SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL EVALUATION OF MIXED LIGAND COMPLEXES OF Pt(IV), Pt(II) AND Pd(II) IONS CONTAINING DIBASIC ACIDS AND HETEROCYCLIC AMINES

PhD Thesis

BY

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KHULNA UNIVERSITY OF ENGINEERING & TECHNOLOGY
KHULNA-9203
JUNE-2014

Dedicated
To
My Beloved Parent
and Teachers

SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL EVALUATION OF MIXED LIGAND COMPLEXES OF Pt(IV), Pt(II) AND Pd(II) IONS CONTAINING DIBASIC ACIDS AND HETEROCYCLIC AMINES

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A thesis submitted in partial fulfillment of the requirements for the degree of doctor of philosophy in department of chemistry, khulna university of engineering & technology

DEPARTMENT OF CHEMISTRY
KHULNA UNIVERSITY OF ENGINEERING & TECHNOLOGY
KHULNA-9203
JUNE-2014

Declaration

This is to certify that the thesis work entitled "SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL EVALUATION OF MIXED LIGAND COMPLEXES OF Pt(IV), Pt(II) AND Pd(II) IONS CONTAINING DIBASIC ACIDS AND HETEROCYCLIC AMINES" has been carried out in partial fulfillment of the requirement for PhD degree in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above thesis work or any part of this work has not been submitted anywhere for the award of any degree or diploma. No other person's work has been used without due acknowledgement.

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Md. Belayet Hossain

Abstract

Mixed ligand complexes of dibasic acid and heterocyclic amine with transition metal ions have been synthesized and characterized. Research was devoted to the synthesis and characterization of mixed ligand complexes of Pt(II), Pt(IV) and Pd(II) ions with some dibasic acid (*viz.*, malonic acid, oxalic acid and phthalic acid) as primary and heterocyclic bases, (*viz.*, quinoline (Q), *iso*-quinoline (IQ), pyridine (Py), 2-aminopyridine (2apy) and 4-picoline (4-pico) as secondary ligands. The general formula of the complexes are as follows; [MLL^1] (where M = Pt(IV) (1-8), Pt(II) (13), Pd(II) (9-12,14-17); L=2$C_3H_2O_4$, malonato (1-4), 2C_2O_4, oxalato (5-8), $C_8H_4O_4$, phthalato (9-13), oxalato C_2O_4(14-17); and L^1 =2C_9H_7N, quinoline (1, 5, 9, 14), 2C_9H_7N, *iso*-quinoline (2, 6, 10,15), 2C_5H_5N, pyridine (3, 7, 11, 16) , 2C_6H_7N, 4-picoline (4, 8, 13), $C_5H_6N_2$, 2-aminopyridine (12, 17)). Complexes were characterized by elemental analysis, conductivity, magnetic measurement, infrared and electronic spectroscopic studies. All the complexes were isolated in the ethanolic solution as amorphous solid. All the synthesized complexes are colored. The complexes, all were slightly soluble in water and methanol but are readily soluble in DMF and DMSO. Single crystal of the complexes could not be isolated from any solution. The conductance values of the complexes were in the range (10.35 – 12.85) Ω^{-1} cm^2 mol^{-1} indicated that these complexes were non-electrolyte in nature. Melting points of the complexes were in the range 240 to 270(± 5°C) while those of the ligands were -15 to 211 (± 5°C) which indicate the strong indication of coordination of the ligands and formation of the complexes. The υ(OCO)asym mode of Pt(IV), Pt(II) and Pd(II) complexes of oxalato, malonato & phthalato is found as a very strong-to-strong band at 1575.7-1708.9 cm^{-1}, and the corresponding υ(OCO)sym one is exhibited at 1363.6- 1410.9 cm^{-1}. Two υ(OCO) stretching symmetrical and asymmetrical lie lower than the free ion values and the frequency difference between these two modes is 198–317 cm^{-1}. From the frequency difference it is evident that the carboxylate group acts as a monodentate ligand. Further, the presence of MO (O = Oxygen in deprotonated dibasic acid) bonding is evident from the appearance of νM-O modes at 500.0-557.4 cm^{-1} in the spectra of the complexes. The presence of M-N bonding in the complexes is evident from the appearance of $\nu_{M\text{-}N}$ modes at 421.4 – 476.4 cm^{-1}. Shifting of infrared spectra of aminopyridine to ~3320.2-3345.3 cm^{-1} and ~3056.0-3061.8 cm^{-1} in the mixed ligand complexes is indicated the coordination

through amino nitrogen to the metal ions. By comparing the data of elemental analysis, magnetic moment, spectroscopic analysis the proposed empirical formula of the synthesized complexes can be following: $[Pt(MA)_2(Q)_2]$(1), $[Pt(MA)_2(IQ)_2]$(2), $[Pt(MA)_2(Py)_2]$(3), $[Pt(MA)_2(4\text{-pico})_2]$(4), $[Pt(OX)_2(Q)_2]$(5), $[Pt(OX)_2(IQ)_2]$(6), $[Pt(OX)_2(Py)_2]$(7), $[Pt(OX)_2(4\text{-pico})_2]$(8), $[Pd(Ph)(Q)_2]$(9), $[Pd(Ph)(IQ)_2]$(10), $[Pd(Ph)(Py)_2]$(11), $[Pd(Ph)(2\text{-apy})]$(12), $[Pt(Ph)(4\text{-pico})_2]$(13), $[Pd(OX)(Q)_2]$(14), $[Pd(OX)(IQ)_2]$(15), $[Pd(OX)(Py)_2]$(16) and $[Pd(OX)(2\text{-apy})]$(17) where, MA = Deprotonated malonic acid, OX = Deprotonated oxalic acid, Ph = Deprotonated phthalic acid, Q = quinoline , IQ = *iso*-quinoline, Py = pyridine, 4-pico = 4-picoline, 2-apy = 2-aminopyridine. The magnetic moment values of the complexes indicated that these complexes are diamagnetic. This diamagnetism is supported by the small negative values obtained for their magnetic susceptibility. The electronic spectra of the Pt(IV) complex gave three bands at 36,000, 39,650 and 41,000 cm^{-1} corresponding to the transitions $^1A_{1g} \rightarrow {}^1T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. In addition to the d-d transitions, the Pt (IV) complexes obtained two charge transfer bands at 39000 and 50000 cm^{-1}. The electronic spectra of the Pd (II) complex showed three spin allowed d-d transitions and two charge transfer bands. The bands were obtained at 22203-23055, 28155-28500, 31000-31350, 34500-35005 and 40000-40205 cm^{-1} corresponding to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{1g} \rightarrow {}^1E_g$, $^1A_{1g} \rightarrow {}^1A_{2u}$ and $^1A_{1g} \rightarrow {}^1E_u$ respectively. The Pt(II) complex gave three bands at 36000, 39650 and 41000 cm^{-1} corresponding to the transitions $^1A_{1g} \rightarrow {}^1B_{1u}$, $^1A_{1g} \rightarrow {}^1E_u$ and $^1A_{1g} \rightarrow {}^1A_{2u}$ respectively. Electronic spectra and magnetic measurement confirmed that Pt (IV) (1-8) complexes are octahedral structure and Pt (II) (13) & Pd (II) (9-12, 14-17) complexes are square planar structure. From the antibacterial screening it is seen that all complexes have antibacterial activity against Gram-positive (*Listeria monocytogenes, Staphylococcus aureus, Enterococcus faecalis*) and Gram-negative (*Pseudomonas aeruginosa, Salmonella bovismorbificans, Salmonella typhi, Escherichia coli*) bacteria through disc diffusion method. Complexes $[Pt(MA)_2(4\text{-pico})_2]$ showed the highest antibacterial activity against all bacteria tested. The complexes 1, 6 and 11 showed the lowest inhibition zones against *Staphylococcus aureus, Listeria monocytogenes & Enterococcus faecalis* corresponding to zone sizes of 8, 11 and 10 mm respectively. The complexes 2, 7 & 11 exhibited no zone inhibition against *Staphylococcus aureus, Salmonella typhi and Salmonella bovismorbificans*. All the synthesized complexes have shown mild to moderate antibacterial activity. The highest and the lowest activities were found in complex 4 and complex 11 respectively.

Symbol and Abbreviations

OXH_2 : Oxalic acid
PAH_2 : Phthalic acid
MOH_2 : Malonic acid
Q : Quinoline
IQ : *iso*- quinoline
Py : Pyridine
4-Pico : 4-picoline
2-apy : 2-aminopyridine
DMSO : Dimethylsulphoxide
DMF : *N,N′*-dimethyl formamide
IR : Infrared
g : Gram
ν : Absorption maximum
% : Percent
mL : milliliter
K : Kelvin
— : Upward
┈┈ : Downward

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List of Publications

1. Md. Belayet Hossain, Md. Abdus Salam, Farzana Siddiquee and M. A. Yousuf, "Synthesis, Characterization and Antibacterial Activity of Mixed Ligand Complexes of Pd(II) Ions with Oxalic Acid and Heterocyclic Amines" Bangladesh Pharmaceutical Journal, Vol.17(1): 46-50, 2014.

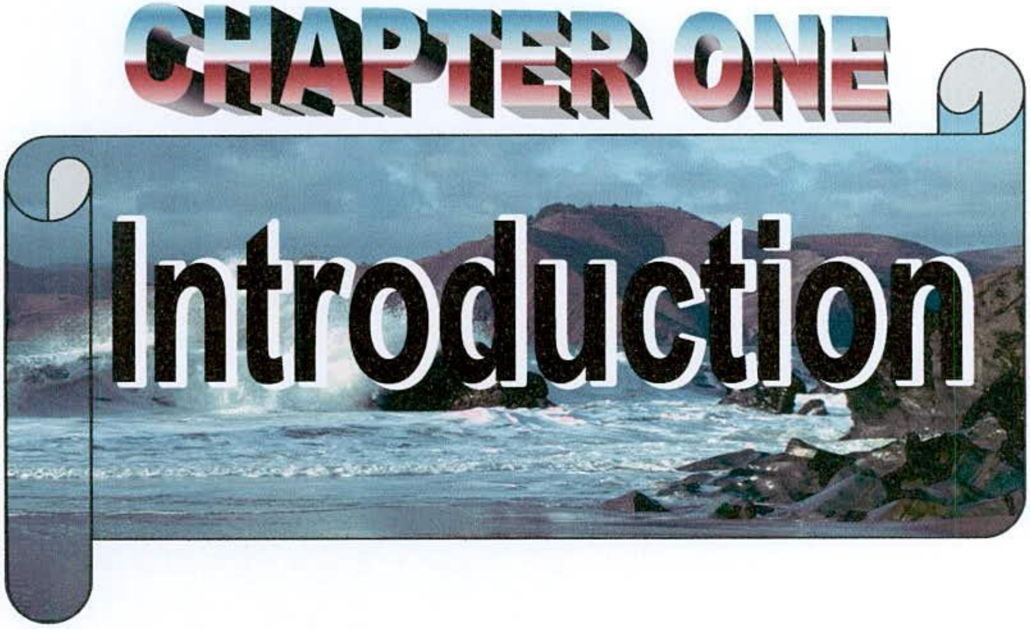
2. Md. Belayet Hossain, Md Abdus Salam and M. A.Yousuf, "Synthesis, Characterization and Antibacterial Studies of Mixed Ligand Complexes of Pt(IV) Ion with Malonic Acid and Heterocyclic Amines" Journal of Bangladesh Chemical Society, Vol. 26(2), 187-194, 2014.

3. Md. Belayet Hossain, Md Abdus Salam and M. A. Yousuf, "Synthesis, Characterization and Antibacterial Studies of the Mixed Ligands Complexes of Pd(II) & Pt(II) Ions with Phthalic Acid and Heterocyclic Amines" Bangladesh Pharmaceutical Journal, Vol. 17 No 2 (Accepted).

4. Md. Belayet Hossain, Md Abdus Salam, M. A. Yousuf and Abdur Rashed, "Characterization and Antibacterial Studies of the Mixed Ligands Complexes of Pd(II) Ion with Phthalic Acid and Heterocyclic Amines" Journal of Engineering Science, Vol. 4 No 2 (Accepted).

CHAPTER ONE

Introduction



Introduction

Content

1.1 The Mixed Ligand Metal Complex
1.2 Carboxylato Ligands
1.3 Heterocyclic Amine Ligands
1.4 Biologically Active Ligands

1. Introduction

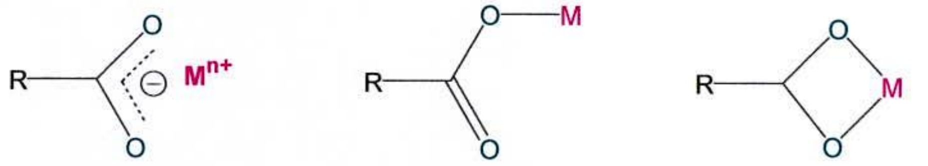
1.1 The Mixed Ligand Metal Complex

Mixed ligand metal complexes are the compounds in which metal ion is simultaneously bonded to two or more different kinds of ligands. These complexes are generally formed in most solutions which contain metal ions and have more than one kind of ligands having sufficiently small number of donor atoms. The mixed ligand metal complexes are likely to be important as models for metalloenzyme-substrate complexes and also as components of the multi-metal-multi-ligand systems in biological fluids and thus provide a strong impetus for increasing interest in this area. Marcus, Y *et al.*[1] have observed that the addition of another, B ligand to a complex MB Perrin which already bears a B ligand is more difficult than adding B to a complex MA, which contains a different ligand, A. The stability of the mixed ligand complex depends on the ligand stability factors and shape of ligands.

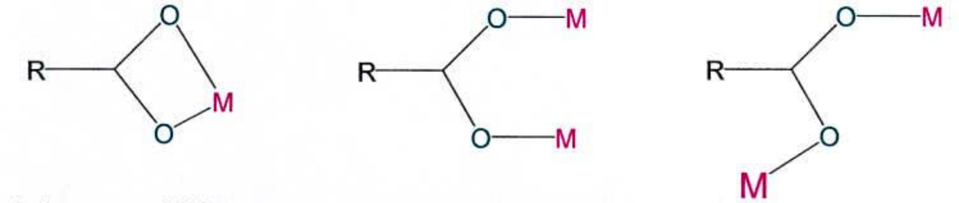
In complex compound, the co-ordination number of the central metal atom/ion is co-ordinated with various types of ligands. The co-ordination number is occupied according to the power of the ligand. First ligand is called primary ligand and the second ligand is called the secondary ligand respectively.

1.2 Carboxylato Ligands

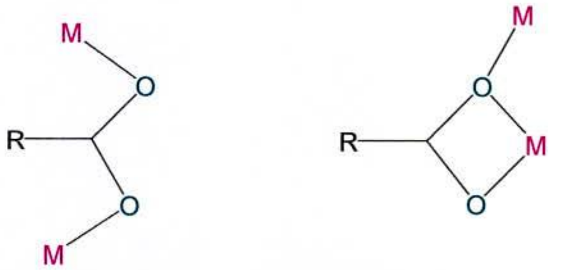
Carboxylate chemistry is indispensable for the construction of inorganic motifs having interesting material properties[2]. Among the various ligands, multidentate O-donor ligands like carboxylic acid can act as good building blocks in constructing metal–organic frameworks, which possess carboxylate groups and exhibit varied coordinate modes. Some possible coordination modes for metal carboxylate complexes are shown in figure 1.1[3].



(A) Ionic (B) Monodentate (C) Sym.bidentate



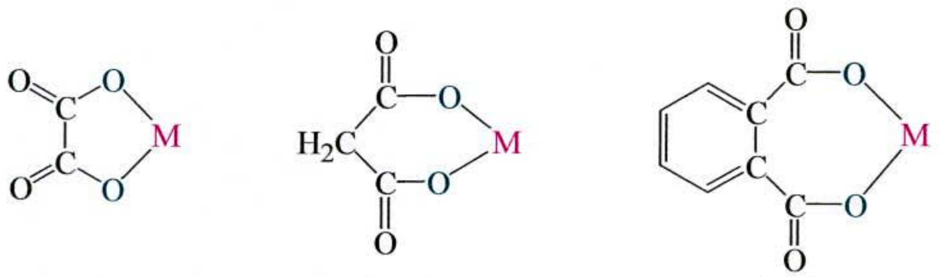
(D) Asym.bidentate (E) Sym-Sym bridging (F) Sym-Anti bridging



(G) Anti-Anti bridging (H) Monodentate terminal briging

Figure 1.1: Coordination mode of carboxylate group

Among the different coordination modes, chelating, monodentate, and bridging are the three modes which generally decide the structural features of inorganic carboxylato complexes[4-5] and they have also been studied from the theoretical point of view [6]. The carboxylate group having bis(unidentate) bridged complexes is known as the secondary part in polynuclear carboxylato complexes[7-10]. Transition metal complexes of dicarboxylic acid such as, malonic acid, maleic acid, malic acid, phthalic acid have been used as dicarboxylate or chelating ligands [11-14]. Although dicarboxylic acid have no co-ordination position but under suitable condition (slightly alkaline medium) these acids loose protons from both the carboxyl group and act as dinegative bidentate ligands. They tend to form 5, 6, 7, 8 and 9 membered chelate rings in their respective cases (figure 1.2).

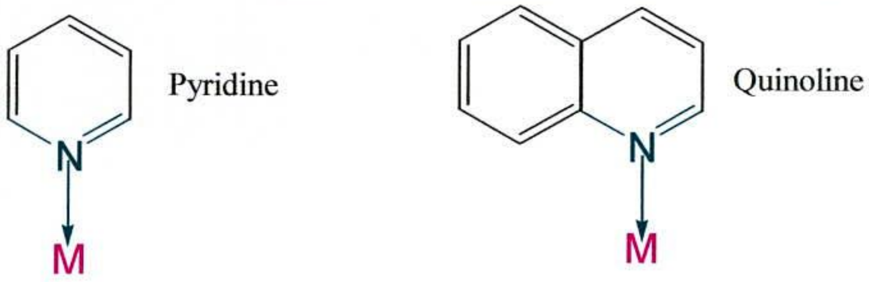


oxalato malonato phthalato

Figure 1.2: Dibasic acids co-ordinet with metal ion

1.3 Heterocyclic Amine Ligands

Heterocyclic amines are common ligands for complexation. The heterocyclic amines although possess tertiary nitrogen, co-ordinate readily with metal atoms (figure 1.3).



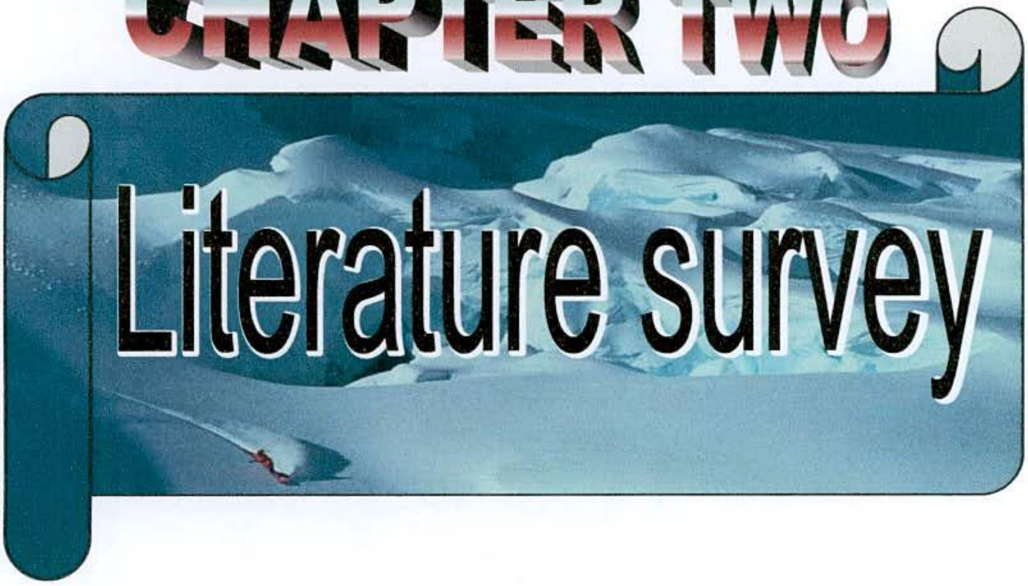
Pyridine Quinoline

Fig 1.3: Tertiary nitrogen co-ordinate with metal atoms.

1.4 Biologically Active Ligands

The ligands attached to the compounds which are very essential for life form are called biological active ligands. The synthetic macro cyclic complexes, particularly with tetradentate nitrogen donor ions, are most important from the biological viewpoint mainly due to their structural similarities to the natural macro cyclic complexes, like, vitamin B_{12}, chlorophyll, hemoglobin, etc. Special compound such as hemoglobin forms bonds with protein through oxygen, act as ligand. Moreover, myoglobin, glycoprotein (Sugar + Protein = Glycoprotein) etc are involve in many important biological process, which play important and multifarious role in biological systems[15-19]. The intriguing mode of function of these natural systems is now well understood. The vital functions performed by the natural systems can largely be determined by the nature of the metal ions enclosed in it. For example, the catalytic properties of vitamin B_{12} and its coenzyme are due to the ability of the cobalt ion to act as a storehouse for an electron which can be released or accepted as required. The metal ion in natural macrocyclic complexes are trapped in such a complicated structure that the fundamental properties of these metal ions are still not well understood. It is, therefore, reasonable to synthesize simple macrocyclic complexes which can be considered as model compounds. Some of these compounds could mimic the properties of their natural counterparts and investigations with them would provide us an easier approach to the study of fundamental properties of metal ions encapsulated in the macrocyclic environment. The rapid developing field of bio-inorganic chemistry is centered on the presence of metal complexes in living systems.

CHAPTER TWO



Literature survey

Literature survey

Content
2.1 Previous Work
2.2 Aim of the Work

2.1 Previous Work

Now-a-days, metal complexes are the most active research field of inorganic chemistry. A survey of articles in recent uses of the journal of inorganic chemistry indicates that perhaps 70% could be considered to deal with metal complexes. Progress in this area of chemistry has received an added impetus because of its many applications to chemical industry and biology. It has been clearly understood and supported that many of the chemical elements including metal ions control a vast range of biological processes going a new dimension to co-ordination chemistry [20].

Transition metals have an important role in medicinal biochemistry[21–25]. The complexes of transition metals have a significant importance that can be utilized as drugs to treat several human diseases like, carcinomas[26], lymphomas[27], anti-inflammatory[28], diabetes[29], and neurological disorders[30]. Transition metals exhibit different oxidation states and can interact with a number of negatively charged molecules. This activity of transition metals has started the development of metal based drugs with promising pharmacological applications and may offer unique therapeutic opportunities. A number of transition metals metal complexes with dicarboxylic acid have been prepared and characterized.[31-35]

Angel and co-workers reported that syntheses and structural, spectroscopic and magnetic characterization of two new Bis(imidazol-2-yl)methylaminomethane (BIMAM) containing copper(II) oxalato derivatives in which oxalato ligands show different coordinating behavior and whose 3D solid-state networks are held together by a combination of H-bonding and aromatic-aromatic interactions provided by the convenient structural features of BIMAM and oxalate[36]. The structures of solid uranium(VI) oxalato compounds reveal different modes of bonding of the ligand chelated through one oxygen from each carboxylate group[37], coordinated through two oxygen atoms of the same carboxylate group or bonded to a single carboxylate oxygen. In most of these structures, the oxalate is bridging different uranyl units. The composition of the complexes have previously been determined by equilibrium analytical methods[38] but with different conclusions as to the stability of the $UO_2[oxalate]_3^{-4}$ complex.

Research works using malonate as bridging ligand in copper(II) complexes have shown the versatility of this ligand[39-42]. The structural complexity in its metal complexes is associated with the simultaneous adoption of chelating bidentate and different carboxylato-bridging coordination modes. The use of $[Cu(mal)_2]^{2-}$ as a complex ligand allowed the preparation of dimers[39], trimers[42], and one[41] and two-dimensional[40] complexes whose structure and magnetic properties were subject of recent investigation.

Santiago *et al*[43] reported that novel malonato-bridged copper(II) complexes were prepared and characterized by elemental analyses, electronic spectra, magnetic susceptibilities and X-ray structure analysis. An exhaustive survey of the existing literature reveals that a very little has been done on the metal complexes of malonic & oxalic acid[42, 44].

A very few survey has been done on the Pt(IV) & Ni(II) complexes of phthalic acid[14]. The study on the metal complexes of heterocyclic amine bases have been carried out[11-14] they have suggested that reactivity of these complexes depend on the nature of heterocyclic amine bases. Complexes of substituted phenanthrolines with pentacoordinate palladium carboxylate were studied, and the structure of $[Pd(Phen)_2(CO_2CH_3)](PF_6)$ was reported[45]. Polypyridyl ruthenium (III) complexes based on 2,2′-bipyridine, 1,10-phenanthroline ligands possess interesting photophysical, photochemical, and electrochemical characteristics[46-47] which make them appealing for the construction of luminescent sensors and photoactive molecular-scale devices[48-49]. Nicolas and coworkers undertaken a study on a new type of mixed ligand Pt(II) complexes with pyrimidine and sulfoxide ligands. They have reported the synthesis and characterization of complexes the types *cis*- and *trans*-$Pt(R_2SO)(pm)Cl_2$. These compounds were prepared from the reaction of

$K[Pt(R_2SO)Cl_3]$ with pyrimidine in water for the *trans* isomer and in methanol for the *cis* compound. The first product is *trans* complex, which then isomerizes to *cis* isomer. The isomerization is quite slow in water especially with more bulky ligands but much faster in an organic solvent. In the second part of the research project, they isolated and characterized a new type of pyrimidine-bridged binuclear complexes with sulfoxide ligands[50].

Moreover, metal complexes of heterocyclic amine bases have been study by several workers[51-58]. Several mixed-ligand complexes of Pd(II) and Pt(II) have been prepared and characterized by elemental analysis, conductivity measurements, Infra-red, electronic absorption and ^{1}H-NMR spectroscopic techniques by Anbalagan *et al* [59]. Puthraya and his coworkers[60] have reported some complexes with formula $[Pd(bipy)(AA)_2]$ where bipy is 2, 2′ = bipyridine and AA is an anion of glycine, L- alanine, L-leucine, L-proline, L-serine, L-lysine, L-asparagine or L-glutamine.

Iwona and coworkers carried out synthesis, molecular structure characterization, and *in vivo* cytotoxic effect of $[PtCl_2(6\text{-}mp)_2]$ and $[PtCl_4(dbtp)_2]$ against B_{16} mouse melanoma cells[61]. They decided to test new Pt(IV) compounds with different heterocyclic ligands which provide better solubility in water. It was demonstrated that the presence of the tert-butyl group in the 5 and 7 positions of the heterocyclic ring is likely to be a major factor in the improvement of the antitumor activity of Pt(II) and Pt(IV) compounds[62-64]. Aleksandrov were synthesized and crystal structure determination of tetranuclear platinum(II)complex $[Pt_4(m\text{-}CH_3COO)_5(m\text{-}NO)_2(m\text{-}NO_2)]$. They explain the bridging acetate groups are easily substituted by other carboxylate groups (of benzoic, picolinic, and trichloro- and trifluoroacetic acids) and ethylenediamine[65].

There are many report of metal complexes containing carboxylic or dicarboxylic groups have both salt forming and coordinating properties. The reported complexes are generally insoluble in polar solvents and soluble in non-polar solvents and hence are very important form analytical, industrial and pharmaceutical point of view[66-71].

A very few survey has been done on the Pd(II) complexes with the tridentate dianionic ligand pyridine-2,6-dicarboxylate[72]. Eryazici and co-workers were synthesized of some square-planar Pd(II), Pt(II), and Au(III) terpyridine complexes. They were determined physical properties, supramolecular constructs, and biomedical activities[73]. There are many reports on Pd(II) complexes of heterocyclic amine with structural & magneto structural characterization[74-81].

