STUDIES ON
THE COMPLEXES OF RUTHENIUM (III) AND RUTHENIUM (II) WITH DIMETHYLSULPHOXIDE AND SOME MONODENTATE AND BIDENTATE LIGANDS

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Chem.
Dis.

Dedicated
to
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I certify that the thesis entitled "Studies on the Complexes of Ruthenium(III) and Ruthenium(II) with dimethylsulphoxide and some monodentate and bidentate ligands", submitted by Mr. Uma Charan Sarma for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigations carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

Date: 29/8/88

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Signature of the Supervisor

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Uma Charan Sarma.
Uma Charan Sarma

CONTENTS

ABBREVIATIONS

abt : *o*-aminobenzenethiolate

acac : acetylacetonate

acacH : acetylacetone/Pentane-2,4-dione

aq : aquated

ba : benzoylacetonate

bdk : β -diketonate

bipy : 2,2'-bipyridyl

BM : Bohr Megneton

bu : butyl

Conc. : Concentrated

CD : Circular Dichroism

CT : Charge transfer

CV : Cyclic Voltammetry

D : Diamagnetic

d : decomposes

DM : dipolemoment

dbm : dibeuzoylmethanate

depe : 1,2-*bis*(diethylphosphino)ethane

depp : 1,3-*bis*(diethylphosphino)propane

diars : *o*-phenylene *bis* dimethylarsine

diphos : 1,2 *bis*(diphenylphosphino)ethane

DMF : N,N'-dimethylformamide

dmpe : 1,2-*bis*(dimethylphosphino)ethane

dtc : diethyldithiocarbamate

EDA : ethylene-1,2-*bis* diphenylarsine

EPR : electron paramagnetic resonance

en : ethylenediamine

Et : ethyl

fac : facial

g : gram

h : hour

IR : infrared

L : ligand

(L-L) : bidentate ligand

M : central metal in a compound

MW : molecular weight

m : medium

MeOH : methanol

mer : meridional

Me_2SO : dimethylsulphoxide

Me : methyl

m mol : milimol

MO : molecular orbital

m.p. : melting point

^1H NMR : Proton nuclear magnetic resonance

nm : nenometer

ox : oxalate

Ph : phenyl

PDA : *o*-phenylenediamine

phen : 1,10-phenanthroline

p p.m : parts per million

pr : propyl

py : pyridine
R : Raman
RT : room temperature
s : strong
sh : shoulder
T : temperature
THF : tetrahydrofuran
TMS : tetramethylsilane
UV : ultraviolet
UV-VIS : ultraviolet-visible
w : weak
QAS : Tris-(2-diphenylarsinophenyl)arsine

ABSTRACT

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ABSTRACT

The thesis describes the results of investigations involving the synthesis, characterization and structural assessments of some ruthenium(III) and ruthenium(II) complexes containing dimethylsulphoxide and some monodentate or bidentate ligands. The contents of the thesis have been distributed over seven chapters.

Chapter I, gives 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 the chemistry of ruthenium and in particular, emphasizes the interest in the chemistry of the metal in oxidation states III and II. Need for more studies in ruthenium(III) chemistry is also highlighted. The importance of synthesis and study of ruthenium(III) and ruthenium(II) complexes containing a weak donor ligand, viz. dimethylsulphoxide has been emphasized. The ambidentate nature of dimethylsulphoxide has been explained and possibility of formation of either S-bonded or

O-bonded complexes with ruthenium(III) and ruthenium(II) has been explored in terms of HSAB principle. A brief review of the literature of reported compounds of ruthenium(III) and ruthenium(II) containing Me_2SO (Me_2SO = dimethylsulphoxide) and/or halides, and their chemical and physical properties has been made. Need to make use of ruthenium triiodide as the source material, for the synthesis of iodide containing ruthenium(III) and ruthenium(II) complexes has been voiced and justified. In this chapter, the scope of the work on the chosen aspects of ruthenium(III) and ruthenium(II) chemistry has been projected.

The new results described in Chapters II to VII have been prefaced with a brief introduction. In Chapter II, the synthesis and characterization of complexes of ruthenium(III) with dimethylsulphoxide, having compositions, $[Ru_2Cl_6(Me_2SO)_4]$1, two linkage isomers, *viz*. *mer* $[RuCl_3(Me_2SO)_3]$2 and *fac* $[RuCl_3(Me_2SO)_3]$3 are discussed. Compound 1 is synthesized by a reaction of commercial ruthenium-trichloride with dimethylsulphoxide, whereas compounds 2 and 3 by reactions of commercial ruthenium trichloride with dimethylsulphoxide in the presence of conc.HCl. With the help of IR spectra, the mode of coordination of Me_2SO molecules in these complexes has been assigned. The dimeric compound, $[Ru_2Cl_6(Me_2SO)_4]$1, and *mer* $[RuCl_3(Me_2SO)_3]$2 have both sulphur and oxygen bonded Me_2SO groups, whereas the *fac* $[RuCl_3(Me_2SO)_3]$3 has all S-bonded Me_2SO

molecules. Compound 1, seems to have chloro-bridges and weak Ruthenium(III) —— Ruthenium(III) interaction. Magnetic moment values (1.6 - 1.9 BM) of compounds 2 and 3 justify that the metal ion is a low-spin d^5, Ruthenium(III) system. A low value of magnetic moment (1.1 BM per ruthenium atom) for the compound 1 at room temperature is explained due to weak antiferromagnetic interaction of two ruthenium(III) ions, through the bridging chlorides. With the help of EPR spectra in powder form at room temperature and in frozen solution at liquid nitrogen temperature and far IR spectra, structural assignments as above, for the compounds 1, 2 and 3 have been made. A ruthenium(III) compound *viz*. $[RuCl_3(Me_2SO)_3]$ reported by Antonov et al[1], on reinvestigation is found to be same as compound 1, *viz*. $[Ru_2Cl_6(Me_2SO)_4]$.

