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Synthesis and structural characterizatinof Pd(II) and Pt(II) complexes with N ,P and S donors.

A Thesis
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By

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Abstract

Taking in account the basic ideas in coordination chemistry governing the structure and reactivity of these compounds especially those of Palladium and Platinum complexes, a new set of Pd(II) and Pt(II) square planar complexes with varying structural isomerism have been prepared and studied. Their structure and spectral behavior have been discussed based on hard and soft acid base principles, back π-bonding, and redox behavior. Another $MCl_2(DMSO)_2$ [M=Pd (II) or Pt (II) complexes were prepared and used as starting materials to prepare the following types of complexes ;

(1)- The reaction of both trans –Pd and cis- Pt complexes with Dithiooxamide (DTO) in ethanol gave cis MCl_2 (DTO)-N, S).

(2)- The reaction of cis –MCl_2 (DTO) with a series of neutral N-and P-donor ligand s in ethanol gave new complexes with different geometries;

* Triphenylphosphine (PPh_3) and triphenylamine (NPh_3) replace the Cl-trans to N of DTO giving N-trans-[MCl (L) (DTO-N, S)], (L=PPh_3 or NPh_3).

 * The reaction of linear Benzidine (Bnz) and $3,3^-,5,5^-$ tetremethylbenzidine (TMBnz) with MCl_2 (DTO) in ethanol gave the tetra nuclear cage complexes [M_4 (DTO)$_4$L$_4$] Cl_4. [L=Bnz orTMBnz]

*$2,2^-$ –dibyridyl (dipy) react with cis –$PtCl_2(DMSO)_2$ in ethanol to give PtCl2 (Dipy), the later gave the ionic mixed ligand complex [Pt(Dipy) (DTO-N,S)]Cl upon reaction with DTO in ethanol.

All the prepared complexes were studied using FT-IR, UV-Vis spectroscopy, and magnetic susceptibility measurement. The metal content was determined using Atomic Absorption apparatus.

The structural changes were discussed, and the tools of basic ideas of coordination with the aid of group's theoretical calculations for some complexes show to be very helpfull in understanding the structural change.

The antibacterial activity against *Escherichia Coli* and *Staphylococcus aureus*, of all the prepared compounds, were pursued.

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Supervisor Certification

We certify that this thesis was prepared by **"Adel Ahmed Awad"**, under our supervision at Al-Nahrain University, College of Science, in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

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Date: /   /2005

We, the Examining Committee, certify that we have read this thesis and examined the student in its contents, and that , according to our opinion ,it is accepted as a thesis for the degree of Master of Science in Chemistry.

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Introduction

1.1-Coordination Chemistry –structural consideration:-

Without the armory of physical methods available to the modern chemist, in particular X-ray crystallography, the early workers were obliged to rely on purely chemical methods to identify the more important of the stereochemistry. They did this during the next 20year, mainly by preparing vast numbers of complexes of various metals of such stereochemistry that the number of isomers which could be produced would distinguish between alternative stereochemistry [1].

The more important factors determining the most favorable coordination number for a particular metal and ligand are summarized below. However it is important to realize that, with so many factors involved, it is not difficult to provide facile explanation of varying degrees of plausibility for most experimented observations, and it is therefore prudent to treat such explanation with caution.

If electrostatic forces are dominate the attraction between the metal and the ligands should exceed the destabilizing repulsions between the ligand, the attraction are proportional to the product of the charges on the metal and the ligand whereas the repulsions are proportional to the square of the ligandcharge.

The concept of the coordinate bond as an interaction between a cation and anion or molecule possessing a lone pair of electrons can be accepted before specifying nature of the interaction indeed ,it is now evident that in different complexes the bond can span the whole range from electrostatic to covalent character[2] .

One of the earliest correlations was the Irving-Williams series of stability for a given ligand, the stability of complexes with dipositive

metal ion follows the order $Ba^{+2} < Sr^{+2} < Ca^{+2} < Mg^{+2} < Sc^{+2} < Ti^{+2} < V^{+2} < Cr^{+2} < Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$

This order arises in part from decreases in size across the series and in part from the ligand field effects.

A second observation is that certain ligands form their most stable complexes with metal ions such as Ag^+ , Hg^{+2} , and pt^{+2} but other ligands seem to prefers ions such as Al^{+3} , Ti^{+4}, and Co^{+3}. Ligands and metal ions were classified as belonging to type (a) or (b) according to their preferential bonding [3]. Class (a) metal ions include those of alkali metals, and lighter transition metal in higher oxidation states such as Ti^{+4}, Cr^{+3}, and hydrogen ion, H^+.

Class (b) metal ions include those of heaver transition metals, and those in lower oxidation states such as Ca^+, Ag^+,.... Pd^{+2} and Pt^{+2}. According to their preferences toward either class (a) or (b), respectively

Tendency to complexes with Class (a) metal ion.	Tendency to complexes with class(b) metal ion
N>>P>As>Sb	N<<P>As>Sb
O>>S>Se>Te	O<<S<Se≈Te
F>Cl>Br>I	F<Cl<Br<I

for example , phosphines (R_3P) and thioethers (R_2S) have much greater tendency to coordination with Hg^{+2} ,Pd^{+2} and Pt^{+2} but ammonia , amines (R_3N) prefer Be^{+2} , Ti^{+4} and Co^{+3}. Pearson[4] has suggest the terms "hard" and "soft" to describe the members of class (a) and (b).

A thorough discussion of the factors operating in hard and soft interactions will be postponed temporarily but may be noted now that the hard species , both acids and bases , tend to be small , slightly polarizable species and soft acid and base tend to be large and more polarizable .

Pearson has suggested a simple rule (sometimes called Pearson's principle) for predicting the stability of complexes formed between acids and bases.

Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases. It should be noted that his statement is not an explanation or a theory, but a simple rule of thump which enable the user to predict qualitatively the relative stability of acid- base adducts.

An important point to remember in considering the information is that the terms hard and soft are relative and that there is no sharp dividing line between them.

This is illustrated in part by the third theory,"borderline" for both acids and bases. But even within a group of hard or soft, not all will have equivalent hardness or softness.

Thus although all alkali metal ions are hard, the larger more polarizable cesium ion will be somewhat softer than the lithium ion. Similarly, although nitrogen is usually hard because of its small size, the presence of polarizable substituents can affect its behavior. Pyridine, for example, is sufficiently softer than ammonia to be considered borderline [5].

Hardness and softness refer to special stability of hard-hard and soft-soft interactions and should be carefully distinguished from inherent acid or base.

It is possible for a strong acid or base to displace a weaker one, even though this appears to violate the principle of hard and soft acids and basis strength. For example, the stronger, softer base, the sulfite ion, can displace the weak, hard base, fluoride ion, from the hard acid, the proton, H^+.

The Irving-Williams series of increasing stability (Ba^{2+}) to (Cu^{2+}) is a measure of increasing inherent acidity of the metal (largely due to decreasing size). Super-imposed upon this is a hardness-softness factor in

which the softer species coming later in the series (greater number of d-electron) favor ligands (S>N>O). The harder alkaline earth and early transition metals ion (few or no d-electron) preferentially bind in the order (O>N>S) [6]

Although the hard-soft rule is basically a pragmatic one allowing the prediction of chemical properties, it is of interest to investigate the theoretical basis of the effect.

In this regard, there is no complete unanimity among chemists concerning the relative importance of the various possible factors that might affect the strength of hard-hard and soft-soft interactions [7].

1.2-Palladium and platinum complexes:-

1.2.1-Palladium Complexes:

Palladium is one of the (4d) transition elements and has the outer electronic configuration ($4d^{10}$) with completely filled (4d) shell which is quite easy to break. The most characteristic feature in its chemistry is its similarity with platinum, its (5d) congener.

It differs from platinum in that it is more reactive and this is reflected in the chemistry of the metal in various oxidation states. Palladium has a well-established chemistry in the (0, I, II) and (IV) oxidation state.

Palladium (IV) complexes are less stable than the corresponding platinum compounds and are readily reduced to palladium (II). Palladium (II) is the dominate oxidation state and usually the compounds are diamagnetic with low spin (d^8). It is generally regarded as a class b (soft) metal and this is reflected in the rich chemistry with sulfhur and phosphorus donor ligand. However, palladium (II) will also complex with hard ligands such as

oxygen and nitrogen. There is also an extensive organometallic chemistry of palladium (II), which has been dealt within a companion volume [8].

Palladium (II) is a class b or "soft" metal ion and therefore generally forms stronger complexes with sulphur donors than with oxygen donor ligands. A comparison of the complexes of the simple oxygen and sulphur ligands shows that (H_2O) and (ROH) form more stable complexes than (H_2S) and (RSH) that (OH^-) forms complexes comparably more stablethan (SH^-),and that (R_2O) and (RO^{1-}) form very much less stable complexes than (R_2S) and (RS^-) [9].

Another contribution to the strength of the palladium (II) sulphur bond could be made by (π) back-donation of electron density from the metal atom .The empty, relatively low energy (d) orbital on sulphur, on the other hand, both electrostatic and covalent descriptions of the (σ) bonding in the complexes of the anionic ligand suggest that the stability should decrease in the order $RO^- > RS^-$. whereas in fact the reverse is found experimentally complexes of palladium (II) with sulphur. Selenium donor ligands generally exhibit similar stabilities, though the actual stability sequence within this group of donor atoms depends on the nature of the other ligands bound of the metal.

Ligands such as sulphite ions, thiosulphate ions that bind to palladium (II) through a sulphur atom generally exhibit a high trans effect as deduced from   preparative studies [10].

However, the trans influence of these ligands is negligible; thus has been deduced, for example, from (IR) stretching frequencies of Pd--Cl bond.

Palladium (II), as a soft metal ion, does not form strong bond with oxygen donors and therefore complexes with unidentate ligands readily undergo substitution reactions.

The chelate effect leads to a greater number of stable complexes for bidentate ligands. Oxygen donor can also be stabilized by incorporation

in a bidentate ligand with other more strongly binding atoms such as nitrogen or sulphur [11].

A wide variety of organic compounds contain nitrogen atoms which are capable of acting as donors in coordination complexes .The strength of the palladium nitrogen bond has led to a large number of stable compounds being prepared. The absence of σ character d orbital for nitrogen leads to the bonds being exclusively in character in the majority of the complexes. The largest class of complexes of this type's [PdX$_2$L$_2$] (x=halide, L=amine), the complexes being readily prepared by addition of the amine with [PdCl$_2$] or [PdCl$_2$ (PhCN) $_2$] inorganic solution. Complexes of the majority of simple amines have been prepared including   recently those of hydroxyl amine [12], aziridine [13] and the trimethyl amine [14]. Normally the Trans isomer (or mixture of isomers) is isolated, though by control of the conditions the pure cis isomer may be obtained.

1.٢ .2-Platinum complexes.

In its compounds platinum can be mono, di, tri, tetra and hexa valent. The tetra valent platinum being the most important in analytical practice.

The synthesis and characterization of certain mixed ligand complexes of platinum (II) and of ligands intermediates required therefore are described. Previous studies of the synthesized and characterized numerous mixed lingand complexes of platinum involving both σ and π bonding mono and bidentate ligands and/ or intermediates were reported but not adequately characterized [15].The one of ligand can have a marked effect upon the binding of another to the same metal atom, as shown in substitution reactions of platinum (II) complexes, where ligands exert

directing effects very similar to those observed in aromatic substitutions [16]. For our purpose the most significant stretching frequency (υ) is that of the bond between the metal atom and ligand atom of the detector ligand. In a series of alkyl platinum complexes trans[pt^{II}XMe (PR$_3$)$_2$] (X=univalent acid radical), it was found that υ(pt-c) of the platinum-methyl bond decreased with increasing trans-effect of the anionic ligand X [17]. However, the trend of these υ(pt-c) values also follows the electro negativities of X, so there is no necessarily any real relation between the trans-directing power of X and the platinum-carbon bond strength in this series of compounds.

We have now extended our studies to uncharged ligands of widely different trans effects, electro negativities, and double-bonding abilities. Detector ligands were chloride and bromide in the series of complexes cis- and trans [PtX$_2$L$_2$], where L: neutral ligand.

In the cis-isomer cis-[PtX$_2$L$_2$], υ(Pt-X) depends greatly on the ligand (L) [18]. There is broad agreement between the patterns for υ(Pt-Cl) and υ(Pt-Br), although several discrepancies exist. Even if some of the υ(Pt-X) frequencies are displaced by coupling with υ (Pt-L), the fact that they have the same relative position is good evidence that we really are studying the effect of (L) upon the strength of the (Pt-X) bond trans to itself [19]. Platinum (II) complexes containing dithiolate (donor) and diimine (accepter) ligand are intensely colored, owing to an absorption that has been attributed to a Pt/S$\rightarrow$ diimine charge-transfer (CT) transition[20,21].. In 1989, complexes luminescent in fluid solution (*e.g.*, Pt (bpy) (tdt): λ_{max}=735 nm; tdt=3, 4-toluenditiolate), probably from a CT excited state.
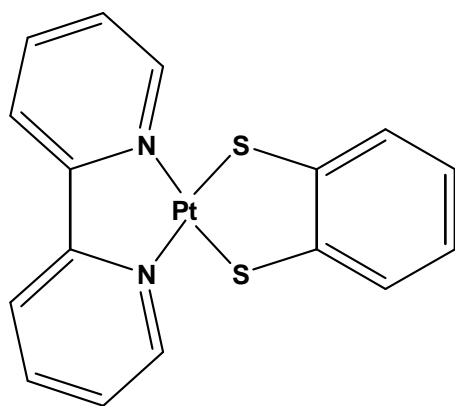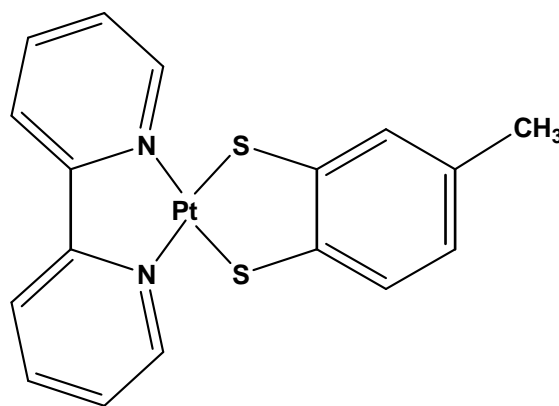
Pt(bpy)(bdt)   **Pt(bpy)(tdt)**

In extensive investigations, Srivastava and co-workers[22] demonstrated that literally dozens of platinum (II) diimine complexes sensitize the formation of singlet oxygen (O_2) from ground-state oxygen ($^3O_2$) In the course of this work, it was established that complexes with thiolate ligands undergo photo induced decomposition in the presence of oxygen [23].

In 1996, the photo oxidation chemistry of two platinum(II) diimine dithionate complexes [Pt(dbbpy)(dpdt)] and Pt(dbbpy)(edt) (dbbpy=4,4′-di-*tert*-buty1-2,2'-bipyridine;dpdt=*meso*-1,2-diphenyl-1,2-ethanedithiolate; edt=1,2- ethanedithiolate)] were examined by Schanze and co-workers[24]. The reactivity of Pt complexes is similar to that of compounds studied by Srivastava; irradiation of an air-saturated solution results in a gradual bleaching of the CT band (466 nm) and other visible charge-transfer features.

1.3- S, N, O and/or P donor ligands:

Several characteristics of palladium (II) chemistry which have promoted recent interest are (1) formation of square-planar complexes and (2) bonding properties intermediate between the first transition series

and the heavy metals. Palladium (II) complexes have played an important role in experimental and theoretical attempts to characterize the electronic structure of square-planar complexes [25,26]. Also, investigations of ligand isomerization and related phenomena have centered around Pd (II) owing to its intermediate bonding properties [27,28]. Previous studies of Pd (II) complexes have been largely restricted to anionic and neutral complexes owing to the absence of convenient method for obtaining the cationic complexes. The preparation and partial characterization of cationic Pd (II) complexes with some common monodentate donors were reported [29,30]. The complex [Pd (DMSO)$_4$] $^{+2}$ is particularly interesting, for it is the first example of a complex containing both sulfur- and oxygen-coordinated dimethylsulphoxides. It was recognized and demonstrated by spectroscopic and X-ray studies [31,32] while DMSO generally associated with metal ion through its oxygen atom, sulfur donation was favored for some cation, such as Pt (II) and Pd (II). Other reports have described complexes of metal ions with sulphoxides in addition to DMSO, most studies have described O complexes, and well-characterized S complexes were known only for DMSO bound to Pt (II) and Pd (II). A number of sulphoxide complexes of platinum (II) have been synthesized, and their infrared and proton magnetic resonance spectra indicate that S is the donor atom. The Pt (II) complexes are of type PtCl$_2$L$_2$ (L= sulphoxide) and far-ir data suggest all have cis configurations except the di-isopropyl sulphoxide complexes. The Pd (II) complexes PdCl$_2$L$_2$ are trans in the solid state but in solution most appear to revert to the halo-bridged binuclear structures Pd$_2$CL$_2$. A large number of compounds containing dimethylsulphoxide (DMSO) as a ligand were prepared [33]. In many cases the structures of the compounds have been infrared from magnetic data and electronic spectra. Realizing at the outset the infrared spectra could also bee of value deducing the structure of many of the compounds .A

possible knowledge of the assignments for DMSO should be known before attempting to assign of observed spectra of the complexes containing DMSO[34] . Complexes of some transition metal and actinide ions with dimethylsulphoxide (DMSO) as ligand exhibit metal-DMSO bonding through the silver atom in the solid phase. Although it is likely that the metal-sulfur bonding is retained when the complex is dissolved (if DMSO is retained as a ligand), there are no studies of solutions to support this expectation at present .Indeed, some studies indicate that change from metal-oxygen to metal-sulfur bonding can occur when the composition of the compound is change[35].

The preparation of large number of dimethylsulphoxide complexes is reported .The structure of some of them have been elucidated on the basis of infrared and visible spectra , magnetic measurement and steric considerations .It appears that oxygen is the donor atom in all cases reported except toward Pd(II) in $[(CH_3)_2SO]_2PdCl_2$ where infrared evidence suggest Pd←S bonding. Sulphoxide ligand has two potential donor atoms. The lighter or more highly charged metal ions favor oxygen coordination while a few heavier charge metals of prefer the sulfur donor site. The proposed [Pd-(DMSO)] X_2 as the first example of a complexes which contains both S- and O-bonded ligands [36,37].

Two S-bonded and two O-bonded ligands in a cis array were inferred primarily from ir spectra. These structural features have now been confirmed by a complex X-ray study[38,39].
The electronic structure of sulphoxides may be represented by a resonance hybrid of the structures:

I   II
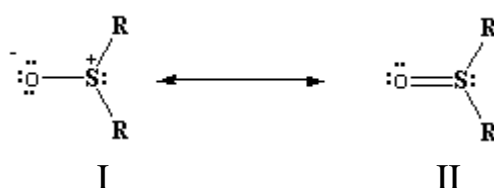
If coordination occurs through oxygen, the contribution of structure I will decrease and result in a decrease in $\upsilon(S=O)$. If coordination occurs through sulfur, the contribution of structure II will decrease and may result in an increase in $\upsilon(S=O)$. It has been concluded that coordination occurs through oxygen in the Co (DMSO) $_6$ ion, since $\upsilon(S=O)$ of this ion absorbs at $1100 – 1053$ cm^{-1} . On the other hand, coordination may occur through sulfur in PdCl$_2$ (DMSO) $_2$ and PtCl$_2$ (DMSO) $_2$. Since $\upsilon(S=O)$ of these compounds (1157-1116 cm) are higher than the value for the free ligand [40].

1.3.1-Dithiooxamide and its metal complexes:-

Dithiooxamide form a class of compounds, which contain the thioamide groups, and contain two soft sulfur atoms beside two hard nitrogen atoms in one molecule [41].

Dithiooxamide, and its derivatives were received more attention during the last decade. The interaction of these ligands with some transition metal ions especially Pd (II), Pt (II) gave a great intersest for versatility from the point of structural.

In 1:1 complexes of N,N$^-$ monosubstituted Dithiooxamide , concluded from infrared spectra that metal such as Ni(II) and Cu (II) are primarily bonded to the N, where as metal such as Hg(II),Pd(II),Pt(II) are bonded to the S atoms .
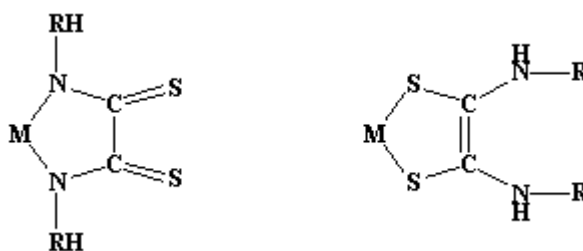
The presence of the "soft" sulfur atoms besides the "hard" nitrogen atom in this thioamide moiety (keeping aside the effects of remainder of the molecules containing it), render these molecules to be potent ligands with a wide diversity and biological importance besides other applications.

The studies of the infrared spectra has shown that in N, N⁻ monosubstituted Dithiooxamide the following canonical forms can be considered [42].
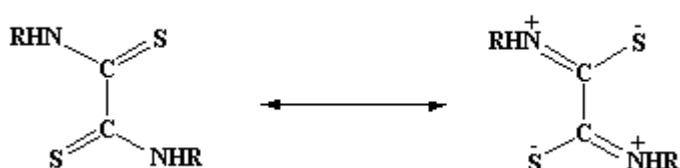
The hydrogen of the thiamine group is removed on complexes formation and the metal can form bonds through both sulfur and nitrogen both these possibilities will be reflected in the spectra of the complexes. Bonding through sulfur will decrease the bond order of the carbon sulfur links toward the value for a single bond; whilst that of the carbon-nitrogen bond approaches the value for double bond if on the contrary a nitrogen-metal bond is formed; just the opposite effect is to be expected.

A through investigation of series of analogue monosubstituted thio-amides seemed to be necessary to resolved doubtful assignments of the (NHCS) group frequencies. It has to be noted that if a bond is attributed to a specific motion of some group of atoms, this should be understood to imploy only a major contribution from that motion [43].

1.3.2-Phosphine complexes:-

The cis-trans isomerization of square planer bis (phosphine) (transition metal) complex has received considerable attention [44]. On reasons for this interest is the importance of these and similar complexes

as catalysts. It is well known that bis (phosphine) platinum (II) complexes are robust and isomer inter conversion normally requires either extended periods of refluxing or catalyses by excess phosphine.

It is not as widely known that analogous palladium (II) complexes are so labile that often mixtures of the isomers exist in solution simultaneously and that isomerization occurs spontaneously requiring only a few minutes with no heating and no catalyses [45].

It has long been known that the cis isomer of square planer platinum (II). Phosphine complexes are thermodynamically more stable than the trans isomers [46] [47]. The trans isomer have, however, been isolated in several cases and the ability to isolate both isomers has been attributed to a kinetic phenomenon (viz, the robust nature of these complexes).

Electronic spectral studies, X-ray crystallography and dipole moment measurement have shown that in general for the platinum complexes, the trans isomer is yellow and the cis isomer is colorless [48].

The tendency of isomerization of the relatively labile palladium complexes make the assignments tenuous since the less polar trans complexes are favored in solvent such as benzene.In fact, more recent studies using infrared spectroscopic techniques show that the cis complexes palladium are indeed more common than originally believed [49,50]

1.4-Infrared spectra of Pd and Pt complexes:-

1.4.1-The neutral complexes of Pd (II) and Pt (II) with sulphoxide donors

A trans S-bonded structure for solid $[Pd (DMSO)_2Cl_2]$ has been proven by a single crystal X-ray studies [51] while a cisS-bonded structure

for [Pt(DMSO)$_2$Cl$_2$] is indicated by IR studies[52].. If the cis configuration is maintained in solution, then the methyl group equivalence probably indicates rapid rotation about both the Pt-S and C-S bonds. Intermolecular exchange has been shown to be slow on the nmr time scale by addition of excess free ligand.

In the palladium complexes [PdL$_2$Cl$_2$] (L= di-n-ethyl and tetra-methylene sulfoxide) [53]. Near and far-Ir data are consistent with a trans sulfur-bonded configuration in every case. Palladium-sulfur stretching modes have been generally assigned to the 400-440 cm^{-1} region however the neutral complexes Pd (TMSO) $_2$Br$_2$ contain no bonds in the far-ir region from 528-364 cm^{-1}. We conclude that the metal sulfur stretching mode in this species is attributable to the strong 364 cm^{-1}bond. Similarly Pd (TMSO)$_2$ Cl$_2$ contains no bond from 526-374 cm^{-1}. The strong band near 357 cm^{-1}, which probably derive most of their intensity from metal-chlorine stretching, may also include the metal-sulfur stretching mode.