2.2 Aim of the Work

The human body contain as many as 81 out of 92 naturally occurring elements[82]. Most of these elements in trace levels which are also of great importance for human physiology indeed some of them are essential for life itself [83]. Such as complex compounds occur in nature, in blood (hemoglobin) which is an iron complex and functions as oxygen carrier of the blood stream similarly the green color of the leaves are due to a complex of magnesium with chlorophyll. Some elements also be toxic even in any concentration is above a certain level. From the nutritional point of view those essential elements, almost found in trace concentration levels play an important role in biochemical processes. In addition to all benefits due to modern technology, the increasing industrial activity is introducing contaminants in food, water and air.

Since modern antibiotic therapy was started, the abuse of antibacterial agents in many fields of human medicine and of zootechnic activities has promoted the progressive development of bacterial resistance[84]. Orally active cephalosporin, cefdinir is of clinical importance for the treatment of bacterial infections[85]. Use of Cisplatin, $[Pt(NH_3)_2Cl_2]$ as an effective anticancer drug and gold salts in treatment of rheumatoid arthritis has increased interest of researchers toward transition metal complexes in order to obtain metal-based drugs exhibiting a high biological activity[86]. Platinum(II) complexes and its derivatives have been widely recognized as potent anticancer agents, effective against different types of cancer *in vitro*[87-88]. After the discovery of its activity, thousands of platinum complexes have been synthesized and tested so far. In one recent study, new Pt based agents have been reported to have distinct features from marketed platinum drugs in several critical aspects[89]. Cisplatin has become a standard drug for the treatment of patients with non-small cell lung cancer. It was one of the most frequently used chemotherapeutic drugs worldwide for long time[90-92]. One way of designing new antitumor prodrugs, related to cisplatin is to change the nature of the central ion and to use six-coordinate octahedral Pt(IV) derivatives. The potential advantage of Pt(IV) complexes in the higher oxidation state is the increased possibility for the Pt(II) moiety reactivity to reach the cellular target before its reduction allowing thus activity with the cell[93]. In addition, potential advantages of Pt(IV) complexes in comparison with Pt(II) compounds are that their lower reactivity decreases the loss of active drug and lowers the incidence of unwanted side reactions leading to toxic side effects in the bloodstream[94]. Studies on the Pt-complexes have been carried out by several workers[95-97]. Palladium(II) complexes on the other hand have been reported to possess antitumor activity at least comparable to cisplatin[98]. Therefore, new metal-based agents like, Pd complexes seem to be promising for the development of novel and improved chemotherapeutic drugs[99]. The ligand environment of transition metals (presented in very low concentration *in vivo*) can be considerably altered upon the administration of a therapeutically effective dose of an antibacterial drug. This change in balance between the metal ion and the ligand may have a profound effect upon the activity of drug against potentially susceptible bacteria. It has also been reported that the transport of organic ligands into the cells can be facilitated by the formation of metal complexes[100]. The literature reveals that chelation causes drastic changes in the biological properties of the ligands and metal moiety[101]. Chelation of metal with inactive substances renders them active and that with active drugs make them more active and less toxic[102-104]. The cefdinir molecule contains the $-NH_2$, –COOH, and –CO functional groups and construction of molecular models indicates that its structure is suitable for chelate formation[100]. There are many reports on the transition metal malonato[105], phthalato[106] and maleato[107] with structural and biological characterization. In the present investigation heterocyclic amines have been used in most of the cases as secondary ligands. It has great importance in biological and industrial fields. Most of the heterocyclic bases are used as corrosion inhibitors and as antibacterial, anticonvulsive, antifungal and antifouling agents[108-112]. Their activity is generally enhanced when they are allowed to form complex with metal ions.

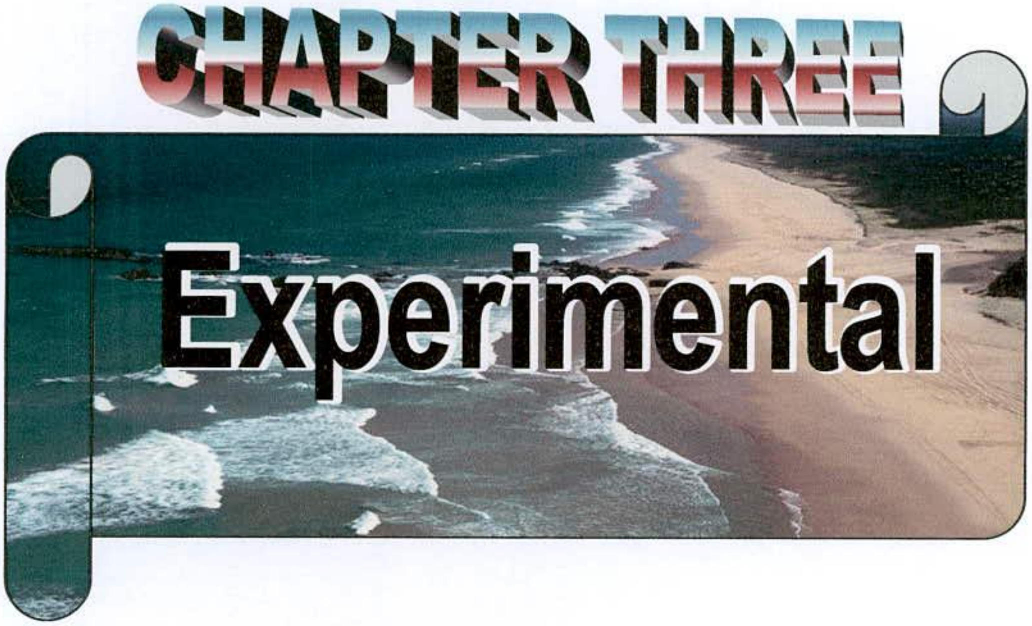
In view of, the above and continuation of previous studies on the synthesis of metal complexes of biologically important ligands, research on mixed ligand complexes of transition metals has been acclimatized as the present topic of the work . The work incorporated in this thesis is on the interaction of some organic ligands with metal ions and there antibacterial studies have been carried out.

We have planned for the synthesis, characterization & biological studies of mixed ligand complexes of Pt(II), Pt(IV), and Pd(II) metal ions containing some dibasic acids (oxalic acid, malonic acid & phthalic acid) and heterocyclic amines (quinoline, *iso*-quinoline, pyridine, 2-aminopyridine & 4-picoline).

Significant progress has been made in the design and synthesis of complexes & the complexes are shown antibacterial activities against the treated bacteria.

CHAPTER THREE

Experimental



Experimental

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	3.7.4	Synthesis of Mixed Ligand Complexes of Pd (II) Ion with Oxalic Acid and Heterocyclic Amines (complex 14-17)

3.1 Chemicals

All the chemicals were of Analytical grade and unless otherwise specified, were used as received. The solvents were purified using conventional methods (discussed in section 3.6). Used chemicals were listed in table 3.1 and 3.2.

Table 3.1: List of Chemicals used

No	**Name of the Chemicals**	**Formula**	**Formula mass**	**Suppliers**	**Purity**
1	Hexachloro platinic acid hydrate	Cl_6H_2Pt	409.8	Sigma-Aldrich (USA)	38% pt
2	Platinum(II) chloride	$PtCl_2$	266.08	Sigma-Aldrich (USA)	99%
3	Palladium(II)Chloride	$PdCl_2$	177.42	E. Merck (Germany)	97%
4	Phthalic acid	$C_8H_6O_4$	166.14	Merck (England)	99%
5	Malonic acid	$C_3H_4O_4$	104.06	Merck (England)	99%
6	Oxalic acid	$C_2H_2O_4.2H_2 O$	126	BDH (England)	99%
7	Quinoline	C_9H_7N	129.16	BDH (England)	pure
8	*iso*-quinoline	C_9H_7N	129.16	BDH (England)	pure
9	Pyridine	C_5H_5N	79.10	Thomas Baker (India)	99.5%
10	2-aminopyridine	$C_5H_6N_2$	74.12	BDH (England)	98%
11	4-picoline	C_6H_7N	93.13	BDH (England)	97%

Table 3.2: List of used solvents

No	Organic solvents	Formula	Suppliers	Purity
1	Absolute ethanol	C_2H_5OH	Sigma-Aldrich (USA)	99%
2	Acetone	$CH_3COC H_3$	Sigma-Aldrich (USA))	99%
3	Methanol	CH_3OH	Sigma-Aldrich (USA)	99.5%
4	Acetonitrile	CH_3CN	Sigma-Aldrich (USA)	99.5%
5	*N,N'*-Dimethylformamide (DMF)	$HCON(CH_3)_2$	BDH (England)	99.5%
6	Dimethyl sulfoxide (DMSO)	$(CH_3)_2 SO$	BDH (England)	99.5%

3.2 General Method for Synthesis of the Complexes

An ethanolic solution of Pt(II), Pt(IV) and Pd(II) ions and dibasic acids (MAH_2, OXH_2, PhH_2) was mixed in the calculated ratio with constant stirring. In finally no precipitate was observed. Then about 25 mL of an ethanolic solution of heterocyclic amine bases (*e.g.*, 2 mmol of quinoline, *iso*-quinoline, pyridine, 4-picoline and 1 mmol of 2- aminopyridine) was added to the resulting solution on the hot plate at 70°C with constant stirring. Volume of the solution was reduced to an half and allowed to cool at room temperature slowly. Precipitate was formed and then it was filtered, washed several times with ethanol. Finally synthesized sample was dried in desiccator over anhydrous $CaCl_2$ and was stored in a sample vial for further investigation.

3.3 Physical Measurements

3.3.1 Weighing

The weighing of the chemicals and samples at different stages were performed on a AND GH-200 electronic balance.

3.3.2 Melting Point Measurement

Melting point of the ligands and complexes were obtained with an electrothermal melting point apparatus model No. AZ 6512.

3.3.3 Conductivity Measurement

Conductivity measurements of the present complexes were carried out in *N,N′*-dimethyl formamide (DMF). The conductivity, *viz.,* the molar conductivities were calculated using the formula:

$$\lambda = \frac{100}{C} \times \text{cell constant} \times \text{Observed conductivity.}$$

10^{-3} M solutions of the complexes were employed for this purpose. The electrical conductance measurements were made at room temperature using a WPACM35 conductivity meter and a dip-cell with platinized electrodes. The cell was calibrated with 0.01N, 0.001N and 0.0001N potassium chloride solution and it had a cell constant of 1.065. The conductance of the pure solvent was determined.

3.3.4 Magnetic Measurements

Magnetic measurements have been carried out in a Sherwood Scientific magnetic susceptibility balance at room temperature.

Working Principle of the Balance

The SHERWOOD SCIENTIFIC magnetic susceptibility Balance is the result of collaboration with Professor D.F. Evens of Imperial College, London and is designed as a replacement for a traditional Gouy balance system. The Even's method uses the same configuration as the Gouy method but instead of measuring the force which a magnet exerts on the sample, the equal and opposite force which the sample exerts on a suspended permanent magnet is observed.

The M.S.B. works on the basis of a stationary sample and moving magnets. The pairs of magnets are placed at opposite ends of a beam placing the system in balance. Introduction of the sample between the poles of one pair of magnets produces a deflection of the beam which is registered by means of photo transistor. A current is made to pass through a coil mounted between the poles of the other pair of magnets, producing a force restoring the system to balance. At the position of equilibrium, the current through the coil is proportional to the force exerted on the sample, and can be measured as a voltage drop.

The following general expression for mass susceptibility χ_g in CGS units may be derived in the same manner as for the traditional Gouy method.

$$\chi_g = \frac{1}{M}\,[C(R - R_0) + V_{air}A]$$

where,

C = Constant of proportionality

R = reading obtained for tube plus sample

R_0 = the empty tube reading

I = sample length (cm)

M = weight of the sample (g)

V_{air} = volume susceptibility of the displaced air. For powder samples the air correction turm V_{air} A may normally be ignored.

C, the constant of proportionality is related to the calibration constant of a given balance by the formula.

$$C = \frac{C_{bal}}{10^9}$$

Hence the mass susceptibility, χ_g is calculated by using:

$$\chi_g = \frac{C_{bal} \times I(R - R_0)}{M \times 10^9} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

Calibration of the Balance

The magnetic susceptibility balance must be calibrated at its intended work place. The balance is to be used mainly for solid sample, then as calibrant $Hg[Co(SCN)_4]$ was used with some of the systematic errors in packing.

Procedure:

1. The zero knob of the magnetic susceptibility balance was turned until numerical display shows zero and was inserted calibration sample, $HgCo(SCN)_4$ into sample holder. It was allowed reading in numerical display to settle.
2. Reading was recorded and calibration constant C_{bal} was calibrated from the formula.

$$C_{bal} = \frac{C_{tube}}{(R - R_0)}$$

The constancy of the calibration was checked using a sealed off sample of $MnCl_2$ solution.

Calculation of Results:

The values of diamagnetic correction for the tube was added or subtracted from the observed weight depending upon whether the substance under investigation has positive or negative value of F respectively. The molar susceptibility χ_M was calculated directly by multiplying equation (1) with the molecular weight of the sample substances. The χ_M was corrected introducing the diamagnetic correction terms given in table 3.3.

The magnetic moments μ in Bohr-magneton were calculated. As the measurements of magnetic susceptibilities were made at about constant temperature, Curie-law was used and was calculated from the equation.

$$\mu_{eff} = 2.83\sqrt{\chi_m{}^{corr}.T} \quad \text{B.M.} \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

Thus μ_{eff} obtained is known as effective magnetic moment. All the values and weight were expressed in C.G.S. units.

Table 3.3: Pascal's constant for the elements and molecules

Elements/Molecules	Pascal's Const. Value $\chi_M \times 10^{-6}$ mole^{-1}
H	-2.93
C	-6.00
C (In benzene ring)	-0.24
N (Open chain)	-6.57
N (ring)	-4.61
O	-4.61
S	-15
H_2O	-13

3.4 Analytical

3.4.1 Analysis for Carbon, Hydrogen and Nitrogen

Analyses of the complexes for carbon, hydrogen and nitrogen were carried out by LECO CHEM-932 organic elemental analyzer, University Kebangsaan Malaysia.

3.4.2 Determination Palladium (II)

A known weight (about 0.2g) of the complex of Pd was treated with concentrated H_2SO_4 (5 cm^3) and concentrated HNO_3 (20 cm^3) and the mixture was evaporated to dryness. Finally $HClO_4$ (72%, 20 cm^3) was added and evaporated again to dryness. Then the residue was dissolved in distilled water (250 cm^3) and the metal content was determined complexometrically[113-114]. The process was repeated three times and the average result was taken.

3.4.3 Determination of Platinum

A known weight (about 0.05g) of the complex of Pt was treated with concentrated H_2SO_4 (5 cm^3) and concentrated HNO_3 (20 cm^3) and the mixture was evaporated to dryness. Finally $HClO_4$ (72%, 20 cm^3) was added and evaporated again to dryness. Then the residue was dissolved in distilled water (250 cm^3) and the metal content was determined complexometrically[113-114]. The process was repeated three times and the average result was taken.

3.4.4 Infrared Spectra

Infrared spectra were recorded on FTIR spectrophotometer (IR-Prestrige-21) in the region 4500-400 cm^{-1} using KBr pellets at the Department of Chemistry, University of Dhaka.

The samples were put in an agate mortar, thoroughly powdered with potassium bromide and then transferred in a mini-disc holder and a disc was made by automatic hydraulic press. The KBr disc was mounted in the sample cavity of the machine. The spectra were calibrated against 1601.8 cm^{-1} peak of the polystyrene film. The tentative band assignments of the important IR bands of the various complexes and the concerning ligands have been made empirically on the basis of some standard books.

3.4.5 Electronic Spectra

The electronic spectra were run on a SHIMADZU UV-2550 spectrophotometer. A tungsten lamp was used for visible region while a deuterium lamp was used for UV-region. The instrument can perform absorbance, transmittance, concentration, rate kinetics and standard curve determination at wavelengths from 190 to 800 nm.

The visible and UV spectroscopy is a simple but powerful tool which gives information on the geometries of the complexes. In a typical transition by metal complexes, the observed spectrum in general, consists of a series of crystal field bands which are in the visible region and depends on the donor atom of the ligand and on the metal ion.

The crystal field transitions are of two types, one is the intense spin-allowed transitions and another is the lower intensity spin-forbidden transitions, which appear as shoulders on the spin allowed transitions. The ultraviolet spectrum is complicated and consists of electronic transitions between the ligand and the metal (charge transfer), and also transitions within the ligand itself which are usually π - π^* or σ - π^* transitions. The bands in the electronic spectra represent different vibrational transition according to the electronic charge; each band is made up of a number of fine lines due to the change in rotational energy superposed on the electronic and vibrational energy changes.

3.5 Antibacterial Activity

The bacteria (test organisms) were collected from microbiology laboratory, Fish Inspection & Quality Control, Department of Fisheries, Khulna, Bangladesh. All steps of the work were carried out at this laboratory.

The complexes were screened for antibacterial activity against *Pseudomonas aeruginosa* (Gram negative), *Salmonella bovismorbificans* (Gram-negative), *Salmonella typhi* (Gram-negative), *Escherichia coli* (Gram-negative), *Listeria* *monocytogenes* (Gram-positive), *Staphylococcus aureus* (Gram-positive), *Enterococcus faecalis* (Gram-positive). The activities were carried out with the help of disc diffusion technique [115-116]. Each disc contained 50 µg of compound and it was placed on bacteria inoculated plates. The growth inhibition results were compared with standard antibiotics, Kanamycin.

3.5.1 Culture media

The instant nutrient agar medium was weighed (28 grams), dispersed in one liter of distilled water and allowed soaking for 10 minutes. Swirled to mix and autoclaved at 15 Ib/(inch)^2 (figure 3.1.) pressure at 121°C. After this, the medium was cooled at 47°C.

Figure-3.1: Sterilization of media in the autoclave

3.5.2 Preparation of fresh culture

50 mL of medium was poured in a test tube. The test microorganisms of pure culture were streaked on the nutrient media with the help of sterile loop in an aseptic condition as shown in figure 3.2 and incubated at 37°C for 24 hours. The culture thus obtained was considered fresh culture. Fresh culture of this type was always used throughout the sensitivity testing.

Figure-3.2: Preparation of fresh culture

3.5.3 Preparation of plates

The medium was poured into sterile petridishes in an aseptic condition on a level horizontal surface so as to give a uniform depth of approximately 4 mm and has been shown in figure 3.3. Then the medium had been allowed to cool to room temperature in order to solidify the medium.

Figure-3.3: Preparation of plate

3.5.4 Preparation of discs

Sterile filter paper discs were taken and the test material of known concentration was applied on the discs with the help of a micropipette as shown in figure 3.4. The solvents from the discs were evaporated by hot air blower. In the similar way control discs (containing only the solvents) were also prepared.

Figure-3.4: Preparation of disc

3.5.5 Placement of the discs and incubation

The solidified agar plates were seeded with 70 μL of fresh culture with the help of a micropipette and spread the micro organisms with the help of a sterile spreader in an aseptic condition.

The prepared discs of samples were placed gently on the freshly seeded solidified agar plates with a sterile forceps (Shown in figure 3.5). Standard discs and control discs were also placed on the test plates to compare their effect with tested samples.

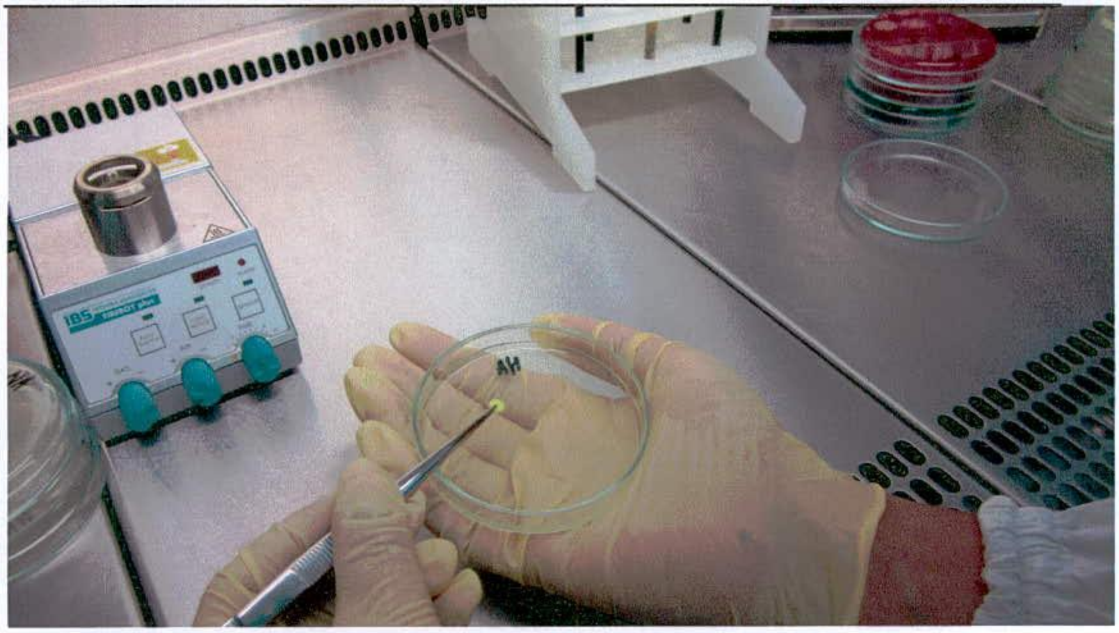


Figure-3.5: Placement of disc on solidified agar plate

Then the plates were kept in a refrigerator at 4°C for 24 hours in order that the materials had sufficient time to diffuse to a considerable area of the plates. After this, the plates were incubated at 37°C for 16 hours (as shown in figure 3.6).

Figure-3.6: Incubation of plate

3.5.6 Calculation of the zone of inhibition

After incubation, the diameter of the zone of inhibition were observed and measured in mm by a transparent scale. Show in Figure 3.7

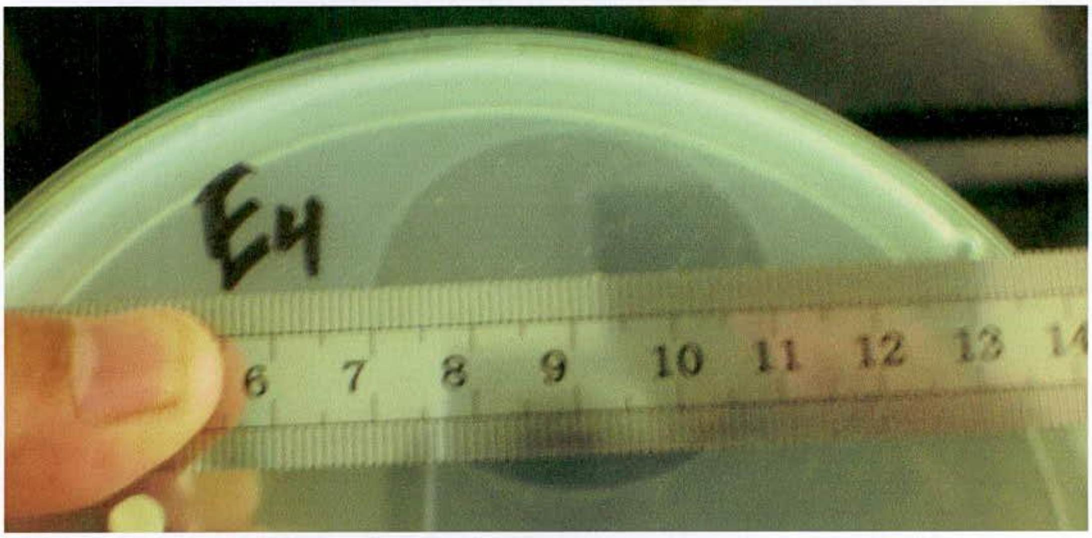


Figure-3.7: Calculation of the zone of inhibition

3.6 Purification of the Solvents

(i) Ethanol

A dry round bottomed flask 2.0L was fitted with a double surface condenser and a calcium chloride drying tube. Clean dry magnesium turnings (5.0 g) and iodine (0.5 g) were placed in the round-bottomed flask followed by 75 mL of commercial absolute ethanol. The mixture was warmed until the iodine had disappeared. Heating was continued until all the magnesium was converted into ethoxide, then 900 mL of absolute ethanol was added and the mixture was refluxed for one hour. After cooling the ethanol was distilled of directly into a vessel in which it was stored, by resembling the condenser for downward distillation via a splash head adapter. Then the ethanol was stored and was used.

(ii) Acetone

The acetone was heated under reflux with successive quantity of potassium per manganese until the violet colored persisted. It was then dried with anhydrous potassium carbonate, filtered from the desiccant and distilled. Precaution was taken to exclude moisture, *i.e.,* a calcium chloride guard tube was used.

3.7.1 Synthesis of Mixed Ligand Complexes of Pt (IV) Ion with Malonic Acid and Heterocyclic Amines (complex 1-4)

A 25 mL of ethanolic solution of the metal salt (PtH_2Cl_6) (1 mmol) and 30 mL ethanolic solution of malonic acid (2 mmol) (for complex 1-4) was mixed with constant stirring. No precipitate was observed. Then 25 mL of an ethanolic solution of 2 mmol of heterocyclic amine bases *e.g.,* quinoline (for complex 1), *iso*-quinoline (for complex 2), pyridine (for complex 3) and 4-picoline (for complex 4) was added to the resulting solution placed on a hot plate at 70°C with constant stirring. The volume of the solution was reduced to an half and allowed to be cooled to room temperature slowly. The precipitates were formed and were filtered, washed several time with ethanol. Finally synthesized sample was dried in desiccator over anhydrous $CaCl_2$ and was stored in a sample vial for further investigation.

3.7.2 Synthesis of Mixed Ligand Complexes of Pt (IV) Ion with Oxalic Acid and Heterocyclic Amines (complex 5-8)

A 25 mL of ethanolic solution of the metal salt (PtH_2Cl_6) (1 mmol) and 30 mL ethanolic solution of oxalic acid (2 mmol) (for complex 5-8) was mixed with constant stirring. No precipitate was observed in the solution. Then 25 mL of an ethanolic solution of 2 mmol of heterocyclic amine bases e.g., quinoline (for complex 5), *iso*-quinoline (for complex 6), pyridine (for complex 7) and 4-picoline (for complex 8) was added to the resulting solution on a hot plate at 70°C with constant stirring. The volume of the solution was reduced to an half and allowed to be cooled to room temperature slowly. The precipitates were formed and were filtered, washed several time with ethanol. Finally synthesized sample was dried in desiccator over anhydrous $CaCl_2$ and was stored in a sample vial for further investigation.

3.7.3 Synthesis of Mixed Ligand Complexes of Pd (II) and Pt (II) Ions with Phthalic Acid and Heterocyclic Amines (complex 9-13)

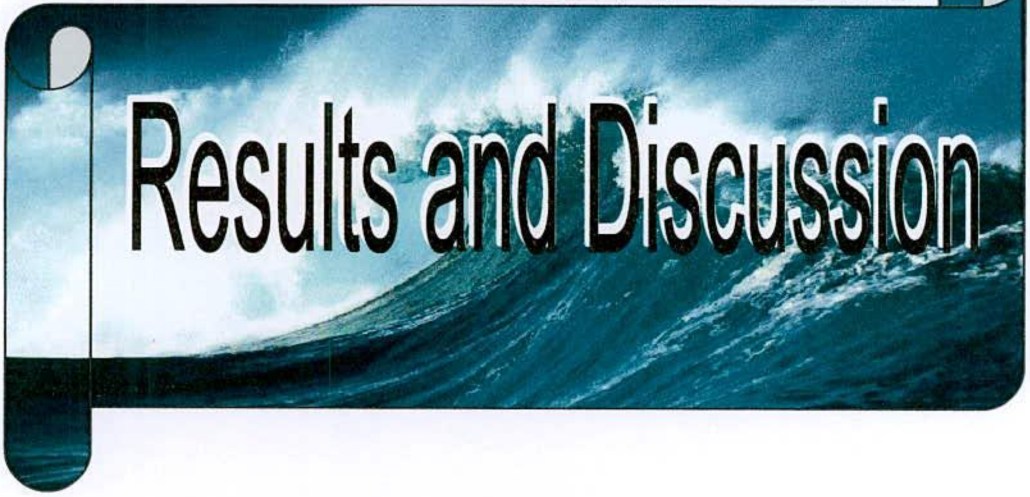
A 25 mL of ethanolic solution of the metal(II) salt {Pd(II) (for complex 9-12) and Pt(II) (for complex 13) } was added to an ethanolic solution (30mL) of phthalic acid (1 mmol) (for complex 9-13), No precipitate was observed. Then 20 mL of an ethanolic solution of heterocyclic amine bases *e.g.,* 2 mmol of, quinoline (for complex 9), *iso*-quinoline (for complex 10), pyridine (for complex 11), 4-picoline(for complex 13) and 1 mmol of 2-apy (for complex 12), was added to the resulting solution on a hot plate at 70°C with constant stirring. The volume of the solution was reduced to an half and allowed to be cooled to room temperature slowly. The precipitates were formed and were filtered, washed several time with ethanol. Finally synthesized sample was dried in desiccator over anhydrous $CaCl_2$ and was stored in a sample vial for further investigation.