The potentiality of the compounds 1, 2 and 3 (the synthesis and characterization of which are described in Chapter II) as precursors for the synthesis of ruthenium(III) complexes is discussed in Chapter III. The above compounds are reacted with some representative mono- and bidentate ligands containing various donor sites, *viz*. N, P, As, O and S atoms. These reactions resulted in the partial or complete substitution of Me_2SO molecules in 1, 2 or 3, depending on the reaction conditions and nature of the incoming ligands. Ligands having S, P or As donor sites and chelates having N and S donors

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[1] P.G. Antonov, Y.N. Kukushkin, V.I. Konnov and B.I. Ionin, *Russ. J. Inorg. Chem.*, 1978, 23, 441

result in complete substitution of Me_2SO molecules, whereas N and O donor ligands generally give partially substituted complexes. In general, complete substitution of coordinated Me_2SO molecules take place, either when the incoming ligand is stronger coordinating than Me_2SO or when the reaction is carried out at a higher temperature (60°C) ligands, such as PPh_3, $AsPh_3$, CS_2 or Et_2NCS_2Na result in the completely substituted products. Compounds containing one or two Me_2SO molecules are generally obtained when nitrogen or oxygen donor ligands, viz. py, bipy, phen, acac, CH_3CN or PDA (PDA = o-phenylenediamine) are treated with compounds 1, 2 or 3 at room temperature condition. However, in some cases, such compounds are obtained even at higher temperature (~ 60°C). New compounds, thus prepared and characterized are $[RuCl_3L_2(Me_2SO)]$ (L = pyridine or acetonitrile; L_2 = 1,10-phenanthroline or 2,2'-bipyridyl) and $[RuCl_2(acac)(Me_2SO)_2]$. All the compounds thus obtained are characterized by the elemental analysis and different physical methods, viz. IR, ^1H NMR, EPR and UV-VIS spectra. In the new compounds described above, Me_2SO is coordinated to the metal through sulphur only (irrespective of starting compounds, either only S-bonded or containing both S- and O-bonded Me_2SO groups. Generally all the compounds are six coordinated with a considerable lowering of symmetry from O_h due to the presence of different type of (mono or bidentate) ligands and different donor sites in a complex.

Studies on the complexes of ruthenium(III) or ruthenium(II) containing bromide and other ligands are relatively much less compared to similar systems containing chloride as one of the ligands. In Chapter IV, at first a brief review on the reported synthesis of ruthenium(III) and ruthenium(II) complexes containing bromide and other ligands is presented. Further, synthesis and characterization of two novel complexes, viz. $[RuBr_3(Me_2SO)_3]$ and $[RuBr_2(Me_2SO)_3]$ are described. $[RuBr_3(Me_2SO)_3]$ is the first example of a compound of ruthenium(III) or ruthenium(II) containing halides and all (three) O-bonded Me_2SO molecules.[2] $[RuBr_3(Me_2SO)_3]$ has been used as precursor for the synthesis of many ruthenium(III) compounds containing bromide and other ligands having donor sites, viz. N, P, As, O and S. Reactions of $[RuBr_3(Me_2SO)_3]$ with such ligands led to a partial or complete substitution of Me_2SO molecules depending on the reaction condition, and the nature of ligands. Some of the new compounds thus synthesized and characterized are, $[RuBr_2(CS_2)(PPh_3)_3]Br$, $[RuBr_2(Et_2NCS_2)(Me_2SO)_2]$, $[RuBr_2(PDA)(Me_2SO)_2]$, $[RuBr_2(PDA)_2(Me_2SO)_2]Br$, $[RuBr_3(py)_3]$ and $[RuBr_3L_2(Me_2SO)]$ (L = py, Me-py; L_2 = bipy). Compounds having P or As donor site or N, S chelate and Me_2SO group/groups have S-bonded Me_2SO wheras compounds containing N donor site, viz. py, Me-py or bipy and Me_2SO group have O-bonded Me_2SO.

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[2] A compound reported by Antonov et al[1] having composition $[RuCl_3(Me_2SO)_3]$ and only S-bonded Me_2SO groups, upon reinvestigation is found to have the composition $[Ru_2Cl_6(Me_2SO)_4]$ and both O- and S-bonded Me_2SO molecules.

$[RuBr_2(Me_2SO)_3]$ has been characterized to have all S-bonded Me_2SO molecules and tentatively it has been assigned to have a trigonal bipyramidal geometry with Me_2SO molecules in the trigonal plane. Some preliminary reactions have been carried out to examine the potentiality of $[RuBr_2(Me_2SO)_3]$, as precursor for the synthesis of ruthenium(II) bromo complexes. Reactions of $[RuBr_2(Me_2SO)_3]$ with strong donor ligands, viz. PPh_3 or $AsPh_3$ result in products which have no coordinated Me_2SO molecules. Nitrogen donor ligands, such as py, bipy, phen result in partially substituted compounds at mild reaction condition and completely substituted compounds under stronger reaction conditions. Compounds thus synthesized are, $[RuBr_2(py)_2(Me_2SO)_2]$, $[RuBr_2(py)_4]$, $[RuBr_2(L\text{-}L)(Me_2SO)_2]$ and $[RuBr_2(L\text{-}L)_2]$ (L-L = bipy, phen). Compounds containing bromide, Me_2SO and the amines have been characterized to have S-bonded Me_2SO molecules, similar to their precursor, viz. $[RuBr_2(Me_2SO)_3]$. The new ruthenium(II) complex, $[RuBr_2(Me_2SO)_3]$ could be used as precursor for the synthesis of many other ruthenium(II) bromo compounds and a molecular oxygen oxidative catalyst like $[RuBr_2(Me_2SO)_4]$.