The preference of Pt (II) and Pd (II) for the sulfur donor site when steric influences are not prohibitive is suggested by the observation that every neutral complex is exclusively sulfur bonded in the solid.

In the Pd (II) chlorides, the enhanced (d-d) π bonding in the cis geometry is apparently insufficient to overcome the interligand repulsions which are larger in the cis configuration, and all of the complexes have the trans structure. in the corresponding [PtL$_2$Cl$_2$] complexes (d-d) π bonding is apparently more effective and cis structure are obtained for all the complexes except with the most sterically demanding ligand, diisoamyl-sulphoxide which yield trans-[Pt(IASO)$_2$Cl$_2$][54].

1.4.2-Cationic complexes of Pd (II) and Pt (II).

Dimethylsulphoxide complexes of Pd (II) and Pt (II). The cationic complexes [Pd(DMSO)$_4$]X$_2$ (X$^-$= BF$_4^-$, ClO$_4^-$) is now known to contain

both S- and O- bonded DMSO in a cis configuration in the solid state. The IR spectrum for [Pt (DMSO) $_4$] (ClO$_4$)$_2$ is very similar to that of the palladium complexes with two strong bands in both S-bonded (1155,1143 cm^{-1}) and O-bonded (897,879 cm^{-1}) νSO regions (The far-IR spectrum contains bands at 517 and 438 cm^{-1} which are assigned to Pt-ligand stretching frequencies[55].

We turn now to the second general class of complexes those in which, the sulphoxide is coordinating through the sulfur atom. The compounds PdCl$_2$.2DMSO and PtCl$_2$.2DMSO appear to be of this type [56]. Their spectra are similar to spectra of O-bonded compounds in the C-H stretching and deformation region. i.e. down to the ~1300 cm^{-1}. Bonds, however, for PdCl$_2$.2DMSO and PtCl$_2$.2DMSO, the SO stretching frequency is higher (1116 cm^{-1}) in the complex than in the free ligand. In the platinum compound there are strong bond at 1157 and 1134 cm^{-1}, one or both of which must be assigned to S-O stretching. In both the platinum and palladium complexes the four strong to medium intensity bond found between ~1025 and ~920 cm^{-1}. may be assigned to CH$_3$ rocking modes. The band at 730 and 683 cm^{-1}. In the palladium compound may presumably be assigned to C-S stretching frequencies. The behavior of these bands in these S-bonded compounds is in a marked contrast to their behavior in the O-bonded compounds. In the latter the C-S stretching bands are generally much weaker (often the symmetric stretches not observed) [57].

The infra-red spectra of dimethylsulphoxide, dimethylsulphoxide – d$_6$, numerous complexes of DMSO –d$_6$ with metal salts are reported and discussed. Assignments are proposed for the bands observed in the region 650-4000 cm^{-1}. The effect of complex formation and sulphoxonium ion formation by dimethylsulphoxide upon its S-O stretching frequency are given a particular attention and it is shown that observed shifts may be

correlated with the occurrence of S- or O- bonding in the adducts by considering the electronic nature of the S-O linkage[58]. The infrared spectra (4000-270) cm^{-1} was recorded and assignments for the main absorption bands were used to determine the ligand donor sites and to comment on the relative acceptor ability of palladium (II). The complex Pd (DMSO)$_4^{+2}$ has the novel feature of containing both sulfur and oxygen bonded dimethylsulphoxide. The IR spectra are most consistent with two sulfur and two oxygen coordination sites in a cis configuration. The solid sulfur bonded complexes trans Pd (DMSO)$_2$Cl$_2$ is found to convert to the cis complex in acetonitrile solution [59]. Further evidence for the presence of mixed sulfur and oxygen coordination sites is supplied by the presence of more IR band than would be expected for four equivalent DMSO ligands. In particular, the spectra regions for δ_s(CSO) and δ_a (CSO) each contain two more bands. In the far-ir there are at least three bands (493,437,420) cm^{-1} that can be associated with Pd-ligand stretching frequencies, while only one would be expected for an idealized D$_4$h symmetry [60].

The splitting of υSO in both the sulfur-bonded and oxygen-bonded regions along with at least three IR active Pd ligand stretching is most consistent with a cis arrangement of a S- and O- bonded DMSO ligands. In order to examine for the possible presence of oxygen bonded DMSO, the deuterated complex Pd[DMSO-d$_6$]$_4^{+2}$ was prepared an tests IR spectrum was recorder. The methyl rocking bands shift ~20 cm^{-1} in the deuterated complex thus clearing the υSO (oxygen bonded) region for inspection. The strong band at 920 and 905 cm^{-1} in the deuterated complex are thus assigned to υSO oxygen-bonded DMSO.

In sulfur bonded bis-DMSO complexes, the DMSO ligand are commonly found in the cis configuration[61][62], the Pd-S bond distance in the cis nitrate complex are significantly shorter than those in the trans-

chloride complex, which is considered to be the result of more favorable d_π-d_π Pd-S bonding in the cis configuration. Assuming that the observed cis structures are the thermodynamically most stable form and do not simply result from kinetic stability, then the presence of the trans structure for Pd (DMSO) $_2$Cl$_2$ is surprising. The trans-configuration of Pd (DMSO) $_2$Cl$_2$ may not be the most stable molecular form but is obtained in the solid state because it leads to more stable crystal form. A study of Pd (DMSO)$_2$Cl$_2$ in solution was under taken to aid in understanding this problem. Their spectrum for solid trans- Pd (DMSO) $_2$Cl$_2$ has a single S-O at 1116 cm^{-1} and single Pd-Cl and Pd-S stretches at 415 and 353 cm^{-1}, respectively [63]. A single S-O stretching frequency at 1125 cm^{-1} in DMSO solution indicates retention the trans-structure in DMSO solvent[64]

1.4.3-Dithiooxamid complexes of Pd (II) & (Pt).

The differences between the IR spectra of the ligand and those of the complexes. The υ(NH) at 3200 cm^{-1}, in the thio-amide II and V bands prove the existence of (RNHCS) groups in the complex. The split thio-amid I,III and IV bands are caused by different (CN) and (CS) groups, vis the (CN) and (CS) groups linked to the metal and on the other hand the (CN) and (CS) groups which are not linked. As the double bond character of the different (CN) and (CS) groups is not equal, split bands can be expected in the region of the (CN) and (CS) absorption [65].

The absence of any (NH) group is shown be the absence of υ (NH), thio-amide (II) and thio-amide v bands.

Thio-amide I, III, and IV band are not split as we observe in the proposed structure only one kind of (CN) and (CS) groups. The lowering of the thio-amide III and IV and the absorptions is the region 400-200 cm^{-1} assigned to υ_a (spds), υ_s(spds) and δ (NCS), are due to the Pd-sulfur bonding,. The absorption in the region 1100cm^{-1}, 1250 cm^{-1} different

from the absorptions of the ligand, can be explained by very strong coordinate bonds between Pd^{+2} and nitrogen, which result in an increase in intensity of the R-N vibrations [66]

The palladium thio-cyanide complexes of biphenyl(2-dimethylaminoethyl, phosphine is a non electrolyte in both acetone and DMF. The infrared spectrum (Nujol mull) of the solid displays a strong, sharp bands at 2126 cm^{-1} and a second, relativity broader peak at 2108 cm^{-1}, indicating the presence of two different types of coordinated thio-cyanide ions. In dichloromethane solution the complex shows two destined bands at 2127 and 2087 cm^{-1} from a comparison with the infrared spectrum of the palladium bromide complex, the weak absorption at 816 cm^{-1} in the spectrum of the thio-cyanate complex is a assigned to the C-S Stretching frequency of an N bonded thio-cyanate [67].

1.5-Polynuclear complexes:

There has been great interest in supramolecular transition metal chemistry science. Self-assembly through coordinate bond formation has proven to be powerful tool for constructing rings, polymers, and networks. Some of these compounds have potential used in the context of molecular recognition, catalysis, size-selective guest transportation, optical material, molecular magnetism, semiconductors, and conductors [68]. Variation of ligand structure and coordination geometry gives rise to the variety of supramolecular structures, and it is now possible to predict the product structures in many cases. For example, the combination of bis- or poly (pyridine) ligands with square planar palladium (II) and platinum (II) centers has yielded an impressive range of polygons, cages, and catenaes. If the metal is constrained to have cis stereochemistry and a linear bipyridine ligand is used, a molecular square is formed, but angular

or flexible bipyridine derivatives can give dimers, trimers, or polymers [69].

.   Organic amides have proved to be useful in self-assembly through hydrogen bonding, and the products have relevance to biological systems. For example, oligoamides have been designed that can fold to give single or double helices as well as other supramolecular assemblies. In addition, amide-linked catenanes, rotaxanes, and knots have been prepared by template synthesis [70]. Cyclic peptides can self-assemble to give interesting supramolecular structure; most notably to give nanotubes via amide-amide hydrogen bonding. This reports the self-assembly of binuclear, tri-nuclear, or poly-nuclear complexes from cis-blocked palladium (II) or platinum (II) centers with the amidopyridine ligands. The major purpose was to investigate the effect ligand structure on the nature of the resulting self-assembly. The ligands are designed to have different degrees of flexibility and orientation of the pyridyl donor groups while retaining the amido groups that can take part in hydrogen bonding. Preliminary accounts of parts of this work have been published [71].

The reaction of cis-blocked Palladium (II) and platinum (II) precursors with strictly linear bipyridyl ligands is known to give molecular squares by 4+4 self-assembly, but angular or flexible bis (pyridyl) ligands can yield cyclic dimers or trimers by 2+2 or 3+3 self-assembly. In one case, involving the more labile palladium (II), equilibrium between molecular triangles and squares was established [72].

The (pyridyl) ligands, dimers, trimers, and polymers (but no cyclic tetramers) have been characterized, and further supramolecular association is often observed through hydrogen bonding of the amide groups. Self-assembled metallomacrocycles have attracted a great amount of attention because of there shape- and size-selective encapsulating properties, with potential applications in catalysis, sensing devices,

molecular electronics, and small molecule transport. The synthesis of these compounds softens proceeds in excellent yields, high selectivity, and few steps using simple metal centers and bidentate ligands as building blocks. For example, cis-blocked, square planar palladium (II) and platinum (II) complexes with bidentate or tridentate pyridine-based ligands have been used to prepare molecular boxes and cages that are soluble in either water or organic solvents. Although there has been much interest in the metal molecular triangle, as the simplest such polygon, there are still relatively few examples and fewer studies of the binding properties of these compounds [73].

Synthesis and magnetic properties of heteropolymetalic complexes with two different paramagnetic centers have attracted considerable attention. Interest in this field is a fundamental requirement, not only for gaining some insight into the structural and electronic factors governing magnetic exchange interaction between paramagnetic centers, but also for obtaining information about designing and synthesizing molecule-based magnets and investigating the spin-exchange mechanism between paramagnetic metal ions. Compared with the number of studies dealing with hetero nuclear systems comprising d-transition metal ions, relatively few studies dealing with hetero metal complexes containing d-transition metal ions.

1.6-Groups theory:

In order to use the symmetry properties of molecules in solving problems connected with molecular structure and bonding, it is necessary to have some acquaintance with the branch of mathematics known as group theory. A group, in the mathematical sense, is a collection of

elements having certain properties in common which enable a wide variety of algebraic manipulations to be carried out on collection.

The frequency data come from two main sources; infrared absorption and Raman scattering spectroscopy .These are complementary, and in almost all cases it necessary to use both, to obtain all the requisite information[74].

1.7-Bioinorganic Chemistry:

Bioinorganic chemistry is a rapidly developing filed and there is enormous potential for application in medicine. Medicinal inorganic chemistry offers real possibilities to pharmaceutical industries, which have traditionally been dominated by organic chemistry alone, for the discovery of truly novel drugs with new mechanisms of action[75].

1.7.1-Clinical Platinum Complexes:

Platinum complexes are now amongst the most widely used drugs for the treatment of cancer. Four injectable Pt^{II} compounds have been approved for clinical use and several other cis-diamines complexes are on clinical trials, including an oral Pt^{IV} complexes Today cisplatin is one of the most widely used anticancer drugs[75].

1.8 Aim of the work

In view of the potential biological activity of divalent square planer palladium and platinum complexes with N, S, and P- donor ligands it was decided to prepare some new complexes of these two metal ions and to study their structural behavior.

A number of N,S-, N,N- , N- or P-donor ligands are to be used to coordinate to Pd (II) or Pt (II), the resulting complexes are to be isolated and characterized using the available conventional techniques, and following different routes, as follows:

i. Isolation and studying the starting complexes MCl_2 $(DMSO)_2$ (M= Pd(II) or Pt(II)).

ii. Preparation and isolation of $MCl_2(DTO)$ (DTO= dithiooaxmide)

iii. Reacting $MCl_2(DTO)$ with the mono-dentate PPh_3 and NPh_3, and the linear bi-dentate benzidine, and 3,3ˉ,5,5ˉ, tetramethyl benzidine

iv. Reacting 2,2ˉ-dipyridyl as bi-dentate N,N-donor with $PtCl_2(DMSO)_2$, the resulting complex is to be reacted with DTO as N,S-, N,N- , or S,S-donor ligands.

The basic ideas governing the structure and reactivity of coordination chemistry are to be used to illustrate the type of bonding and isomerism.

2.1-Instrumentation

A)-Metal analysis:

The metal content of the complexes was measured using atomic absorption technique by *Pye Unicam* of *Philips scientific instrument* which employed the Hallow cathode lamp of *Pye Unicam Ltd. Cambridge.*

(B) –Infrared spectrophotometer:

The i.r. spectra of the prepared compounds were recorded using *Perking –Elmer 1130* infrared spectrophotometer as CsI disc in the range $(4000—250)$ cm^{-1}.

(C)- Magnetic susceptibility measurements:

The magnetic susceptibility values for the prepared complexes were obtained at room temperature using (Faraday Method, by placing the sample in small Pyrex container suspended from a balance through a fine, Nylon thread to the center of electric magnet. For this purpose, *Bruker Magnet B.M6* had been employed. The diamagnetic correction factor(D) was calculated using Pascal constants.

(D)-Electronic Absorption Spectra:

The electronic spectra of the complexes were obtained using *Shimadzu Uv-Vis-160A* Ultra-Violet Spectrophotometer at room temperature using quartz cells of 1.0 cm^{-1} length and using ethanol or DMSO as solvent.

(E)- Melting Points:

Gallencamp M.F.B 600.010F melting point apparatus were used to measure the melting points of all the prepared compounds.

2.2 Chemicals

2.2.1 Supplied chemicals:

Chemicals	Purity %	Company
2,2-dipyridyl	98%	Merck
3,3⁻,5,5⁻--Tetramethyl Benzidine	98%	BDH
Acetone	99%	BDH
Benzidine	98%	Fluka
Chloroform	97%	BDH
Diethyl ether	90%	BDH
Dimethylsulphoxide	98%	BDH
Dithiooxamide	98%	BDH
Ethanol	95%	BDH
Hydrazinedihydrochloride	85%	BDH
Methanol	95%	BDH
Palladium(II)chloride	60%Palladium	BDH
Potassiumheax-chloroplatinate(IV)	Lab. Chemicals	M&B
Triphenylamine(Ph$_3$N)	98%	BDH
Triphenylphosphine(Ph$_3$P)	98%	BDH

2.3.1-Preparation of starting material

A-1: Trans –dichlorobis(Dimethylsulphoxide) palladium (II) (A1).

This complex was prepared by dissolving 0.025g(0.762mmol) of palladium (II) chloride in 5 ml of Dimethylsulphoxide at50C^0 .The product was separated upon addition of anhydrous diethyl ether with stirring. The precipitate was dried under vacuum for 5 hours at room temperature. The product was yellow in color [76].

A.2:- Potassium tetrachloroplatinate (II) (AII):-

To a suspension 0.303g (20mmol) of potassium hexa-chloroplatinate (IV) in 4 ml of water small portions of 0.03g (10mmol) of hydrazine dihydrochloride, were added gradually .The mixture was stirred mechanically while the temperature was raised to 50 -65C.over a period of 5 -10 minutes. The temperature was maintained until only a small amount of yellow potassium hexa-chloroplatinate (IV) remained. The temperature was then raised to 80 – 90C for the completion of the reaction. The mixture was cooled in an ice bath and filtered to remove unreacted potassium hexa-chloroplatinate (IV). The precipitate was washed with several portion of water till it became colorless; the washing were combined with the original red filtrate. The resulting solution was evaporated to dryness a red crystalline needles were formed [77].

A.3-Cis-dichlorobis (Dimethylsulphoxide) platinum (II) (AIII).

The neutral platinum sulphoxide complex was prepared by adding (9mmol) 0.395g of Dimethylsulphoxide to an aqueous solution of (3mmol) 0.414g of AII in 10ml of water, the solution was allowed to stand at room temperature until yellow crystals precipitated.

The complex was filtered washed with water, ethanol, and diethyl ether and dried under vacuum for 4hours [76].

2.3.2-.Preparation of Pt (II) and Pd (II) complexes:-

B.1-Cis Dichloro (Dithiooxamide) platinum (II), BI.

Dithiooxamide 0.056g (4mmol) was dissolved in 6 ml of hot ethanol. To the resulting brown solution 0.2g (4mmol) of A III was added and the mixture was refluxed for 2 hours and cooled. The resulting red brown precipitation was filtered washed with diethyl ether several times & dried under vacuum .

B.2-Cis Dichloro (Dithiooxamide) palladium (II), BII.

Dithiooxamide 0.1g (9mmol)was dissolved in 6 ml of hot ethanol. To the resulting brown solution 0.3g(9mmol) of ○AI was added. The mixture was refluxed for 2 hours and cooled. The resulting black-brown precipitate was filtered washed with diethyl ether several times & dried under vacuum.

B3-Dithiooxamide (Triphenylphosphine) Palladium (II) chloride (BIII):

This complex was prepared by dissolving 0.1g (3.36mmol)of BII in warm ethanol which was then added to 0.088g (3.36mmol) of (Ph$_3$P) dissolved in acetone. The mixture was heated with stirring yielding brown crystalline precipitate, which was filtered and washed with diethyl ether and dried under vacuum for 3hours.

B-4. Dithiooxamide (Triphenylphosphine) Platinum (II) chloride (BIV):

This complex was prepared by dissolving 0.1g (2.59mmol) BI in warm ethanol which was then added to 0.0678g (2.59mmol) of (Ph$_3$P) dissolved in acetone. The mixture was heated with stirring yielding black-brown crystalline precipitate, which was filtered and washed with diethyl ether and dried under vacuum for 3hours.

B-5. Dithiooxamide (Triphenylamine) Palladium (II) chloride (BV):

This complex was prepared by dissolving 0.1g (3.36mmol) BII in warm ethanol which was then added to 0.082g (3.36mmol) of (Ph$_3$N) dissolved in acetone the mixture was heated with stirring yielding red-brown precipitate, which was filtered and washed with diethyl ether and dried under vacuum for 3hours.

B-6 Dithiooxamide (Triphenylamine) Platinum (II) chloride (BVI):

This complex was prepared by dissolving 0.1g (2.59mmol) BI in warm ethanol which was then added to 0.0635g (2.59mmol) of (Ph$_3$N) dissolved in acetone the mixture was heated with stirring yielding violet crystalline precipitate, which was filtered and washed with diethyl ether and dried under vacuum for 3hours.

B7- Tetra chloro [dithiooxamideplatinum (II)] tetra [N, N-benzidine] GI.

This complex was prepared by dissolving 0.1g (2.59mol) of B1 in ethanol and with mild heating it gave red brown solution, to which 0.047g (2.59mol) of benzidine dissolved in (4ml) hot ethanol was added with stirring at about 60C for 1 hour.

The resulting violet solution was cooled to room temperature, a violet crystals was formed, which were then, washed several times with diethyl ether and dried under vacuum for 3hours.

B8- Tetra -chloro [dithiooxamidepalladium (II)] tetra [N, N-benzidine] GII.

This complex was prepared by dissolving 0.1g (3,36mol)of BII in ethanol and with mild heating it gave red brown solution, to which 0.063g (3.36mol) of benzidine dissolved in (4ml) hot ethanol was added with stirring at about60C for 1 hour .The resulting violet solution was cooled to room temperature, a violet crystals was formed, which were then,

washed several times with diethyl ether and dried under vacuum for 3hours.

B9- Tetra chloro [dithiooxamidepalladium (II)] tetra [3,3⁻,5,5⁻ tetremethylbenzidine] GIII.

Dissolving BII 0.12g (3.36mol) in ethanol under with mild heating gave is red brown solution, to which 0.08g (3.36mol) of benzidine dissolved in (4ml) hot ethanol was added with stirring at about60C for 1 hour.

The resulting violet solution was cooled to room temperature, a violet brown crystal was formed, which were then, washed several times with diethyl ether and dried under vacuum for 3hours.

B.10- Tetra chloro [dithiooxamideplatinum (II)] tetra [3,3⁻,5,5⁻ tetremethylbenzidin] GIV.

Dissolving BI 0.12g (2.59mol) in ethanol under with mild heating gave red brown solution, to which 0.0622g (2.59mol) of benzidine dissolved in (4ml) hot ethanol was added with stirring at about60C^{0} for 1 hour .

The resulting violet solution was cooled to room temperature, a violet brown crystal was formed, which were then, washed several times with diethyl ether and dried under vacuum for 3hour.

B.11-Dichloro (2, 2⁻-dibyridyl) Platinum (II) HI.

To a solution of 0.1g (2.9mmol) dissolved in warm ethanol, 0.045g (2.9mmol) of 2,2⁻-dipyridyl solution in 6ml ethanol was added .The resulting yellow solution was heated with stirring .A yellow precipitate

was formed on cooling ,which was washed with diethyl ether and dried under vacuum for 3hours.

B.12-Dithiooxamide (2, 2⁻-dibyridyl) Platinum (II) chloride HII.

