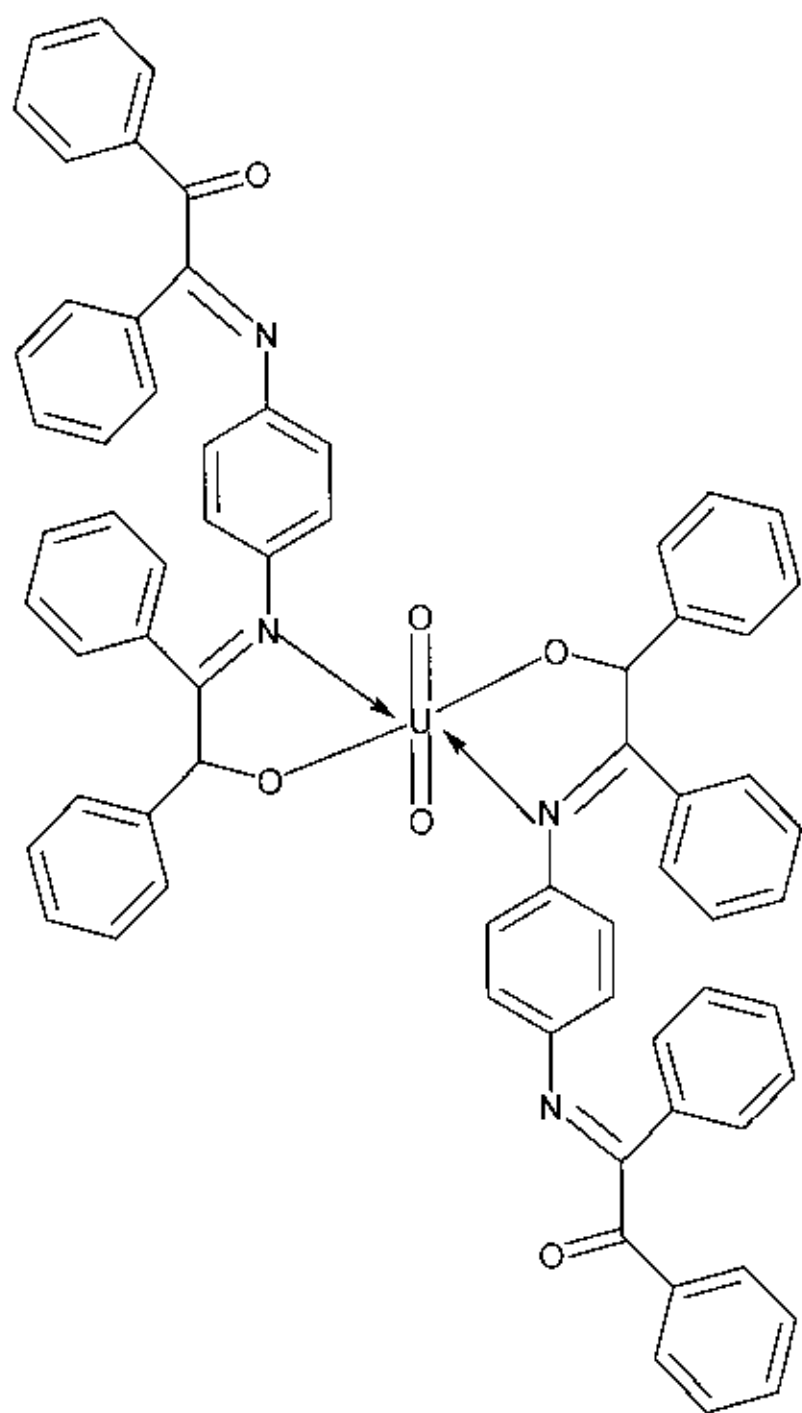
Structure of $UO_2 (L^3)_2 .8H_2O$ Complex
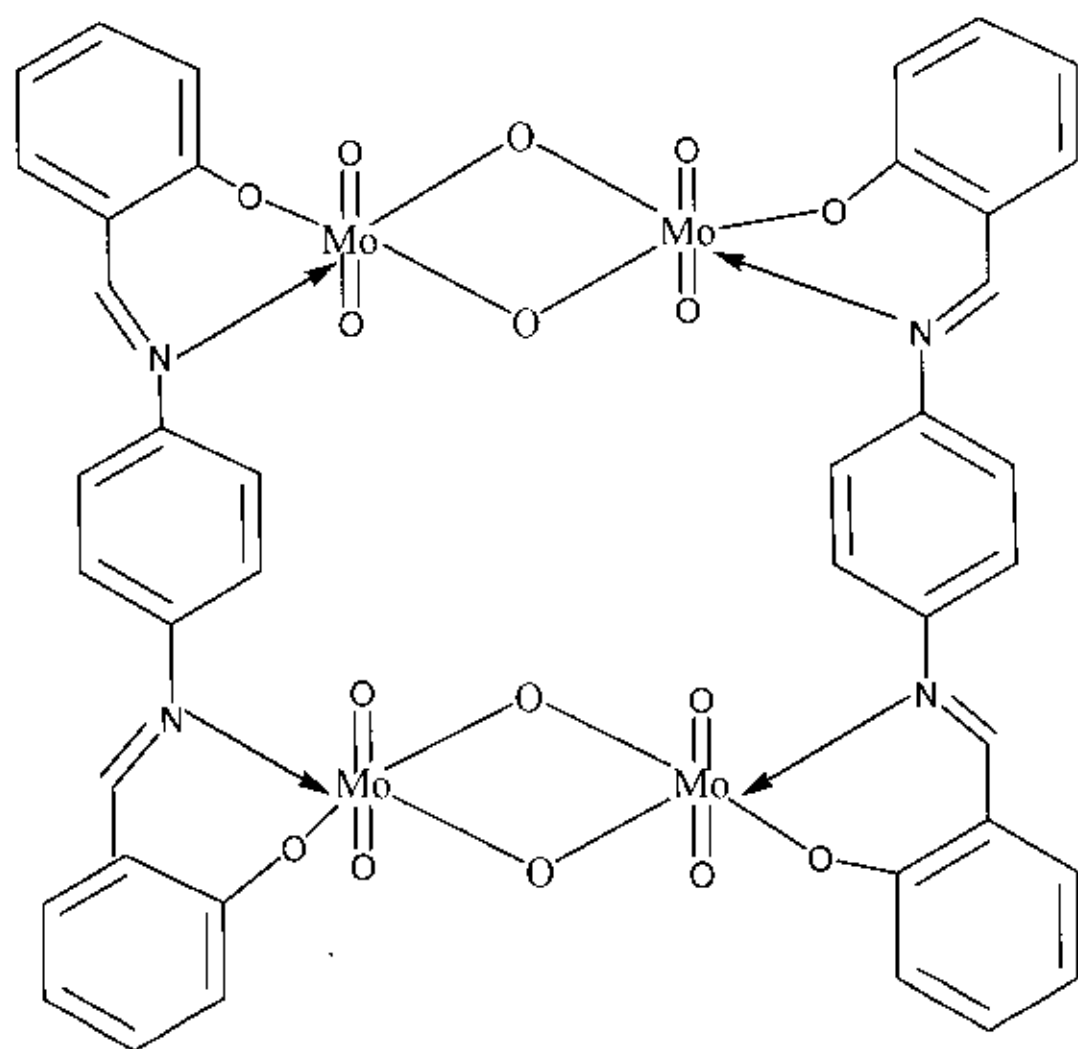
