CHAPTER-IV

PREPARATION AND SPECTRAL STUDIES OF PALLADIUM(II), RHODIUM(III) AND RUTHENIUM(III) COMPLEXES OF QBD, MQBD, QBO, MQBO, NQTC AND MNQTC.
4.1 Introduction and literature survey of palladium(II) complexes

Palladium has attracted much attention as because it is a source of an increasing stream of new compounds of high intrinsic interest, particularly with respect to bonding and structure. The interest in coordination chemistry of square planar $d^8$ palladium complexes involving nitrogen, sulphur or oxygen donor ligands has grown in recent years because of their electronic properties, the application of those compounds in organometallic chemistry, analytical chemistry, catalysis and relevance to bioinorganic systems.1,2

A large numbers of both four and five coordinated palladium complexes have been studied by Orschin and Schmidt.3 Majority of divalent palladium complexes with coordination number four are square planar are slightly distorted, which may be due to the palladium(II) exhibits large crystal fields splitting, since it is possible to leave empty $d_{x^2-y^2}$ orbital, which could be left empty to give a diamagnetic products. Lott and Ramussen4 reported a few Pd(II) complexes having tetrahedral geometry.

A general survey of literature reveals that, a large number of ligands containing nitrogen, oxygen or sulphur atoms have been reviewed. A brief review of some of the important ligands and their complexes with palladium are given in the following paragraphs. The ligands are: dimethyl sulphoxide, ethyleneamine, 1,10-phenanthroline, saqlicylaldoxime, 2-(2'-thienyl)-pyridine, 4-benzylamide theosemicarbazide, 2-hydroxyl-1-naphthaldoxime, 1-(3-pyridyl)-1,3-butanedione, o-phenylene-bis(methylphenylarsine), N,N-dimethyl-3-aminopropanethiolate, pyridine-2-theol, theocarbamide, N-(2-methoxy)benzidencyclohexylamine, trichalco[n]ferrocenophanes, 2-mercapto-1-methylimidazole, azetidine, N,N-dimethyl-2-(or 3) thiophene carbothiamide, N-methylcyclohexyldithiocarbamate, 1,4-dithia-18-crown-6, cis-(benzylthiol)stilbenethiolate, 2,3-bis-(hydroxylimino)-
1,2,3,4-tetrahydropyrido[2,3-b]pyrazine\(^{25}\), chloro-[2,6-di(2-imidazoline-2-yl)pyridine]\(^{26}\).

Byers\(^{30,31}\) reviewed the coordination chemistry of palladium with various ligands reported during the year 1992 and 1993.

The complexes of \(\alpha\)-vanilline and \(\alpha\)-vallin semicarbazone with Pd(II) have been reported by Hingorani et.al.\(^{32}\). The isolation and structure of Pd(II) complex of 2-acetylpyridine thiosemicarbazone has been investigated\(^{33}\). The organopalladium chemistry contain the bidentate nitrogen donor ligand dimethyl-N,N,N',N'-tetramethylethylenediamine has been reported\(^{34}\).

Recently reported Pd(II) complexes of different ligands and their structural developments are briefly summarized in the following paragraphs. N-(2-hydroxyphenyl)-salicylamide(H\(_3\)L\(^{1}\)) and N-(2-hydroxy-5-chloro-phenyl) salicylamide (H\(_3\)L\(^{2}\)) formed diamagnetic Pd(II) complexes of the composition (PBu\(_4\))\(_2\)[M(L)(H\(_2\)L)](where PBu\(_4\)=tetraethylphosphonium ion; M=Ni, Pd; L=L\(^{1}\),L\(^{2}\)). Single crystal analysis for (PBu\(_4\))\(_2\)[Pd(L\(^{1}\))(H\(_2\)L\(^{1}\))] revealed that one ligand (L\(^{1}\))\(^{3-}\) coordinated tetradeutately and the other ligand (H\(_2\)L\(^{1}\)) coordinates unidentately at the phenolic oxygen of the salicylamide entity, affording a planar configuration around the metal ion\(^{35}\). Delima et.al.\(^{36}\) reported the crystal structure of Pd(II) complexes of 1-bis(diphenylphosphene)ferrocene.

Synthesis and characterization of some dimethyl sulphoxide complexes of Pd with the type [PdL\(_2\)(DMSO)\(_2\)](ClO\(_4\))\(_2\) and [PdL\(_2\)(DMSO)Cl](ClO\(_4\)) (where L=1,10-phenanthroline, 2,2'-dipyridyl or L=triphenylphosphine) were reported\(^{37}\). In which L\(_2\) and L act as auxiliary ligands. IR spectroscopy reveals that DMSO is bounded to Pd through S atom. Serindag\(^{38}\) synthesized the Pd(II) complexes of crown ether functionalized aminomethyl phosphene and characterized by employing \(^{31}\)P and \(^{1}\)H-
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NMR, mass spectra and micro analytical methods. Chandra and Singh investigated a few complexes of Pd(II) of 16-membered dibenzotetraaza macrocycles via non-template method using m-phenylenediamine and 2-propymal.

Eight complexes of the formulae $[\text{M}(\text{N-N})(\text{DHBA})]$ (where $\text{M}=$Pd(II) or Pt(II); $\text{N-N}=2,2'$-biquinoline, 2,2'-bipyridine, 4,7-diphenyl-1,10-phenanthroline, 1,10-phenanthroline and DHBA is the dianion of 3,4-dihydroxybenzoic acid) were found to show a ligand to ligand charge transfer (LLCT) band. Schumann et al. reported the preparation and characterizations of new bis-dichloropalladium(II) complexes of $\alpha$-w-dicarboxylicacid-bis(1,2,4-triaminobutane-$N^4$). Riger and Collins have synthesized the stable complexes of the formula trans-$[\text{Pd(CN)}_2(\text{CN(H)CH}_2\text{CH}_2\text{O})_2]\text{Pd(Pet}_3)\text{ER}$, where $\text{ER}=\text{OC}_6\text{H}_5$, $\text{SCH}_3$, p-$\text{SC}_6\text{H}_4\text{CH}_3$. A solid state structure of complex shows that the theolate ligand is in a coplanar arrangement with the palladium coordination sphere. Kernbach and Fehlhammer reported the X-ray crystal studies of trans-$[\text{Pd(CN)}_2(\text{CN(H)CH}_2\text{CH}_2\text{O})_2]$.