HI 0.1g (2.36mmol) was dissolved in 6 ml ethanol, then DTO 0.028g (2.36mmol) dissolved in ethanol was added with stirring to which was filtered washed with diethyl ether. A red precipitate was formed on cooling and dried under vacuum for 4 hours.
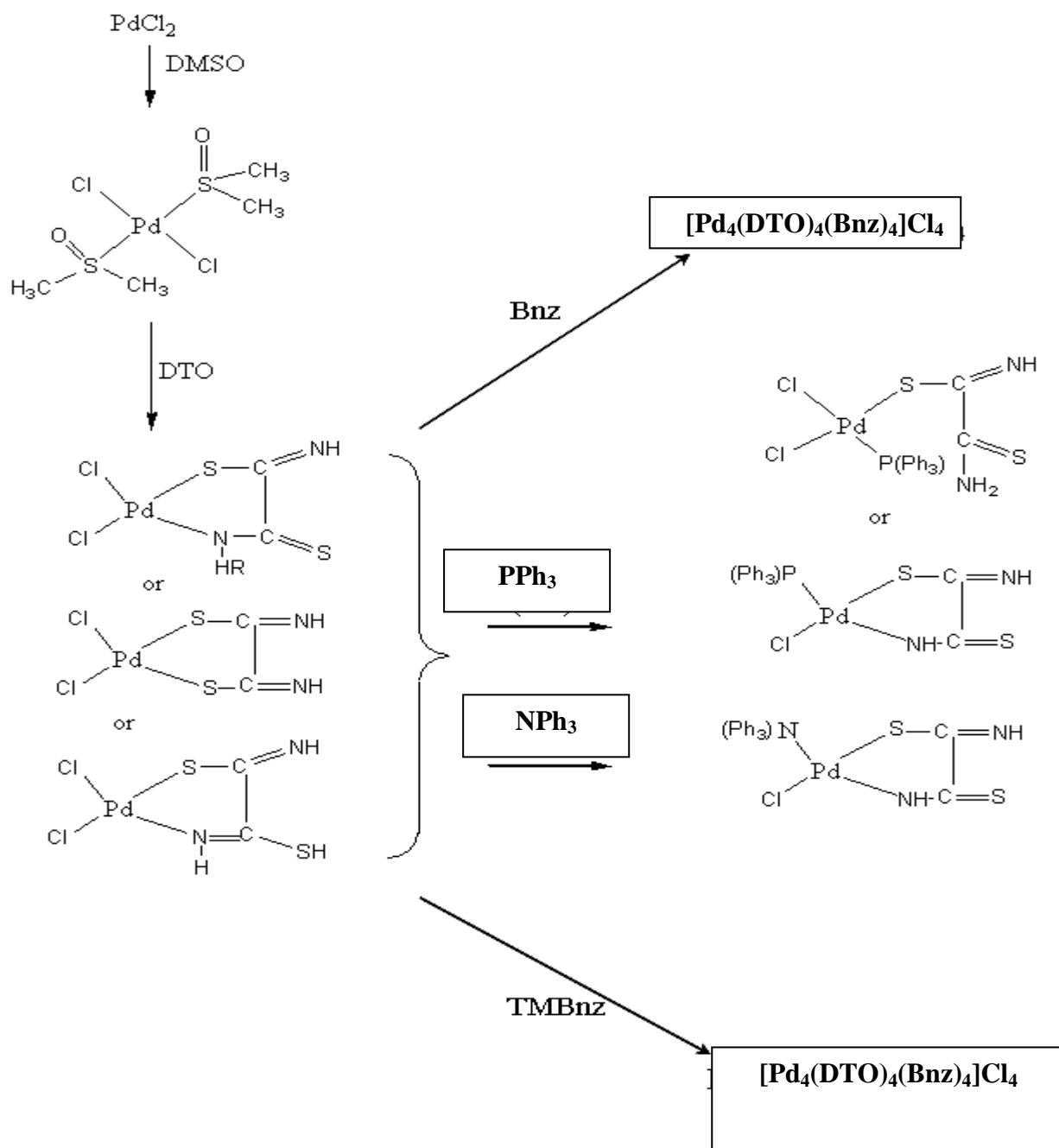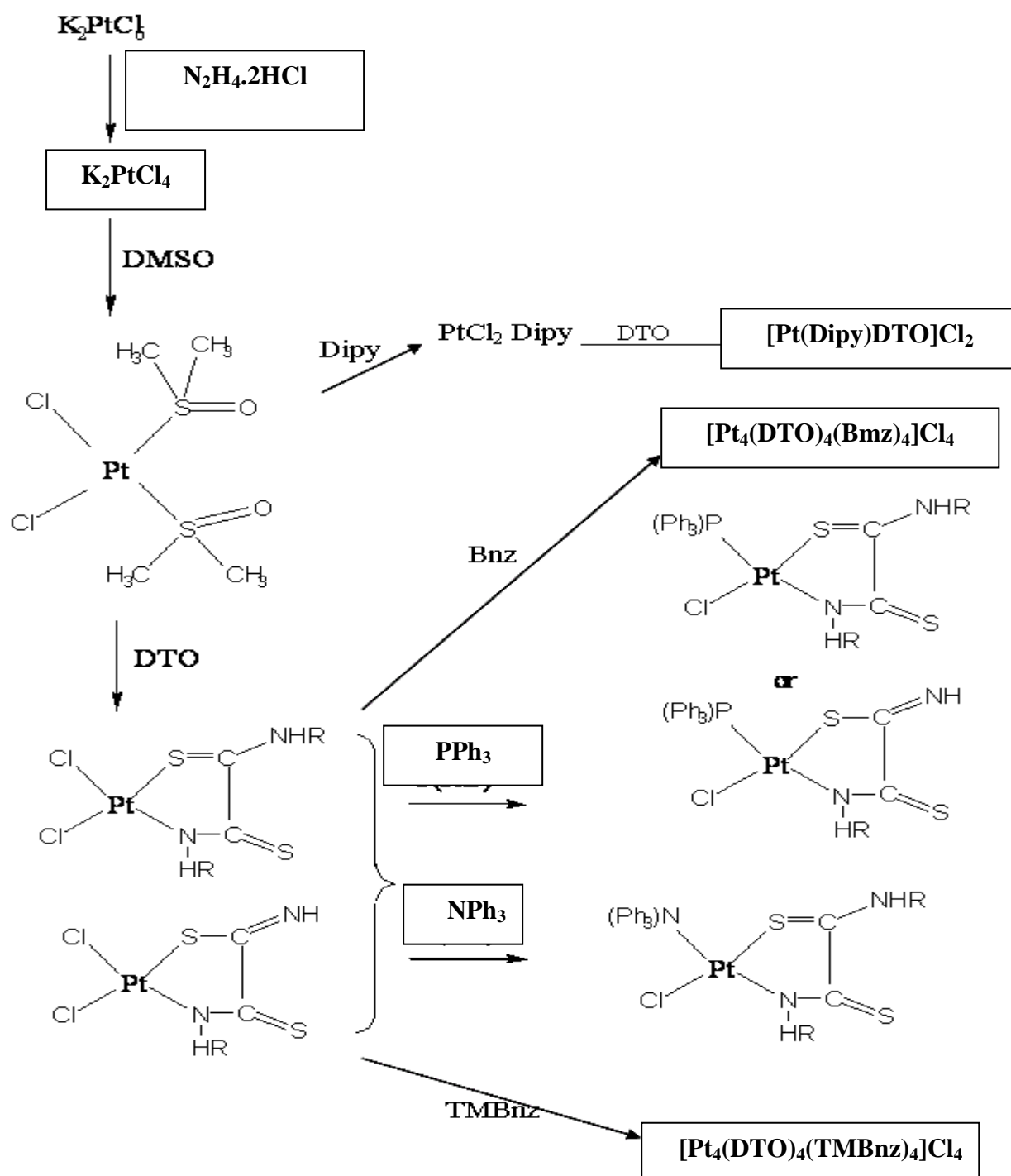
3.1-Preparation of the metal complexes:

3.1.1- Preparation of the Platinum (II) complexes:

The reaction of hot DMSO with potassium tetrachloroplatinum (II), which in turn was prepared by reduction of potassium hexa-chloroplatinum (IV) by Hydrazinedihydrochloride, gave yellow needle-like crystals, stable toward air the moisture. The executed geometry of the resulting complex is cis-square planar [PtCl$_2$ (DMSO)$_2$] [78,79].

When [PtCl$_2$ (DMSO)$_2$] was reacted with Dithiooxamide (DTO) in ethanol under reflux condition, it gave a brown fine powder with good air and moisture stability in which the two labile DMSO molecules were substituted by one chelating DTO molecule giving two exchangeable chloro atoms. This fact was utilized to prepare four different complexes using four nitrogen and phosphorous donor neutral ligands i.e.triphenylphosphine, triphenylamine, Benzidine,and 3,3$^-$,5,5$^-$ tetra-methylbenzidin.

The two monodenate entering ligands, Ph$_3$P and Ph$_3$N, may react with [PtCl$_2$DTO] in either of three possible ways, which include, first the displacement of one chloro atoms (trans to S or trans to N of DTO),second breaking and displacing the coordinated amino group of the DTO, third breaking and displacing the coordinated sulfur of the DTO.

The last too ways of reaction are the least probable, because the Pt-N and Pt-S bonds are stronger than Pt-Cl [80]. So we were left with the first choice with the problem of substituting the trans-S or trans-N chloro atoms. The spectral studies will be used to solve this problem. The result of reacting equimolar quantities of PtCl$_2$DTO with Ph$_3$P or Ph$_3$N in acetone at room temperature was the precipitation of brown and violet fine crystals respectively, which were both stable toward air and moisture.

Benzidine and its derivative (3,3ʹ,5,5ʹ-tetramethylBenzidine) were selected to prepare a cage complex of tetra nuclear platinum, since these ligands are linear with respected to the position of the two amino groups, which make possible the formation of the tetramers, in addition to the suitability of the starting platinum complex[81]. Therefore $PtCl_2$(DTO) was choosen to synthesize the desired cage complexes, since it contain the two labile chloride ions at cis-position, the other two cis-position are coordinative inert.

The reaction of Benzidine or tetra methyl Benzidine with $PtCl_2$ (DTO) in hot ethanol gave brown and violet fine crystalline powders respectively. It was noticed that the reaction with naked Benzidine was faster than the tetra substituted Benzedrine; this was attributed to the steric hindrance of the substitutions.

Another route for preparing a mixed ligand complex of platinum was followed, in which 2, 2ʹ-dibyridyl complex [$PtCl_2$ (dipy)] was prepared in the first step by reaction equimolar quantities of [$PtCl_2$ (DMSO) $_2$] and dibyridyl in hot ethanol giving bright yellow crystalline powder. In the second step DTO was reacted with the dibyridyl complex in hot ethanol in 1:1 mol ratio, a red crystalline powder was obtained which was also stable toward air and moisture.

3.1.2-Preparation of Palladium (II) complex:

Palladium is the closely related analogue of Platinum, however there are some differences in the chemistries of these two element. Of these differences is the higher rate of substitution reaction of Pd (II) compared to that of Pt (II) (10^5 times), and the stereochemistry of square planar complexes (cis vs. trans)[82]. The same preparation protocol which was the case if Pt (II) was followed to prepare the complexes Pd (II). Some notes were pointed out, the first was that all the reaction steps in

the case of Pd(II) were faster corresponding to that of Pt(II) complexes, the second was the difference in the stereochemistry of PdCl$_2$(DMSO)$_2$,being trans, while PtCl$_2$(DMSO)$_2$ was of cis geometry ,the third point was the difference in the color of the corresponding complexes[82].

3.2- Physical and spectroscopic study

3.2.1-Infra-red spectra

All the spectra were recorded in the solid state using CsI disk technique in the rang 4000-250 cm^{-1}.

A-Dimethyl sulfoxide complexes:

Infrared spectral studies of DMSO complexes have proven useful in distinguishing between coordination through the oxygen or sulfur donor site [83]. Previous structure determination studies of trans PdCl$_2$ (DMSO) $_2$ have demonstrated that DMSO `coordinate through S-atoms. The trans configuration of PdCl$_2$ (DMSO) $_2$ may not be the most stable molecular form but is obtained in the solid state because it leads to a more stable crystal form [84,85].

The FT-IR spectrum of our starting complex PdCl$_2$(DMSO)$_2$, fig (1)and table, shows a sharp strong single S=O stretching at 1116 cm^{-1} and a well defined bands for Pd-S and Pd-Cl stretching at 414 and 349 cm, respectively. The bands appeared at 2912cm^{-1} and 1406cm^{-1} may be attributed to CH$_3$ stretching. These i.r. spectral data in accordance with the expected trans-, S-bonded DMSO.

Inspection of the spectral i.r. data of PtCl$_2$(DMSO)$_2$,fig(2)and table (1), show that DMSO is coordinated to Pt through it's S-atom and in cis-

configuration ,since two stretching vibration of Pt-Cl bond appeared at 309 and 334cm^{-1}.

Table (1) The FT.IR of Pd(II) and Pt (II) with DMSO complexes.

Sample	νS=O	νCH3	σCH3	VM-Cl	V M-S
DMSO	1050	2998 2971	1414		
Trans-PdCl$_2$(DMSO)$_2$	1116	2912	1406	349	414
Cis-PtCl$_2$(DMSO)$_2$	1157	3010 2920	1409	309 334	434

This was expected following the solid state studies of several workers [86] [87].

On comparison of the νS=O in Pd –complex with that in Pt –complex, it can be seen that the later frequency came at 41cm^{-1} higher in its position. We think that this difference make further evidence for the cis configuration of the Pt-complex VS. the trans configuration of the Pd complex, i.e. .B .VS- A, where S=sulphoxide.
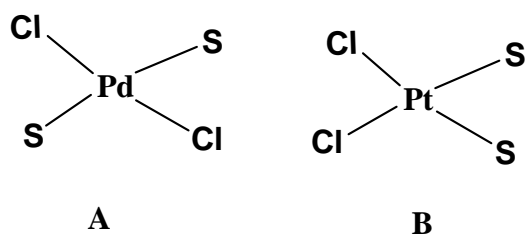
On taking the trans-influence of Cl to be mutually equal in A, but it affect the S=O bond order indirectly by it's back π- bonding in B

lessening the back donation from Pt to the π or vacant d-orbital of S-atom leading to the decrease in bond length of S=O.

As required by group theoretical calculation, structure A (D$_2$h) yield one vPd-Cl as i.r.action, while B (C$_2$v) yielded two vPt-Cl as i.r.active bands, as illustrated by the following calculation:

Structure A

D$_2$h	E	C$_2$(z)	C$_2$(y)	C$_2$(x)	i	σ(xy)	σ(xz)	σ(yz)		
A$_1$g	1	1	1	1	1	1	1	1		x,y,z
B$_1$g	1	1	-1	-1	1	1	-1	-1	Rz	xy
B$_2$g	1	-1	1	-1	1	-1	1	-1	Ry	zx
B$_3$g	1	-1	-1	1	1	-1	-1	1	Rx	yz
Au	1	1	1	1	-1	-1	-1	-1		
B$_1$u	1	1	-1	-1	-1	-1	1	1	Tz	
B$_2$u	1	-1	1	-1	-1	1	-1	1	Ty	
B$_3$u	1	-1	-1	1	-1	1	1	-1	Tx	
Γt(Pd-Cl)st	2	0	2	0	0	2	0	2		

a$_p$=(1/g)ΣnRx(R)xp(R)

a$_p$= any irreducible representation p.

g =is the number of symmetry operations in the the point group.

X$_p$(R), and x(R)= The characters of the operation R in the reducible and irreducible representation, respectively.

n = number of symmetry.

$$aA_g = \frac{1}{8}[(2\times1\times1)+(0\times1\times1)+(2\times1\times1)+(0\times1\times1)+(0\times1\times1)$$

$$+(2\times1\times1)+(0\times1\times1)+(2\times1\times1)]=\frac{1}{8}[8]=1$$

$$a\,B_{1g} = \frac{1}{8}[(2)+(-2)+(2)+(-2)] = 0$$

$$a\,B_{2g} = \frac{1}{8}[(2)+(2)+(-2)+(-2)] = 0$$

$$a\,B_{3g} = \frac{1}{8}[(2)+(-2)+(-2)+(2)] = 0$$

$$a\,A_u = \frac{1}{8}[(2)+(2)+(-2)+(-2)] = 0$$

$$a\,B_{1u} = \frac{1}{8}[(2)+(-2)+(-2)+(2)] = 0$$

$$a\,B_{2u} = \frac{1}{8}[(2)+(2)+(2)+(2)] = 1$$

$$\mathbf{a}\,B_{3u} = \frac{1}{8}[(2)+(-2)+(2)+(-2)] = 0$$

$$\therefore \ \Gamma(Pd-Cl)_{st} = A_g + B_{2u}$$

Inspection of the character table of the D_{2h} point group, it can be seen that A_g mode is i.r. inactive, while B_{2u} is i.r. active, so only one i.r. band is expected.

Structure B

C_2v1	E	C_2	$\sigma_V(xz)$	$\sigma_V(yz)$		
A1	1	1	1	1	Tz	x^2,y^2,z^2
A2	1	1	-1	-1	Rz	xy
B1	1	-1	1	-1	Tx,Ry	zx
B2	1	-1	-1	1	Ty,Rx	yz
Γ(Pt-Cl)st	2	0	2	0		

$$a\,A_1 = \frac{1}{4}\left[(2)+(0)+(2)+(0)\right]=1$$

$$a\,A_2 = \frac{1}{4}\left[(2)+(0)+(-2)+(0)\right]=0$$

$$a\,B_1 = \frac{1}{4}\left[(2)+(0)+(2)+(0)\right]=1$$

$$\mathbf{a}\,B_2 = \frac{1}{4}\left[(2)+(0)+(-2)+(0)\right]=0$$

$$\therefore\ \ \Gamma(Pt-Cl)_{st} = A_1 + B_1$$

A_1 mode is i.r. active and B_1 mode is i.r. active. There fore, two i.r. bands are expected to appear.

3.2.2-Dithiooxamide (DTO) and its metal complexes.

Dithiooxamide molecule contain two thioamidegroups linked directed toward other, and because these groups can be found as thion and thiol forms, and also it can be considered as 1,2-dithiol molecule, it's coordination behavior is somewhat, but the i.r. spectral study may be helpful in this respect[88].

The hydrogen of the thioamide group is removed on complex formation in some cases and the metal can form bonds through both sulfur and nitrogen. Both these possibilities will be reflected in the spectra of the complexes. Bonding through sulfur will decrease the bond order of the carbon sulfur links toward the value for a single bond. If on the contrary a nitrogen metal bond is formed, just the opposite effect is to be expected[89]. Therefore, a difference between the infra-red spectra of DTO itself and those of its metal complexes, can be confined to the regions of the four thioamide bands in addition to the regions 3200, and 500 cm$^{-1.}$

Thioamides bands

The thioamide bands of DTO have been fully discussed previously. Where the four bands have been assigned as follows; band (I) is due to v(CN) (major) +δ (NH) (major), band (II) due to v (CN) and v (CS), band (III) and (IV) are due to v(N-C-S) and v(C=S) frequencies respectively. The frequency at 3200 cm^{-1} region was assigned to v (NH).) Fig's (3) (4) show the spectra of DTO and its metal complexes. Table (2) gives the most diagnostic frequencies of the DTO and its metal complexes [90, 91].

The following changes were noticed for metal complex spectra:

All the characteristic bands of DMSO disappeared in the spectra of the prepared DTO complexes of Pd (II) and Pt (II). The differences between the i.r. spectra of the ligand and those of the complexes are given in table (2).

1. Pd(II) complex: The thioamide I, and II bands undergo splitting in the spectrum of Pd(II) complex which is caused by different (CN) and (CS) groups; i.e.; the (CN) and (CS) groups coordinated to the metal and those (CN) and (CS) groups which are not coordinated. As the double bond character of the different (CN) and (CS) groups is not equal, split bands were noticed in the region of the intensity and frequency of thioamides. Band (I) by 49cm$^{-1,}$ and (II) by 92cm^{-1} and there is adecrease by 101 cm^{-1} and 83 cm^{-1}of bands (III) and (IV) respectively in the complex compared to that in the ligand , and the appearance of two bands at 500 and 450 cm^{-1} which refer to ν(Pt-N) and (Pd-S) bands respectively. These changes refer to the coordination of Pd(II) through both atoms; i.e. nitrogen and sulfur, and the following structure can be suggested.
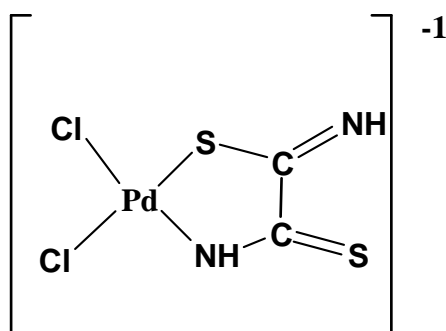
2-For the Pt (II) complex: The thioamide band (I) underwent splitting into two bands 1620 cm^{-1} and 1571 cm^{-1} .Thioamide band (II) was noticed at higher frequency by 31cm^{-1}from that of the ligand ,while band (III) showed a decrease in frequency by 87cm^{-1}, and band (IV) show also a decrease in position by 14 cm^{-1}. This indicate the coordination of Pt (II) through both nitrogen and sulfur atoms. It should be pointed that there is one type of CN and CS groups due to the different behavior of the

relative intensity and magnitude of the shift compared with those of Pd complex .The Pt-N, Pt –S band appeared at 468 and 420cm^{-1}respectively. On (Pt-Cl) band was noticed at 297 cm^{-1}, the other expected (Pt-Cl) could not noticed, because it was obscured by strong bands in this region. According to this discussion the following structure can be suggested.
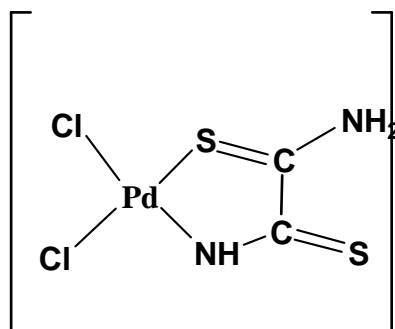
Table (2) The FT.IR of Pd(II) and Pt (II) with DTO complexes

Sample	VNH	Thioamide I δNH+vC=N	Thioamide II vC=N+vC=S	Thioamide III vN-C-S	Thioamide IV vC-S	M-Cl	M-N	M-S
DTO	3200	1585	1429	1196	835			
PdCl$_2$(DTO)	3140	1620-1571	1496-1404	1095	752	290-330	500	450
PtCl$_2$(DTO)	3311	1620-1571	1460	1109	821	297	468	420

3.2.3- *Triphenylphosphine and Triphenylamine complexes of B1 and B2 complexes.*

As the neutral P-donating (Ph$_3$P) or N-donating (Ph$_3$N) react with BI or BII in 1:1 mole ratio ,either one chloride is substituted ,or one of the coordinating bonds of DTO (N or S) is broken. Considering the ligand field strength of the donor atoms (according to chelating effect), the first possibility is more probable.

In the case of palladium complex (BII), the spectrum of BII complex with Ph$_3$P, fig (5), shows a set of new well-characterized bands, when two sharp and strong bands appeared at 750and 696 cm^{-1} due to monosubstituted phenyl groups. The band characteristic of νΦ –P appeared at 1437 cm^{-1}, which is about 63cm lower than that for the free Ph$_3$P. If the isomerism of the new complex is considered, two possibilities are expected:

N-isomer   S-isomer   )=DTO
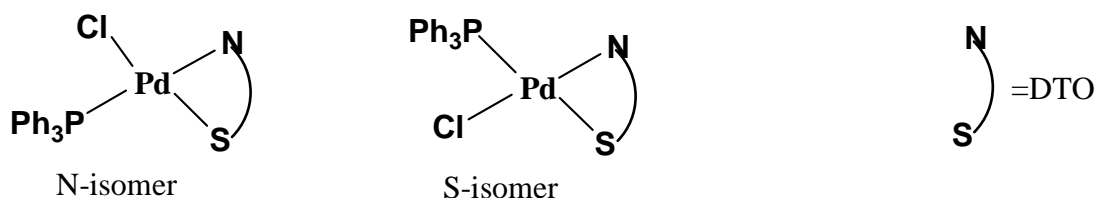
Since N atom is stronger as trans- director than S-atom, the N-isomer is more probable than S-isomer. The νPd-Cl was noticed at 351cm$^{-1(93)}$.

The spectrum of BII with Ph3N, fig (6), show the substituted pattern of phenyl groups at 754 and 696 cm^{-1}, as sharp bands. The νΦ –N appeared at 1280cm^{-1}, which is about 20cm^{-1} lower than that for the free NPh$_3$, indicating the coordination ofd N to the metal. The νPd-Cl appeared at 326 cm^{-1}

, following the isomerization possibilities discussed above, N-isomer is expected.
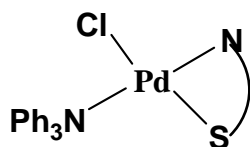
Inspection of the spectra of BI complexes with Ph_3P and Ph_3N show that fig's (7) (8) nearly identical charges were took place as that noticed and discussed in the case of BII complexes.

The expected structures for platinum complexes are:

3.2.4 Polynuclear cage complexes of Pd (II) & Pt (II)

The self-assembly of complex cationic structures by combination of cis-blocked square planar palladium (II) or platinum(II) with ligand having bridging amide units has been discussed in section 1.4 .

As it has referred to, different self-assembled metallomacrocycles can be obtained with high selectivity, and few steps using simple metal centers and bidentate ligand as building block [94-95]-. For example molecular triangle can, in principle, be formed according to the three methods shown in Scheme:

$$\alpha = 80 - 90^{\circ}$$
$$\beta = 120 - 180^{\circ}$$
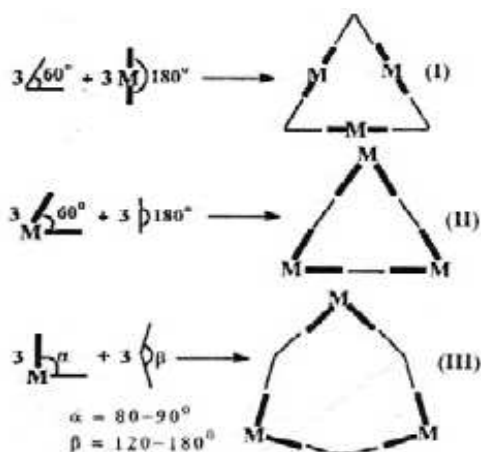
In our present work method II is followed with modification, where the metal center was with natural bond angle of 90°, i.e .BII (PdCl$_2$DTO) or BI (PtCl$_2$DTO), and liner bridging ligands, which include benzidine and tetramethylbenzidin. This should lead to the formation of tetra nuclear metallomacrocycles [95].

The physical properties and metal analysis data are shown in table (3). The value of Pd or Pt content formed in the prepared samples came in a good agreement with required (calculated) value for [Pd$_4$(DTO)$_4$(Benz)]Cl$_4$,[Pd$_4$(DTO)$_4$(TMBNZ)$_4$]Cl$_4$ or [Pt$_4$(DTO)$_4$(Benz)$_4$]Cl$_4$,[Pt$_4$(DTO)$_4$ (TMBNZ)$_4$]Cl$_4$, complexes respectively.