Structure of $(MoO_3)_4 (H_2L^4)_2$ Complex
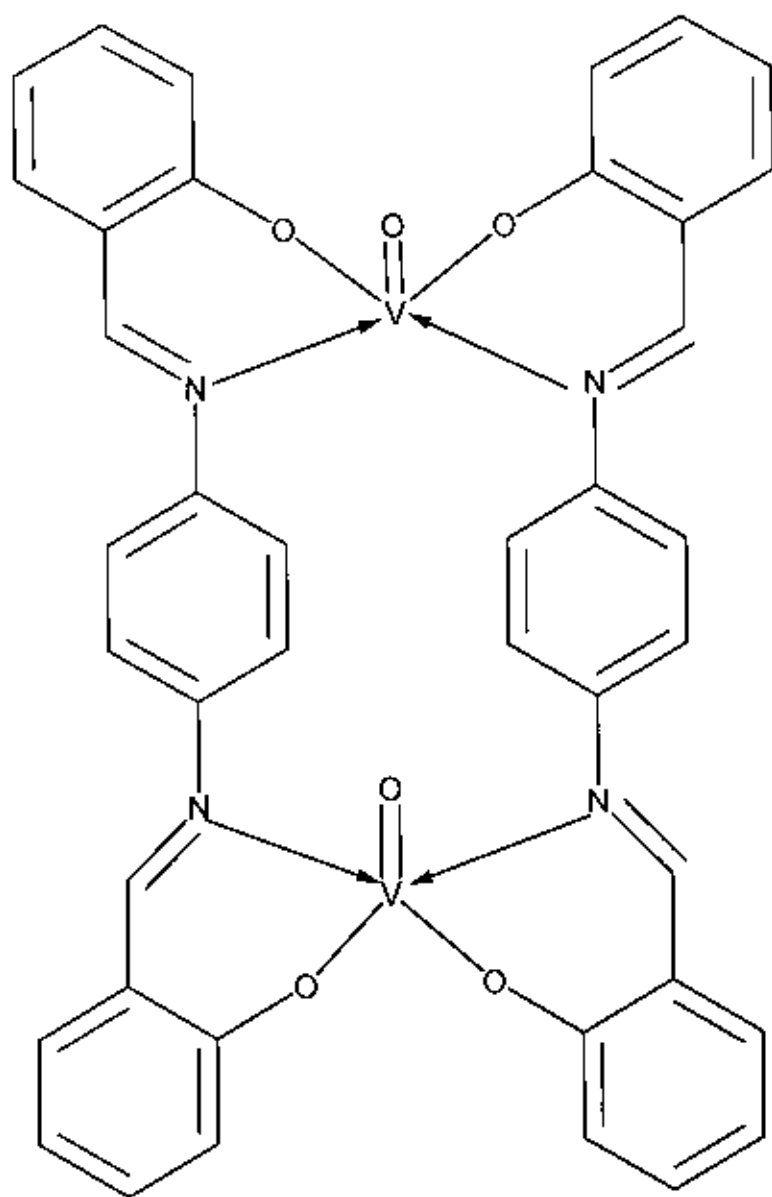
Structure of $(VO\,H_2L^4)_2\,.2H_2O$ Complex
