Synthesis, Characterization and Reactivity Studies of Some Mixed Ligand Complexes of Ruthenium (II) and Rhodium (III)

and

Novel Synthesis and Crystal Structure of Hydrotris(3,5-Dimethylpyrazolyl)Borate 1-Iminomethyl-3,5-Dimethylpyrazole Copper (II) Perchlorate

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A Thesis

submitted in fulfilment of the requirement for the Degree of

Doctor of Philosophy

To

North-Eastern Hill University

SHILLONG, INDIA

DECEMBER, 2000

To

My Parents and

Beloved pallavi sarkhel

DECLARATION

North-Eastern Hill University

December,2000

I **Prashanta Sarkhel**, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form the basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University / Institute.

This is being submitted to the North-Eastern Hill University for the degree of **Doctor of Philosophy** in Chemistry.

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CONTENTS

ABSTRACT

SYNTHESIS, CHARACTERIZATION AND REACTIVITY STUDIES OF SOME MIXED LIGAND COMPLEXES OF RUTHENIUM(II) AND RHODIUM(III)

AND

NOVEL SYNTHESIS AND CRYSTAL STRUCTURE OF HYDRO TRIS(3,5-DIMETHYLPYRAZOLYL)BORATE 1-IMINOMETHYL-3,5-DIMETHYLPYRAZOLE COPPER(II) PERCHLORATE

The thesis presents the results of investigations involving the synthesis, characterization and reactivity studies of (i) some mono and binuclear ruthenium(II) trifluoroacetato/arene complexes containing mono or bidentate co-ligands (ii) rhodium(III) complexes containing acetylacetonate and mono or bidentate ligands and (iii) novel synthesis, characterization and crystal structure of copper (II) amidine complex. The content of the thesis have been distributed over seven chapters.

Chapter 1 presents a brief introduction pertaining to the work described in the thesis. It describes in general, the rapid growth and diversification of interest in the study of chemistry of ruthenium and rhodium. The importance of ruthenium(II) complexes containing trifluoroacetato or arenes and other mono or bidentate ligands have been emphasized in this chapter.

The interest in β-diketonato complex due to the variety in bonding modes, their reactivity and catalytic activity and applications in various industrial processes is also described in Chapter 1. Apart from these, various complexes of copper with hydrotris(pyrazolyl)borate have been discussed with regards to their different synthetic methodologies, reactivity studies and structural aspects. Need to develop method to synthesize copper(II) amidine complex have been justified.

Chapter 2 describes the details of the methods of elemental analyses as well as the particulars of the instruments/equipments used for the characterization and structural assessment of the compounds which are described in chapter 3 to 7. The instruments/equipments used are : Infra-red, UV-visible spectrophotometers, ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR and ESR spectrometers, Conductivity meter, Vibrating Sample Magnetometer, Cyclic Voltameter and single crystal X-ray diffractrometer.

Chapter 3 of the thesis addresses to the simple and efficient methods for the synthesis of some mono and binuclear ruthenium(II) trifluoroacetato complexes containing nitrogen donor co-ligands of the type $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ and $[Ru\ (O_2CCF_3)_2L_4]$ (L = pyridine, 2-methylpyridine

or 3-methylpyridine) and $[Ru(L\text{-}L)_3](O_2CCF_3)_2$ (L-L = 2,2'-bipyridine or 1,10-phenanthroline). The characterization and structural assignments of the above complexes have been described, by making use of the elemental analyses and various physical measurements, as described in chapter 2. The IR spectra of the complexes containing trifluoroacetate show a strong absorption in the region 1630-1640 cm^{-1} for bridging, 1675-1690 cm^{-1} for unidentate and 1660-1670 cm^{-1} for ionic $\nu_{(OCO)asym}$ mode of vibration of the trifluoroacetato group(s). ^{1}H and ^{13}C NMR spectra of these complexes show signals in the aromatic region due to pyridine and substituted pyridines and ^{19}F NMR spectra of the complexes show signals due to fluorine in the region δ -76.00 to -77.00. The electrochemical studies show quasi reversible oxidation at $E°_{1/2}$ = 0.15 to 0.19 V for the mononuclear and at $E°_{1/2}$ = 0.80 to 0.90 V for the binuclear ruthenium(II) trifluoroacetato complexes, which is in conformity with the metal to ligand charge transfer bands observed in the electronic absorption spectra of the two systems.

Chapter 4 continues with ruthenium(II) trifluroacetato complexes with some of the co-ligands. The complexes are of the type $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$, $[Ru(O_2CCF_3)_2(CO)(EPh_3)_3]$ (E = P or As) , $[Ru(O_2CCF_3)_2(Me_2SO)_3]$ and $[Ru(O_2CCF_3)_2(Me_2SO)(EPh_3)_2]$ (E = P or As). The bonding modes of trifluoroacetate(s) have been diagnosed with the help of IR and ^{19}F NMR spectral studies. Except $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ in all other complexes trifluoroacetate is bonded to the metal in a unidentate

fashion. The dimethylsulphoxide groups in $[Ru(O_2CCF_3)_2(Me_2SO)_3]$ and $[Ru(O_2CCF_3)_2(Me_2SO)(EPh_3)_2]$ (E = P or As) are found to be S-bonded as interpreted from the infrared and ^1H NMR data of the complexes.

In **Chapter 5** is described, the reactivity studies $[(p\text{-cymene})RuCl_2]_2$ and $[(p\text{-cymene})RuCl_2(EPh_3)]$ (E = P or As) with 4,4'bipyridine , which resulted in the formation of bridging binuclear complexes of the type $[\{(p\text{-cymene})RuCl_2\}_2(\mu\text{-}4,4'bipy)]$ and $[\{(p\text{-cymene})RuCl(EPh_3)\}_2(\mu\text{-}4,4'bipy)](BF_4)_2$ (E = P or As). Reaction of $[(p\text{-cymene})RuCl_2(PPh_3)]$ with imidazole yielded $[(p\text{-cymene})RuCl\ (PPh_3)(Im)](BF_4)$ (Im = Imidazole). All the complexes have been characterized with the help of elemental analysis and various physical methods described in chapter 2. The ^1H NMR studies confirm the presence of bridging 4,4'-bipyridine in the binuclear complexes.

Chapter 6 of the thesis presents the synthesis and characterization of $[RhCl_2(acac)(py)_2]$, $[RhBr_2(acac)(L)_2]$ (L = PPh_3, $AsPh_3$ or py) and $[RhBr_2(acac)(L\text{-}L)]$ (L-L = bipy or phen). The bromo acetylacetonato complexes of rhodium (III) were synthesized by a metathetic reaction of $[RhCl_2(acac)(acacH)]$ with LiBr *in situ,* followed by the addition of neutral monodentate / bidentate ligands. All the complexes were characterized with the help of analytical data and various physical methods as mentioned above. $[RhBr_2(acac)(L\text{-}L)]$ (L-L = bipy or phen) are found to have *cis*-geometry which was characterized by well resolved ^1H NMR spectra of the complexes.

Chapter 7 deals with the synthesis of a new copper(II) amidine complex *viz.* $[Tp^*CuL]ClO_4$ (Tp* = Hydrotris(3,5-dimethylpyrazolyl)borate and L = 1-Methylcarbaldimino-3,5-dimethylpyrazole). The Ligand(L) has been generated *in situ* by a condensation reaction of acetonitrile with 3,5-dimethylpyrazole activated by Cu(II). The X-ray crystal structure shows that the complex is monoclinic, space group Pc, a = 10.2879(7) A°, b = 7.8877(7) A°, c = 17.1301(14) A°, β = 96.896(6)°, V= 1380.01$A^{\circ 3}$, Z = 2, R = 0.388 and Rw = 0.1041. The three nitrogen atoms of Tp* and two nitrogen atoms of L are coordinating with Cu making a distorted square pyramidal geometry around the metal center. The compound has also been characterized by IR, UV-vis, ESR spectroscopies and Cyclic Voltametry.

The results of studies described in chapters 3,4,5,6 and 7 have been published, while a part of the work described in chapter 4 and 5 has been communicated for publication.

CHAPTER 1

Chapter 1

Introduction

Chemistry of ruthenium and rhodium complexes have shown growing interest among researchers during the past three decades, due to their applications in diverse fields such as homogenous catalysis, organic synthesis, material science, clusters, electrochemistry, biology and medicine. This is reflected in the publications of several monographs and reviews on different facets of the chemistry of these metals [1-14].

The chemistry of ruthenium complexes has been evoking interest among the inorganic chemists due to their interesting molecular structures and physical and chemical behaviors too [4-6]. One of the most important and useful collection on ruthenium chemistry is a monograph by Seddon and Seddon [6]. Several other reviews on the organometallic chemistry, photochemistry, thermodynamics, medicinal applications and catalytic behavior of ruthenium and its complexes have also appeared, which justify rapidly growing and diversifying interest in ruthenium [7-14]. Ruthenium has $4d^7 5s^1$ electronic configuration. It has the widest range of oxidation states (from -2 to +8) compared to all other elements in the Periodic table [3-6]. Among these,+2 and +3 oxidation states are the most common ones [1-6].

Some of the important and interesting compounds of ruthenium(II) and ruthenium(III) are $[Ru(NH_3)_5(N_2)]Cl_2$ [15], $[Ru(NO)_2(PPh_3)_2]$ [16-18], $[RuCl_2(PPh_3)_3]$ [13,19], $[RuX_2(Me_2SO)_4]$ [20-21], $[RuX_3(PPh_3)_3]$ [22-23] (X = Cl or Br), and $[Ru(acac)_3]$ [24-26]. The importance of these compounds is due to their various physical, chemical , catalytic and structural behaviors. These compounds are good precursors also, for the synthesis of many ruthenium(II) or ruthenium(III) complexes [21,23,27]. $[Ru(bipy)_3]^{2+}$ and other related diimine complexes [6,12] are extensively used as sensitizers in photodriven chemical and physical processes such as photoinduced decomposition of water into hydrogen and oxygen. Such complexes are playing a key role in the development of photochemistry, photophysics,

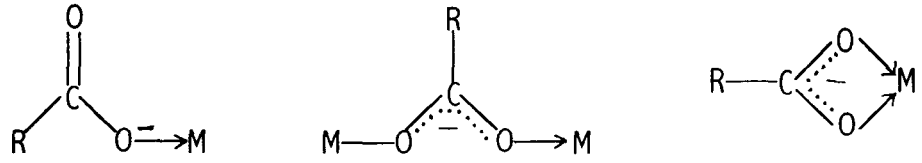
photocatalysis, photoelectrochemistry, chemi-and electrochemiluminescence and electron energy transfer. A number of Ru(III) amine and imine complexes *viz.* $[Ru(NH_3)_6]Cl_3$, $[RuBr(NH_3)_5]Br_2$, $[Ru(hypoxanthine)(NH_3)_5]Cl_3$ and $(ImH)[RuCl_4(Im)_2]$ (Im = imidazole) have shown antitumor activity [28].

Some (but by no means all) of the most notable examples of exciting new chemistry of ruthenium include :

- A reaction between $[Ru(CO)_5]$ and buckministerfullerene, C_{60}, in toluene produces $[Ru(CO)_4(\eta^2\text{-}C_{60})]$ [29].
- Molecular wires with directional photoinduced electron transfer, based on alkyne -substituted terpyridine ligands, have been developed. Complexes include such species as $[(terpy)Ru(\mu\text{-terpy-}C_4\text{-terpy})M((\mu\text{-terpy-}C_4\text{-terpy})Ru(terpy)]^{6+}$, (M = Fe, Co or Zn ; terpy = 2,2':6',2"-terpyridine) [30-31].
- A perfluorinated ruthenium(II) phthalocyanine complex, $[Ru(F_{16}Pc)]$ has been encapsulated in zeolite NaX, and used (in the presence of t-butylhydroperoxide) to oxidise cyclohexane at room temperature [32], while a simple water-soluble Ru(II) phthalocyanine complex , $K_3[Ru(Pc)L_2]$ (LH = diphenyl(phenyl-3-sulphonic acid) phosphine , is an exceptionally active agent for photodynamic cancer therapy [33].

- $[Ru(CO)_6]^{2+}$ has been prepared for the first time, as a thermally stable $[Sb_2F_{11}]^-$ salt, by the reductive carbonylation of $Ru(SO_3F)$ under one atmosphere of carbon monoxide at 60° to 90° C [34].
- Sr_2RuO_4 has been shown to be a copper-free superconductor [35,36].
- Gratzel has developed an efficient nanocrystalline photovoltaic device, using cis-di(thiocyanato)bis(2,2'-bipyridine-4,4'-dicarboxylato ruthenate(II) as the sensitiser [37].
- In perhaps one of the most elegant synthetic studies in ruthenium chemistry of the twentieth century, Newkome and co-workers have prepared ruthenium-containing dendrimers containing twelve ruthenium atoms [38]. Similarly from E.C. Constable's research group an 18-ruthenium dendrimer is also reported [39].

The carboxylato ligand finds wide application in transition metal chemistry due to various modes of coordination with metal ions [4-6]. Different modes of binding of carboxylates with a metal M, have been shown in Fig. 1.1.



(a) Unidentate (b) Bidentate Bridging (c) Bidentate Chelated

Figure 1.1 Various modes of bonding of carboxylates

Carboxylato complexes also feature extensively in homogenous catalytic systems [40-49] . The ligand characteristics of carboxylate anions and the structural features of many metal carboxylato complexes are of considerable theoretical interest [50-51]. A large number of metal carboxylates have been synthesised, but binuclear metal carboxylates $[M_2(\mu\text{-}O_2CR)_4]$ (where M = Cr, Co, W, Ru, Rh and Cu ; R = alkyl or aryl) [52-62] represent an important class of transition metal complexes. Binuclear carboxylato complexes have been used for the synthesis of diverse coordination and organometallic compounds [3,63-65]. Main types of the reactions include (a) those in which the $[M_2(\mu\text{-}O_2CR)_4]$ unit is retained [66,67]; (b) those where substitution of some or all the carboxylate ligands occurs (with or without redox processes at the M_2^{4+} core) [58] and (c) those where the binuclear unit is cleaved [58]. Tetra-μ-carboxylato-diruthenium complexes are known to exist both as homovalent Ru_2(II,II) and mixed valent Ru_2(II, III) species [55,58,68]. The first reported synthesis of the homovalent Ru_2^{4+} compounds of the type $[Ru_2(\mu\text{-}O_2CR)_4]$ (R = H, Me, Et, CH_2Cl or Ph) and the mixed valence Ru_2^{5+} core polymeric species $[Ru_2(\mu\text{-}O_2CMe)_4Cl]_n$ were from G. Wilkinson's group [58,69].

Trifluoroacetato complexes of ruthenium(II) and ruthenium(III) are of contemporary research interest. Some mixed ligand ruthenium trifluoroacetato complexes reported in the literature are :

$[Ru_2(\mu\text{-}O_2CCF_3)_4(tempo)_2]$ (tempo = 2,2',6,6'-tetramethylpiperidine-1-oxyl) [66], $[Ru(O_2CCF_3)_2(PPh_3)_2L]$, {L = PF_3, $PF_2(NMe_2)$} [67], $[RuH(O_2CCF_3)(PF_3)_2(PPh_3)_2]$ [67], $[Ru(O_2CCF_3)_2\{PF_2(O_2CCF_3)\}(PF_3)(PPh_3)]^+$ [67], $[Ru(O_2CCF_3)_2\{PF_2(NMe_2)\}_2(PPh_3)]$ [67], $[RuH(O_2CCF_3)(PPh_3)_3]$ [70], $[Ru(O_2CCF_3)(CO)(PPh_3)_2L]$ (L = H^-, NO_3^-, acac, hfacac) [71], $[RuH(O_2CCF_3)(CO)(PPh_3)_3]$ [71], $[RuH(O_2CCF_3)(CO)_2(PPh_3)_2]$ [71], $[Ru(O_2CCF_3)_2(CO)_2(PPh_3)_2]$ [71], $[Ru(O_2CCF_3)(NO)(PPh_3)_2]$ [71], $[RuH(O_2CCF_3)(NO)(PPh_3)_2]$ [71].

Some of the mixed ligand perfluorocarboxylato complexes of ruthenium have shown good homogenous catalytic activity in oligomerisation and hydrogenation of acetylenes [43], selective hydrogenation of alk-1-enes [44], hydrogenation of aldehydes and ketones [45-47] and dehydrogenation of primary, secondary and cyclic alcohols [48].

In view of the importance of carboxylato and perfluorocarboxylato complexes, an attempt has been made to synthesize and characterize some trifluoroacetato complexes of ruthenium(II) containing nitrogen donor ligands, such as pyridine, substituted pyridines and diimines, which is described in chapter 3 of the thesis.

Dimethylsulphoxide being an ambidentate ligand, can coordinate to a metal ion either through the oxygen atom or through the sulphur atom [72]. It was observed that sulphoxides coordinate to hard metals *via* the oxygen and to soft metals *via* the sulphur atom [73]. Ruthenium(II) and ruthenium(III) are not categorized clearly, either as hard or as soft acid,

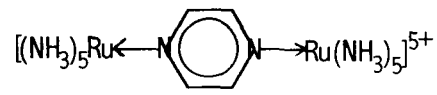
instead these are borderline metal ions among the two distinct categories of hard and soft acids [74]. Dimethylsulphoxide is a weak donor ligand, which can be easily replaced either wholly or partially by other ligands in a metal complex. The chemistry of halogeno dimethylsulphoxide complexes of ruthenium(II) and ruthenium(III) has been studied extensively [20,21,75-82]. Some of the important ruthenium(II) complexes with dimethylsulphoxide are : $[RuX_2(Me_2SO)_4]$ (X = Cl, Br or I) [21,76,81-82] and $[RuBr_2(Me_2SO)_3]$ [83]. They are also used as precursors for the synthesis of several ruthenium(II) complexes [20-21,84-85]. Ruthenium(II) complexes containing dimethylsulphoxide ligands are reported also for their catalytic activity e.g. oxidation of thioethers to sulphoxides with molecular oxygen [86-87] and hydrogenation of acrylamide to 1-aminopropane [88].

Few dimethylsulphoxide complexes of ruthenium(II) and ruthenium(III) *viz.* *cis*-$[RuCl_2(Me_2SO)_4]$, *trans*-$Na[RuCl_4(Me_2SO)(Im)]$ and *mer*-$[RuCl_3(Me_2SO)L]$ (L = NH_3, Im) exhibit antitumor activity and are relatively non-toxic [28,89-91]. In view of this, an attempt has been made to synthesize and characterize some ruthenium(II) complexes containing dimethylsulphoxide and trifluoroacetate. The findings of this work are described in chapter 4.

Arene as ligand has proven to serve effectively as an activating factor in hydrogen abstraction, generation of coordinatively unsaturated species by the liberation of ligands and stabilization of reactive intermediates. In recent years, the influence of arene ruthenium complexes in organic synthesis has

increased its importance due to their role as catalysts in various homogeneous reactions [92-98]. Arene ruthenium complexes are also very useful synthetic precursors for the synthesis of many zerovalent [99] and divalent [100-101] ruthenium compounds. Much of the earlier work was concerned with complexes of zerovalent metals and it was found that although the hydrocarbon ligands retain their aromatic character, they are generally deactivated towards electrophilic attack and activated towards nucleophilic attack relative to the free ligand [102]. Besides their novel structures and catalytic activity, arene ruthenium compounds also seem interesting because they offer an opportunity to investigate reactions of aromatic molecules coordinated to metal ions in different oxidation states [100-102].

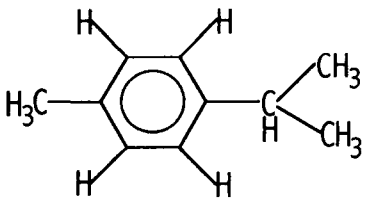
Inorganic chemists have been interested in the study of molecules in which two (or more) metal centers, linked by a bridging ligand of some sort, show a pronounced electronic interactions [103]. A beginning in this area was made by Creutz and Taube in early seventies [104], when they described $[\{(NH_3)_5Ru\}_2(\mu\text{-pyz})]^{5+}$ (pyz = pyrazine) ion. Following this



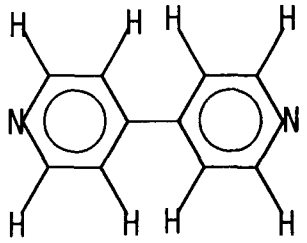
Creutz-Taube ion

discovery, a large number of complexes containing two Ru(II) or Ru(III) fragments have been reported with different bridging ligands. Very few

work is reported in the literature on arene ruthenium complexes containing bridging ligands [105-108]. In view of this, it was attempted to synthesize and characterize (p-cymene)ruthenium complexes containing 4,4'-bipyridine as bridging ligand.The results of the investigation are described in chapter 5.



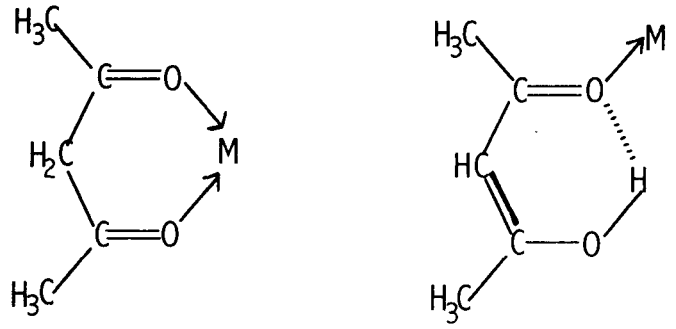
p-cymene



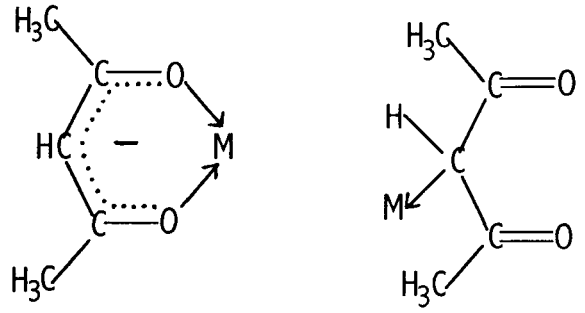
4,4'-Bipyridine

Ligands of the β-diketone type have played an important role in the development and practice of coordination chemistry [109-110]. Acetylacetone is the simplest β-diketone and forms compounds with most of the transition and non-transition metal ions [110]. The importance of metal acetylacetonato complexes is due to the variety in bonding modes displayed by acetylacetone molecule when coordinated to a metal ion [111]. Different bonding modes of acetylacetone/acetylacetonate are presented in Fig. 1.2.

The role of metal-acetylacetonates as catalyst in important organic reactions, such as polymerisation, hydrogenation, oligomerisation and isomerisation of olefins, hydrosilation of alkynes and oxidation of alcohols are well recognised [112-113]. Metal acetylacetonato complexes have also found application in various industrial processes e.g as additives in rubber, plastic and paint industries [114] and also as semiconductors [115]



(a) Keto form (b) Enol Form



(c) Chelated (d) C-bonded

Figure 1.2 Various modes of bonding of acetylacetone/acetylacetonate

and antioxidants [116]. Their ability to function as probes for NMR spectroscopic studies has rendered them as a useful class of NMR shift reagents [117]. The properties of β-diketone complexes, *viz.* the volatility and solubility in organic solvents are significant. Based on their volatile nature, yet another application of β-diketone complexes has recently

attracted active attention of researchers. This involves chemical vapor deposition (CVD) technique for making high quality film super conductors or superconducting ceramics and materials for micro-electronics applications [118-119].

A scrutiny of the literature reveals that there are few reports of the complexes of Rh(I), Rh(II) and Rh(III) containing acetylacetonate and other monodentate ligands [120-122]. Some mixed halogeno-β-diketonato complexes of Rh(III) are : $[RhCl(acac)_2(PPh_3)]$ [123] and $[RhCl(hfacac)_2]$ [124]. Few compounds of Rh(III) containing acetylacetone/acetylacetonate, chloride and other coligands have been reported from our research group [125], but no report on the synthesis of rhodium(III) complexes containing acetylacetonate, bromide and other co-ligands is available. Looking at the importance of β-diketonato complexes, work in this area was taken up. chapter 6 of the thesis describes the synthesis and characterization of some mixed ligand rhodium(III) acetylacetonato complexes.

In the early seventies S. Trofimenko synthesised a new class of ligands, known as poly(pyrazolyl)borate. The coordination chemistry of such ligands are being studied since then [126-127]. One compound of this class of ligands is hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) as shown in Fig. 1.3. Complexes containing poly(prazolyl)borate ligands have been extensively studied by inorganic, organometallic and bioinorganic chemists [126-127]. They have unusual structural features and chemical behavior. The complexes of copper(II) and copper(I) with tris(pyrazolyl)borate systems have been extensively used as models for biomimetic studies [128-129].

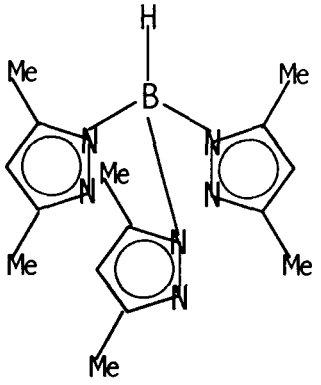


Figure 1.3 Hydrotris (3,5-dimethylpyrazoly)borate (Tp*)

It is interesting to note that the insertion of a nitrile group to an N-H moeity in presence of Cu(II) ion, gives rise to copper amidine complex which is otherwise difficult to synthesise, because imines with no substitution on the nitrogen atom are seldom available. Copper amidine complexes of this kind are rare [130] while there are some reports on other transition metals *viz.* ruthenium [131-132].

In chapter 7, is described the synthesis of a new five coordinate copper(II) complex, $[Tp^*CuL]ClO_4$ (L = 1-methylcarbaldimino-3,5-dimethylpyrazole). The structure of L, is given in Fig. 1.4.

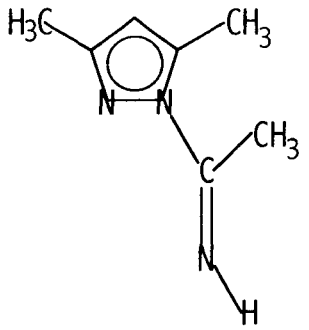


Figure 1.4 1-methylcarbaldimino-3,5-dimethylpyrazole(L)

The ligand(L) has been generated in situ through the condensation of 3,5-dimethylpyrazole and acetonitrile under the influence of copper(II). The structure of the complex has been established by X-ray single crystal structure determination. It is also characterised by IR, UV-vis, EPR spectroscopies and cyclic voltametric studies.

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CHAPTER 2

Chapter 2

Methods of Elemental Analysis and Particulars of Instruments used for the characterization and structural assessment of the compounds

In this chapter methods employed for the quantitative analysis of various constituents in the compounds and the particulars of the instruments used for the characterization and structural assessment of the synthesized compounds are described.

2.1 Elemental Analysis

2.1.1 Carbon, Hydrogen and Nitrogen analysis

Carbon, Hydrogen and Nitrogen contents of the compounds were analyzed from the following Micro analytical laboratories.

(i) Regional Sophisticated Instruments Center, North-Eastern Hill university, Shillong.

(ii) Regional Sophisticated Instrumentation Center, Central Drug Research Institute, Lucknow.

(iii) Department of Inorganic Chemistry, Indian Association for Cultivation of Sciences, Jadavpur, Calcutta.

2.1.2 Chloride or Bromide Estimation

Chloride or Bromide was estimated by two different standard methods as reported in the literature [1].

Method 1 (Gravimetric method)

An accurately weighed amount of the compound was decomposed by heating with a melt of potassium nitrate and potassium hydroxide mixture (1:8) at around 800°C in a platinum crucible. It was cooled and extracted with water and then acidified with dilute nitric acid. The solution was digested on a water-bath for about an hour and filtered. Silver nitrate (0.1 M)

solution was added to the filtrate to precipitate silver chloride /silver bromide. The solution was further digested on a water-bath for one hour for coagulation of the precipitate. The precipitate was filtered through a sintered glass crucible (G-4), washed with very dilute nitric acid (1%) to free from silver nitrate and dried to a constant weight at 120°C. The precipitate was weighed as silver chloride or silver bromide

Method 2 (Volhard' s method)

An accurately weighed amount (~0.1g) of the compound containing chloride was decomposed with 100 cm^3 of 2% sodium hydroxide solution. The mixture was heated on a water-bath for 30 minutes to ensure complete decomposition. The hydrated metal oxide thus formed was separated by filtration and washed several times with water. The filtrate and the washings were collected for chloride estimation. The alkali chloride solution was neutralized with dilute nitric acid (1:1) and acidified chloride solution was then treated with an excess of standard silver nitrate solution. The suspension was heated to almost boiling and then stirred vigorously. The precipitated silver chloride was separated out by filtration and washed several times with water. The filtrate and the washings were collected and the unreacted silver nitrate was titrated with standard potassium thiocyanate solution, the volume of excess silver nitrate was calculated and this was separated from the volume of silver nitrate initially added. The difference is the volume of silver nitrate solution consumed for the precipitation of silver chloride.

2.2 Particulars of Instruments

2.2.1 Melting Point

Melting point of the compounds was measured using a Toshniwal CL 0302 melting point apparatus.

2.2.2 Conductance

The molar conductance measurements were made in a Wayne-Kerr Automatic Precision B905 conductometer. Solutions of milimolar strength were made in chloroform, acetonitrile. methanol, or dimethylsulfoxide.

2.2.3 Magnetic measurements

Magnetic susceptibilities of the complexes were measured on an EG & G PARC Vibrating Sample Magnetometer model-155 at room temperature in powder form.

2.2.4 Infra-red Spectra

The infra-red (IR) spectra of the compounds were recorded in KBr on the following spectrophotometer.

(i) Perkin Elmer model 297 in the range 4000-600 cm^{-1}

(ii) Perkin Elmer model 983 in the range 4000-400 cm^{-1}

(iii) FT-IR Bomen DA8 in the range 4000 -400 cm^{-1}

(iv) FT-IR Nicolet model 410 in the range 4000-600 cm^{-1}

2.2.5 Electronic Absorption Spectra

The UV-visible spectra were recorded on the following spectrophotometers in the region 1000 – 200 nm

(i) Hitachi model – 330 spectrophotometer

(ii) Beckman DU model 650 spectrophotometer

Milimolar solutions in chloroform, acetonitrile, methanol or dimethylsulphoxide were used for the measurements.

2.2.6 Nuclear Magnetic Resonance (NMR) Spectra

^{1}H NMR spectra of the compounds were recorded on the following spectrometer in various deutrated solvent viz. $CDCl_3$, CD_3CN, or $(CD_3)_2SO$.

(i) Varian –390, 90 MHz spectrometer

(ii) Brucker ACF-300, 300 MHz FT spectrometer

^{13}C and ^{31}P NMR spectra of the complexes were recorded on a Brucker ACF-300, 300 MHz FT spectrometer in $CDCl_3$ or CD_3CN.

^{19}F NMR spectra were recorded on an AMX-400 FT spectrometer. Tetramethylsilane was used as an internal standard for ^{1}H, and ^{13}C NMR, whereas H_3PO_4, and $CFCl_3$ were used as internal standards for ^{31}P and ^{19}F NMR spectra respectively.

2.2.8 Electrochemical measurements

The electrochemical measurements were carried out using a PAR model 370-4 electrochemistry system which includes the 174A polarographic analyser, 175 universal programmer, RE0074-X-Y recorder, 173 potentiostat, 170 digital coulometer and 377A cell system. The three electrode measurements were done with a planar Beckman model 39273 platinum inlay working electrode, a platinum wire auxiliary electrode and a saturated calomel electrode as reference. All the measurements were made at room temperature (298K) and the reported potentials are uncorrected for junction contribution. The electron-transfer properties of the complexes have been studied voltametrically in acetonitrile or chloroform solution at a platinum electrode in the range +1.5 to –1.5 V. All potentials are referenced to the saturated calomel electrode (SCE).

2.2.9 X-ray Determination

A green prismatic crystal of [Tp*CuL]ClO_4 was mounted on a glass fiber and used for the data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of $23.418 < \theta < 45.765$ in a Enraf Nonius CAD 4 automatic diffractometer [4]. Data were collected at 293K using CuKα ($\lambda = 1.54184$ A°) and the ω scan technique and corrected

for lorentz and polarisation effects [5]. A semi-empirical absorption correction (ϕ scan) was made.

The structure was solved by Patterson methods [7] and subsequent difference Fourier maps were refined on F^2 by a full matrix least-squares procedure using anisotropic displacement parameters [8]. All hydrogen atoms were located from difference Fourier maps except those of the methyl groups which were located in their calculated positions (C-H 0.96 A°). The located H atoms were refined isotropically, whereas the calculated H atoms were refined using a riding model and an absolute configuration was established [9]. Atomic scattering factors were obtained from "International Tables for X-ray Crystallography" [10]. Computer programs PLATON [11], ZORTEP [12] and SCHAKAL [13] were used for molecular graphics.