Not many ruthenium(III) and ruthenium(II) iodo compounds are synthesized compared to their chloro analogues. In Chapter V, firstly a brief review on the reported synthesis of ruthenium(III) and ruthenium(II) complexes containing iodide and other ligands is presented. Synthesis of ruthenium triiodide is described by a little modification of earlier methods. It is insoluble in non-coordinating organic solvents. Ruthenium triiodide, thus synthesized has been used as precursor for the synthesis of ruthenium(II) compounds, viz. $[RuI_2L_4]$ (L = Me_2SO, py or CH_3CN), $[RuI_2(CS)(PPh_3)_3]$ and $[RuI_2(PPh_3)_2(CH_3CN)_2]$. The synthesis is achieved by dissolving RuI_3 in a coordinating solvent like Me_2SO, py or CH_3CN. Above mentioned complexes are characterized as mentioned earlier for other compounds. $[RuI_2(Me_2SO)_4]$ is characterized to have all Me_2SO molecules bonded to the metal through the sulphur atom. $[RuI_2(Me_2SO)_4]$ and $[RuI_2(CH_3CN)_4]$ are used as source materials for the synthesis of other complexes containing iodide ligands. The complexes, thus synthesized and characterized are, $[RuI_2L_2(Me_2SO)_2]$ (L_2 = py_2, bipy, phen) $[RuI_2(py)_4]$, $[RuI_2(bipy)_2]$, $[RuI_2(CH_3CN)_2(PPh_3)_2]$, $[RuI_2(PPh_3)_2(Me_2SO)]$, $[RuI_2(CH_3CN)_3(Me_2SO)]$, $[Ru(Et_2NCS_2)_2(Me_2SO)_2]$. Among the compounds mentioned above, compounds containing Me_2SO molecules have S-bonded Me_2SO only, similar to the parent compound, viz. $[RuI_2(Me_2SO)_4]$.

In Chapter VI, some cationic and anionic complexes of ruthenium(III) containing Me_2SO, are described. Cationic complexes described are $[Ru(Me_2SO)_6]X_3$ (X = ClO_4, BPh_4) and anionic complexes are $[Me_4N][RuCl_4(Me_2SO)_2]$ and $[Et_4N][RuBr_4(Me_2SO)_2]$. With the help of IR and EPR spectral studies, $[Ru(Me_2SO)_6]^{3+}$ is characterized to have three S-bonded and three O-bonded molecules; arranged to give a facial geometry having a C_{3v} symmetry group. $[Ru(Me_2SO)_6]^{3+}$

is synthesized from ruthenium(III) compounds containing either only S-bonded or containing both S- and O-bonded Me_2SO molecules. The anionic complex, $[Me_4N][RuCl_4(Me_2SO)_2]$ is synthesized from <u>fac</u> or <u>mer</u> $[RuCl_3(Me_2SO)_3]$ and characterized to have the Me_2SO molecules bonded through the S-atom and seems to have a <u>cis</u> geometry. $[Et_4N][RuBr_4(Me_2SO)_2]$ is synthesized from $[RuBr_3(Me_2SO)_3]$ and characterized to have the Me_2SO molecules bonded to the metal through the O-atom and seems to have a <u>cis</u> geometry.

Some convenient syntheses of 2,2'-bipyridyl and 1,10-phenanthroline complexes of ruthenium(III) and (II) are described in Chapter VII. $[Ru(L-L)_3]X_2$ (L-L = phen or bipy; X = Cl, Br, ClO_4 or BPh_4) are synthesized from <u>fac</u> or <u>mer</u> $[RuCl_3(Me_2SO)_3]$ or $[RuBr_3(Me_2SO)_3]$, using excess of the diimines. $[Ru(bipy)_2Cl_2]Cl.2H_2O$ is obtained by a reaction of <u>fac</u> or <u>mer</u> $[RuCl_3(Me_2SO)_3]$ with 2,2'-bipyridyl (molar ratio, 1:2). Further, a novel compound of ruthenium(III) containing 1,10-phenanthroline and bromide, <u>viz</u>. $[Ru(phen)_2Br_2]Br$ is synthesized from $[RuBr_3(Me_2SO)_3]$ and characterized. By the metathetic substitution, $[Ru(phen)_2Br_2]X$ (X = ClO_4 or BPh_4) are also obtained and characterized.

Most part of the work described in Chapters II, III, IV and V have been published in "POLYHEDRON" while the rest is under communication.

CHAPTER I

CHAPTER I

INTRODUCTION

Interest in the chemistry of ruthenium appears to be growing very rapidly during the last decade. This is reflected in the publication of several reviews on different facets of the chemistry of the metal. The pioneering work in this field is by W.P. Griffith.[1] Subsequent reviews by Gmelin[2], Livingstone[3] and Cotton and Wilkinson[4] contribute more to the chemistry of ruthenium. One of the latest and most useful collection on ruthenium chemistry is a monograph by Seddon and Seddon.[5] Seddon has covered the chemistry of ruthenium till 1981 in his subsequent reviews.[6-8] The latest review by Schröder and Stephenson[9] covers the coordination chemistry of ruthenium till the middle of 1984. Several other reviews[10-17] on the organometallic chemistry, photochemistry, thermodynamics and medical applications of ruthenium and its compounds have also appeared which justify rapidly growing and diversifying interest in ruthenium.