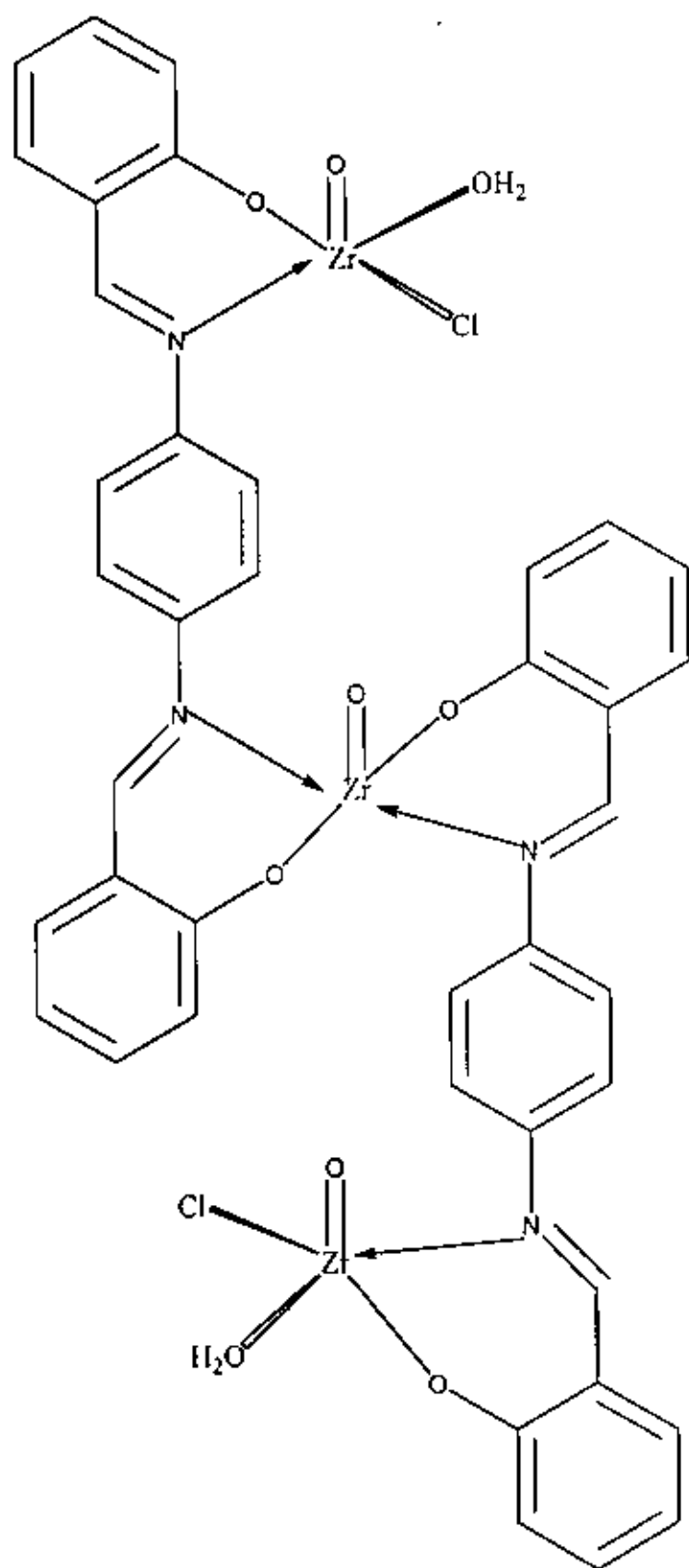
Structure of $(ZrO)_3 (H_2L^4.Cl.H_2O)_2 .9H_2O$ Complex
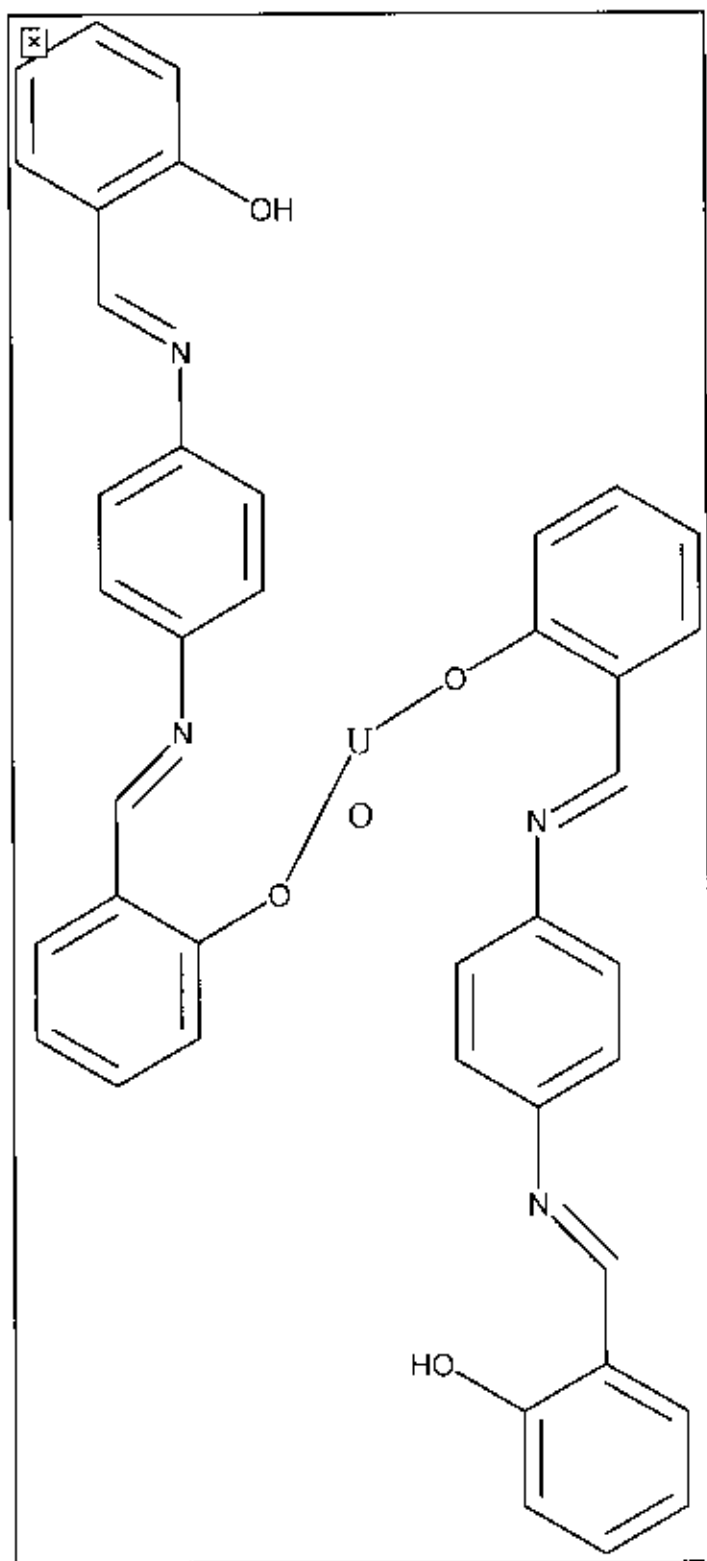