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CHAPTER 3

Chapter 3

Convenient synthesis, Characterisation and Studies of some Mono and Binuclear Ruthenium(II) trifluoroacetato complexes containing nitrogen donor co-ligands

3.1 Introduction

Carboxylato compounds of ruthenium(II) and ruthenium(III) have attracted much attention due to their structural variety, catalytic activity and extensive chemistry[1-11]. Binuclear carboxylato compounds of the type $[M_2(\mu\text{-}O_2CCR)_4L_2]$ (M = Cr, Mo, W or Rh ; R = alkyl or aryl) have been used for the synthesis of diverse coordination and organometallic compounds [12-15]. Trifluoroacetato complexes of ruthenium(II) and ruthenium(III) are of contemporary research interest. Some of the binuclear,

Ru(II)-Ru(II) and Ru(II)-Ru(III) complexes reported recently, containing bridging trifluoroacetato groups are, $[Ru_2(\mu\text{-}O_2CCF_3)_4(O_2CCF_3)]_n$ [16], $[Ru_2(\mu\text{-}O_2CCF_3)_4]$ [16] and $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ [16,17] (L = thf, Me_2CO or 2,2',6,6'- trimethylpyridine-N-oxyl). These have been prepared by three step synthetic routes : (i) preparation of $[Ru_2(\mu\text{-}O_2CCH_3)_4]$ by a reaction of ruthenium trichloride with glacial acetic acid and sodium carbonate. (ii) followed by a reaction of $[Ru_2(\mu\text{-}O_2CCH_3)_4]$ with K_2CO_3 to give $\{K_3[Ru_2(\mu\text{-}O_2CO)_4].6H_2O\}_n$ and (iii) finally treatment of the ruthenium carbonate with trifluoroacetic acid and trifluoroacetic anhydride mixture at different conditions to yield the binuclear complexes mentioned above.

Mononuclear ruthenium(II) trifluoroacetato complexes containing some monodentate ligands were reported by the (i) reaction of ruthenium(II) dihydrido/chlorohydrido/dichloro complexes containing tertiary phosphine and/or carbonyl groups with trifluoroacetic acid [18,19] (ii) reaction of low oxidation state ruthenium carbonyls or nitrosyls containing triphenylphosphine with trifluoroacetic acid [18]. Some mononuclear ruthenium(II) trifluoroacetato complexes of the type $[Ru(O_2CCF_3)_2L_4]$ [16] were prepared by the reactions of the binuclear species mentioned above, with monodentate ligands, *viz* CH_3CN, ^tBuNC, py, CO and PPh_3.

The present work describes convenient methods for the synthesis of binuclear and mononuclear ruthenium(II) trifluoroacetato complexes containing nitrogen donor co-ligands of the type, $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ and $[Ru(O_2CCF_3)_2L_4]$ (L = pyridine, 2-methylpyridine or 3-methylpyridine).

Attempts to synthesise similar complexes using bidentate ligands resulted in the formation of the complexes of the type $[Ru(L\text{-}L)_3](O_2CCF_3)_2$ (L-L = 2,2'-bipyridine or 1,10-phenanthroline).

3.2 Experimental

All solvents were freshly distilled before use. $RuCl_3nH_2O$ was obtained from Arora-Mathey Ltd., Calcutta. Chemicals used were of Analar grade. Silver trifluoroacetate was prepared by a reaction of silver carbonate with trifluoroacetic acid.

3.2.1 Preparation of $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ (L = py, 2-Mepy or 3-Mepy)

To a solution of $RuCl_3nH_2O$ (0.10g, 0.38 mmol) in ethanol (15 cm^3), $Ag(O_2CCF_3)$ (0.25g, 1.13 mmol) was added and the mixture was boiled under reflux on a water-bath for 6h. A green solution was obtained, which was cooled and filtered. The filtrate was evaporated to dryness on a water-bath and the residue was dissolved in ethanol (20cm^3) and filtered again to remove silver chloride, if any. A green solution of ruthenium trifluoroacetate was obtained. Pyridine(py), 2-methylpyridine(2-Mepy) or 3-methylpyridine(3-Mepy) (0.5 cm^3) *as appropriate* was added to the filtrate, which was maintained under reflux on a water-bath for 2h. A brown crystalline compound separated out, which was isolated by centrifugation,

washed with dry ether and dried *in vacuo*. Yield : 0.14g, (45%) for $[Ru_2(\mu\text{-}O_2CCF_3)_4(py)_2]$, 0.13g (40%) for $[Ru_2(\mu\text{-}O_2CCF_3)_4(2\text{-}Mepy)_2]$, 0.15g (47%) for $[Ru_2(\mu\text{-}O_2CCF_3)_4(3\text{-}Mepy)_2]$.

3.2.2 Preparation of $[Ru(O_2CCF_3)_2L_4]$ (L = py, 2-Mepy or 3-Mepy)

The mother liquor obtained after separating the compound $[Ru(\mu\text{-}O_2CCF_3)_4L_2]$ (L = py, 2-Mepy or 3-Mepy), reported in the previous preparations, was concentrated to *ca.*. 5 cm^3 by heating, cooled and kept at room temperature for 3 days. A yellow compound crystallised out, which was separated out by centrifugation, washed with acetone several times and dried *in vacuo*. Yield : 0.08g (32%) for $[Ru(O_2CCF_3)_2(py)_4]$, 0.05g (19%) for $[Ru(O_2CCF_3)_2(2\text{-}Mepy)_4]$, 0.07g (26%) for $[Ru(O_2CCF_3)_2(3\text{-}Mepy)_4]$.

3.2.3 Preparation of $[Ru(L\text{-}L)_3](O_2CCF_3)_2nH_2O$ (when L-L = 2,2'-bipyridine, n = 3 and L-L = 1,10- phenanthroline, n = 6)

2,2'-Bipyridine (bipy) or 1,10-Phenanthroline (phen), *as appropriate* was added in a molar ratio $RuCl_3nH_2O$: L-L = 1 : 3 , to an ethanolic solution of ruthenium trifluoroacetate obtained, as in the preparation (3.2.1). The mixture was refluxed on a water-bath for 3h. The green solution turned to a brown solution. It was concentrated to *ca.* 2 cm^3 and cooled to room temperature. A compound was precipitated by the addition of dry

diethylether, which was isolated by centrifugation, washed with dry ether and dried *in vacuo*. Yield : 0.24g, (74%) for $[Ru(bipy)_3](O_2CCF_3)_2.3H_2O$, 0.28g (75%) for $[Ru(phen)_3](O_2CCF_3)_2.6H_2O$.

3.3 Results and Discussion

Ruthenium trifluoroacetato complexes with monodentate co-ligands such as pyridine, 2-methylpyridine or 3-methylpyridine have been prepared by a simpler method than the reported ones [16-21]. An ethanolic solution of ruthenium trifluoroacetate obtained by the metathesis of ruthenium trichloride with silver trifluoroacetate was treated with the monodentate ligand. Care was taken to completely remove the chloride as silver chloride. Reactions of the ethanolic solution of ruthenium trifluoroacetate with monodentate nitrogen donor ligands under different conditions yielded binuclear and mononuclear ruthenium(II) complexes of the type $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ and $[Ru(O_2CCF_3)_2L_4]$ where L = py, 2-Mepy or 3-Mepy. Previous attempts by Lindsay et al. [16] to obtain ruthenium trifluoroacetate complexes by the metathesis of $[Ru_2(\mu\text{-}O_2CCH_3)_4]$ with excess of $Ag(O_2CCF_3)$ were reported to be unsuccessful. A green mass, obtained by evaporating the solution of ruthenium trifluoroacetate, gave an analytical composition closely resembling to $Ru(O_2CCF_3)_2$. IR spectrum of the same shows absorptions at 1631 and 1427 cm^{-1} which could be assigned

to $\nu_{(OCO)asym}$ and $\nu_{(OCO)sym}$ respectively. Large value of $\Delta\nu = (\nu_{(OCO)\ asym} - \nu_{(OCO)sym})$ (Table 3.2) indicates symmetric bridging trifluoroacetato groups [16]. The electronic absorption spectrum of the green mass in ethanol showed bands at 880, 318(sh) and 260 nm. The presence of 880 nm band is indicative of the dimeric nature of $[Ru_2]^{4+}$ species (*vide infra*), which is necessary for the presence of bridging trifluoroacetato groups. Presence of absorptions at 318 nm and 260 nm are assigned to charge transfer bands (*vide infra*).

3.3.1 $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ (L = py, 2-Mepy or 3-Mepy).

Reactions of the green ethanolic ruthenium trifluoroacetate solution with pyridine and substituted pyridines yielded two products *viz.* $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ and $[Ru(O_2CCF_3)_2L_4]$ (L = py, 2-Mepy or 3-Mepy). $[Ru_2(\mu\text{-}O_2CCF_3)_4(py)_2]$ is insoluble in most of the organic solvents, whereas the substituted pyridine analogues are soluble in some of the organic solvents *viz.* chloroform and acetonitrile. Molar conductivity measurements (Table 3.1) of $[Ru_2(\mu\text{-}O_2CCF_3)_4\ L_2]$ (L = 2-Mepy or 3-Mepy) in chloroform conforms to their non electrolytic nature.

IR spectra of the complexes (Table 3.2, Fig. 3.1) showed a strong band around 1635 cm^{-1} which could be assigned to $\nu_{(OCO)asym}$ for a bridging or a chelating trifluoroacetate group. A band of medium intensity was also observed around 1445 cm^{-1} which may be due to a combination of $\nu_{(OCO)sym}$ of trifluoracetato and $\nu_{C\text{-}C}$ of pyridine. A preference of symmetric bridging

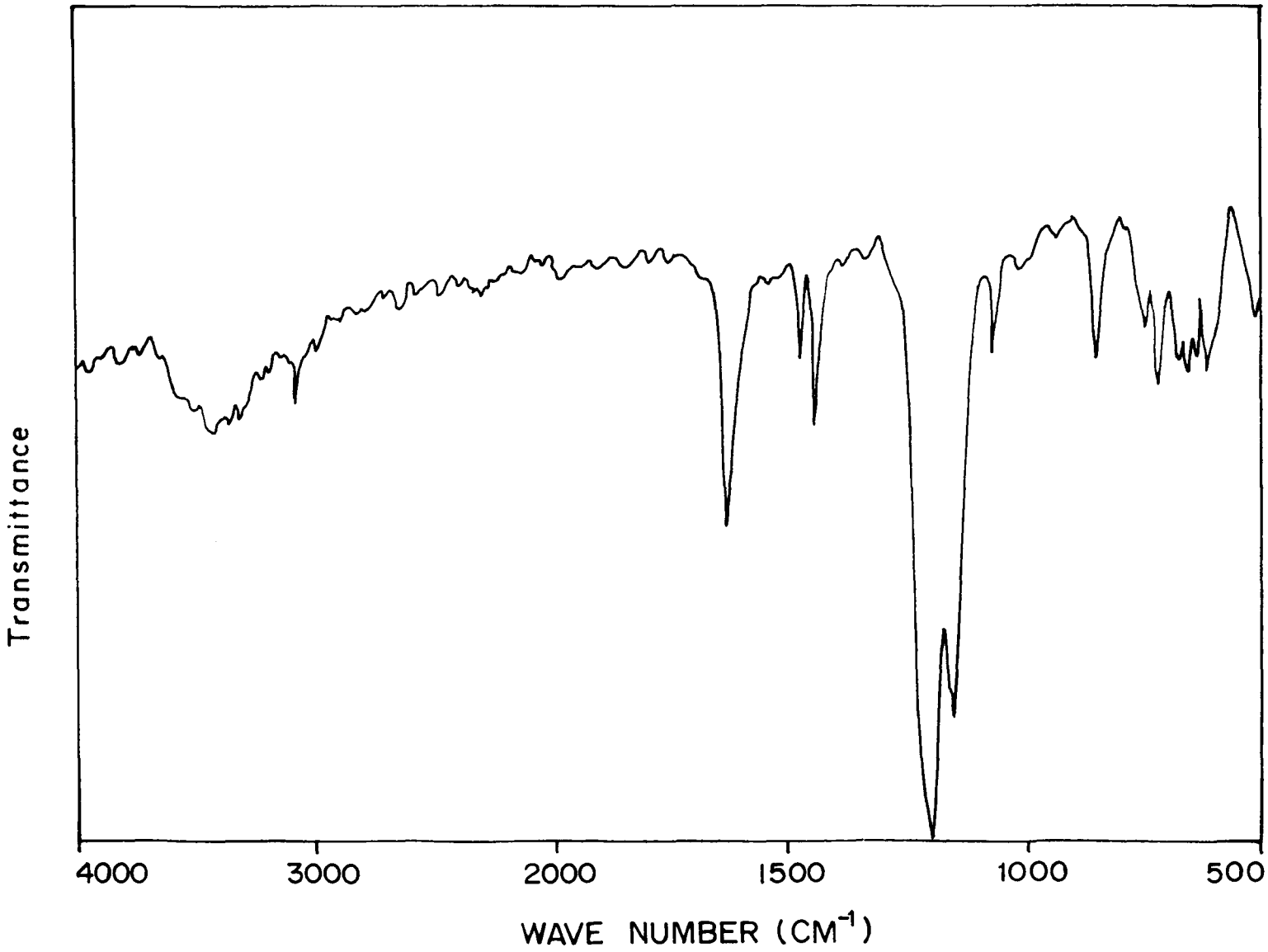


Figure 3.1 Infra-red spectrum of $[Ru_2(\mu\text{-}O_2CCF_3)_4(py)_2]$ using KBr pellet

coordination of trifluoroacetato groups to the two ruthenium centres, over a chelating trifluoroacetato group is due to (i) the similarity of IR spectra of these compounds with that of the green mass (*vide supra*) (ii) similar IR data are reported in the literature for analogous compounds having bridging trifluoroacetato groups [16] and (iii) the relatively large $\Delta\nu$ ($\nu_{(OCO)asym}$ - $\nu_{(OCO)sym}$) for the $O_2CCF_3^-$ [22]. Bands, characteristics of pyridine and substituted pyridines and $\nu_{C\text{-}F}$ (Table 3.2) were also observed for these complexes.

The magnetic measurements of $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ (L = py, 2-Mepy or 3-Mepy) in powder form at room temperature showed diamagnetic behaviour. This magnetic behaviour is not in confirmity with the reported Ru_2^{4+} species as in $[Ru_2(\mu\text{-}O_2CCF_3)_4]$ and $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ (L = thf, Me_2CO or 2,2',6,6'-trimetylpyridine-N-oxyl) [16,17]. The magnetic behaviour of the above reported compounds corresponds to two unpaired electrons per binuclear unit assigned to the electronic configuration $\sigma^2\pi^4\delta^2\pi^{*3}\delta^{*1}$ or $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*3}$ as predicted by Norman et al. (Fig. 3.2 (a),(b)) [22]. The unique diamagnetic behaviour of the binuclear unit in the $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ (L = py, 2-Mepy or 3-Mepy) complexes, Ru_2^{4+} suggests a $\sigma^2\pi^4\delta^2\pi^{*4}$ electronic configuration (Fig. 3.2(c)), which is presumably due to the mixing of metal-metal orbitals and metal-ligand orbitals and this mixing perturbs the normal $\delta^* < \pi^*$ ordering, which is predicted by metal-metal bonding considerations alone [22]. Similar observations has been reported for the triazenido bridging Ru_2^{4+} species [16].

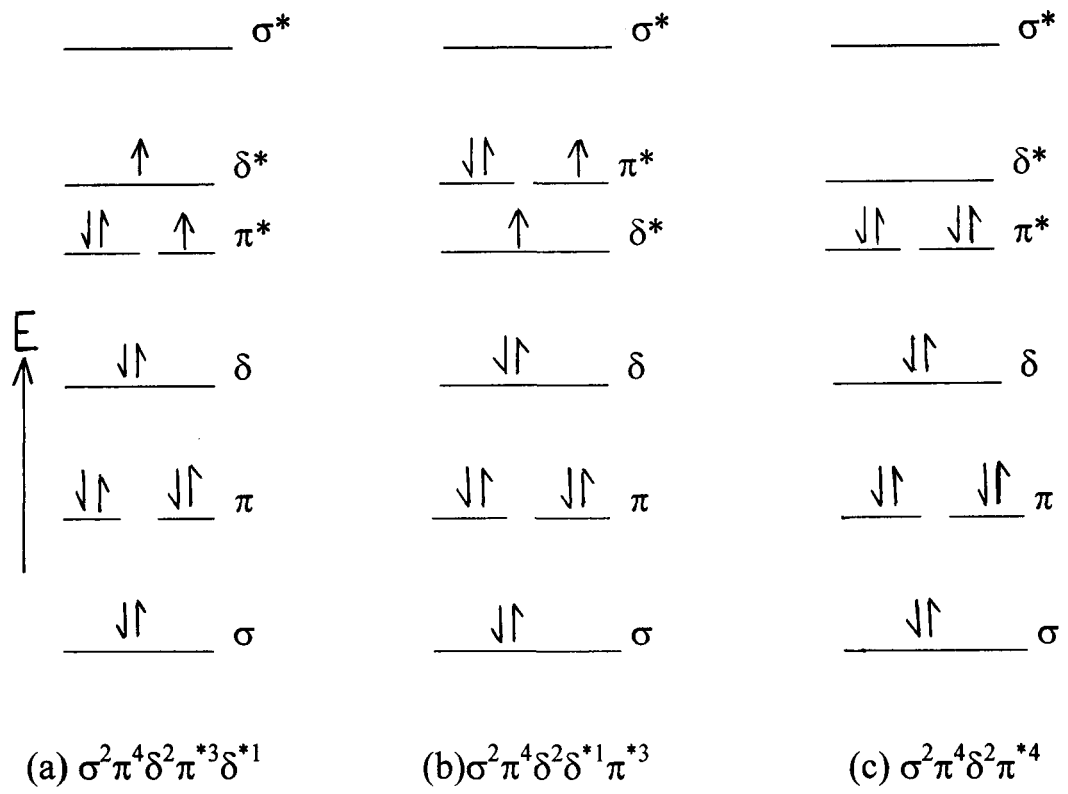


Figure 3.2 Electronic configuration of binuclear Ru_2^{4+} species according to Norman et al. [22]

The ^1H NMR spectrum of $[Ru_2(\mu\text{-}O_2CCF_3)_4(3\text{-Mepy})_2]$ (Fig. 3.3) in $CDCl_3$ showed a sharp singlet at δ 2.59 assigned to the methyl group of 3-methylpyridine. Other signals observed are at δ 7.77(t) and 7.89(d) corresponding to 5H and 4H of aromatic protons respectively and at δ 8.70 (s & d) corresponding to 2H and 6H of aromatic protons. Upon coordination, a shift towards the lower field was observed for all the proton signals in 3-methylpyridine compared to the free ligand [23]. ^{19}F NMR spectra of

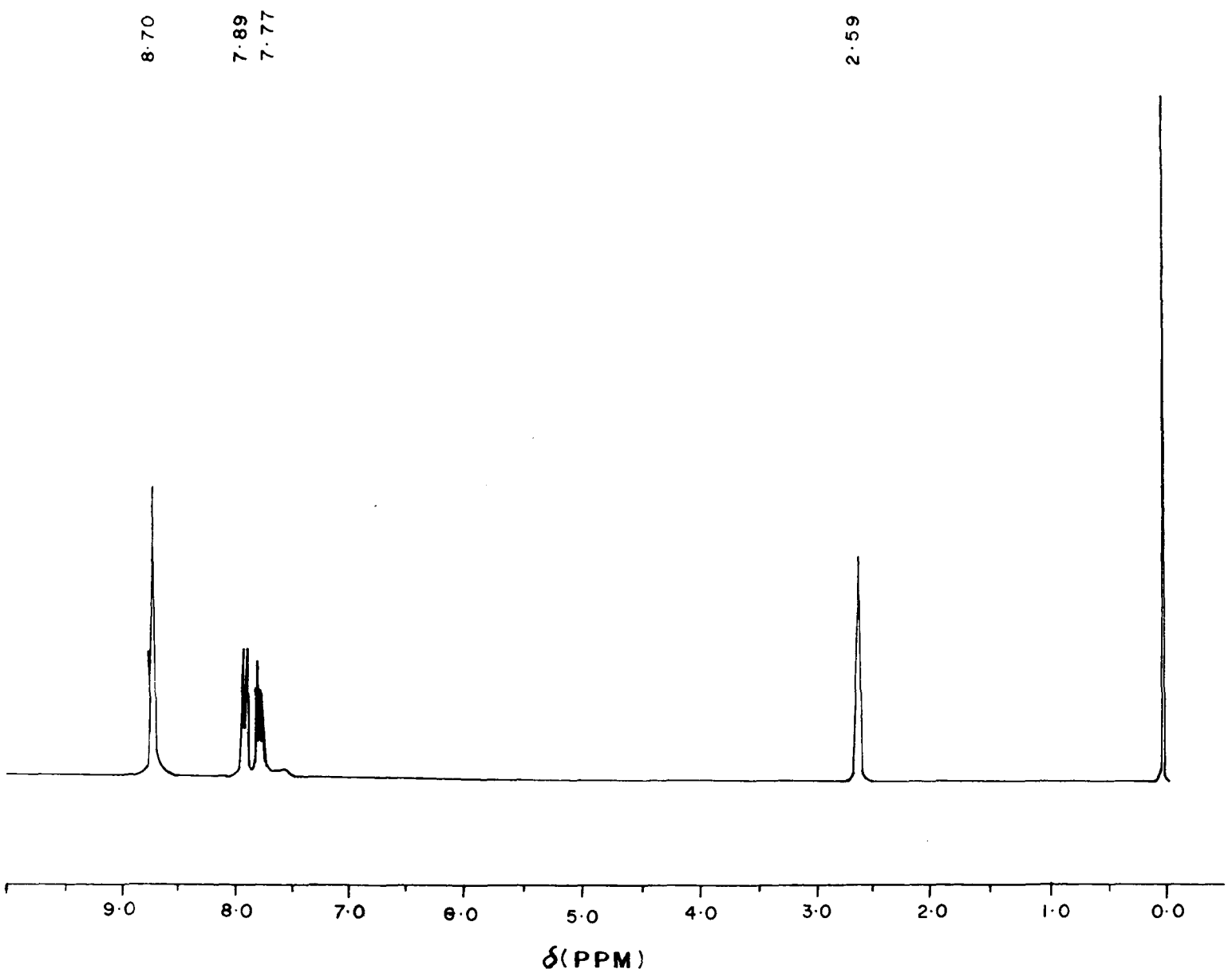


Figure 3.3 ^{1}H NMR of $[Ru_2(\mu\text{-}O_2CCF_3)_4(3\text{-}Mepy)_2]$ in $CDCl_3$

$[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ (L = 2-Mepy or 3-Mepy) in $CDCl_3$ showed a sharp singlet at δ -76.76 which is assigned to the three equivalent fluorine atoms in trifluoroacetato groups [16]. The electronic absorption spectra of $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ (L = 2-Mepy or 3-Mepy) (Table 3.3, Fig. 3.4(a)) in chloroform showed a broad band around 900 nm (ε_{max} = 2.8 x 10^2 dm^3 $mol^{-1}cm^{-1}$), a sharp band at 320 nm (ε_{max} = 3 x 10^3 $dm^3mol^{-1}cm^{-1}$) and one or two bands below 300 nm ε_{max} = 3.5 – 5.0 x 10^3 $dm^3mol^{-1}cm^{-1}$). The band at 900 nm is of the d-d type and may be assigned to the δ - δ* type of transition, (Fig. 3.2) as predicted by Norman et al. [22]. The band at 320 nm is of a charge-transfer nature and may be assigned to Ru - Ru(π*) → Ligand(π*) transition. Absorption below 280 nm may be assigned to the intraligand (π → π*) transitions. Cyclic voltammograms of $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ (L = 2-Mepy or 3-Mepy) (Table 3.4, Fig. 3.5) in CH_3CN using TBAP (tetrabutylammonium perchlorate) as supporting electrolyte, showed only one quasi-reversible oxidation wave at a positive potential ($E°_{1/2}$ = 0.8 to 0.9 V) corresponding to $Ru^{II}Ru^{II}$ -$Ru^{II}Ru^{III}$ oxidation *vs* SCE. On varying the scan rate from 0.02 to 0.2 $Vsec^{-1}$, a change in the ΔE_p value from (0.06 – 0.20 V) is observed, whereas $E°_{1/2}$ remains constant, confirming the quasi-reversibility of the system. No further oxidation ($Ru^{II}Ru^{III} \rightarrow Ru^{III}Ru^{III}$) is observed in the acetonitrile medium, which may be due to the extra- stability of the binuclear ($Ru^{II}Ru^{III}$) system as predicted by Norman et al. [22].

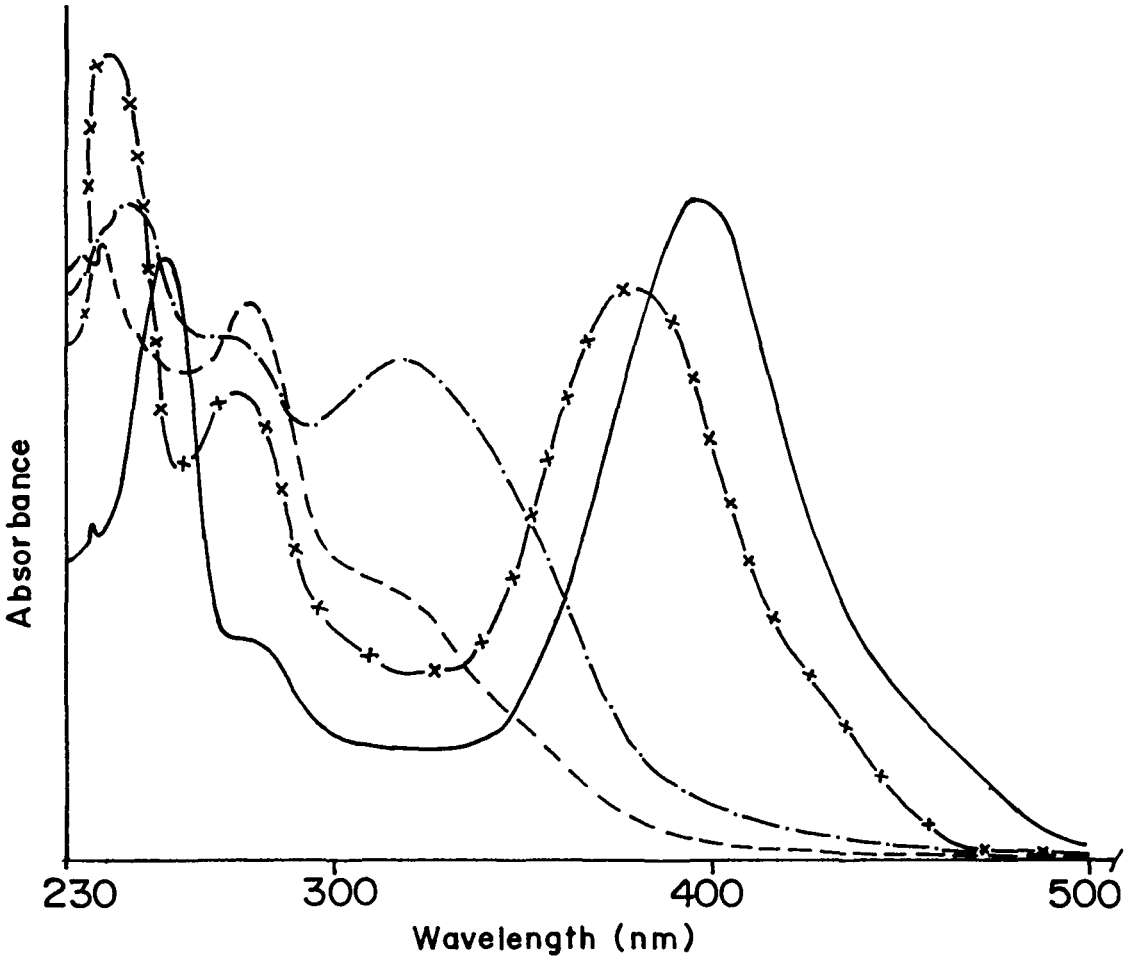


Figure 3.4 UV-visible spectra of (a) $[Ru_2(\mu\text{-}O_2CCF_3)_4(3\text{-}Mepy)_2]$ (·····), and $[Ru_2(\mu\text{-}O_2CCF_3)_4(2\text{-}Mepy)_2]$(-----) (b) $[Ru(O_2CCF_3)_2(py)_4]$ (-x-x-x) and $[Ru(O_2CCF_3)_2(3\text{-}Mepy)_4]$ (—) recorded in $CHCl_3$

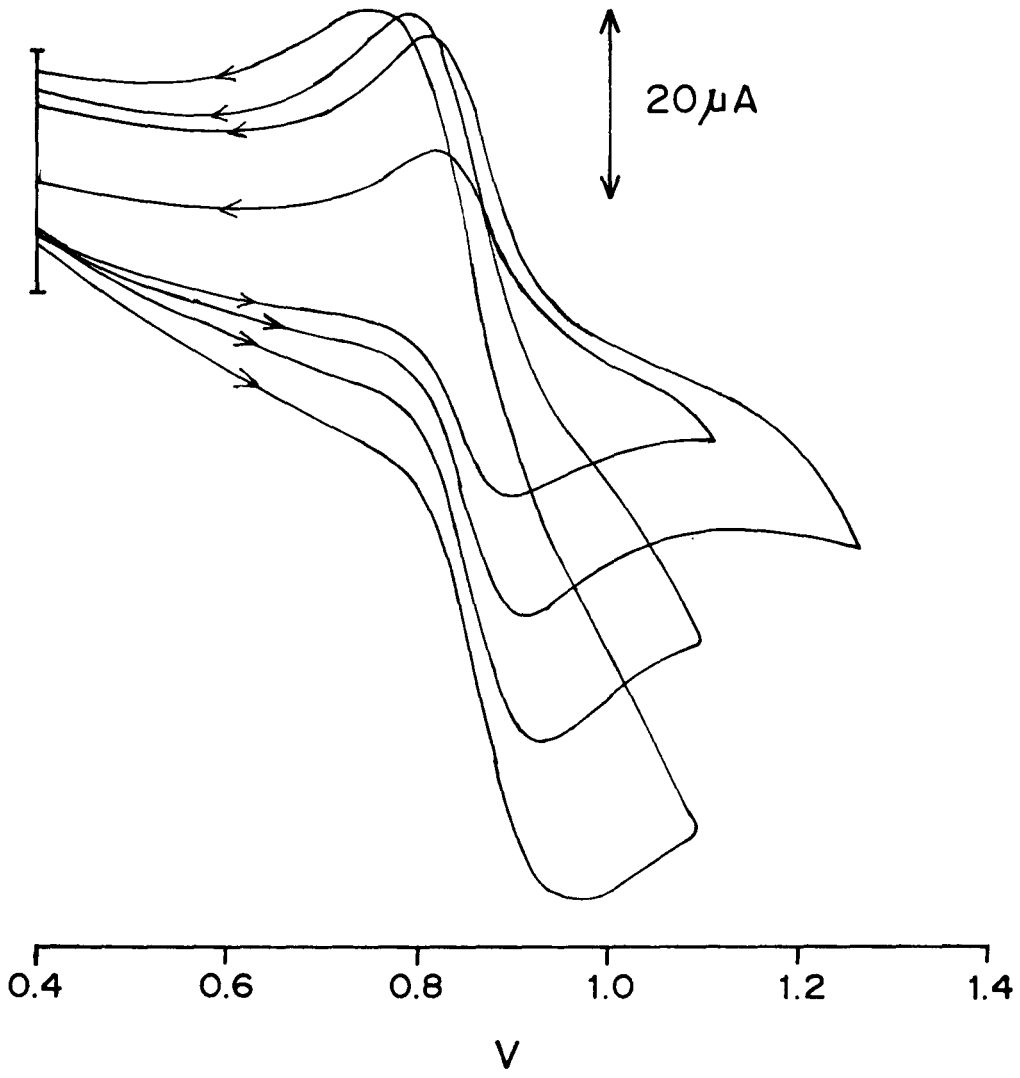


Figure 3.5 Cyclic voltammograms of $[Ru_2(\mu\text{-}O_2CCF_3)_4(3\text{-}Mepy)_2]$ in acetonitrile at room temperature, scan rates: 20, 50, 100 and 200 mV/s

3.3.2 *trans*-$[Ru(O_2CCF_3)_2L_4]$ (L = py, 2-Mepy or 3-Mepy)