Oberhauser et al. synthesized novel Pd(II) complexes containing the ligand $\text{cis}$-$1,2$-$\text{bis}$-(diphenylphosphino)ethane[\text{cis}-\text{dppen}] and characterized by X-ray diffraction, NMR $^{13\text{P}}(\text{H})$, IR spectroscopy and elemental analysis. A single crystal structure determination of the complex (butane-$1,4$-diyl)$(\text{N,N}^1,\text{N}^1$-tetramethyl-ethylenediamine)$\text{Pd(II)}$ has shown that crystals are orthorhombic. The square planar complex has puckered $\text{Pd(CH}_2)\text{C}_4$ and $\text{PdNMe}_2\text{C}_2\text{CH}_2\text{NMe}_2$ rings.

Downard et al. isolated the chelating tetrazole containing ligands and their complexes with Pd(II) and Ru(II). $^1$H-NMR, electronic and cyclic voltametry have been used to study the nature of the metal ligand interactions in the complexes. Perera et al. reported the synthesis and characterization of Pd(II) complexes of 4-ter-butyl-2-diphenylphosphinocyclohexanone N,N-dimethylhydrazone. A few bis(3-
nitro-1,5-diarylformazane)Pd(II) chelates have been prepared by reacting an acetonic solution of the corresponding 3-nitroformazan with Pd(II) chlorides\(^{48}\). The spectral studies revealed that the coordination of the metal ion occurs through the nitrogen atoms. The structure of these chelates contains two symmetric six membered CN\(_4\)Pd rings.

Demertzi et al.\(^{49}\) reported the Pd(II) complexes of 2-acetylpyridine-N(4)-dimethylthiosemicarbazone (HAc4DM)]. A spectroscopic study indicates that the metal forms bonds with pyridyl nitrogen, azomethine nitrogen and thiolate sulphur atoms of the ligands. Selvakumar and Vancheesan\(^{50}\) have studied the reaction of various A-tetraloneketamines (L) with palladium acetate in CHCl\(_3\). Khandelwal et al.\(^{51}\) prepared and characterized the novel Pd(II) complexes of oroganotellurium ligand, 2(2-pyridoethyl-telluro)ethyl pyridine (L) of the type [PdCl(L)]Cl. The complex has square planar geometry around the palladium with the (N, Te, N) ligand coordinated in a tridentate mode. Bis(3-aminopropyl)telluride (L) and its complexes with Pd(II) of the types [PdCl(L)]Cl and [PdMeL]Cl have been isolated and characterized using IR, multinuclear NMR\({^1}\text{H} \text{and} {^{125}}\text{Te}({^1}\text{H})\) as well as molar conductivity data. The complexes exhibit square planar geometry around Pd(II) metal with (N, Te, N) ligand coordinated in tridentate mode\(^{52}\).

Kahraman and Irez\(^{53}\) studied the synthesis of N-(2-methylpyridyl)diaminoglyoxime derivatives and their Pd(II) complexes. The square planar geometry was proposed for the resulting complex by using spectral studies. Khandelwal et al.\(^{54}\) investigated the novel Pd(II) complexes of bis(4-methoxyphenyltelluro)methane. The structure of the complex was confirmed by X-ray diffraction studies. Fregona et al.\(^{55}\) reported that the palladium dihalides reacted with N,N-dimethylselenourea (dmsu) yielding complexes of the general formula [Pd(dmsu)\(_4\)]\(_2\), [Pd(dmsu)\(_4\)X]X,
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[Pd(dmsu)\(_4\)X\(_2\)] (X=Cl or Br) and characterized. The crystal structures of both modifications have been determined by X-ray crystallography. A few complexes of Pd(II) with N-(2-pyridyl)-3-carboxypropaneamid and N-(2-(pyridyl)-2-carboxybenzamide derived from 2-aminopyridine has been prepared and characterized. Spectral studies show that the pyridine nitrogen atom involved in coordination.

More recently reported Pd(II) complexes of different ligands and their structural developments are briefly summarized in the following paragraphs.

Reiss et.al.\(^{57}\) synthesized the complexes of bivalent Pd and Pt with 6-aryl-3-cyano-4-trifluoromethylpyridine-2(1H)-thione. Molar conductivities in nitromethane suggested that the complexes to be non-conducting. IR and NMR investigations show that the thiones are bonded to the metal ion through the sulfur atom. The thiones and their complexes possess antimicrobial activities.

Kriza et.al.\(^{58}\) reported the complex compounds of ions with d\(^6\), d\(^7\), d\(^8\) and d\(^{10}\) electronic configuration with 3-N-dibenzo furylthiourea. The complexes are found to be of the type [MLCl\(_2\)], where M=Co(II), Ni(II), Pd(II) or Pt(II). The thioamide acts as bidentate ligand using both sulfur and nitrogen atoms as donors. The bacteriostatic activities of the thioamide and the complexes have been determined against selected bacteria.

Padhye et.al.\(^{59}\) isolated coordinatively unsaturated metal complexes of the stoichiometry [M(HL)Cl] and [Fe(HL)Cl\(_2\)].2H\(_2\)O, where M=Cu(II), Ni(II), Pd(II) and Pt(II); HL=tridentate anion of 4-hydroxy-3-methyl-1,2-naphthoquinone-1-thiosemicarbazone(H\(_2\)L). The X-ray crystal structure for H\(_2\)L has been determined. The Cu(II), Ni(II), Pd(II) and Pt(II) complexes are found to possess square planar geometries, where as Fe(III) complex possesses a square pyramidal configuration. The \textit{in vitro} activity of the synthesized compounds examined against human breast
cancer cell line MCF-7 clearly indicates that the metal complexation enhances antitumour activity, the highest being for the copper complex.

Ramachandra and Narayana\textsuperscript{60} reported complexing behaviour of 4-vanillideneamino-3-methyl-5-mercapto-1,2,4-triazole towards Ag(I), Zn(II), Pb(II), Cd(II), Hg(II), Co(II), Ni(II), Pd(II), Rh(III) and Ir(III). Octahedral structure for Co(II), Ni(II), Rh(III) and Ir(III) complexes, square planar structure for Pd(II) complex, tetrahedral structure for Zn(II), Cd(II) and Pb(II) complexes and linear polymeric structure for Ag(I) complex have been proposed.