3.7.4 Synthesis of Mixed Ligand Complexes of Pd (II) Ion with Oxalic Acid and Heterocyclic Amines (complex 14-17)

A 25 mL of ethanolic solution of the metal salt ($PdCl_2$) (1 mmol) and 30 mL ethanolic solution oxalic acid (1 mmol) (for complex 14-17) was mixed with constant stirring. No precipitate was observed in the solution. Then 25 mL of an ethanolic solution of heterocyclic amine bases *e.g.,* 2 mmol of quinoline (for complex 14), *iso*-quinoline (for complex 15), pyridine (for complex 16) and 1 mmol of 2-aminopyridine (for complex 17) was added to the resulting solution on a hot plate at 70°C with constant stirring. The volume of the solution was reduced to an half and allowed to be cooled to room temperature slowly. The precipitates were formed and were filtered, washed several time with ethanol. Finally synthesized sample was dried in desiccator over anhydrous $CaCl_2$ and was stored in a sample vial for further investigation.

CHAPTER FOUR

Results and Discussion



Results and Discussion 1

Characterization of Mixed Ligand Complexes of Pt (IV) Ion with Malonic Acid and Heterocyclic Amines [Complex 1-4]

Content

4.1.1 **Physical Properties**
4.1.1.1 **Solubility**
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4.1.1.3 **Conductivity Measurement**
4.1.1.4 **Magnetic Moment Measurement**
4.1.2 **Elemental Analysis**
4.1.3 **Infrared Spectra Studies**
4.1.4 **Electronic Spectra Studies**

Mixed ligand complexes of Pt(IV) ion with malonic acid (MOH_2) as primary and heterocyclic amines, *viz.* quinoline (Q), *iso*-quinoline (IQ), pyridine (Py) and 4-pico (4-picoline) as secondary ligands have been synthesized and characterized by several physico-chemical and spectroscopic analysis. Complexes of Pt(IV) ion with malonic acid (MOH_2) and heterocyclic amines were synthesized by a very simple experimental method; in ethanolic solution at room temperature as discussed in chapter III. It is revealed that the syntheses of all the complexes of Pt (IV) followed the following general chemical reactions.

$$\mathrm{Pt\,H_2Cl_6} + 2\,\mathrm{MAH_2} \rightarrow [\mathrm{Pt^{4+}} + 2\mathrm{MA^-} + 6\mathrm{H^+} + 6\mathrm{Cl^-}] \text{ (Resulting Solution)}$$

$$[\mathrm{Pt^{4+}} + 2\mathrm{MA^-} + 6\mathrm{H^+} + 6\mathrm{Cl^-}] + 2\mathrm{L} \rightarrow [\mathrm{Pt(MA)_2L_2}] + 6\mathrm{HCl} \quad \text{(For complexes 1-4)}$$

where, MAH_2 =malonic acid L = monodented base, *viz.,* quinoline, Q (for complex 1), *iso*-quinoline, IQ (for complex 2), pyridine, Py (for complex 3), 4-picoline ,4-pico (for complex 4). Physico-chemical properties, elemental analysis, magnetic and spectroscopic data were used to propose probable structures, and the complexes are reported here for the first time.

4.1.1 Physical Properties

4.1.1.1 Solubility

Solubility of a compound depends on the mode of interaction between solute and solvent molecules (*e.g.,* dipole-dipole interaction, lattice energy, lattice enthalpy, solvation energy, temperature and pressure). A compound will be soluble only when the lattice enthalpy is lower than the solvation energy. The solubility of the complexes was examined in the usual manner. The complexes were all slightly soluble in water and methanol but are soluble in DMF and DMSO (table 4.1.1).

Table 4.1.1: Solubility of the synthesized complexes

Complex No.	Complexes	Water		Methanol		DMF		DMSO	
		Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
1	$[Pt(IV)(MA)_2(Q)_2]$	+/-	+/-	+/-	+/-	+	+	+	+
2	$[Pt(IV)(MA)_2(IQ)_2]$	+/-	+/-	+/-	+/-	+	+	+	+
3	$[Pt(IV)(MA)_2(Py)_2]$	+/-	+/-	+/-	+/-	+	+	+	+
4	$[Pt(IV)(MA)_2(4\text{-pico})_2]$	+/-	+/-	+/-	+/-	+	+	+	+

Here, +/- = Slightly soluble and + = Soluble

4.1.1.2 Color & Melting point

All the synthesized complexes (complex 1-4) are colored amorphous powder. Single crystal of the complexes could not be isolated from any solution. Complexes 1 and 3 *i.e.,* Pt(IV) with (malonic acid + quinoline) and (malonic acid + pyridine) are orange in colored but Complexes 2 and 4 *i.e.,* Pt(IV) with (malonic acid + *iso*-quinoline) and (malonic acid + 4-picoline) are yellow-orange in colored (shown in table 4.1.2). Melting point of complex-1, $Pt(IV)(MA)_2(Q)_2$ is 268± 5°C while the melting point of the ligands, malonic acid is 135-136°C and quinoline is -15°C which indicates the strong indication of coordination of the ligands and formation of the complex. Similarly for the melting point of complex-2 is 255± 5°C while that for *iso*-quinoline is 26-28°C melting point of complex-3 is 260± 5°C while that for pyridine is -41.8°C and melting point of complex-4 is 258±5°C while that for 4-picoline is 2.4°C also indicate the formation of the complexes. Data for the melting points of the complexes has been tabulated in table 4.1.2.

4.1.1.3 Conductivity Measurement

The molar conductance values were measured in *N,N'*-dimethyl formamide. The conductance values of the complexes were in the range (10.35–12.60) Ω^{-1} cm^2 $mole^{-1}$ indicated that these complexes were non-electrolyte in nature[11, 14]. The conductance values are given in table 4.1.2.

4.1.1.4 Magnetic Moment Measurement

The magnetic moment values of the synthesized complexes indicated that these complexes are diamagnetic (table 4.1.2). This diamagnetism is supported by the small negative values obtained for their magnetic susceptibility. It appears from the magnetic moment data that the complexes of Pt(IV) ion display diamagnetic property and an octahedral geometry[14, 61-62] with d^2sp^3 hybridization. The following schematic diagram represents the hybridization in the complexes (1-4).

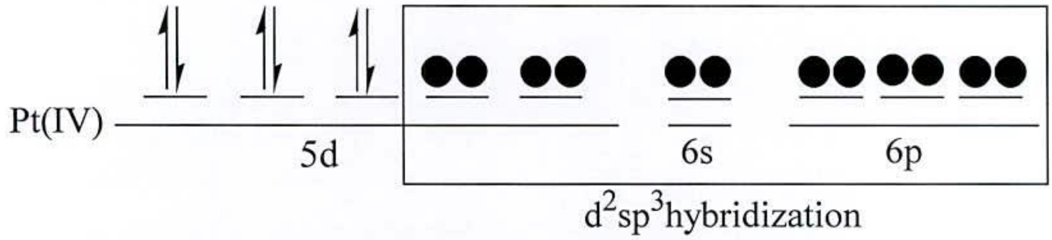


Table 4.1.2: Physical properties of the complexes

Complex No.	Complexes	Color	Melting point or decomposition temperature (± 5°C)	Molar conductance (ohm^{-1} cm^2 mol^{-1})	magnetic moment
1	$[Pt(IV)(MA)_2(Q)_2]$	Orange	268	10.35	Dia
2	$[Pt(IV)(MA)_2(IQ)_2]$	Yellow Orange	255	12.60	Dia
3	$[Pt(IV)(MA)_2(Py)_2]$	Orange	260	11.85	Dia
4	$[Pt(IV)(MA)_2(4\text{-pico})_2]$	Yellow Orange	258	10.60	Dia

Here, Dia = Diamagnetic, MA = Deprotonated malonic acid, Q = quinoline, IQ = *iso*-quinoline, Py = pyridine and 4-pico = 4-picoline.

4.1.2 Elemental Analysis

Elemental analysis is the prime tool for the formulation of a new chemical species. The formulations of the synthesized complexes were done on the basis of elemental analysis. Elemental analyses of the synthesized mixed ligand complexes were performed for platinum, carbon, hydrogen and nitrogen. The microanalysis of carbon, hydrogen and nitrogen were carried out by an organic elemental analyzer. Platinum was determined by weighing as the oxide produced by direct ignition. The elemental analyses data of the complexes are given in table 4.1.3. It is seen that the analytical data are in good agreement with the proposed empirical formula of the present complexes.

Table 4.1.3: Elemental analyses of the complexes

Com. No.	Yields %	Metal %		Carbon %		Hydrogen %		Nitrogen %	
		Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
1	67	29.67	29.70	43.83	43.80	2.76	2.85	4.26	4.25
2	65	29.67	29.65	43.83	43.78	2.76	2.82	4.26	4.27
3	78	35.00	34.91	34.47	34.52	2.53	2.55	5.03	5.03
4	76	33.33	33.28	36.92	37.02	3.10	3.21	4.79	4.78

4.1.3 Infrared Spectra Studies

In the Infrared spectra two strong bands at ~1737.9 cm^{-1} for asymmetric stretching of υ(C=O) and at ~1436.9 cm^{-1} for symmetric stretching of υ(C=O) revealed the presence of free carboxylic group of malonic acid. Upon coordination or chelation of carboxylic group to central metal ions both these υ(C=O) bands shifted to relatively shorter frequencies. It is seen that two new bands relating to the asymmetric stretching [υ(OCO)asym] and symmetric stretching [υ(OCO)sym] shifted in the regions 1704.1–1708.9 cm^{-1} and 1373.3–1410.9 cm^{-1} respectively. The shifting of these two infrared bands of can strongly be attributed to coordination of the carboxylic group as well as the formation of the complexes[117-118].

The magnitude of the separation between these two bands [Δ(OCO) cm^{-1}] has been used, tentatively, as a help in the determination of the nature of the carboxylate coordination[118].

$$\Delta(OCO)= [\upsilon(OCO)asym- \upsilon(OCO)sym]\ cm^{-1}$$

Characterization of the coordination mode of carboxylate based on the IR spectrum of the metal complex has been discussed previously by Deacon and Philips[119]. Coordination modes were classified as (1) Ionic acetates (*e.g.* those of alkali metals having Δ(OCO) values of *ca.* 165 cm^{-1} and for ionic trifluoroacetates, the Δ(OCO) value was *ca.* 235 cm^{-1}); (2) Δ(OCO) values <105 cm^{-1} indicating symmetric chelating carboxylate coordination; complexes in which the carboxylates bridge metal–metal bonds may also exhibit values in this region; (3) Δ(OCO) values substantially less than the ionic values (<150 cm^{-1}) indicating the presence of chelating or bridging carboxylates; monodentate carboxylates containing hydrogen bonds may also fall into this category; (4) Δ(OCO) values of transition metal complexes similar to that of ionic acetates (*ca.* 165 cm^{-1}) were found to be untrustworthy as many examples of each type of coordination mode were found in this category; and (5) Δ(OCO) values of >200 cm^{-1} indicate monodentate coordination. This large difference in energy is thought to arise from the bonding of one oxygen atom to the metal with the other oxygen-free, increasing the energy of the asymmetric stretching mode. There have been many contradictions to the Δ(OCO) assignments[119-120], primarily concerned with locating the exact position of the Δ(OCO)sym absorption band, and, as such, great care is required when using these guidelines. Tentative assignments for the coordination modes of carboxylate ligands (malonate) with Pt(IV) based on Δ(OCO) values, are listed in table 4.1.4.

The *υ*(OCO)asym mode of Pt(IV) complexes of malonate is found as a very strong-to-strong band at 1704.1–1708.9 cm^{-1}, and the corresponding *υ*(OCO)sym one is exhibited at 1373.3–1410.9 cm^{-1}. As the two *υ*(OCO) stretching symmetrical and asymmetrical lie lower than the free ion values and the frequency difference between these two modes is 293.2–333.7 cm^{-1}, it becomes evident that the carboxylate group acts as monodentate ligand[117-119]. Further, the presence of M−O (O = Oxygen in deprotonated malonic acid) bonding is evident from the appearance of *ν*M−O modes at 505.4-557.4 cm^{-1}.

The characteristic ring vibration of the heterocyclic amines in the range 1400-1600 cm^{-1} generally show significant changes on complexation but in our present complexes these bands could not be distinguished because of overlapping with $\nu_{C=O}$ and $\nu_{C\text{-}O}$ stretching bands. The in-plane and out-plane ring deformation modes of the heterocyclic amines observed at ~520 and ~720 cm^{-1} respectively undergo a positive shift in mixed ligand complexes conforming thereby a co-ordination through nitrogen. The presence of M–N bonding in the complexes is evident from the appearance of $\nu_{M\text{-}N}$ modes at 460.0–476.4 cm^{-1} in the spectra of the complexes. Major I.R. spectral data for the complexes are given in table 4.1.4.

Table 4.1.4: Infrared spectral data of the complexes (cm^{-1})

Com. No.	*υ*(OH)	*υ*(OCO) asym (cm^{-1})	*υ*(OCO) sym (cm^{-1})	Δ(OCO) (cm^{-1})	*υ*(M-O) (cm^{-1})	*υ*(M-N) (cm^{-1})
1	-	1704.1	1410.9	293.2	557.4	476.4
2	-	1708.9	1400.0	308.9	510.0	460.0
3	-	1707.0	1390.0	317.0	510.0	4650
4	-	1707.0	1373.3	333.7	505.4	470.0

4.1.4 Electronic Spectra Studies

The survey of the existing literature reveals that the complexes of $5d^6$ metal ions are generally diamagnetic in nature. The absorption spectra of diamagnetic octahedrally coordinated d^6 metal ion complexes give rise to two spin-allowed $^1T_{1g}$ and $^1T_{2g}$ and two spin forbidden $^3T_{1g}$ and $^3T_{2g}$ excited states. Three d-d transitions have been observed in the spectra of each Pt(IV) compound. These are spin-allowed bands involving transition $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ and the third one (every broad spin-prohibited) is due to $^1A_{1g} \rightarrow {}^3T_{1g}$. These three bands were obtained in the case of our complexes are given in table 4.1.5. By using the descent-in-symmetry method, the following three equations may be given corresponding to these three transitions.

$$10\,Dq - C = ({}^1A_{1g} \rightarrow {}^1T_{1g})\Delta E$$

$$10\,Dq + 16\,B - C = ({}^1A_{1g} \rightarrow {}^1T_{2g})\Delta E$$

$$10\,Dq - 3C = ({}^1A_{1g} \rightarrow {}^3T_{1g})\Delta E$$

Table 4.1.5: Electronic spectral data (cm^{-1}) of octahedral platinum (IV) complexes

Complex No	Spectral band (cm^{-1}) with assignment		
	$^1A_{1g}\rightarrow{}^3T_{1g}$	$^1A_{1g}\rightarrow{}^1T_{1g}$	$^1A_{1g}\rightarrow{}^1T_{2g}$
1	19055	27040	35200
2	18988	26992	35140
3	19022	27000	35300
4	19000	27030	35000

In addition to the d-d transitions, the Pt(IV) complexes obtained two charge transfer bands at 39000 and 50000 cm^{-1}. These have been assigned as ligand to metal charge transfer band, since empty ligand orbitals are expected to be at energies too high to participate to any extent in bonding. All these bands are consistent with the octahedral stereochemistry of Pt(IV) compounds[14, 61-62].

From the above discussion, it is evident that the synthesized Pt(IV) complexes are Octahedral in structure and the probable structures of the complexes have been shown in figures 4.1.1-4.1.4.

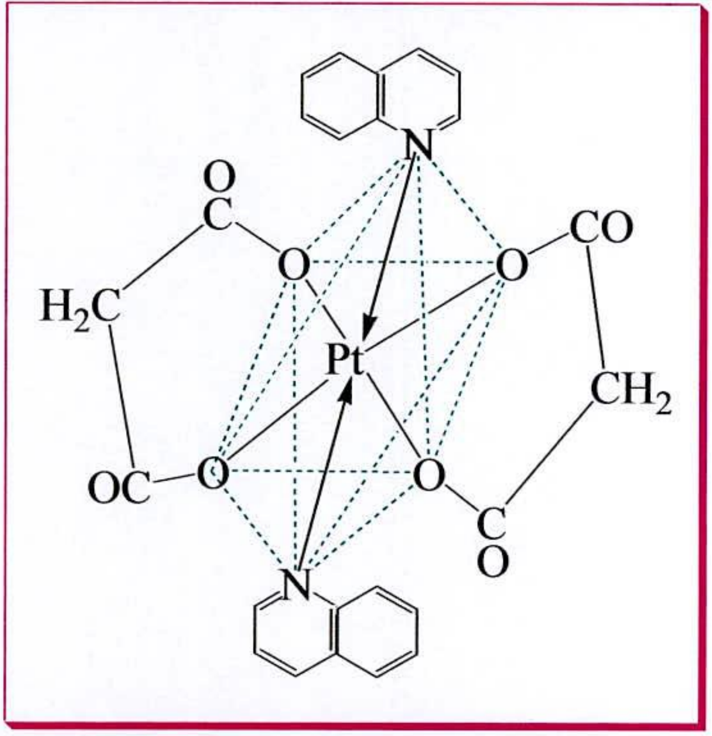


Figure 4.1.1(a): Probable structure of the complex-1, $[Pt(IV)(MA)_2(Q)_2]$

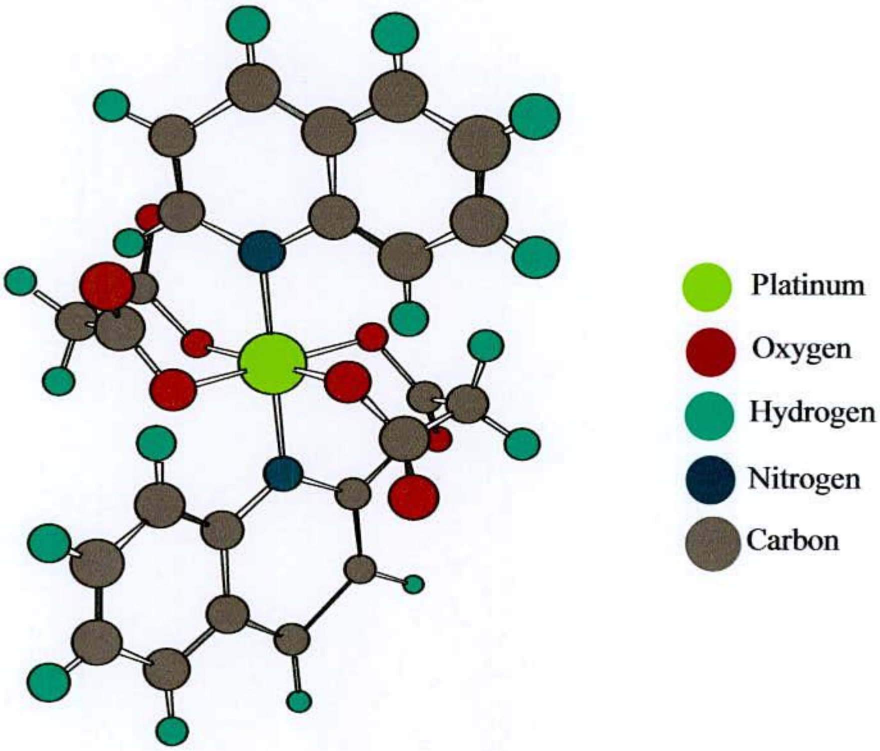


Figure 4.1.1(b): Probable ball and stick model of the complex-1, $[Pt(IV)(MA)_2(Q)_2]$

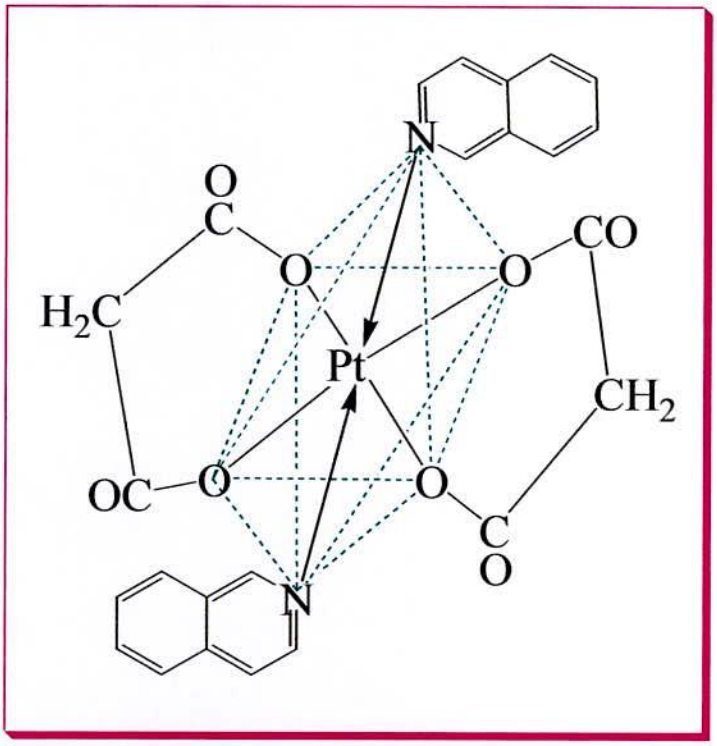


Figure 4.1.2(a): Probable structure of the complex-2, $[Pt(IV)(MA)_2(IQ)_2]$

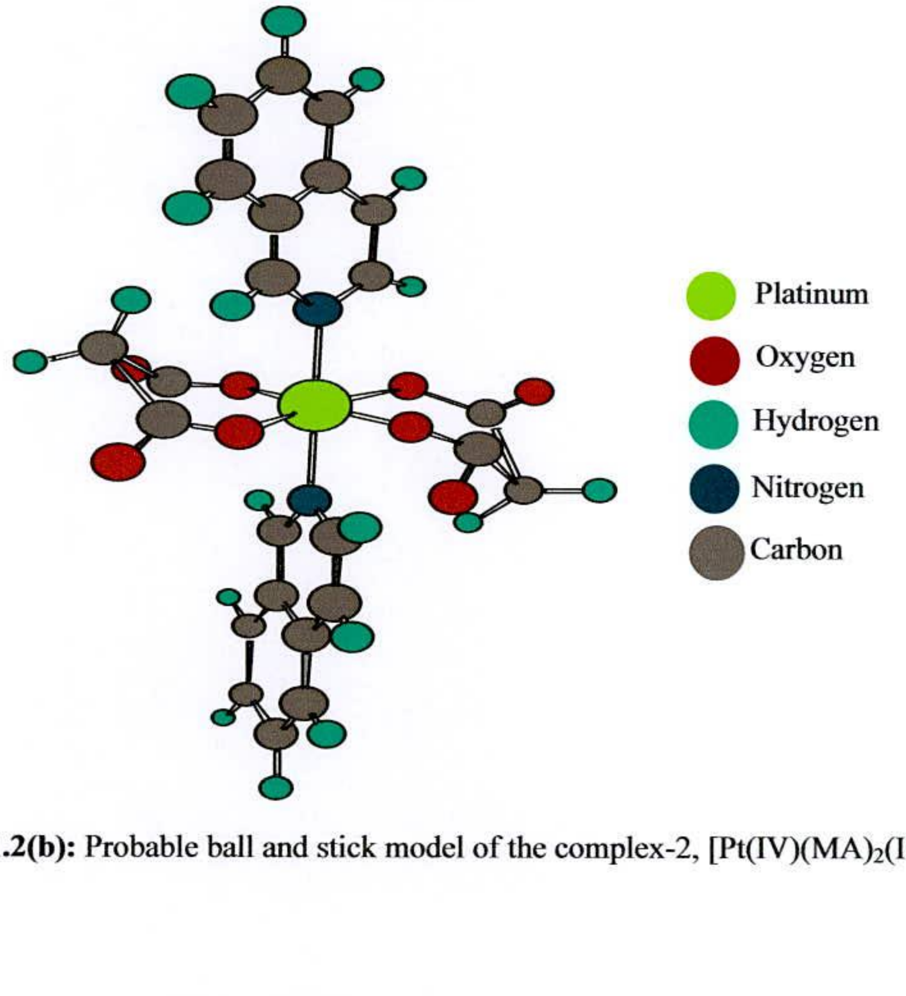


Figure 4.1.2(b): Probable ball and stick model of the complex-2, $[Pt(IV)(MA)_2(IQ)_2]$

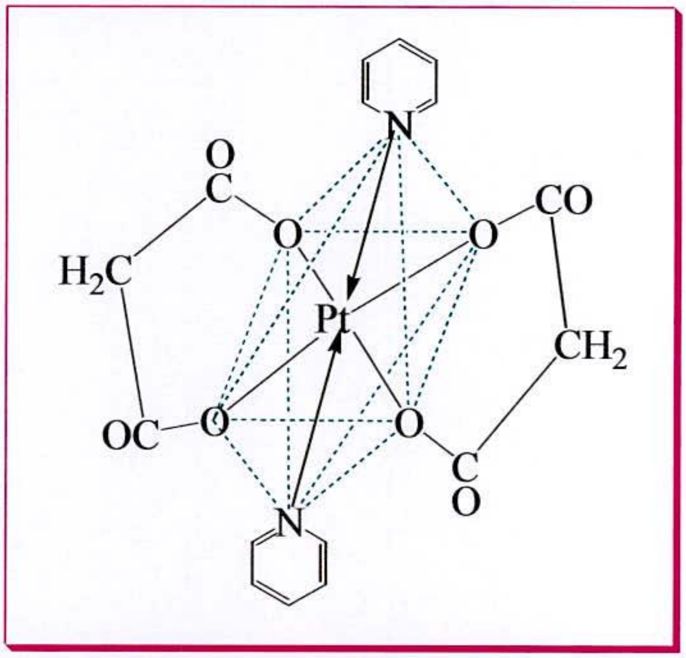


Figure 4.1.3(a): Probable structure of the complex-3, $[Pt(IV)(MA)_2(Py)_2]$

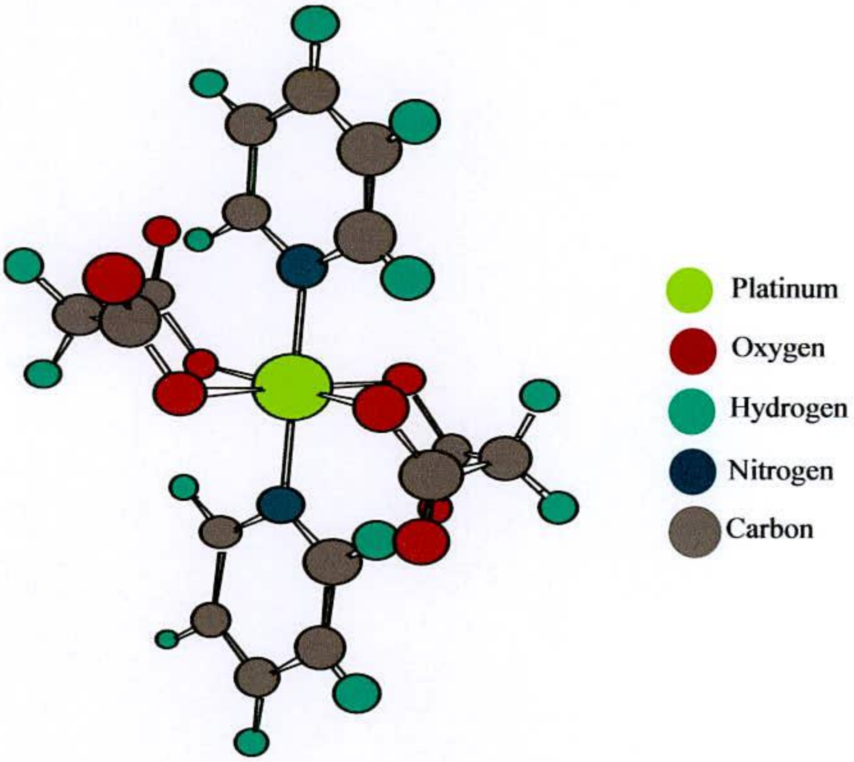


Figure 4.1.3(b): Probable ball and stick model of the complex-3, $[Pt(IV)(MA)_2(Py)_2]$