The chemistry of ruthenium is known in the oxidation states ranging from VIII to II.[1-5] Most extensively studied compounds of ruthenium belong to the oxidation states II and III.[1-5] Some of the important compounds of ruthenium(II) and ruthenium(III) are $[RuCl_2(PPh_3)_3]$,[17-19] $[Ru(bipy)_3]^{2+}$,[14,20] cis $[RuCl_2(Me_2SO)_4]$,[21,22] trans $[RuBr_2(Me_2SO)_4]$,[21,23-25] $[RuX_3(EPh_3)_3]$ and $[RuX_3(EPh_3)_2(MeOH)]$, (X = Cl or Br, E = P or As).[18,26-29] The importance of these compounds is due to their various physical, chemical and structural behaviours. For example, $[RuCl_2(PPh_3)_3]$, has a distorted square pyramidal structure[30] and is a good catalyst for various homogeneous reactions, viz oxidation, hydrogenation, dehydrogenation, hydrosilylation and isomerization.[17] The homogeneous catalytic properties are due to the coordinative unsaturation of the compound. Besides its catalytic behaviour, it has been found to be excellent starting compound for the synthesis of a large number of ruthenium(II) complexes, particularly those containing π -acid ligands.[17]

$[Ru(bipy)_3]^{2+}$ and other related diimine complexes[14,20] are being considered as promising candidates for the role of ideal photocatalyst for the visible light photo induced decomposition of water into dihydrogen and oxygen. Such complexes are playing a key role in the development of photochemistry, photophysics, photocatalysis, electrochemistry, photoelectrochemistry, chemi- and electrochemi luminescence and electron energy transfer. The interest in this field could be well imagined that, despite literally hundreds of publications on the photophysics and photochemistry of $[\mathrm{Ru(bipy)_3}]^{2+}$ have appeared, there still does not yet exist an unambiguously correct assignment of either the electronic absorption or the luminescence spectrum for $[\mathrm{Ru(bipy)_3}]^{2+}$.[14,20]

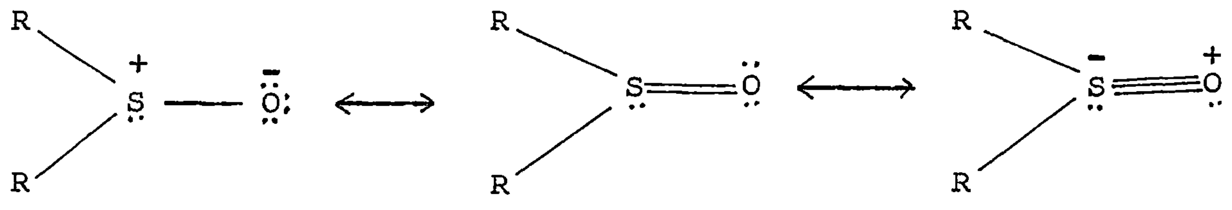
cis $[\mathrm{RuCl_2(Me_2SO)_4}]$ is characterized to have a distorted octahedral geometry,[31] with the two chlorides in the *cis* positions and having three S-bonded and one O-bonded $\mathrm{Me_2SO}$ molecule. It has been used as a precursor for the synthesis of many ruthenium(II) complexes.[22,32-35] *cis* $[\mathrm{RuCl_2(Me_2SO)_4}]$ and *trans* $[\mathrm{RuBr_2(Me_2SO)_4}]$ have been investigated for their catalytic activity towards molecular oxygen oxidation of thioethers to the sulphoxides.[36,37] The interest aroused by the new antitumour agent, *viz*, *cis* $[\mathrm{Pt(NH_3)_2Cl_2}]$, has spread to ruthenium complexes, and *cis* $[\mathrm{RuCl_2(Me_2SO)_4}]$ in particular, appears to be attracting some attention.[38] Ruthenium(III) complexes of the type, $[\mathrm{RuX_3(EPh_3)_3}]$ and $[\mathrm{RuX_3(EPh_3)_2(MeOH)}]$ (X = Cl or Br; E = P or As) have been used as precursors for the synthesis of ruthenium(III) complexes.[23,29,39-44] Recently $[\mathrm{Ru(H_2O)_6}][\mathrm{C_7H_7SO_3}]_n$[45] and $[\mathrm{Ru(DMF)_6}][\mathrm{CF_3SO_3}]_n$[46] (n =2or 3) have been synthesized and their potential as precursors is being explored.

Examples of ruthenium(II) and ruthenium(III) complexes, cited above, convincingly show their importance in inorganic chemistry. One finds that much larger contribution has been made to the study of the chemistry of ruthenium(II) than that of ruthenium(III).

The source material for the synthesis of ruthenium(II) and ruthenium(III) compounds is commercial ruthenium trichloride. However, the reaction products of ruthenium trichloride with ligands, mostly yielded ruthenium(II) complexes. Commercial ruthenium trichloride generally gets reduced to ruthenium(II) even with a mild reducing agent. In most such cases, the ligands themselves act as agents for reducing ruthenium(III) to ruthenium(II) One of the most widely studied complex, viz. $[RuCl_2(PPh_3)_3]$ was synthesized by the refluxing of a methanolic solution of commercial ruthenium trichloride with triphenylphosphine.[18,19] Thus the studies on the ruthenium(III) complexes are relatively less compared to that of ruthenium(II). Hence, in the present work, an attempt has been made to synthesize and study mostly complexes of ruthenium(III). In the course of investigation, some of the reactions have resulted in the formation of ruthenium(II) complexes as well. Ruthenium(III) is a d^5 system forming only low spin complexes. These complexes have generally one unpaired electron which shows a magnetic moment $\sim$ 1.9 BM and the single unpaired electron gives EPR signals which sometimes are very characteristic to make proper structural assignments to the complexes.[47]

In the present work, most complexes of ruthenium(III) and some complexes of ruthenium(II) have been studied with some weak donor ligands,[48] such as dimethylsulphoxide and acetonitrile. Most of the work centres around Me_2SO. Me_2SO being an ambidentate ligand, coordinates to a metal ion either through oxygen or through sulphur atom.[49,50] Besides X-ray crystallographic studies, simple physical methods, viz. IR and ^1H NMR spectral studies have been used extensively to diognise the bonding behaviour of Me_2SO molecules. Recently electron spectroscopy for chemical analysis (ESCA) has been applied to the study of ambidentate coordination in sulphoxide complexes.[51]