Infrared spectral study showed the following changes:

A-Benzidine complexes:

Benzidine complexes of both BII and BI fig's (9,10), showed similar characteristics, where a new bands appeared which characterize the coordination of the Benzidine with Pd and Pt in BII and BI respectively,ν N-H at 3327 cm^{-1} of primary aromatic amine . The νC-N of the Benzidine appeared at 1286 and 1274cm^{-1} in BII and BI, while C-H in-plane bending vibration appeared at 1097and 1016 cm^{-1} for BII and BI,

and C-H out-of plane bending vibration appeared at 651 and642 cm^{-1} for BII and BI respectively. All the above mentioned bands were not formed in the spectra of BI and BII alone. In addition, the band due to v M-N at (500 cm^{-1}) became more intense in the spectra of the cage complexes of BII and BI which indicate the formation more than one M-N bond.

B- 3,3ˉ,5,5ˉ-tetramethylbenzidin (TMBnz) complexes:

The two spectra of (TMBnz) with BI and BII, fig's (11) (12) did not show appreciable changes compared to those of (Bnz) complexes of B1 and B2, except the appearance of new band at 2910 cm^{-1} characteristic of vC-H of the methyl group.

3.2-5- Dipyridyl (dipy) complex.

The complexes PtCl$_2$ (Dipy), which was first prepared, showed a spectrum, fig (13) containing the characteristic bands of Dipyridyl ,at 1606 and 1475 cm^{-1} (due to vC=N &v C=C of the ring), and 3087 cm^{-1} (due to vC-H. This indicates the coordination of Dibyridyl with Pt by using the far-ir to indicates of the showed ,fig(14).

The final mixed ligand Pt (DTO) (Dipy), complex showed ,fig(14), the characteristic bands of DTO , bands: I at 1572 ,II at 1461, III at 1113, and IV at 823 cm^{-1} in addition to the new band due to vPd-S at 420 cm^{-1} . The band due to vC=N of Dipy, which was strong in the spectrum of Pt(dipy) Cl$_2$ became weak and slightly higher in its position (Δv=+14 cm^{-1})1n the Pt (DTO) (Dipy),which may be due to replacement of two Pt-Cl groups by Pt-N and Pt-S of the incoming DTO ligand.

3.3 Electronic spectra and magnetic properties

Electronic absorption spectra of transition metal complexes are usually attributed to the partially filled d-orbital of the metal. The energy required for such transitions is that of the near uv and visible region. Charge transfer spectra are due to the metal under certain conditions. Study of electronic spectra of complexes helps in the determination of structure of those complexes through the electronic interaction of the metal d-orbital and orbital of the ligand. In our case, the spectra were recorded at (200-1100) nm using Dimethylsulphoxid (DMSO) or ethanol as a solvent.

Measuring magnetic susceptibility contributes to the determination of structure of the complexes. In addition, these measurements provide information about the type of bonding and strength of ligand field of complexes by giving information about the number of unpaired electronics.

The effective magnetic spin of the complexes was measured using spin only magnetic moment according to the following equation.

$$\mu_{s.o} = 2\sqrt{s(s+1)}B.M$$

Where, S=n/2 (n= no. of unpaired electrons).

The results obtained from this equation were compared to the actual values obtained through magnetic measurements.

These values were corrected for diamagnetic effects using the following relationship:-

$$\mu_{eff} = 2.828\sqrt{X_A.T}$$

$$X_A = X_M + D*$$

$$X_M = X_g * M.wt$$

Where, T =Absolute temperature (298K), X_A = Atomic susceptibility

X_M =Molar susceptibility, X_g = Gramic susceptibility

D = Correction factor

The U.V-Vis spectra of the transion metal with partially filled d-orbital are generally characterized by charge –transfer (C.T) bands which involve an electron transfer from M to L during optical excitation by which the oxidation number of the central ion is changed by one, while the ligand filled bands correspond to the same oxidation number in the excited and the ground state. These redox process bands are strong and their wave numbers decreases (or wav length increasers), the more oxidizing the central ion and the more reducing the ligand.

The Pd (II) and Pt (II) ions are considered to be weaker as oxidizing and more stable than their tetravalent states. The transition metal ions have been arranged according to the shifting toward higher wavelength of the first strong band of their halide complexes (C.T. bands), and increasing in "oxidizing power" in the same direction, briefly as:

Ir (III)>Pt (IV)>Rh (III)>PT (II)>Pd (IV)>Pd (II)>Fe (III)>Cu (II),

This is undoubtedly determined by the oxidizing character of the central ion [94].

The first strong band in the spectra of all the Pd (II) and Pt (II) complexes Figs (15) prepared in this work is assigned as (L-MCT) band. The spectra of same complexes of Pd (II) of Pt (II) show same weak ligand filled bands, but their interpretation is not certain, this is a general feature of the spectra of spin –paired complexes in that the amount of information which can be obtained from them is a good deal less than that available from spin -free complexes.

On inspection of the electronic spectra of complexes prepared in the present work, a number of points can be pointed out:

(a)- The first strong C.T.band in the spectra of Pt (II) complexes (appeared at 250-300nm) appeared at shorter wavelength in comparison with the corresponding Pd (II) complexes, as seen in fig's (16), (17), (18), (19),(20),(21) the $\Delta \lambda$ cane in the range 7-40nm depending on the type of ligand.

(b)-On the comparison of spectra of cis $-PtCl_2(DMSO)_2$ and trans $-PdCl_2(DMSO)_2$,appreciable change took place , thin may be due to the cis –trans –isomerism effect , where the expected in wavelength in case of Pd over that of Pt in compensated by sharing the M-L C-T donation equally between the two S-atoms ,while it is in one direction ,i.e. toward one S-atoms in case of Pt as seen in the following representation .
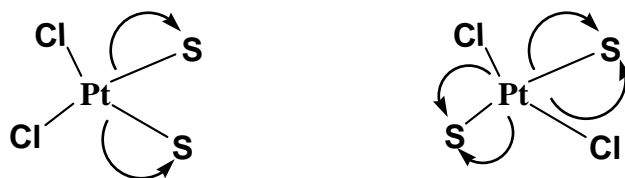
(c) The only band which undergo a change in the case of Pt complexes $PtCl_2$ (dipy) and Pt (dipy) (DTO) in the d- d transition band which came at 412 and 404 nm respectively. This shift is expected since the ligand field effect in DTO complex is strong than that of dichloride complexes. This is more indicated by changing the color from yellow [for $PtCl_2$ (dipy)] to red for[Pt (dipy) (DTO)] Cl_2. The measured magnetic moment for the studies complexes showed that all of them were diamagnetic with

the magnetic moment (μ.eff) to be zero; this indicates the formation square planar geometry for complexes show in these Tables (3) and (4).

Table (4) The physical data of Pd(II) complexes

Symbol	Color	Yiel%	M.P	Matel analysis	
				M%Calc	M%Found
AI	Yellow-orange	89	189-190	31.9	30.98
BII	Black-Brown	82	223-225	36.00	35.65
BIII	Brown	90	234-236d	19.08	18.9
BV	Red-Brown	86	230-233d	19.67	19.65
GII	Violet	80	>209-210d	22.28	22.21
GIII	Brown	75	219-220d	19.93	19.9

Table (5) The physical data of Pt(II) complexes

Symbol	Color	Yield%	M.P	Matel analysis	
				M%Calc	M%Found
AIII	Needle-Yellow-	93	194-196	46.2	46.00
BI	Red-Brown	85	229-230	50.77	50.23
BIV	Violet-Brown	80	240-242d	30.19	30.02
BVI	Violet	90	>237-238d	30.99	30.99
GI	Violet-	86	214-216d	34.33	34.21
GIV	Violet-Brown	70	223-224d	31.33	31.27
HI	Yellow	65	220-222d	46.21	46.10
HII	Red	70	>230-232d	36.10	35.98
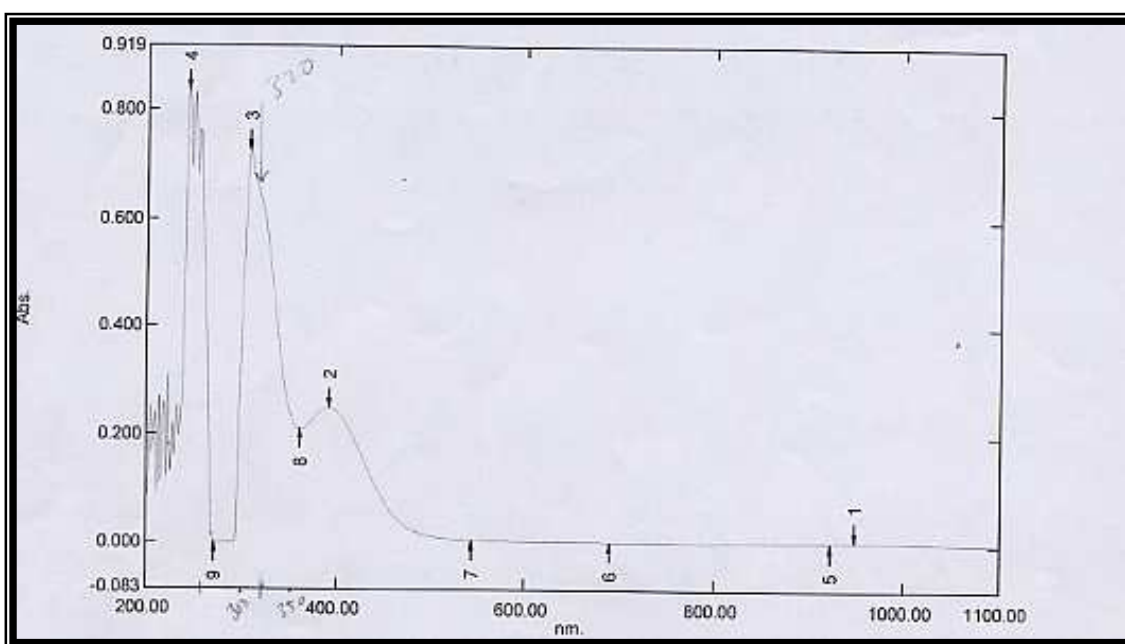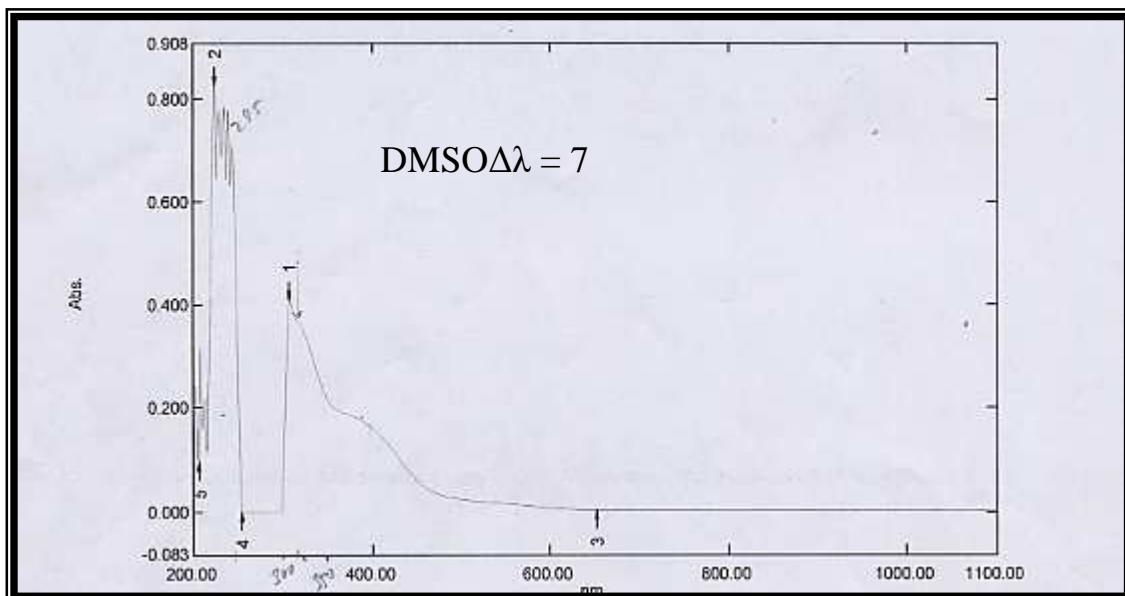
Fig. (15): Electronic spectra of AI and AIII.
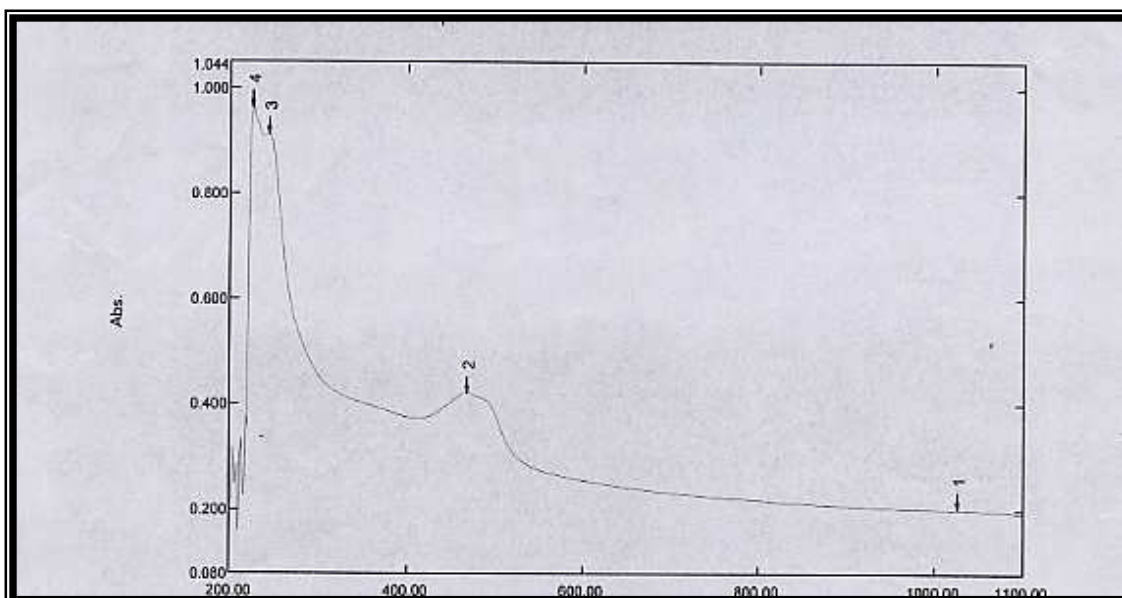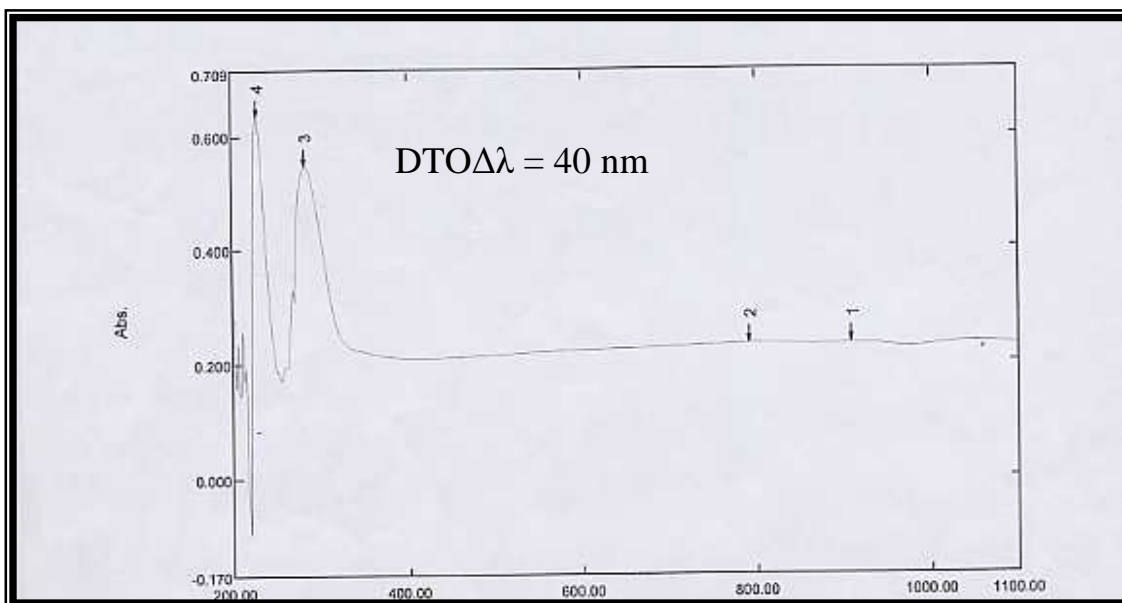
Fig. (16): Electronic spectra of BI and BII.
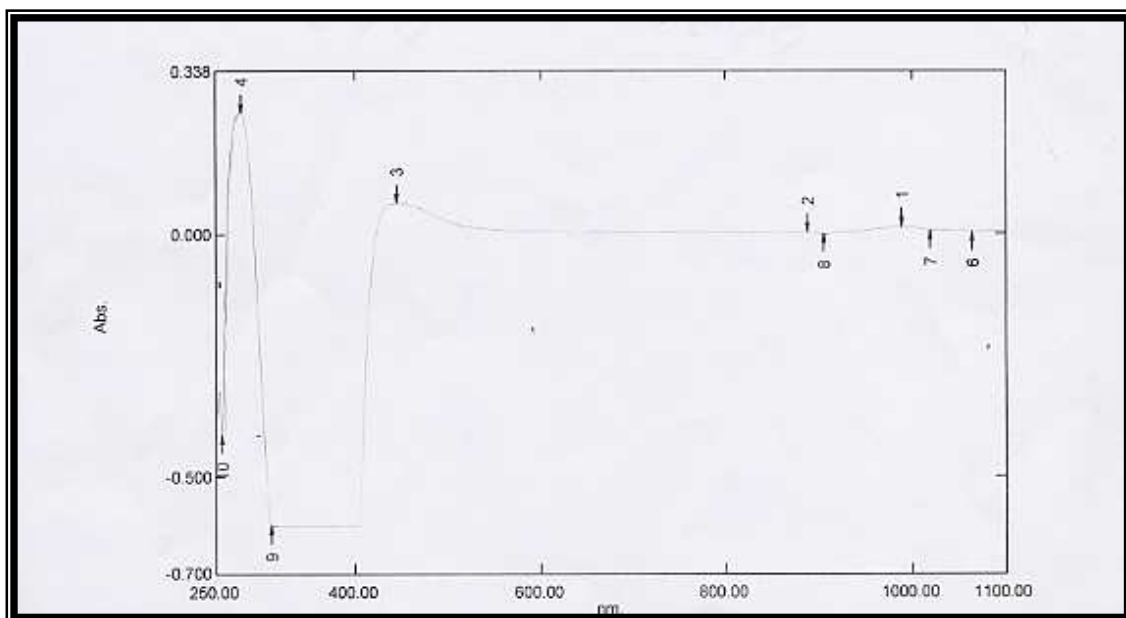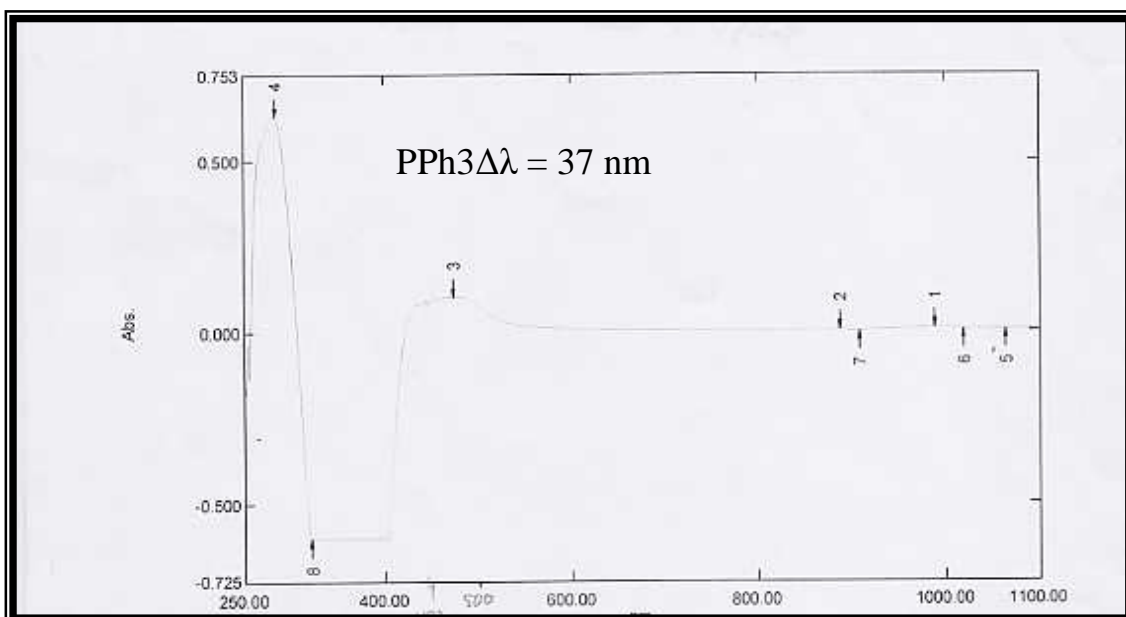
Fig. (17): Electronic spectra of BII and BIV.

NPh3Δλ = 7 nm
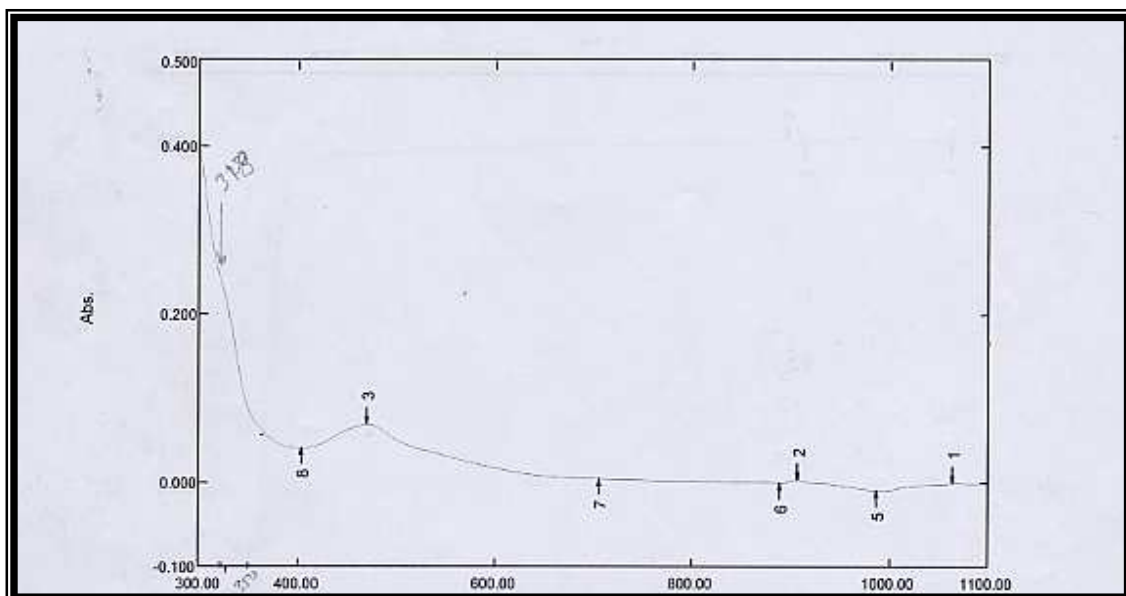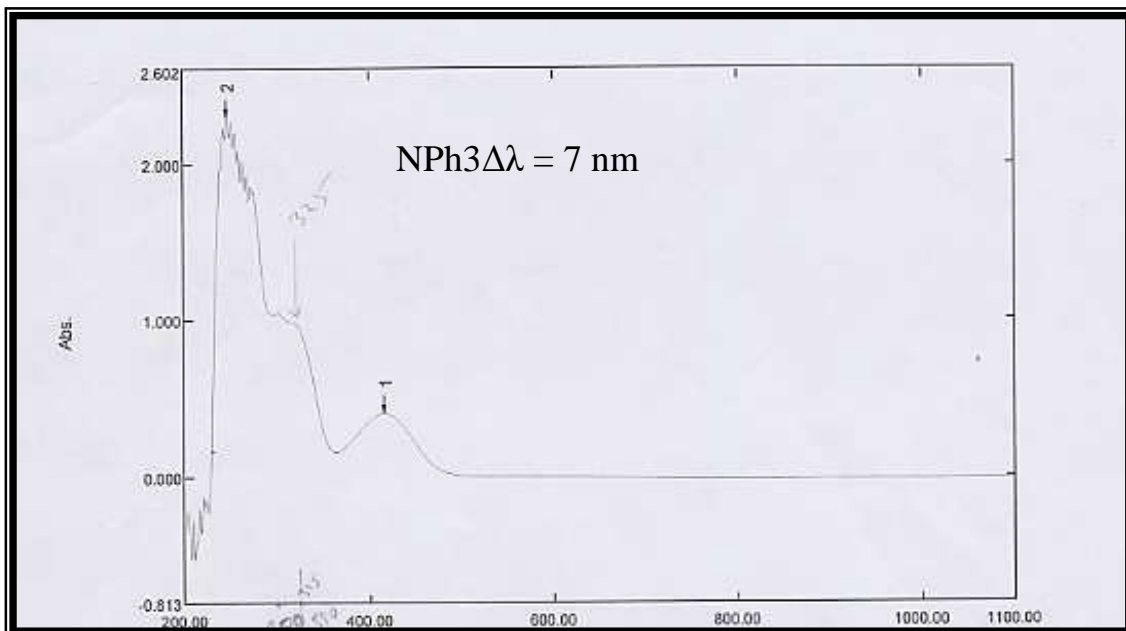
Fig. (18): Electronic spectra of BV and BVI.