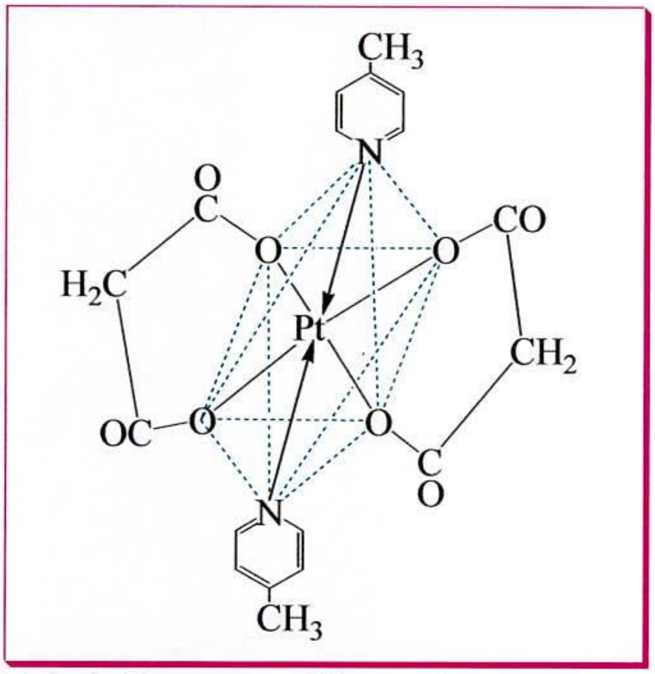


Figure 4.1.4(a): Probable structure of the complex-4, [Pt(IV)(MA)$_2$(4-Pico)$_2$]

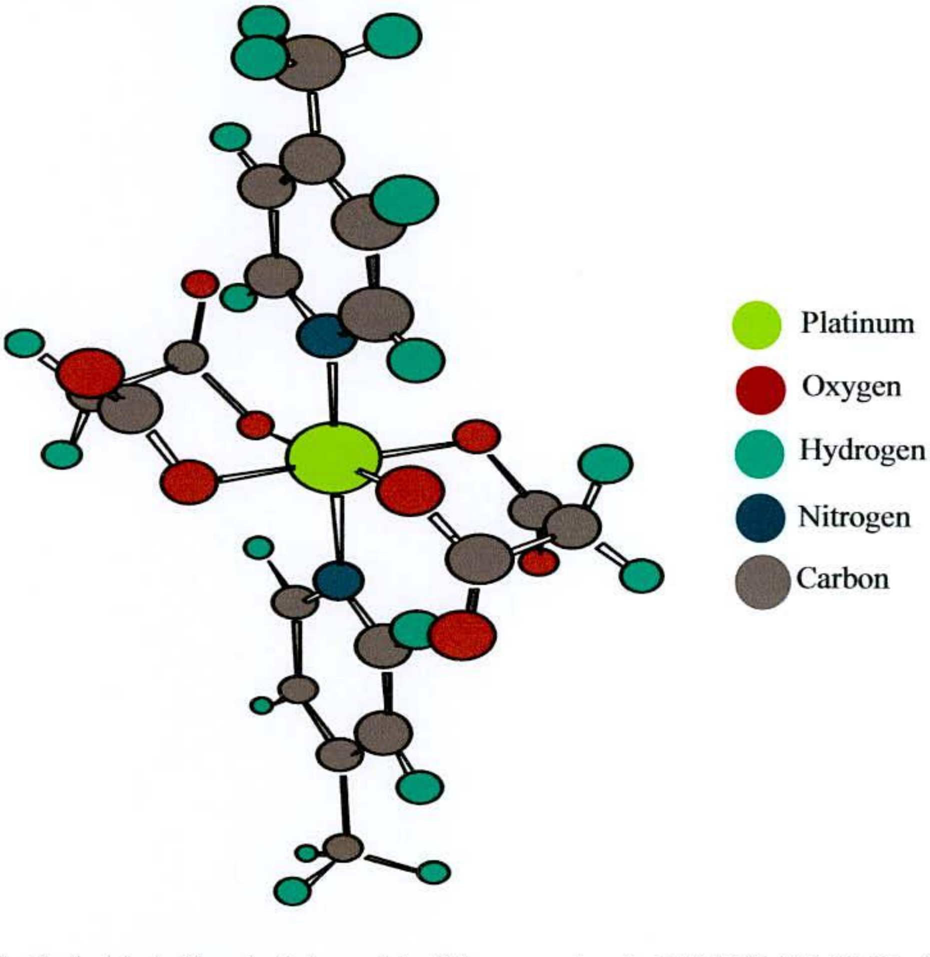


Figure 4.1.4(b): Probable ball and stick model of the complex-4, [Pt(IV)(MA)$_2$(4-Pico)$_2$].

Results and Discussion 2

Characterization of Mixed Ligand Complexes of Pt (IV) Ion with Oxalic Acid and Heterocyclic Amines [Complex 5-8]

Content

4.2.1 Physical Properties
4.2.1.1 Solubility
4.2.1.2 Color & Melting point
4.2.1.3 Conductivity Measurement
4.2.1.4 Magnetic Moment Measurement
4.2.2 Elemental Analysis
4.2.3 Infrared Spectra Studies
4.2.4 Electronic Spectra Studies

Mixed ligand complexes of Pt(IV) ion with oxalic acid (OXH_2) as primary and heterocyclic amines, *viz*. quinoline (Q), *iso*-quinoline (IQ), pyridine (Py) and 4-pico(4-picoline) as secondary ligands have been synthesized and characterized by several physico-chemical and spectroscopic analysis. Complexes of Pt(IV) ion with oxalic acid (OXH_2) and heterocyclic amines were synthesized by a very simple experimental method; in ethanolic solution at room temperature as discussed in chapter III. It is revealed that the syntheses of all the complexes of Pt (IV) followed the following general chemical reactions.

$$\mathrm{Pt\,H_2Cl_6} + 2\,\mathrm{OXH_2} \rightarrow [\mathrm{Pt}^{4+} + 2\mathrm{OX}^{-} + 6\mathrm{H}^{+} + 6\mathrm{Cl}^{-}] \text{ (Resulting Solution)}$$

$$[\mathrm{Pt}^{4+} + 2\mathrm{OX}^{-} + 6\mathrm{H}^{+} + 6\mathrm{Cl}^{-}] + 2\mathrm{L} \rightarrow [\mathrm{Pt(OX)_2L_2}] + 6\mathrm{HCl} \quad \text{(For complexes 5-8)}$$

where, OXH_2 =oxalic acid L = monodented base, *viz.,* quinoline, Q (for complex 1), *iso*-quinoline, IQ (for complex 2), pyridine, Py (for complex 3), 4-picoline ,4-pico (for complex 4). Physico-chemical properties, elemental analysis, magnetic and spectroscopic data were used to propose probable structures, and the complexes are reported here for the first time.

4.2.1 Physical Properties

4.2.1.1 Solubility

Solubility of a compound depends on the mode of interaction between solute and solvent molecules (*e.g.,* dipole-dipole interaction, lattice energy, lattice enthalpy, solvation energy, temperature and pressure). A compound will be soluble only when the lattice enthalpy is lower than the solvation energy. The solubility of the complexes was examined in the usual manner. The complexes were all slightly soluble in water and methanol but are soluble in DMF and DMSO.(table 4.2.1)

Table 4.2.1: Solubility of the synthesized complexes

Complex No.	Complexes	Water		Methanol		DMF		DMSO	
		Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
5	$[Pt(IV)(OX)_2(Q)_2]$	+/-	+/-	+/-	+/-	+	+	+	+
6	$[Pt(IV)(OX)_2(IQ)_2]$	+/-	+/-	+/-	+/-	+	+	+	+
7	$[Pt(IV)(OX)_2(Py)_2]$	+/-	+/-	+/-	+/-	+	+	+	+
8	$[Pt(IV)(OX)_2(4\text{-pico})_2]$	+/-	+/-	+/-	+/-	+	+	+	+

Here, +/- = Slightly soluble and + = Soluble

4.2.1.2 Color & Melting point

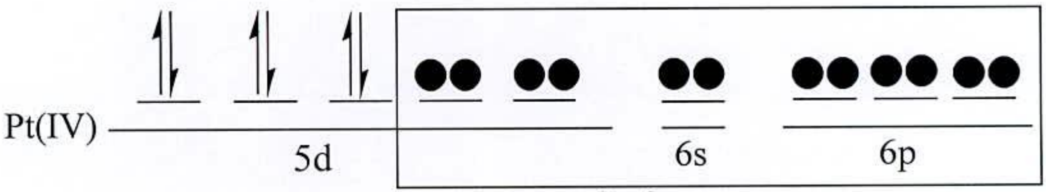
All the synthesized complexes (complex 5-8) are colored amorphous powder. Single crystal of the complexes could not be isolated from any solution. Complex 5, Pt(IV) with (oxalic acid + quinoline) is orange in colored , Complexes 6 and 7 *i.e.,* Pt(IV) with (oxalic acid + *iso*-quinoline) and (oxalic acid + pyridine) are yellow in colored & Complex 8, Pt(IV) with (oxalic acid + 4-picoline) is yellow-orange in colored (shown in table 4.2.2). Melting point of complex-5, $Pt(IV)(OX)_2(Q)_2$ is 260± 5°C while the melting point of the ligands, oxalic acid is 102-103°C and quinoline is -15°C which indicates the strong indication of coordination of the ligands and formation of the complex. Similarly for the melting point of complex-6 is 240± 5°C while that for *iso*-quinoline is 26-28°C melting point of complex-7 is 265± 5°C while that for pyridine is -41.8°C and melting point of complex-8 is 270±5°C while that for 4-picoline is 2.4°C also indicate the formation of the complexes. Data for the melting points of the complexes has been tabulated in table 4.2.2.

4.2.1.3 Conductivity Measurement

The molar conductance were measured in *N,N'*-dimethyl formamide. The conductance values of the complexes were in the range (10.60 – 12.85) Ω^{-1} cm^2 $mole^{-1}$ indicated that these complexes were non-electrolyte in nature[11,14]. The conductance values are given in table 4.2.2

4.2.1.4 Magnetic Moment Measurement

The magnetic moment values of the synthesized complexes indicated that these complexes are diamagnetic (table 4.2.2). This diamagnetism is supported by the small negative values obtained for their magnetic susceptibility. It appears from the magnetic moment data that the complexes of Pt(IV) ion display diamagnetic property and an octahedral geometry[14, 61-62] with d^2sp^3 hybridization. The following schematic diagram represents the hybridization in the complexes (5-9).



d^2sp^3hybridization

Table 4.2.2: Physical properties of the complexes

Complexes No.	Complexes	Color	Melting point or decomposition temperature (± 5°C)	Molar conductance (ohm^{-1} cm^{2} mol^{-1})	magnetic moment
5	$[Pt(IV)(OX)_2(Q)_2]$	Orange	260	10.85	Dia
6	$[Pt(IV)(OX)_2(IQ)_2]$	Yellow	240	11.65	Dia
7	$[Pt(IV)(OX)_2(Py)_2]$	Yellow	265	12.85	Dia
8	$[Pt(IV)(OX)_2(4\text{-}pico)_2]$	Yellow Orange	270	10.60	Dia

where, Dia = Diamagnetic, OX = Deprotonated oxalic acid, Q=quinoline , IQ= *iso*-quinoline, Py=pyridine, 4-pico=4-picoline.

4.2.2 Elemental Analysis

Elemental analysis is the prime tool for the formulation of a new chemical species. The formulations of the synthesized complexes were done on the basis of elemental analysis. Elemental analyses of the synthesized mixed ligand complexes were performed for platinum, carbon, hydrogen and nitrogen. The microanalysis of carbon, hydrogen and nitrogen were carried out by an organic elemental analyzer. Platinum was determined by weighing as the oxide produced by direct ignition. The elemental analyses data of the complexes are given in table 4.2.3. It is seen that the analytical data are in good agreement with the proposed empirical formula of the present complexes.

Table 4.2.3: Elemental analyses of the complexes

Com. No.	Yields %	Metal %		Carbon %		Hydrogen %		Nitrogen %	
		Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
5	65	31.00	30.90	41.97	42.04	2.24	2.28	4.45	4.48
6	62	31.00	31.08	41.97	41.88	2.24	2.33	4.45	4.45
7	71	36.86	36.90	31.76	31.76	1.90	2.01	5.30	5.35
8	74	35.00	35.00	34.47	34.55	2.53	2.52	5.03	5.00

4.2.3 Infrared Spectra Studies

The position of the strong C=O absorption band in the carboxylic acid group of the free carboxylic acid of oxalic acid, 1692.5 cm^{-1} and 1441.8 cm^{-1}. Upon chelating to center metal ions, this υ(C=O) band shifted or disappears and two new bands relating to the asymmetric [υ(OCO)asym] and symmetric [υ(OCO)sym] stretches appear in the regions 1600.0–1606.6 and 1377.1–1393.5 cm^{-1}, respectively[117-118] . The magnitude of the separation between these two bands [Δ(OCO) cm^{-1}] has been used, tentatively, as a help in the determination of the nature of the carboxylate coordination[118].

$$\Delta(OCO)= [\upsilon(OCO)asym- \upsilon(OCO)sym]\ cm^{-1}$$

Characterization of the coordination mode of carboxylate based on the IR spectrum of the metal complex has been discussed previously by Deacon and Philips[119]. Coordination modes were classified as (1) Ionic acetates (*e.g.* those of alkali metals) having Δ(OCO) values of *ca.* 165 cm^{-1} (for ionic trifluoroacetates, the Δ(OCO) value was *ca.* 235 cm^{-1}); (2) Δ(OCO) values <105 cm^{-1} indicating symmetric chelating carboxylate coordination; complexes in which the carboxylates bridge short metal–metal bonds may also exhibit values in this region; (3) Δ(OCO) values substantially less than the ionic values (<150 cm^{-1}) indicating the presence of chelating or bridging carboxylates; monodentate carboxylates containing hydrogen bonds may also fall into this category; (4) Δ(OCO) values of transition metal complexes similar to that of ionic acetates (*ca.* 165 cm^{-1}) were found to be untrustworthy as many examples of each type of coordination mode were found in this category; and (5) Δ(OCO) values of >200 cm^{-1} indicate monodentate coordination. This large difference in energy is thought to arise from the bonding of one oxygen atom to the metal with the other oxygen-free, increasing the energy of the asymmetric stretching mode. There have been many contradictions to the Δ(OCO) assignments[119-120], primarily concerned with locating the exact position of the Δ(OCO)sym absorption band, and, as such, great care is required when using these guidelines. Tentative assignments for the coordination modes of carboxylate ligands (oxalate) with Pt(IV) based on Δ(OCO) values, are listed in table 4.2.4.

The υ(OCO)asym mode of Pt(IV) complexes of oxalate is found as a very strong-to-strong band at 1600.0–1606.6 cm^{-1}, and the corresponding υ(OCO)sym one is exhibited at 1377.1–1393.5 cm^{-1}. As the two υ(OCO) stretching symmetrical and asymmetrical lie lower than the free ion values and the frequency difference between these two modes is 201.5–229.5 cm^{-1}, it becomes evident that the carboxylate group acts as a monodentate ligand[117-119]. Further, the presence of M–O (O = Oxygen in deprotonated oxalic acid) bonding is evident from the appearance of ν M–O modes at 500.0–519.8 cm^{-1}.

The characteristic ring vibration of the heterocyclic amines in the range 1400-1600 cm^{-1} generally show significant changes on complexation but in our present complexes these bands could not be distinguished because of overlapping with $\nu_{C=O}$ and $\nu_{C\text{-}O}$ stretching bands. The in-plane and out plane ring deformation modes of the heterocyclic amines observed at ~ 520 and ~ 720 cm^{-1} respectively undergo a positive shift in mixed ligand complexes conforming thereby a co-ordination through nitrogen. The presence of M-N bonding in the complexes is evident form the appearance of $\nu_{M\text{-}N}$ modes at 445.5 – 461.9 cm^{-1} in the spectra of the complexes. Major I.R. spectral data for the complexes are given in table 4.2.4.

Table 4.2.4: Infrared spectral data of the complexes (cm^{-1})

Com. No.	υ(OH)	υ(OCO) asym	υ(OCO) sym	Δ(OCO)	υ(M-O)	υ(M-N)
5	-	1600.0	1392.5	207.5	519.8	461.9
6	-	1595.0	1393.5	201.5	519.8	461.9
7	-	1600.0	1390.0	210.0	500.0	460.0
8	-	1606.6	1377.1	229.5	504.4	445.5

4.2.4 Electronic Spectra Studies

The survey of the existing literature reveals that the complexes of $5d^6$ metal ions are generally diamagnetic in nature. The absorption spectra of diamagnetic octahedrally coordinated d^6 metal ion complexes give rise to two spin-allowed $^1T_{1g}$ and $^1T_{2g}$ and two spin forbidden $^3T_{1g}$ and $^3T_{2g}$ excited states. Three d-d transitions have been observed in the spectra of each Pt(IV) compound. These are spin-allowed bands involving transition $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ and the third one (every broad spin-prohibited) is due to $^1A_{1g} \rightarrow {}^3T_{1g}$. These three bands were obtained in the case of our complexes are given in table 4.2.5. By using the descent-in-symmetry method, the following three equations may be given corresponding to these three transitions.

$$10\ Dq - C = ({}^1A_{1g} \rightarrow {}^1T_{1g})\ \Delta E$$

$$10\ Dq + 16\ B - C = ({}^1A_{1g} \rightarrow {}^1T_{2g})\ \Delta E$$

$$10\ Dq - 3C = ({}^1A_{1g} \rightarrow {}^3T_{1g})\ \Delta E$$

In addition to the d-d transitions, the Pt(IV) complexes obtained two charge transfer bands at 39050 and 50000 cm^{-1}. These have been assigned as ligand to metal charge transfer band, since empty ligand orbitals are expected to be at energies too high to participate to any extent in bonding. All these bands are consistent with the octahedral stereochemistry of Pt(IV) compound[14, 61-62].

Table 4.2.5: Electronic spectral data (cm^{-1}) of octahedral platinum (IV) complexes

Complex No.	Spectral band (cm^{-1}) with assignment		
	$^1A_{1g}\rightarrow{}^3T_{1g}$	$^1A_{1g}\rightarrow{}^1T_{1g}$	$^1A_{1g}\rightarrow{}^1T_{2g}$
5	19005	27075	35210
6	18995	26980	35160
7	19045	27065	35300
8	19065	27040	35030

From the above discussion, it is evident that the synthesized Pt(IV) complexes are Octahedral in structure and the probable structures of the complexes have been shown in figures 4.2.1-4.2.4.

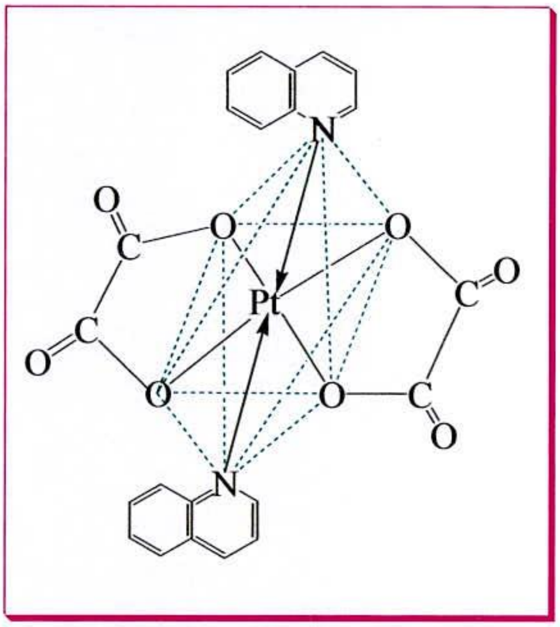


Figure 4.2.1(a): Probable structure of the complex-5, $[Pt(IV)(OX)_2(Q)_2]$

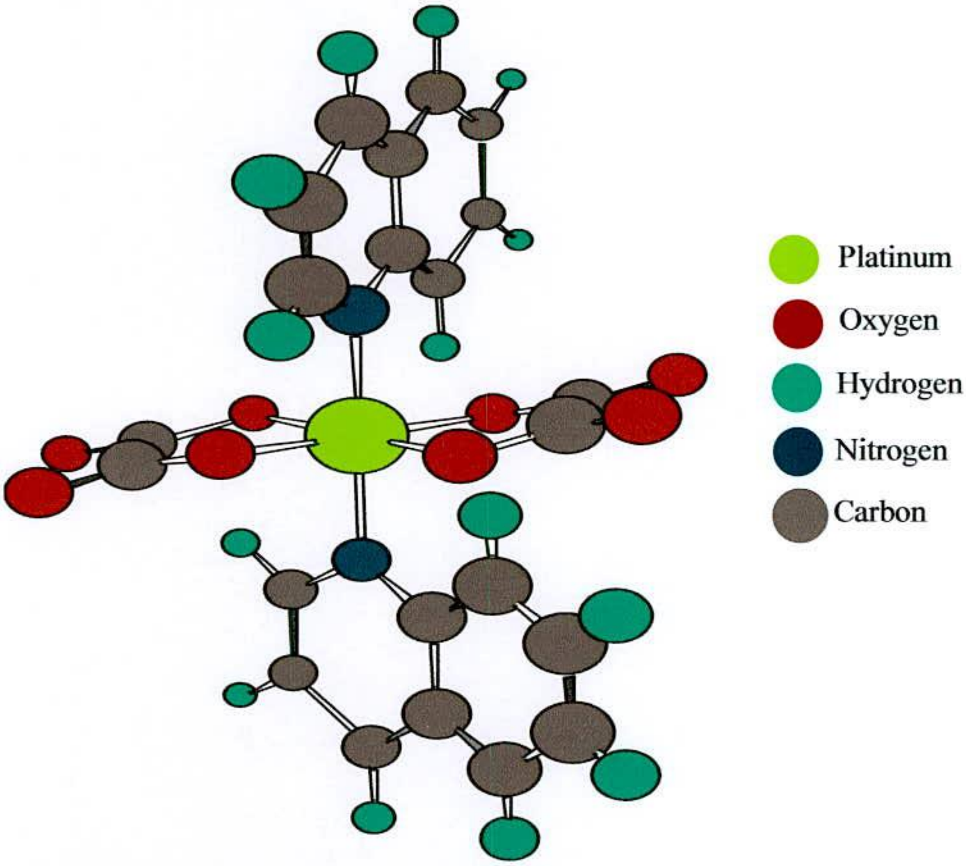


Figure 4.2.1(b): Probable ball and stick model of the complex-5, $[Pt(IV)(OX)_2(Q)_2]$

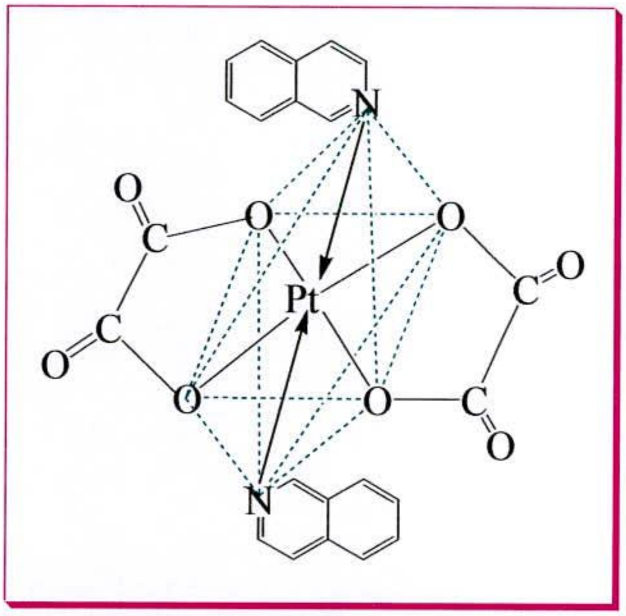


Figure 4.2.2(a): Probable structure of the complex-6, [Pt(IV)$(OX)_2(IQ)_2$]

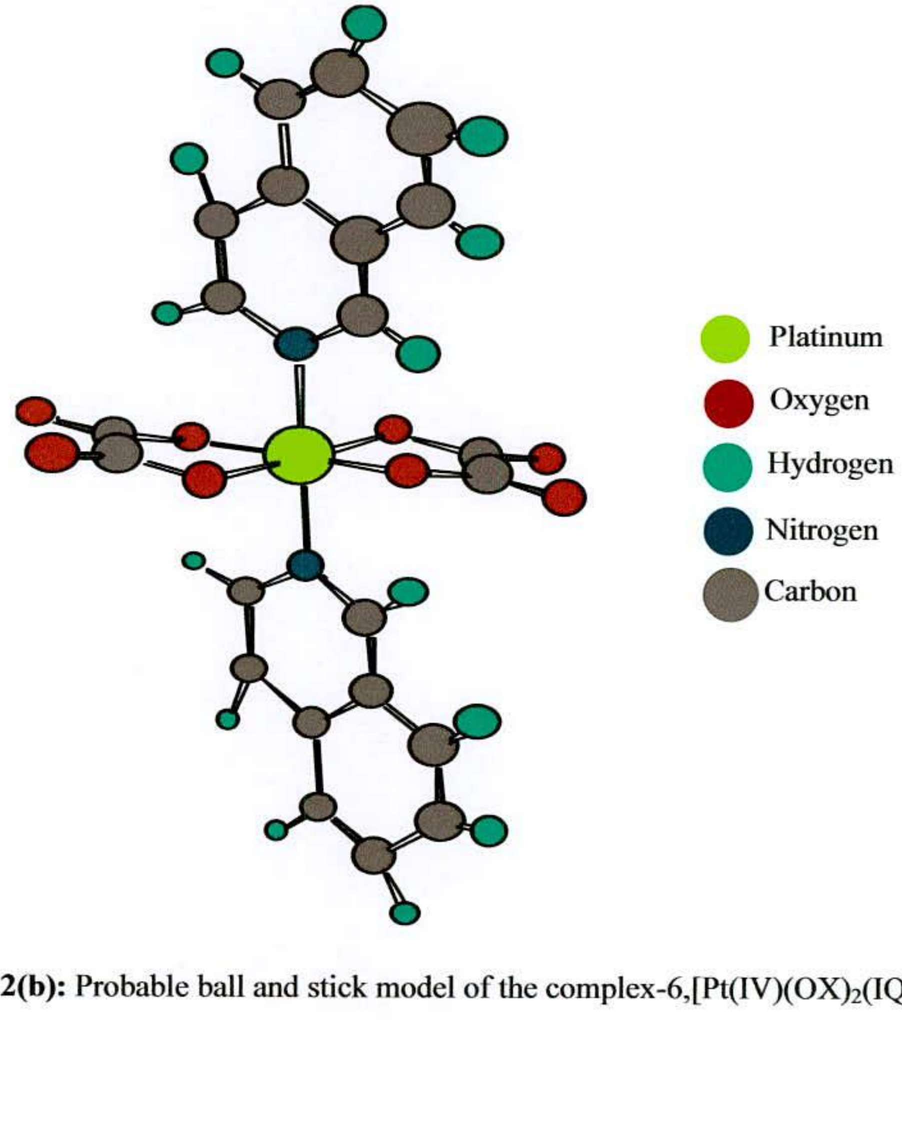


Figure 4.2.2(b): Probable ball and stick model of the complex-6,[Pt(IV)$(OX)_2(IQ)_2$]