Two of the most successful chemotherapeutic agents used in the treatment of several neoplasias are bleomycin and cisplatin. Both drugs attack the DNA leading to the cancer cells death via different mechanisms. Papakyriakou et al.\textsuperscript{61} undertaken NMR and circular dichroism studies on the complexes formed between bleomycin and Pt(II) or Pd(II).

Leka et al.\textsuperscript{62} reported the complexes of platinum(II) and palladium(II) with a new polydentate dithiocarbamate ligand, 3-dithiocarboxy-3-aza-5-aminopentanoate (daap), of the type [M(daap)\textsubscript{2}].nH\textsubscript{2}O (M=Zn(II), Cd(II), n=2; or M=Pt(II), Pd(II), n=0). Elemental analysis, IR and UV/Vis spectroscopy, as well as magnetic measurements have been used to characterize the complexes. The spectra of complexes suggest a bidentate coordination of ligand to the metal ions via sulphur atoms of deprotonated dithiocarbamato group.

Complexes of Zn(II), Pd(II) and Pt(II) with 2\textsuperscript{'}-[1-(2-pyridinyl)ethylidene]oxamohydrazide (Hapsox) were synthesized and their structures were determined by Andelkovic et al.\textsuperscript{63}. All complexes were of neutral type with two Hapsox ligands coordinated to Zn(II) and one Hapsox ligand coordinated to Pd(II) or Pt(II). In each case, the polydentate was coordinated via pyridine and hydrazone nitrogen's and
oxygen, forming an octahedral geometry around Zn(II), and square planar geometry around Pd(II) and Pt(II). The structure determination was performed by IR, $^1$H-NMR and $^{13}$C-NMR spectroscopy.

4.2 Introduction and literature survey of rhodium(III) complexes

The coordination chemistry of rhodium(III) is currently of great interest, since some of these complexes have been found to possess antitumour activity and can be used as potential models for a number of important catalytic systems.

Number of rhodium(III) complexes with different ligands have been reviewed. The rhodium complexes of various ligands have been extensively reported as potential catalyst in certain hydrogenation and dehydrogenation reactions. The macrocyclic chemistry of rhodium has been extensively investigated in biological systems. Rh(III) complexes of N-heterocyclic ligands have received special interest for their potential use as electron transfer agents in the storage of radiant energy.

A large number of rhodium(III) complexes with variety of complexing agents have been investigated. Some of the important ligands used are: 2-pyridinethiol, phosphine, $n^1$-ylidieneamine, 1,2-naphthaquinonemonoxime, thiosemicarbazones, nucleic acid bases, nucleosides, pentamine trifluoromethanesulphonate-o, 2,2'-biquinoline, 2-(2'-pyridyl)quinoline, 4-amino-3-mercapto-1,2,4-triazole, chalcosemicarbazones, 5-methyl-3,7-diazanonance-1,5,9-triamine and dimethylglyoximate.

Recently, Dreos et.al. reported the synthesis and characterization of a series of [RM(DBPh$_2$)$_2$(H$_2$O)] complexes (where M=Co or Rh) and the X-ray structure of the dinuclear [n-PrRh(DH)(DBPh$_2$)]$_2$ obtained by recrystallization of [n-PrRh(DBPh$_2$)$_2$](H$_2$O) in non coordinating solvent.
The structures of the compounds \([\text{Rh(bpy)}_2(\text{py})(\text{Cl})](\text{ClO}_4)_2\) and \([\text{Rh(phen)}_2(\text{py})(\text{Cl})](\text{ClO}_4)_2\) were determined by single crystal X-ray diffraction by Kim et al.\(^{90}\). Both complexes show a six coordinate rhodium with two bpy or phen ligands in the \(\text{cis}\) configuration.

Lee et al.\(^{91}\) synthesized and characterized a new complex of the type \([\text{Rh(PA)}_2\text{Cl}_2]\text{Cl}_2\text{H}_2\text{O}\) (where PA=Phenylpyridin-2-methyleneamine). The complex shows high intensity bands in the UV region, and these are assigned to spin allowed \(\pi-\pi^*\) transitions. The medium intensity absorption band profile in the lower energy region can be explained by convolution of spin-allowed CT and d-d transitions.

Nastasovic et al.\(^{92}\) synthesized macroporous crosslinked poly(glycidyl methacrylatecoethylene glycol dimethacrylate). The sorption rate and capacity of modified copolymer, p(GME)-en for Rh(III), Au(III) and Pt(IV) ions were determined in batch experiments under noncompetitive conditions.

Qaseer\(^{93}\) reported Rh(III) complexes containing 2-(2'-pyridyl)quinoline (PQ) prepared by the reaction of RhCl\(_3\cdot6\text{H}_2\text{O}\) and PQ in 1:2 mole ratio followed by addition of an excess of sodium salts to the reaction mixture. The new complexes \(\text{cis-}[\text{RhX}_2(\text{PQ})_2]\text{Y}\) (where \(\text{X}=\text{NO}_2^-, \text{Y}=\text{PF}_6^-, \text{X}=\text{SCN}^-\) or \(\text{NO}_3^-, \text{Y}=\text{Cl}^-; \text{X}=\text{Y}=\text{I}^-\)) and \(\text{cis-}[\text{Rh(N}_3)_2(\text{H}_2\text{O})_2(\text{PQ})]\text{PF}_6\) were characterized by elemental analysis, conductivity measurements, IR, \(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR spectra.

### 4.3 Introduction and literature survey of ruthenium(III) complexes

With their high reactivity, ruthenium compounds are among the most widely used homogenous catalysts or catalyst precursor for such reactions as alkene hydrogenation, isomerization, hydroformylation, polymerization and the oxidation of various organic substrates\(^{94-97}\). Exhaustive reviews on the complexes of ruthenium(III) are available\(^{98,99}\). A large number of chloro and amine complexes of ruthenium(III)
Preparation and Spectral studies of Pd(n), Rh(III) and Ru(III) have been reported. The ruthenium complexes of various ligands and their properties are extensively reviewed. The spatial structure of DNA by the application of tris(2,2'-bipyridyl) ruthenium(III) complex has been investigated.

Many octahedral complexes of ruthenium(III) with different ligands have been reported. Some of such ligands include: trimethylenemethane, 6-fluoro-2-oxopyridine, 2,2'-bipyridine, 2,3-bis(2-pyridyl)pyrazine, hydrazone of 2,6-diacetylpyrididine. N,N'-dimethyl-N,N'-bis(2-pyridylimethyl)ethylenediamine, N,N-(2-diphenylphosphinoethyl)-N-benzylamine.