BnzΔλ = 20 nm
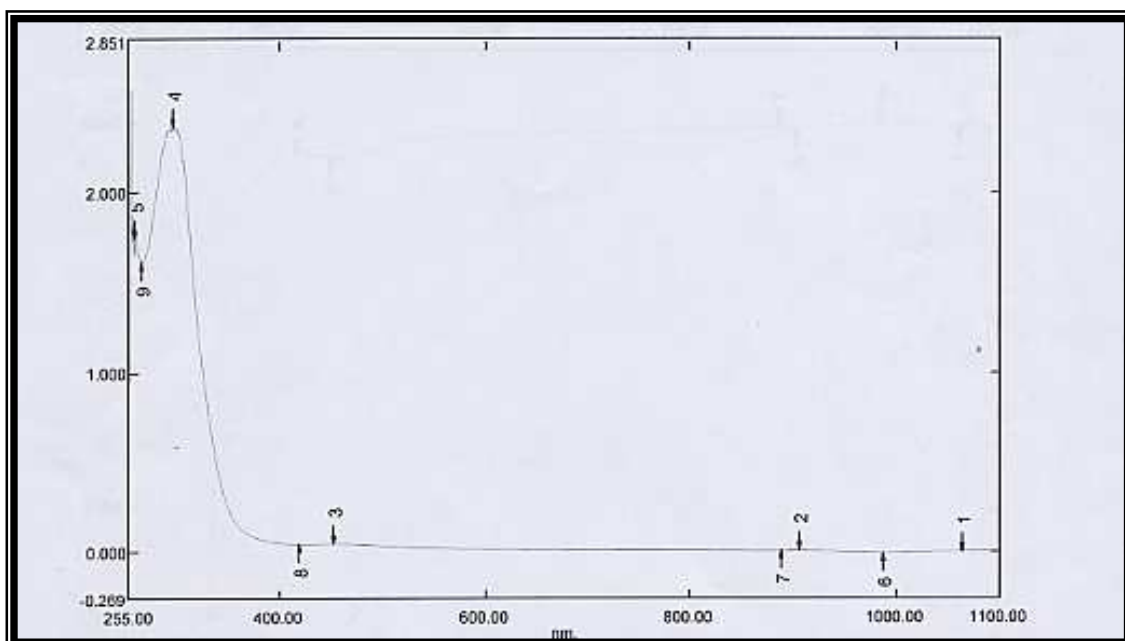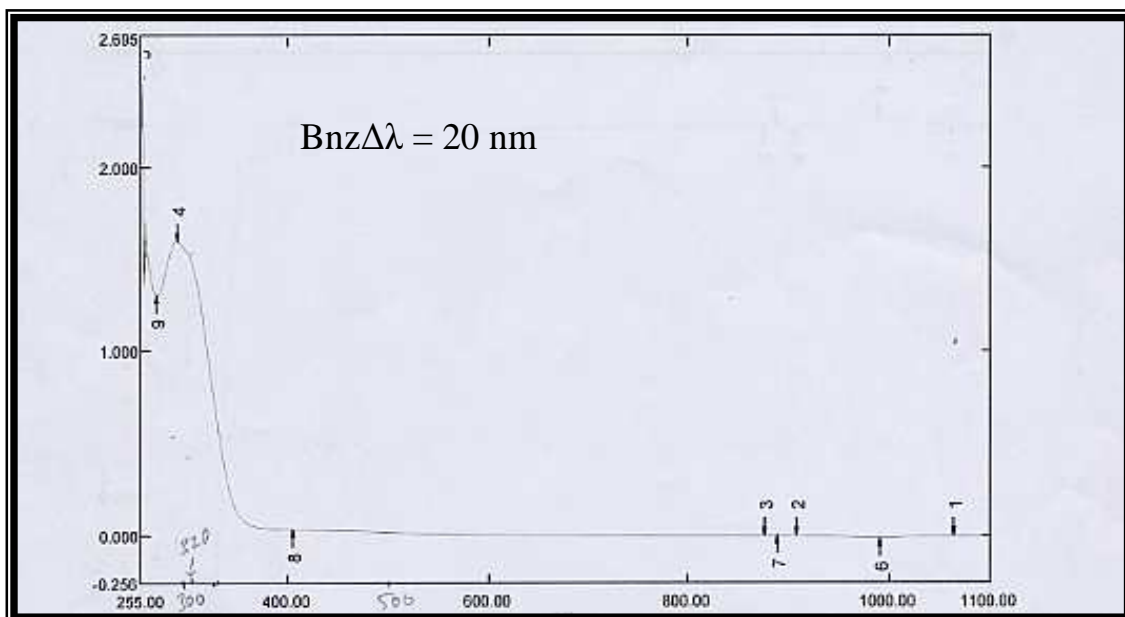
Fig. (19): Electronic spectra of GI and GII.

TMBnzΔλ = 20 nm
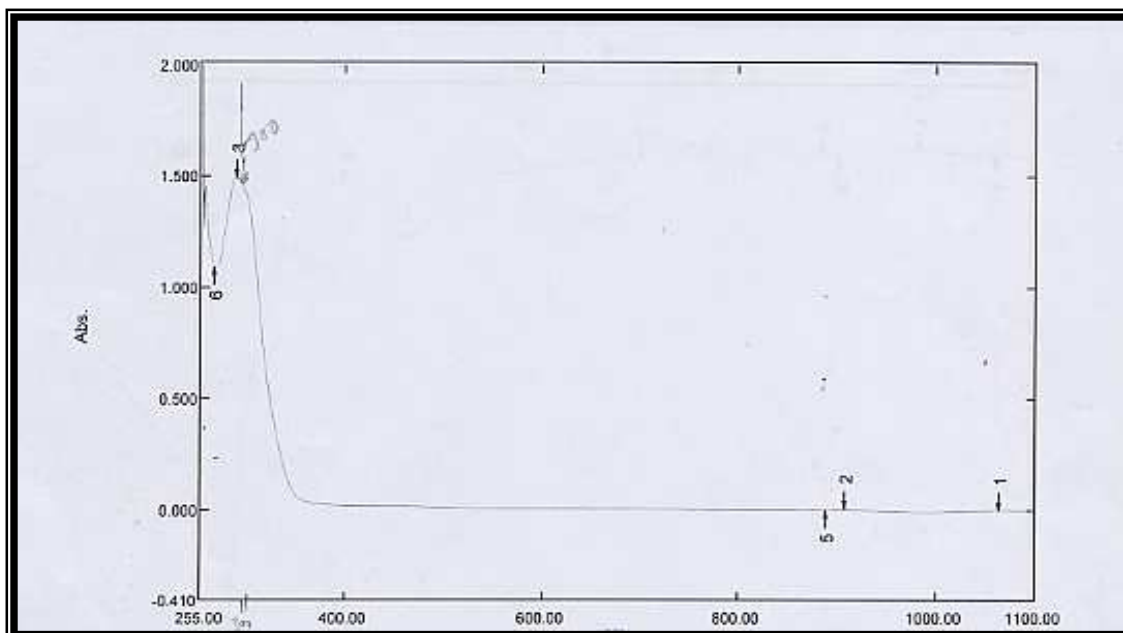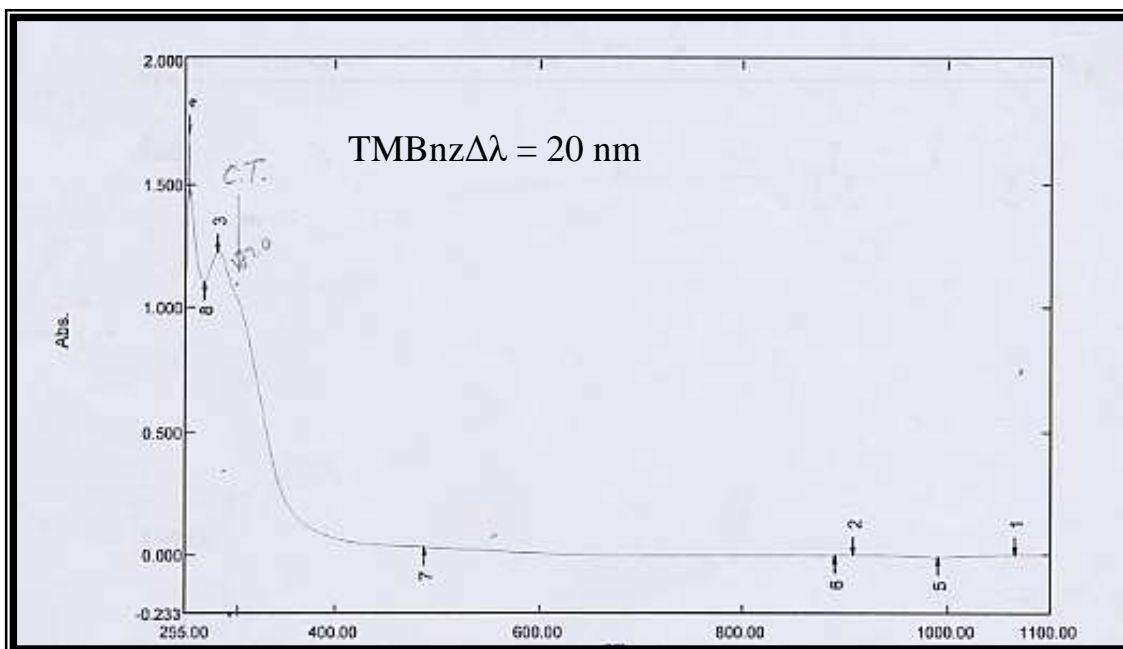
Fig. (20): Electronic spectra of GIII and GIV.
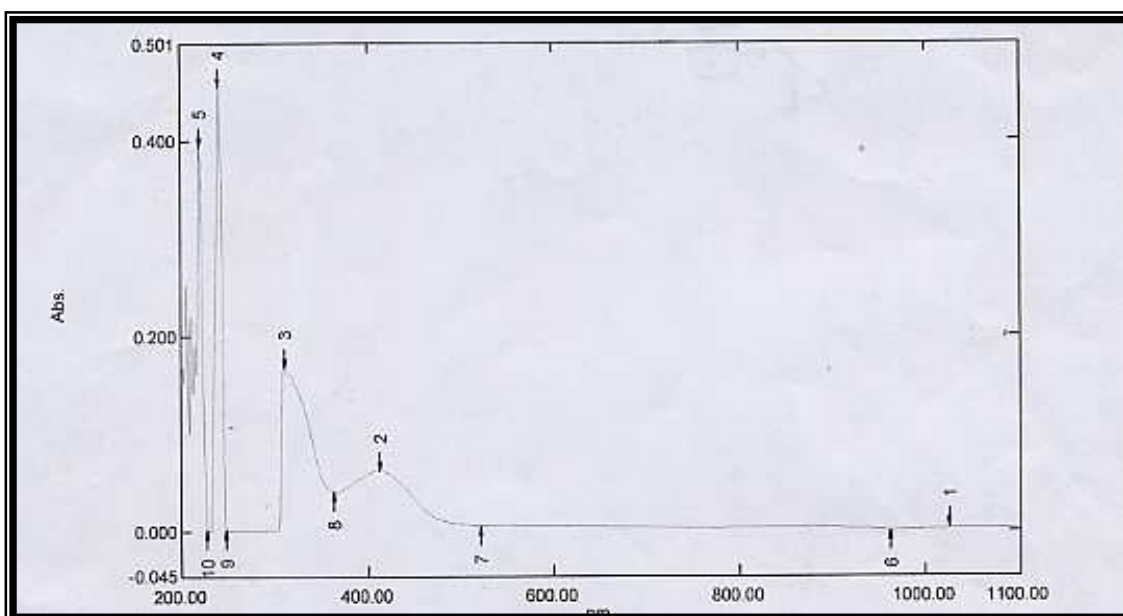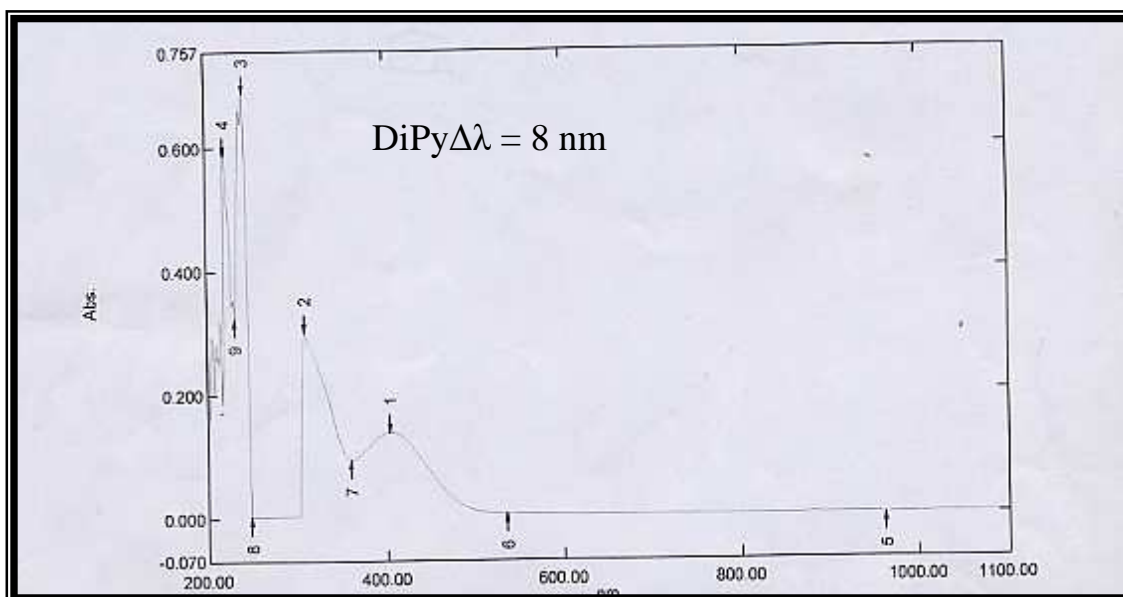
Fig. (21): Electronic spectra of HI and HII.

4.1-Biological Activity

The empirical use of inorganic substances in medicine has its origins in antiquities. Nevertheless, it is only in recent times, following development in chemistry, biochemistry and related disciplines, that logical bases have been established for understanding the roles of the inorganic species in medicines, and promise for the logical design of inorganic therapeutic agents that are relatively innocuous to the host, while being toxic to unwanted types of cell components.

In spite of the large amount of literature dealing with the metal metabolism of living organisms, only limited attempt appear to have been made to bring together what might be described as ***inorganic medical chemistry***. This topic includes the impact of pharmaceuticals on the metal composition of cells and tissues, the use of metal-containing agents in therapeutics, and the external control of the concentrations of essentials and toxic metal ions in living organisms. Certain metal complexes are active at low concentrations against a range of bacteria, fungi, and viruses.

It is clear that metal cheats can act in a number of ways. Thus they may inactivate a virus by occupying sites on its surface which would normally be utilized in the initiation of the infection of the host cell. The first step in the infection would be an adsorption reaction involving electrostatic interactions. Alternatively, the complex cations may penetrate the cell wall and prevent virus reproduction. Also it was found that side effects associated with anti-cancer drugs, e.g. cis-platin, can be minimized if technique could be developed to give constant low concentrations of the drug in vivo. Possibilities have involved in vivo reduction of Pt (IV) complexes, the break down of the polymeric platinum compounds and the slow removal of the inert blocking ligands. [96,97]

The transition metals have many a characteristic property of which is the ability.

To have multiple oxidation states, and having a strong tendency to from Ionic and neutral complexes of varying degrees of complexity. This can fruitfully be utilized in selective preparation of a very wide range of chemotherapeutic agents containing transition metals and study the complexing behavior of biological ligands involved in various biological processes, also to model mathematically and chemically biological systems with such compounds, and finally to control and optimize these systems [98] . Taking this into consideration we put forward the basic requirements achieved by preview researchers in the field of metal therapy and tried to choose accordingly our new potent materials. Other complexes chosen our work were to explore the possibility of finding out other requirements not investigated before. This has been achieved by synthesizing a considerable number of new heterocyclic transition metal complexes, i.e. Pd (II) and Pt (II).

4.2 Chemicals

1- Dimethylsulphoxide (DMSO).

2- Nutrient agar medium from *Maknus Lab. Company.*

3- Solutions of the new tested compound in DMSO

4.3 Apparatus

1- Petridish.

2- Incubator type *Memmert incubator.*

3- Autoclave from *Hiraymama Company.*

4.4 Types of bacteria

1- *Esherichia coli* (Gram negative).

2- *Staphvlocoous aureus* (Gram positive).

Method

A- Standard drugs

A number of Known antibiotics drugs Table (4.1) were taken as standard to compare their activity with that of the new ligands and complexes. These antibiotics cover a wide range of structural variety.

B- Preparation of Nutrient agar medium

(20 g) of dry nutrient agar were added to (1L) of distilled water in conical flask and stirred the solution with heating until it completely dissolve. The flask was Stoppard by cotton and the medium was sterilized by placing it in an autoclave for (20 mm) at 121 ^{0}C under pressure of 15 bound/inch. After that the medium was cooled to *(45-55)^{0}C* and placed in Petri dish about *(15-20)* ml for each one, and was left to cooled and solidified. Therefore the medium was ready for bacteria growth. The studied bacteria were placed on the nutrient agar surface using the loop and by streaking processor. After that the disc saturated with the tested compound solution was placed in the dishes which were then incubated for 24 hour, at 37C^0.

4.5 Results Discussion:

In this research many compounds were studied and characterized .All of these compounds are soft so that they could penetrate bacterial .Bacteria which are

studied are **_Staph_.aureus** and **_E-Coli_.** The bacterial cell wall of these we bacteria consist of lipofilac,cell walls of negative bacteria are far more complexes than those of positive bacteria. But since all of the prepared compounds are soft, that could form covalent bonds that are capable of penetrating the cell of interest, thus it manifests a biological activity. The results showed that there are compounds of high biological activity as could be read in the table (4.2).

Table (4.2) shows the activity of the new ligand and their complexes on the growth of the studied bacteria, the results show the following observations:

1. L_1 was highly active against **Staph.aureus** only, L_2 inactive against both bacteria while L_3 was highly active against **Staph.aureus** and moderately active against **E-CoIi**. L_1=[Pph$_3$,TMBnz,Dipy],L_2=[Bnz,DTO] L_3=Nph$_3$.

2.The Pd (II) complexes of (AI)show high a wider spectrum of activity against only active in **E-Coli** ,but Pt (II) complexes A(III)in active in both against of bacteria compared with the ligand as using the control.

3-The five complexes BI,BII,BIII,GII and H1 of Pt(II) and Pd (II) as shown high activity against both type of bacteria compared with that of their ligand .

4-The behavior of the four complexes BV, GI, GIII and HII show the in active against both bacteria as the compared with the ligand.

5-the BVI and GIV complexes were moderately active against **E-Coli** only, while BIV complexes were moderately active against **Staph-aureus** only.

6.The observation reflect the different effect of introducing the metal ion on the ligand structure, were some metal ions inhainse activity while others retard it. This phenomenon is known as synergistic effect. The following figures show the various activities obtained by different metal ion complex.

Fig.(22):-Effect of AI ,AIII,BI,BII,BII and BIV on **Staph. aureus**
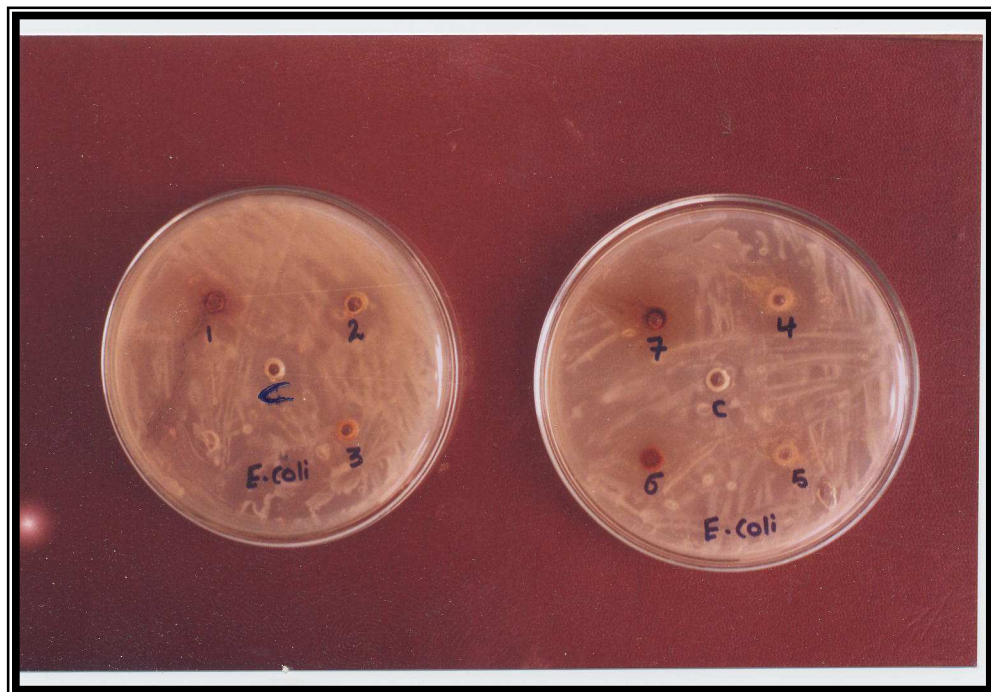
Fig.(23):-Effect of AI and AIII,BI,BII,BII and BIV on **E-Coli**
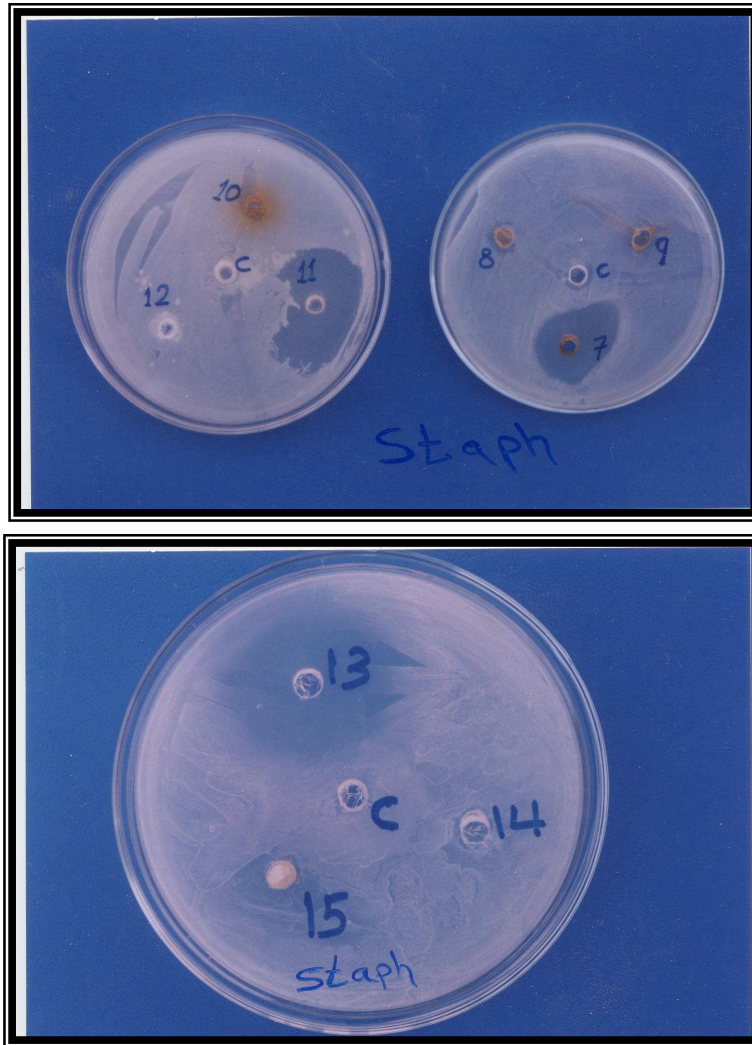
Fig.(24):-Effect of BV,BVI,GI,GII,GIII,GIV ,HI,HII and DTOon

Staph.aureu
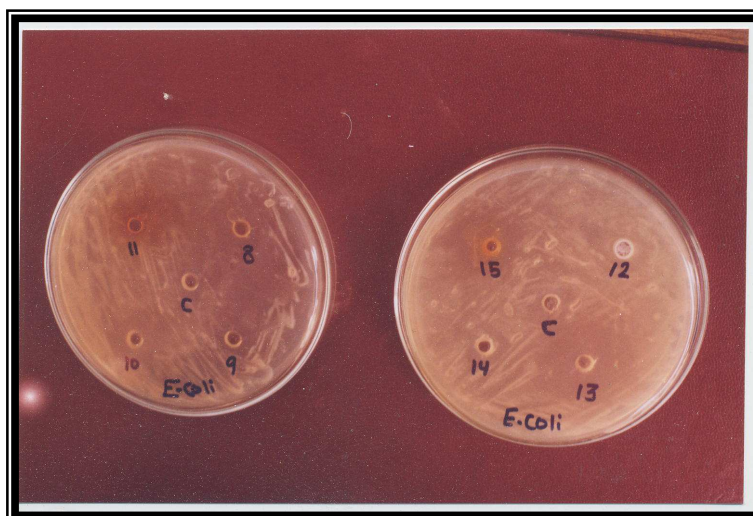
Fig.(25):-Effect of BV,BVI,GI,GII,GIII, GIV ,HI,HII and DTO on **E-Coli**

Fig.(26):-Effect of Nph3,Pph3,Bnz, TMBnz,and Dipy on **Staph. aureus**

Fig.(27):-Effect of Nph3,Pph3,Bnz, TMBnz,and Dipy on **E-Coli**

Table (4.1) Biological activity for known anti-biotic drugs

Anti-biotic drugs	Staphylococcus aureus	Escherichia Coli
Erythromycin	+ + +	-
Chioramphenical	+ + +	-
Tetracycline	+ + +	-
Ampicillin	+ + +	-
Fusidic acid	+ + +	-
Amoxicillin	+ + +	-
Neomycin	-	++
Refadin	-	-
Streptomycin	-	-

(-)   No inhibition

(+)   Inhibition zone (6- 8) mm

(++) Inhibition zone (8-10) mm

(+++) Inhibition zone (>10) mm.