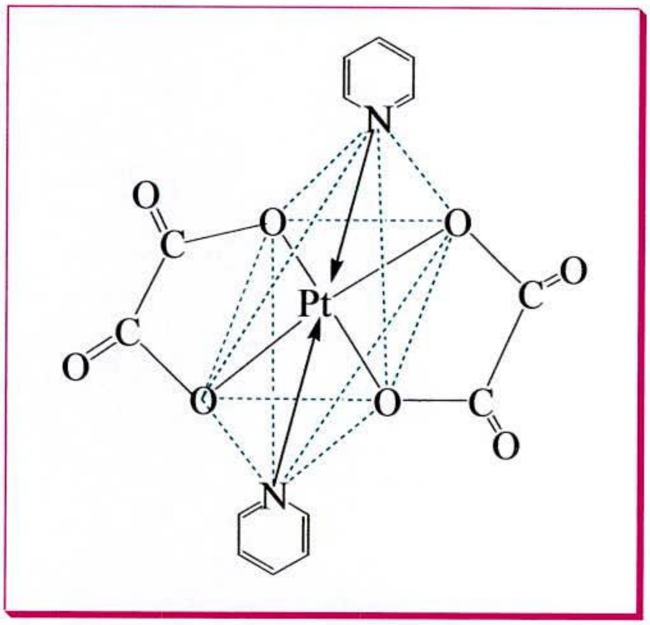


Figure 4.2.3(a): Probable structure of the complex-7, [Pt(IV)(OX)$_2$(Py)$_2$]

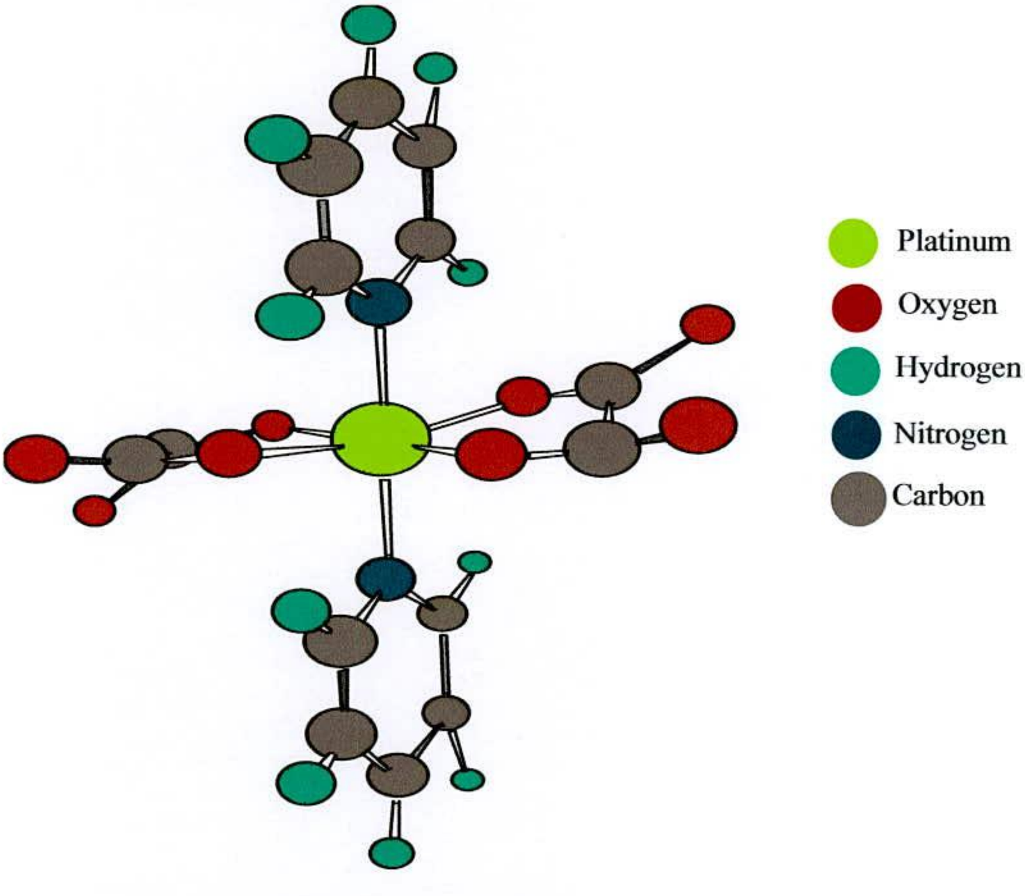


Figure 4.2.3(b): Probable ball and stick model of the complex-7, [Pt(IV)(OX)$_2$(Py)$_2$]

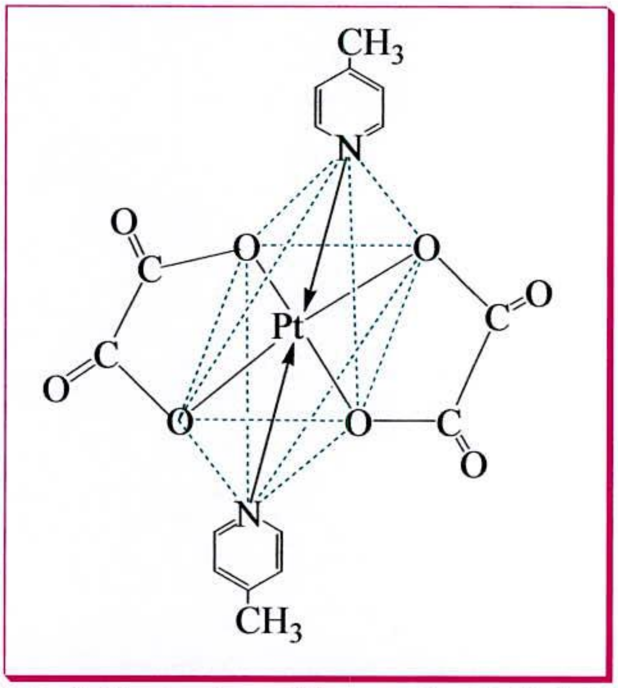


Figure 4.2.4(a): Probable structure of the complex-8, [Pt(IV)(OX)$_2$(4-pico)$_2$]

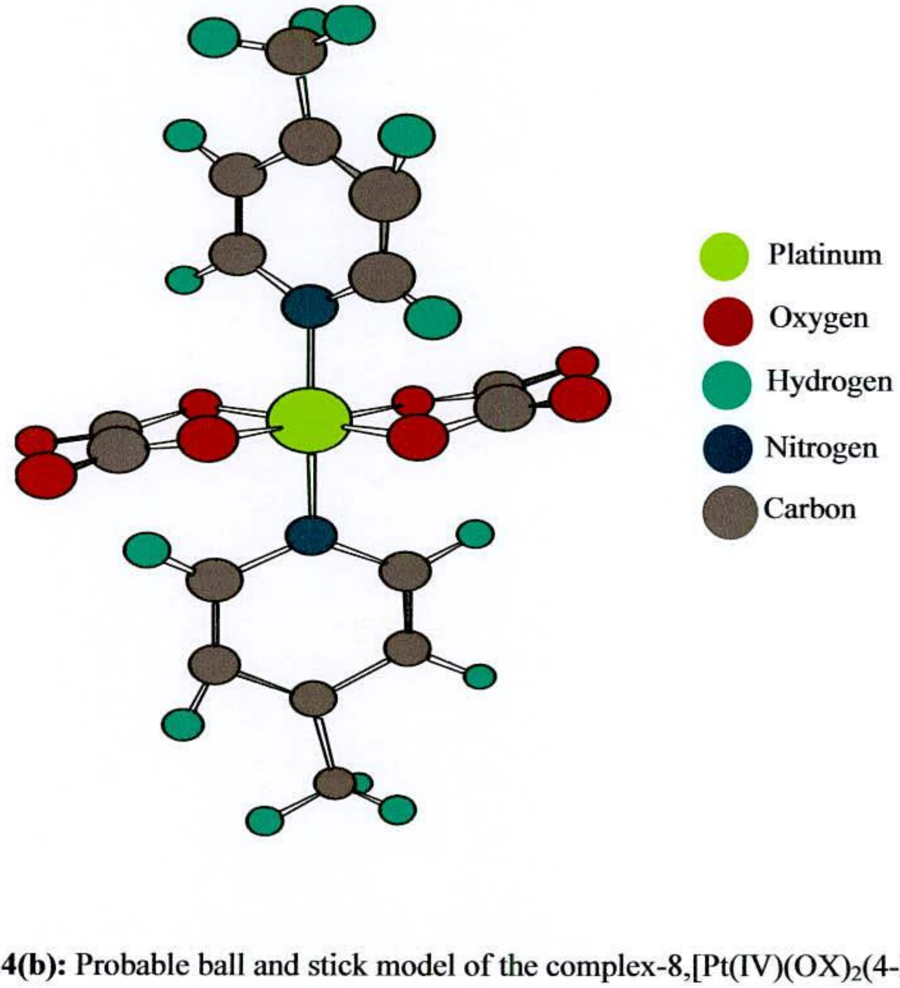


Figure 4.2.4(b): Probable ball and stick model of the complex-8,[Pt(IV)(OX)$_2$(4-Pico)$_2$]

Results and Discussion 3

Characterization of Mixed Ligand Complexes of Pd (II) & Pt(II) Ion with Phthalic Acid and Heterocyclic Amines [Complex 9-13]

Content

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4.3.2 Elemental Analysis
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4.3.4 Electronic Spectra Studies

Mixed ligand complexes of Pt(II) & Pd(II) ion with phthalic acid (PhH_2) as primary and heterocyclic amines, *viz*. quinoline (Q), *iso*-Quinoline (IQ), Pyridine (Py) and 4-picoline (4-pico) 2-aminopyridine (2apy) as secondary ligands have been synthesized and characterized by several physico-chemical and spectroscopic analysis. Complexes of Pt(II) & Pd(II) ion with phthalic acid (PhH_2) and heterocyclic amines were synthesized by a very simple experimental method; in ethanolic solution at room temperature as discussed in chapter III. It is revealed that the syntheses complexes of Pd(II) & Pt(II) followed the following general chemical reactions.

For Pd(II) complexes

$$PdCl_2 + PhH_2 \rightarrow [Pd^{2+} + Ph^- + 2H^+ + 2Cl^-] \text{ (Resulting Solution)}$$

$$[Pd^{2+} + Ph^- + 2H^+ + 2Cl^-] + 2L \rightarrow [Pd(Ph)L_2] + 2HCl \qquad \text{[For complexes 9-11]}$$

$$[Pd^{2+} + Ph^- + 2H^+ + 2Cl + L^1 \rightarrow [Pd(Ph)L^1] + 2HCl \text{ [For complexes 12]}$$

For Pt(II) complexes

$$PtCl_2 + PhH_2 \rightarrow [Pt^{2+} + Ph^- + 2H^+ + 2Cl^-] \text{ (Resulting Solution)}$$

$$[Pd^{2+} + Ph^- + 2H^+ + 2Cl^-] + 2L \rightarrow [Pt(Ph)L_2] + 2HCl \qquad \text{[For complexes 13]}$$

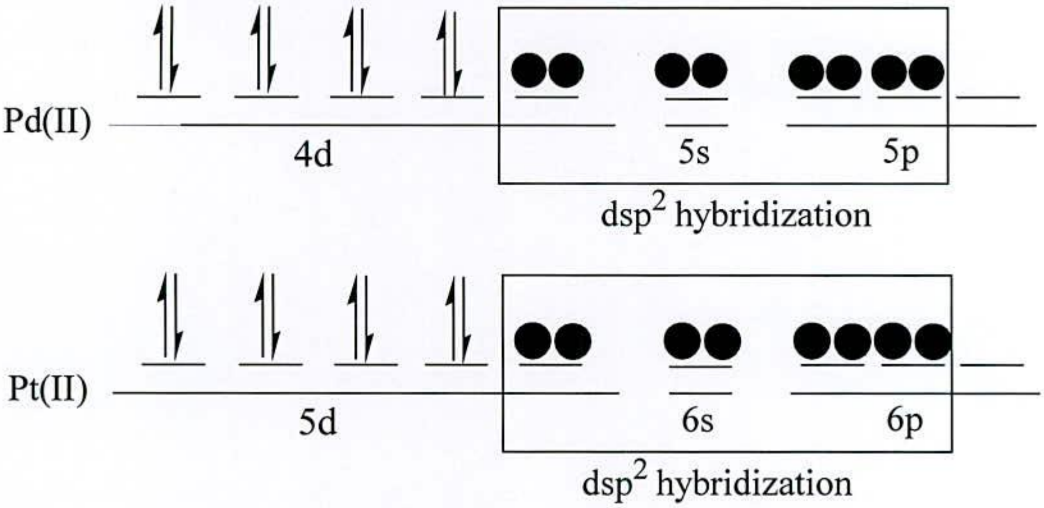
where, PhH_2 = phthlic acid L = monodented base, *viz* – quinoline, Q (for complex 9), *iso*-quinoline, IQ (for complex 10), pyridine, Py (for complex 11), 4-picoline ,4-pico (for complex 13) L^1 = bidented base , 2-aminopyridine, 2apy (for complex 12). Physico-chemical indicates the strong indication of coordination of the ligands and formation of the complex. Similarly for the melting point of complex-10 is 255± 5°C while that for *iso*-quinoline is 26-28°C melting point of complex-11 is 260± 5°C while that for pyridine is -41.8°C melting point of complex-12 is 258±5°C while that for 2-aminopyridine is 59-60°C and melting point of complex-13 is 250±5°C while that for 4-picoline is 2.4°C also indicate the formation of the complexes. Data for the melting points of the complexes has been tabulated in table 4.3.2.

4.3.1.3 Conductivity Measurement

The molar conductance were measured in *N,N'*-dimethyl formamide. The conductance values of the Pt(II) and Pd(II) complexes were in the range (10.65 – 11.65) Ω^{-1} cm^2 mole^{-1} indicated that these complexes were non-electrolyte in nature[11,14]. The conductance values are given in tables 4.3.1.

4.3.1.4 Magnetic Moment Measurement

The magnetic moment values of the synthesized complexes indicated that these complexes are diamagnetic (table 4.3.2). This diamagnetism is supported by the small negative values obtained for their magnetic susceptibility. The observed magnetic moment indicate that these complexes are square planar[60, 67, 73, 121] with dsp^2 hybridization. The following schematic diagram represents the hybridization in the complexes.



properties, elemental analysis, magnetic and spectroscopic data were used to propose probable structures, and the complexes are reported here for the first time.

4.3.1 Physical Properties

4.3.1.1 Solubility

Solubility of a compound depends on the mode of interaction between solute and solvent molecules (e.g., dipole-dipole interaction, lattice energy, lattice enthalpy, solvation energy, temperature and pressure). A compound will be soluble only when the lattice enthalpy is lower than the solvation energy. The solubility of the complexes was examined in the usual manner. The complexes were all slightly soluble in water and methanol but are soluble in DMF and DMSO.(table 4.3.1)

Table 4.3.1: Solubility of the synthesized complexes

Complex No.	Complexes	Water		Methanol		DMF		DMSO	
		Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
9	[Pd(II)(Ph)(Q)$_2$]	+/-	+/-	+/-	+/-	+	+	+	+
10	[Pd(II)(Ph)(IQ)$_2$]	+/-	+/-	+/-	+/-	+	+	+	+
11	[Pd(II)(Ph)(Py)$_2$]	+/-	+/-	+/-	+/-	+	+	+	+
12	[Pd(II)(Ph)(2-apy)]	+/-	+/-	+/-	+/-	+	+	+	+
13	[Pt(II)(Ph)(4-pico)$_2$]	+/-	+/-	+/-	+/-	+	+	+	+

Here, +/- = Slightly soluble and + = Soluble

4.3.1.2 Color & Melting point

All the synthesized complexes (complex 9-13) are colored amorphous powder. Single crystal of the complexes could not be isolated from any solution. Complexes 9,10 and 12 *i.e.,* Pd(II) with (phthalic acid + quinoline), (phthalic acid + pyridine) and (phthalic acid + 2-aminopyridine) are yellow-green in colored, Complexes 10, Pd(II) with (phthalic acid + *iso*-quinoline) is khaki in colored and Pt(II) with (phthalic acid + 4-picoline) is yellow in colored (shown in table 4.3.2). Melting point of complex-9, Pd(II)(Ph)(Q)$_2$ is 268± 5°C while the melting point of the ligands, phthalic acid is 210-211°C and quinoline is -15°C which

Table 4.3.2: Physical properties of the complexes

Complexes No.	Complexes	Color	Melting point or decomposition temperature (± 5°C)	Molar conductance $(ohm^{-1}\ cm^2\ mol^{-1})$	magnetic moment
9	$[Pd(II)(Ph)(Q)_2]$	Yellow Green	268	11.65	Dia
10	$[Pd(II)(Ph)(IQ)_2]$	Khaki	255	11.60	Dia
11	$[Pd(II)(Ph)(Py)_2]$	Yellow Green	260	10.80	Dia
12	$[Pd(II)(Ph)(2\text{-}apy)]$	Yellow Green	258	11.30	Dia
13	$[Pt(II)(Ph)(4\text{-}pico)_2]$	Yellow	250	10.65	Dia

where, Dia = Diamagnetic, Ph= Deprotonated phthalic acid, Q=quinoline , IQ= *iso*-quinoline, Py=pyridine, 4-pico=4-picoline, 2-apy=2-amino pyridine.

4.3.2 Elemental Analysis

Elemental analysis is the prime tool for the formulation of a new chemical species. The formulations of the synthesized complexes were done on the basis of elemental analysis. Elemental analyses of the synthesized mixed ligand complexes were performed for palladium, platinum, carbon, hydrogen and nitrogen. The microanalysis of carbon, hydrogen and nitrogen were carried out by an organic elemental analyzer. Palladium & platinum were determined by weighing as the oxide produced by direct ignition. The elemental analyses data of the complexes are given in table 4.3.3. It is seen that the analytical data are in good agreement with the proposed empirical formula of the present complexes.

Table 4.3.3: Elemental analyses of the complexes

Com. No.	Yields %	Metal %		Carbon %		Hydrogen %		Nitrogen %	
		Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
9	65	20.20	20.25	59.27	59.22	3.06	3.11	5.32	5.30
10	61	20.20	20.30	59.27	59.25	3.06	3.10	5.32	5.30
11	72	24.82	24.85	50.42	50.35	3.29	3.35	6.54	6.50
12	67	29.18	29.10	42.81	42.75	2.76	2.70	7.68	7.70
13	72	35.77	35.70	44.03	44.13	3.33	3.40	5.14	5.11

4.3.3 Infrared Spectra Studies

The position of the strong C=O absorption band in the carboxylic acid group of the free carboxylic acid of phtalic acid,1686.8 and 1404.2 cm^{-1}. Upon chelating to center metal ions, this υ(C=O) band shifted or disappears and two new bands relating to the asymmetric [υ(OCO)asym] and symmetric [υ(OCO)sym] stretches appear in the regions 1633.6–1606.6 and 1399.3–1363.6 cm^{-1}, respectively[117-118]. The magnitude of the separation between these two bands [Δ(OCO) cm^{-1}] has been used, tentatively, as a help in the determination of the nature of the carboxylate coordination[118].

$$\Delta(OCO) = [\upsilon(OCO)asym - \upsilon(OCO)sym]\ cm^{-1}$$

Characterization of the coordination mode of carboxylate based on the IR spectrum of the metal complex has been discussed previously by Deacon and Philips[119]. Coordination modes were classified as (1) Ionic acetates (*e.g.* those of alkali metals) having Δ(OCO) values of *ca.* 165 cm^{-1} (for ionic trifluoroacetates, the Δ(OCO) value was *ca.* 235 cm^{-1}); (2) Δ(OCO) values <105 cm^{-1} indicating symmetric chelating carboxylate coordination; complexes in which the carboxylates bridge metal–metal bonds may also exhibit values in this region; (3) Δ(OCO) values substantially less than the ionic values (<150 cm^{-1}) indicating the presence of chelating or bridging carboxylates; monodentate carboxylates containing hydrogen bonds may also fall into this category; (4) Δ(OCO) values of transition metal complexes similar to that of ionic acetates (*ca.* 165 cm^{-1}) were found to be untrustworthy as many examples of each type of coordination mode were found in this category; and (5) Δ(OCO) values of >200 cm^{-1} indicate monodentate coordination. This large difference in energy is thought to arise from the bonding of one oxygen atom to the metal with the other oxygen-free, increasing the energy of the asymmetric stretching mode. There have been many contradictions to the Δ(OCO) assignments[119-120], primarily concerned with locating the exact position of the Δ(OCO)sym absorption band, and, as such, great care is required when using these guidelines. Tentative assignments for the coordination modes of carboxylate ligands (phthalate) with Pt(II) and Pd(II), based on Δ(OCO) values, are listed in table 4.3.4.

The υ(OCO)asym mode of Pt(II) and Pd(II) complexes of phthalate is found as a very strong-to-strong band at 1633.6–1606.6 cm-1, and the corresponding υ(OCO)sym one is exhibited at 1399.3–1363.6 cm-1. As the two υ(OCO) stretching symmetrical and asymmetrical lie lower than the free ion values and the frequency difference between these two modes is 220.0–260.3 cm^{-1}, it becomes evident that the carboxylate group acts as a monodentate ligand[118-120]. Further, the presence of M–O (O = Oxygen in deprotonated phthalic acid) bonding is evident from the appearance of ν M–O modes at 510.0–537.1 cm^{-1}.

The characteristic ring vibration of the heterocyclic amines in the range 1400-1600 cm^{-1} generally show significant changes on complexation but in our present complexes these bands could not be distinguished because of overlapping with $\nu_{C=O}$ and $\nu_{C\text{-}O}$ stretching bands. The in-plane and out plane ring deformation modes of the heterocyclic amines observed at ~ 520 and ~ 720 cm^{-1} respectively undergo a positive shift in mixed ligand complexes conforming thereby a co-ordination through nitrogen. The presence of M-N bonding in the complexes are evident form the appearance of $\nu_{M\text{-}N}$ modes at 421.4 – 470.0 cm^{-1}. The infrared spectrum of amino pyridine shows ν_{NH_2} modes at ~ 3443.96 and ~ 3193.21 cm^{-1}. Both of these bands are shifted to lower frequencies in the complex-12 at ~ 3320.2 cm^{-1} & ~ 3056.0 cm^{-1} which indicate the coordination with amino nitrogen[8-14,122]. Major I.R. spectral data for the complexes are given in table 4.3.4.

Table 4.3.4: Infrared spectral data of the complexes (cm^{-1})

Com. No.	υ(OH)	υ(N-H)	υ(OCO) asym	υ(OCO) sym	Δ(OCO)	υ(M-O)	υ(M-N)
9	-	-	1653.5	1399.3	254.2	510.1	440.0
10	-	-	1606.6	1363.6	243.0	523.6	431.1
11	-	-	1659.6	1399.3	260.3	512.1	421.4
12	-	3320.2 3056.0	1633.6	1385.8	247.8	537.1	463.8
13	-	-	1610.0	1390.0	220.0	510.0	470.0

4.3.4 Electronic Spectra Studies

The spectra of the Pd(II) complex in DMSO showed three spin allowed d-d transitions and two charge transfer bands. The bands were obtained at 22203-23050, 28155-28500, 31000-31300, 34500-35005 and 40000-40200 cm^{-1} corresponding to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$,$^1A_{1g} \rightarrow {}^1B_{1g}$,$^1A_{1g} \rightarrow {}^1E_g$,$^1A_{1g} \rightarrow {}^1A_{2u}$ & $^1A_{1g} \rightarrow {}^1E_u$ respectively, which indicates square planar stereochemistry[59-60, 68-69, 71, 73]. Electronic spectral data for the Pd(II) complexes are given in table 4.3.5.

Table 4.3.5: Electronic spectral data (cm^{-1}) of square-planar palladium (II) complexes

Complex No	**Spectral band (cm^{-1}) with assignment**				
	$^1A_{1g} \rightarrow {}^1A_{2g}$	$^1A_{1g} \rightarrow {}^1B_{1g}$	$^1A_{1g} \rightarrow {}^1E_g$,	$^1A_{1g} \rightarrow {}^1A_{2u}$	$^1A_{1g} \rightarrow {}^1E_u$
9	22,203	28,155	31,115	35,005	40,155
10	23000	28500	31000	34500	40000
11	23050	28300	31000	34800	40000
12	22800	28300	31300	35000	40200

The Pt(II) complex gave three bands at 36,000, 39,650 and 41,000 cm^{-1} corresponding to the transitions $^1A_{1g} \rightarrow {}^1B_{1u}$, $^1A_{1g} \rightarrow {}^1E_u$ and $^1A_{1g} \rightarrow {}^1A_{2u}$ respectively. All of these bands are characteristic of a square-planar Pt(II) complex[59, 67, 69, 73]. Electronic spectral data for the Pt(II) complexes are given in table 4.3.6.

Table 4.3.6: Electronic spectral data (cm^{-1}) of square-planar platinum (II) complexes

Com. No*	Spectral band (cm^{-1}) with assignment		
	$^1A_{1g} \rightarrow {}^1B_{1u}$	$^1A_{1g} \rightarrow {}^1E_u$	$^1A_{1g} \rightarrow {}^1A_{2u}$
13	36,000	39,650	41,000

From the above discussion, it is evident that the synthesized Pd(II) & Pt(II) complexes are square-planar in structure and the probable structures of the complexes have been shown in figures 4.3.1-4.3.5.