Structure of UO$_2$ (H$_2$L$^4$)$_2$ Complex
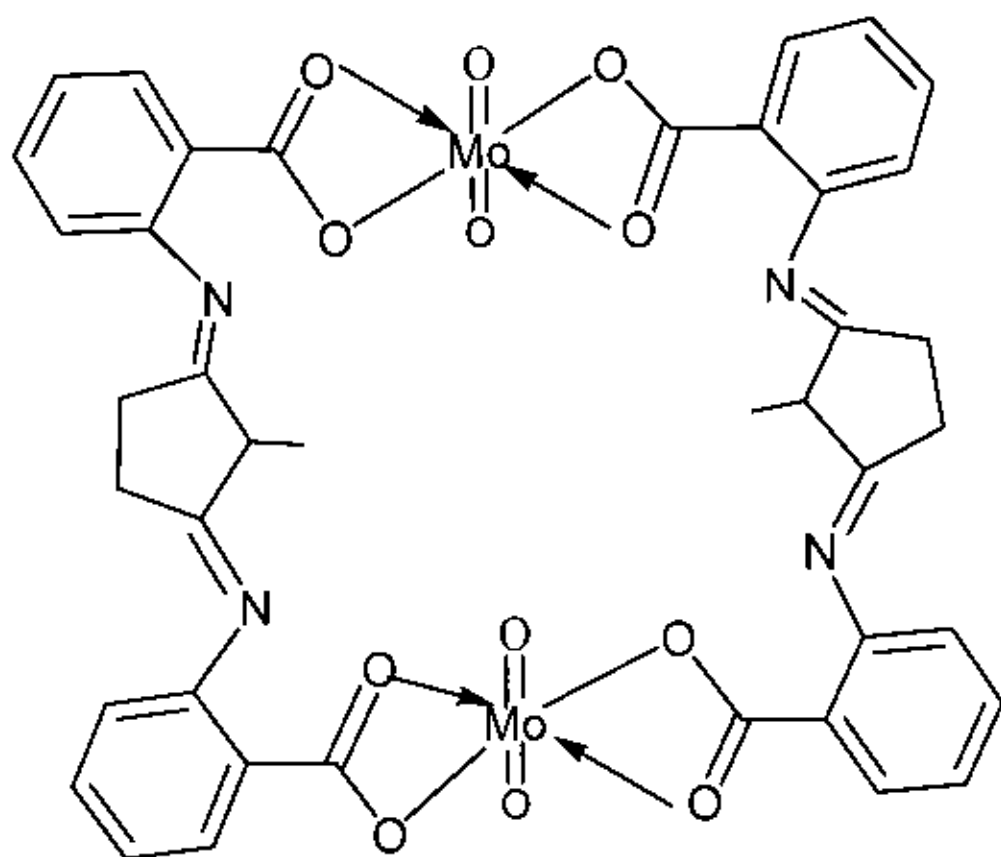
Structure of $(MoO_2H_2L^5)_2.16H_2O$ Complex
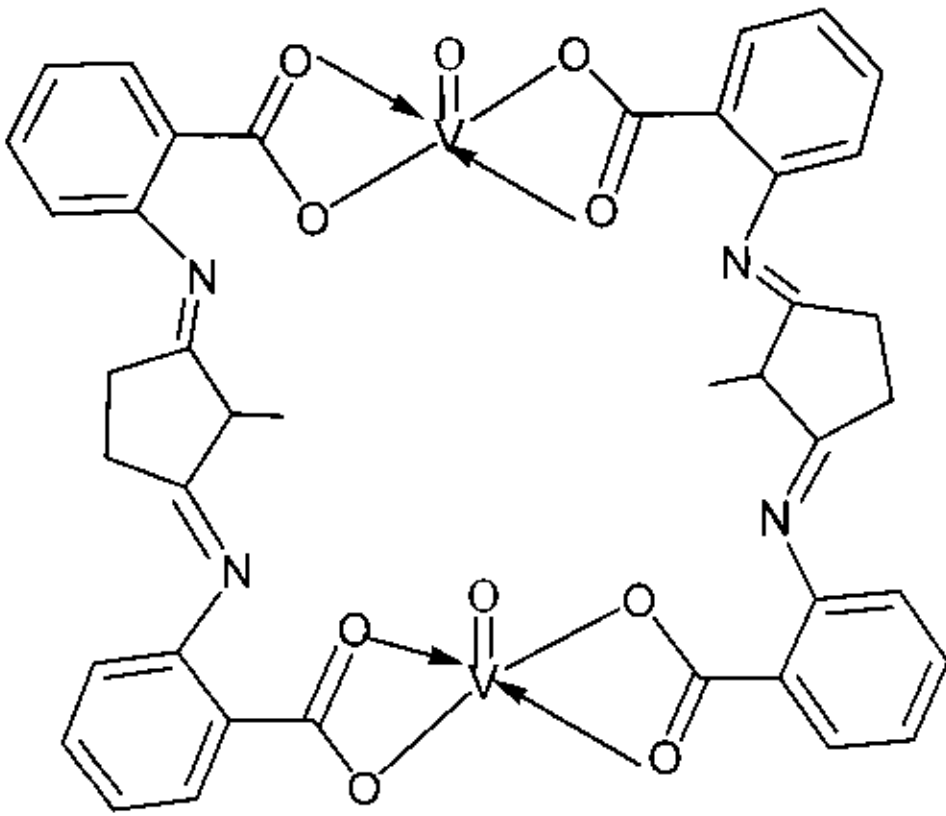
Structure of $(VO \: H_2L^5)_2 \cdot 6H_2O$ Complex