Complexes of the composition $[Ru(O_2CCF_3)_2L_4]$ (L = 2-Mepy or 3-Mepy) presented in this work are new, whereas complex with L = py, was reported from Wilkinson's group [16] by a reaction of $[Ru_2(O_2CCF_3)_4]$ with pyridine. Conductivity measurements of the complexes (Table 3.1) conform to their molecular nature. IR spectra of the complexes (Table 3.2, Fig. 3.6) showed bands around 1680 and 1410 cm^{-1} attributable to $\nu_{(OCO)asym}$ and $\nu_{(OCO)sym}$ modes of vibration respectively of trifluoroacetato groups. Large $\Delta\nu$ value (270 cm^{-1}) clearly indicates a unidentate type of bonding for the trifluoroacetate anions [15,16]. Characteristic bands of pyridines / substituted pyridines and $\nu_{C\text{-}F}$ were also observed in the complexes. ^1H , ^{13}C and ^{19}F NMR spectral studies (Table 3.3, Fig.3.7,8,9) of $[Ru(O_2CCF_3)_2L_4]$ (L = py or 3-Mepy) are in conformity with the *trans*-trifluoroacetato groups. ^1H NMR spectra of $[Ru(O_2CCF_3)_2L_4]$ (L = py or 3-Mepy) in $CDCl_3$ showed signals at δ 8.40(s & d), 7.78(d) and 7.24(t) for pyridine and at δ 8.35 (s & d), 7.38(d) and 6.95(t) for 3-methylpyridine aromatic protons. A sharp singlet at δ 2.18(s) is attributable to the methyl protons of 3-methylpyridine. The ^{13}C NMR spectra of $[Ru(O_2CCF_3)_2L_4]$ (L = py or 3-Mepy) showed signals at δ 157.5, 136.0 and 124.4 for pyridine and at δ 158.0, 155.1, 134.8, 132.6, 122.5, and 18.4 for 3-methylpyridine. A shift towards low field δ 7-8 is observed for pyridine and 3-methylpyridine in ^{13}C NMR spectra of the above complexes compared to that of the free

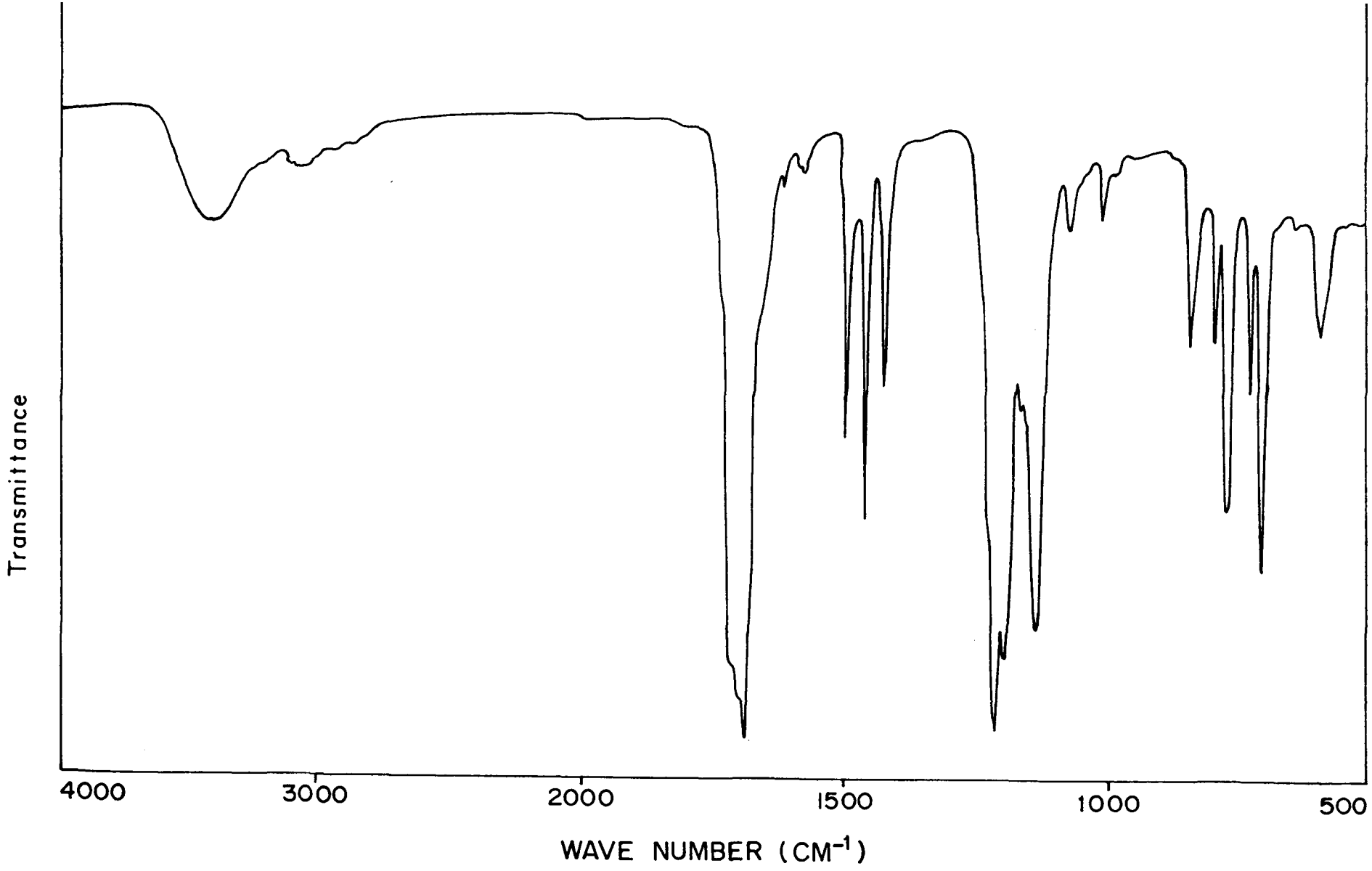


Figure 3.6 Infra-red spectrum of $[Ru(O_2CCF_3)_2(3\text{-Mepy})_4]$ using KBr pellet

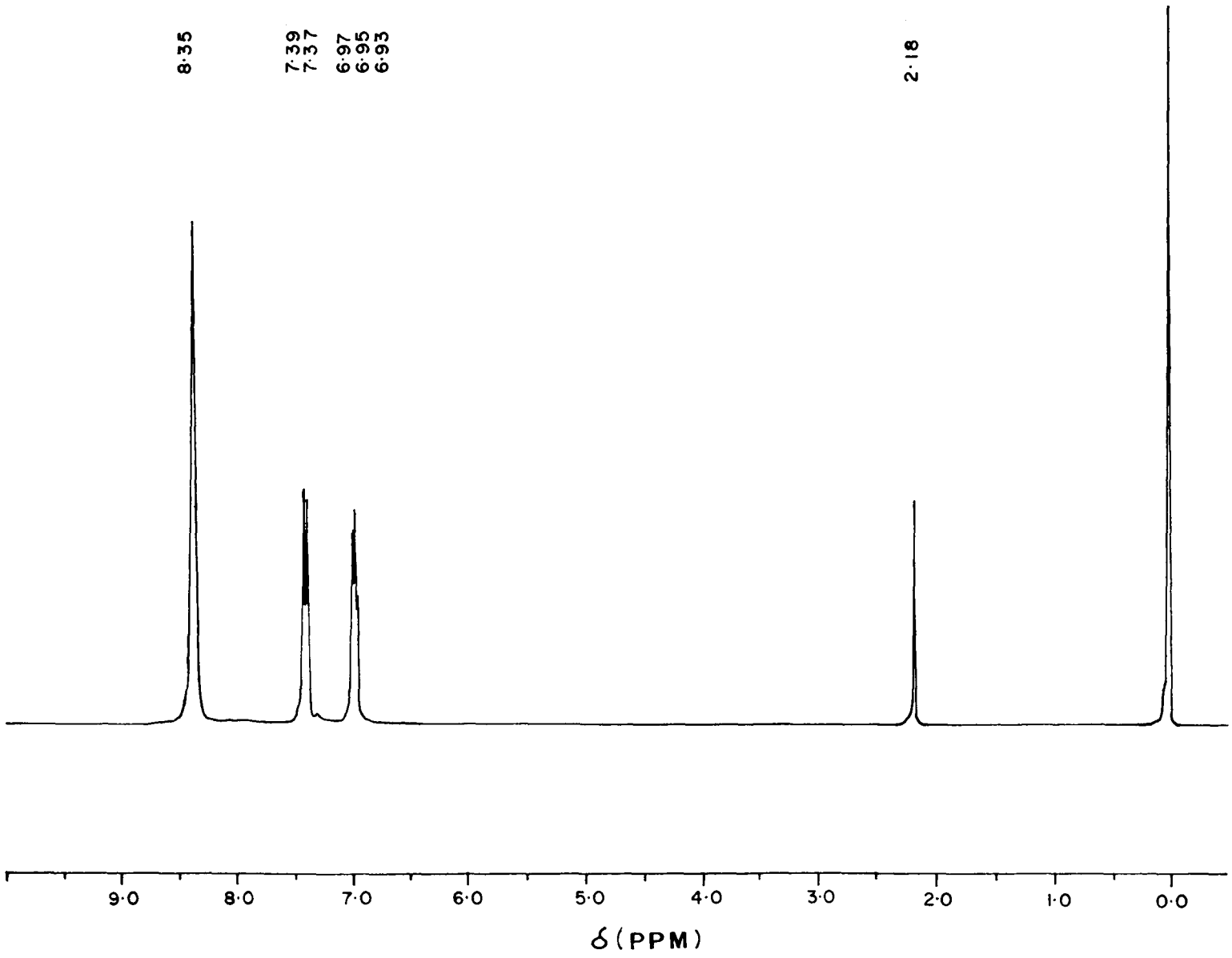


Figure 3.7 ^{1}H NMR spectrum of $[Ru(O_2CCF_3)_2(3\text{-Mepy})_4]$ in $CDCl_3$

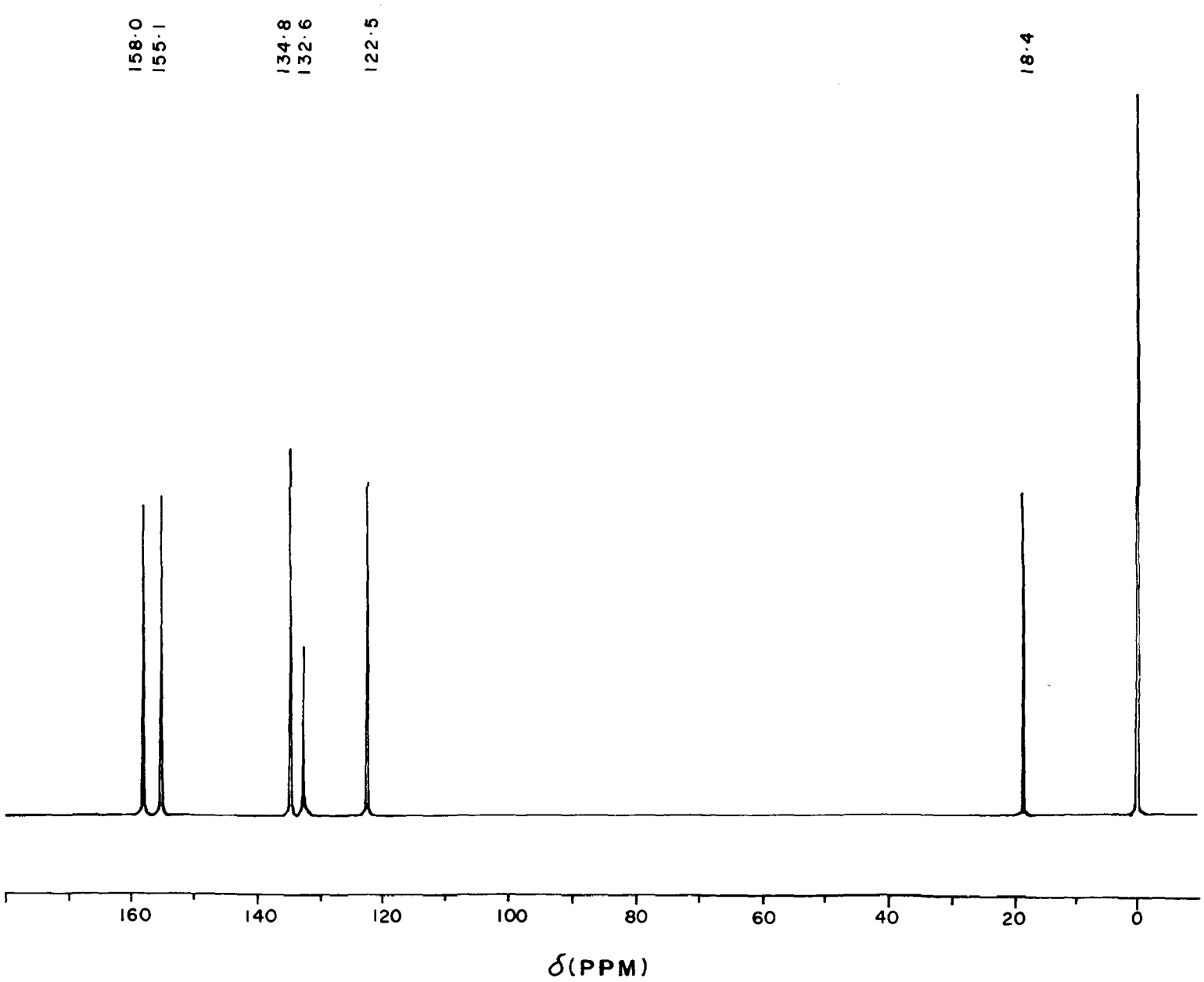


Figure 3.8 ^{13}C NMR spectrum of $[Ru(O_2CCF_3)_2(3\text{-Mepy})_4]$ in $CDCl_3$

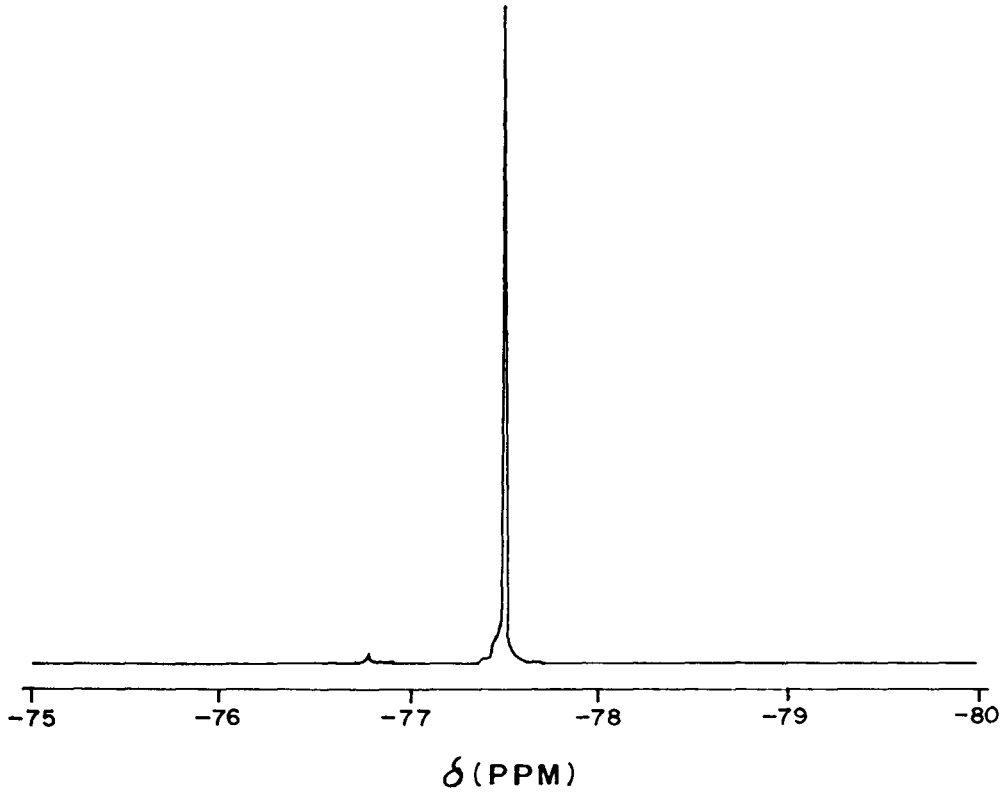
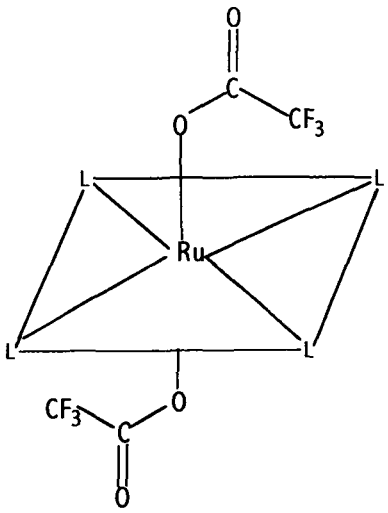


Figure 3.9 ^{19}F NMR spectrum of $[Ru(O_2CCF_3)_2(3\text{-Mepy})_4]$ in $CDCl_3$

pyridines [23]. The ^{19}F NMR spectra of $[Ru(O_2CCF_3)_2L_4]$ (L= py or 3-Mepy) showed a sharp singlet at δ -77.35 and δ -77.49 for L = py and 3-Mepy respectively, indicating a *trans* arrangement for the trifluoroacetato groups as in Fig. 3.10.



L = py, 2-Mepy or 3-Mepy

Figure 3.10 Structure of *trans*-$[Ru(O_2CCF_3)_2L_4]$ (L = py, 2-Mepy or 3-Mepy).

Diamagnetic nature of these complexes in powder form at room temperature, is assigned to a low spin d^6 configuration of the Ru(II) system. The electronic absorption spectra of *trans*-$[Ru(O_2CCF_3)_2L_4]$ (L = py, 2-Mepy or 3-Mepy) (Table 3.3, Fig. 3.4(b)) in chloroform showed an intense

band around 390 nm (ε_{max} = 7-9 x 10^3 $dm^3mol^{-1}cm^{-1}$), which could be assigned to metal → ligand (pyridine or substituted pyridines) charge transfer transition. Bands below 300 nm (ε_{max} = 10^3 -10^4 $dm^3mol^{-1}cm^{-1}$) may be assigned to intraligand transitions. The cyclic voltammograms of $[Ru(O_2CCF_3)_2L_4]$ (L = py, 2-Mepy or 3-Mepy) (Table 4, Fig. 3.11) in acetonitrile using TBAP as supporting electrolyte showed one quasi-reversible oxidation peak at a positive potential ($E°_{1/2}$ = 0.15 to 0.19 V) corresponding to Ru(II)/Ru(III) couple *vs* SCE. On changing the scan rate from 0.02 to 0.2 Vs^{-1}, a change in the ΔE_p values (0.08 to 0.20 V) is observed whereas $E°_{1/2}$ remains constant, thereby confirming the quasi-reversible nature of the system. The oxidation of the metal Ru(II) → Ru(III) in these complexes is observed at a lower potential ($E°_{1/2}$ = 0.15 to 0.19 V) compared to that of $Ru^{II}Ru^{II}$ → $Ru^{II}Ru^{III}$, ($E°_{1/2}$ = 0.8 to 0.9 V) the binuclear species (*vide supra*). This observation is in conformity with the metal to ligand charge transfer bands observed in the two systems. The lower oxidation potential ($E°_{1/2}$ = 0.15 to 0.19 V) peak for Ru(II) → Ru(III) is consistent with the high wavelength (380 nm) or low energy band in the electronic absorption spectrum, whereas the higher oxidation potential ($E°_{1/2}$ = 0.8 to 0.9 V) peak for $Ru^{II}Ru^{II}$ → $Ru^{II}Ru^{III}$ is consistent with the low wavelength (320 nm) or high energy band in the electronic absorption spectrum

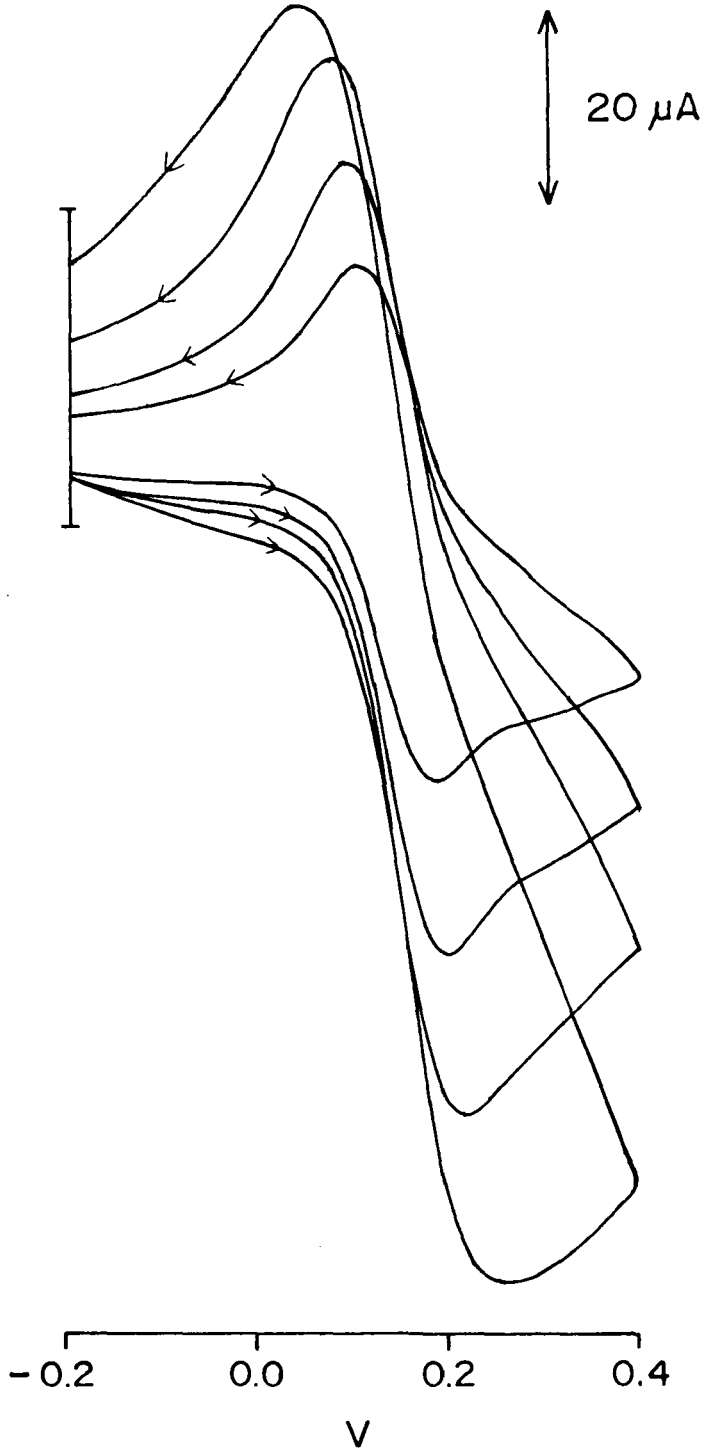


Figure 3.11 Cyclic voltammograms of $[Ru(O_2CCF_3)_2(3\text{-Mepy})_4]$ in acetonitrile at room temperature, scan rates : 20, 50, 100 and 200 mV/s

3.3.3 $[Ru(L\text{-}L)_3](O_2CCF_3)_2.nH_2O$ (L-L = 2,2'-bipyridine, n = 3; L-L = 1,10-phenanthroline, n = 6)

Reaction of a methanolic solution of ruthenium trifluoroacetate with bisimine ligands, *viz.* 2,2'-bipyridine or 1,10-phenanthroline in different molar ratios of Ru : bisimine (1 : 1 to 1 : 5) resulted in the formation of $[Ru(L\text{-}L)_3](O_2CCF_3)_2$ (L-L = bipy or phen) only. Low yield of the product was obtained when bisimine was used in lower molar ratio. Molar conductance of these complexes (Table 3.1) in acetonitrile and methanol conform to their 1 : 2 electrolytic behaviour. Diamagnetic nature of these complexes in powder form at room temperature is in confirmity with the low spin d^6 systems. IR spectra of these complexes showed a strong band around 1665 cm^{-1} assigned to $\nu_{(OCO)asym}$ mode of vibration for the ionic trifluoroacetato groups [16]. $\nu_{(OCO)sym}$ could not be assigned unambigously due to the presence of bis-imine bands in the region 1400 – 1500 cm^{-1}. The electronic spectra (Table 3.3) and the cyclic voltammetric studies (Table 3.4) are in agreement with those reported for $[Ru(L\text{-}L)_3]^{2+}$ (L-L = bipy or phen) [8].

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Table 3.1 Physical and Analytical data for ruthenium(II) complexes

Complex	Colour	m.p.(°C)	Λ_M $\Omega^{-1}cm^2mol^{-1}$	Analysis(%)[a]		
				C	H	N
$[Ru_2(\mu\text{-}O_2CCF_3)_4(py)_2]$	Brown	Above 350		26.84(26.60)	1.47(1.23)	3.37(3.45)
$[Ru_2(\mu\text{-}O_2CCF_3)_4(2\text{-}Mepy)_2]$	Brown	330[d]	3[b]	28.27(28.57)	1.83(1.67)	3.16(3.33)
$[Ru_2(\mu\text{-}O_2CCF_3)_4(3\text{-}Mepy)_2]$	Brown	330[d]	3[b]	28.26(28.57)	1.73(1.67)	3.54(3.33)
$[Ru(O_2CCF_3)_2(py)_4]$	Yellow	320[d]	5[b]	44.34(44.79)	2.98(3.11)	9.03(8.71)
$[Ru(O_2CCF_3)_2(2\text{-}Mepy)_4]$	Yellow	300[d]	4[b]	48.12(48.06)	4.21(4.01)	8.21(8.01)
$[Ru(O_2CCF_3)_2(3\text{-}Mepy)_4]$	Yellow	310[d]	5[b]	47.95(48.06)	4.23(4.01)	7.95(8.01)
$[Ru(bipy)_3](O_2CCF_3)_23H_2O$	Orange	Above 350	188[c], 294[e]	47.88(48.06)	3.51(3.53)	10.15(9.89)
$[Ru(phen)_3](O_2CCF_3)_26H_2O$	Brown	Above 350	196[c], 222[e]	49.19(49.23)	3.55(3.69)	8.77(8.61)

[a]Calculated values are in parenthesis; [b]In chloroform; [c]In methanol; [d]Decomposition temperature; [e]In acetonitrile

Table 3.2 Selected infrared data[a] (in cm^{-1}) for ruthenium(II) trifluoroacetato complexes

Complex	$\nu_{(OCO)asym}$	$\nu_{(OCO)sym}$	$\Delta\nu^{b}$	$\nu_{(C-F)}$
$[Ru_2(\mu\text{-}O_2CCF_3)_4(py)_2]$	1635	1446	189	1193, 1156
$[Ru_2(\mu\text{-}O_2CCF_3)_4(2\text{-}Mepy)_2]$	1630	1447	183	1203, 1155
$[Ru_2(\mu\text{-}O_2CCF_3)_4(3\text{-}Mepy)_2]$	1634	1442	192	1197, 1159
$[Ru(O_2CCF_3)_2(py)_4]$	1675	1408	267	1198
$[Ru(O_2CCF_3)_2(2\text{-}Mepy)_4]$	1679	1410	269	1208
$[Ru(O_2CCF_3)_2(3\text{-}Mepy)_4]$	1682	1410	272	1203
$[Ru(bipy)_3](O_2CCF_3)_2 3H_2O$	1665			1194, 1157
$[Ru(phen)_3](O_2CCF_3)_2 6H_2O$	1669			1195, 1162

[a]as KBr disc; [b]$\Delta\nu = (\nu_{(OCO)\,asym} - \nu_{(OCO)sym})$,

Table 3.3 NMR and UV-visible spectral data of ruthenium(II) trifluoroacetato complexes

Complex	NMR[a] δ(ppm)	UV-visible $\lambda_{MAX}(\varepsilon)$ nm
$[Ru_2(\mu\text{-}O_2CCF_3)_4(2\text{-}Mepy)_2]$[d]	δ(^{19}F) : -76.74(s)	900[b](290), 320(2720), 275(5080)
$[Ru_2(\mu\text{-}O_2CCF_3)_4(3\text{-}Mepy)_2]$[d]	δ(^{19}F) : -76.78(s) δ(^{1}H) : 8.70(s,d), 7.89(d), 7.77(t), 2.59(s).	900[b](270), 320(3360) 278(3600), 250(4500)
$[Ru(O_2CCF_3)_2(py)_4]$[d]	δ(^{19}F) : -77.35(s) δ(^{1}H) : 8.40(d), 7.78(t), 7.24(t) δ(^{13}C) : 157.5, 136.0, 124.4	380(9100), 274(7430), 240((12660)
$[Ru(O_2CCF_3)_2(2\text{-}Mepy)_4]$[d]		392(7445), 280(5400)
$[Ru(O_2CCF_3)_2(3\text{-}Mepy)_4]$[d]	δ(^{19}F) : -77.49(s) δ(^{1}H) : 8.35(s,d), 7.38(d), 6.95(t), 2.18(s) δ(^{13}C) : 158.0, 155.1, 134.8, 132.6, 122.5, 18.4	396(7260), 284(4380) 256(6590)
$[Ru(bipy)_3](O_2CCF_3)_23H_2O$[e]		446(13330),420[sh](11170), 390[sh](8730),350[sh](5290), 284(87090)
$[Ru(phen)_3](O_2CCF_3)_26H_2O$[e]		448(20000), 414[sh](19750), 310[sh](5122), 285(9300), 258(86000)

[a]s : singlet, d : doublet, t : triplet, q : quartet; δ(^{1}H) and δ(^{13}C) in ppm relative to $Si(CH_3)_4$; δ(^{19}F) in ppm relative to $CFCl_3$; [b]broad ; [sh]shoulder ; [d]UV-visible spectra in chloroform and [e]UV-visible spectra in methanol.

Table 3.4 Cyclic voltammetric data of ruthenium(II) complexes

Complex	$E^{a,d}_{pa}$(V)	$E^{b,d}_{pc}$(V)	$\Delta E^{c,d}_{p}$(V)	$E^{\circ e}_{1/2}$(V)
$[Ru_2(\mu\text{-}O_2CCF_3)_4(2\text{-}Mepy)_2]$	0.87	0.75	0.12	0.81
$[Ru_2(\mu\text{-}O_2CCF_3)_4(3\text{-}Mepy)_2]$	0.91	0.81	0.10	0.86
$[Ru(O_2CCF_3)_2(py)_4]$	0.24	0.14	0.10	0.19
$[Ru(O_2CCF_3)_2(2\text{-}Mepy)_4]$	0.20	0.10	0.10	0.15
$[Ru(O_2CCF_3)_2(3\text{-}Mepy)_4]$	0.20	0.09	0.11	0.15
$[Ru(bipy)_3](O_2CCF_3)_2\ 3H_2O$	1.36	1.26	0.10	1.31
$[Ru(phen)_3](O_2CCF_3)_2\ 6H_2O$	1.41	1.26	0.15	1.33

All $E^\circ_{1/2}$ values are referenced with respect to a saturated calomel electrode ; [a]CV, oxidation ; [b]CV reduction ; [c]E_{pa}-E_{pc} ; [d]Function of scan rate (0.02, 0.05, 0.10, 0.20 Vs^{-1}) values listed were obtained at scan rate = 0.05 Vs^{-1} ; [e](formal) redox potential. 0.1M tetrabutylammonium perchlorate used as a supporting electrolyte at room temperature.

CHAPTER 4

Chapter 4

Synthesis, Characterization and Reactivity Studies of some Ruthenium(II) trifluoroacetato complexes containing triphenylphosphine, triphenylarsine or dimethylsulphoxide

4.1 Introduction

Carboxylato complexes of platinum group of metals are useful synthetic precursors owing to the lability of the carboxylate ligands [1,2]. A large number of ruthenium carboxylato complexes have been synthesised and most of the known mononuclear acetato complexes contain triphenylphosphine as co-ligand [3]. Ruthenium acetato complexes also display various catalytic properties [2,4-14]. Interest in the chemistry of

trifluoroacetato complexes of ruthenium(II) and ruthenium(III) is reflected by the reported work in this area of research [15-20]. Some ruthenium(II) trifluoroacetato complexes containing tertiary phosphine and other monodentate ligands reported are : $[Ru(O_2CCF_3)_2(PPh_3)_2]$ [9], $[RuH(O_2CCF_3)(PPh_3)_3]$ [17(a)], $[Ru(O_2CCF_3)_2(CO)_n(PPh_3)_2]$ (where n= 1 or 2) [17(a,b)], $[RuH(O_2CCF_3)(CO)(PPh_3)_n]$ (n = 1 or 2) [17(a,b)], $[RuH(O_2CCF_3)(CO)_2(PPh_3)_2]$ [17(b)], $[Ru(O_2CCF_3)(CO)(PPh_3)_2L]$, (Cl, NO_3^-, acac, facfac, CH_3SO_3) [17(a,b,c)], $[Ru(O_2CCF_3)_2(PPh_3)_2L]$ (L = PF_3 or $PF_2(NMe_2)$) [18], $[Ru(O_2CCF_3)_2(PPh_3)\{PF_2(NMe_2)\}_2]$ [18], and *cis*-$[RuH(O_2CCF_3)(PPh_3)_2(PF_3)_2]$[18].

Most of the ruthenium(II) complexes containing trifluoroacetato group(s) listed above contain one or more molecules of triphenylphosphine. Compounds containing ruthenium(II), trifluoroacetato group(s) and having weak donor ligand, such as dimethylsulphoxide are not reported. The dimethylsulphoxide complexes of ruthenium(II) containing chloro or bromo anionic ligands are reported to be good catalysts for various homogenous oxidation reactions [21-24]. In view of this, it was felt that the synthesis and reactivity studies of ruthenium(II) trifluoroacetato complexes containing dimethylsulphoxide will be important and interesting.