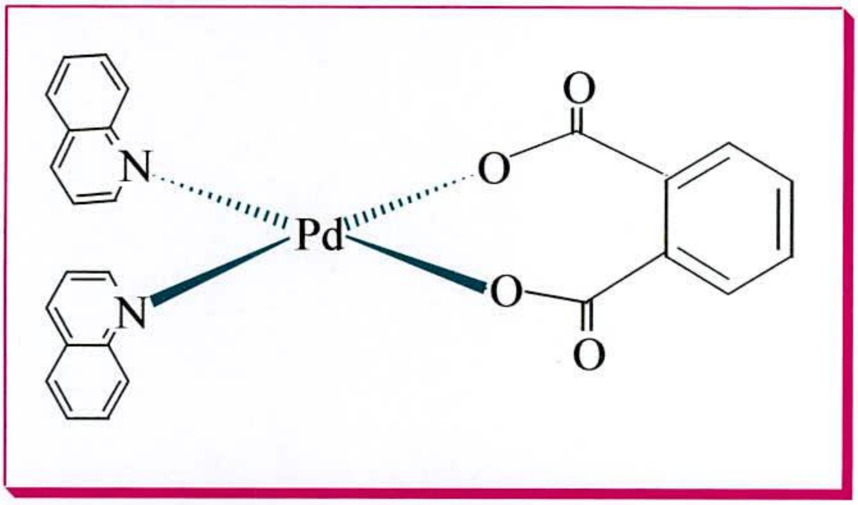


Figure 4.3.1(a): Probable structure of the complex-9, $[Pd(II)(Ph)(Q)_2]$

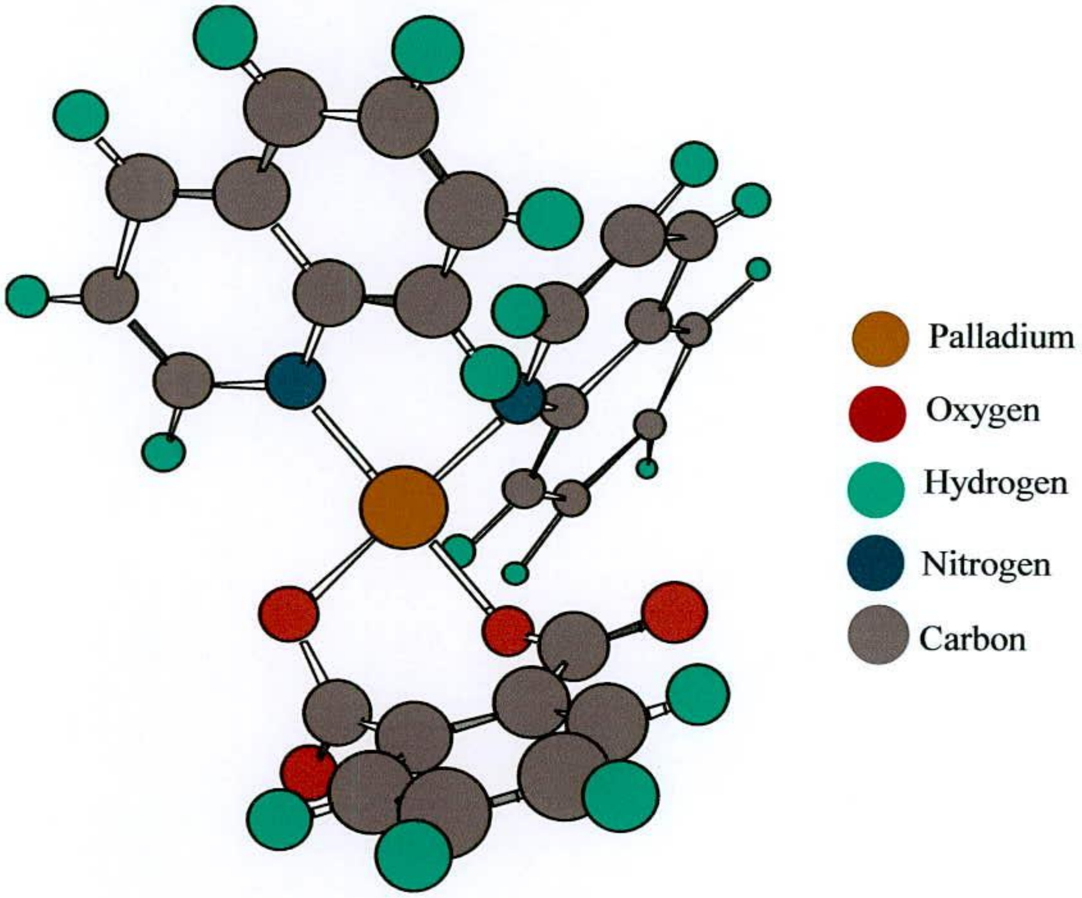


Figure 4.3.1(b): Probable ball and stick model of the complex-9, $[Pd(II)(Ph)(Q)_2]$

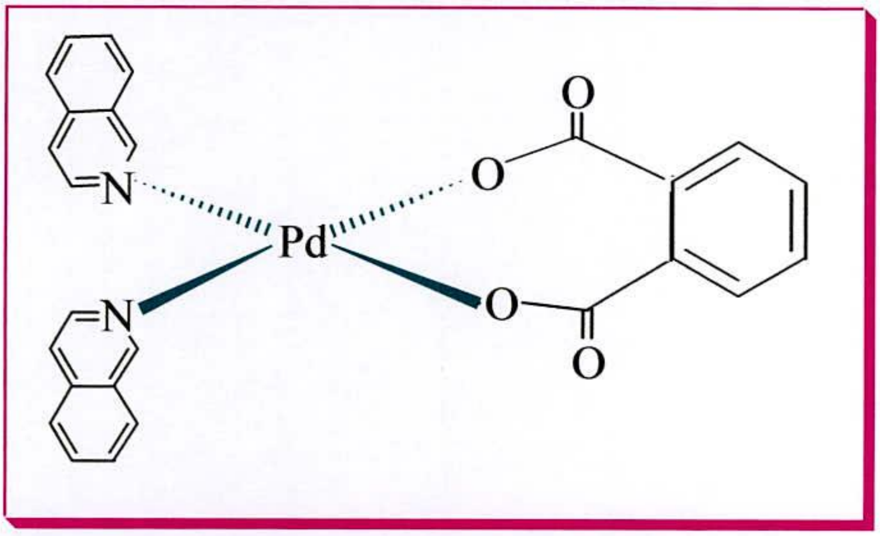


Figure 4.3.2(a): Probable structure of the complex-10, [Pd(II)(Ph)(IQ)$_2$]

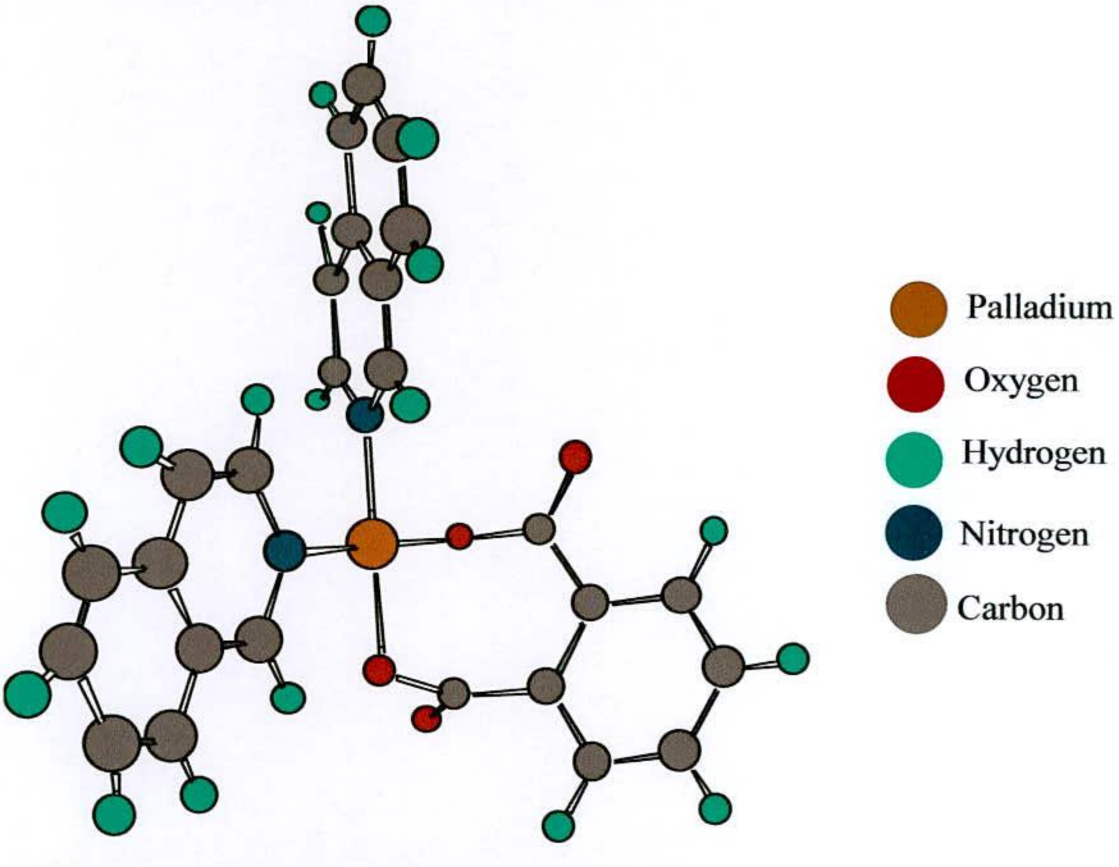


Figure 4.3.2(b): Probable ball and stick model of the complex-10, [Pd(II)(Ph)(IQ)$_2$]

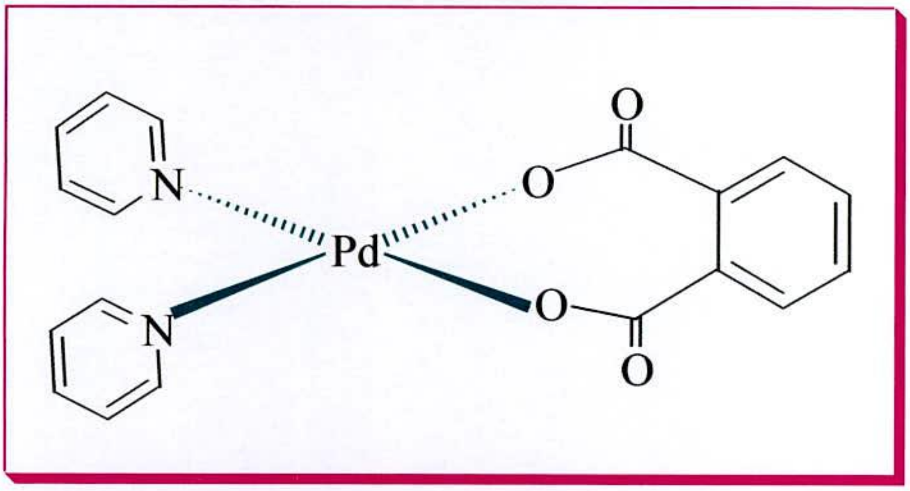


Figure 4.3.3(a): Probable structure of the complex-11, $[Pd(II)(Ph)(Py)_2]$

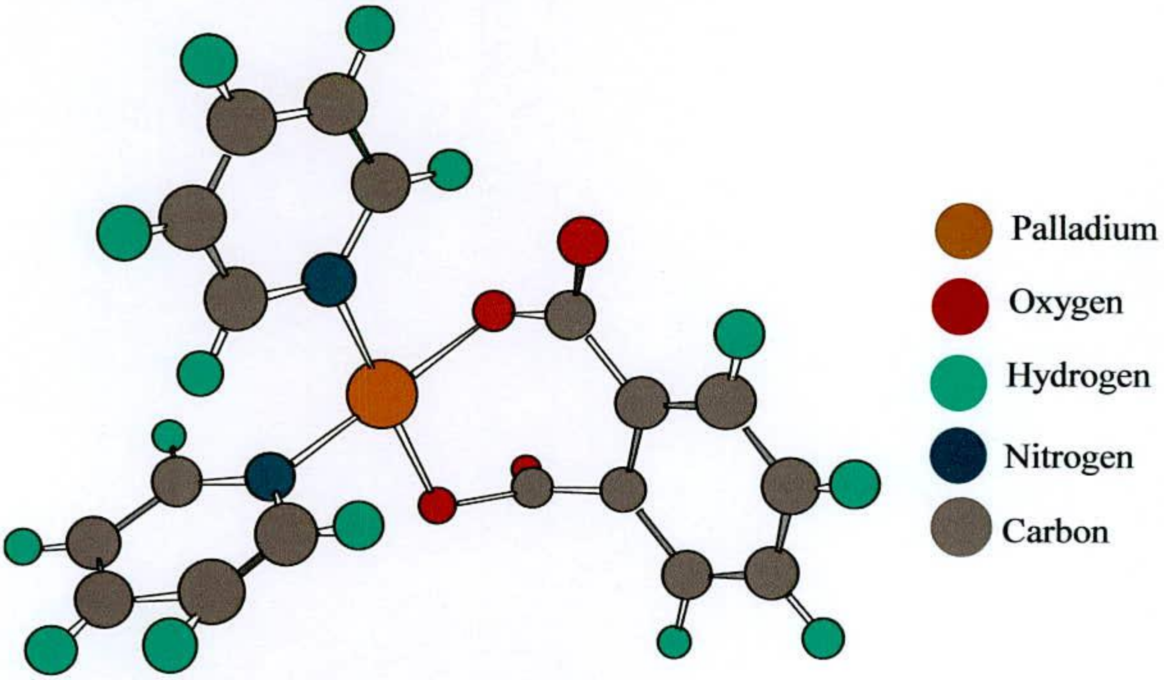


Figure 4.3.3(b): Probable ball and stick model of the complex-11, $[Pd(II)(Ph)(Py)_2]$

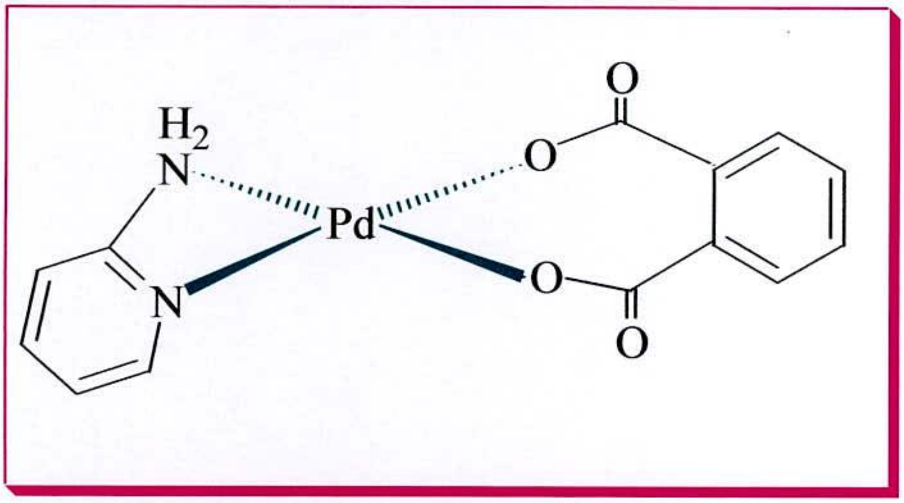


Figure 4.3.4(a): Probable structure of the complex-12, [Pd(II)(Ph)(2-apy)]

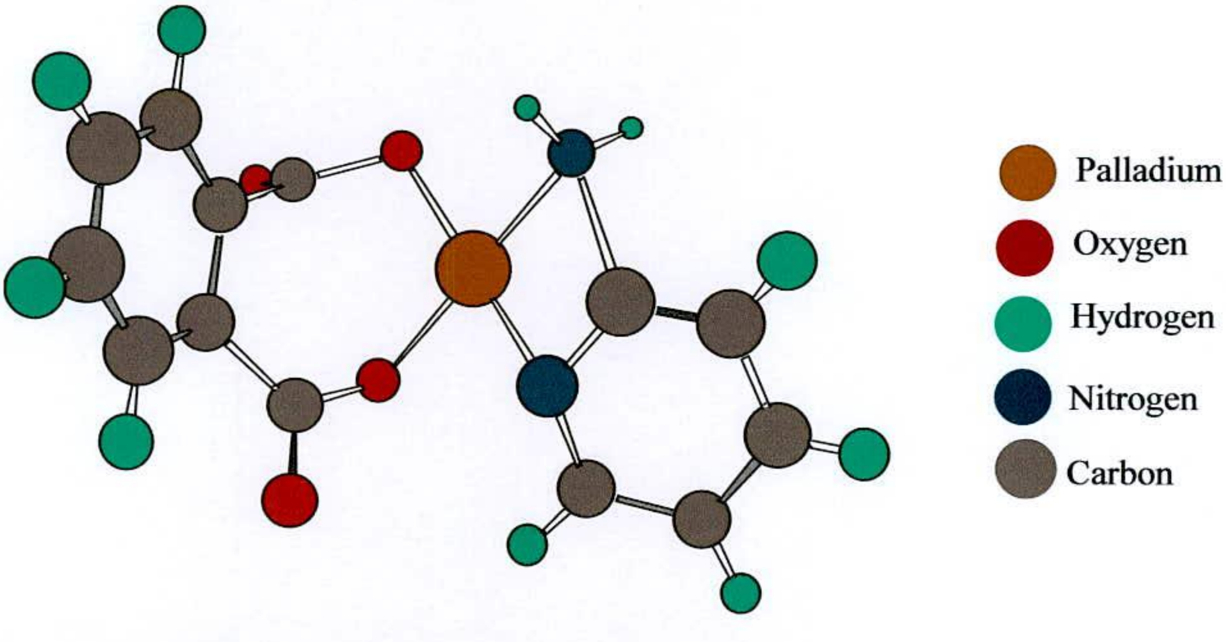


Figure 4.3.4(b): Probable ball and stick model of the complex-12, [Pd(II)(Ph)(2-apy)]

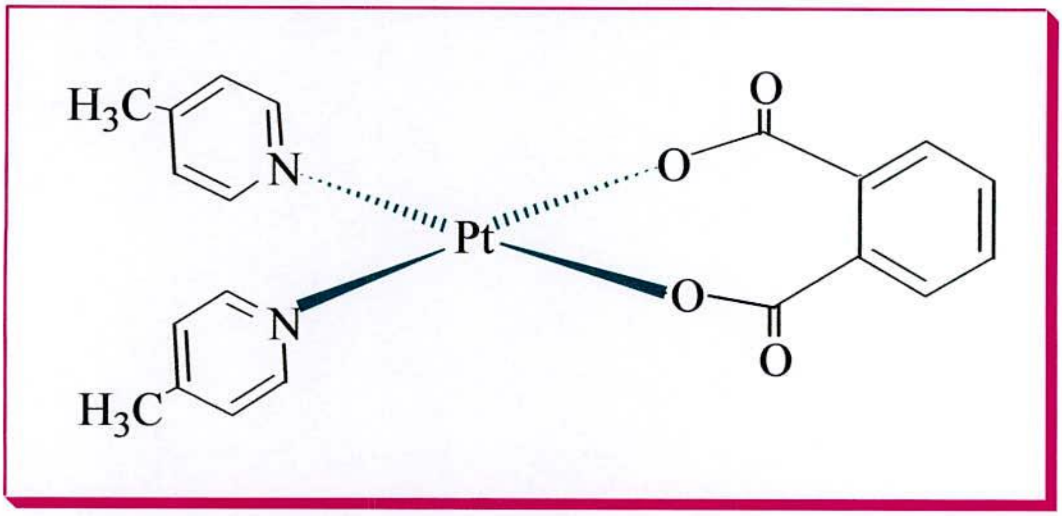


Figure 4.3.5(a): Probable structure of the complex-13, [Pt(II)(Ph)(4-pico)$_2$]

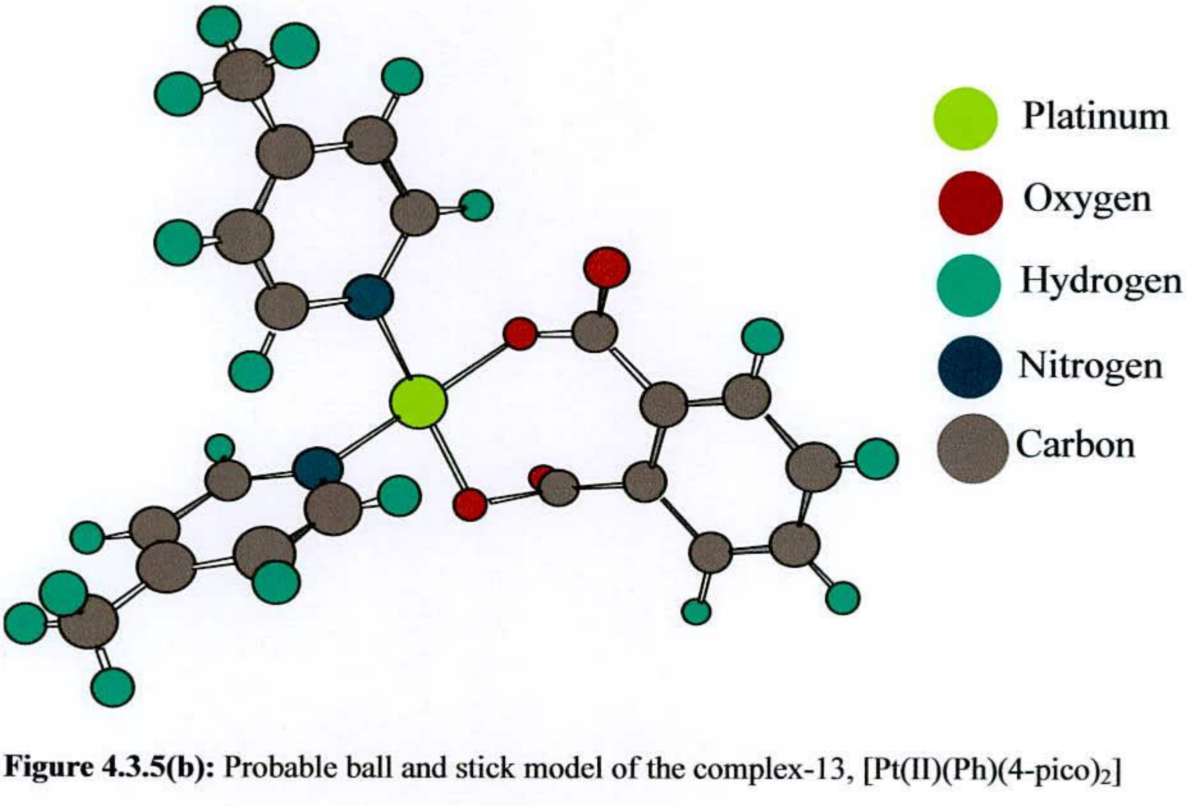


Figure 4.3.5(b): Probable ball and stick model of the complex-13, [Pt(II)(Ph)(4-pico)$_2$]

Results and Discussion 4

Characterization of Mixed Ligand Complexes of Pd (II) Ion with Oxalic Acid and Heterocyclic Amines [Complex 14-17]

Content

4.4.1 Physical Properties
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4.4.1.2 Color & Melting point
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4.4.1.4 Magnetic Moment
4.4.2 Elemental Analysis
4.4.3 Infrared Spectra Studies
4.4.4 Electronic Spectra Studies

Mixed ligand complexes of Pd(II) ion with oxalic acid (OXH_2) as primary and heterocyclic amines, *viz.* quinoline (Q), *iso*-Quinoline (IQ), Pyridine (Py) 2-aminopyridine (2-apy) as secondary ligands have been synthesized and characterized by several physico-chemical and spectroscopic analysis. Complexes of Pd(II) ion with oxalic acid (OXH_2) and heterocyclic amines were synthesized by a very simple experimental method; in ethanolic solution at room temperature as discussed in chapter III. It is revealed that the syntheses of all the complexes of Pd(II) followed the following general chemical reactions.

$$PdCl_2 + OXH_2 \rightarrow [Pd^{2+} + OX^{-} + 2H^{+} + 2Cl^{-}] \text{ (Resulting Solution)}$$

$$[Pd^{2+} + OX^{-} + 2H^{+} + 2Cl^{-}] + 2L \rightarrow [Pd(OX)L_2] + 2HCl \quad \text{[For complexes 14-16]}$$

$$[Pd^{2+} + OX^{-} + 2H^{+} + 2Cl^{-}] + L^1 \rightarrow [Pd(OX)L^1] + 2HCl \quad \text{[For complexes 17]}$$

where, OXH_2 = oxalic acid, L = monodented base, *viz* – quinoline, Q (for complex 14), *iso*-quinoline, IQ (for complex 15), pyridine, Py (For complex 16) and L^1 = bidented base, 2-aminopyridine, 2apy (For complex 17) Physico-chemical properties, elemental analysis, magnetic and spectroscopic data were used to propose probable structures, and the complexes are reported here for the first time.

4.4.1 Physical Properties

4.4.1.1 Solubility

Solubility of a compound depends on the mode of interaction between solute and solvent molecules (e.g., dipole-dipole interaction, lattice energy, lattice enthalpy, solvation energy, temperature and pressure). A compound will be soluble only when the lattice enthalpy is lower than the solvation energy. The solubility of the complexes was examined in the usual manner. The complexes were all slightly soluble in water and methanol but are soluble in DMF and DMSO (table 4.4.1).

Table 4.4.1: Solubility of the synthesized complexes

Complex No.	**Complexes**	**Water**		**Methanol**		**DMF**		**DMSO**	
		Cold	**Hot**	**Cold**	**Hot**	**Cold**	**Hot**	**Cold**	**Hot**
14	[Pd(II)(OX)(Q)$_2$]	+/-	+/-	+/-	+/-	+	+	+	+
15	[Pd(II)(OX)(IQ)$_2$]	+/-	+/-	+/-	+/-	+	+	+	+
16	[Pd(II)(OX)(Py)$_2$]	+/-	+/-	+/-	+/-	+	+	+	+
17	[Pd(II)(OX)(2-apy)]	+/-	+/-	+/-	+/-	+	+	+	+

Here, +/- = Slightly soluble and + = Soluble

4.4.1.2 Color & Melting point

All the synthesized complexes (complex 14-17) are colored amorphous powder. Single crystal of the complexes could not be isolated from any solution. Complexes 14 , Pd(II) with (oxalic acid + quinoline) is yellow in colored , Complexes 15 , Pd(II) with (oxalic acid + *iso*-quinoline) is apricot in colored and Complexes 16 and 17 *i.e.*, Pd(II) with (oxalic acid + pyridine) and (oxalic acid + 2-aminopyridine) are yellow-orange in colored (shown in table 4.4.2). Melting point of complex-14, Pd(II)(OX)(Q)$_2$is 270± 5°C while the melting point of the ligands, oxalic acid is 102-103°C and quinoline is -15°C which indicates the strong indication of coordination of the ligands and formation of the complex. Similarly for the melting point of complex-15 is 255± 5°C while that for *iso*-quinoline is 26-28°C melting point of complex-16 is 265± 5°C while that for pyridine is -41.8°C and melting point of complex-17 is 250±5°C while that for 2-aminopyridine is 59-60°C also indicate the formation of the complexes. Data for the melting points of the complexes has been tabulated in table 4.4.2.

4.4.1.3 Conductivity Measurement

The molar conductance were measured in *N,N′*-dimethyl formamide. The conductance values of the Pd(II) complexes were in the range (10.65 – 12.40) Ω^{-1} cm^2 mole^{-1} indicated that these complexes were non-electrolyte in nature[11,14]. The conductance values are given in table 4.4.2.

4.4.1.4 Magnetic Moment Measurement

The magnetic moment values of the synthesized complexes indicated that these complexes are diamagnetic (table 4.4.2). This diamagnetism is supported by the small negative values obtained for their magnetic susceptibility. The observed magnetic moment indicate that these complexes are square planar[60, 67, 73, 121] with dsp^2 hybridization. The following schematic diagram represents the hybridization in the complexes(14-17).

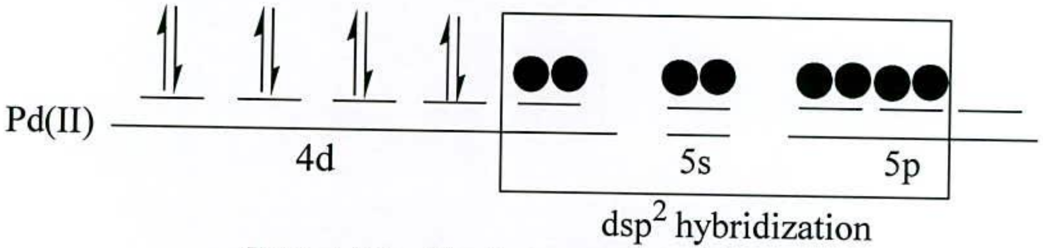


Table 4.4.2: Physical properties of the complexes

Complexes No.	Complexes	Color	Melting point or decomposition temperature (± 5°C)	Molar conductance (ohm^{-1} cm^2 mol^{-1})	magnetic moment
14	$[Pd(II)(OX)(Q)_2]$	Yellow	270	10.75	Dia
15	$[Pd(II)(OX)(IQ)_2]$	Apricot	255	12.40	Dia
16	$[Pd(II)(OX)(Py)_2]$	Yellow Green	265	11.35	Dia
17	[Pd(II)(OX)(2-apy)]	Yellow Green	250	10.65	Dia

where, Dia = Diamagnetic, OX = Deprotonated oxalic acid, Q =quinoline , IQ = *iso*-quinoline, Py=pyridine, 2-apy=2-amino pyridine.

4.4.2 Elemental Analysis

Elemental analysis is the prime tool for the formulation of a new chemical species. The formulations of the synthesized complexes were done on the basis of elemental analysis. Elemental analyses of the synthesized mixed ligand complexes were performed for Palladium, carbon, hydrogen and nitrogen. The microanalysis of carbon, hydrogen and nitrogen were carried out by an organic elemental analyzer. Palladium was determined by weighing as the oxide produced by direct ignition. The elemental analyses data of the complexes are given in table 4.4.3. It is seen that the analytical data are in good agreement with the proposed empirical formula of the present complexes.