In terms of explaining the ambidentate donor ability of sulphoxides, one may like to represent the simple sulphoxides, R_2SO, as a resonance hybrid of the following three canonical forms:-



(i) (ii) (iii)

The corollary of this is, that O-bonding is a result of dominant contribution of form (i) and S-bonding, a result of dominant contribution of form (iii). A compilation of the available physical data of Me_2SO and its transition metal complexes,[50] show that this is not so, and that form (i) makes a dominant contribution to the resonance hybrid in both, the free molecules and its O-bonded complexes, while form (ii) makes a dominant contribution in S-bonding. It seems likely that O-bonding results from electron donation from a Sp^2 hybrid orbital on oxygen and that S-bonding involves donation from a Sp^3 hybrid orbital on sulphur.[50] It is generally observed that sulphoxides coordinate to hard metals, *via* oxygen and to soft metals *via* sulphur,[50,52] exactly as expected in terms of the HSAB principle.

Ruthenium(II) and ruthenium(III) metal ions are not clearly categorised either as hard or as soft bases.[48] Instead, these are the border line metal ions among the two distinct categories of hard and soft bases. Some of the well characterized complexes of ruthenium(II) and ruthenium(III) containing Me_2SO and/or halides having all S-bonded Me_2SO groups reported are $[RuBr_2(Me_2SO)_4]$[25] $[RuI_2(Me_2SO)_4]$[53] and $[NMe_2H_2][RuCl_3(Me_2SO)_3]$.[54] The complexes, *cis* $[RuCl_2(Me_2SO)_4]$[31] and $[Ru(Me_2SO)_6][BF_4]_2$[55] are reported to contain three S-bonded and the rest O-bonded Me_2SO molecules. Only one report of a ruthenium(III) complex having all O-bonded Me_2SO molecules, *viz* $[RuCl_3(Me_2SO)_3]$ has been made by Antonov *et al.*,[56] where characterization of the complex has not been satisfactory. Looking at the borderline behaviour of ruthenium(II) and ruthenium(III) it has been thought interesting to investigate more into the chemistry of the complexes of Me_2SO with ruthenium(II) and ruthenium(III).

Besides the ambidentate donor properties of Me_2SO and its reported complexes with ruthenium(II) and ruthenium(III) having either S-bonded or containing both S- and O-bonded Me_2SO molecules, the interest in the chemistry of Me_2SO complexes of ruthenium is due to other reasons also. Me_2SO is a weak donor ligand[48] which is relatively easily replaced by other ligands. Due to which complexes of ruthenium(II) or ruthenium(III) with Me_2SO, could be used as precursors for the synthesis of ruthenium(II) and ruthenium(III) complexes, either containing Me_2SO and other ligands or containing only other ligands. cis $[RuCl_2(Me_2SO)_4]$[22,32-35] and trans $[RuBr_2(Me_2SO)_4]$[37] have been used as precursors for the synthesis of many ruthenium(II) complexes. Further, sulphoxide complexes of transition metals are being developed as homogeneous catalysts for a variety of organic transformations, including the hydrogenation, hydroformylation and oligomerization of olefines.[50] cis $[RuCl_2(Me_2SO)_4]$ and trans $[RuBr_2(Me_2SO)_4]$[36,37] have been used as molecular oxygen oxidative catalyst for the oxidation of thioethers to sulphoxides. It is observed that cis $[RuCl_2(Me_2SO)_4]$, $[RuCl_3(Me_2SO)_3]^-$ and $[Ru(Me_2SO)_6]^{2+}$ catalyse the hydrogenation of acrylamide to 1-amino propane.[54,55,57] Similarly, other ruthenium(II) and ruthenium(III) complexes with Me_2SO may be found to be good catalysts for some of the homogenous catalytic reactions, mentioned above.

Looking at the importance of the chemistry of ruthenium(II) and ruthenium(III) complexes with monodentate ligands, especially of the weak donor type, synthesis and physico chemical studies of the complexes of ruthenium(II) and ruthenium(III) with one of the weak donor ligands, viz. dimethylsulphoxide, has been taken up. In this process some complexes of ruthenium(III) containing Me_2SO and halides (chloride or bromide) and some complexes of ruthenium(II) with Me_2SO and halides (bromide or iodide) have been synthesized and their structural assignments made on the basis of available physical methods. Some of these complexes are used as precursors for the synthesis of ruthenium(II) and ruthenium(III) complexes containing one or two molecules of Me_2SO and other ligand molecules. In some cases completely substituted (Me_2SO) compounds have also been obtained. Some of the compounds obtained by such methods were reported earlier by different methods and most others are new. These new compounds are studied for their structural assignments by various physical methods.

Some of the well characterized cationic or anionic complexes of ruthenium(II) containing either Me_2SO or Me_2SO and halides reported are $[Ru(Me_2SO)_6]X_2$ ($X = BF_4, ClO_4, BPh_4$)[22,55,58] and $[NMe_2H_2][RuCl_3(Me_2SO)_3]$.[54] There is a report on ruthenium(III) complexes of similar types, as well.[59] However the report on ruthenium(III) complexes is not satisfactory and convincing, and in most cases the reported syntheses are not repeatable. Hence, study has been taken up to synthesize and characterize ruthenium(III) cationic and anionic complexes similar to ruthenium(II) complexes mentioned above.