In this chapter, we have described synthesis of some ruthenium(II) trifluoroacetato complexes containing monodentate ligands *viz.* triphenylphosphine, triphenylarsine, carbon monoxide or dimethylsulphoxide. These complexes have been characterized using various analytical and physical methods.

4.2 Experimental

All chemicals used are of AR or chemically pure grade. Solvents were purified prior to use by the standard methods. $RuCl_3nH_2O$ was used as received from Arora-Mathey Ltd., Calcutta. $[RuCl_2(Me_2SO)_4]$ was prepared according to the reported method [25].

4.2.1 Preparation of $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$

To a solution of $RuCl_3nH_2O$ (0.1g, 0.38 mmol) in ethanol(15 cm^3), $Ag(O_2CCF_3)$ (0.25g, 1.13 mmol) was added and the mixture was boiled under reflux on a water-bath for 6h. A green solution obtained, which was cooled and filtered. The filtrate was evaporated to dryness on a water-bath and the crude green mass was dissolved in ethanol(20 cm^3) and filtered again to remove silver chloride, if any. A green solution of ruthenium trifluoroacetate was obtained. A solution of triphenylphosphine (0.8g, 3.05 mmol) in ethanol(15 cm^3) was added to the ruthenium trifluoroacetate solution and the mixture was refluxed on a water-bath for 1h. A brown-yellow compound separated out which was isolated by centrifugation, washed several times with diethylether and dried *in vacuo*. Yield : 0.32g (60%).

4.2.2 Preparation of $[Ru(O_2CCF_3)_2(CO)(EPh_3)_3]$ (E = P or As)

Ruthenium trifluoroacetate solution, obtained as mentioned above (section 4.2.1), was evaporated to dryness on a water-bath. The green residue was dissolved in 2-ethoxyethanol(20 cm^3) and the solution was refluxed on a heating mantle for 2h. EPh_3 (E = P or As) was added (molar ratio Ru : EPh_3 = 1 : 8) to the hot solution and refluxed the mixture for 8h. A pale yellow colour solution was obtained, which was kept at room temperature for 2 days. A white crystalline solid crystallized out which was separated by centrifugation, washed with methanol and ether successively and dried *in vacuo*. Yield : 0.28g (64%) for $[Ru(O_2CCF_3)_2(CO)(PPh_3)_3]$ and 0.39g (80%) for $[Ru(O_2CCF_3)_2(CO)(AsPh_3)_3]$.

4.2.3. Preparation of $[Ru(Me_2SO)_3(O_2CCF_3)_2]$

To a solution of $[Ru(Me_2SO)_4Cl_2]$ (1.00 g, 2.07 mmol) in methanol (50 cm^3) , $Ag(O_2CCF_3)$ (0.95 g, 4.30 mmol) was added. The mixture was stirred at room temperature for 6h. AgCl precipitated out, which was separated by filtration. The filtrate was slowly evaporated at room temperature. Pale yellow crystalline solid obtained, which was washed with acetone and dry diethylether and dried *in vacuo*.Yield : 0.50g (43%).

4.2.4 Reaction of $[Ru(Me_2SO)_3(O_2CCF_3)_2]$ with triphenylphosphine

(i) A methanolic solution (25 cm^3) of $[Ru(Me_2SO)_3(O_2CCF_3)_2]$ (0.25 g, 0.44 mmol), was added to a solution of triphenylphosphine (0.47 g, 1.76 mmol) in methanol (20 cm^3). The mixture was stirred at room temperature for 6h, when a light yellow compound separated out. The compound was isolated by centrifugation, washed with dry diethylether and dried *in vacuo*. Yield : 0.24g (58%) of $[Ru(Me_2SO)(O_2CCF_3)_2(PPh_3)_2]$.

(ii) A reaction similar to 4.2.4(i) was carried out, except the mixture was refluxed on a water-bath for 3h. A brownish-yellow coloured compound separated out which was isolated by centrifugation, washed with dry diethylether several times and dried *in vacuo.* Yield : 0.30g (79%) of $[Ru(O_2CCF_3)_2(PPh_3)_2]$.

4.2.5 Reaction of $[Ru(Me_2SO)_3(O_2CCF_3)_2]$ with triphenylarsine

A solution of $[Ru(Me_2SO)_3(O_2CCF_3)_2]$ (0.25 g, 0.44 mmol) in methanol (20 cm^3) was added to a methanolic solution (20 cm^3) of triphenylarsine (0.55g, 1.79 mmol). The mixture was refluxed on a water-bath for 6h, when a light yellow compound separated out, which was isolated by centrifugation, washed with dry diethylether and dried *in vacuo*. Yield : 0.25g (55%) of $[Ru(Me_2SO)(O_2CCF_3)_2(AsPh_3)_2]$.

4.3 Results and Discussion

The green mass of ruthenium(II) trifluoroacetate is dimeric with bridging trifluoroacetates (*vide* chapter 3). A reaction of which with triphenylphosphine or triphenylarsine resulted in the formation of monomeric ruthenium(II) complexes. Cleavage of Ru-Ru bond is reported in binuclear carboxylato bridged species in presence of a tertiary phosphine [15]. When a reaction was carried out in ethanol medium, $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ was obtained, whereas 2-ethoxyethanol medium resulted in the formation of $[Ru(O_2CCF_3)_2(CO)(EPh_3)_3]$ (E = P or As). Reaction in 2-ethoxyethanol medium have been reported to yield carbonyl containing complexes [26]. Molar conductance value of $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ in acetonitrile (Table 4.1) conforms to its 1:1 electrolytic nature, while the carbonyl containing complexes are non-electrolytes. IR spectrum of $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ (Table 4.2, Fig. 4.1), shows two strong bands at 1670 and 1610 cm^{-1} which are assigned to $\nu_{(OCO)asym}$ mode of vibration for the ionic and chelated trifluoroacetato groups respectively [15,27]. $\nu_{(OCO)sym}$ for the unidentate coordination of trifluoroacetate is also expected around 1670 cm^{-1}. Since the molar conductivity measurement confirms that the complex is 1:1 electrolyte, hence 1670 cm^{-1} band is preferred to $\nu_{(OCO)asym}$ ionic over the unidentate trifluroacetate. IR spectra of $[Ru(O_2CCF_3)_2(CO)(EPh_3)_3]$ (E = P or As).(Table 4.2, Fig. 4.2) show two strong bands ~1915 and ~1690 cm^{-1} which may be assigned to $\nu_{(CO)}$ of the carbonyl group and $\nu_{(OCO)asym}$ of the

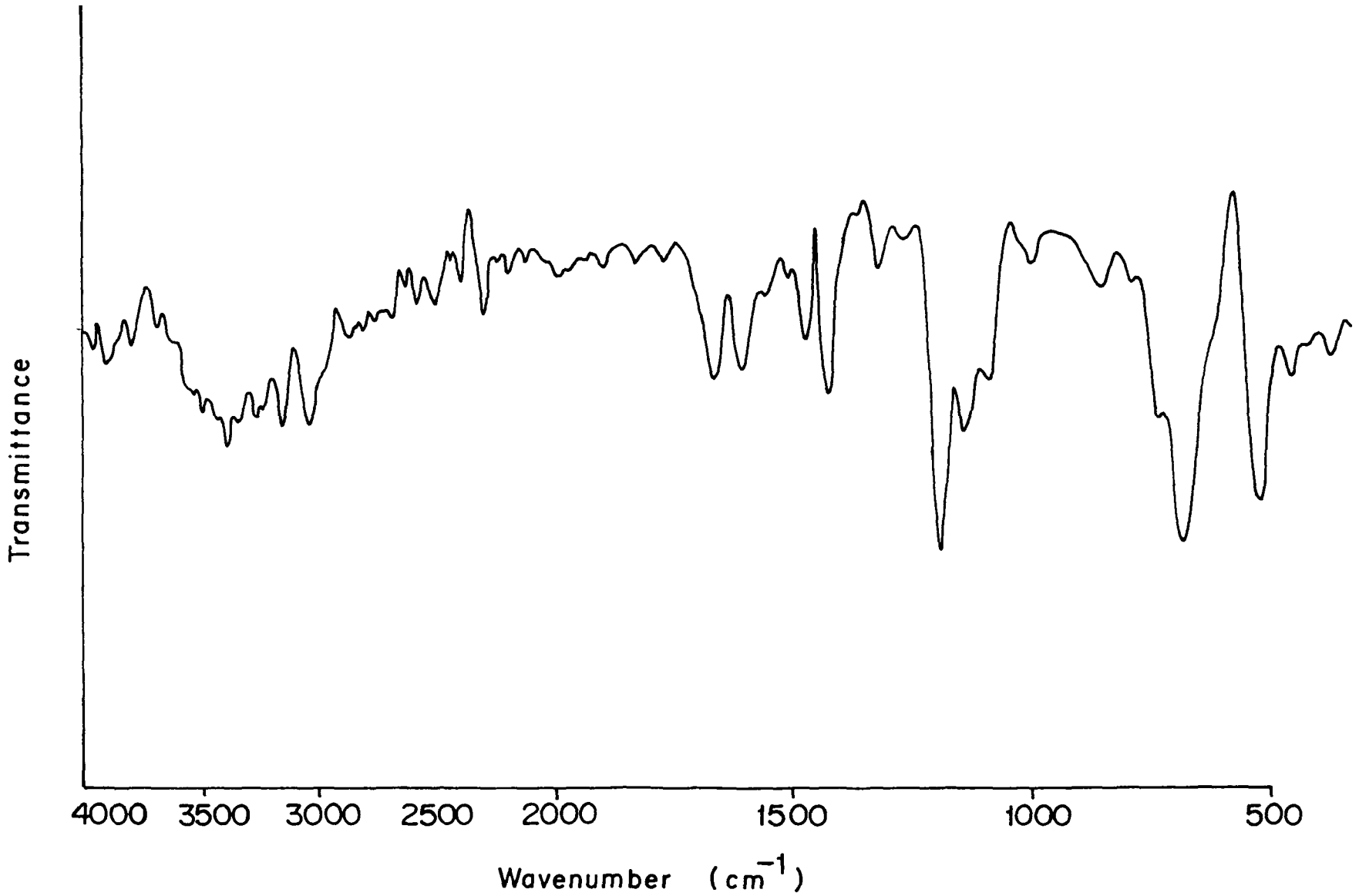

Figure 4.1 Infra-red spectrum of $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ recorded using KBr pellet

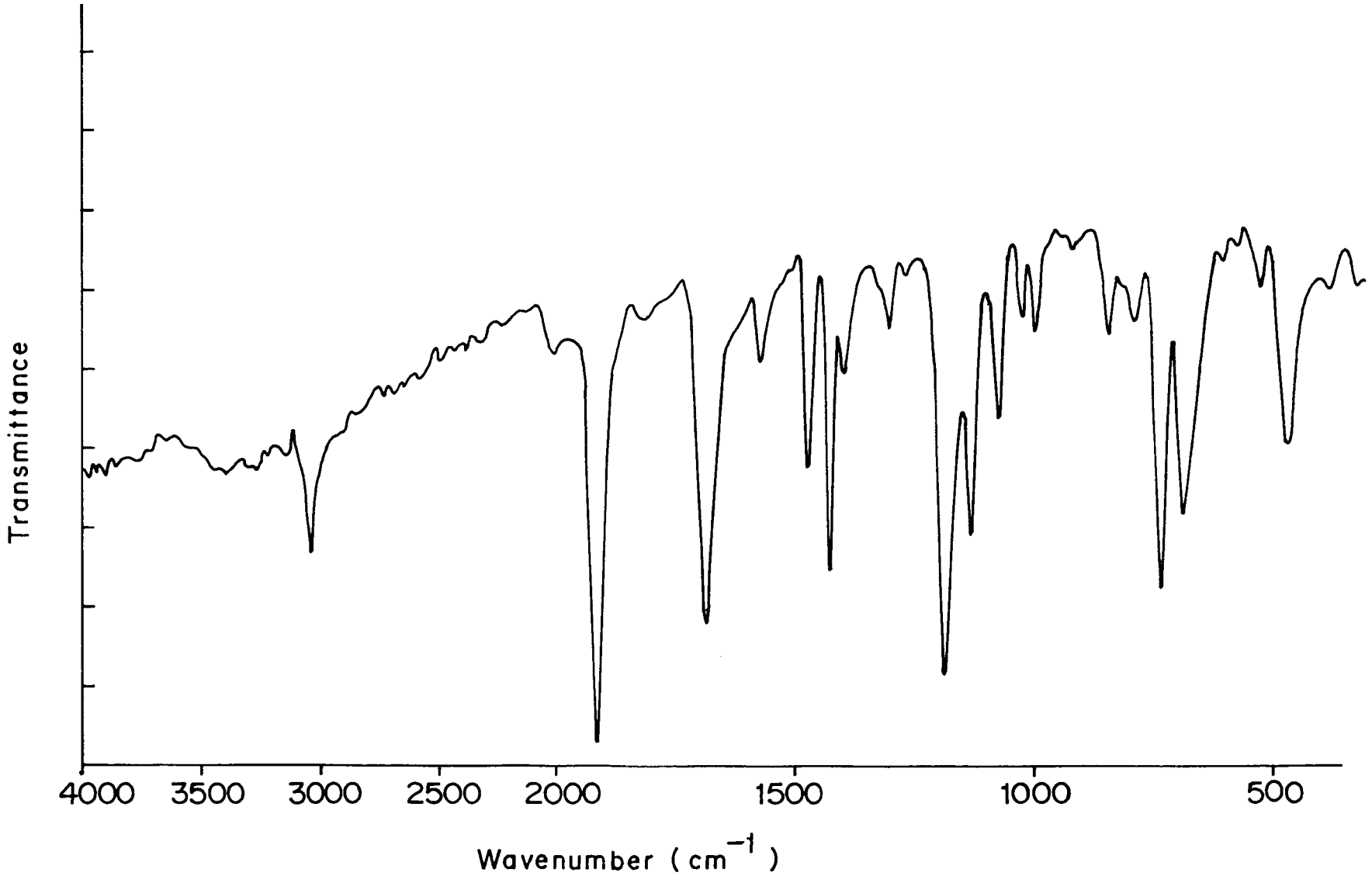

Figure 4.2 Infra-red spectrum of $[Ru(O_2CCF_3)_2(CO)(AsPh_3)_3]$ recorded using KBr pellet

unidentate trifluoroacetato group respectively [15, 27-28]. IR absorption bands due to $\nu_{(OCO)sym}$ are expected in the range *ca.* 1390–1440 cm^{-1}. Triphenylphosphine and triphenylarsine have also strong absorptions in this region. Hence an assignment exclusively due to $\nu_{(OCO)sym}$ mode of vibration of trifluroacetate is not possible.

^{19}F NMR spectrum of $[Ru(O_2CCF_3)_2(PPh_3)_4](O_2CCF_3)$ in $CDCl_3$ (Table 4.3, Fig. 4.3) shows signals at δ -76.80, -76.45 and -76.25. Signal at δ -76.80 may be assigned to CF_3 of the ionic trifluoroacetate and signals at δ -76.45 and δ -76.25 due to the CF_3 of the coordinated trifluoroacetato group. The intensity ratio of the signals due to the ionic and the coordinated trifluoroacetato group is 1:1. Presence of signals at two fields (at δ -76.45 and δ -76.25) for the coordinated trifluoroacetato group may be explained due to the partial change in the coordination behavior of trifluoroacetate in $CDCl_3$ solution, from chelated to unidentate because of steric hindrance of coordinated triphenylphosphine molecules [18]. ^{19}F NMR spectra of $[Ru(O_2CCF_3)_2(CO)(EPh_3)_3]$ (E = P or As) show a sharp singlet at δ -74.86 and δ -75.08 for the triphenylphosphine and triphenylarsine containing complex respectively, confirming that both the trifluoroacetato groups in each of the complexes are coordinated in a similar fashion. Magnetic susceptibility measurements of $[Ru(O_2CCF_3)_2(PPh_3)_4](O_2CCF_3)$ and $[Ru(O_2CCF_3)_2(CO)(EPh_3)_3]$ (E = P or As) in powder form at room temperature show that the complexes are diamagnetic, thereby conforming to the low spin Ru(II), d^6 system.

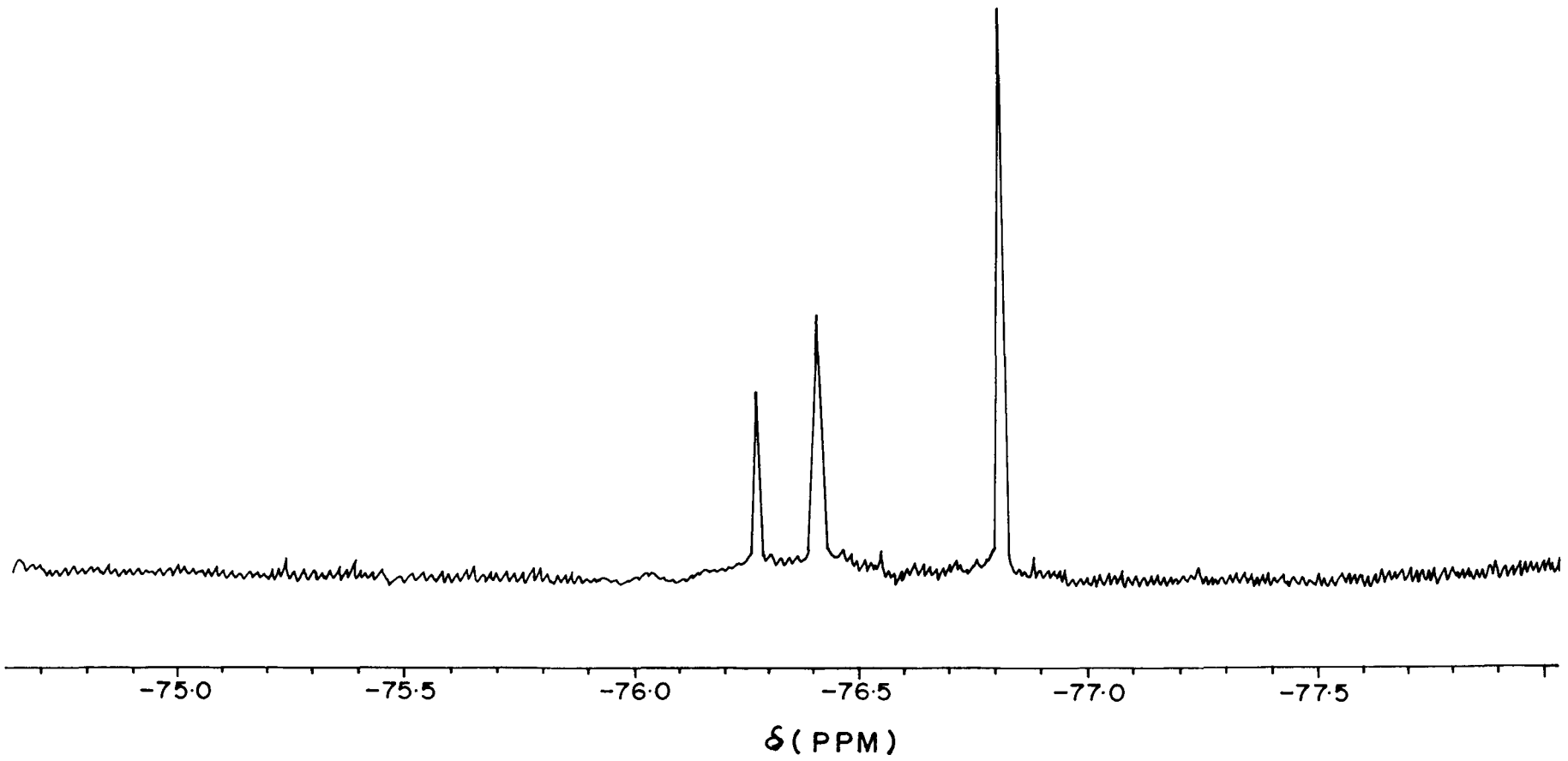

Figure 4.3 ^{19}F NMR spectrum of $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ in $CDCl_3$

The cyclic voltametric studies in acetonitrile of $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ and $[Ru(O_2CCF_3)_2(CO)(EPh_3)_3]$ (E = P or As) show one irreversible oxidation peak at a positive potential of 0.76 V and 0.56V (Fig. 4.4) respectively, inferring thereby that the trivalent state of ruthenium in all these complexes is unstable.The electronic absorption spectrum of $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ in chloroform (Fig. 4.5) shows a broad absorption band around 560 nm (ε = 1020 $dm^3mol^{-1}cm^{-1}$) and a shoulder around 380 nm. The former band may be assigned to a combination of d-d transition ($^1A_{1g} \rightarrow {}^1T_{1g}$ or $^1T_{2g}$) and a metal to ligand charge transfer transition and the later one to a metal to ligand charge transfer transition only [29].

A metathesis of chloride in *cis*-$[Ru(Me_2SO)_4Cl_2]$ by $Ag(O_2CCF_3)$ at room temperature resulted in the formation of $[Ru(Me_2SO)_3(O_2CCF_3)_2]$. The compound is diamagnetic and non-electrolytic in nature (Table 4.1), thereby confirming a low spin d^6, Ru(II) system having non-ionic trifluoroactates. The infrared spectrum of $[Ru(Me_2SO)_3(O_2CCF_3)_2]$ (Table 4.2, Fig. 4.6) showed strong and sharp bands at 1680 and 1425 cm^{-1} which could be assigned to $\nu_{(OCO)asym}$ and $\nu_{(OCO)sym}$ respectively of the trifluoroacetates. The large $\Delta\nu$ value (253 cm^{-1}) (*vide supra*, section 3.3) clearly indicates unidentate mode of bonding of trifluoroacetato groups [15,27]. Further, the spectrum shows one more strong and sharp band at 1116 cm^{-1} which is characteristic of $\nu_{(SO)}$ of the S-bonded dimethylsulphoxide groups [25]. No

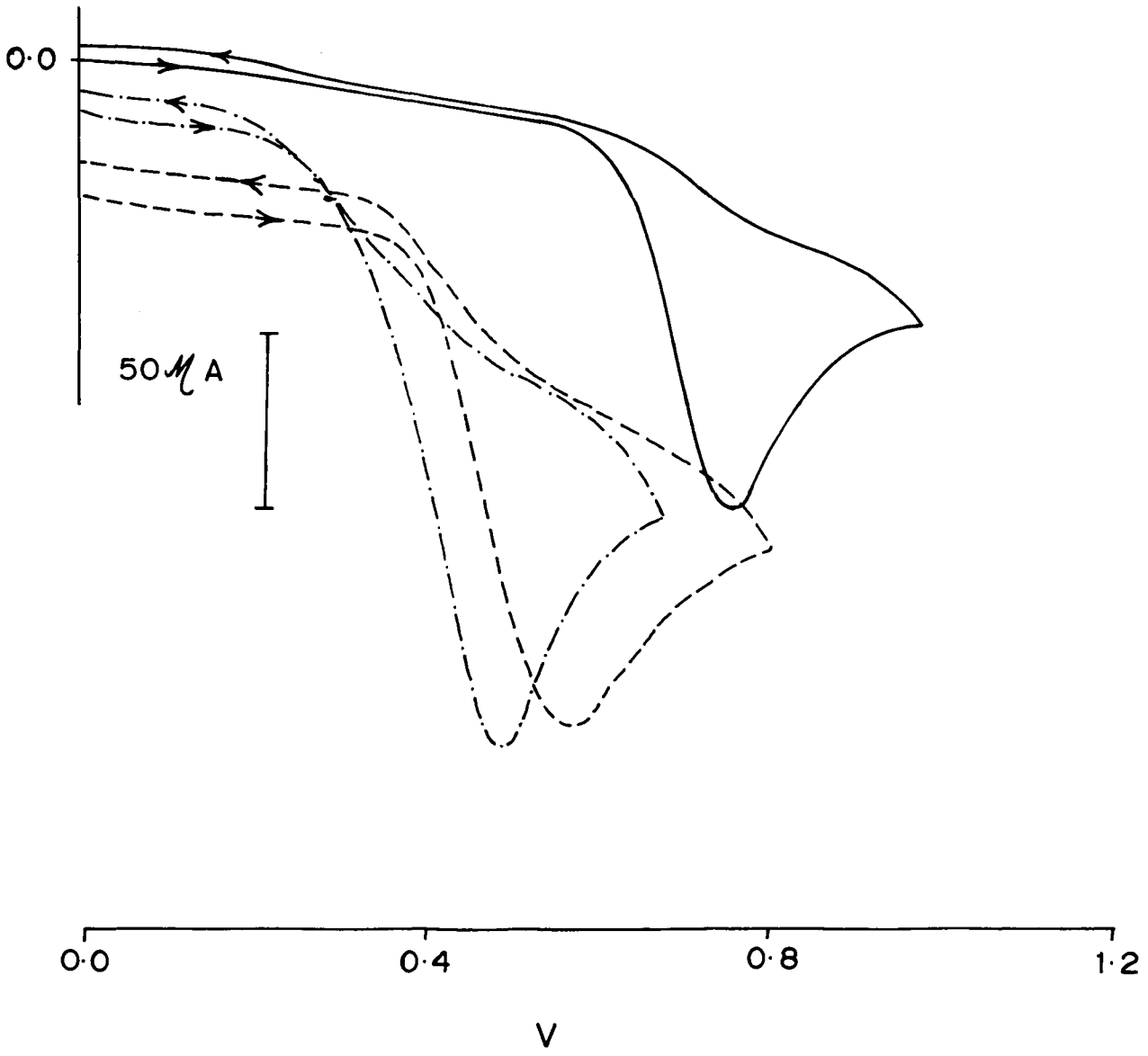

Figure 4.4 Cyclic voltammograms of $[Ru(O_2CCF_3)_2(CO)(AsPh_3)_3$ (——) $[Ru(O_2CCF_3)_2(CO)(PPh_3)_3]$ (----) and $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ (·-·-·-·) in acetonitrile at room temperature, scan rate 50 mV/s

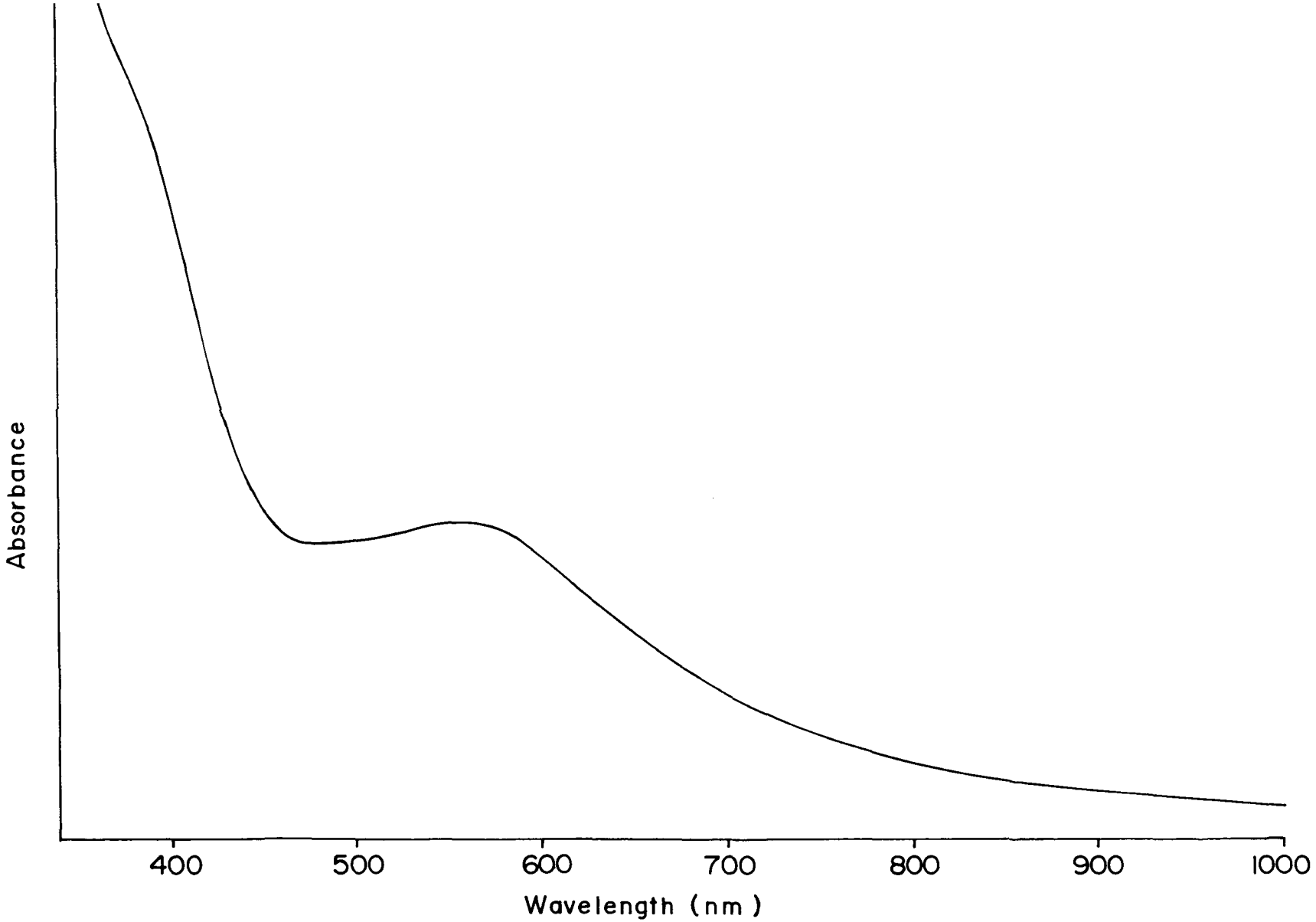

Figure 4.5 Electronic absorption spectrum of $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ recorded in $CHCl_3$

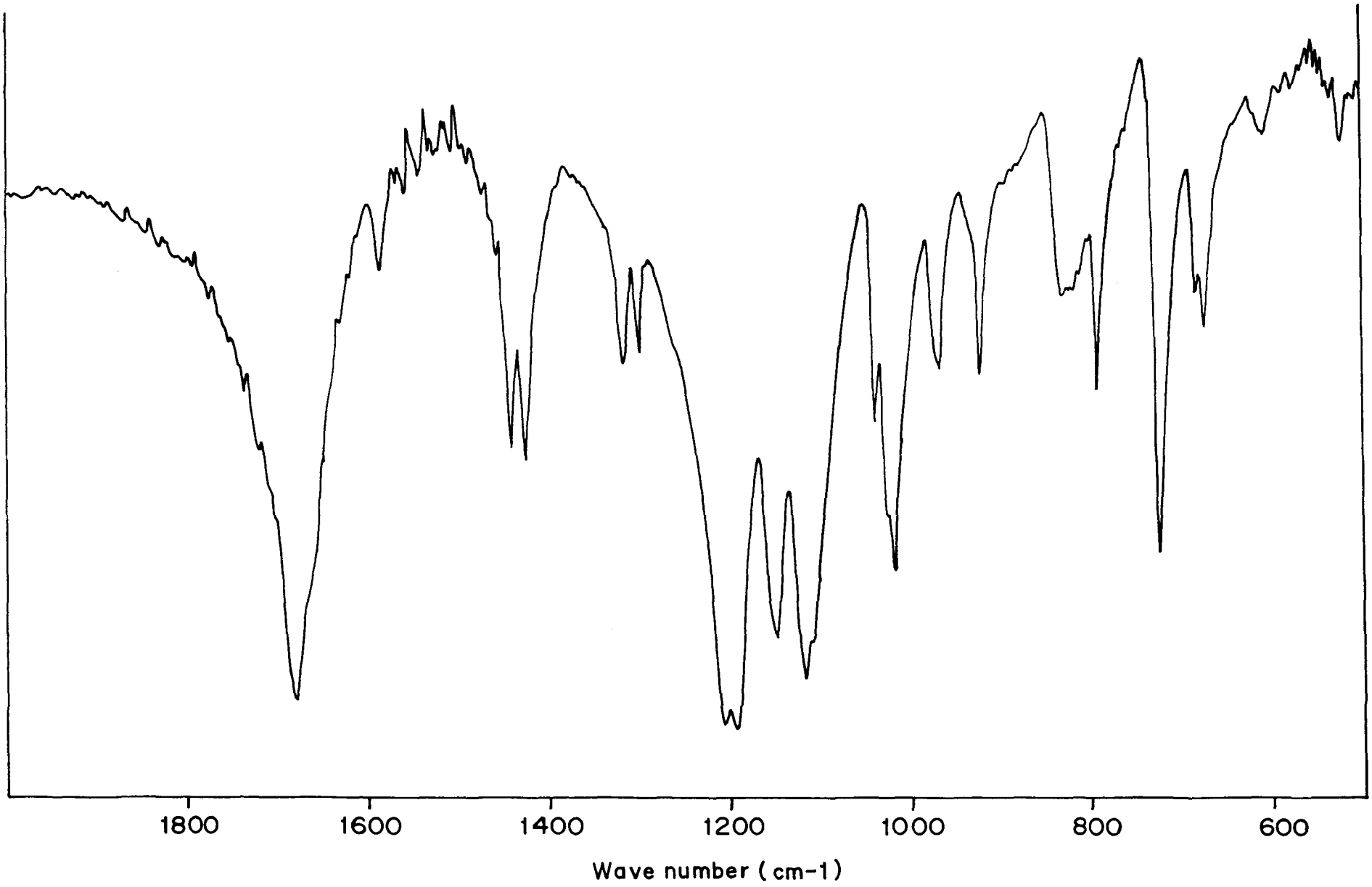

Figure 4.6 Infra-red spectrum of $[Ru(O_2CCF_3)_2(Me_2SO)_3]$ recorded using KBr pellet

band in the region 1000 to 900 cm^{-1} was observed, thereby confirming the absence of any O-bonded dimethylsulphoxide molecule. Thus all three dimethylsulphoxide molecules are only S-bonded. The ^1H NMR study further confirms the composition and the S-bonded nature of dimethylsulphoxide molecules. ^1H NMR (Table 4.3, Fig. 4.7) in $CDCl_3$ showed three sharp singlets of equal intensity at δ 3.29, 3.31 and 3.33. The presence of three singlets of equal intensity in the region is assignable to the methyl protons of three dimethylsulphoxide molecules. Signals due to methyl protons of S-bonded dimethylsulphoxide are observed between δ 3.0 to δ 3.4 whereas O-bonded dimethylsulphoxide shows signals at δ lower than δ 3.0 [25].