Table 4.4.3: Elemental analyses of the complexes

Com. No.	Yields %	Metal %		Carbon %		Hydrogen %		Nitrogen %	
		Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
14	61	23.51	23.45	53.05	52.89	3.12	3.21	6.19	6.18
15	65	23.51	23.41	53.05	52.92	3.12	3.18	6.19	6.13
16	70	30.18	30.02	40.87	40.95	2.86	2.93	7.95	7.85
17	65	36.88	36.75	29.13	29.00	2.10	2.21	9.71	9.65

4.4.3 Infrared Spectra Studies

The position of the strong C=O absorption band in the carboxylic acid group of the free carboxylic acid of oxalic acid, 1692.6 and 1441.8 cm^{-1}. Upon chelating to center metal ions, this υ(C=O) band shifted or disappears and two new bands relating to the asymmetric [υ(OCO)asym] and symmetric [υ(OCO)sym] stretches appear in the regions 1610.5–1575.7 and 1389.6-1379.1 cm^{-1} respectively[117-118] . The magnitude of the separation between these two bands [Δ(OCO) cm^{-1}] has been used, tentatively, as a help in the determination of the nature of the carboxylate coordination[118].

$$\Delta(OCO)= [\upsilon(OCO)asym- \upsilon(OCO)sym]\ cm^{-1}$$

Characterization of the coordination mode of carboxylate based on the IR spectrum of the metal complex has been discussed previously by Deacon and Philips[119]. Coordination modes were classified as (1) Ionic acetates (*e.g.* those of alkali metals) having Δ(OCO) values of *ca.* 165 cm^{-1} (for ionic trifluoroacetates, the Δ(OCO) value was *ca.* 235 cm^{-1}); (2) Δ(OCO) values <105 cm^{-1} indicating symmetric chelating carboxylate coordination; complexes in which the carboxylates bridge metal–metal bonds may also exhibit values in this region; (3) Δ(OCO) values substantially less than the ionic values (<150 cm^{-1}) indicating the presence of chelating or bridging carboxylates; monodentate carboxylates containing hydrogen bonds may also fall into this category; (4) Δ(OCO) values of transition metal complexes similar to that of ionic acetates (*ca.* 165 cm^{-1}) were found to be untrustworthy as many examples of each type of coordination mode were found in this category; and (5) Δ(OCO) values of >200 cm^{-1} indicate monodentate coordination. This large difference in energy is thought to arise from the bonding of one oxygen atom to the metal with the other oxygen-free, increasing the energy of the asymmetric stretching mode. There have been many contradictions to the Δ(OCO) assignments[119-120], primarily concerned with locating the exact position of the Δ(OCO)sym absorption band, and, as such, great care is required when using these guidelines. Tentative assignments for the coordination modes of carboxylate ligands (oxalate) with Pd(II) based on Δ(OCO) values, are listed in table 4.4.4.

The υ(OCO)asym mode of Pd(II) complexes of oxalate is found as a very strong-to-strong band at 1610.5–1575.7 cm^{-1}, and the corresponding υ(OCO)sym one is exhibited at 1389.6-1379.1 cm^{-1}. As the two υ(OCO) stretching symmetrical and asymmetrical lie lower than the free ion values and the frequency difference between these two modes is 197.7–231.4 cm^{-1} it becomes evident that the carboxylate group acts as a monodentate ligand[117-119]. Further, the presence of M–O (O = Oxygen in deprotonated oxalic acid) bonding is evident from the appearance of ν M–O modes at 500.5−520.0 cm^{-1}.

The characteristic ring vibration of the heterocyclic amines in the range 1400-1600 cm^{-1} generally show significant changes on complexation but in our present complexes these bands could not be distinguished because of overlapping with $\nu_{C=O}$ and ν_{C-O} stretching bands. The in-plane and out plane ring deformation modes of the heterocyclic amines observed at ~ 520 and ~ 720 cm^{-1} respectively undergo a positive shift in mixed ligand complexes conforming thereby a co-ordination through nitrogen. The presence of M-N bonding in the complexes are evident form the appearance of ν_{M-N} modes at 455.0 – 469.6 cm^{-1}. The infrared spectrum of amino pyridine shows ν_{NH_2} modes at ~ 3443.96 and ~ 3193.21 cm^{-1}. Both of these bands are shifted to lower frequencies in the complex-17 at ~3345.3 cm^{-1} & ~3061.8 cm^{-1} which indicate the coordination with amino nitrogen[8-14, 122].Major I.R. spectral data for the complexes are given in table 4.4.4

Table 4.4.4: Infrared spectral data of the complexes (cm^{-1}).

Com. No.	υ(OH)	υ(N-H)	υ(OCO) asym	υ(OCO) sym	Δ(OCO)	υ(M-O)	υ(M-N)
14	-	-	1610.5	1379.1	231.4	510.0	460.0
15	-	-	1610.0	1379.1	230.9	500.5	455.0
16	-	-	1575.7	1378.0	197.7	520.0	469.6
17	-	3345.3 3061.8	1599.8	1389.6	210.2	513.0	463.8

4.4.4 Electronic Spectra Studies

The spectra of the Pd(II) complex in DMSO showed three spin allowed d-d transitions and two charge transfer bands. The bands were obtained at 22220-23055, 28155-28500, 31000-31350, 34500-35000 and 40050-40205 cm^{-1} corresponding to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$,$^1A_{1g} \rightarrow {}^1B_{1g}$,$^1A_{1g} \rightarrow {}^1E_g$,$^1A_{1g} \rightarrow {}^1A_{2u}$ & $^1A_{1g} \rightarrow {}^1E_u$ respectively, which indicates square planar stereochemistry[59-60, 68-69, 71, 73]. Electronic spectral data for the complexes are given in table 4.4.5

Table 4.4.5: Electronic spectral data (cm^{-1}) of square-planar palladium (II) complexes

Complexes No	**Spectral band (cm^{-1}) with assignment**				
	$^1A_{1g} \rightarrow {}^1A_{2g}$	$^1A_{1g} \rightarrow {}^1B_{1g}$	$^1A_{1g} \rightarrow {}^1E_g$,	$^1A_{1g} \rightarrow {}^1A_{2u}$	$^1A_{1g} \rightarrow {}^1E_u$
14	22220	28500	31115	35000	40165
15	23040	28,155	31050	34505	40050
16	23055	28350	31000	34850	40100
17	22750	28400	31350	35000	40205

From the above discussion, it is evident that the Synthesized Pd(II) complexes are square planer in structure and the probable structures of the complexes have been shown in figures 4.4.1-4.4.4.

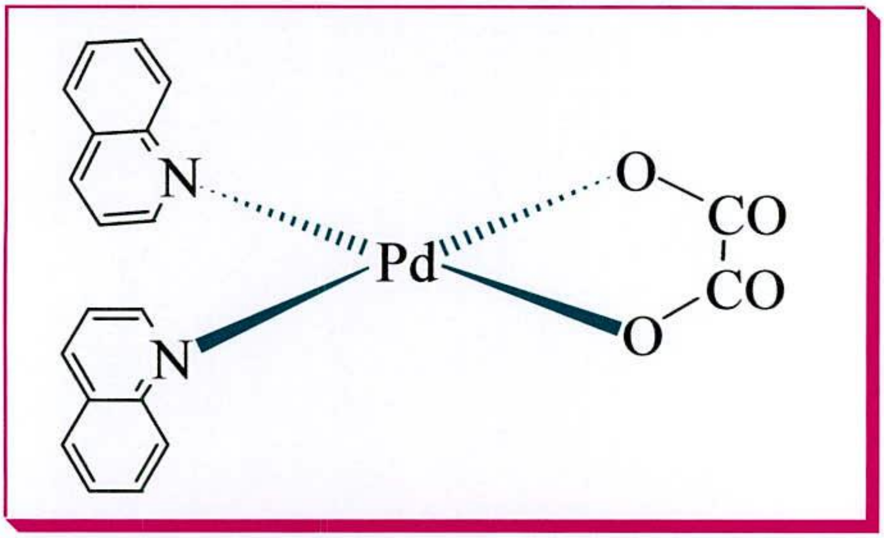


Figure 4.4.1(a): Probable structure of the complex-14, $[Pd(II)(OX)(Q)_2]$

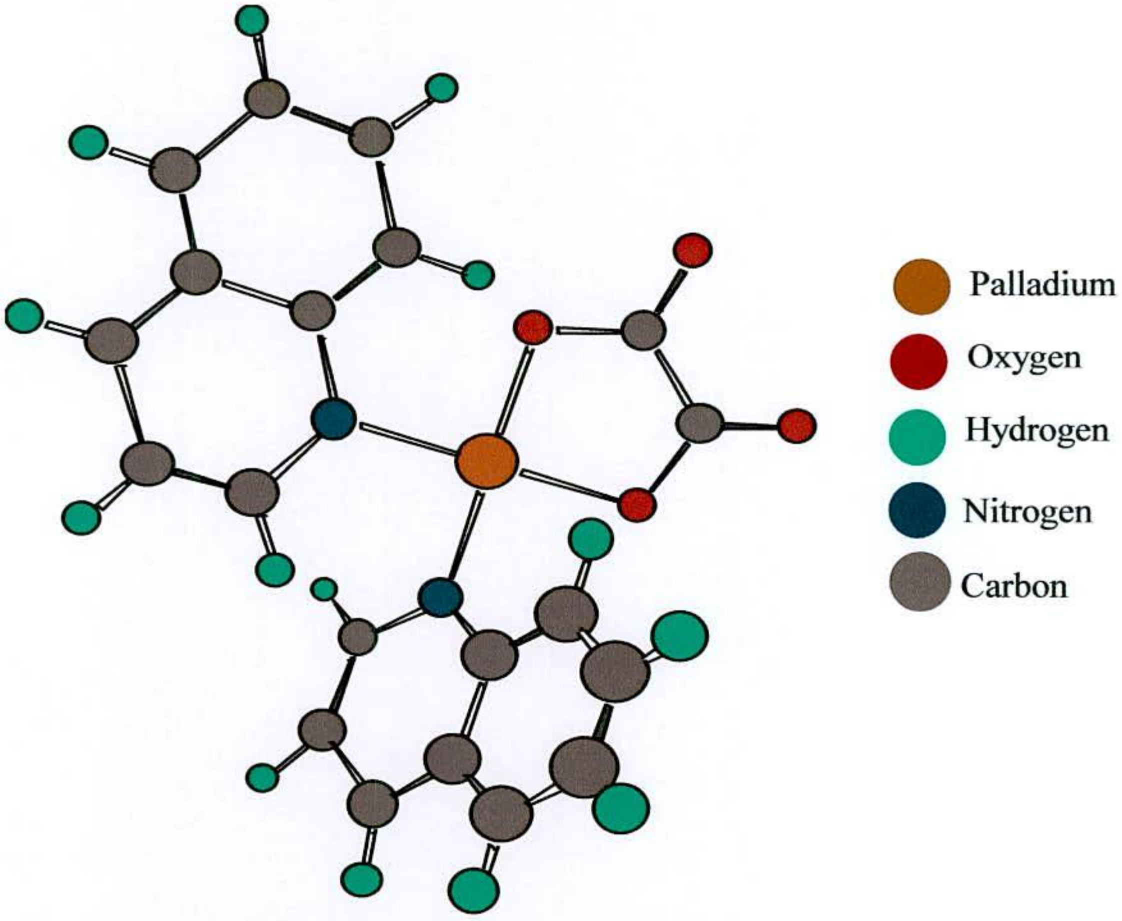


Figure 4.4.1(b): Probable ball and stick model of the complex-14, $[Pd(II)(OX)(Q)_2]$

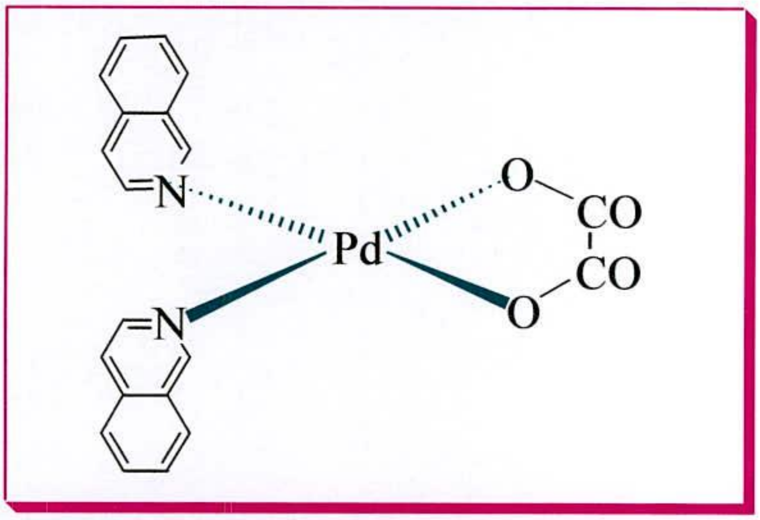


Figure 4.4.2(a): Probable structure of the complex-15, $[Pd(II)(OX)(IQ)_2]$

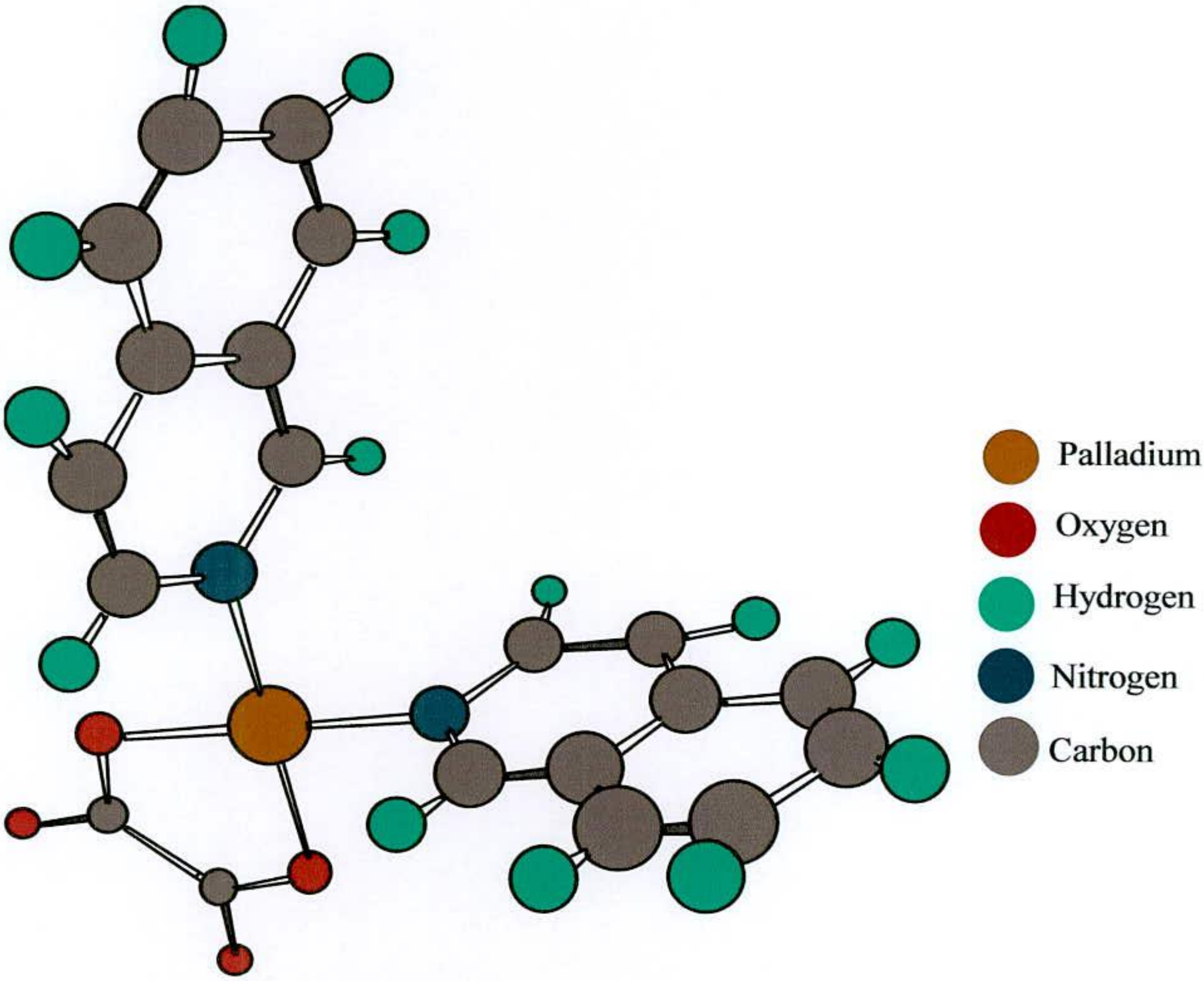


Figure 4.4.2(b): Probable ball and stick model of the complex-15, $[Pd(II)(OX)(IQ)_2]$

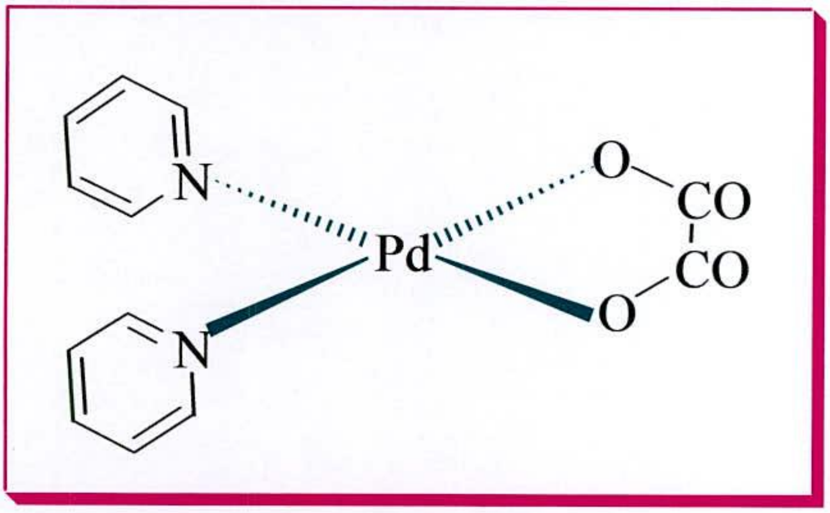


Figure 4.4.3(a): Probable structure of the complex-16, [Pd(II)(OX)(Py)$_2$]

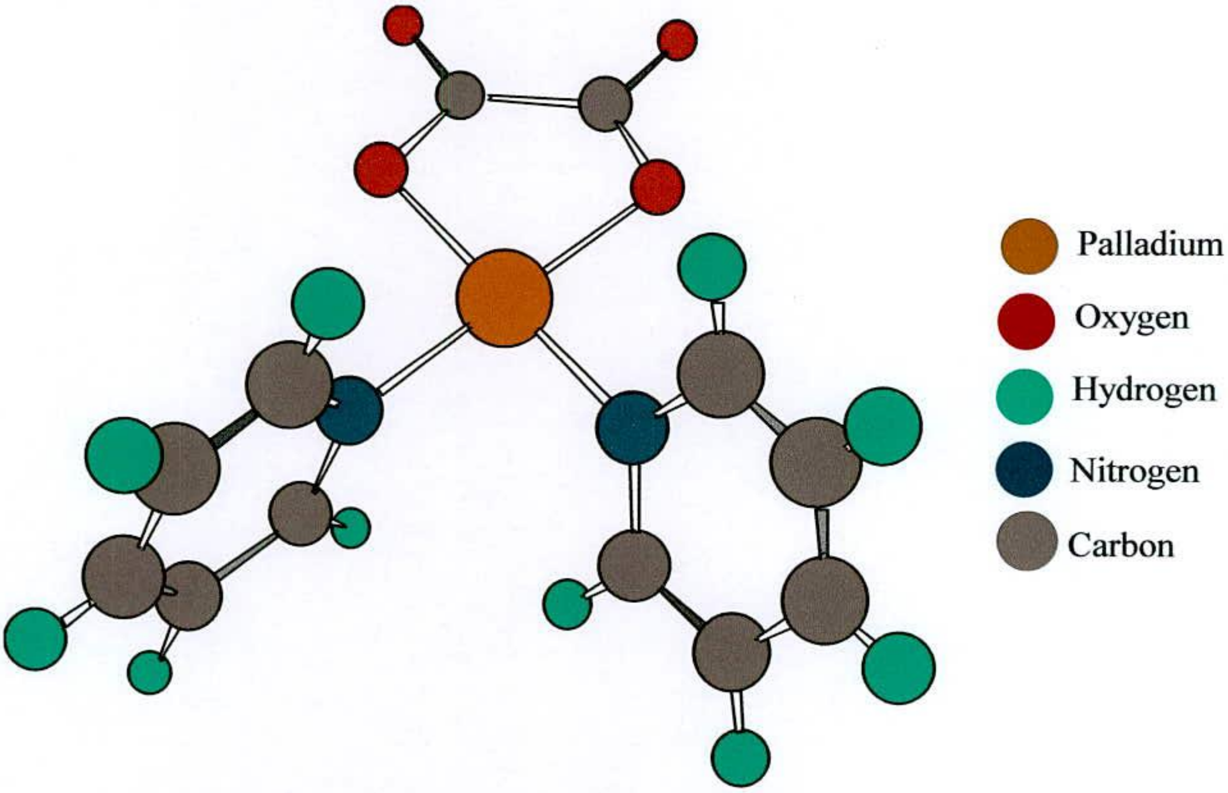


Figure 4.4.3(b): Probable ball and stick model of the complex-16, [Pd(II)(OX)(Py)$_2$]

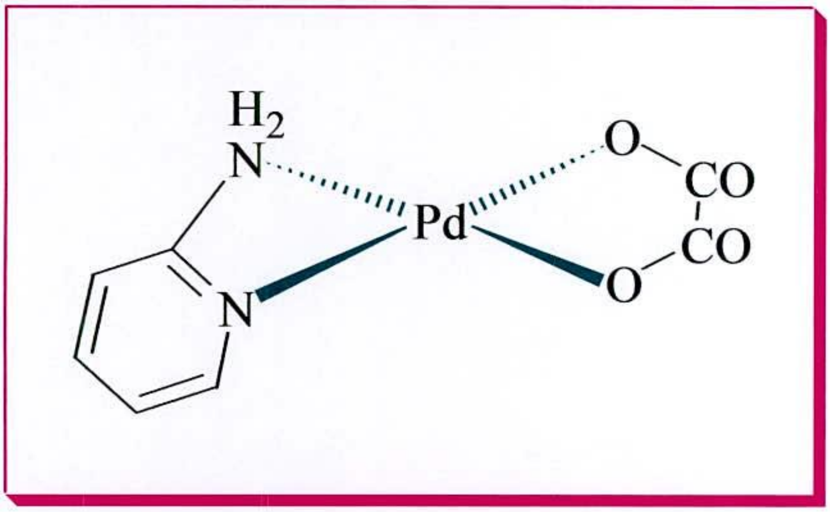


Figure 4.4.4(a): Probable structure of the complex-17, [Pd(II)(OX)(2-apy)]

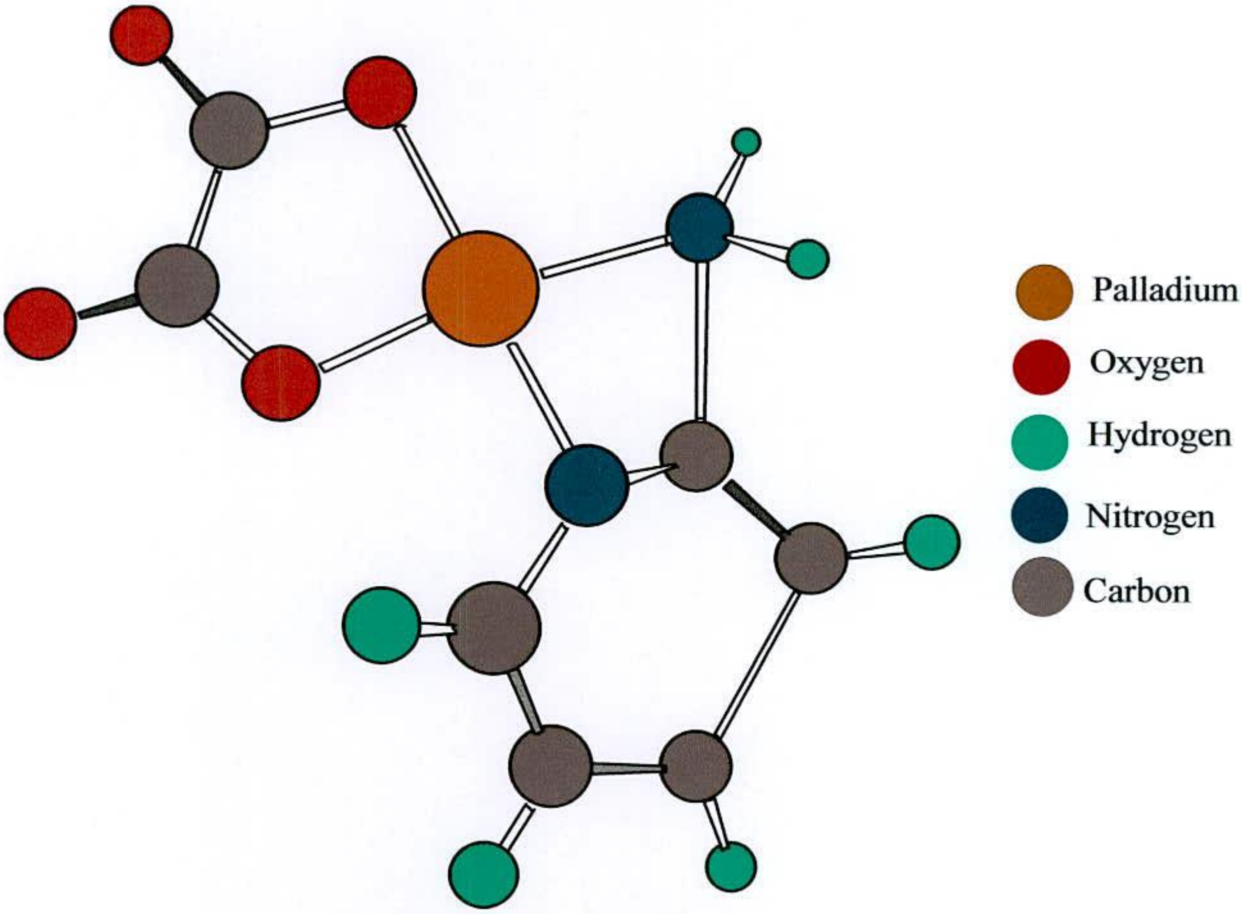


Figure 4.4.4(b): Probable ball and stick model of the complex-17, [Pd(II)(OX)(2-apy)]

Results and Discussion 5

Antibacterial Activity of The Mixed Ligand Pt(II), Pt(IV) & Pd(II) Complexes(1-17)

4.5.1 Antibacterial Screening

The present chapter describes the antibacterial activity of mixed ligand complexes of Pt(II), Pt(IV), & Pd(II) ions with some dibasic acids (malonic acid, oxalic acid & phthalic acid) as primary and heterocyclic amines, viz. quinoline (Q), *iso*-quinoline (IQ), pyridine (Py), 2-aminopyridine (2-apy), 4-pico(4-picoline) as secondary ligands. Disc diffusion method was employed for the antibacterial studies and the detail method was discussed in chapter III.