Many authors have reported the isolation and characterization of Ru(III) complexes of ligands containing nitrogen, oxygen or sulphur donor atoms. Some of these are mentioned in the following paragraphs.

Broomhead and Lynch investigated the synthesis and X-ray crystal structure of pentamine(1-thiolate-choso-undecahydrododecacarborane)-Ru(III) dehydrate. Synthesis and spectral studies of Ru(III) complexes with mono, di-(seleno)bis(β-diketone) and imido di(thiocarbonic acid-o-alkyl) ester has been reported. Complexes of Ru(III) with thioester, sulfoxide and benzoate axial ligands have been prepared and characterized by use of spectral and volumetric studies. The IR data suggest that the coordination form through sulphur atom. Mosny et al. synthesized and characterized a variety of ruthenium complexes with degradation resistant ligand tri-2-pyridylamine. A series of neutral ligands viz., 2-(2-thienylpyridine), 2-(2-methylaminoethyl)pyridine, 2-acetylpyrrole and N,N'-ethylene-bis(2'-aminobenzamide reacts with [Ru(NH3)3N2]Br2 and form Ru(II) complexes by substituting the dinitrogen and three ammonia molecules forming [RuLn(NH3)2]Br (n=1 or 2). The complexes have been characterized by using spectral studies. The synthesis and characterization of the complex [Ru(tppz)(4,4'- (CH3)2bpy)Cl+] where tppz = 2,3,5,6-
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tetrakis (2-pyridyl) pyrazine has been reported\textsuperscript{119}. The ruthenium atom is in a highly distorted octahedral environment. The distortion is evident in the $^1$H NMR spectra by the shifts of characteristics resonances and downfield relative to ligand.

Two Ru-nitrosylporphyrins \{(TPP)Ru(NO)(H$_2$O)\}BF$_4$ and \{(TPP)Ru(NO)(ONO)\} (ONO), where TPP is dianion of 5,10,15,20-tetraphenyl porphyrin were synthesized and characterized by spectroscopic and electrochemical method\textsuperscript{120}. Low-spin Ru(III) complexes \{RuX(Eph$_3$)(LL$^1$)\} (X=Cl, Br; E=P, As; LL$^1$=schiff bases) were isolated and characterized\textsuperscript{121}. Aneetha et.al.\textsuperscript{122} have synthesized and characterized a number of dinuclear ruthenium(III) complexes of dinucleating ligands.

Recently, Collins et.al.\textsuperscript{123} reported the use of $^1$H NMR spectroscopy to study the oligonucleotide binding of the $\Delta$ enantiomers of [Ru(phen)$_2$L]$^{2+}$ where the bidentate ligand L is 1,10-phenanthroline, dipyrldo[3,2-$d$:2'3'-f]quinoxaline or dipyrldo-[3,2-$a$:2'3'-c](6,7,8,9-tetrahydro)phenazine. The data from one- and two-dimensional NMR experiments of the oligonucleotide-metal complex binding suggest that all the three ruthenium(II) polypyridyl complexes bind in the DNA minor groove.

Stein et.al.\textsuperscript{124} reported synthesis and electrochemical characterization of bimetallic ruthenium complexes with the bridging $\eta^2$ ($\sigma$, $\sigma$)-1,3-butadiyne-1,4-diyl ligand. The bis(ruthenium)alkyne complex \{cis-$\{\text{RuCl(bpy)}_2(\mu-C≡C-)\}_2$\} was obtained by treatment of one equivalent of either 1,4-bis(trimethylsilyl)-1,3-butadiene or bis(trimethylsilyl)acetylene with two equivalents of cis-$\{\text{RuCl}_2$(bpy)$_2$\}$_2$H$_2$O, NaF and NaBF$_4$ salts in methanol/CH$_2$Cl$_2$ mixture (10/1) in 52% and 35%, respectively.

Mahesh and Ram\textsuperscript{125} chemically modified the chloromethylated styrene-divinylbenzene copolymer with ethylenediaminetetraacetic acid ligand. Catalytically active polymer containing Ru(III) moieties were synthesized from this polymeric
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ligand. They were characterized using FTIR, UV-Vis, ESR and TGA. The polymer bound complex was used to study hydrogenation of 1-hexene to n-hexane under mild conditions. Influence of [1-hexene], [catalyst], temperature and nature of the solvent on the rate of the reaction were investigated.

Lemiesz reported the effect of an anticancer ruthenium complex, \( \text{trans-indazolium-(bis-indazole)tetrachlororuthenate(III)} \) \( (\text{HInd[RuInd}_2\text{Cl}_4]) \), on conformation of cytochrome C, the state of the heme moiety, formation of the protein dimer and on folding state of apocytochrome C.

Slim and Sleiman reported the synthesis, characterization and avidin binding properties of two novel ruthenium complexes, \( [\text{Ru(bpy)}_2(\text{phen-biotin})][\text{PF}_6]_2 \) and \( [\text{Ru(phen)}_2(\text{phen-biotin})][\text{PF}_6]_2 \) where \( \text{bpy}=2,2’\text{-bipyridine; phen}=1,10\text{-phenanthroline, phen-biotin}=5-(10\text{-amidobiotinyl})-(1,10\text{-phenanthroline}) \). It is observed that both biotinylated compounds bind to avidin through their biotin moieties with high affinity and in a 4:1 ratio.

Zhong and Yuan synthesized a novel binuclear complex \( [(\text{bpy})_2\text{Ru(\mu-bipp)}\text{Ru(bpy)}_2](\text{ClO}_4)_4 \), where \( \text{bpy}=2,2’\text{-bipyridine and bipp}=2,9\text{-bis}(2\text{-imidazo}[4,5-f][1,10\text{-phenanthroline})-1,10\text{-phenanthroline} \). Photophysical results reveal that this complex interacts with CT DNA with intrinsic binding constant \( 2.6 \times 10^5 \text{ M}^{-1} \) in the buffer containing 5 mM Tris and 50 mM NaCl.