$[Ru(Me_2SO)_3(O_2CCF_3)_2]$ has been used as a precursor for the synthesis of compounds having trifluoroacetate(s), dimethylsulphoxide(s) and other monodentate ligands. The compound is fairly soluble in most of the organic solvents, thereby making its reactivity studies more convenient. The reactions of $[Ru(Me_2SO)_3(O_2CCF_3)_2]$ with triphenylphosphine and triphenylarsine at room temperature and at refluxing condition yielded in part or complete substitution of dimethylsulphoxide groups. When a reaction of $[Ru(Me_2SO)_3(O_2CCF_3)_2]$ was carried out with triphenylphosphine using Ru : PPh_3 in molar ratio 1:2 or 1:4 at the boiling condition of methanol, complete substitution of dimethylsulphoxide took place and the resultant complex has a composition $[Ru(PPh_3)_2(O_2CCF_3)_2]$ similar to the one reported in the literature [9]. The infrared spectrum (Table 4.2) of the compound showed a strong and sharp band at 1620 cm^{-1} characteristic of

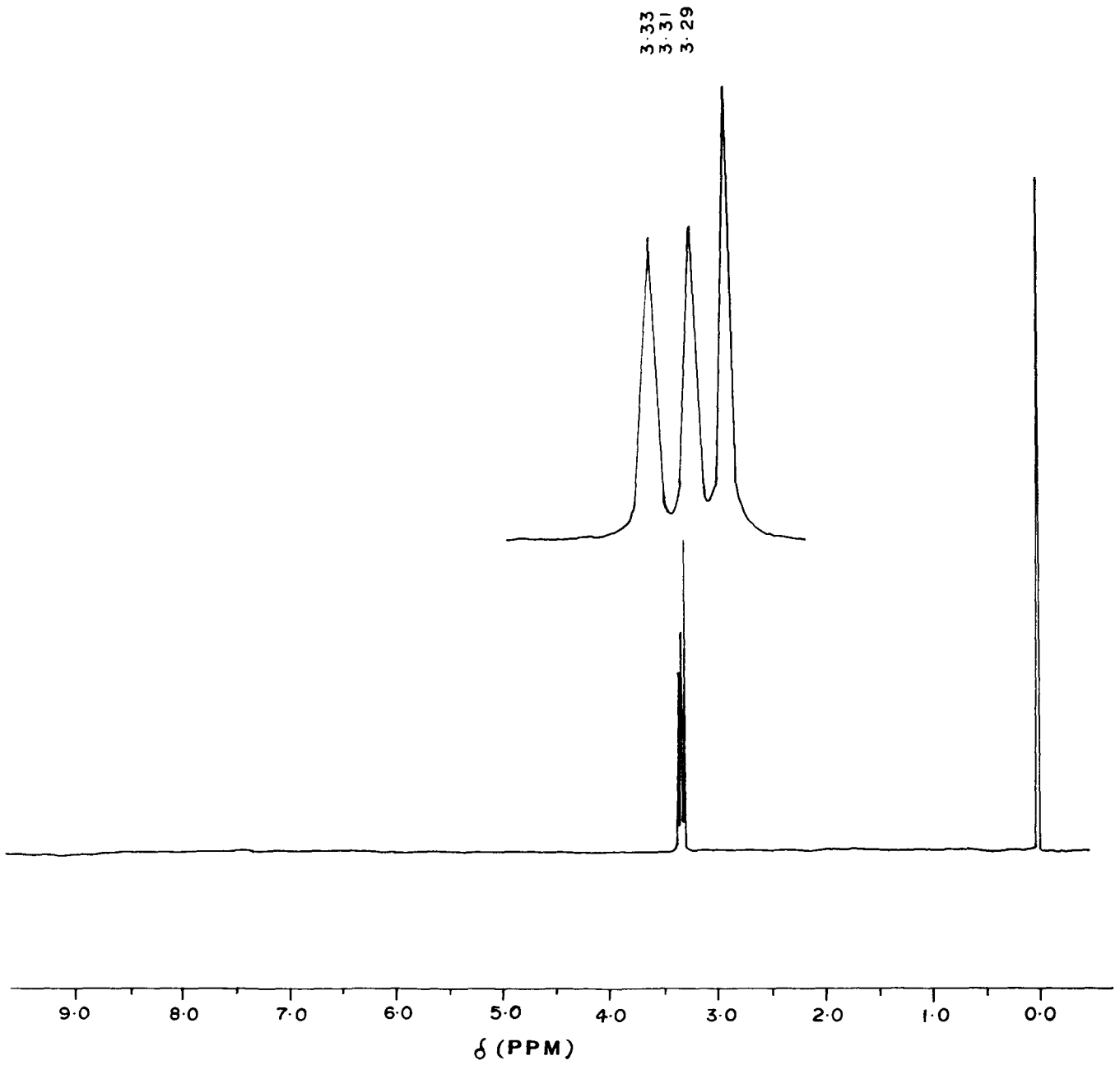

Figure 4.7 ^{1}H NMR spectrum of $[Ru(O_2CCF_3)_2(Me_2SO)_3]$ in $CDCl_3$

$\nu_{(OCO)asym}$ of chelated trifluoroacetato group [15,27]. Characteristic $\nu_{(SO)}$ bands due to coordinated dimethylsulphoxide were absent. The ^1H NMR spectrum of $[Ru(PPh_3)_2(O_2CCF_3)_2]$ showed multiplets in the region δ 7.43 to 7.70 characteristics of the aromatic protons of the triphenylphosphine groups.

A reaction of $[Ru(Me_2SO)_3(O_2CCF_3)_2]$ with triphenylarsine at room temperature or at refluxing condition in methanol, or with triphenylphosphine at room temperature, resulted in the substitution of two molecules of dimethylsulphoxide., thereby forming $[Ru(Me_2SO)(EPh_3)_2(O_2CCF_3)_2]$ (where E = P or As). Low molar conductance values of the complexes (Table 4.1) is indicative of its non-electrolytic nature. The magnetic susceptibility measurements in powder form at room temperature showed diamagnetism confirming that the ruthenium is in low spin, +2 state having d^6 configuration. The IR spectra of $[Ru(Me_2SO)(EPh_3)_2(O_2CCF_3)_2]$ (E = P or As) (Table 4.2, Fig 4.8) showed a strong band ~1680 cm^{-1} and a medium sharp band ~1435 cm^{-1}. The former band is assignable to $\nu_{(OCO)asym}$ whereas the later one is due to a combination of $\nu_{(OCO)sym}$ of trifluoroacetate and characteristic absorption due to triphenylphosphine or triphenylarsine in the complex. Large $\Delta\nu$ (245 cm^{-1}) value (*vide supra*, section 3.3) indicates that the trifluoroacetato groups are bonded to ruthenium in a unidentate manner. Further, one medium intensity band at ~1110 cm^{-1} is also observed, which is attributable to $\nu_{(SO)}$ of the S-bonded dimethylsulphoxide group. All other characteristic bands due to triphenylphosphine or triphenylarsine were also observed in the spectrum.

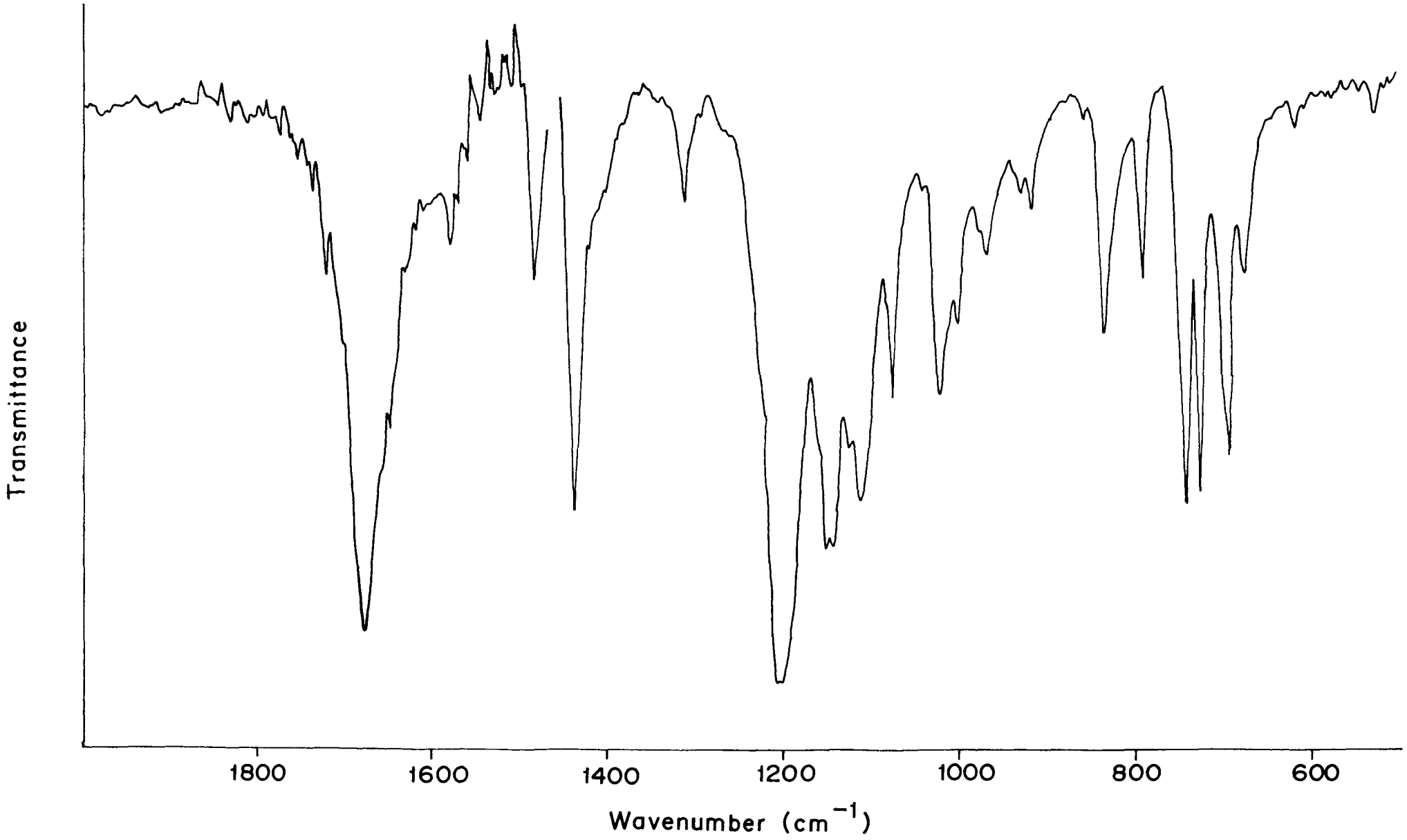

Figure 4.8 Infra-red spectrum of $[Ru(O_2CCF_3)_2(Me_2SO)(AsPh_3)_2]$ recorded using KBr pellet

The ^1H NMR spectra of $[Ru(Me_2SO)(EPh_3)_2(O_2CCF_3)_2]$ (where E = P or As) in $CDCl_3$ (Table 4.3, Fig. 4.9) showed a sharp singlet ~δ 3.0 and multiplets in the region δ 7.1 to 7.6. The singlet ~δ 3.0 may be assigned to the methyl protons of the S-bonded dimethylsulphoxide molecule, whereas multiplets between δ 7.1 to 7.6 are due to the protons of phenyl groups in triphenylphosphine or triphenylarsine. The ratio of the area under the signals ~δ 3.0 and the signals between δ 7.1 to 7.6 is around 1:5, thereby confirming that the complex is having one dimethylsulphoxide and two triphenylphosphine or triphenylarsine groups coordinated to it.

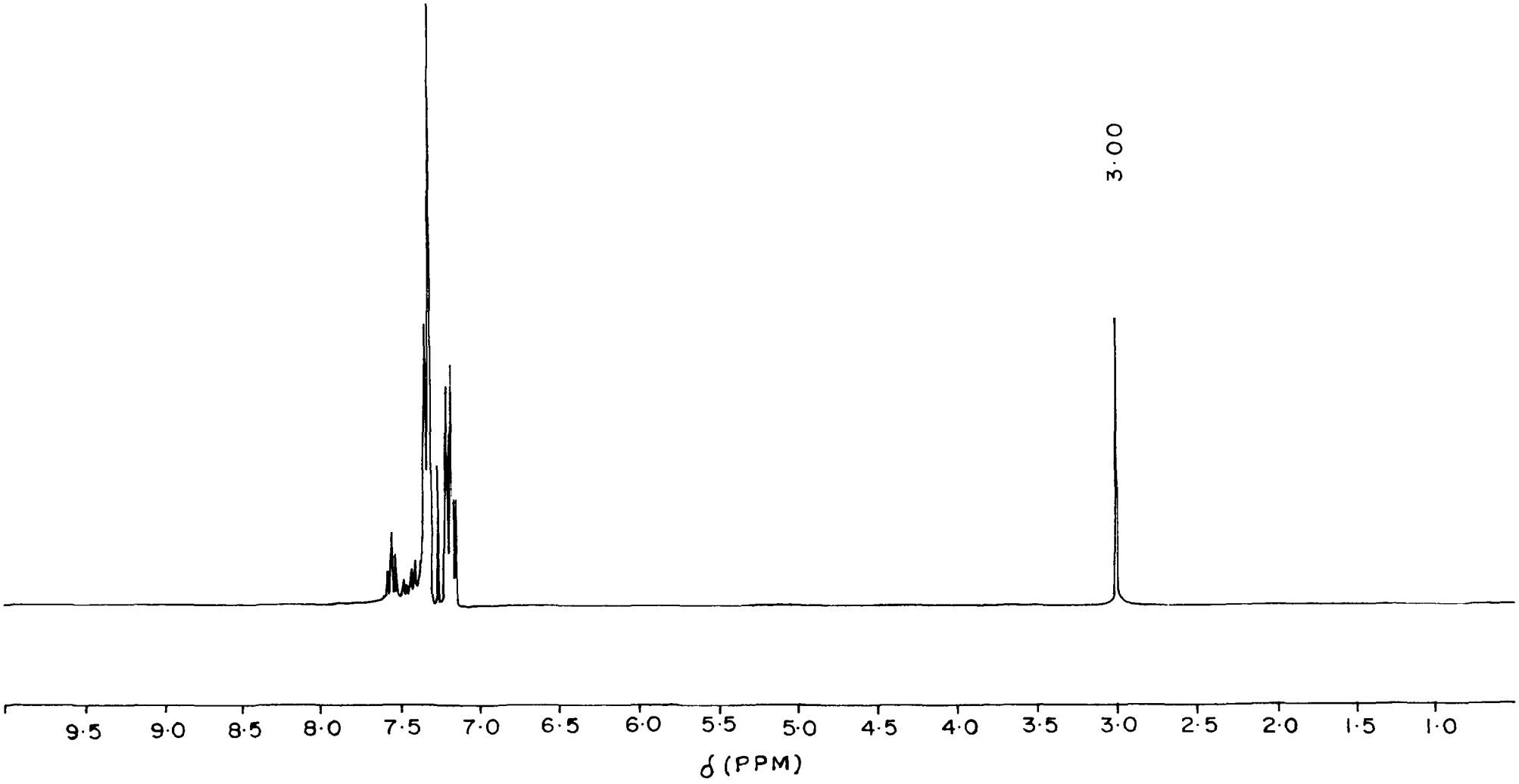

Figure 4.9 ^{1}H NMR spectrum of $[Ru(O_2CCF_3)_2(Me_2SO)(AsPh_3)_2]$ in $CDCl_3$

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Table 4.1 Physical and Analytical data of ruthenium(II) trifluoroacetato complexes

Complex	Colour	M.P. (°C)	Λ_M $\Omega^{-1}cm^2mol^{-1}$	Analysis(%)[a] C	H
$[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$	Brownish Yellow	185[d]	140[b]	66.0 (66.3)	4.5 (4.4)
$[Ru(O_2CCF_3)_2(CO)(PPh_3)_3]$	White	205[d]	10[b]	55.4 (55.6)	3.7 (3.5)
$[Ru(O_2CCF_3)_2(CO)(AsPh_3)_3]$	White	220[d]	12[b]	62.2 (62.1)	4.0 (3.9)
$[Ru(O_2CCF_3)_2(Me_2SO)_3]$	Pale yellow	158	18[c]	22.1 (21.4)	3.6 (3.2)
$[Ru(O_2CCF_3)_2(Me_2SO)(PPh_3)_2]$	light yellow	169	25[c]	54.0 (54.2)	2.1 (2.3)
$[Ru(O_2CCF_3)_2(Me_2SO)(AsPh_3)_2]$	light yellow	195	28[c]	48.5 (49.6)	2.6 (2.1)
$[Ru(O_2CCF_3)_2(PPh_3)_2]$	Brownish yellow	215	21[c]	67.0 (67.1)	4.2 (4.0)

[a]Calculated values in parenthesis; [b]Measured in acetonitrile ; [c]Measured in chloroform

[d]Decomposition temerature

Table 4.2 Some important infra-red spectral bands (in cm^{-1}) of ruthenium(II) trifluoroacetato complexes

Complex	$\nu_{(CO))}$	$\nu_{(OCO)asym}$	$\nu_{(OCO)} + \nu_{(C-C)}$	$\nu_{(C-F)}$	$\nu_{(SO)}$
$[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$		1670, 1610,	1475, 1427	1195, 1135	
$[Ru(O_2CCF_3)_2(CO)(PPh_3)_3]$	1913	1690	1483, 1432	1184, 1128	
$[Ru(O_2CCF_3)_2(CO)(AsPh_3)_3]$	1916	1686	1471, 1431	1196, 1138	
$[Ru(O_2CCF_3)_2(Me_2SO)_3]$		1680	1442, 1426	1193, 1148,	1116
$[Ru(O_2CCF_3)_2(Me_2SO)(PPh_3)_2]$		1678	1484, 1435	1193, 1148,	1110
$[Ru(O_2CCF_3)_2(Me_2SO)(AsPh_3)_2]$		1677	1483, 1438	1196, 1142,	1110
$[Ru(O_2CCF_3)_2(PPh_3)_2]$		1620	1480, 1432	1195, 1139	

Table 4.3 ^{1}H and ^{19}F NMR spectral data of ruthenium(II) trifluoroacetato complexes

Complex	δ(ppm)[a]
$[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$	^{19}F : -76.75(s), -74.45(s), -76.25(s)
$[Ru(O_2CCF_3)_2(CO)(PPh_3)_3]$	^{19}F : -74.86(s)
$[Ru(O_2CCF_3)_2(CO)(AsPh_3)_3]$	^{19}F : -75.08(s)
$[Ru(O_2CCF_3)_2(Me_2SO)_3]$	^{1}H : 3.29(s), 3.31(s), 3.33(s)
$[Ru(O_2CCF_3)_2(Me_2SO)(PPh_3)_2]$	^{1}H : 2.97(s), 7.16 - 7.36(m)
$[Ru(O_2CCF_3)_2(Me_2SO)(AsPh_3)_2]$	^{1}H : 3.00(s), 7.16 - 7.55(m)
$[Ru(O_2CCF_3)_2(PPh_3)_2]$	^{1}H : 7.43 - 7.70(m)

[a] Spectra recorded in $CDCl_3$

CHAPTER 5

Chapter 5

Synthesis, Characterization and Reactivity studies of (p-cymene)Ruthenium(II) complexes with 4,4'- bipyridine and Imidazole ligands

5.1 Introduction

In the last two decades, the chemistry of $[(arene)RuX_2]_2$ (arene = benzene and substituted benzenes, X = halides and pseudo halides) have been studied extensively [1-5]. These complexes attracted much attention due to their reactivity towards various nucleophiles [2a,6-8]. Ruthenium arene complexes also exhibit various homogeneous catalytic activity [9-14]. Moreover the chemistry of these complexes are very similar to their

cyclopentadienyl ruthenium analogues [3,14-15]. In the literature, very few reports are available on ruthenium arene complexes containing bridging ligands [16-19]. Some of the arene ruthenium complexes containing bridging ligands reported are : $[\{(\eta^6\text{-}C_6Me_6)Cl_2Ru\}_2(\mu\text{-CNPy})]$ (CNPy = cyanopyridine) [16(a)], $[\{(\eta^6\text{-}C_6Me_6)Cl_2Ru\}_2(\mu\text{-DCBT})]$ (DCBT = 1,4-dicyno-*trans*-2-butene)[16(b)], $[(\eta^6\text{-arene})Ru(\mu\text{-OMe})_2(\mu\text{-pz})Ru(\eta^6\text{-arene})]^+$ and $[(\eta^6\text{-arene})Ru(\mu\text{-OH})(\mu\text{-pz})_2Ru(\eta^6\text{-arene})]^+$ (arene = p-cymene or hexamethylbenzene) [17, 19(c)] $[(\eta^6\text{-benzene})Ru(\mu\text{-Cl})_2(\mu\text{-pz})Ru(\eta^6\text{-benzene})]^+$, $[(\eta^6\text{-benzene})Ru(\mu\text{-Cl})(\mu\text{-pz})_2Ru(\eta^6\text{-benzene})]$ (pz = pyrazole) [18(a)], $[\{(\eta^6\text{-benzene})ClRu(\mu\text{-adeH})\}_4]Cl_4$, $[(\eta^6\text{-benzene})ClRu(\mu\text{-6made})]_4$, $[(\eta^6\text{-benzene})Cl_2Ru(\mu\text{-3-apzH})RuCl_2(\eta^6\text{-benzene})]$, $[(\eta^6\text{-benzene})ClRu(\mu\text{-Cl})(\mu_3\text{-3-apz})RuCl(\eta^6\text{-benzene})]^{2+}$, $[(\eta^6\text{-benzene})ClRu(\mu\text{-Im})]_n$ (ade = adenine, 6made = N^6-methyladenine, 3-apz = 3-aminopyrazole, Im = imidazole) [18(b)]. 4,4'-bipyridine is a useful bridging ligand for synthesizing various di and polynuclear complexes [20-26].

This chapter describes the reactivity of $[(p\text{-cymene})RuCl_2]_2$ and $[(p\text{-cymene})Ru(EPh_3)Cl_2]$ (E = P or As) with 4, 4'-bipyridine which resulted in the bridged complexes of the type $[(p\text{-cymene})RuCl_2(\mu\text{-}4,4'\text{-bipy})Cl_2Ru(p\text{-cymene})]$ and $[(p\text{-cymene})Ru(EPh_3)Cl(4,4'\text{-bipy})Cl(EPh_3)Ru(p\text{-cymene})](BF_4)_2$ (E = P or As) respectively. Reaction of $[(p\text{-cymene})Ru(PPh_3)Cl_2]$ with imidazole yielded $[(p\text{-cymene})Ru(PPh_3)(Im)Cl]BF_4$ (Im = imidazole). All these complexes have been characterized with the help of analytical data (Table 5.1) and various spectroscopic techniques.

5.2 Experimental

All the solvents were dried by standard methods. Ruthenium trichloride trihydrate was obtained from Arora Mathey Ltd. and used without further purification. $[(p\text{-cymene})RuCl_2]_2$ and $[(p\text{-cymene})Ru(EPh_3)Cl_2]$ (E = P or As) were prepared according to the literature methods [2(a), 2(c)].

5.2.1 Preparation of [(p-cymene) $Cl_2Ru(\mu\text{-}4,4'\text{-bipy})Ru\ Cl_2$ (p-cymene)]

To a suspension of $[(p\text{-cymene})RuCl_2]_2$ (0.20 g, 0.33 mmol) in methanol (20 cm^3) was added a little excess of 4,4'-bipyridine (0.07 g, 0.45 mmol) and the resulting mixture was refluxed on a water-bath for three hours. An orange compound separated out, which was isolated by filtration, and washed with ethanol and diethyl ether and dried *in vacuum*. Yield: 0.15g (60%).

5.2.2 Preparation of $[\{(p\text{-cymene})Ru(EPh_3)Cl\}_2(\mu\text{-}4,4'\text{-bipy})](BF_4)_2$ (E = P or As)

4,4'-Bipyridine (0.014g, 0.09 mmol) and sodium tetrafluoroborate (0.02g, 0.18 mmol) were added to a suspension of $[(p\text{-cymene})Ru(EPh_3)Cl_2]$ {(E = P(0.10g, 0.18 mmol) or As(0.11g, 0.18 mmol)} in methanol (20 cm^3). The resulting mixture was refluxed on a water-bath for 5 hours. The solution was cooled to room temperature, when an orange colour product

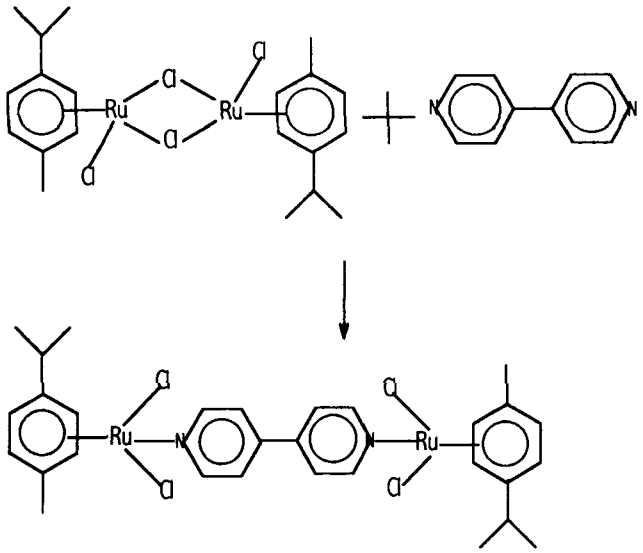
out, which was isolated by filtration, washed with ethanol and diethyl ether and dried *in vacuo*. Yield: 0.08 g, (65%) for [{(p-cymene)Ru(PPh_3)Cl}$_2$(μ-4,4'-bipy)](BF_4)$_2$; 0.085g, (70%) for [{(p-cymene)Ru($AsPh_3$)Cl}$_2$(μ-4,4'-bipy)](BF_4)$_2$.

5.2.3 Preparation of [(p-cymene)Ru(PPh_3)(Im)Cl]BF_4 (Im = imidazole)

Imidazole (0.03g, 0.44 mmol) and sodium tetrafluroborate (0.05g, 0.45 mmol) were added to a methanolic solution of [(p-cymene)Ru(PPh_3)Cl_2] (0.20g, 0.35 mmol). The resulting solution was refluxed on a water-bath for 6 hours. An orange colour solution, which appeared after refluxing was concentrated to *ca.* 5 cm^3 and kept overnight. A yellow compound deposited, which was isolated by filtration washed with hexane and dried *in vacuum*. Yield : 0.15g, (62 %).

5.3 Results and Discussion

[{(p-cymene)$RuCl_2$}$_2$(μ-4,4'-bipy)] has been synthesised by a reaction of [(p-cymene)$RuCl_2$]$_2$ with 4,4'-bipyridine in 1 : 1 molar ratio at refluxing condition in methanol. This air stable complex is sparingly soluble in polar solvents such as chloroform, acetonitrile etc. and insoluble in non-polar solvents. The conductivity measurement of the complex in acetonitrile show molar conductance value of the order 7-10 $\Omega^{-1}cm^2mol^{-1}$ which conforms to the covalent nature of chloro groups bonded to ruthenium.



The magnetic susceptibility measurement in powder form at room temperature shows diamagnetic behaviour confirming to a low spin d^6 configuration of the Ru(II) system. The IR spectrum of the complex shows a medium sharp band at 822 cm^{-1}, which is characteristic of 4,4'-bipyridine. The ^1H NMR spectrum of complex (Table 5.2, Fig. 5.1) exhibited two doublets at δ 7.07 and 9.03 for 4, 4'-bipyridine. The p-cymene group in the complex shows a singlet for the methyl group at δ 2.08, a sharp doublet at δ 1.33 for the methyl groups of isopropyl, septet for proton of isopropyl at δ 2.98 and two doublets for ring protons at δ 5.28 and 5.51 respectively [7].