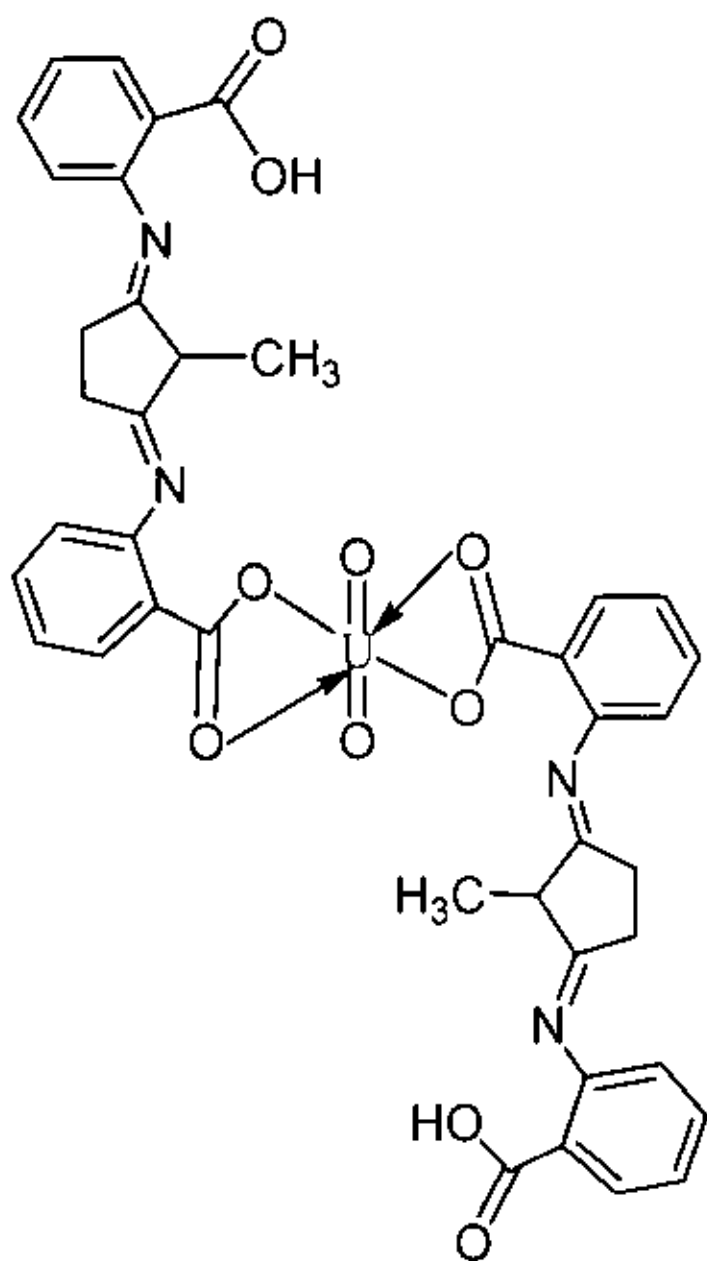
Structure of $UO_2 (H_2L^5)_2 . 8H_2O$ Complex
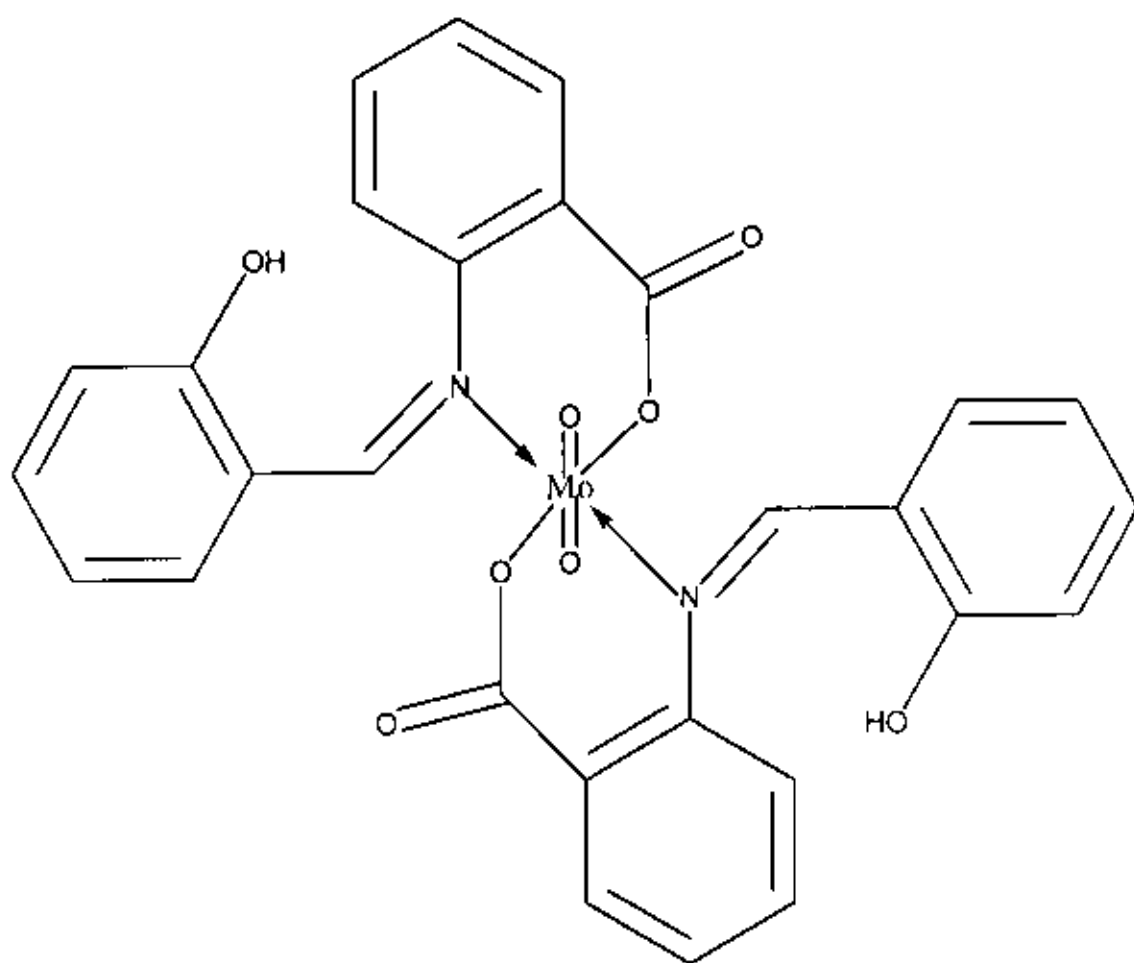