Deshpande and Kumbhar presented the synthesis and characterization of mixed ligand complexes of the type \( [\text{Ru(N-N)}_2(\text{dzdf})]\text{Cl}_2 \), where \( \text{N-N} \) is \( 2,2’\text{-bipyridine(bpy), 1,10-phenanthroline(phen) and 9-diazo-4,5-diazofluorene(dzdf).} \) Binding of these complexes with CT-DNA has been investigated by absorption spectroscopy, steady-state emission spectroscopy and viscosity measurements. The
complex \([\text{Ru(phen)}_2(\text{dzdf})]\text{Cl}_2\) binds with CT-DNA through an intercalative binding mode, while the complex \([\text{Ru(bpy)}_2(\text{dzdf})]\text{Cl}_2\) binds electrostatically.

The above literature survey reveals that the complexes of Pd(II), Rh(III), Ru(III) with QBD, MQBD, QBO, MQBO, NQTC and MNQTC have not been previously investigated. Therefore, the author has reported the synthesis and characterization of new Pd(II), Rh(III), Ru(III) complexes with QBD, MQBD, QBO, MQBO, NQTC and MNQTC as primary ligands and chloride as a secondary ligand.

4.4 Experimental

4.4.1 Estimation of metal ion

a. Estimation of palladium

The palladium content of the complexes was determined by heating a known weight of the complex with 5 ml of concentrated nitric acid and 3 ml of hydrogen peroxide (6% w/v). The dissolution and heating were repeated until a clear solution was obtained. The amount of palladium present in the complex was then determined by dimethylglyoxime method\(^{183}\).

b. Estimation of ruthenium and rhodium

The analyses of the rhodium and ruthenium ion in the complexes were carried out by dissolving a known amount of the complex in concentrated nitric acid followed by evaporation of the solution to dryness, extraction with distilled water and estimation of the metal ions in solution by the method given in literature\(^{184}\).

4.4.2 Complexing agents

The complexing agents QBD, MQBD, QBO, MQBO, NQTC and MNQTC were used for the preparation of palladium(II), rhodium(III) and ruthenium(III) complexes. A detailed account of these reagents is presented in Chapter II.
4.43 Preparation of complexes

a. General procedure for the preparation of Pd(II) complexes

The complexes were prepared by mixing an ethanolic solution of the metal dichloride with the corresponding ligand in hot ethanol in a 1:1 molar ratio. The resultant solution was refluxed at 110 °C for three hours. When the corresponding metal complex precipitated, it was filtered, washed several times with ethanol and dried under reduced pressure.

b. General procedure for the preparation of Rh(III) complexes

The complexes were prepared by refluxing the rhodium(III) chloride trihydrate (5 mmol) and the corresponding ligand (10 mmol) in ethanol (75 ml) for 2-3 hours. When the metal complex precipitated, it was filtered, washed several times with hot water, warm ethanol and dried at 110-130 °C.

c. General procedure for the preparation of Ru(III) complexes

A mixture containing RuCl₃·3H₂O (2.5 mmol) and corresponding ligand (5 mmol) was refluxed in methanol for 5 hours. The solution was cooled to room temperature. After evaporation of the solvent, the solid was collected, washed with methanol and dried under suction.

4.5 Results and discussion

The analytical data presented in the Tables 4.1 and 4.2 reveals that the complexes synthesized from QBD, MQBD, QBO, MQBO, NQTC and MNQTC possess 1:1 (metal:ligand) stoichiometry for Pd(II) complexes and 1:2 (metal:ligand) stoichiometry for Rh(III) and Ru(III) complexes with the general molecular formulae [PdLCl₂] and [ML₂Cl₂], where M=Rh(III) or Ru(III); L=QBD, MQBD, QBO, MQBO, NQTC or MNQTC.
Palladium(II) and Ruthenium(III) complexes with NQTC and MNQTC are yellow in colour and with QBD, MQBD, QBO and MQBO are brown to brownish red. The rhodium(III) complexes with all ligands show deep reddish colour. These characteristic colour of the Pd(II), Rh(III) and Ru(III) complexes indicate that the ligands have high ligand field strength in forming the complexes in which d-d transitions are largely obscured by the more intense charge transfer bands.

All the complexes of QBD, MQBD, QBO, MQBO, NQTC and MNQTC are freely soluble in DMF and DMSO but sparingly soluble in water, methanol and practically insoluble in benzene, chloroform, acetone, carbontetrachloride and ether. All these complexes are stable towards air and moisture.

4.51 Molar conductance

The molar conductance values of all the complexes were determined in 10^{-3} M DMF and are tabulated in Table 4.1. The conductivity values of Pd(II) complexes are in the range 32.8-22.8 mhos cm^2 mol^{-1} indicating the non-electrolytic nature of the complexes. The molar conductance values of rhodium(III) and ruthenium(III) complexes were found to be quite low (15.5-25.4 mhos cm^2 mol^{-1}), showing thereby these complexes have covalent behaviour. The observed very small conductance values show that practically no interaction occurs between the solvent and the dissolved complex. Thus the chloride ions in all these complexes are coordinated to metal ion and are not present outside the coordination sphere. This is consistent with the stoichiometry assumed for the complexes on the basis of analytical data.
Table 4.1: Yield, molecular weight and molar conductance data of Pd(II), Rh(III) and Ru(III) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Yield %</th>
<th>Molecular weight found</th>
<th>$\Omega_M$ mhos.cm$^2$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(QBD)Cl$_2$]</td>
<td>78</td>
<td>422.60</td>
<td>22.8</td>
</tr>
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<td>830.81</td>
<td>23.1</td>
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</tbody>
</table>

4.52 Magnetic susceptibility measurements$^{118, 122, 132-135}$

Magnetic susceptibility measurements of all these new complexes were determined using Guoy balance at room temperature and the values are given in Table 4.2. The magnetic moment value shows that the [Pd(L)Cl$_2$] (where L= QBD, MQBD, QBO, MQBO, NQTC or MNQTC) complexes are diamagnetic, which corresponds to the +2 oxidation state of palladium.
Magnetic moment values of \([\text{RhL}_2\text{Cl}_2]\) (where \(L = \text{QBD, MQBD, QBO, MQBO, NQTC or MNQTC}\)) complexes are found to be in the range 1.81-1.86 BM. These results are consistent with the octahedral structures proposed for the paramagnetic Rh(III) complexes.

The magnetic susceptibility data indicates that the new ruthenium(III) complexes are paramagnetic with one unpaired electron. The values are in the range 1.81-1.92 BM that is lower than the predicted value of 2.1 BM. This low value may be due to low symmetry ligand fields or electron delocalization. This observed value is very close to the spin only value for one unpaired electron. This suggests the low spin \(d^5\) configuration for ruthenium(III) ion in an octahedral environment.