The electronic absorption spectrum of complex (Fig. 5.2) showed two absorptions at 325 nm and 410 nm having ε value of the order of 10^4. The absorption at 410 nm may be assigned to MLCT transition arising due to

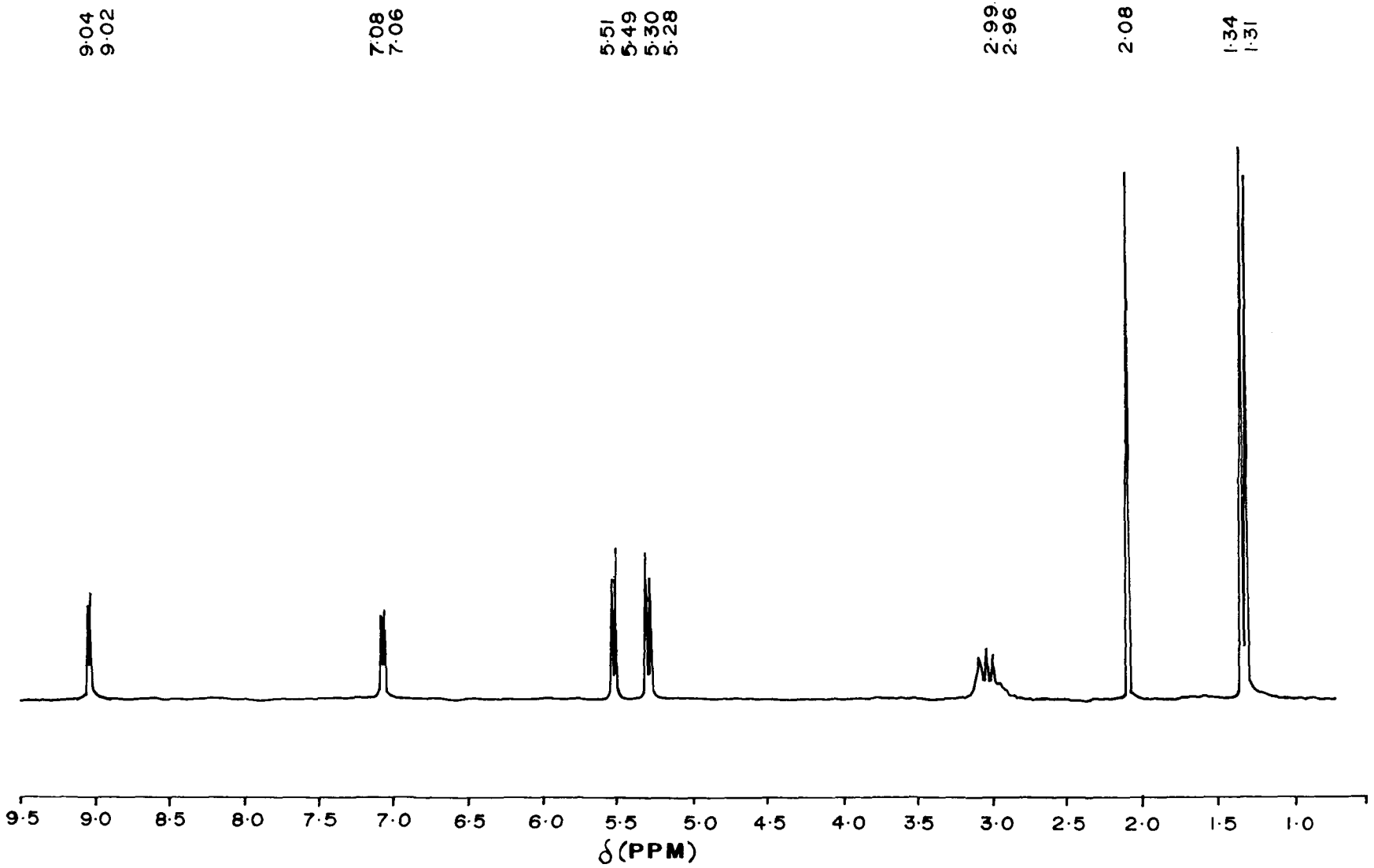


Figure 5.1 ^{1}H NMR spectrum of [{(p-cymene)$RuCl_2$}$_2$(μ-4,4'-bipy)] in $CDCl_3$

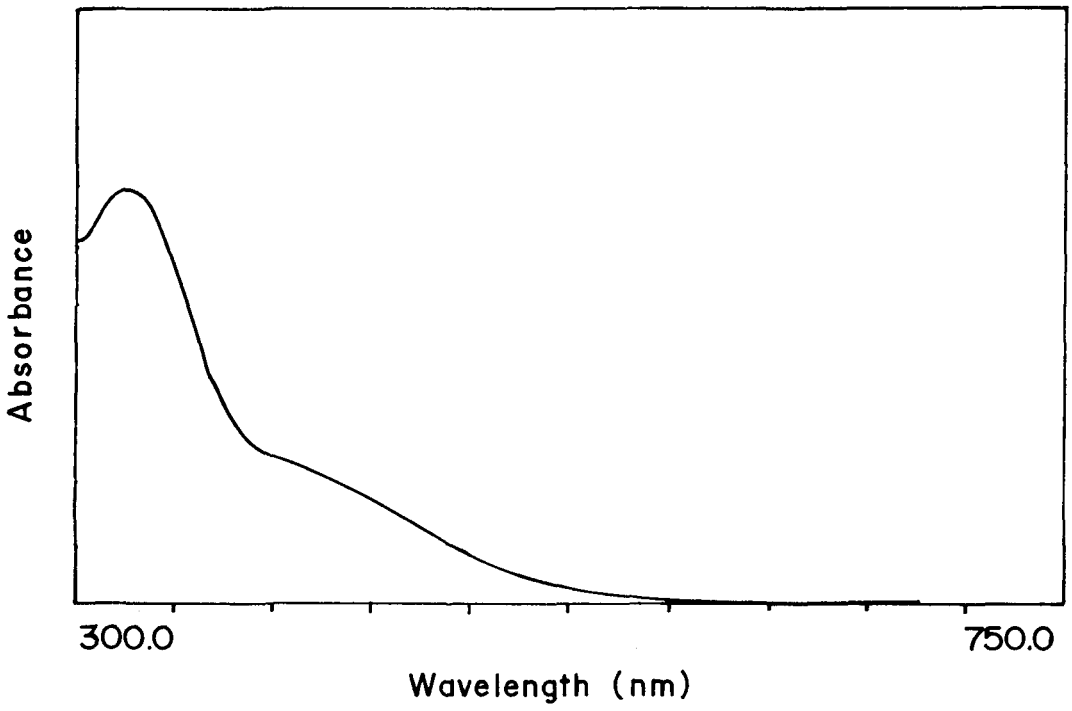
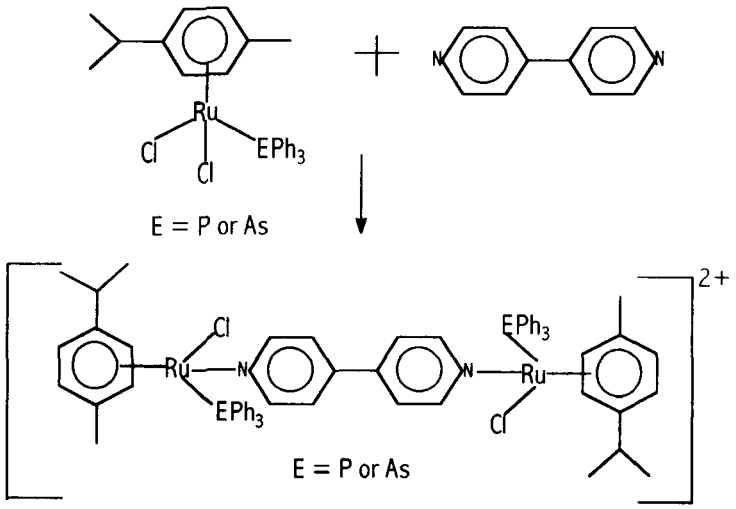


Figure 5.2 Electronic absorption spectrum of [{(p-cymene)$RuCl_2$}$_2$(μ-4,4'-bipy)] in chloroform

transfer of charge density from the filled t_{2g} orbitals of metal to low lying π^* orbitals of bipyridine ligand while the band at 325 nm may be due to $\pi \rightarrow \pi^*$ type of transition of 4,4'bipyridine [27].

[(p-cymene)Ru(EPh_3)Cl_2] (E = P or As), on treatment with 4,4'-bipyridine yielded bridged complex having molecular composition [{(p-cymene)Ru(EPh_3)Cl}$_2$(4,4'-bipy)](BF_4)$_2$ (E = P, As).



Conductivity measurements of these complexes (Table 5.1) in acetonitrile show molar conductance values around 180 $\Omega^{-1}cm^2mol^{-1}$, thereby confirming 1 : 2 electrolytic nature of the complexes. The magnetic susceptibility measurements of these complexes show diamagnetism thereby indicating that ruthenium is in low spin +2 oxidation state having d^6 configuration.

The IR spectra of these complexes showed an absorption at 823 cm^{-1}, which is characteristic of 4,4'-bipyridine ligand. A strong broad band around 1080 cm^{-1} was also observed, which is attributable to a combination of ν_{B-F} and band due to triphenylphosphine or triphenylarsine. Characteristic absorption bands due to p-cymene and triphenylphosphine or triphenylarsine were also observed in the complexes. The ^1H NMR spectra of the complexes (Table 5.2, Fig. 5.3) exhibited one singlet around δ 1.7 for the methyl protons, two doublets around δ 1.2 for methyl protons of isopropyl group, a septet around δ 2.5 for proton of isopropyl group and two pairs of doublets in the region δ 5.35 - 5.55 and δ 5.90 - 6.15 were attributed to the ring protons of the p-cymene group respectively. The split in the ring proton and isopropyl group may be due to the loss of planarity of p-cymene group. A similar pattern was observed in the case of substitution of Schiff base ligands [7]. Two doublets in the region δ 8.40 to δ 9.10 were also observed, which are assigned to the protons of the bridging 4,4'-bipyridine. Signals for phenyl groups of phosphine and arsine ligands were also observed in their ^1H NMR spectra. ^{31}P NMR spectrum of the complex [{(p-cymene)$Ru(PPh_3)Cl\}_2$(4,4'-bipy)]$(BF_4)_2$ exhibited single sharp peak at δ 37.8 which is attributed to the presence of triphenylphosphine group.

A reaction of [(p-cymene)$RuCl_2(PPh_3)$] with imidazole in presence of sodium tetrafluoroborate in methanol resulted a monomeric complex having composition [(p-cymene)$RuCl(PPh_3)$(Im)](BF_4).

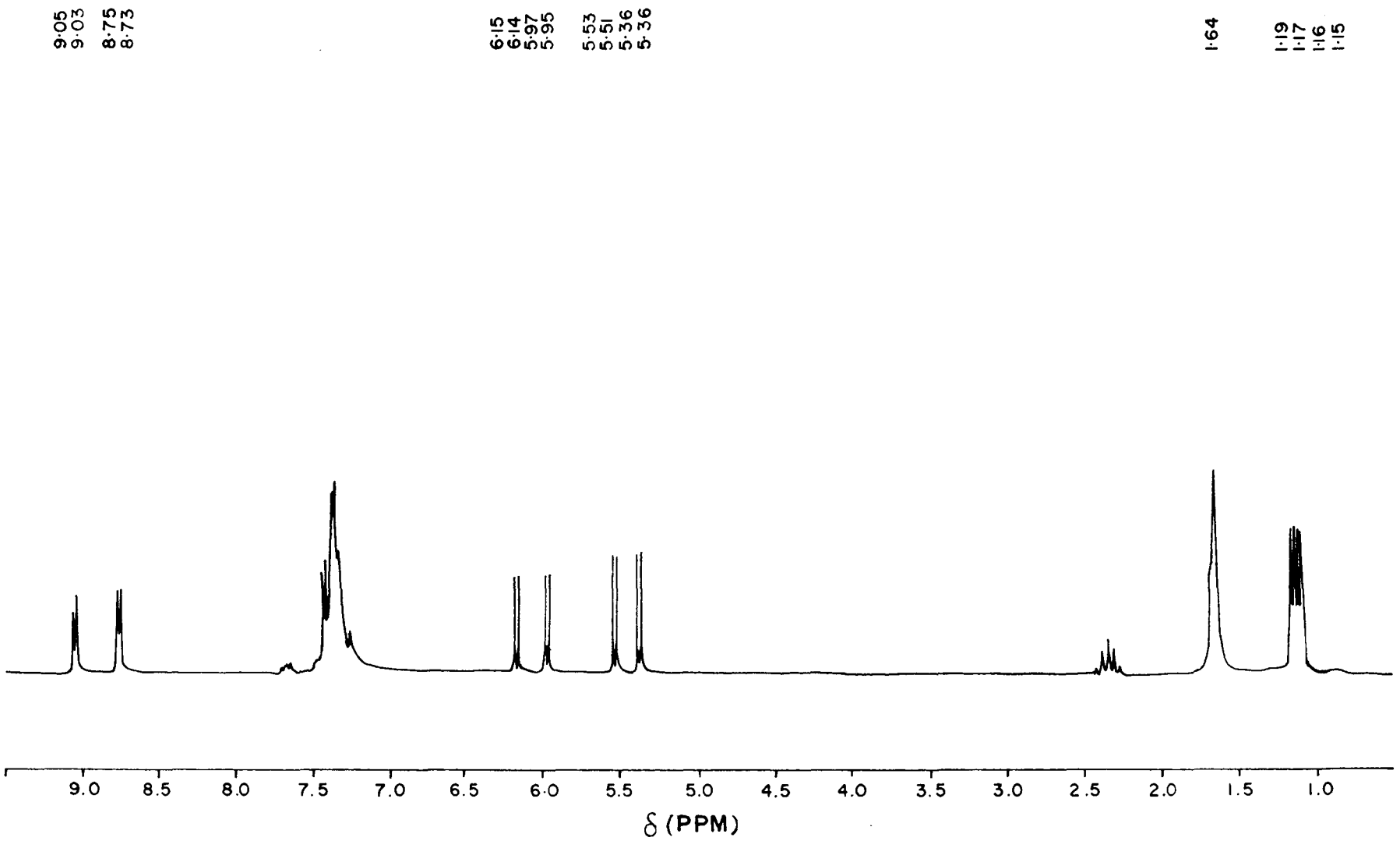
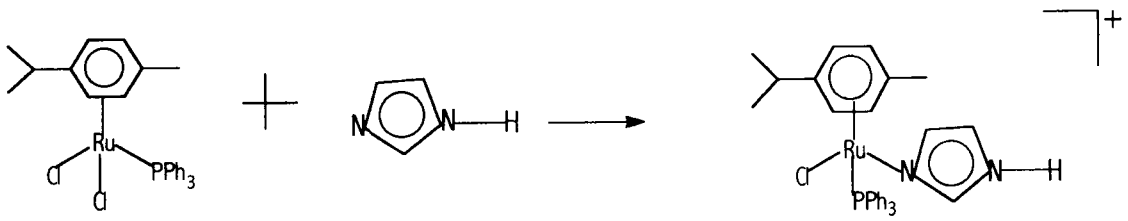
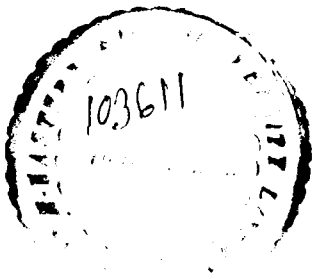


Figure 5.3 ^{1}H NMR spectrum of [{(p-cymene)RuCl(PPh$_3$)}$_2$(μ-4,4'-bipy)](BF$_4$)$_2$ in $CDCl_3$



The conductivity measurement of the complex (Table 5.1) in acetonitrile conforms to 1:1 electrolytic nature. The diamagnetic behaviour of the complex indicates that ruthenium is in +2 oxidation state having low spin d^6 configuration. The IR spectrum of the complex showed a strong broad band around 1090 cm^{-1} (*vide supra*). Other characteristic bands due to imidazole and triphenylphosphine were also observed in the complex. The ^1H NMR spectrum of the complex (Table 5.2, Fig. 5.4) shows one singlet at δ 1.71 due to methyl protons, two doublets in the region δ 1.06 – 1.12 for the methyl protons of isopropyl group. A septet at δ 2.4 for the proton of isopropyl group and two doublet of doublets were also observed in the region δ 5.03 - 5.42 and δ 5.68 - 5.81 ppm due to aromatic protons of p-cymene group. Signals due to phenyl groups of phosphine are also observed as multiplets in the region δ 7.3 - 7.4. The three C-H protons of imidazole were observed at δ 6.78, 7.15 and 8.04 as singlets and a broad singlet at δ 12.80 was observed for the N-H proton. ^{31}P NMR spectrum of the complex shows a sharp singlet at δ 36.45 due to the presence of triphenylphosphine group. The electronic spectrum of the complex exhibited a strong intensity band at 340 nm having ε value 10,000 which may be due to metal to ligand charge transfer band.



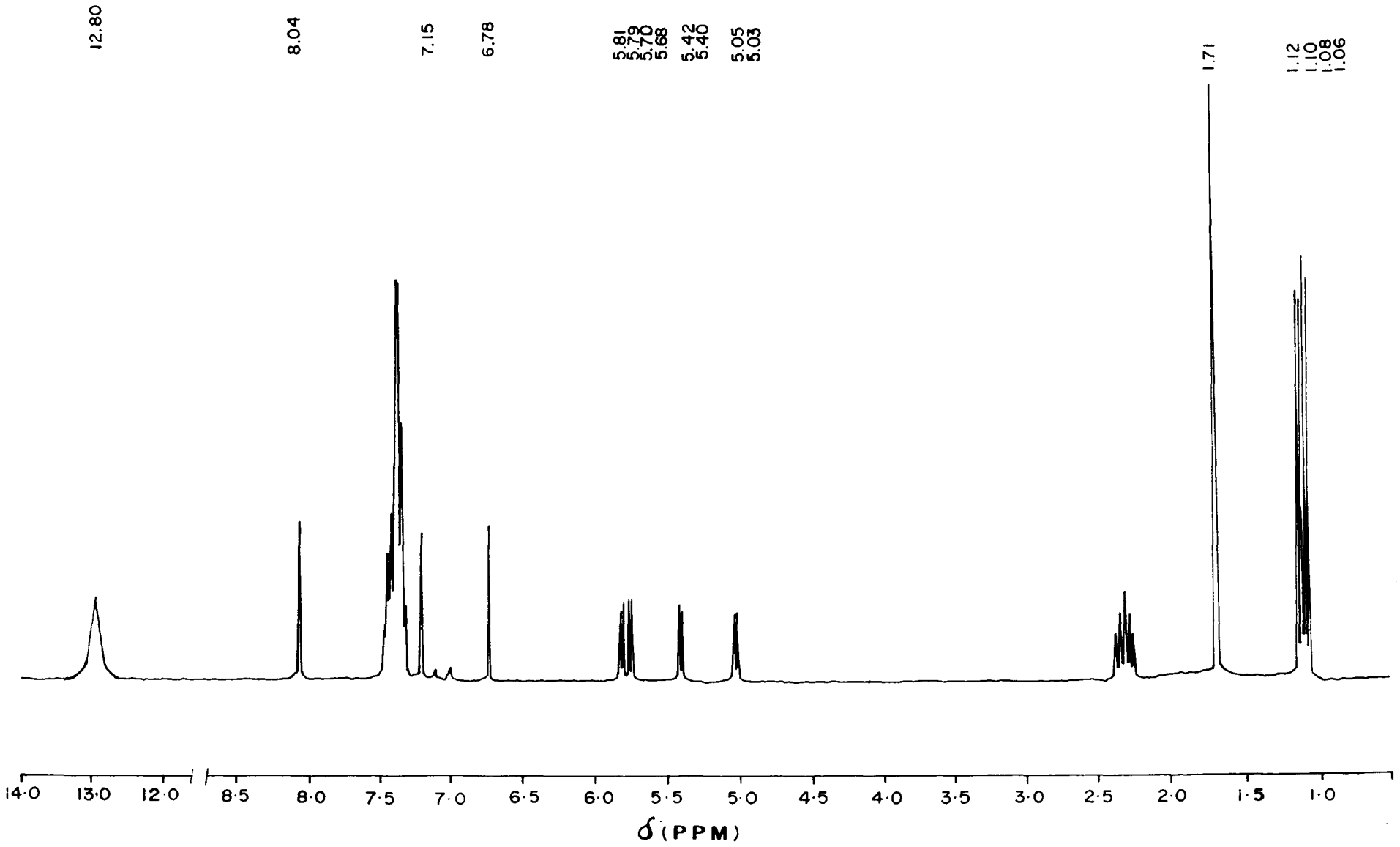


Figure 5.4 ^{1}H NMR spectrum of [(p-cymene)RuCl(PPh_3)(ImH)](BF_4) in $CDCl_3$

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Table 5.1 Physical and Analytical data of some (p-cymene)ruthenium(II) complexes

Complex	Colour	Λ_M [b]	Analysis(%)[a]		
		$\Omega^{-1}cm^2mol^{-1}$	C	H	N
$[\{(p\text{-cymene})RuCl_2\}_2(\mu\text{-}4,4'\text{-bipy})]$	Orange	10	46.46 (46.87)	4.59 (4.69)	3.91 (3.64)
$[\{(p\text{-cymene})RuCl(PPh_3)\}_2(\mu\text{-}4,4'\text{-bipy})](BF_4)_2$	Orange	180	56.21 (56.77)	4.62 (4.73)	2.35 (2.01)
$[\{(p\text{-cymene})RuCl(AsPh_3)\}_2(\mu\text{-}4,4'\text{-bipy})](BF_4)_2$	Orange	195	53.06 (53.40)	4.20 (4.45)	2.16 (1.89)
$[(p\text{-cymene})RuCl(PPh_3)(Im)](BF_4)$	Yellow	125	54.60 (54.11)	4.76 (4.80)	4.64 (4.07)

[a]Calculated values are in parenthesis ; [b]measured in acetonitrile solution.

Table 5.2 ^{1}H and NMR spectral data of the ruthenium(II) complexes

Complex	δ(ppm)[a]
[{(p-cymene)$RuCl_2$}$_2$(μ-4,4'-bipy)]	1.33 { d, J(HH) 6.9 Hz }, 2.08 (s), 2.98 (sept.), 5.28 {d, J(HH) 6.0 Hz }, 5.51{d, J(HH) 6.0 Hz},7.07{d,J(HH) 6.5Hz}, 9.03 {d, J(HH) 6.5Hz}.
[{(p-cymene)$RuCl(PPh_3)$}$_2$(μ-4,4'-bipy)]$^{2+}$	1.10{dd,J(HH)2.9 and 2.8 Hz},1.60(s), 2.40 (sept.), 5.30 - 5.50 {dd, J(HH) 6.0 and 7.1Hz}, 5.90 - 6.10{dd, J(HH) 6.0 and 7.6 Hz}, 8.70{d, J(HH) 6.1 Hz}, 9.03 {d, J(HH) 6.7Hz}, 7.20-7.40 (m)
[{(p-cymene)$RuCl(AsPh_3)$}$_2$(μ-4,4'-bipy)]$^{2+}$	1.20{dd, J(HH) 3.1 and 3.3 Hz},1.80 (s), 2.60 (sept.), 5.30 - 5.55 {dd, J(HH) 6.5 and 7.1Hz }, 5.90 - 6.15{dd, J(HH) 6.4 and 7.3 Hz }, 8.40 { d, J(HH) 6.8Hz }, 9.10 {d, J(HH) 6.9Hz }, 7.50-7.70 (m)
[(p-cymene)$RuCl(PPh_3)(Im)$]$^{+}$	1.06-1.12{two d, J(HH)6.9 and 7.0 Hz}, 1.71 (s), 2.40 (sept.), 5.03 - 5.42 { dd, J(HH) 6.0 and 6.2Hz }, 5.68 - 5.81 { dd, J(HH) 6.1 and 6.2 Hz}, 6.78(d),7.15(d), 8.04(d), 12.8 (br., s), 7.30-7.40(m)

[a]Measured in $CDCl_3$

CHAPTER 6

Chapter 6

Synthesis, Characterization and Studies of some rhodium(III) complexes containing acetylacetone and mono or bidentate ligands

6.1 Introduction

The coordination compounds of transition metals with β-diketonates and substituted β-diketonates have been extensively investigated with regard to their stability, structure and reactivity studies.Continuing our interest in the chemistry of acetylacetonate/acetylacetonato complexes of platinum group of metals, after having studied complexes with ruthenium [1-2], we extended studies to the next member of platinum metals i.e. Rhodium. Literature survey reveals that complexes of rhodium with β-diketonates have

been studied in the oxidation state +1, +2 and +3. Rhodium(I) complexes containing β-diketonate and other unidentate ligands include, $[Rh(CO)(\beta\text{-dik})(PPh_3)_2]$ [3-4], $[Rh(CO)(\beta\text{-dik})L]$ (L = PPh_3 or $AsPh_3$) [5-7], $[Rh(CO)(\beta\text{-dik})]$ [5], $[Rh(\beta\text{-dik})(PPh_3)_n]$ [4,8] (n = 2 or 3), $[Rh(CO)_2(\beta\text{-dik})]$ [9-12] and $[Rh(acac)(C_2H_4)_2]$ [13]. The rhodium(II) complexes reported are $[Rh(O_2CCH_3)(tfacac)L_2]$ (L = H_2O or py) [4-16]. Reported complexes of rhodium(III) with β-diketonates are $[Rh(\beta\text{-dik})_3]$ (β-dik = acac, tfacac, hfacac and 3-NO_2acac) [17-24]. Mixed halogeno-β-diketonato complexes of Rh(III) reported are $[RhCl(hfacac)_2]$ [25] and $[RhCl(acac)_2(PPh_3)]$[26]. Most of the β-diketonato complexes of rhodium have no other anions other than β-diketonate(s). Some examples of complexes containing β-diketonato and an anion such as chloride are reported above. In our laboratory, work on $[RhCl_2(acac)(acacH)$ and systems of the type $[RhCl_2(acac)L_2]$ (where L = PPh_3 or $AsPh_3$; L_2 = 2,2'-bipyridine or 1,10-phenanthroline) and $M_2[RhCl_4(acac)]$ (M = NMe_4 or Cs) have been carried out [27]. Studies on mixed ligand complexes of Ru(II) containing halides, acetylacetonate and neutral donor ligands reveal that the bromo analogues of $[RuCl_2(acac)L_2]$ (L = PPh_3 or $AsPh_3$) show much better catalytic activity towards oxidation of PPh_3 and $AsPh_3$ [2]. In view of the above, it was thought of extending the synthesis and structural studies on the bromo analogues of $[RhCl_2(acac)L_2]$. Present work describes the synthesis, characterisation and structural assessment of some new Rh(III) complexes of the type $[RhBr_2(acac)L_2]$ (where L = PPh_3 , $AsPh_3$ or py ; L_2 = bipy or phen) and $[RhCl_2(acac)(py)_2]$.

6.2 Experimetal

Rhodium trichloride trihydrate was obtained from Arora-Mathey Ltd., Calcutta. All solvents were freshly distilled before use and other chemicals used were of Analar or extra-purity grade.

6.2.1 Preparation of $[RhCl_2(acac)(acacH)]$

A solution of rhodium trichloride trihydrate (0.20g, 0.76 mmol) in acetylacetone (5 cm^3) was heated on a water-bath at *ca.* 85°C for 4h, when a clear reddish brown solution was obtained. The solution was concentrated to about half its volume on a water-bath and cooled to room temperature. On addition of dry diethylether, a yellowish brown compound precipitated out. It was centrifuged, washed three to four times with diethylether and dried *in vacuo*. Yield : 0.20g, (71%).

6.2.2 Preparation of $[RhCl_2(acac)(py)_2]$

A solution of $[RhCl_2(acac)(acacH)]$ (0.20g, 0.54 mmol) was made in ethanol (10 cm^3) by warming. Pyridine (0.5 cm^3) was added to the clear solution and the reaction mixture was refluxed on a water-bath for 2h. On cooling, a compound was obtained, which was separated by centrifugation, washed successively with ethanol and ether and dried *in vacuo*. Yield : 0.11g, (45%).

6.2.3 Preparation of $[RhBr_2(acac)(PPh_3)_2]$

Lithium bromide (0.20g, 0.23 mmol) was added to a solution of $[RhCl_2(acac)(acacH)]$ (0.20g, 0.54 mmol) in ethanol (15 cm^3) and the solution was refluxed on a water-bath for 1h. It was cooled and centrifuged. To the clear solution, a solution of triphenylphosphine (0.30g, 1.15 mmol) was added and the mixture was stirred at room temperature for 3 h. A brown compound separated out, which was centrifuged, washed with ethanol and ether and dried *in vacuo*. Yield : 0.17g, (35%).

6.2.4 Preparation of $[RhBr_2(acac)L_2]$ (L = $AsPh_3$ or py)

Lithium bromide (0.20g, 0.23 mmol) was added to a solution of $[RhCl_2(acac)(acacH)]$ (0.20g, 0.54 mmol) in ethanol (15 cm^3) and the mixture was refluxed on a water-bath for 1 h. To the clear solution, obtained after centrifugation, a solution of the ligand (L) (molar ratio Rh : L = 1 : 2) was added and further refluxed the mixture for 3h on a water-bath. A compound separated out after concentrating the solution (~ 2 cm^3) , which was centrifuged washed with ethanol and then with ether and dried *in vacuo*. Yield : 0.24g, (45%) for $[RhBr_2(acac)(AsPh_3)_2]$; 0.13 g, (45%) for $[RhBr_2(acac)(py)_2]$

6.2.5 Preparation of [$RhBr_2(acac)(L\text{-}L)$] (L-L = 2,2'-bipyridine or 1,10-phenanthroline)

The preparation of of [$RhBr_2(acac)(L\text{-}L)$] is similar to that in 6.2.4, except the solution of ligand (L-L) in ethanol (10 cm^3) was added in a molar ratio Rh : L-L = 1 :1, to the mixture. The product obtained was washed with ether and dried *in vacuo*. Yield : 0.10g, (65%) for [$RhBr_2(acac)(bipy)$] ; 0.18 g, (60%) for [$RhBr_2(acac)(phen)$].

6.3 Results and Discussion

[$RhCl_2(acac)(acacH)$] is soluble in many organic solvents, *viz.* methanol, ethanol, chloroform and acetonitrile, permitting a wide range of its reactivity studies. Neutral acetylacetone is weakly coordinated to the metal ion. Hence in a solution , [$RhCl_2(acac)$] or [$RhCl_2(acac)(S)_2$] (S = solvent molecule) is obtained. A reaction of [$RhCl_2(acac)(acacH)$] with pyridine resulted in the formation of [$RhCl_2(acac)(py)_2$]. The molar conductance value of the complex in acetonitrile at room temperature (Table 6.1) was very low, confirming that the chlorides are covalently bonded to the metal ion. The diamagnetic behaviour of the complex indicates no change in the oxidation state of the metal Rh(III) during the substitution reaction.

The absence of the IR band at 1620 cm^{-1} for [$RhCl_2(acac)(py)_2$] (Table 6.2) confirms the absence of neutral acetylacetone molecule [1]. However presence of two bands at 1550 and 1515 cm^{-1} are, assignable to the combination of $\nu_{(C\text{-}O)}$ and $\nu_{(C\text{-}C)}$. Other characteristic bands of the O-bonded

chelated acetylacetonato groups were also observed. Two bands were observed at 1470 and 321 cm^{-1} which are assigned to $\nu_{(Rh-O)}$ and $\nu_{(Rh-Cl)}$ respectively [28]. All characteristic absorptions due to pyridine were also present.

The ^1H NMR spectrum of $[RhCl_2(acac)(py)_2]$ in dmso-d_6 (Fig. 6.1, Table 6.3) showed several signals in the region δ 2.20 to δ 2.60, which are attributable to the methyl protons of acetylacetonato group. Three singlets were observed in the region δ 5.45 to δ 5.80 which could be assigned to the methine poton of the acetylacetone group. The presence of three signals in δ 5.45 to 5.80 region and many signals in δ 2.20 to δ 2.60 region could be due to three possible isomers of $[RhCl_2(acac)(py)_2]$ (Fig. 6.2).

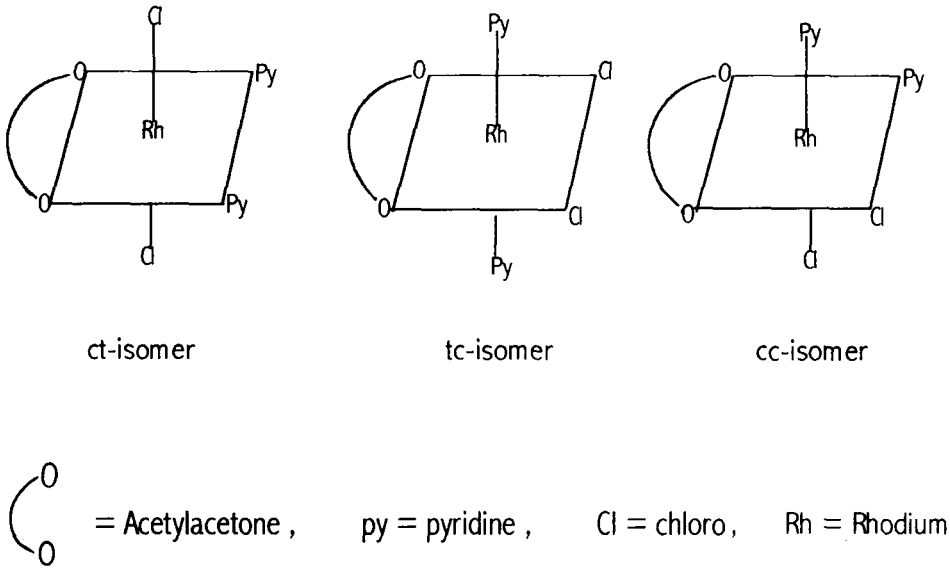

Figure 6.2 Isomers of $[RhCl_2(acac)(py)_2]$

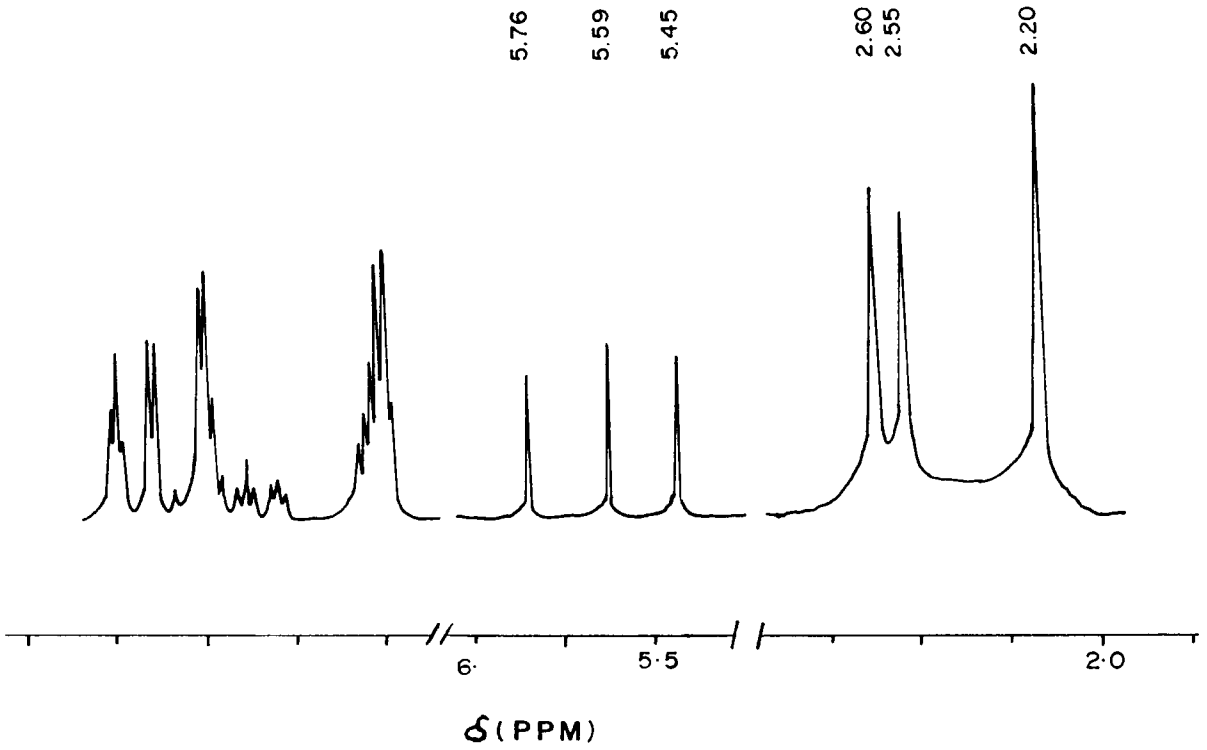

Figure 6.1 ^{1}H NMR spectrum of $[RhCl_2(acac)(py)_2]$ in dmso-d^6

Presence of mixture of isomers in the sample was also evident from the signals due to aromatic protons of the pyridine molecules observed in the region δ 7.61 to δ 8.30. Attempts to separate three isomers were not successful. The electronic absorption spectrum of $[RhCl_2(acac)(py)_2]$ (Table 6.2) showed one band at 313 nm attributable to metal → ligand charge transfer transition [29]. The cyclic voltammograms of $[RhCl_2(acac)(py)_2]$ (Table 6.4) showed one irreversible oxidation wave at a positive potential ($E°_{1/2}$ = 1.1 V) and one irreversible reduction wave at negative potential ($E°_{1/2}$ = -1.15 V). The oxidation wave may be due to Rh(IV) / Rh(III) couple [30], whereas the wave at $E°_{1/2}$ = -1.15 V may be attributed to the reduction of the ligand, *viz.* pyridine [31].