Studies on the complexes of ruthenium(II) and ruthenium(III) containing iodide as one of the ligands is very scarce, even though the existance of RuI_3 was reported at the beginning of this century.[60] Practically, no use of RuI_3 as the starting material for the synthesis of ruthenium(II) and ruthenium(III) complexes containing iodide as one of the ligands has been made. It is probably due to the insolubility of RuI_3 in most of the common non-coordinating organic solvents. Hence the study has been taken up, where RuI_3 is made soluble in coordinating type organic solvents, viz. Me_2SO, CH_3CN or pyridine and in this process, complexes of ruthenium(II) containing iodide and the weak donor ligands, such as Me_2SO, CH_3CN or pyridine are obtained. As these ligands are of the weak donor type, these could be replaced by other ligands in a relatively non-coordinating solvent medium (where these iodo complexes are soluble). Hence some ruthenium(II) complexes containing iodide as one of the ligands have been synthesized and their potentiality as precursor has also been explored.

Ruthenium(II) complexes of diimines of the type $[Ru(L-L)_3]^{2+}$ (L-L = bipy, phen etc) are of interest because of their key role in the development of photochemistry, photophysics, photocatalysis etc.[14,20] Most of the methods of syntheses described for such complexes make use of ruthenium(III) or ruthenium(IV) compounds, viz. commercial $RuCl_3.xH_2O$, $K_2[RuCl_5(H_2O)]$, $K_2[RuCl_6]$ or $K_4[Ru_2OCl_{10}]$.[61] A simpler method has been evolved where complete substitution of chloride and Me_2SO is carried out by the diimines in some ruthenium(III) complexes and the products obtained are characterized by comparing the physical properties with the reported compounds.

Synthesis of ruthenium(III) complexes containing (mono, bis or tris) 2,2' bipyridyl or 1,10-phenanthroline is generally achieved in two steps.[62] The first step involves the synthesis of the ruthenium(II) analogue of the desired compound and in the second step, oxidation of ruthenium(II) compounds to ruthenium(III) compound is achieved by one of the oxidising agents such as chlorine, a cerium(IV) compound, Pb(IV) oxide or silver nitrate. One such compound is $[Ru(bipy)_2Cl_2]Cl.2H_2O$. Easier method of synthesizing such compounds have been achieved, where substitution of coordinated ligands, viz. Me_2SO and X^- (X = Cl or Br), in easily synthesized and very stable ruthenium(III) complexes of the type $[RuX_3(Me_2SO)_3]$ (X = Cl or Br), by the diimine has been carried out. Besides, obtaining the reported $[Ru(bipy)_2Cl_2]Cl.2H_2O$,[63-65] a new compound $[Ru(phen)_2Br_2]Br$ has also been synthesized and characterized.

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CHAPTER II

CHAPTER II

SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF RUTHENIUM(III) WITH CHLORIDE AND DIMETHYLSULPHOXIDE : $[RuCl_3(Me_2SO)_2]_2$ AND *fac* AND *mer* ISOMERS OF $[RuCl_3(Me_2SO)_3]$

A complex of ruthenium(II) with dimethylsulphoxide *viz.* $[RuCl_2(Me_2SO)_4]$, was reported by James *et al.*[1] A simpler method of preparation for the same was later reported,[2] and the complex was used as precursor for the synthesis of many ruthenium(II) complexes.[2-5] The structure of $[RuCl_2(Me_2SO)_4]$ was determined by X-ray diffraction technique,[6] and was shown to have a *cis* arrangement of the chloride ligands with three S-bonded Me_2SO ligands and one O-bonded Me_2SO, mutually *cis* to each chloro ligand. A similar complex of ruthenium(III), *viz.* $[RuCl_3(Me_2SO)_3]$ was first reported from Wilkinson's group,[7] using blue solution of ruthenium(II). However, they[2] later reported that the preparation was unrepeatable. Antonov *et al.*[8] reported its preparation and some physical characteristics. They reported that all the three Me_2SO molecules were bonded to ruthenium(III) through the oxygen atoms.

Most of the physical data reported conform with the composition and the facial structure of the complex. However, the lowering of the magnetic-moment value (μ_{eff} = 1.0 B.M.) and sharp line ^{1}H NMR spectrum at room temperature are intriguing. Two reports on other ruthenium(III) complexes with Me_2SO by Bora and Singh[9-10] describe $[Ru(Me_2SO)_6]X_3$, (X = Cl, Br or ClO_4) and M $[RuCl_4(Me_2SO)_2]$, (M = Na or Bu_4N). These complexes require further investigation for complete characterization.

Thus looking at the informations available on $[RuCl_3(Me_2SO)_3]$ and other ruthenium(III) complexes with Me_2SO, a thorough and exhaustive study of Me_2SO complexes of ruthenium(III) has been taken up. In this chapter, synthesis of three compounds of ruthenium(III) with Me_2SO and chloride ligands are described. Characterization and structural assignments have been made using analytical data and various physical methods. Potentiality of these compounds as precursors for the synthesis of ruthenium(III) complexes has been explored and described in Chapter III.

EXPERIMENTAL

All the solvents were freshly distilled before use. Ruthenium trichloride trihydrate was obtained from Aurora Matthey Ltd. Calcutta.

ANALYSES

(a) Carbon and Hydrogen Carbon and hydrogen were analysed by microanalytical methods. The analyses were obtained from the Microanalytical Laboratory, Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow.

(b) Chloride Chloride was estimated by the standard method.[11] An accurately weighed amount of the complex was decomposed by heating with a melt of KNO_3 and KOH mixture (1:8) at around ~ 800°C. It was cooled and extracted with water and then acidified with dilute HNO_3. It was then digested on a water-bath for about one hour and filtered. Silver nitrate solution (0.1M) was added to the filtrate to precipitate silver chloride. The mixture was 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 HNO_3 (1:100) to free from silver nitrate and dried to a constant weight at 120°C. The precipitate was weighed as silver chloride. Analytical data are presented in Table II.1.

MELTING POINT

Melting points were recorded using capilliary method, and are presented in Table II.1. Melting points are uncorrected.