Table (4.2) Biological activity for ligands and its complexes at(conc.1mg/ml) in DMSO as asolvent.

Symbols	Staphylococcus aureus	Escherichia Coli
DMSO	-	-
AI	-	+
AIII	-	-
BI	+++	++
BII	+	+
BIII	+++	++
BIV	+	-
BV	-	-
BVI	-	++
GI	-	-
GII	+++	+++
GIII	-	-
GIV	-	+
HI	+++	++
HII	-	-
DTO	-	-
Pph$_3$	+++	-
Nph$_3$	-	+
Bnz	-	-
TMBnz	+	-
Dipy	+	-

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List of abbreviation

DMSO   **Dimethylsulphoxide**

DTO   **Dithiooxamide**
PPh$_3$ **Triphenylphosphine**

Nph$_3$ **Triphenylamine**

Bnz   **Benzidine**

TMBnz   **3,3ˉ,5,5ˉTetramethylBenzidine**

Dipy   **2, 2ˉDipyridyl**

ν   **Stretching**
ν$_s$ **Symmetrical Stretching**
ν$_{as}$ **ASymmetrical Stretching**
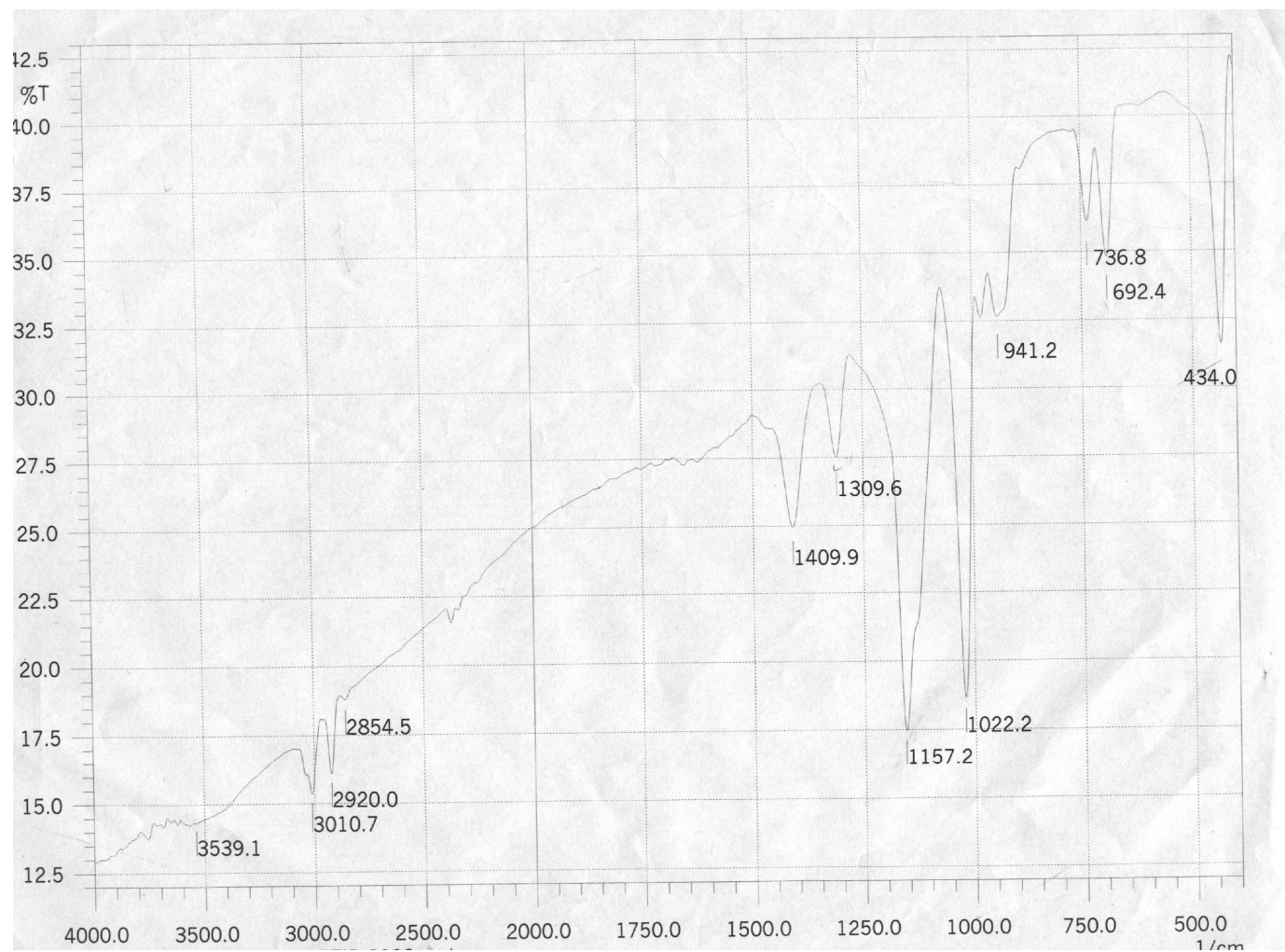
Fig. (1): Cis-Pt(DMSO)₂Cl₂
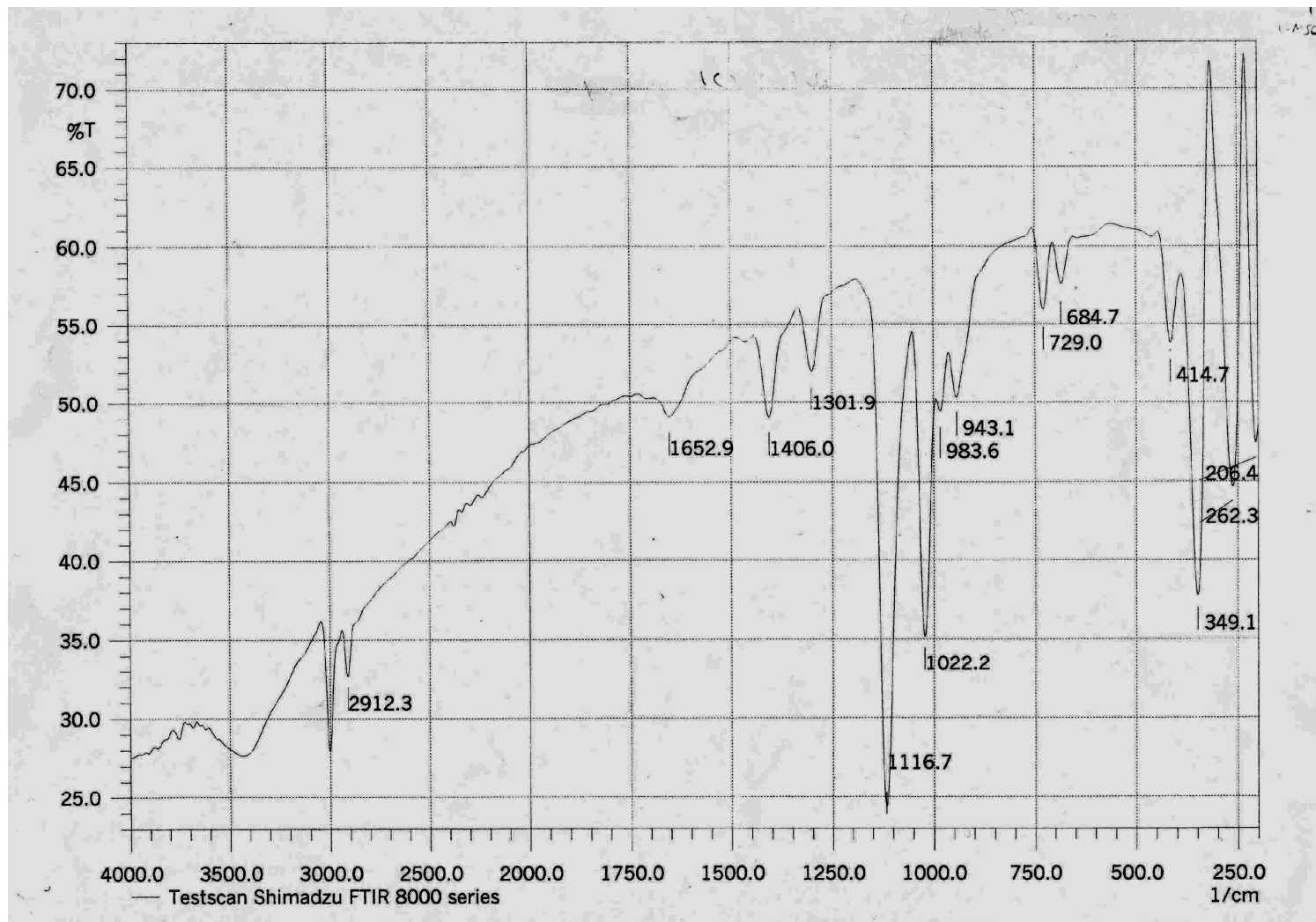
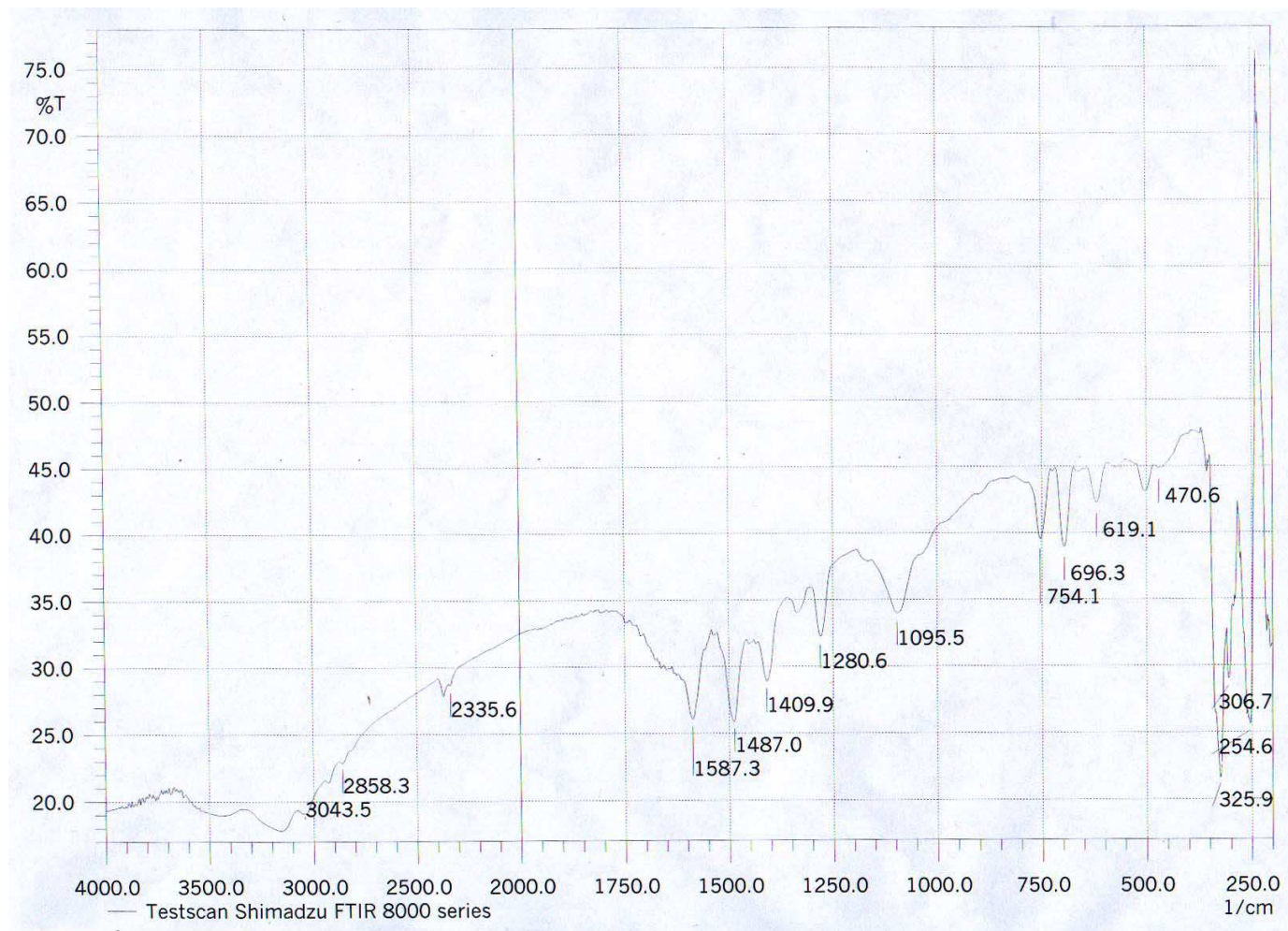**Fig. (2): Trans- PdCl$_2$(DMSO)$_2$**
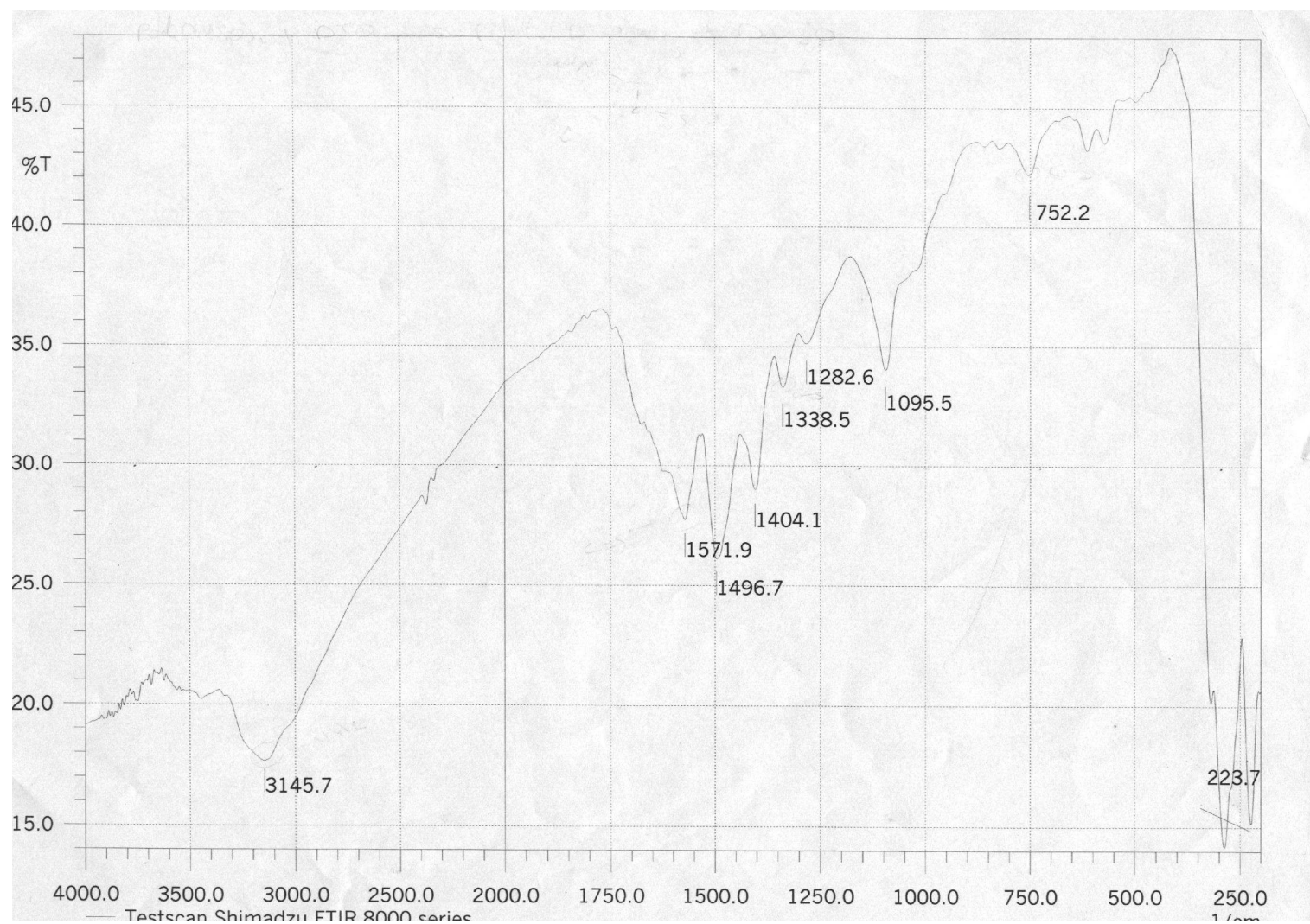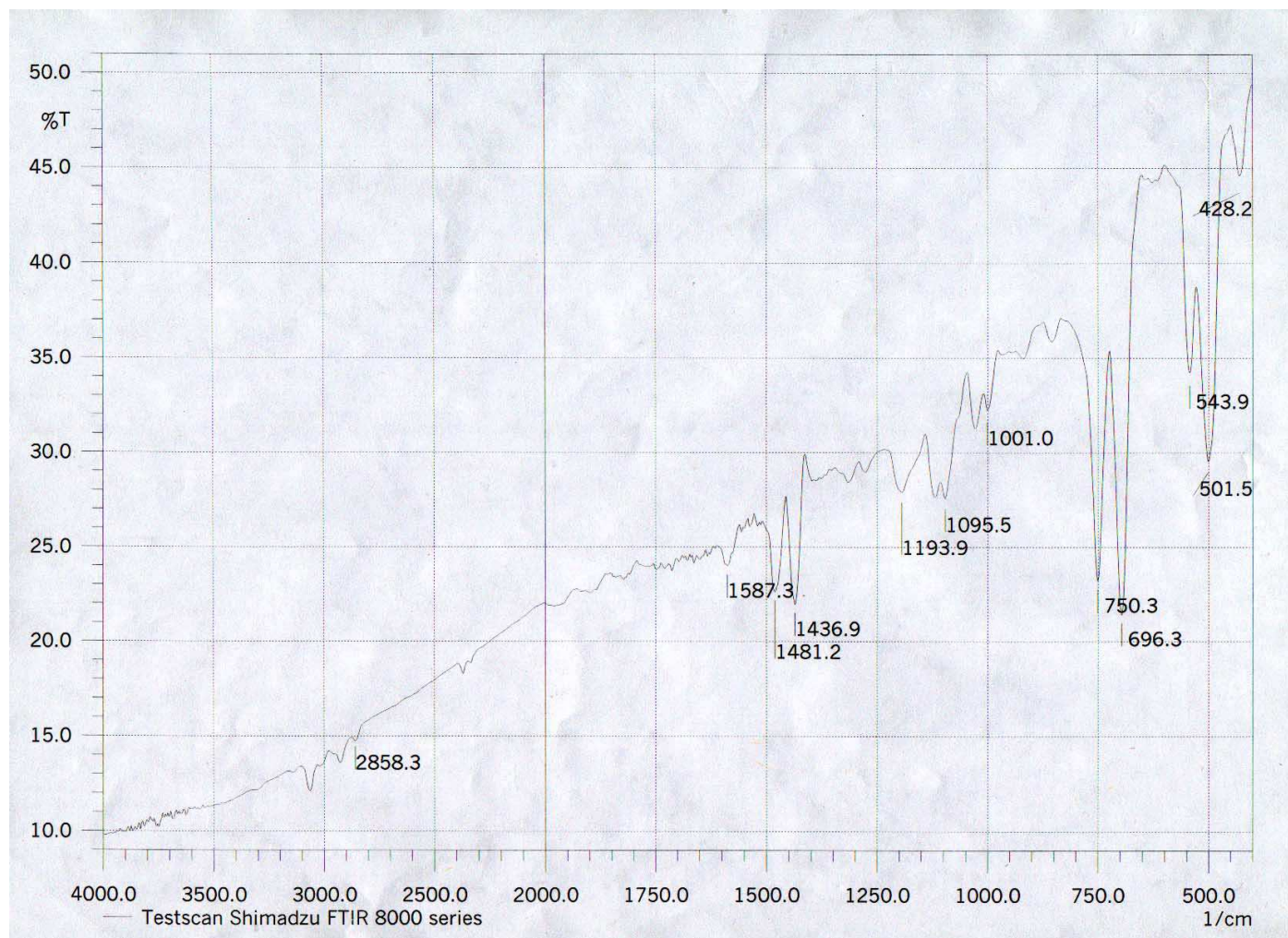
Fig. (3): PdCl₂(DTO)
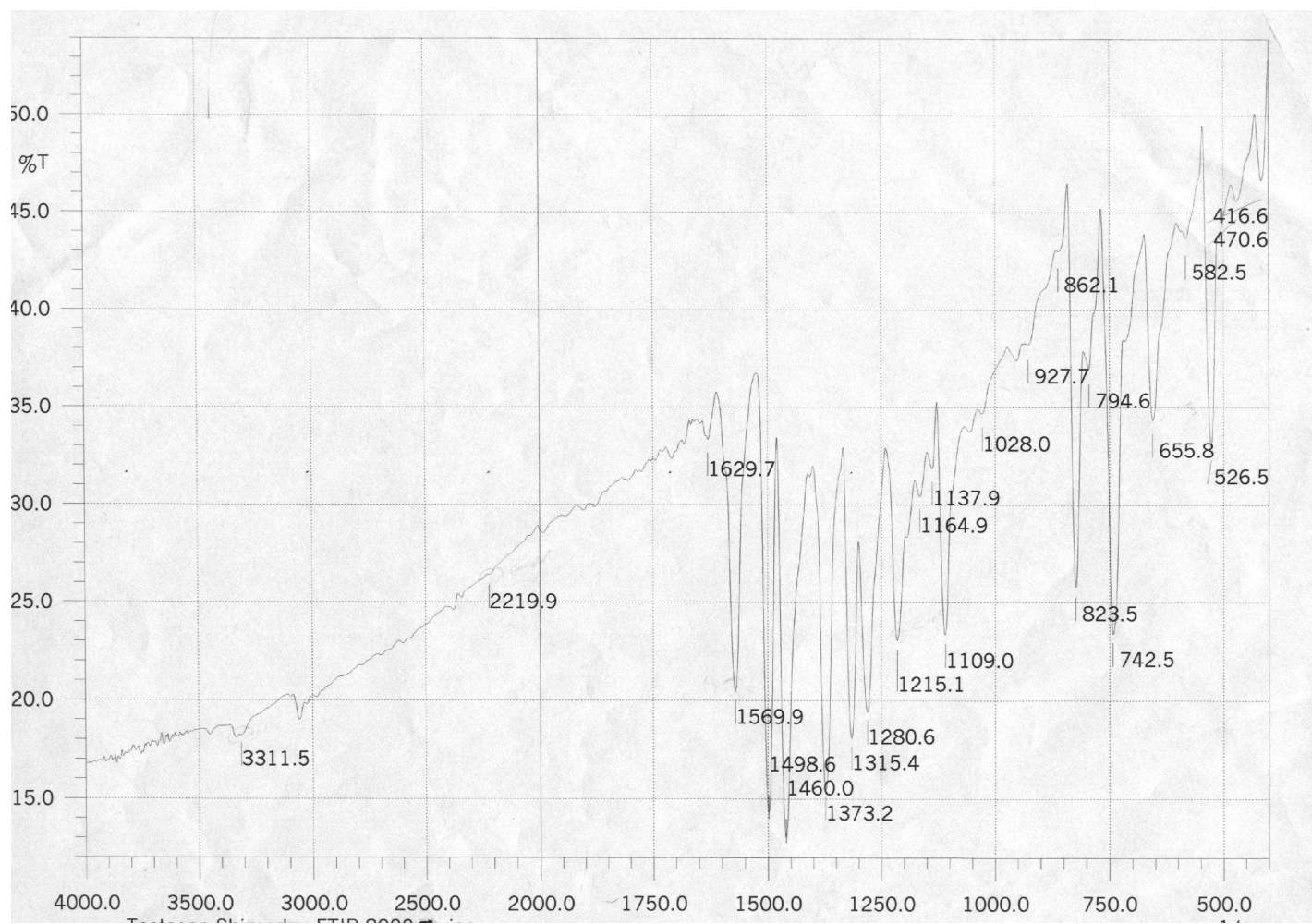
Fig. (4): PtCl₂ (DTO)
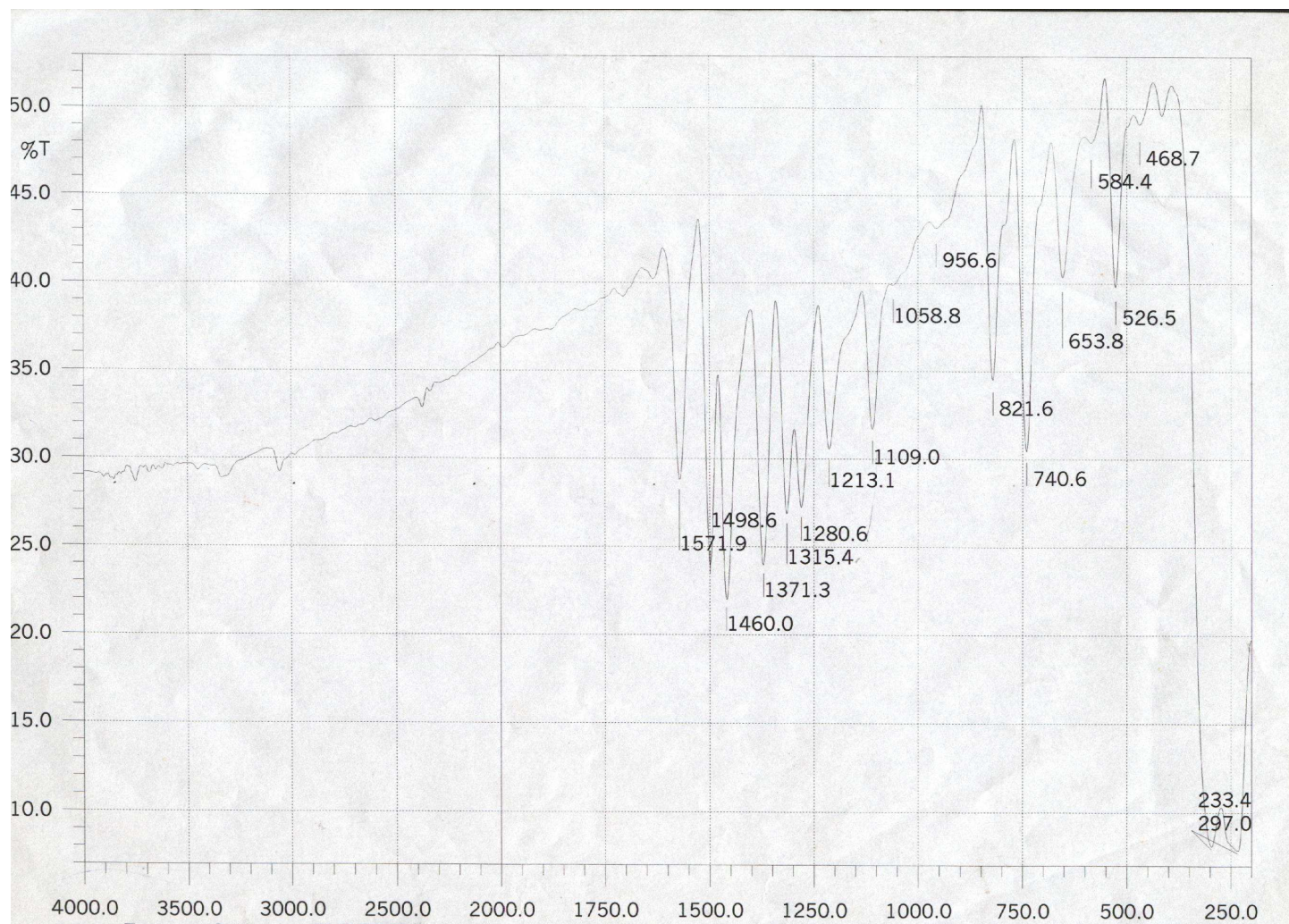
Fig. (5): PtCl2(DTO)
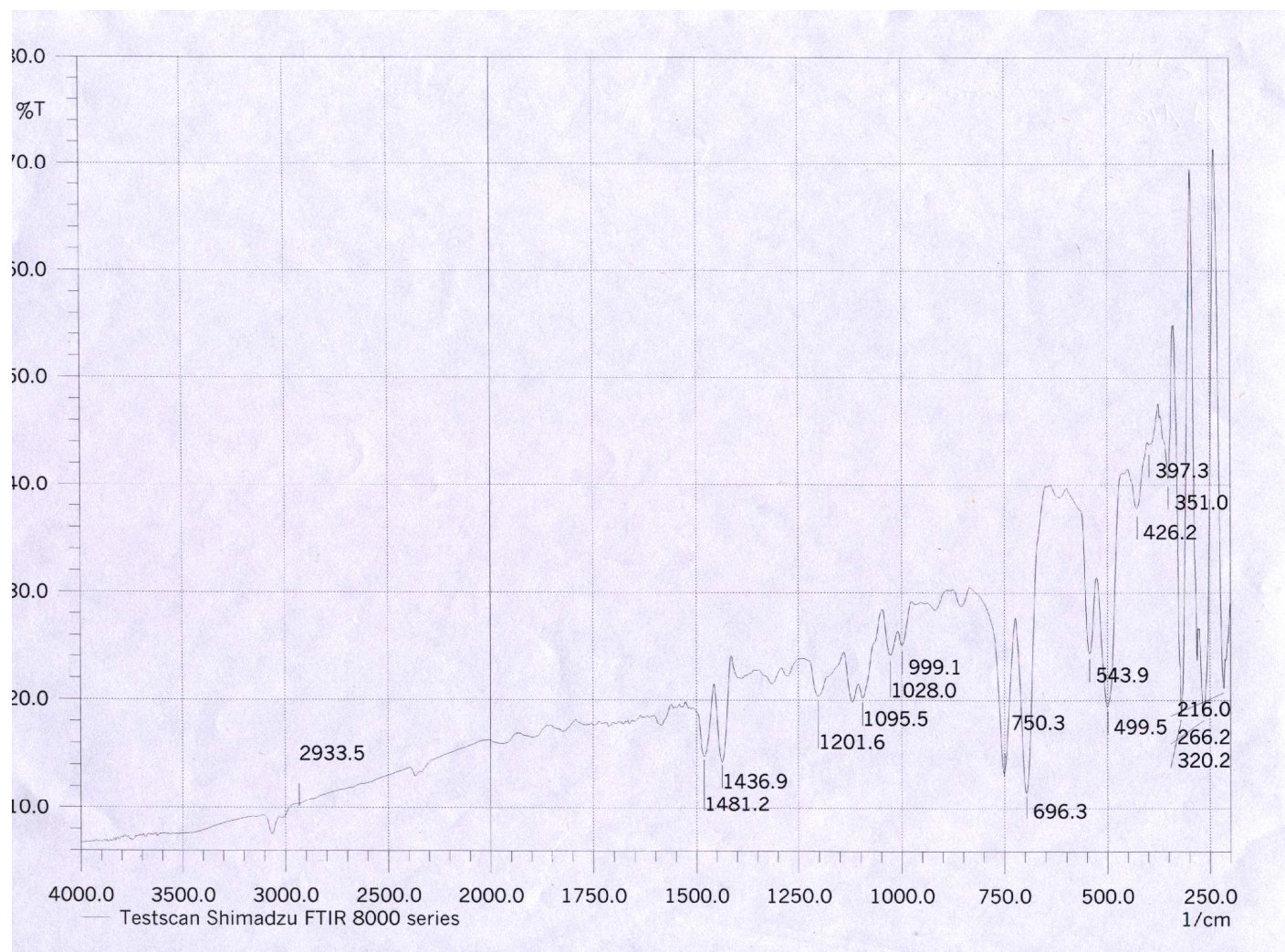
Fig. (6): PdCl₂(DTO) P(ph₃)
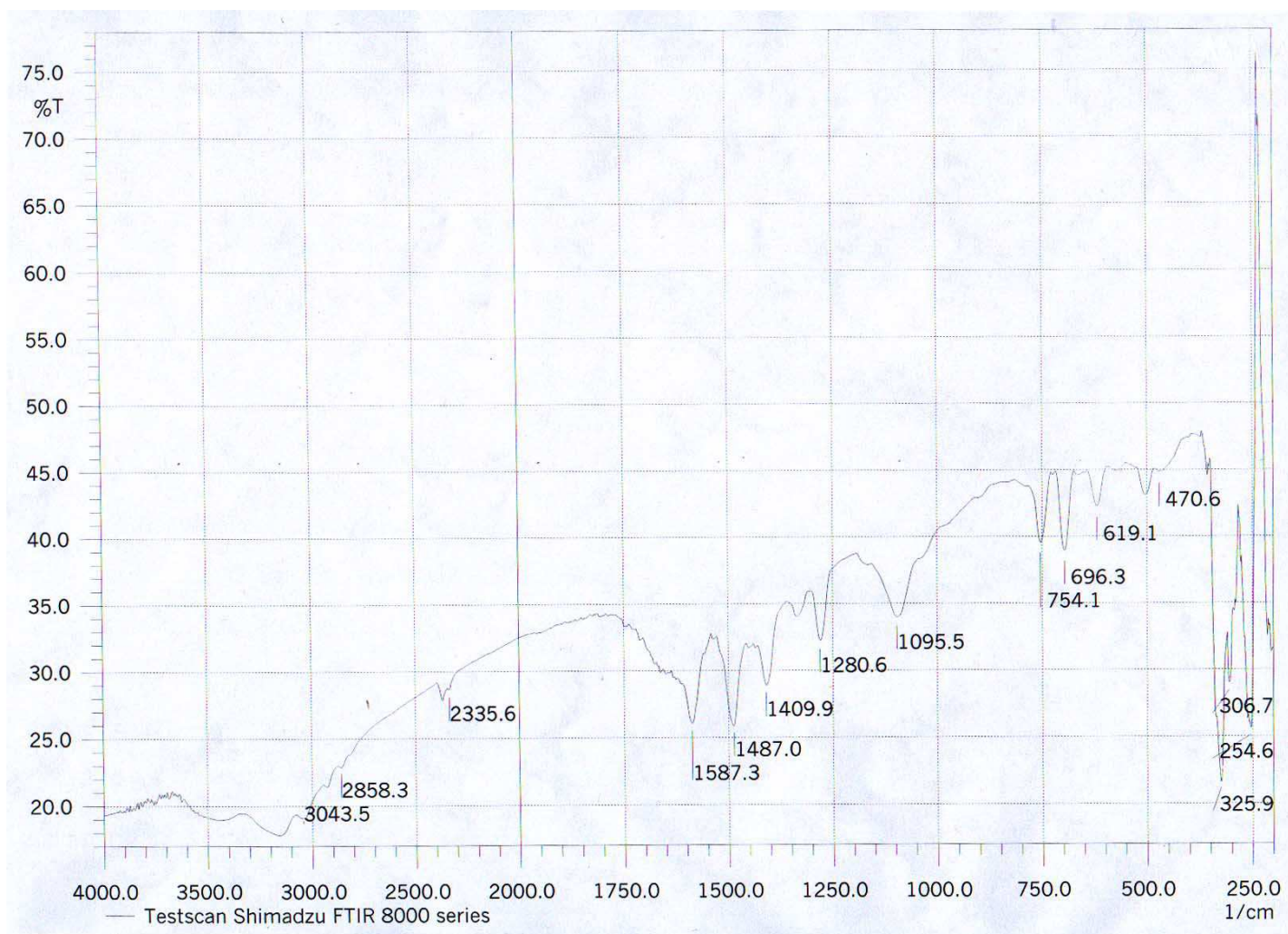
Fig. (7): PdCl$_2$(DTO) N(ph$_3$)