Our attempts to isolate the bromo analogue of $[RhCl_2(acac)(acacH)]$ by the metathesis of chloride in $[RhCl_2(acac)(acacH)]$ using LiBr, were not successful. However, when a metathesis of the chloride in $[RhCl_2(acac)(acacH)]$ by LiBr was carried out *in-situ* , followed by the addition of neutral donor ligands, complexes of the type $[RhBr_2(acac)L_2]$ (L = PPh_3, $AsPh_3$ or py) were obtained. These complexes showed diamagnetic behavior at room temperature, attributed to a low spin d^6 configuration of Rh(III). These are non electrolytes (Table 6.1) thereby confirming covalent nature of bromide in the complexes.

The IR spectra of $[RhBr_2(acac)L_2]$ (L = PPh_3, $AsPh_3$ or py) (Table 6.2, Fig. 6.3) showed two sharp bands in the region 1560-1510 cm^{-1}, characteristic of a chelated O-bonded acetylacetonato group [2]. Further, one more absorption band in 470-450 cm^{-1} region was also observed which may

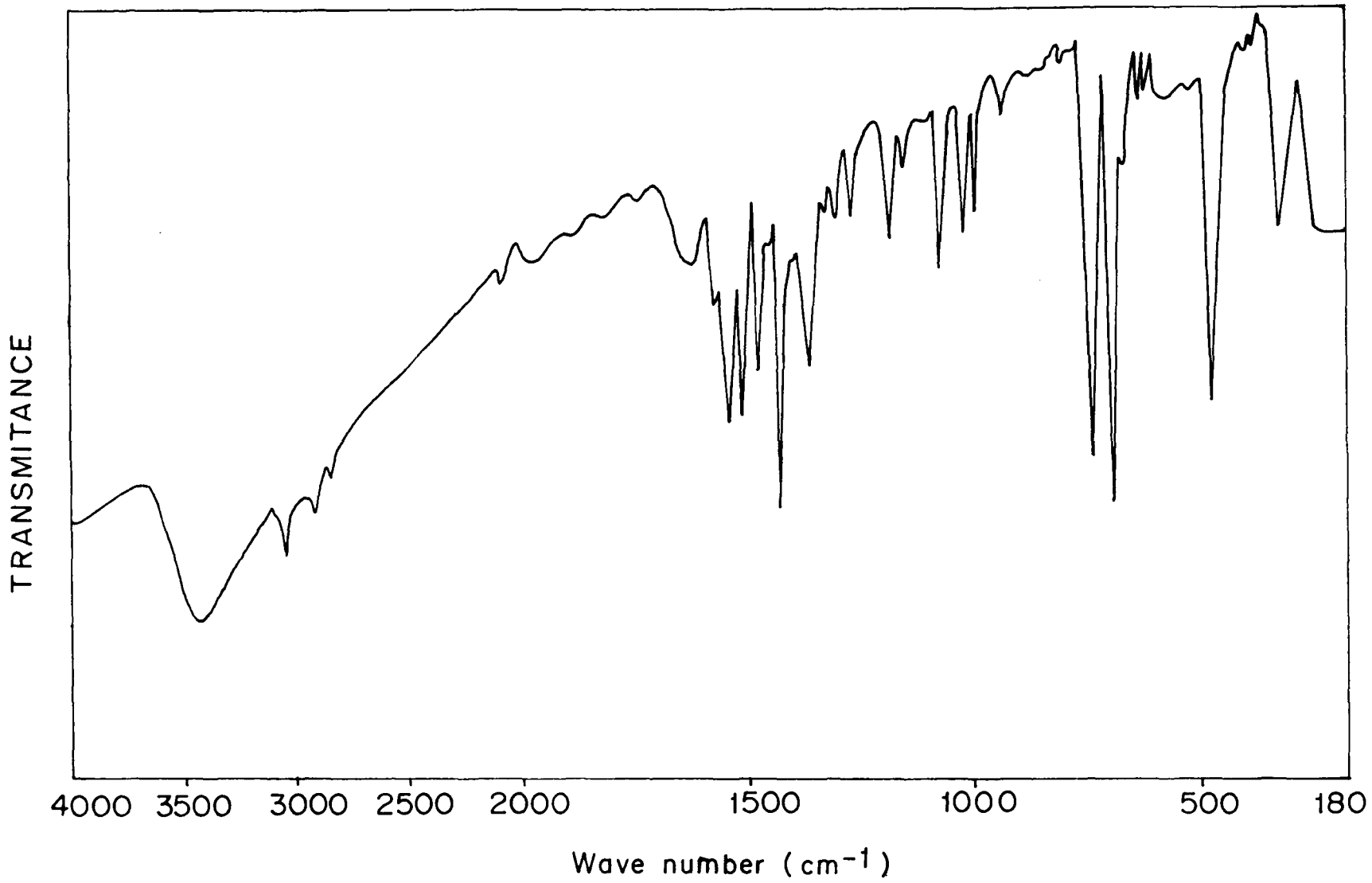

Figure 6.3 Infra-red spectrum of $[RhBr_2(acac)(AsPh_3)_2]$ using KBr disc

be assigned to ν_{Rh-O} [28]. Characteristic absorptions of the ligands were also observed.

The ^1H NMR spectra of $[RhBr_2(acac)L_2]$ (L = PPh_3 or $AsPh_3$) (Table 6.3) showed one singlet between δ 1.9 and δ 2.1 and between δ 4.9 and δ 5.2, which are assigned due to the methyl and the methine protons respectively of the acetylacetonate. Multiplets around δ 7.7 are characteristic of aromatic protons of triphenylphosphine or triphenylarsine. The spectra are similar to their chloro analogues [27]. The electronic absorption spectra of $[RhBr_2(acac)L_2]$ (L = PPh_3, $AsPh_3$ or py) (Table 6.2) showed one absorption band in the region 320 nm to 335 nm having ε value in the range 10^3 to 10^4 which may be assigned to metal → ligand charge transfer transition [27].

A reaction of $[RhCl_2(acac)(acacH)]$ with 2,2'-bipyridine or 1,10-phenanthroline in presence of LiBr resulted in the formation of $[RhBr_2(acac)(L\text{-}L)]$ (L-L = bipy or phen). Molar conductance measurements of these complexes in acetonitrile at room temperature gave a very low values (Λ_M = 10 –12 $\Omega^{-1}cm^2mol^{-1}$) conforming that the bromides are covalently bonded to the metal ion. Complexes are diamagnetic, thereby confirming no change in the oxidation state of the metal during the substitution reactions. The IR spectra of the complexes (Table 6.2, Fig. 6.4), showed two bands in the region 1560-1510 cm^{-1} characteristic of chelated O-bonded acetylacetonato group. Besides the above, all other absorption due to ligands (L-L) were also present. The ^1H NMR spectra of $[RhBr_2(acac)(L\text{-}L)]$ (L-L = bipy or phen) (Table 6.3, Fig. 6.5) are very useful in assigning the geometry of the complexes. The spectra show two

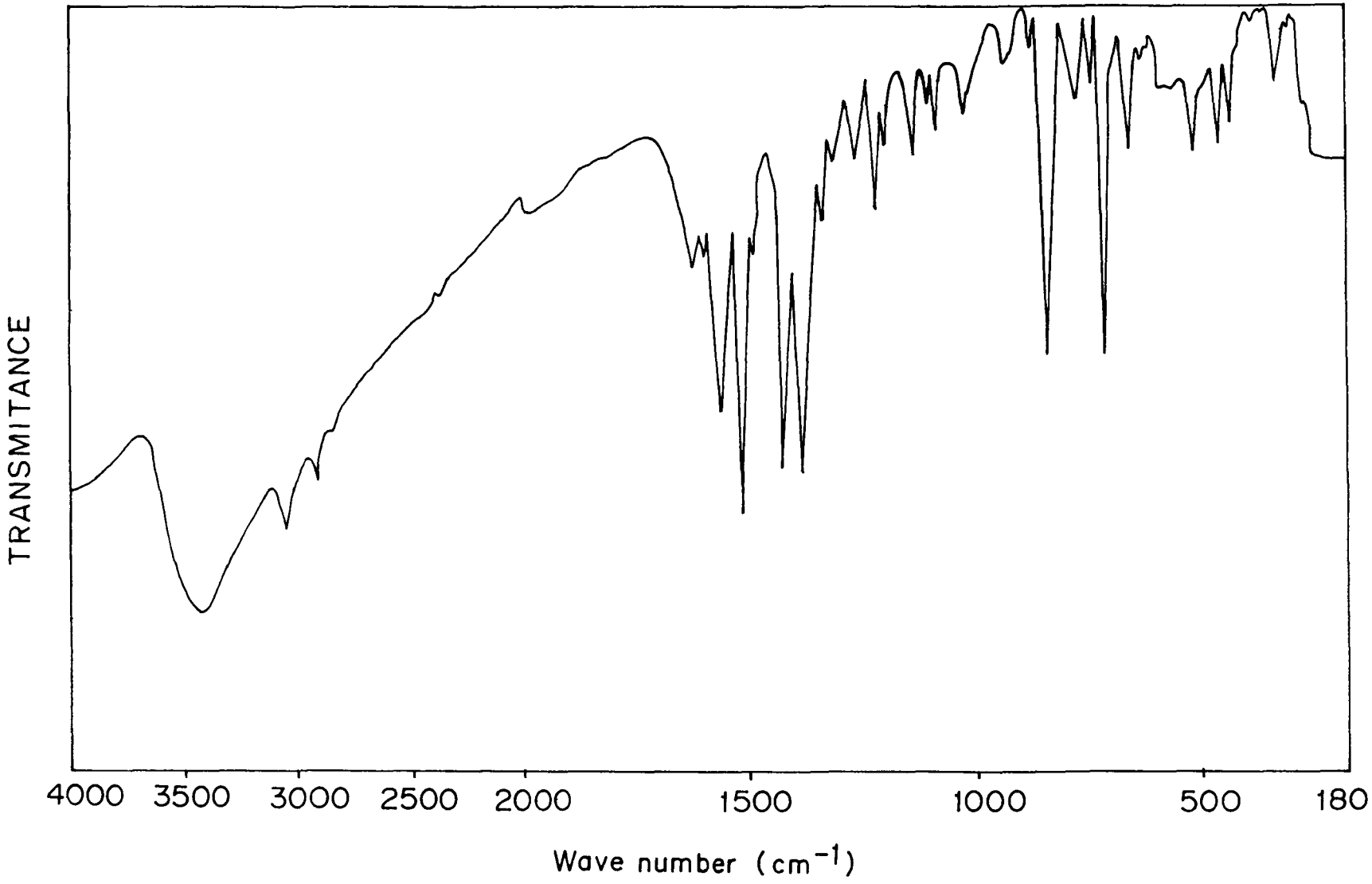

Figure 6.4 Infra-red spectrum of $[RhBr_2(acac)(bipy)]$ using KBr disc

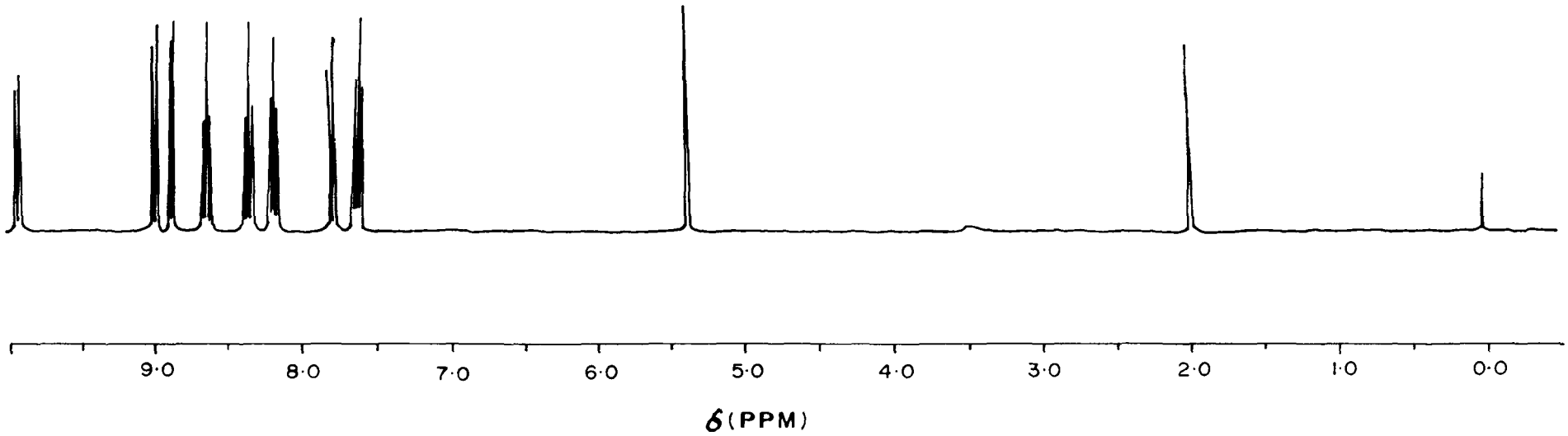

Figure 6.5 ^{1}H NMR spectrum of $[RhBr_2(acac)(bipy)]$ in $CDCl_3$

singlets around δ 2.0 and δ 5.4 having ratio of the protons 6 : 1 assigned to the six methyl protons and one methine proton respectively of the acetylacetonato group. Further ^{1}H NMR due to 2,2'-bipyridine or 1,10-phenanthroline coordinated to rhodium showed eight well resolved separate signals for each of the eight protons of the diimine in the region δ 7.50 to δ 9.90. If we assume a geometry with the bromide ligands in the trans position, presence of a C_2 axis across acac-Rh-(L-L), envisages four protons on either side of the axis are equivalent and hence only four separate signals should be observed. Presence of eight signals of equal intensities is expected when the two bromides are cis to each other, thereby making acac$^-$ and bipy or phen to occupy cis position only. Hence a cis geometry for the diimine substituted complexes (Fig. 6.6) is proposed.

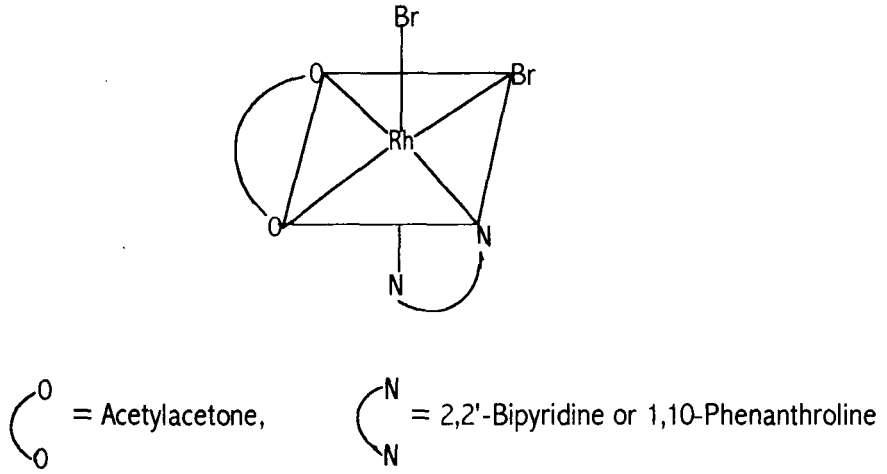

Figure 6.6 Structure of *cis*-[$RhBr_2$(acac)(L-L)] (L-L = bipy or phen)

The electronic absorption spectra of $[RhBr_2(acac)(L\text{-}L)]$ (L-L = bipy or phen) (Fig. 6.7, Table 6.2) showed two absorption bands in the region 300 nm to 350 nm with ε values of the order of 10^4. These bands may be assigned to Rh→ligand ($acac^-$, bipy or phen) charge transfer transition.

7.3.1 Electrochemical Studies

The cyclic voltammograms of $[RhBr_2(acac)L_2]$(L = $AsPh_3$ or py) (Table 6.4, Fig. 6.8) show two oxidation waves. The oxidation wave at a lower potential ($E°_{1/2}$ = 0.60V for $AsPh_3$ and $E°_{1/2}$ = 0.75 V for py) is irreversible whereas at higher potential ($E°_{1/2}$ = 0.75V, ΔE_p = 100 mV for $AsPh_3$and $E°_{1/2}$ = 0.98 V, ΔE_p = 160 mV for py) is quasi-reversible. Both of the complexes showed one irreversible reduction wave at $E°_{1/2}$ = -1.4 V which may be attributed to the ligand reduction in the complexes. In case $[RhBr_2(acac)(phen)]$ (Table 6.4, Fig. 6.9) two irreversible oxidation waves at $E°_{1/2}$ = 0.96 V and 1.32 V are observed. An irreversible reduction wave at $E°_{1/2}$ = -1.20 V for the complex may be assigned to the reduction of 1,10-phenanthroline. A report on the cyclic voltametric studies of $[Rh(acac)_3]$ describes a metal based irreversible oxidation at $E°_{1/2}$ = 1.74 V assigned to Rh(IV)/Rh(III) couple [30]. In the light of the above, oxidation waves observed are most likely due to metal based oxidations.

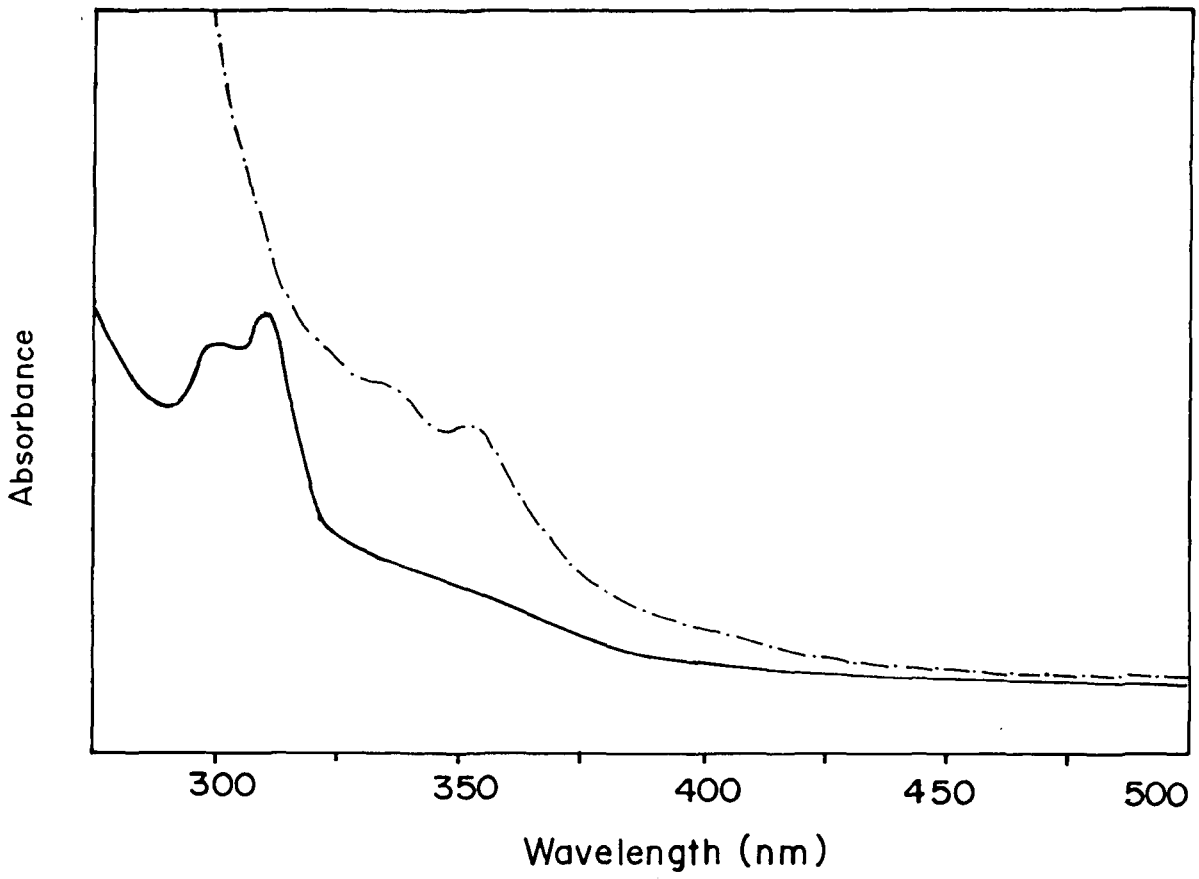

Figure 6.7 Electronic absorption spectra of [$RhBr_2$(acac)(bipy)] (_____) and [$RhBr_2$(acac)(phen)] (----------) in acetonitrile

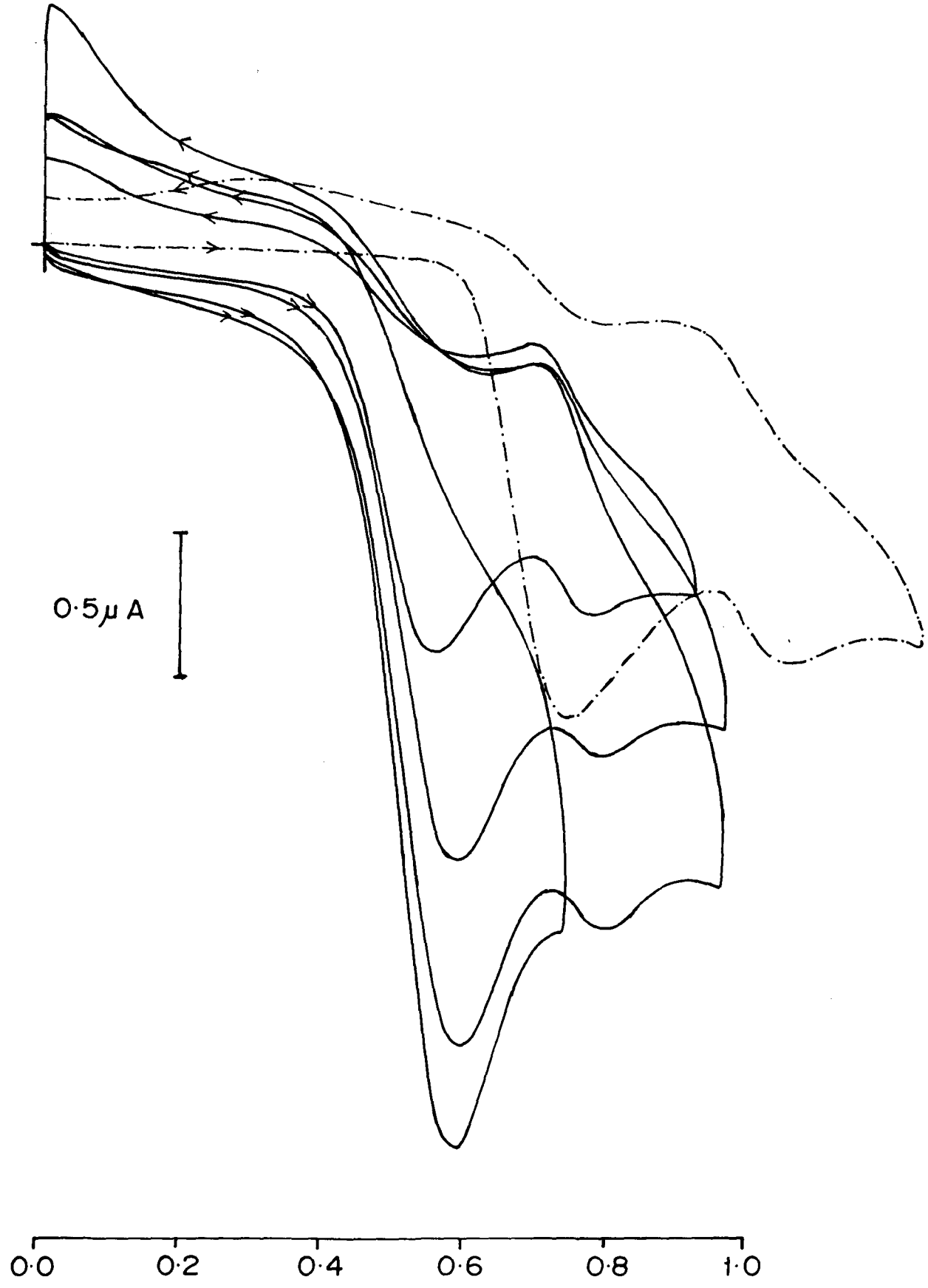

Figure 6.8 Cyclic voltammograms of [$RhBr_2(acac)(AsPh_3)_2$] (_____) at different scan rates:20, 50, 100, 200 mV/s and [$RhBr_2(acac)(py)_2$] (----------) at scan rate 50 mV/s in CH_3CN at room temperature

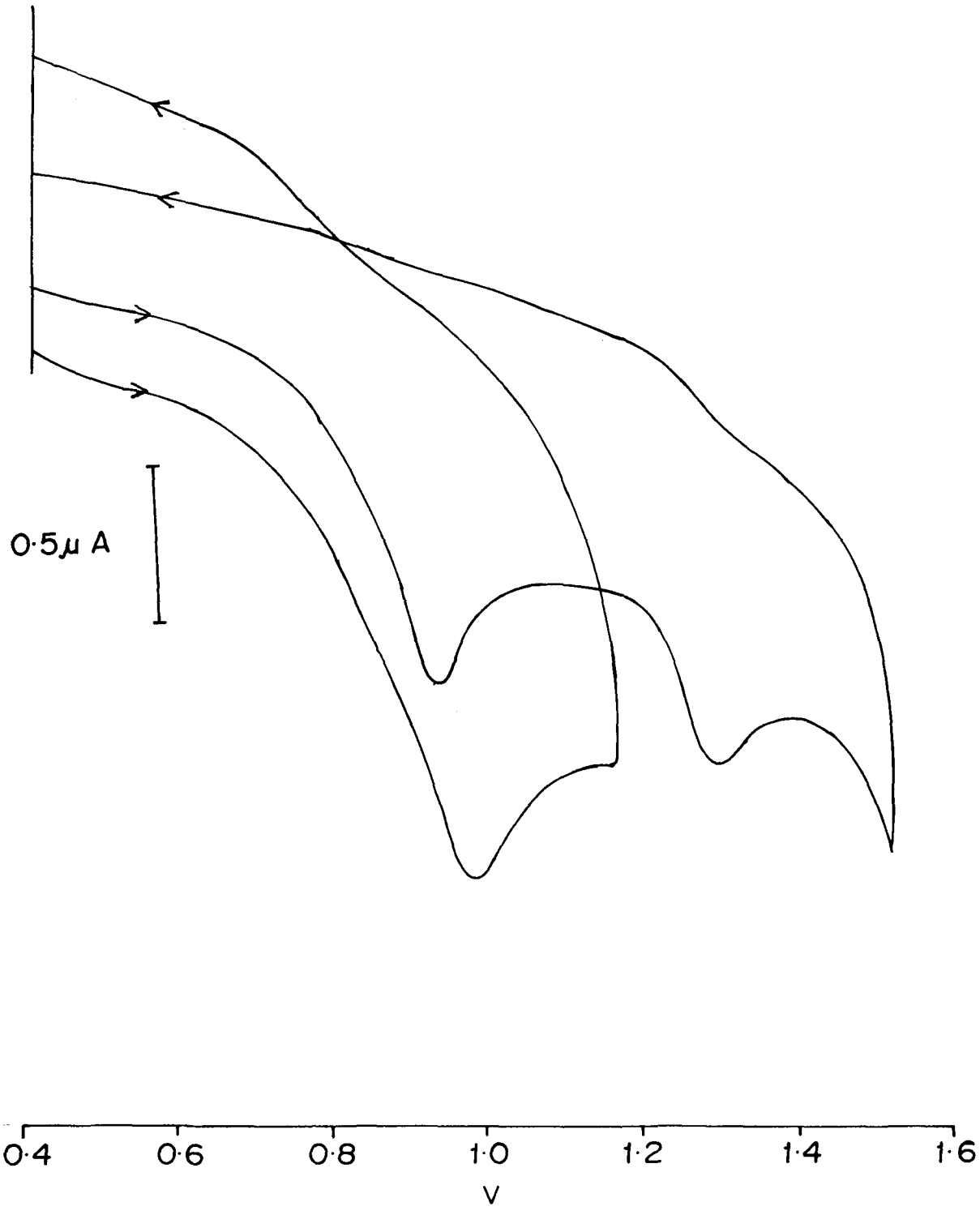

Figure 6.9 Cyclic voltammogram of [$RhBr_2(acac)(phen)$] in acetonitrile at room temperature, scan rates 20, 50, mV/s

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Table 6.1 Physical and Analytical data of Rhodium(III) complexes

Compound	Colour	M.P. (°C)	Λ_M $\Omega^{-1}mol^{-1}cm^2$	Analysis(%)[a]			
				C	H	N	Cl/Br
$[RhCl_2(acac)(acacH)]$	Light brown	310[d]	10	31.8(32.2)	3.8(4.0)		19.5(19.0)
$[RhCl_2(acac)(py)_2]$	Brown	135[d]	7	41.3(41.8)	3.5(3.9)	6.1(6.5)	16.0(16.5)
$[RhBr_2(acac)(PPh_3)_2]$	Brown	195	5	55.0(55.5)	4.0(4.2)		17.6(18.1)
$[RhBr_2(acac)(AsPh_3)_2]$	Brown	198	5	49.9(50.5)	3.2(3.8)		17.1(16.4)
$[RhBr_2(acac)(py)_2]$	Brown	Above 250	16	34.1(34.6)	3.0(3.3)	5.3(5.4)	29.9(30.8)
$[RhBr_2(acac)(bipy)]$	Orange	Above 250	12	34.5(34.7)	3.0(2.9)	5.2(5.4)	30.5(30.9)
$[RhBr_2(acac)(phen)]$	Yellowish brown	Above 250	10	37.5(37.6)	2.1(2.8)	5.0(5.3)	29.3(29.5)

[a] Calculated values are in parenthesis ; [d] Decomposition temperature

Table 6.2 Important infrared and electronic absorption spectral data of Rhodium(III) complexes

Compound	Infra-red bands(cm^{-1})	UV-Vis[c], λ_{max}, nm, (ε)
$[RhCl_2(acac)(acacH)]$[b]	1700, 1625, 1555, 1514, 470, 365	
$[RhCl_2(acac)(acacH)]$[a]	1620, 1565, 1516, 476, 364	315(6100), 217[sh](10,800)
$[RhCl_2(acac)(py)_2]$[a]	1550, 1515, 470, 321	313(3140)
$[RhBr_2(acac)(PPh_3)_2]$[a]	1556, 1515, 458	332(10,200)
$[RhBr_2(acac)(AsPh_3)_2]$[a]	1540, 1515, 473	335(12,850)
$[RhBr_2(acac)(py)_2]$[a]	1550, 1515, 469	321[sh](1720)
$[RhBr_2(acac)(bipy)]$[a]	1556, 1515, 457	312(18,200), 302(17020)
$[RhBr_2(acac)(phen)]$[a]	1558, 1513, 460	350(3140), 336(3570), 270(30,000)

[a] as KBr pellets ; [b] in chloroform ; [c] UV-vis spectra were taken in acetonitrile ; [sh] shoulder

Table 6.3 ^{1}H NMR spectra of Rhodium(III) complexes

Compound	δ(ppm)
$[RhCl_2(acac)(acacH)]^a$	2.25(s), 2.38(s), 5.35(s)
$[RhCl_2(acac)(py)_2]^b$	2.20(s), 2.55(s), 2.60(s), 5.45(s), 5.59(s), 5.76(s), 7.61-8.30(m)
$[RhBr_2(acac)(PPh_3)_2]^b$	1.90(s), 5.20(s), 7.60(m)
$[RhBr_2(acac)(AsPh_3)_2]^a$	2.13(s), 4.95(s), 7.80(m)
$[RhBr_2(acac)(bipy)]^b$	1.97(s), 5.36(s), 7.50(t), 7.60(d), 8.16(t), 8.31(t), 8.58(t), 8.83(d), 8.95(d), 9.89(d)
$[RhBr_2(acac)(phen)]^c$	2.10(s), 5.40(s), 7.62(m), 7.82(d), 8.24(d), 8.35(m), 8.39(m), 8.67(d), 9.05(d), 9.35(d)

[a] Measured in $CDCl_3$, [b]Measured in $(CD_3)_2SO$, [c]Measured in CD_3CN

Table 6.4 Cyclic Voltametric measurement data for the oxidation and reduction of Rhodium(III) complexes

Compound	Oxidation		Reduction	
	E_p^{ox}	E_p^{red}	E_p^{red}	E_p^{ox}
$[RhCl_2(acac)(py)_2]$	+1.1	-	-1.15	-
$[RhBr_2(acac)(py)_2]$	+0.75	-	-1.40	-
	+1.06	0.90		
$[RhBr_2(acac)(AsPh_3)_2]$	+0.60	-	-1.40	-
	+0.80	0.70		
$[RhBr_2(acac)(phen)]$	+0.96	-	-1.20	-
	+1.32	-		

Conditions : acetonitrile solvent , Tetrabutylammonium perchlorate as supporting electrolyte , scan rate = 100 mVs^{-1}, E_p^{ox} = Oxidation peak potential, E_p^{red} = reduction peak potential.