MOLAR CONDUCTANCE MEASUREMENTS

Molar conductance measurements were made on a Systronic digital direct reading conductivity meter 304. Solutions of milimolar strength were made in acetonitrile or nitro methane. Molar conductance data are presented in Table II.1.

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Bulk magnetic susceptibility measurements at room temperature ($\sim$ 25 °C), were carried out using a Faraday balance at Tata Institute of Fundamental Research, Bombay or using a Vibrating Sample Magnetometer, EG G. PARC, Model 155 at Indian Association for Cultivation of Science, Jadavpur, Calcutta. μ_{eff} values have been reported in Table II.1.

ELECTRON PARAMAGNETIC RESONANCE

EPR spectra were recorded (i) in the powder form at room temperature and (ii) in acetonitrile, chloroform or methanol solution at liquid nitrogen temperature using a Varian E-104 spectrometer.

PROTON MAGNETIC RESONANCE

^{1}H NMR spectra were recorded at Regional Sophisticated Instrumentation Centre, NEHU, Shillong at room temperature on a Varian EM-390, 90 MHz spectrometer, in deuterated solvents using tetramethylsilane as internal standard.

INFRARED SPECTRA

Infrared spectra were recorded at Regional Sophisticated Instrumentation Centre, NEHU, Shillong in KBr pellets on a Perkin Elmer-297 IR spectrophotometer in the range 4000-600 cm^{-1} and in both KBr and CsI pellets on a Perkin Elmer-983 IR spectrophotometer in the range 4000-200 cm^{-1}. Important IR absorption bands are given in Table II.2.

ELECTRONIC ABSORPTION SPECTRA

Electronic absorption spectra were recorded in solution at Regional Sophisticated Instrumentation Centre, NEHU, Shillong, using (i) a Beckmann-26 Spectrophotometer in the range 800-200 nm, or (ii) Cary-2390 spectrophotometer in the range 1200-200 nm. Electronic spectra were recorded using Hitachi-330 spectrophotometer also, in the range 1200-200 nm.

PREPARATIONS

$[Ru_2Cl_6(Me_2SO)_4]$ 1

Method A : Dimethylsulphoxide (1.5 cm^3) was added to hydrated ruthenium trichloride (0.25g, 1 mmol) and warmed on a water-bath (~ 15-20 min) to get a clear dark red solution. The solution was cooled to room temperature and acetone was added with stirring when brownish-red coloured compound precipitated out. It was centrifuged and washed 2-3 times with acetone and dried in vacuo. Yield 0.3g, 75%. It was analysed for $[Ru_2Cl_6(Me_2SO)_4]$.

Method B : Compound 1 was obtained also, when a solution of hydrated ruthenium trichloride in dimethylsulphoxide (at room temperature) was precipitated with acetone.

mer $[RuCl_3(Me_2SO)_3]$, Dark Orange, 2

Method A : Conc. HCl (5 cm^3) was added to a solution of hydrated ruthenium trichloride (0.25g, 1 mmol) in dimethylsulphoxide (1.5 cm^3). The mixture was refluxed on an oil-bath (130-140°C) for 1 $\frac{1}{2}$ h and slowly cooled to room temperature when a compound separated out. It was centrifuged and carefully washed twice with very little (0.1 - 0.2 cm^3) ice cold acetone (acetone soluble) and dried in vacuo. Yield : 0.33g, 80%. It was analysed for $[RuCl_3(Me_2SO)_3]$.

Method B : If the reaction mixture of method A was heated on a water-bath for about 4 h, instead of refluxing on an oil-bath and cooled, compound 2 separated out.

fac $[RuCl_3(Me_2SO)_3]$, yellow, 3

Method A : Conc. HCl (5 cm^3) was added to a solution of hydrated ruthenium trichloride (0.25g, 1 mmol) in dimethylsulphoxide (1.5 cm^3). The mixture was heated on a water-bath (~ 85 °C) for 30 min. The solution was concentrated to 1 cm^3 by heating on a water-bath and cooled overnight at 10°C. Yellow needle-shaped crystals separated out. These were centrifuged, washed 2-3 times with acetone and dried *in vacuo*. Yield 0.33g, 80%. It was analysed for $[RuCl_3(Me_2SO)_3]$.

Method B : **3**, in the powder form, could be precipitated out by the addition of acetone under constant stirring to the concentrated solution (1 cm^3) obtained as in Method A above.

Method C : Mother-liquor, obtained after removing **2**, was concentrated on a water-bath to about 1 cm^3 and was ice-cooled. Acetone was added to it with continuous stirring, which yielded small quantity of **3**.

RESULTS AND DISCUSSION

The only ruthenium(III) complex containing chloride and dimethylsulphoxide ligands, *viz*. $[RuCl_3(Me_2SO)_3]$ was first reported from Wilkinson's group,[7] using blue solution of ruthenium(II). However, they[2] later reported the unrepeatability of the reaction. Much later Antonov *et al*.[8] have reported its preparation. We have been able to synthesize two isomers of the formula $[RuCl_3(Me_2SO)_3]$, and one compound of the formula $[Ru_2Cl_6(Me_2SO)_4]$. We attempted to prepare

$[RuCl_3(Me_2SO)_3]$ according to Antonov's method, but obtained $[Ru_2Cl_6(Me_2SO)_4]$ only. In fact, a closer look at the preparative methods of Antonov and compound 1 of ours, reveals a great similarity except that we have used a smaller volume of dimethylsulphoxide, but large excess compared to the ruthenium trichloride used (~ 12 mmol for 1 mmol of $RuCl_3.xH_2O$). Normally reactions carried out at higher temperature (i.e. refluxing of Me_2SO), even for short period (5 min) without using conc. HCl, yielded ruthenium(II) complexes, viz. $[RuCl_2(Me_2SO)_4]$.[2] When the reaction was carried out at a lower temperature (water-bath temperature, ~ 70-80°C), a ruthenium(III) complex with dimethylsulphoxide, viz. $[Ru_2Cl_6(Me_2SO)_4]$ was obtained by us. However, if the reaction was carried out in the presence of conc. HCl, two isomers of the composition $[RuCl_3(Me_2SO)_3]$ were obtained. A reaction of dimethylsulphoxide and ruthenium trichloride in conc. HCl at a higher temperature (heating in oil-bath, 130°-140°C) for $1\frac{1}{2}$ h or at lower temperature (water-bath temperature) for 4 h yielded an orange-red isomer 2, whereas the reaction at water-bath temperature for about 30 min gave a yellow isomer 3.