Fig. (8): PdCl2(DTO) N(ph3)
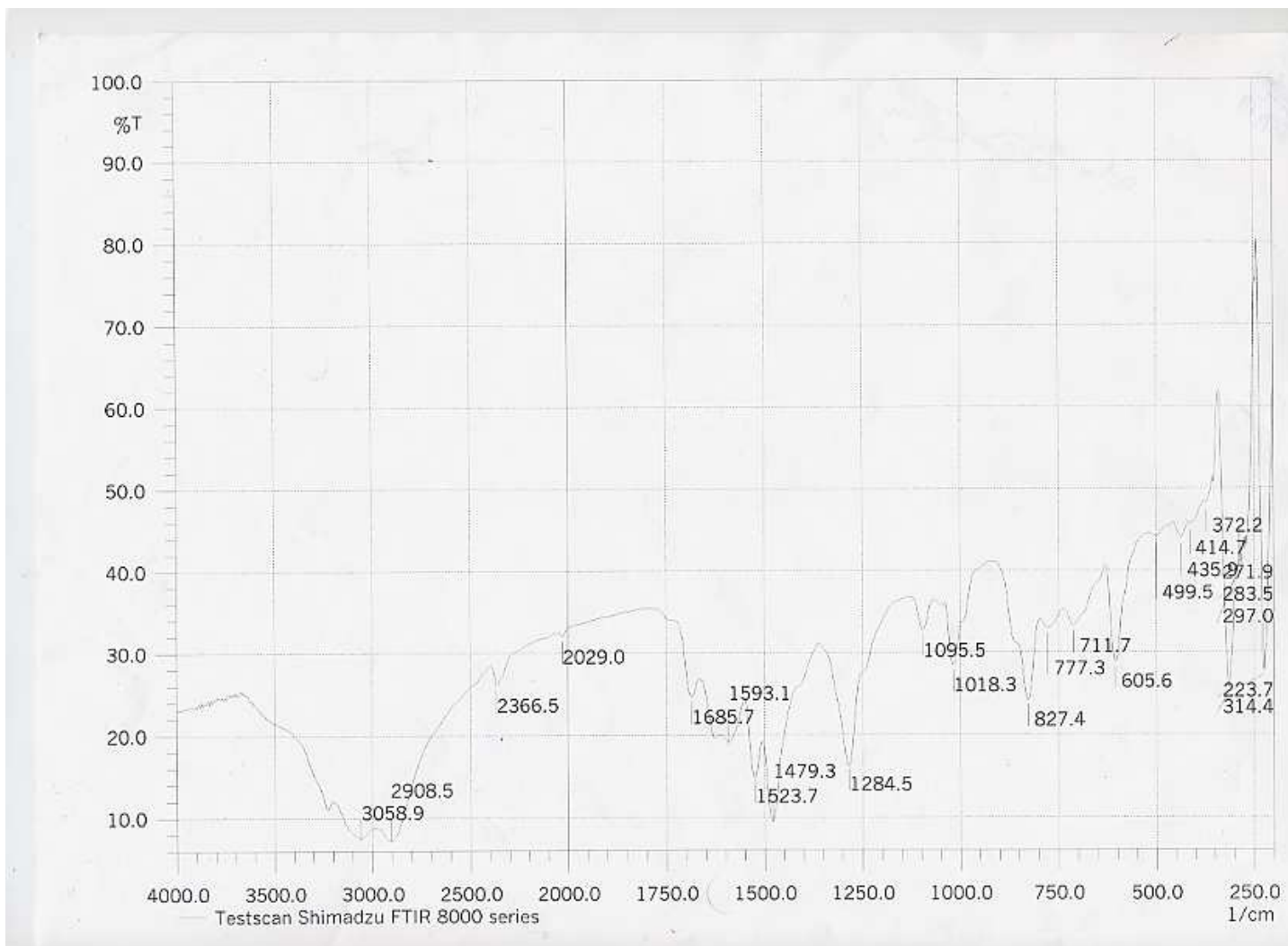
Fig. (9): PtCl₂(DTO) P(ph₃)
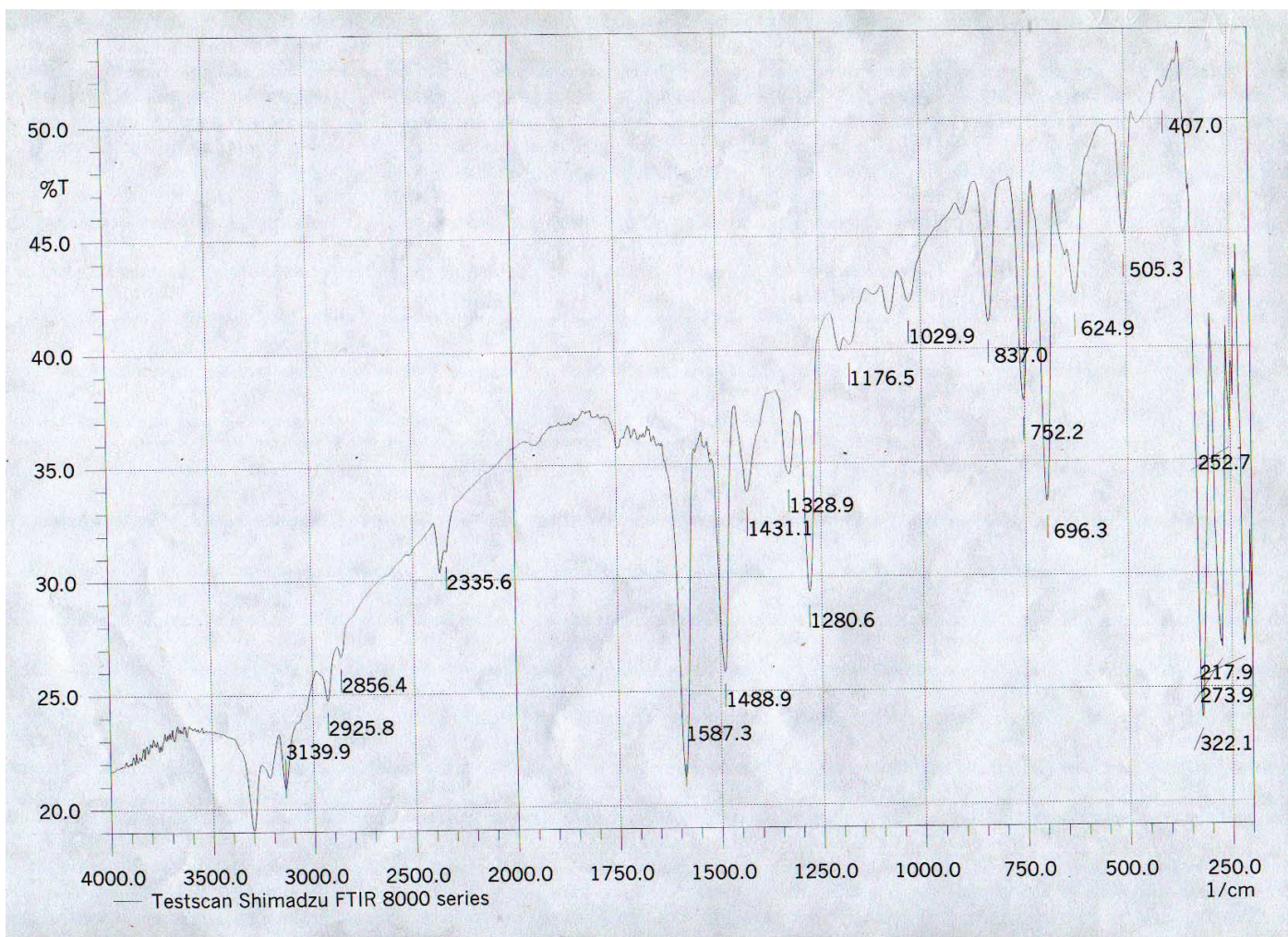
Fig. (9): PtCl$_2$(DTO) N(ph$_3$)
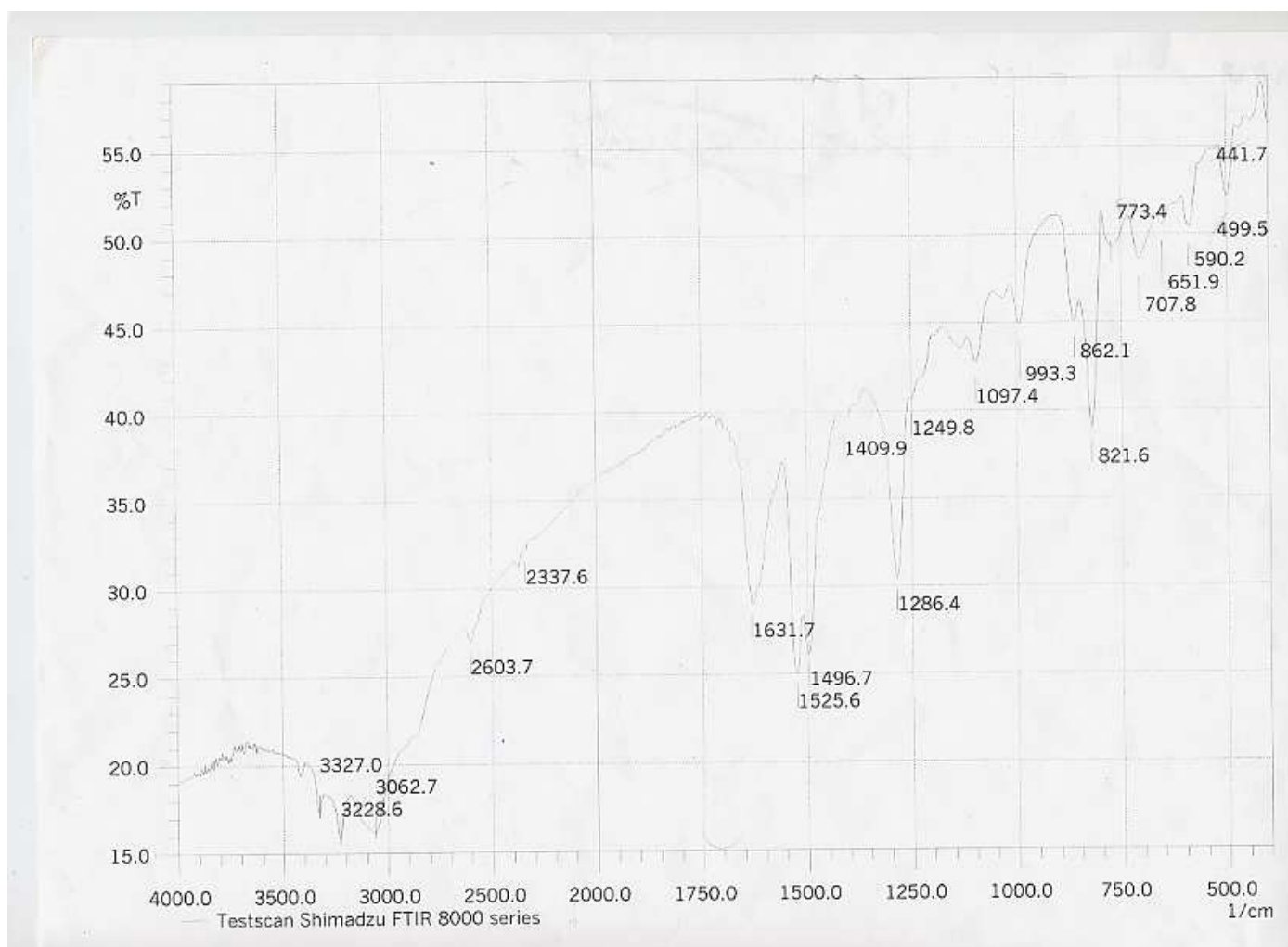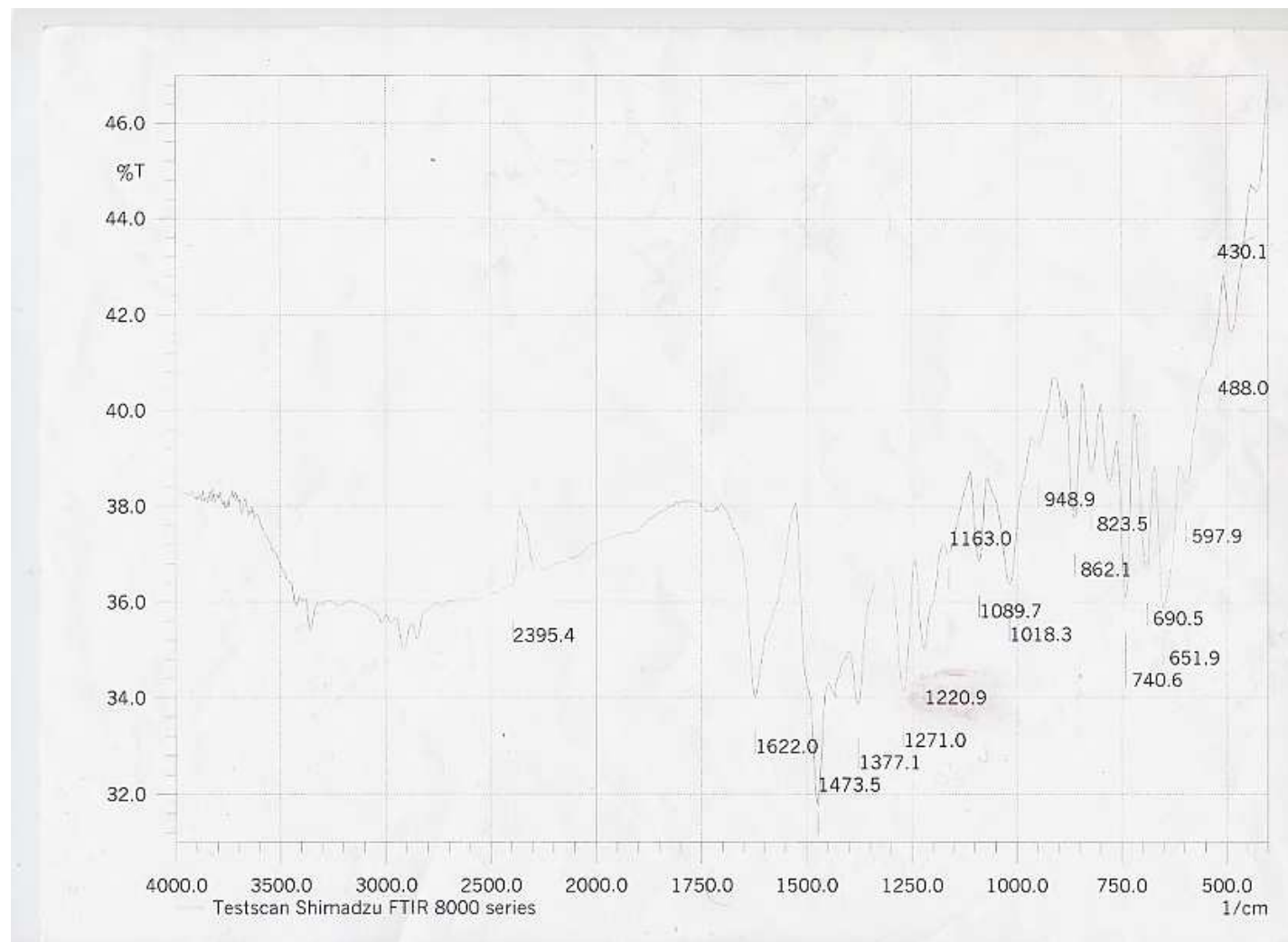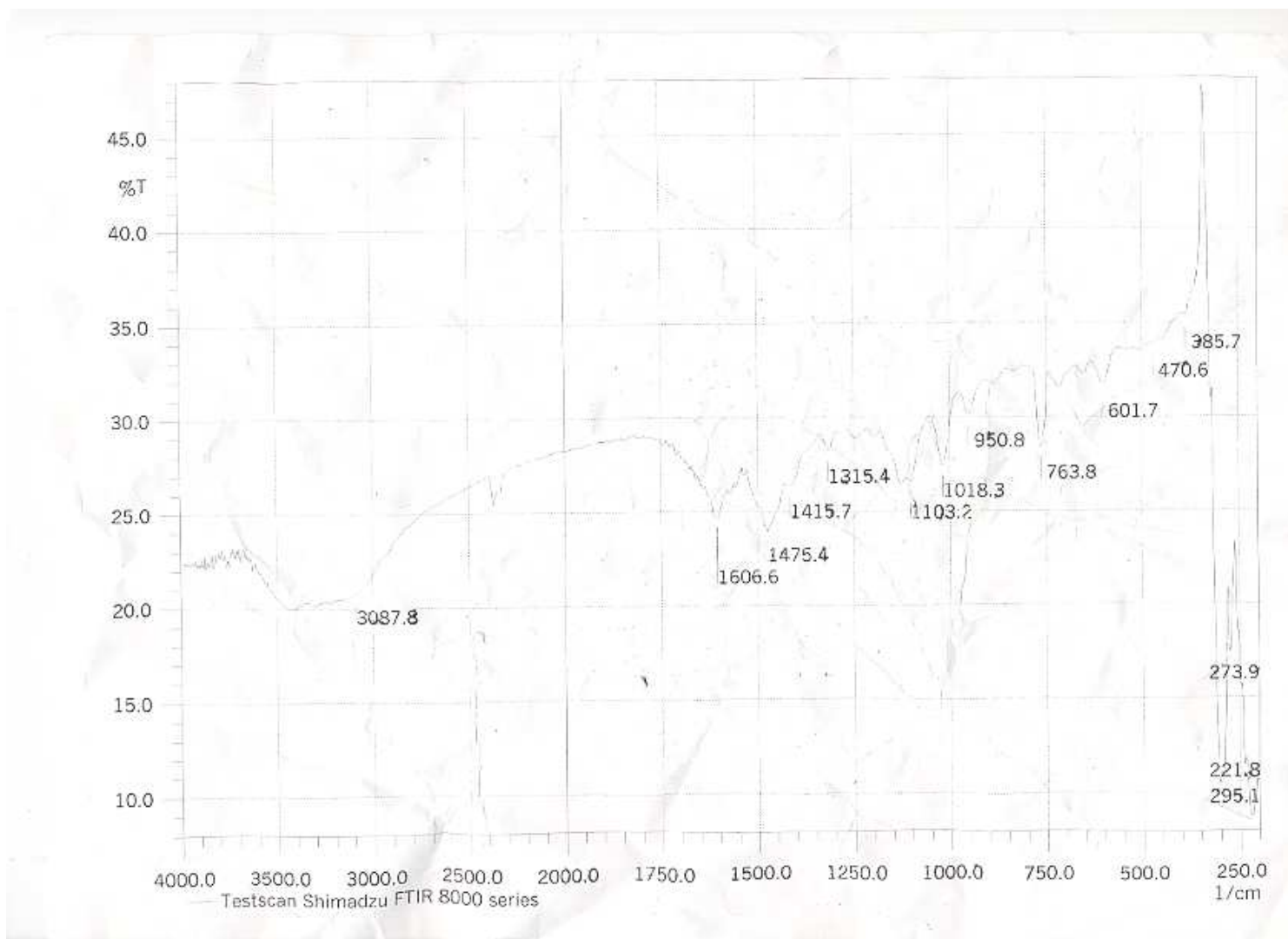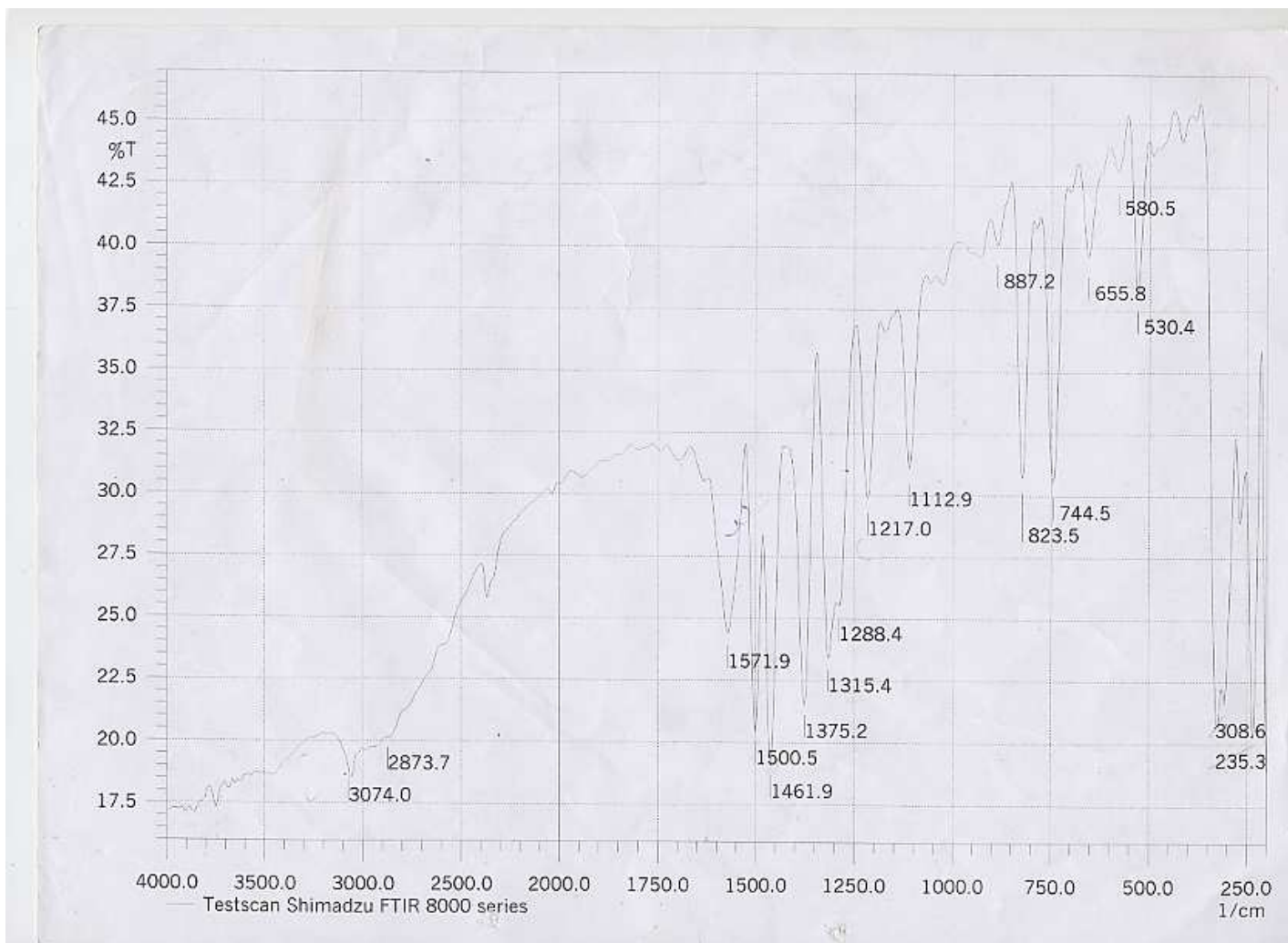
Fig. (10): **Pd(DTO)Bnz**
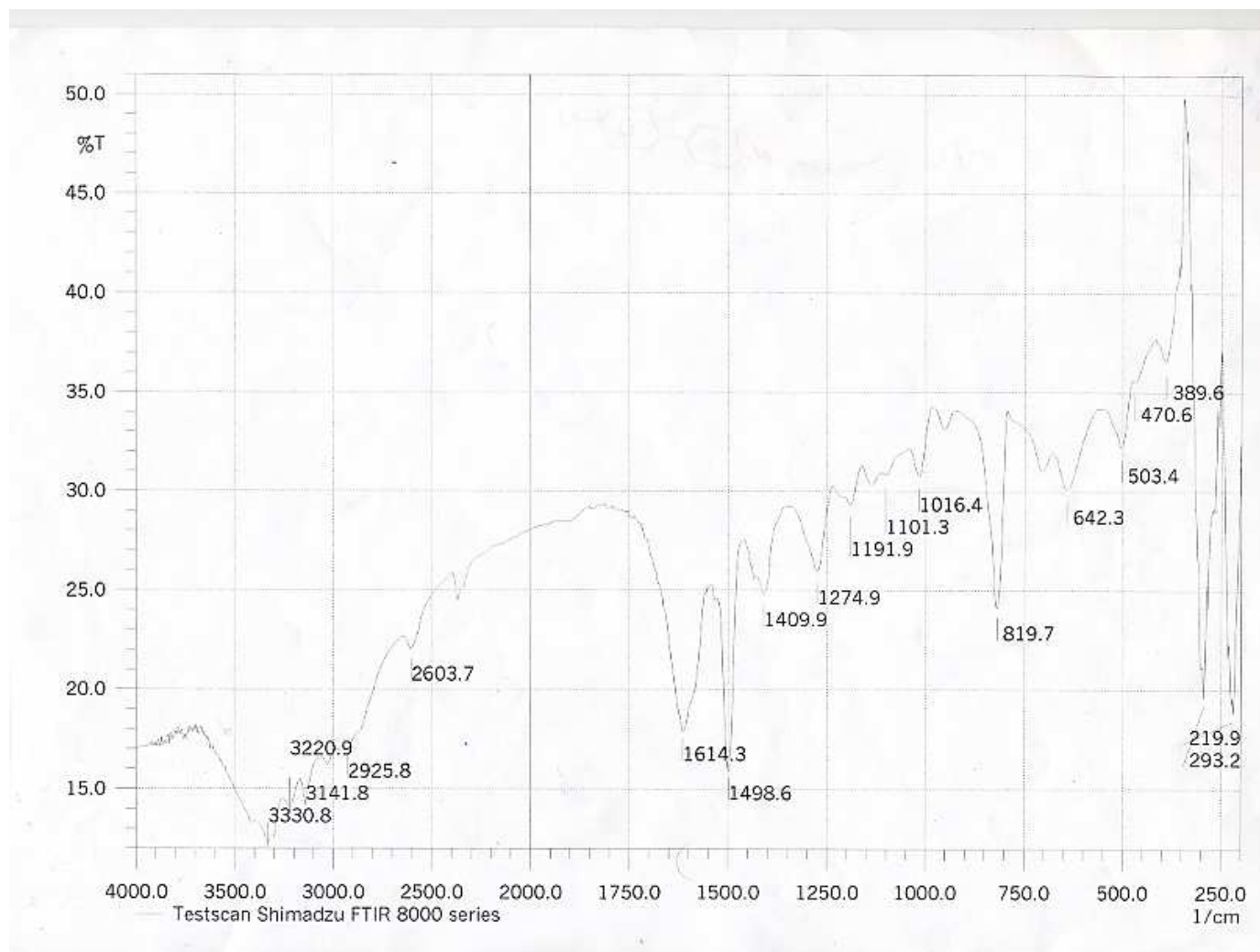
Fig. (11): **Pt(DTO)Bnz**