4.5.1 Antibacterial Screening

Biological studies were observed in the antibacterial activities of the targeted compounds against Gram-positive (*Listeria monocytogenes*, *Staphylococcus aureus*, *Enterococcus faecalis)* and Gram-negative (*Pseudomonas aeruginosa*, *Salmonella bovismorbificans*, *Salmonella typhi*, *Escherichia coli)*. Result from the agar disc diffusion tests for antibacterial activities of target compounds are presented in tables 4.5.1-4.5.4, and illustrated in figures 4.5.5-4.5.10 respectively. The diameters of zone of inhibition (in mm) of the standard drug kanamycin against bacteria *Pseudomonas aeruginosa* (Gram-negative), *Salmonella bovismorbificans* (Gram-negative), *Salmonella typhi* (Gram-negative), *Escherichia coli* (Gram-negative), *Listeria monocytogenes* (Gram-positive), *Staphylococcus aureus* (Gram-positive), *Enterococcus faecalis* (Gram-positive) were found to be 22, 22, 20, 20, 25, 23, and 21 mm respectively & the graphical comparision of zone of inhibition of the complexes with standard against the microorganisms are shown in figures 4.5.1-4.5.4. Under identical conditions table 4.5.1 shows that complex 1 has 20, 15, 20, 30, 31,08 and 25 mm, complex 2 has 25, 18, 19, 32, 25, 0 and 28 mm, complex 3 has 38, 25, 21, 45, 29, 28 and 45 mm, complex 4 has 45, 28, 25, 48, 40, 21 and 40 mm, table 4.5.2 shows that complex 5 has 20, 24, 32, 24, 32, 23 and 25 mm, complex 6 has 20, 31, 30, 30, 11, 34 and 22 mm, complex 7 has 25, 25, 0, 32, 14, 22 and 24 mm, complex 8 has 40, 32, 22, 38, 42, 32 and 18 mm, table 4.5.3 shows that complex 9 has 18, 23, 28, 12, 24, 30 and 31 mm, complex 10 has 19, 23, 26, 28, 22, 17 and 21 mm, complex 11 has 12, 0, 21, 23, 26, 18 and 10 mm, complex 12 has 38, 25, 21, 30, 21, 34 and 21 mm, complex 13 has 32, 33, 33, 40, 41, 42 and 27 mm, table 4.5.4 shows that complex 14 has 11, 18, 16, 23, 31, 23 and 15 mm, complex 15 has 23, 16, 17, 19, 26, 22 and 21 mm, complex 16 has 21, 22, 25, 16, 19, 32 and 25 mm, complex 17 has 34, 42, 26, 28, 38, 35 and 41 mm, against *Pseudomonas aeruginosa, Salmonella bovismorbificans*, *Salmonella typhi*, *Escherichia coli*, *Listeria monocytogenes*, *Staphylococcus aureus*, *Enterococcus faecalis* respectively. The complexes containing 2-aminopyridine and 4-picoline as secondary ligands are much more microbial active than the other complexes. Moreover, the complexes $[Pt(MA)_2(4\text{-pico})_2]$ showed the highest antibacterial activity against all bacteria tested. The complexes 1, 6 and 11 showed the lowest inhibition zones against *Staphylococcus aureus, Salmonella typhi & Enterococcus faecalis* corresponding to zone sizes of 8 and 10 mm respectively. The complexes 2, 7 and 11 no zone inhibition against *Staphylococcus aureus, Salmonella typhi and Salmonella bovismorbificans* was found. Among the tested complexes, all were shown more or less antibacterial activities against the treated bacteria. The highest and the lowest antibacterial activities were found in complex 4 and complex 11 respectively against all the treated bacteria.

It may be concluded that from the data most of the complexes were found to be efficient antibacterial agent.

Table 4.5.1: Antibacterial activity of the complexes (1-4)

Bacteria code	Name of the bacteria	Diameter of inhibition zone of bacteria in different complexes (mm)				
		1	**2**	**3**	**4**	**Kanamycin 30μg/disc**
A	*Pseudomonas aeruginosa* (-ve)	20	25	38	45	22
B	*Salmonella bovismorbificans*(-ve)	15	18	25	28	22
C	*Salmonella typhi* (-ve)	20	19	21	25	20
D	*Escherichia coli* (-ve)	30	32	45	48	20
E	*Listeria monocytogenes*(+ve)	31	25	29	40	25
F	*Staphylococcus aureus* (+ve)	08	0	28	21	23
G	*Enterococcus faecalis*(+ve)	25	28	45	40	21

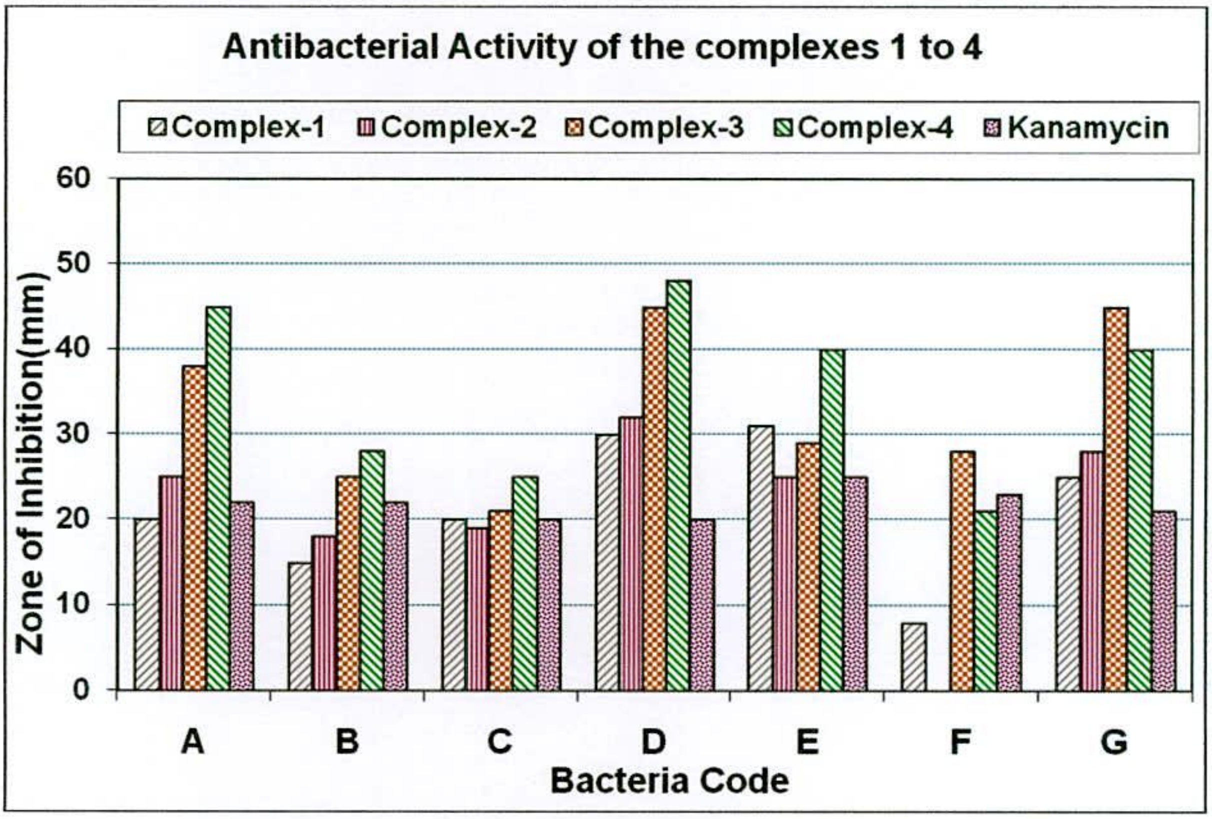


Figure 4.5.1: Graphical comparision of zone of inhibition of the complexes 1-4 with standard (Kanamycin)

Table 4.5.2: Antibacterial activity of the complexes (5-8)

Bacteria code	Name of the bacteria	Diameter of inhibition zone of bacteria in different complexes (mm)				
		5	**6**	**7**	**8**	**Kanamycin 30µg/disc**
A	*Pseudomonas aeruginosa* (-ve)	20	20	25	40	22
B	*Salmonella bovismorbificans*(-ve)	24	31	25	32	22
C	*Salmonella typhi* (-ve)	32	30	0	22	20
D	*Escherichia coli* (-ve)	24	30	32	38	20
E	*Listeria monocytogenes*(+ve)	32	11	14	42	25
F	*Staphylococcus aureus* (+ve)	23	34	22	32	23
G	*Enterococcus faecalis*(+ve)	21	22	24	18	21

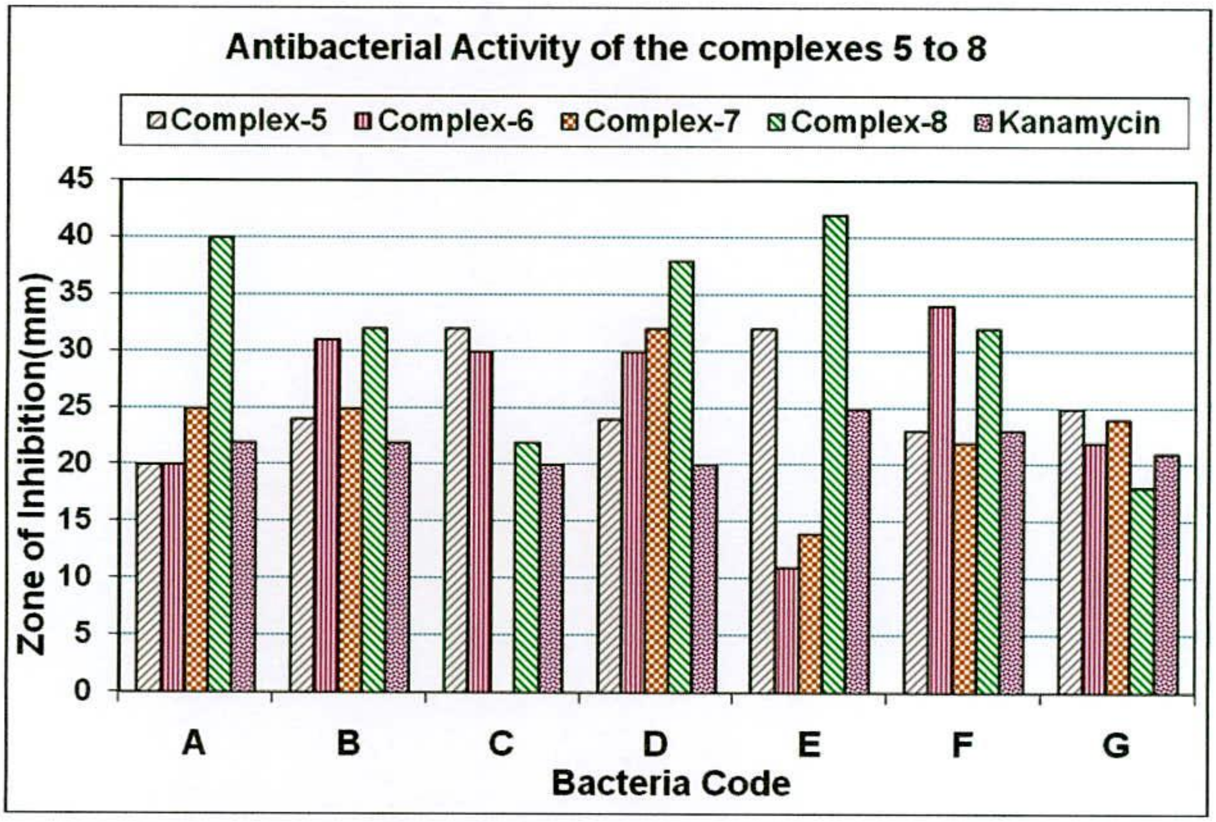


Figure 4.5.2: Graphical comparision of zone of inhibition of the complexes 5-8 with standard (Kanamycin)

Table 4.5.3: Antibacterial activity of the complexes (9-13)

Bacteria code	Name of the bacteria	Diameter of inhibition zone of bacteria in different complexes (mm)					
		9	**10**	**11**	**12**	**13**	**Kanamycin 30μg/disc**
A	*Pseudomonas aeruginosa* (-ve)	18	19	12	38	32	22
B	*Salmonella bovismorbificans*(-ve)	23	23	0	25	33	22
C	*Salmonella typhi* (-ve)	28	26	21	21	33	20
D	*Escherichia coli* (-ve)	12	28	23	30	40	20
E	*Listeria monocytogenes*(+ve)	24	22	26	21	41	25
F	*Staphylococcus aureus* (+ve)	30	17	18	34	12	23
G	*Enterococcus faecalis*(+ve)	31	21	10	12	27	21

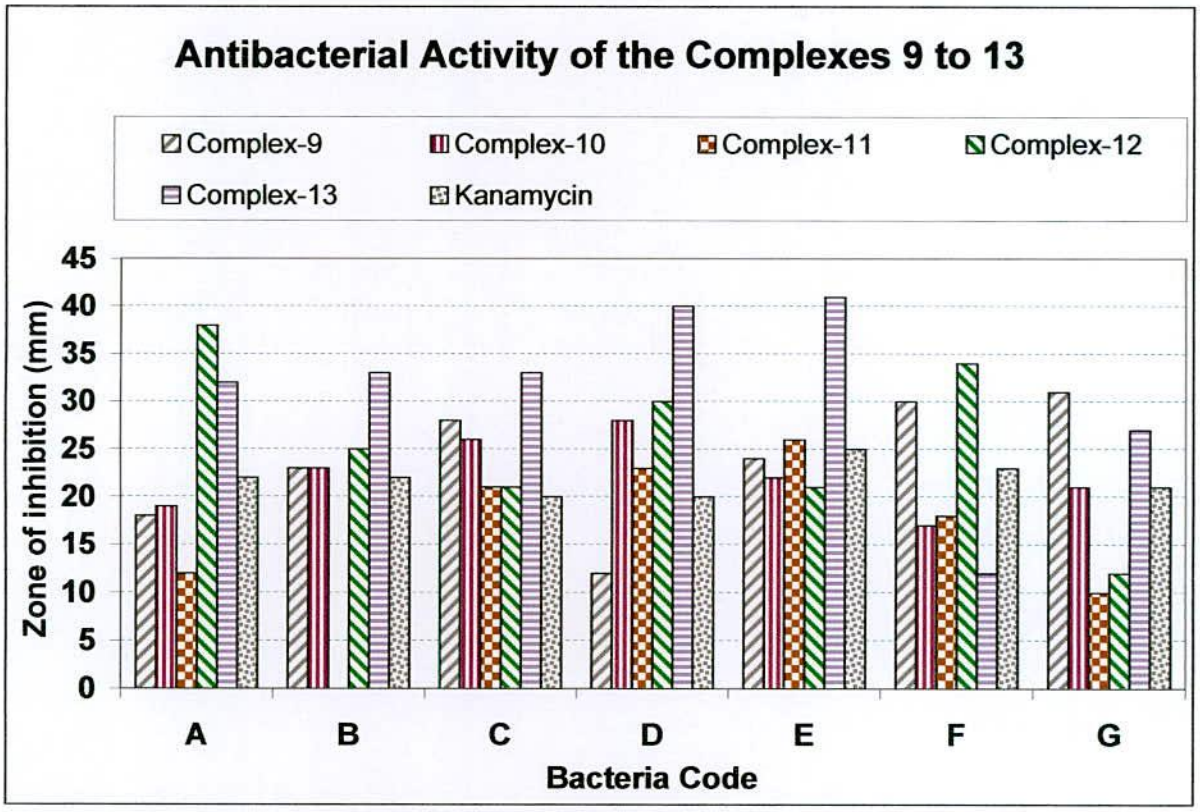


Figure 4.5.3: Graphical comparision of zone of inhibition of the complexes 9-13 with standard (Kanamycin)

Table 4.5.4: Antibacterial activity of the complexes (14-17)

Bacteria code	Name of the bacteria	Diameter of inhibition zone of bacteria in different complexes (mm)				
		14	**15**	**16**	**17**	**Kanamycin 30μg/disc**
A	*Pseudomonas aeruginosa* (-ve)	11	23	21	34	22
B	*Salmonella bovismorbificans*(-ve)	18	16	22	42	22
C	*Salmonella typhi* (-ve)	16	17	25	26	20
D	*Escherichia coli* (-ve)	23	19	16	28	20
E	*Listeria monocytogenes*(+ve)	31	26	19	38	25
F	*Staphylococcus aureus* (+ve)	23	22	32	25	23
G	*Enterococcus faecalis*(+ve)	15	21	25	41	21

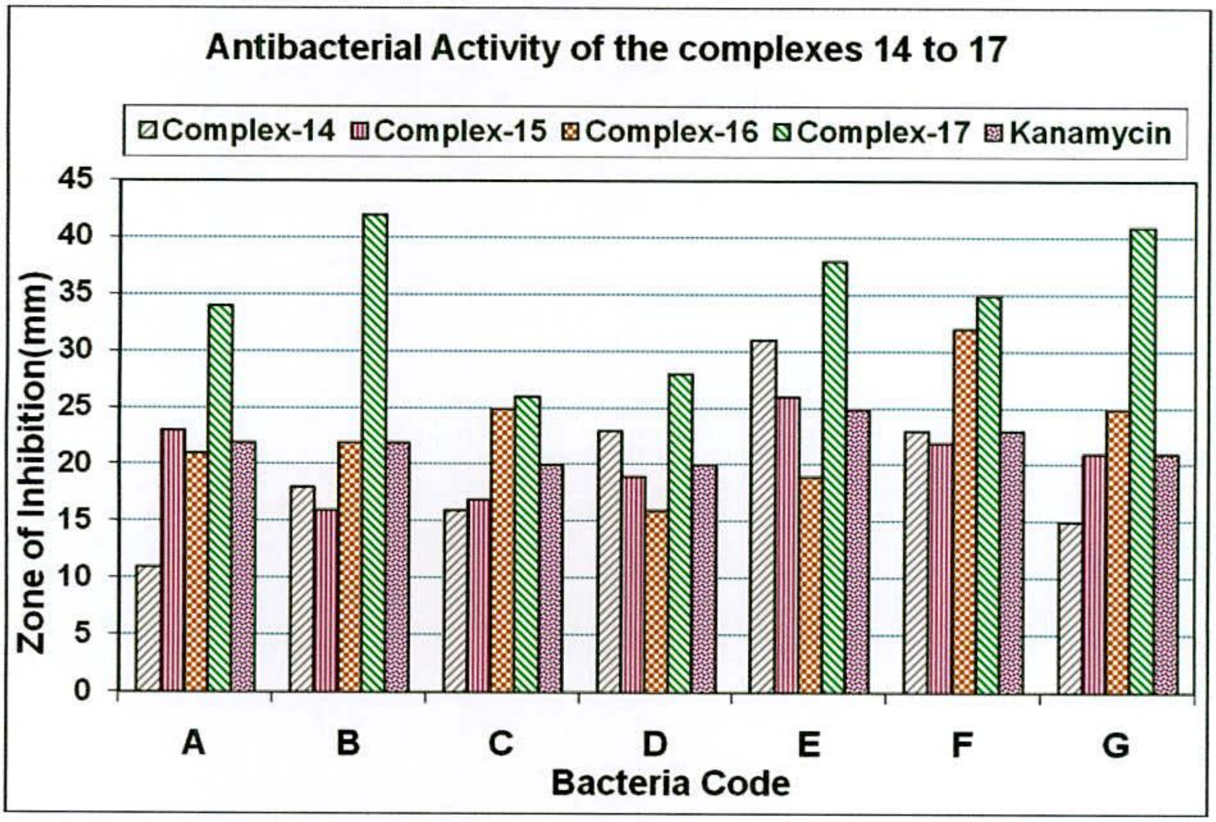


Figure 4.5.4: Graphical comparision of zone of inhibition of the complexes 14-17 with standard (Kanamycin)

Figure-4.5.5: Photographic representation of zone of inhibition of complexes **1** and **2** respectively against the bacteria *Listeria monocytogenes.*

Figure- 4.5.6: Photographic representation of zone of inhibition of complexes **5** and **6** respectively against the bacteria *Escherichia coli.*

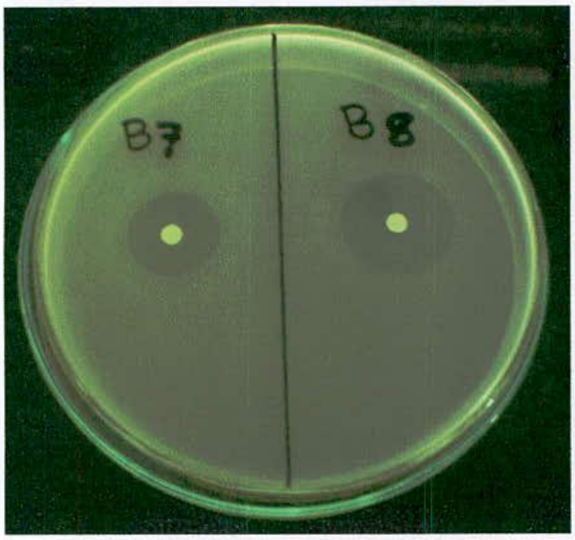


Figure- 4.5.7: Photographic representation of zone of inhibition of complexes **7** and **8** respectively against the bacteria *Salmonella bovismorbificans.*

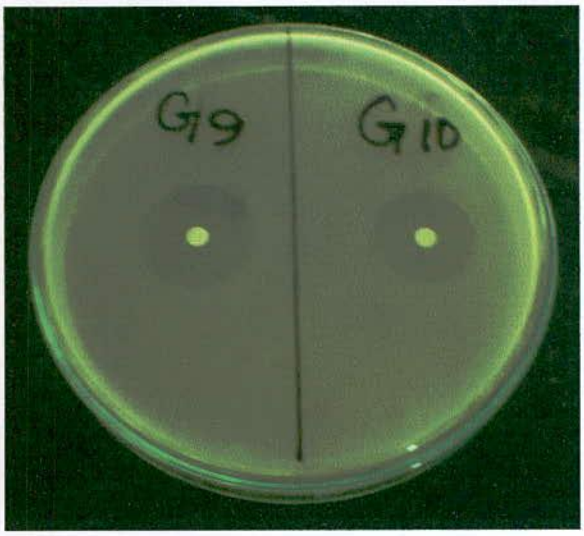


Figure- 4.5.8: Photographic representation of zone of inhibition of complexes **9** and **10** respectively against the bacteria *Enterococcus faecalis.*

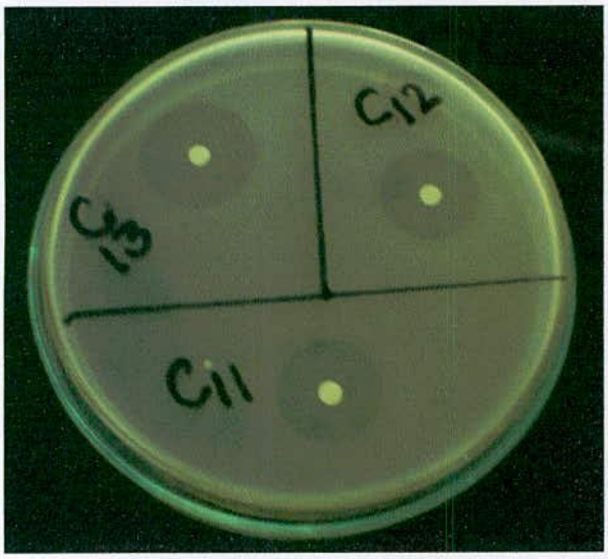
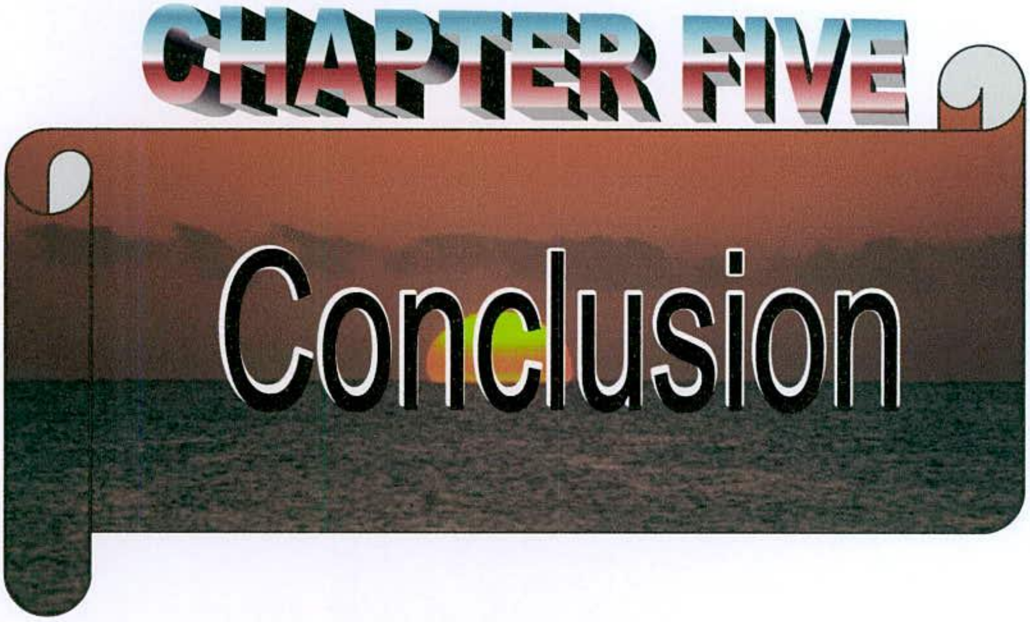


Figure- 4.5.9: Photographic representation of zone of inhibition of complexes **11, 12** and **13** respectively against the bacteria *Salmonella typhi.*

Figure- 4.5.10: Photographic representation of zone of inhibition of complexes **14** and **15** respectively against the bacteria *Staphylococcus aureus.*

CHAPTER FIVE

Conclusion



5. Conclusion

Mixed ligand complexes of platinum (II), platinum (IV), Palladium (II) ions with some dibasic acid (*viz.*, malonic acid, oxalic acid and phthalic acid) as primary and heterocyclic bases, *viz.*, quinoline(Q), *iso*-quinoline (IQ), pyridine (Py), 2-aminopyridine (2apy) and 4-picoline (4-pico) as secondary ligands were synthesized. By comparing the data of elemental analysis, magnetic moment, spectroscopic analysis the proposed empirical formula of the synthesized complexes can be following:

$[Pt(MA)_2(Q)_2]$(1), $[Pt(MA)_2(IQ)_2]$(2), $[Pt(MA)_2(Py)_2]$(3), $[Pt(MA)_2(4\text{-pico})_2]$(4), $[Pt(OX)_2(Q)_2]$(5), $[Pt(OX)_2(IQ)_2]$(6), $[Pt(OX)_2(Py)_2]$(7), $[Pt(OX)_2(4\text{-pico})_2]$(8), $[Pd(Ph)(Q)_2]$(9), $[Pd(Ph)(IQ)_2]$(10), $[Pd(Ph)(Py)_2]$(11), $[Pd(Ph)(2\text{-apy})]$(12), $[Pt(Ph)(4\text{-pico})_2]$(13), $[Pd(OX)(Q)_2]$(14), $[Pd(OX)(IQ)_2]$(15), $[Pd(OX)(Py)_2]$(16) and $[Pd(OX)(2\text{-apy})]$(17) where, MA = Deprotonated malonic acid, OX = Deprotonated oxalic acid, Ph = Deprotonated phthalic acid, Q = quinoline , IQ = *iso*-quinoline, Py = pyridine, 4-pico = 4-picoline, 2-apy = 2-aminopyridine.

All the complexes were isolated in the ethanolic solution as amorphous solid. All the synthesized complexes are colored and readily soluble in DMF and DMSO. The conductance values attributed that the complexes were non-electrolyte in nature. The analytical data are in good agreement with the proposed empirical formula of the present complexes. The infrared spectra of the complexes confirmed the coordination of metal ion with ligands. The small negative values of magnetic moment of the complexes indicated that all the synthesized complexes are diamagnetic. From the Magnetic moment and electronic spectra of the complexes are assignable that the Pt(IV) (1-8) complexes are octahedral structure and Pt(II) (13) & Pd(II) (9-12,14-17) complexes are square planar structure.

Their anti-bacterial activity had been evaluated. Disc diffusion methods were employed for antibacterial assays against seven pathogenic bacteria (thee gram positive and four gram negative), the complexe-4 shows the highest anti bacterial activity against all bacterial tested.

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