CHAPTER 7

Chapter 7

Copper(II) catalysed condensation of 3,5-dimethyl-pyrazole and acetonitrile : isolation of a new copper(II) amidine complex

7.1 Introduction

Acetonitrile serves as a ligand in a number of coordination compounds. Inspite of the presence of a reactive nitrile group, it has been found to be a good solvent. Acetonitrile undergoes addition reactions at the nitrile group with a suitable substrate such as amine, in the presence of a Lewis acid [1-3]. Compounds with the activated nitrile group, for example Cl_3CCN and NH_2CN react with the amines even in the absence of Lewis acid [4,5]. Activation of nitrile group also occurs by its coordination to a

metal. A recent review article [6] comprehends the reactions of coordinated transition metal nitriles. It is interesting to note that the insertion of a nitrile group to an N-H moiety in presence of a metal ion, gives rise to amidine metal complexes [7]. In this chapter , we describe the synthesis of a new copper(II) amidine complex, $[Tp^*CuL]ClO_4$ (Tp^* = hydrotris(3,5-dimethylpyrazolyl)borate and L = 1-methylcarbaldimino-3,5-dimethylpyrazole). 1-methylcarbaldimino-3,5-dimethylpyrazole is formed *in situ* by the condensation of acetonitrile with 3,5-dimethylpyrazole(DMPZ) under the influence of copper(II) ion.

7.2 Experimental

All chemicals were of reagent grade and used without further purification.Sodium borohydride, acetylacetone and hydrazine hydrate were purchased from s.d.fine-chem. India. Cupric perchlorate was prepared by the reaction of $CuCO_3$ with $HClO_4$. 3,5-Dimethylpyrazole was prepared by the condensation of acetylacetone and hydrazine hydrate.

7.2.1 Preparation of Sodium Hydrotris(3,5-dimethylpyrazolyl)borate

An intimate mixture of 1.0 g (26.43 mmol) sodium borohydride and 10.17g (105.77 mmol) 3,5-dimethylpyrazole was heated slowly at 195°C with constant stirring. A cupious amount of hydrogen gas was evolved. The

temperature was maintained at 190 - 195°C for 4h to get a solid mass. The solid was crushed to powder and washed with warm(40°C) toluene. The solid was used without further purification. Yield : 80 % , m.p. : 320° C.

7.2.2 Preparation of [Tp*CuL]ClO_4

A solution of sodium hydrotris(3,5-dimethylpyrazolyl)borate (NaTp*) (0.22g, 0.69 mmol) in dichloromethane (15 cm^3) was added to a solution of $Cu(ClO_4)_2.6H_2O$ (0.25g. 0.67 mmol) in acetonitrile (15 cm^3) and the mixture was stirred for 4h at room temperature when a green solution was obtained. On evaporation of the solvent at room temperature, a green micro crystalline product separated out. It was purified by passing through a silica gel column using dichloromethane - acetonitrile (9 : 1) as eluent. Yield : 0.20g, (50%). Anal. : Found : C = 44.23, H = 5.58, N = 21.11% ; Calcd. for $C_{22}H_{33}BClCuN_9O_4$, C = 44.18, H = 5.61, N = 21.14%.

7.2.3 X-ray structure determination

X-ray quality crystals were developed by keeping a saturated solution of the compound in acetonitrile for several days at 5° C. Table 7.1 summarizes the crystal data and details of structure solution and refinement parameters. The cell constants and an orientation matrix for data collection

were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of $23.418 < \theta < 45.765$ in an Enraf Nonius CAD4 automatic diffractometer. Data were collected at 293 K using CuKα (λ = 1.5418 A°) and the ω scan technique, and corrected for Lorentz and polarisation effects. A semi-empirical absorption correction (psi scan) was made. The structure was solved by Patterson methods and subsequent difference Fourier maps are refined on F^2 by a full-matrix least squares procedure using anisotropic displacement parameters. All hydrogen atoms were located from difference Fourier maps except those of the methyl groups which were located in their calculated positions (C-H 0.96A°) . The located hydrogen atoms were refined isotropically, whereas the calculated hydrogen atoms were refined using a riding model. The absolute configuration was established. Atomic positional parameters for the non-hydrogen atoms are listed in Table 7.2.

7.3. Results and Discussion

[Tp*CuL]ClO_4 has been synthesized by a reaction of cupric perchlorate with NaTp* in acetonitrile-dichloromethane medium at room temperature. The formation of 1-methtlcarbaldimino-3,5-dimethylpyrazole(L) presumably takes place by the condensation of DMPZ with acetonitrile activated by Cu(II) ion, in view of the following facts. DMPZ remains unchanged for several days in acetonitrile solution at room

temperature. The non-Lewis acid catalysed addition of amines to nitriles require the presence of an activating group [4,5] and acetonitrile has been found to be an excellent solvent in such reactions [4]. In acetonitrile or dichloromethane NaTp* decomposes producing DMPZ. The decomposition of polypyrazolylborate in solution has been evidenced in the literature [7-10]. The plausible mechanism of the reaction may be one among the following (i) initial coordination of both DMPZ and acetonitrile to Cu(II), followed by their condensation, forming a C-N linkage and amidine by the nucleophilic attack of DMPZ on the nitrile carbon of acetonitrile (ii) nucleophilic attack of the coordinated DMPZ on the nitrile carbon of the solvent acetonitrile, with the *in situ* generation of amidine and its coordination to the metal (iii) nucleophillic attack of DMPZ present in the solvent on the nitrile carbon of the coordinated acetonitrile, with the *in situ* generation of amidine and its coordination to the metal center. For reactions closely related to this, the mechanism of the first kind has been reported [7, 11-12].

The perspective view of the complex cation is presented in Fig. 7.1. Three nitrogen atoms of Tp* and two nitrogen atoms of L are coordinating with the copper making a distorted square pyramidal geometry around the metal center. The ligand Tp* is coordinated in a tridentate chelated fashion. The molecule shows an axial elongation as expected for Jahn-Teller distortion susceptible copper(II) ion , with Cu(1)-N(32) bond distance [2.153(2) A°] being significantly longer than the other Cu-N bonds [av. 2.022(3) A°]. The bond length of special significance is the appreciably

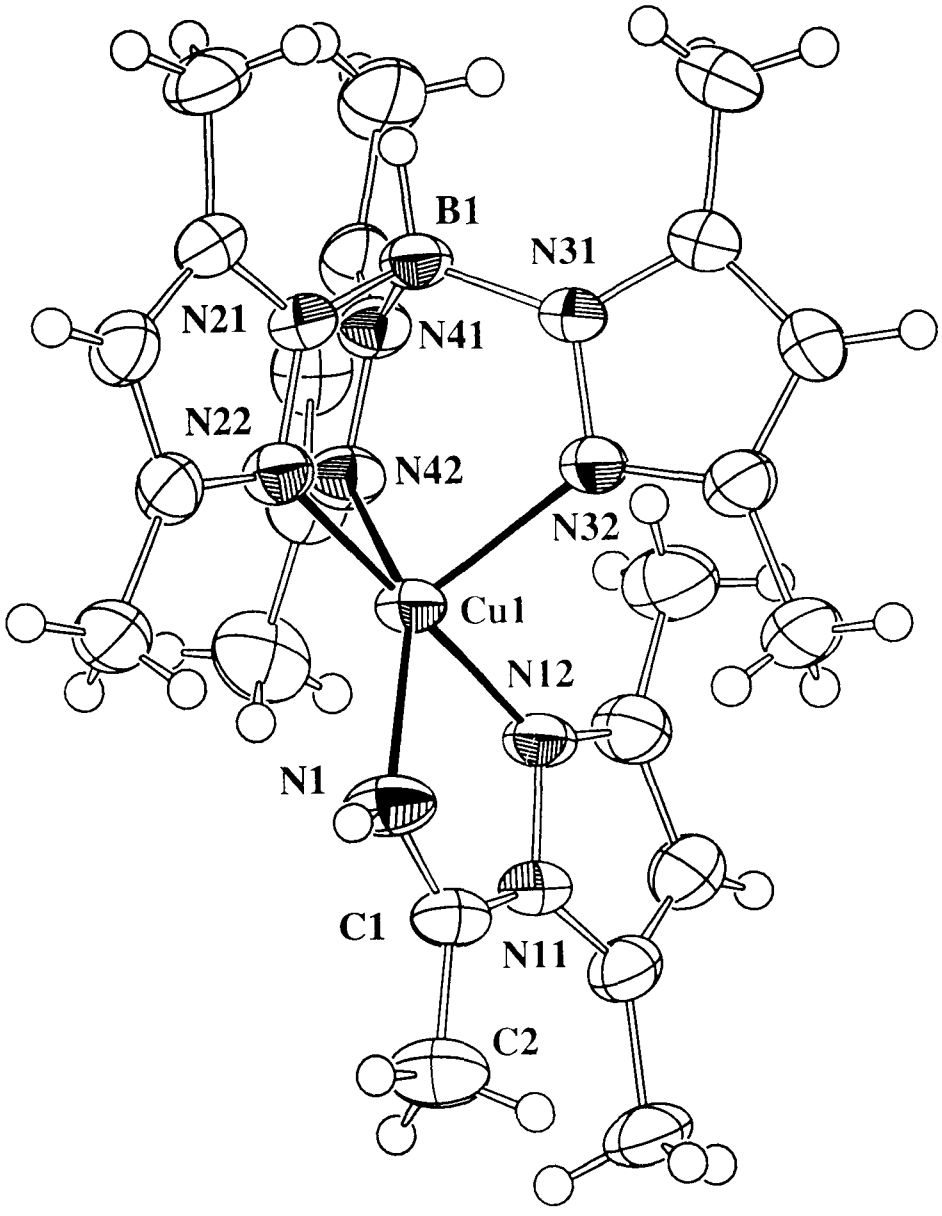

Figure 7.1 Perspective view of $[Tp^*CuL]^+$ with atom numbering scheme

short [1.276(6) A°] amidine C=N bond compared to the average [1.342(5) A°] C-N bond distance of the pyrazolyl rings in the compound and C(1)-N(11) bond length [1.393(6) A°] in the amidine ligand, indicating its pronounced double bond character. Another important structural feature is the presence of a hydrogen bond between the hydrogen atom of C=NH moiety and oxygen of the perchlorate ion, having a non-bonding distance 2.34(A°). Selected bond lengths and angles are collected in Table 7.3.

In the IR spectrum (Fig. 7.2), a medium intensity band at 2526 cm^{-1} indicates the presence of the B-H moiety. Another strong band at 1090 cm^{-1} and a medium sharp band at 625 cm^{-1} is characteristic of ν_3 and ν_4 modes of vibration respectively of the ionic perchlorate group. The electronic absorption spectrum (Fig. 7.3) of the compound in acetonitrile displays multiple absorption bands at λ/nm (ε /$dm^3mol^{-1}cm^{-1}$) 217(22,900), 258(2,190), 338(290) and 670br(27). The absorption at 670 nm, assignable to d-d transition is suggestive of the square pyramidal geometry of the Cu(II) compound [13]. [Tp*CuL]ClO_4 exhibits an interesting electrochemical property. The cyclic voltammetric (Fig. 7.4) behavior of the compound in acetonitrile is characterized by a highly quasi-reversible response at $E_{1/2}$ = 0.32 V *vs.* SCE with ΔE_p = 360 mV, which is attributed to Cu^{II}/Cu^{I} couple. It is pertinent to mention that Cu^{II}/Cu^{I} couple occuring at such high potential is rare although not unprecedented [14]. The irreversible ligand reduction occurs at negative potential. The compound registers a normal value of room temperature solid-state magnetic moment, μ = 1.78 BM, for a monomeric

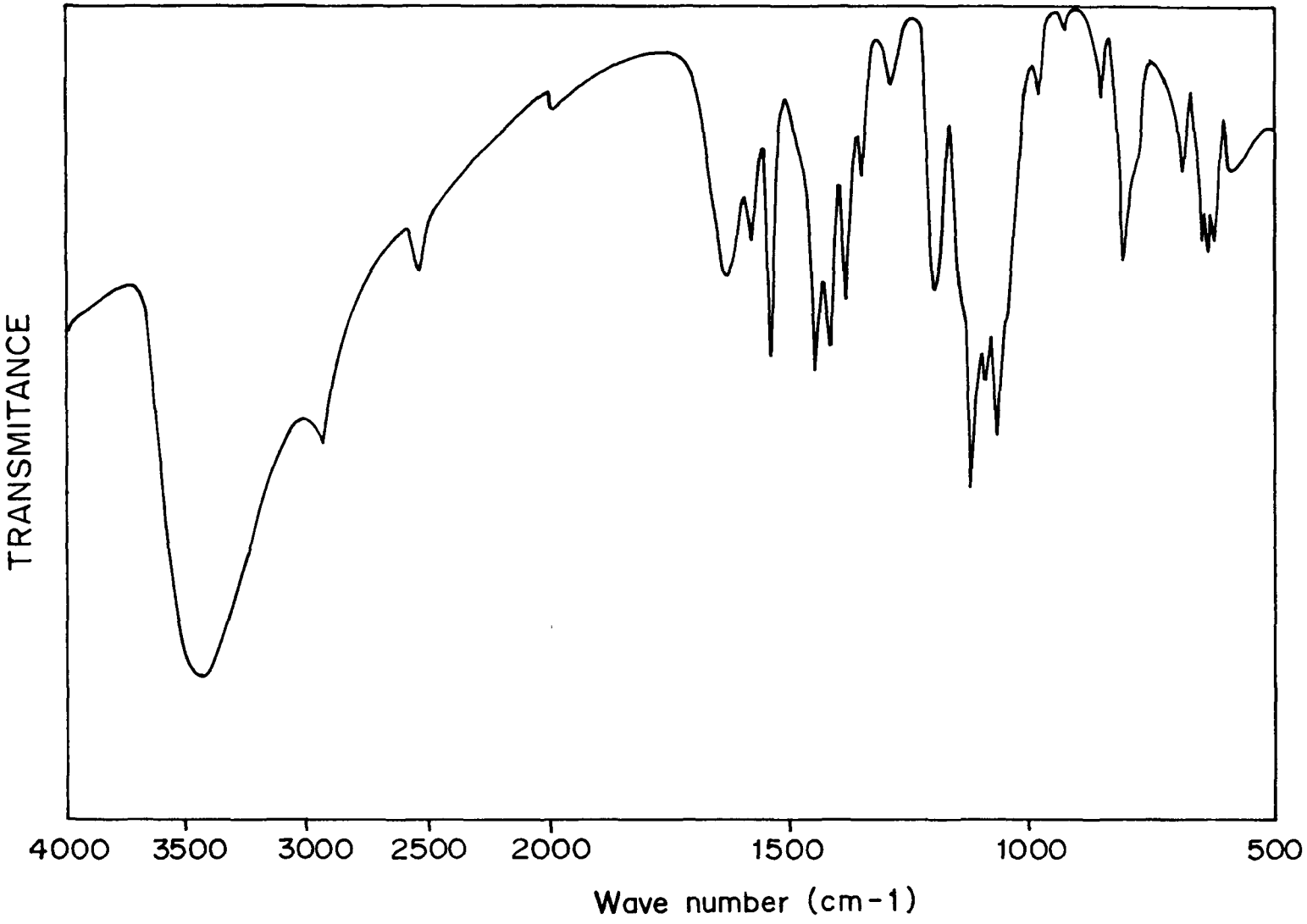

Figure 7.2 Infra-red spectrum of [Tp*CuL]ClO_4 using KBr pellet

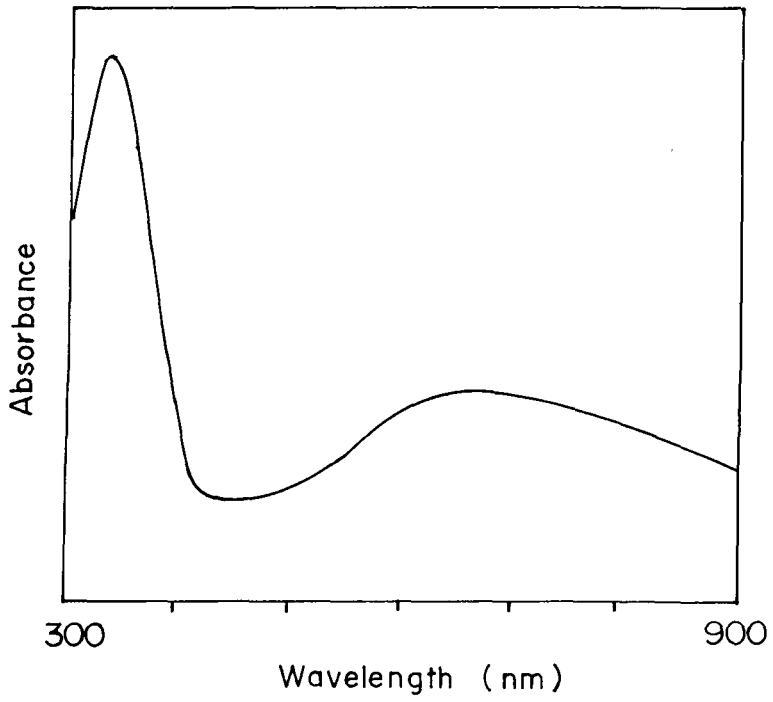

Figure 7.3 Uv-visible spectrum of $[Tp^*CuL]ClO_4$ in CH_3CN

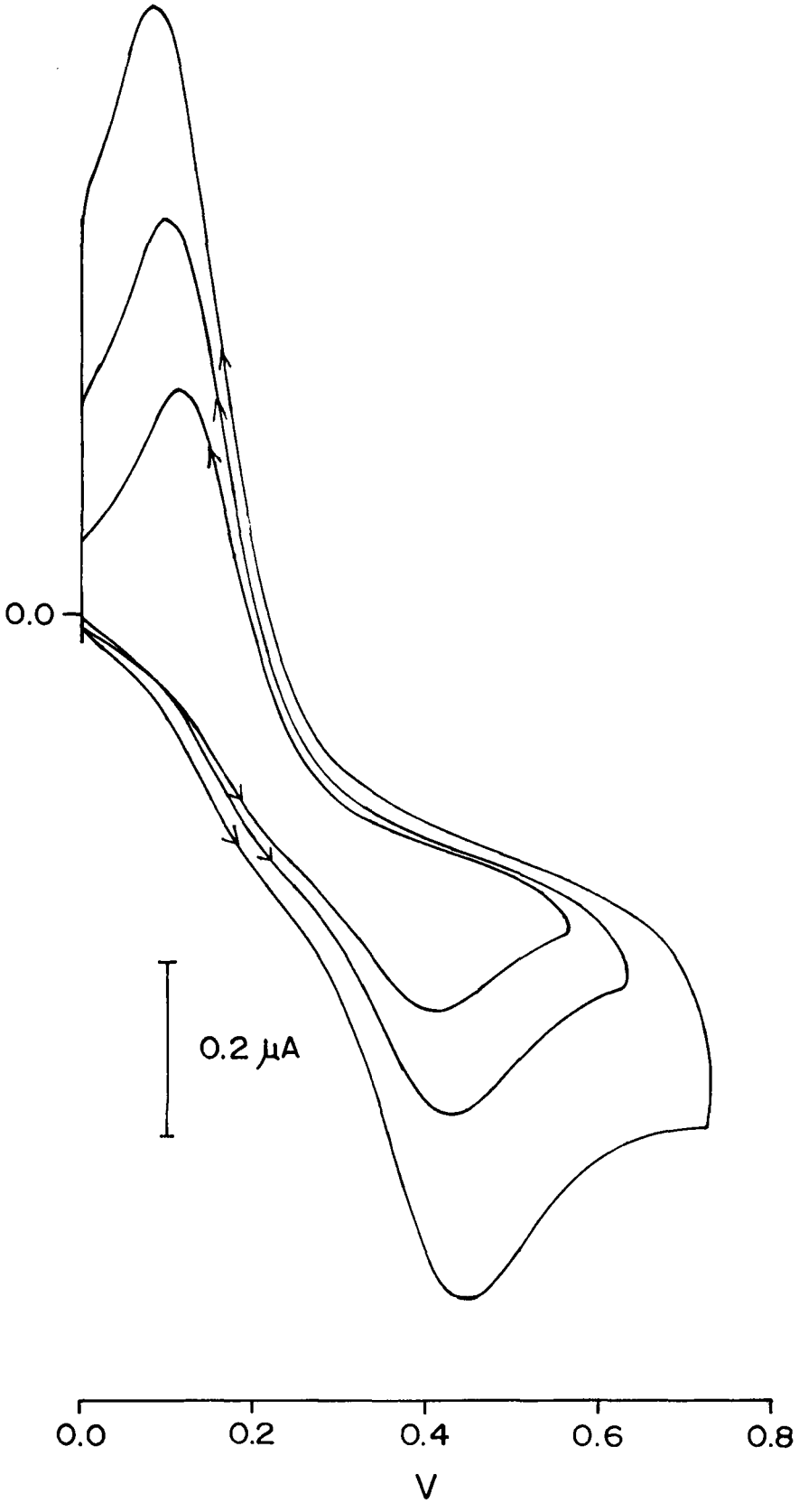

Figure 7.4 Cyclic voltammogram of [Tp*CuL]ClO_4 in acetonitrile at 25°C, scan rate:50, 100 and 200 mV/s.

bivalent copper entity. In the EPR spectrum (Fig. 7.5) the compound exhibits four hyperfine lines with $g_{II} = 2.47$, $g_{\perp} = 2.16$ and $A_{II} = 160 \times 10^{-4}$ cm^{-1} in frozen 50% aqueous –dimethylsulfoxide solution at liquid nitrogen temperature. This spectral feature ($g_{II} > g_{\perp} > 2.03$ and $g_{II}/A_{II} = 154$ cm^{-1}) is consistent with its monomeric square pyramidal stereochemistry [15].

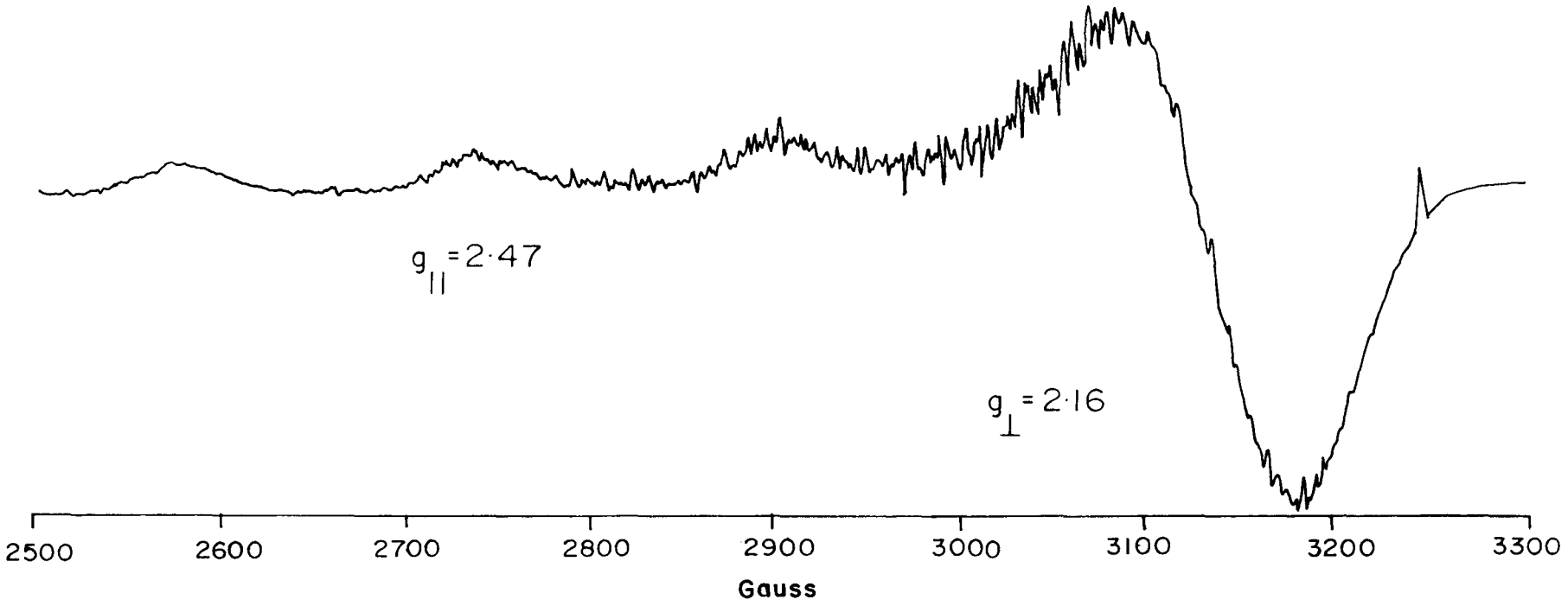

Figure 7.5 EPR spectrum of [Tp*CuL]ClO_4 in frozen aqueous-Me_2SO solution at liquid nitrogen temperature

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Table 7.1 Crystal data, structure and refinement for $[Tp^*CuL]ClO_4$

Empirical formula	$C_{22}H_{33}BClCuN_9O_4$
Formula weight	M = 597.37
Temperature	T = 293(2) K
Crystal System	monoclinic
Space group	Pc
Crystal dimensions (mm)	0.35 x 0.35 x 0.35
Unit cell dimensions	a = 10.2879(7) A°
	b = 7.8877(7) A°, β = 96.896(6)°
	c = 17.1301(14) A°
Volume	U = 1380.01(19) A^{o3}
Z	2
Density (calculated)	1.438 g cm^{-3}
F(000)	622
μ(CuKα)(cm^{-1})	23.95
Radiation	CuKα(λ = 1.5418 A°)
Number of reflections	3046
Number of unique reflections	3045
Goodness-of-fit	1.049
R, Rw	0.388, 0.1041

Table 7.2 Atomic Coordinates ($x10^{-4}$) and equivalent isotropic displacement parameters ($A^{o2} \times 10^{-3}$) for $[Tp^*CuL]ClO_4$

	x	y	z	U(eq)
Cu(1)	5821(1)	5383(1)	3944(1)	36(1)
N(1)	7246(4)	6016(5)	4805(2)	50(1)
N(11)	8492(3)	4269(4)	4171(2)	39(1)
N(12)	7389(3)	4148(5)	3631(2)	40(1)
N(21)	3215(3)	6762(4)	3680(2)	36(1)
N(22)	4241(3)	6576(4)	4270(2)	38(1)
N(31)	4364(3)	6788(4)	2461(2)	36(1)
N(32)	5583(3)	6864(4)	2881(2)	39(1)
N(41)	3544(3)	4041(4)	2971(2)	38(1)
N(42)	4533(3)	3526(4)	3523(2)	41(1)
C(1)	8368(4)	5325(5)	4809(3)	43(1)
C(2)	9494(6)	5560(7)	5422(4)	61(1)
C(12)	6761(6)	2861(9)	2334(3)	70(2)
C(13)	7702(5)	3216(6)	3048(3)	49(1)
C(14)	9023(5)	2699(7)	3211(3)	53(1)

C(15)	9504(4)	3378(5)	3914(3)	45(1)
C(16)	10841(4)	3178(7)	4339(3)	58(1)
C(22)	4741(5)	7335(9)	5676(3)	63(1)
C(23)	3876(4)	7295(6)	4916(2)	43(1)
C(24)	2625(4)	7952(6)	4747(3)	49(1)
C(25)	2232(4)	7606(5)	3965(2)	42(1)
C(26)	969(4)	8018(7)	3485(3)	58(1)
C(32)	7789(5)	7860(9)	2685(4)	69(2)
C(33)	6378(4)	7573(6)	2411(3)	47(1)
C(34)	5667(5)	7966(7)	1687(3)	55(1)
C(35)	4401(4)	7440(6)	1736(2)	46(1)
C(36)	3236(6)	7517(9)	1131(3)	70(2)
C(42)	5477(7)	863(7)	4094(4)	70(2)
C(43)	4532(5)	1845(5)	3529(3)	48(1)
C(44)	3538(5)	1259(6)	2963(3)	46(1)
C(45)	2937(4)	2667(6)	2623(2)	46(1)
C(46)	1822(5)	2818(8)	1979(3)	64(1)
B(1)	3252(4)	5956(6)	2856(3)	38(1)
Cl(1)	-1098(1)	-263(2)	651(1)	60(1)
O(1)	-1711(7)	-1862(6)	548(4)	108(2)
O(2)	-746(13)	329(9)	-44(6)	193(6)
O(3)	-1967(8)	875(7)	943(4)	133(3)
O(4)	-59(11)	-500(19)	1170(10)	244(8)

U(eq) is one third of the trace orthogonalized Uij tensor.

Table 7.3 Selected bond lengths (A°) and angles(°)

Cu(1) - N(1)	2.014(4)	N(1) – C(1)	1.276(6)
Cu(1) - N(12)	2.012(3)	N(11) – C(1)	1.393(6)
Cu(1) - N(22)	2.014(3)	N(12) – C(13)	1.311(5)
Cu(1) - N(42)	2.047(3)	N(12) – C(15)	1.372(5)
Cu(1) - N(32)	2.152(3)	N(21) – C(25)	1.350(5)
		N(22) – C(23)	1.336(5)
		N(31) – C(35)	1.350(5)
		N(32) – C(33)	1.338(5)
		N(41) – C(45)	1.354(5)
		N(42) – C(43)	1.326(5)

N(12) - Cu(1) - N(1)	77.22(15)	N(22) - Cu(1) - N(42)	85.55(14)
N(12) - Cu(1) - N(22)	178.81(15)	N(12) - Cu(1) - N(32)	92.88(13)
N(1) - Cu(1) - N(22)	102.81(15)	N(1) - Cu(1) - N(32)	118.91(16)
N(12) - Cu(1) - N(42)	93.75(14)	N(22) - Cu(1) - N(32)	88.14(13)
N(1) - Cu(1) - N(42)	144.97(16)	N(42) - Cu(1) - N(32)	95.03(13)

D-H	A	d(D-H)	d(H---A)	d(D---A)	<(DHA)
N(1) – H(10)	0(3)#1	0.88(7)	2.34(7)	3.177(7)	157(6)

Symmetry transformations used to generate equivalent atoms :

#1 x+1, -y+1, z+1/2

List of Publications:

1. Synthesis and Catalytic activity of Ruthenium (II) complexes containing acetylacetonate.
   Bipul C. Paul, **Prashanta Sarkhel** and Raj K. Poddar*. J. Coord. Chem., 1995, **36**, 267-272.

2. Mono and Binuclear ruthenium (II) trifluoroacetato complexes containing co-ligands.
   Prashanta Sarkhel, Sekhar Ch. Sarker, A.K.Gupta and Raj K. Poddar* Trans. Met. Chem., 1996, **21**, 250-253.

3. Rhodium (III) complexes containing acetylacetonate and mono or bidentate ligands.
   Prashanta Sarkhel, Bipul C. Paul and Raj K. Poddar* Ind. J. Chem., Sec.A, **38A**, 1999, 150-155.

4. Isolation of a new Copper (II) amidine complex and its characterisation.
   Gagan C. Mandal, **Prashanta Sarkhel**, Raj K. Poddar*, E. Bermejo, Alfonso Castneiras* and P. Sevillano. Ind. J. Chem., 2000 (in press).

5. Reactivity studies of (η^6-p-cymene)Ruthenium complexes with 4,4'-bipyridine and Imidazole ligands.
   Prashanta Sarkhel and K. Mohan Rao*. Ind. J. Chem., Communicated

Symposium /Conference/Workshops attended :

1. ***National symposium on perspective of Inorganic Chemistry.***
   Convenient synthesis, characterization and studies of mono and binuclear Ruthenium (II) trifluoroacetato complexes containing pyridines.
   Prashanta Sarkhel and Raj K. Poddar.
   December 21-22,1995, IACS, Jadavpur, Calcutta.

2. ***Workshop on FT-NMR sponsored by Department of Science and Technology, Govt. of India.***
   June 28-30, 2000, Conducted by RSIC, NEHU, Shillong.

3. ***Introduction to Computer Networks and Internet.***
   September 26-29, 2000, Conducted by the Bio-Informatics Centre, NEHU, Shillong.