Fig. (12): Pd(DTO)TMBnz

Fig. (13): Pt(DTO)TMBnz

Fig. (14): **PtCl$_2$(Dipy)**

Fig. (15): Pt(DTO)(Dipy)

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الإهداء

الى مثلي الاعلى ...وقدوتي في الحياة ...الى نبع المحبة الصافي الى من علمني
معنى العطاء و التضحية

والدي

الى من صبرت وسهرت من اجل راحتي ... الى فيض الحنان الدافق

والدتي

الى من شرفني الله بوجودهم ... الى سندي و مشجعي في الشدائد
الى مهد طفولتي و مرح شبابي ... و أحباب قلبي ...

أخوتي

الى من امتلكت قلبي وكان دعائها لي كالظل... الى نصفي الأخر

خطيبتي

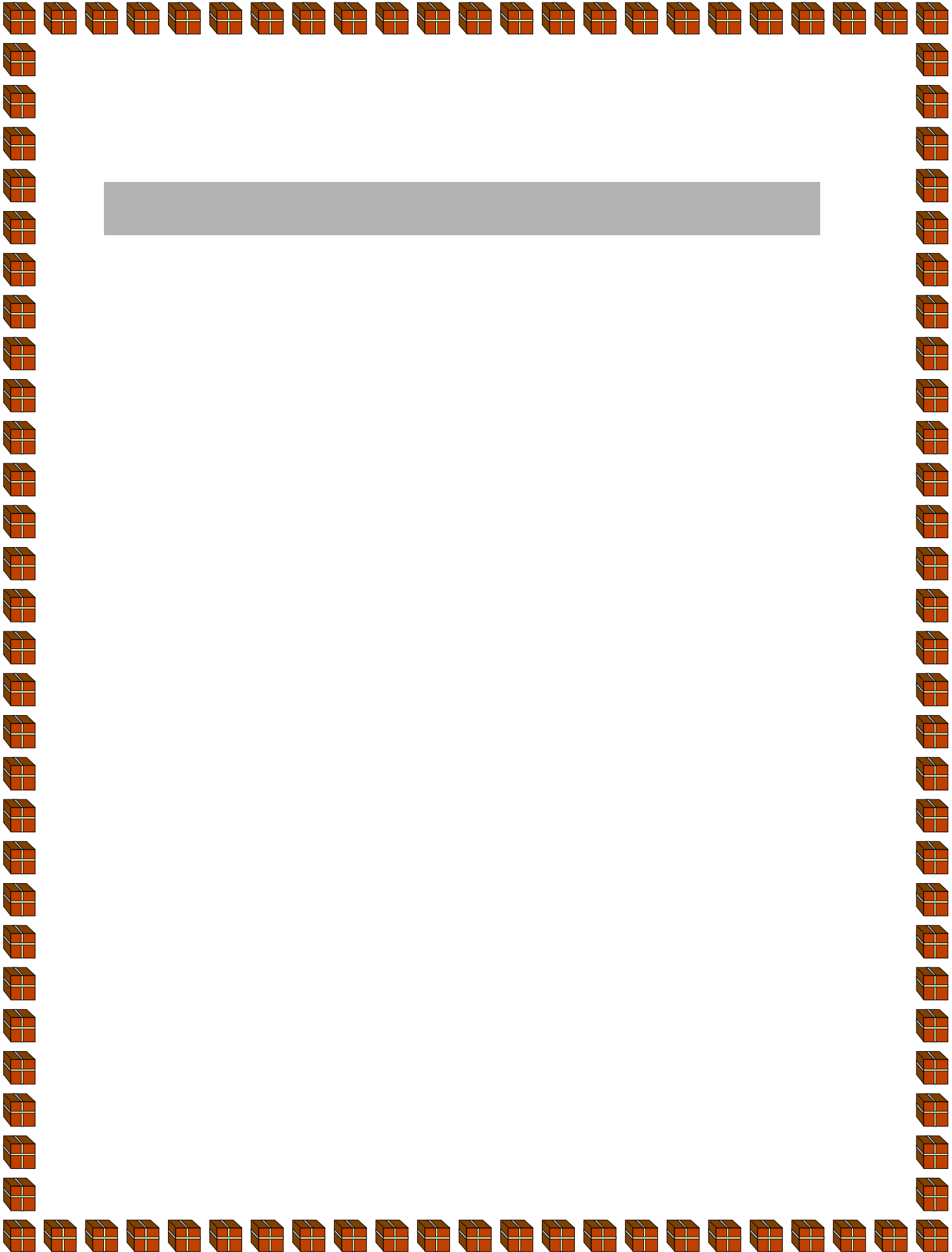الى من رافقوني وكانوا لي أصدقاء وشاركوني في فرحي وشجوني الى
أصدقائي

أهدي هذا الجهد المتواضع

عادل

الأسم: عادل أحمد عواد حمود الدليمي

تأريخ الولادة: 1980/7/10

العنوان: الأنبار ـ الفلوجة ــ الصقلاوية

تأريخ المناقشة:2005/7/21

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الخلاصة

تم في هذا العمل تحضير ودراسة سلسلة جديدة من معقدات البلاديوم الثنائي والبلاتين الثنائي ذات ايزومرية تركيبية مختلفة آخذين بنظر الأعتبار الأفكار و المباديٌ الأساسية التي تحكم تركيب و فاعلية المركبات التناسقية.

تمت مناقشة تركيب هذه المعقدات ودراسة سلوكها الطيفي استناداً الى قاعدة (بيرسن) وتآصر باي الرجوعي والسلوك التأكسدي / الأختزالي أضافة لقواعد أخرى.

جرى تحضير المعقدين [MCl₂(DMSO)₂] ، حيث M=Pd(II) أو Pt(II) ، واستخدامها في تحضير أنواع التالية من المعقدات:

1. أعطى تفاعل كل من معقدي البلاديوم (ترانس) و البلاتين (سيز) مع Dithioxmide(DTO) في الأيثانول المعقدين [cis-[MCl₂(DTO)]-N,S].

2. عند مفاعلة [cis-[MCl₂(DTO)]-N,S] مع سلسلة من الليكاندات المتعادلة المانحة للنتروجين أو الفسفور في الأيثانول تكونت معقدات جديدة وكما يلي:
*عند أضافة ثلاثي فنيل الفوسفين (Ph₃P) أو ثلاثي فنيل الأمين (Ph₃N) جرى أستبدال لذرة الكلور المقابله لنتروجين (DTO) في كلا الحالتين تكون المعقدين -N
N- trans-[MCl(L)(DTO-N,S)] (L=Ph₃P or Ph₃N)

3.أعطى تفاعل الليكاندين المتعادلين ثنائي السن الخطيين Benzidine(Bnz)andN-N'-tetramethylbenzidine(TMBnz)مع المعقدين [MCl₂DTO-N,S] في الأيثانول المعقدين القفصيين رباعي النواة [M4(TO-N,S)₄L'₄]Cl₄ حيث 'L تمثل Bnz أو TMBnz

4. تفاعل الليكاند المتعادل 2,2'-dipyridile (dipy) مع [cis-[PtCl₂(DMSO)₂] في الأيثانول معطياً المعقد المتعادل [PtCl₂dipy] ، والذي أعطى المعقد الأيوني [Pt(dipy)(DTO-N,S)]Cl عند تفاعله مع DTO في الأيثانول.

تم دراسة جميع المعقدات المحضرة بأستخدام مطيافية الأشعة تحت الحمراء و فوق البنفسجية ـالمرئية، و قياسات الحساسية المغناطيسية، تم كذلك تحديد المحتوى الفلزي بتقنية مطيافية الأمتصاص الذري.

5. جرى أستخدام حسابات نظرية الأيزومرلبعض المعقدات أضافةً للقواعد الأخرى في تفسير سلوك المعقدات التركيبي. و قد أظهرت الوسائل المستخدمة كونها ذات فائدة كبيرة في فهم السلوك التركيبي.

تم أستقصاء الفعالية البايولوجية لجميع المعقدات المحضرة تجاه نوعي البكتريا E-coliوStaph.

</div>

بسم الله الرحمن الرحيم

فتعالى الله المَلِكُ الحقُ ولاتَعجَل

بالقرءان من قبلِ ان يُقضي اليك وحيُهُ

وقل ربِ زدني عِلماً

صدق الله العظيم

(سورة طه ١١٤)