4.53 Electronic spectra \(^{130,131,136-140}\)

The electronic spectral data are presented in Tables 4.2(a) & 4.2(b), and the corresponding spectra are produced in Figures 4.1-4.3. Palladium is \(d^8\) system. A square planar geometry is generally found for metal of low spin \(d^8\) system. The ground state for low spin palladium(II) ion is \(^1A_{1g} (=a_{1g}^2, e_g^5, b_{2g}^2)\). The ligand field excited states are \(^3A_{2g}, ^1A_{2g} (b_{2g} \rightarrow b_{1g}), ^3E_g, ^1E_g (e_g \rightarrow b_{1g})\) and \(^3B_{1g}, ^1B_{1g} (a_{1g} \rightarrow b_{1g})\). Therefore, one can expect three spin allowed and spin forbidden transitions in these cases. The intensity bands arising out of transitions \(a_{1g} \rightarrow b_{1g}\) could not be assigned here because the forbidden \(d\-d\) transition are largely masked by the more intense \(L \rightarrow M\) charge transfer bands. The electronic spectrum of Pd(II) complexes gave three bands at 16600, 21300 and 30300 cm\(^{-1}\) may be assigned \(^1A_{1g} \rightarrow ^1A_{2g} (v_1), ^1A_{1g} \rightarrow ^1B_{1g} (v_2)\) and \(^1A_{1g} \rightarrow ^1E_{1g} (v_3)\) transitions, respectively in a square planar configuration around Pd(II).

Rhodium(III) is a \(d^6\) system. The ground state of the octahedral rhodium(III) complex is \(^1A_{1g}\). The singlets excited states are \(^1T_{1g}\) and \(^1T_{2g}\). Thus electronic
transitions correspond to \(^{1}A_{1g} \rightarrow ^{1}T_{1g}\) and \(^{1}A_{1g} \rightarrow ^{1}T_{2g}\) in the increasing order of their energies. The spin forbidden \(^{1}A_{1g} \rightarrow ^{3}T_{1g}\) transition is also observed in Rh(III) complexes. In the present investigation of Rh(III) complexes, the observed electronic bands around 16600, 19400 and 22300 cm\(^{-1}\) are due to the transitions \(^{1}A_{1g} \rightarrow ^{3}T_{1g}\), \(^{1}A_{1g} \rightarrow ^{1}T_{1g}\) and \(^{1}A_{1g} \rightarrow ^{1}T_{2g}\) respectively in an octahedral structure around Rh(III).

The trivalent low spin Ru(III) is a \(d^5\) ion with \(^{2}T_{2g}\) as the ground term and the first excited doublet levels in the order of increasing energy are \(^{2}A_{2g}\) and \(^{2}T_{1g}\) which arise from \(t_{2g}^4 e_g^1\) configuration. The electronic spectra of Ru(III) complexes is often composed of well defined ligand to metal charge transfer bands. Generally, the Ru(III) complexes have high oxidizing properties and hence, the charge transfer bands of the type \(\pi_L \rightarrow t_{2g}(M)\) are prominent in the low energy region which obscure the weaker bands due to d-d transitions. It is therefore, difficult to assign conclusively the bands of Ru(III) complexes which appear in the visible region.

The UV-Visible spectra Ru(III) complexes of the ligands QBD, QBO, NQTC, MQBD, MQBO and MNQTC showed that all complexes exhibit octahedral absorption bands in the region 24800-24570 cm\(^{-1}\). Only charge transfer bands, which masked the weak (spin forbidden as well as spin allowed) bands due to d-d transitions in the visible region. The bands in the range 24800-24570 cm\(^{-1}\) may be attributed to \(^{1}A_{1g} \rightarrow ^{1}T_{1g}\) charge transfer transitions. All the Ru(III) complexes show absorption band ca. 37000 cm\(^{-1}\) corresponding to charge transfer transitions.
Preparation and Spectral studies of Pd(II), Rh(III) and Ru(III)

Figure 4.1: Electronic spectra of [Pd(QBO)Cl₂]_

Table 4.2(a): Analytical and electronic spectral data of Pd(II) complexes

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<th>Electronic spectral data</th>
<th>μeff BM</th>
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Preparation and Spectral studies of Pd(II), Rh(III) and Ru(III).

Figure 4.2: Electronic spectra of [Rh(QBD)Cl]

Figure 4.3: Electronic spectra of [Ru(QBD)Cl]
Table 4.2(b): Analytical and electronic spectral data of Rh(III) and Ru(III) complexes

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<th>Frequency3</th>
<th>Frequency4</th>
<th>Frequency5</th>
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4.54 IR spectra

In order to study the binding mode of ligands to metal ions in the complexes, IR spectrum of the free ligands were compared with the spectra of the metal complexes. The important assignments of ligands and their complexes are summarized in Table 4.3 and Figures 4.4-4.6.
Preparation and Spectral studies of Pd(II), Rh(III) and Ru(III).....

An intense bands observed in the infrared spectra of the free QBD ligand around 1658 and 3330 cm\(^{-1}\) due to \(\nu(C=N)\), \(\nu(NH)\), respectively have been shifted to a lower frequencies by 25-35 cm\(^{-1}\) in the spectra of Pd(II), Rh(III), Ru(III) complexes indicating the coordination of nitrogen atoms of heterocyclic rings. This confirms the bidentate behavior of the ligand.

The ligand bands at 1662 cm\(^{-1}\), 1578 cm\(^{-1}\) and 3332 cm\(^{-1}\) in the IR spectra of MQBD assigned to \(\nu(C=N)\), \(\nu(C=C)\) and \(\nu(NH)\) vibrations, respectively. After complexation, ligand-metal bond is formed through the nitrogen atom of quinoline and that of oxazepine ring. Slight shift of \(\nu(C=N)\) and \(\nu(NH)\) bands to lower wave numbers in the complexes confirmed the coordination of the nitrogen atoms with the metal ions.