Structure of $MoO_2 (H_2L^6)_2 . 12H_2O$ Complex
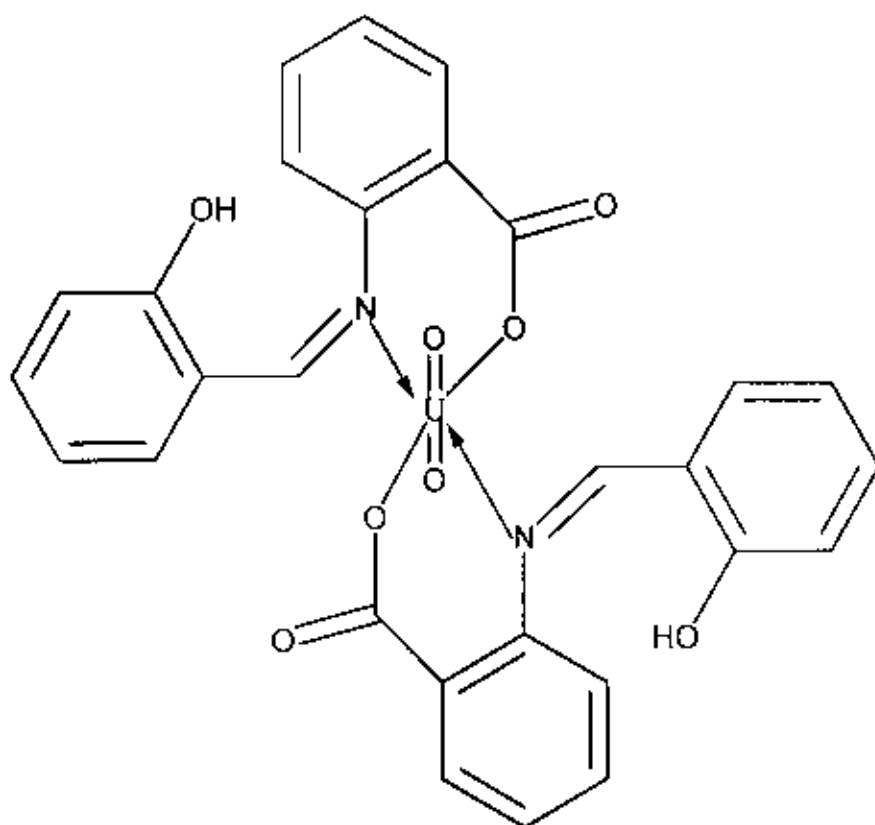
Structure of $UO_2(H_2L^6)_2.4H_2O$ Complex