The free QBO displays a characteristic bands in the regions as mentioned: The \(\nu(C=N)\) at 1651 cm\(^{-1}\), \(\nu(C=C)\) at 1566 cm\(^{-1}\), \(\nu(C-H)\) at 2924 cm\(^{-1}\), \(\nu(COC)\) at 1022 cm\(^{-1}\), respectively. In the IR spectra of the complexes the band at 1651 cm\(^{-1}\) totally disappears indicating the coordination of metal ion through quinoline nitrogen. The band at 1022 cm\(^{-1}\) is also disappears in the complexes indicating the oxygen atom of oxazepine ring is the site of coordination. In addition there were bands that could be attributed to metal-oxygen and metal-nitrogen bonds in the complexes.

The IR spectra of MQBO ligand shows absorption bands in the region of 1025 cm\(^{-1}\), 1569 cm\(^{-1}\) and 3053 cm\(^{-1}\) for \(\nu(COC)\), \(\nu(C=C)\) and \(\nu(C-H)\), respectively. It also shows the band around 1653 cm\(^{-1}\) due to \(\nu(C=N)\) vibrations. In the IR spectra of the complexes the band at 1653 cm\(^{-1}\) suffers a negative shift indicating the coordination through the quinoline nitrogen. Also, the band at 1025 cm\(^{-1}\) disappears in the complexes indicating the oxygen atom of oxazepine ring is the site of coordination.
The infrared spectrum of the ligand NQTC exhibits the bands at 760 and 1710 cm\(^{-1}\) for \(v(\text{CSC})\) and \(v(\text{CHO})\) vibrations, respectively. The band at 1650 cm\(^{-1}\) is characteristic of \(v(\text{C}=\text{N})\) vibrations. The lowering in this frequency (1605-1615 cm\(^{-1}\)), observed in Pd(II), Rh(III) and Ru(III) complexes suggesting the involvement of the quinoline nitrogen atom in coordination. In the IR spectra of the complexes, the band due to \(v(\text{CSC})\) suffers a negative shift to the extent of 15-20 cm\(^{-1}\) indicating the involvement of sulphur atom of the ligand in bonding with metal ions.

The MNQTC ligand shows its characteristics absorption bands at 762, 1713 and 1652 cm\(^{-1}\) regions, are assignable to \(-\text{CSC}-, -\text{H-CH}=0\) and \(\text{C} = \text{N}\) vibrations, respectively. The band at 1652 cm\(^{-1}\) underwent a shift to lower frequency (1608-1620 cm\(^{-1}\)) after complexation, indicating the coordination of quinoline nitrogen to metal atom and this can be explained by the donation of electrons from nitrogen to the empty \(d\)-orbital of the metal atom. Also, in the IR spectra of the complexes, the band due to \(v(\text{CSC})\) suffers a negative shift to the extent of 25-30 cm\(^{-1}\) indicating the involvement of sulphur atom of the ligand in bonding with metal ions.

The Far-IR spectra of the complexes reveal some new bands at ca. 300-310, 340-351 and 320-325 cm\(^{-1}\), which are assignable to Pd-Cl, Rh-Cl and Ru-Cl vibrations, respectively.

**Table 4.3: Some important IR stretching frequencies (cm\(^{-1}\)) of Pd(II) Rh(III) and Ru(III) complexes**

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<th>(v(\text{NH}))</th>
<th>(v(\text{COC}))</th>
<th>(v(\text{CSC}))</th>
<th>(v\text{ M-N})</th>
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<td>--</td>
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<td>--</td>
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<td>--</td>
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<td>--</td>
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<td>738</td>
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<td>320</td>
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</table>
Preparation and Spectral studies of Pd(II), Rh(III) and Ru(III).....

Figure 4.4: IR spectra of [Pd(NQTC)Cl₂] complex.

Figure 4.5: IR spectra of [Rh(NQTC)₂Cl₂] complex.
Preparation and Spectral studies of Pd(II), Rh(III) and Ru(III)...

Figure 4.6: IR spectra of [Ru(NQTC)2Cl2] complex.

4.55 Proton nuclear magnetic resonance spectra

The chemical shift of the representative groups of the QBD, QBO, NQTC, MQBD, MQBO, MNQTC and their complexes are presented in Table 4.4 and Figures 4.7-4.9.

The proton NMR spectra of the ligand QBD in DMSO shows the following signals: multiplet of aromatic protons at 7.2-7.8 δ range and -H-C=N at 8.4 δ. The peak at 10.65 δ is attributed to the -NH group present in the benzodiazepine moiety. The shifting of this peak, observed in the complexes, indicates that the nitrogen atom of the benzodiazepine moiety is the site of coordination. There is no appreciable change in all other signals in these complexes.

The ¹H NMR spectrum of the ligand MQBD exhibits a multiplet signal at 7.1-8.2 δ (m, Ar-H), 10.80 δ (s, N-H), 2.7 δ (s, CH₃) and 8.6 δ (s, H-C=N). In Pd(II), Rh(III) and Ru(III) complexes, the N-H proton is shifted slightly downfield at 10.9 δ which reveals the bonding of the benzodiazepine nitrogen to metal ions.
1H NMR spectra of the ligand QBO exhibit a multiplet signal in the range 7.1-8.0 δ are attributed to aromatic protons. The singlet at 8.3 δ is assigned to H-C=N proton. In the spectra of the complexes, there is no significant difference in the chemical shifts of the protons compared with the free ligand.

1H NMR spectra of the ligand MQBO exhibit a multiplet signal in the range δ 7.3-8.0 are attributed to aromatic protons. The singlets at 8.1 δ and 2.6 δ are assigned to H-C=N proton and methyl group protons, respectively. In the spectrum of the complexes, all the proton NMR signals of the ligand have appeared in their appropriate places as in the free ligand.

1H NMR spectrum of the ligand NQTC in DMSO consists of several signals, which can be assigned as follows: a singlet at δ 9.6 (s, H-C=O) and a multiplet at δ 7.4-8.6 (m, Ar-H). 1H NMR spectra of Pd(II), Rh(III) and Ru(III) complexes exhibit signals remaining in the same position as in the free ligand.

1H NMR spectra of the ligand MNQTC showed singlets at 9.7 ppm, 2.9 ppm and a multiplet in the range 7.5-8.6 ppm due to -CHO, -CH3 and aromatic protons, respectively. In the 1H NMR spectra of the Pd(II), Rh(III) and Ru(III) complexes these signals remains in the same position as in the free ligand.

Thus 1H NMR support the conclusion drawn on the basis of IR data regarding the coordination mode of the ligands QBD, QBO, NQTC, MQBD, MQBO and MNQTC with metal ions.
Figure 4.7: $^1$H NMR spectra of $\text{[Pd(QBD)Cl}_2]$ complex.

Figure 4.8: $^1$H NMR spectra of $\text{[Rh(QBD)_2Cl}_2]$ complex.
Figure 4.9: $^1$H NMR spectra of [Ru(QBD)$_2$Cl$_2$] complex.

Table 4.4: $^1$H NMR spectral data ($\delta$, ppm) of Pd(II), Rh(III) and Ru(III) complexes.

<table>
<thead>
<tr>
<th>Ligand/Complex</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(QBD)Cl$_2$]</td>
<td>10.85 (s, 1H, NH), 8.4 (s, 1H, H-C=N), 7.2-7.8 (m, 9H, Ar-H)</td>
</tr>
<tr>
<td>[Pd(QBO)Cl$_2$]</td>
<td>8.3 (s, 1H, H-C=N), 7.1-8.0 (m, 9H, Ar-H)</td>
</tr>
<tr>
<td>[Pd(NQTC)Cl$_2$]</td>
<td>9.6 (s, 1H, -CHO), 7.4-8.6 (m, 11H, Ar-H)</td>
</tr>
<tr>
<td>[Rh(QBD)$_2$Cl$_2$]</td>
<td>10.9 (s, 1H, NH), 8.4 (s, 1H, H-C=N), 7.2-7.8 (m, 9H, Ar-H)</td>
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<tr>
<td>[Rh(QBO)$_2$Cl$_2$]</td>
<td>8.3 (s, 1H, H-C=N), 7.1-8.0 (m, 9H, Ar-H)</td>
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<tr>
<td>[Rh(NQTC)$_2$Cl$_2$]</td>
<td>9.6 (s, 1H, -CHO), 7.4-8.6 (m, 11H, Ar-H)</td>
</tr>
<tr>
<td>[Ru(QBD)$_2$Cl$_2$]</td>
<td>10.8 (s, 1H, NH), 8.4 (s, 1H, H-C=N), 7.2-7.8 (m, 9H, Ar-H)</td>
</tr>
<tr>
<td>[Ru(QBO)$_2$Cl$_2$]</td>
<td>8.3 (s, 1H, H-C=N), 7.1-8.0 (m, 9H, Ar-H)</td>
</tr>
<tr>
<td>[Ru(NQTC)$_2$Cl$_2$]</td>
<td>9.6 (s, 1H, -CHO), 7.4-8.6 (m, 11H, Ar-H)</td>
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</tbody>
</table>

4.56 X-ray diffraction studies

The X-ray powder diffraction for [Pd(QBD)Cl$_2$] complex has been shown in a typical X-ray pattern (Table 4.5, Figure 4.10). The diffractogram records 14 reflections between 5 and 50° (2θ). The diffraction pattern of this complex has been...
indexed by standard methods and the unit cell parameters were calculated from the indexed data by trail and error method. The unit cell parameters are found to be a=7.02, b=7.2599, c=6.543897 and the value of α=89.20°, β=90.37, γ=90.33. Comparison of values reveals that there is good agreement between the observed and calculated values of 2θ and d value.

![X-ray diffraction spectrum of [Pd(QBD)Cl2] complex.](image)

**Table 4.5: X-ray diffraction data of [Pd(QBD)Cl2]**

<table>
<thead>
<tr>
<th>Peak</th>
<th>d spacing experimental (calculated)</th>
<th>2θ experimental (calculated)</th>
<th>h k l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.2545 (7.2250)</td>
<td>12.20 (12.25)</td>
<td>0 2 0</td>
</tr>
<tr>
<td>2</td>
<td>6.3256 (6.3436)</td>
<td>14.00 (13.96)</td>
<td>0 2 1</td>
</tr>
<tr>
<td>3</td>
<td>4.3301 (4.3301)</td>
<td>20.40 (20.50)</td>
<td>3 0 1</td>
</tr>
<tr>
<td>4</td>
<td>4.0767 (4.0878)</td>
<td>21.80 (21.74)</td>
<td>1 0 3</td>
</tr>
<tr>
<td>5</td>
<td>3.4795 (3.5038)</td>
<td>25.60 (25.42)</td>
<td>2 1 3</td>
</tr>
<tr>
<td>6</td>
<td>3.0582 (3.0841)</td>
<td>29.20 (28.95)</td>
<td>1 0 4</td>
</tr>
<tr>
<td>7</td>
<td>3.0582 (3.0737)</td>
<td>29.20 (29.05)</td>
<td>1 3 3</td>
</tr>
<tr>
<td>8</td>
<td>3.0582 (3.0531)</td>
<td>29.20 (29.25)</td>
<td>4 2 0</td>
</tr>
<tr>
<td>9</td>
<td>2.7967 (2.7925)</td>
<td>32.00 (32.05)</td>
<td>0 5 0</td>
</tr>
<tr>
<td>10</td>
<td>2.7967 (2.7950)</td>
<td>32.00 (32.02)</td>
<td>2 1 4</td>
</tr>
<tr>
<td>11</td>
<td>2.4551 (2.4538)</td>
<td>36.60 (36.62)</td>
<td>0 1 5</td>
</tr>
<tr>
<td>12</td>
<td>2.1127 (2.1310)</td>
<td>42.80 (42.41)</td>
<td>1 3 5</td>
</tr>
<tr>
<td>13</td>
<td>2.1127 (2.1250)</td>
<td>42.80 (42.54)</td>
<td>3 0 5</td>
</tr>
<tr>
<td>14</td>
<td>2.1127 (2.1170)</td>
<td>42.80 (42.71)</td>
<td>4 2 4</td>
</tr>
</tbody>
</table>
4.6 Conclusion

New complexes of the general formulae \([\text{PdLCl}_2]\) and \([\text{ML}_2\text{Cl}_2]\) (where \(\text{M}=\text{Rh(III)}\) or \(\text{Ru(III)}\); \(\text{L}=\text{QBD}, \text{MQBD}, \text{QBO}, \text{MQBO}, \text{NQTC}\) or \(\text{MNQTC}\)) have been isolated and characterized by physico-chemical methods. The molar conductance data indicates the non-electrolytic behaviour of all the complexes. While elemental analyses support their formulations, the spectral and magnetic data suggest the presence of square planar geometry around Pd(II) ion with coordination number four and octahedral environment around Rh(III) and Ru(III) ions with coordination number six.
Reference