# Conclusion

The o-aminobenzoicacid, o-amino phenol, Benzidin and 1,4-phenylenediamine reacts with Benzil, Salicylaldehyde, and 2-methlyc yclopentane-1,3-dione, the reaction produced are the Schiff base ligands $L^1$ $[C_{40}H_{28}N_2O_2]$, $H_2L^2$ $[C_{13}H_{11}NO_2]$, $L^3$ $[C_{34}H_{24}N_2O_2]$ , $H_2L^4$ $[C_{20}H_{16}N_2O_2]$, $H_2L^5$ $[C_{20}H_{16}N_2O_4]$ and $H_2L^6$ $[C_{14}H_{11}NO_3]$ have been prepared by direct condensation. The prepared Schiff base ligands have been reacted with some oxy metal ions $VO^{2+}$, $ZrO^{2+}$, $MoO_2^{2+}$ and $UO_2^{2+}$ and produced the corresponding complexes. The analysis of the Schiff base ligands and their complexes showed that the formation of mononuclear and binuclear metal complexes. Were proposed the geometrical structure of the complexes was depending upon the metal ion and the ligand considered during the preparations. For example, $L^1$ and $H_2L^2$ ligands were reacted with $VO^{2+}$ ion forming the mono- and dinuclear vanadyl complexes respectively. Biological activates of the complexes may also be considered for another study.

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ملخص البحث باللغة العربية

هناك الكثير من التطبيقات على قواعد شيف واستخداماتها حيث أنها اشتملت على العديد من التطبيقات المتنوعة وبالأخص عند ارتباطها ببعض العناصر الانتقالية أو أكاسيدها وذلك بسبب زيادة ثباتها وذوبا نيتها العالية في اغلب المذيبات.

وفي هذا البحث تم تحضير عدد ستة مترابطات (Ligands) لقواعد شيف من نوع $N_2O_2$ وتم تحضير هذه المترابطات وذلك بتكثيف بعض من المركبات الامينية الاروماتية مع عدد من الالدهيدات أو الكيتونات تحصلنا على عدد(16) معقد والتي تم دراستها من حيث الشكل الهندسي و التركيب المتوقع.

وأثبتت الدراسات السابقة أن استخدام معقدات الموليبدنيوم و الفاناديوم و اليورانيوم اظهر أهمية كبيرة في كثير من المجالات الحيوية والطبية والبيولوجية في استخدامها كمضادات حيوية لبعض الكائنات الحية الدقيقة الضارة مثل الفيروسات وعلاج بعض الأمراض مثل السرطان و غيرها.

وقد قسم البحث إلى ثلاثة أجزاء وكانت على النحو التالي :

الفصل الأول المقدمة:

تعتبر قواد شيف من المكبات الهامة في تحضير المترابطات و منها يتم ربطها ببعض العناصر الانتقالية لتكوين معقدات و على سبيل المثال عندما يتم تفاعل الدهيد او كيتون مع مركبات الأمين يتكون مركب ناتج من عملية تكثيف يسمى (بقواعد شيف).

وقد ولحظ في بعض الدراسات السابقة أن قواعد شيف عند ربطها ببعض العناصر الانتقالية قد زادت من فاعليتها البيولوجية و هذه المواد تستخدم كعلاج ضد السرطان ومضادات لأنواع من الفطريات و الميكروبات.

الفصل الثاني الجانب العملي:

يوضح هذا الفصل المواد و المركبات المستخدمة في التحضير وكذلك طرق تحضير المترابطات و معقداتها وفقا لطرق تحضير سابقة.

وهذه المواد هي:

Benzil, Salicylaldehyde,          2-methlycyclopentane-1, 3-dione,

1.4-phenylenediamine          , Benzidin, o-aminobenzoicacid

and o-amino phenol.

اكاسيد العناصر الانتقالية التي تم استخدامها هي :

(ZrO, VO, MoO$_2$ and UO$_2$ )

الفصل الثالث النتائج والمناقشة:

يوضح هذا الفصل نتائج التحاليل التي تم إجراؤها و الجدول رقم (1) يوضح نتائج التحليل العنصري (Elemental analysis) و درجة الانصهار (Melting point) .

والجدول رقم (2) يوضح تحليل طيف الأشعة تحت الحمراء (Infrared spectra) .

والجدول رقم (3) يوضح تحليل الأشعة فوق البنفسجية (Electronic spectra) و تحليل

العزم المغناطيسي (Magnetic moment) .

و قد تم إجراء تحليل طيف الكتلة (Mass spectra)    للمترابطات فقط.

ومن هذه الدراسة تم توقع التراكيب المقترحة لستة عشر معقدا.

ملخص البحث باللغة العربية

# كلية العلوم

## قسم الكيمياء

### عنوان البحث

تحضير و الدراسات الطيفية لبعض مركبات أوكسي
المعادن مع عضاعد الأبين

مقدمة من الطالب

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قسم الكيمياء

سرت – ليبيا

# تحضير والدراسات الطيفية لبعض مركبات أوكسي المعادن مع عضائد الأيمين

بحث مقدم كجزء من متطلبات استكمال درجة الماجستير في علم الكيمياء

إعداد

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