The analytical data (Table II.1) of 1, 2 and 3 conform to the compositions $[Ru_2Cl_6(Me_2SO)_4]$, $[RuCl_3(Me_2SO)_3]$ and $[RuCl_3(Me_2SO)_3]$ respectively. The conductivity measurements of these complexes in acetonitrile and nitromethane, showed molar conductance of the order of 7 to 14 $\Omega^{-1}cm^2mol^{-1}$ which conform to the covalent nature of the chlorides bonded to

Table II.1 Some Physical and Analytical Data of New Ruthenium(III) Complexes

Compounds	Molecular Formula	Colour	M.P.°C	Analytical data[a] (%)			μ eff at R.T. in B M.	Λ_M in $\Omega^{-1}cm^2mol^{-1}$
				C	H	Cl		
<u>1</u>	$[Ru_2Cl_6(Me_2SO)_4]$	Browish red	160-65	13.2 (13.2)	3.4 (3.3)	28.7 (29.3)	1.1	7[b]
<u>2</u>	$[\underline{mer}[RuCl_3(Me_2SO)_3]$	Dark orange	135-40	16.6 (16.3)	4.3 (4.1)	24.0 (24.1)	1.9	14[b]
<u>3</u>	$[\underline{fac}[RuCl_3(Me_2SO)_3]$	Yellow	145-50	16.6 (16.3)	4.2 (4.1)	24.6 (24.1)	1.7	8[b]
Antonov's	$[RuCl_3(Me_2SO)_3]$[d]	Brown to red	-	15.8 (16.3)	- (4.1)	24.8 (24.1)	1.0	15[c]
	$[Ru_2Cl_6(Me_2SO)_4]$[e]	Brownish red	160-65	12.5 (13.2)	3.1 (3.3)	-	-	12[c]

a : Calculated values are in parentheses

b : in acetonitrile

c : in nitromethane

d : Reported by Antonov <u>et</u> <u>al</u>, ref. 8

e : Repeated by us according to Antonov's method

Table II.2 Important IR band positions (in cm^{-1}) and their assignments

1	2	3	Assignments
$[Ru_2Cl_6(Me_2SO)_4]$	mer $[RuCl_3(Me_2SO)_3]$	fac $[RuCl_3(Me_2SO)_3]$	
1427m 1410m	1433-1410m-s	1427m 1413m 1404m	δ_d(CH)
1317m	1320m	1315m	δ_d(CH)
1298m	1295w	1295m	δ_d(CH)
1110m	1113m 1093m	1110sh 1087s 1065m	$\nu_{S=O}$ (S-bonded)
1028m 1019m	1032s 1015m	1037w 1022m	ρ_r(CH)
..	981vs	..	$\nu_{S=O}$ (O-bonded)
985m 950m	936vw	975m	ρ_r(CH)
891vs	..	..	$\nu_{S=O}$ (O-bonded)
723w 683w	725w 683w	725w 680w	ν_a(CS)
504m	471br,s	..	ν_{Ru-O}
430m-w	421m-w	422s	ν_{Ru-S} δ_d(CSO)
376w	380w	385m	δ_a(CSO)
335s	340vs 326s 313m	343s 319s	ν_{Ru-Cl}
	288m	279m	
249m-w	--	--	ν_{Ru-Cl} (bridging)

s, strong; m, medium; w, weak; sh, shoulder.

ruthenium. Molar conductance in water showed very high values (~230 & 370 $\Omega^{-1}cm^2mol^{-1}$ for the monomeric 2 and 3 respectively and 600 $\Omega^{-1}cm^2mol^{-1}$ for the dimeric species 1). It may be due to the decomposition of the complexes in water leading to the formation of $[Ru(H_2O)_6]^{3+}$ and Cl^- ions.

INFRARED SPECTRA

IR spectra of the compound 1, 2 and 3 throw light on the nature of coordination of Me_2SO with ruthenium. Important infrared bands are given in Table II.2 with their most plausible assignments. IR spectra of these compounds are shown in Fig. Nos. II.1, II.2 and II.3. Compound 1 showed a very strong absorption band at 891 cm^{-1} assigned to $\nu_{S=O}$ of the O-bonded Me_2SO, as observed by Antonov et al.[8] A band of medium intensity at 1110 cm^{-1} was also observed which may be assigned to $\nu_{S=O}$ (S-bonded).[2,12] The infrared absorption at 504 cm^{-1} and at 430 cm^{-1} could be assigned to ν_{Ru-O} and ν_{Ru-S} respectively due to O-bonded and S-bonded Me_2SO.[12-16] Finally, a strong band at 335 cm^{-1} could be due to ν_{Ru-Cl} (terminal) and at 249 cm^{-1} due to ν_{Ru-Cl} (bridging).[17] On the basis of infrared spectrum, we may infer that Me_2SO molecules in compound 1 are both O-bonded and S-bonded. The dimerization may take place through chloro-bridges. In compound 2, the bands at 1113 and 1093 cm^{-1} of medium intensity may be assigned

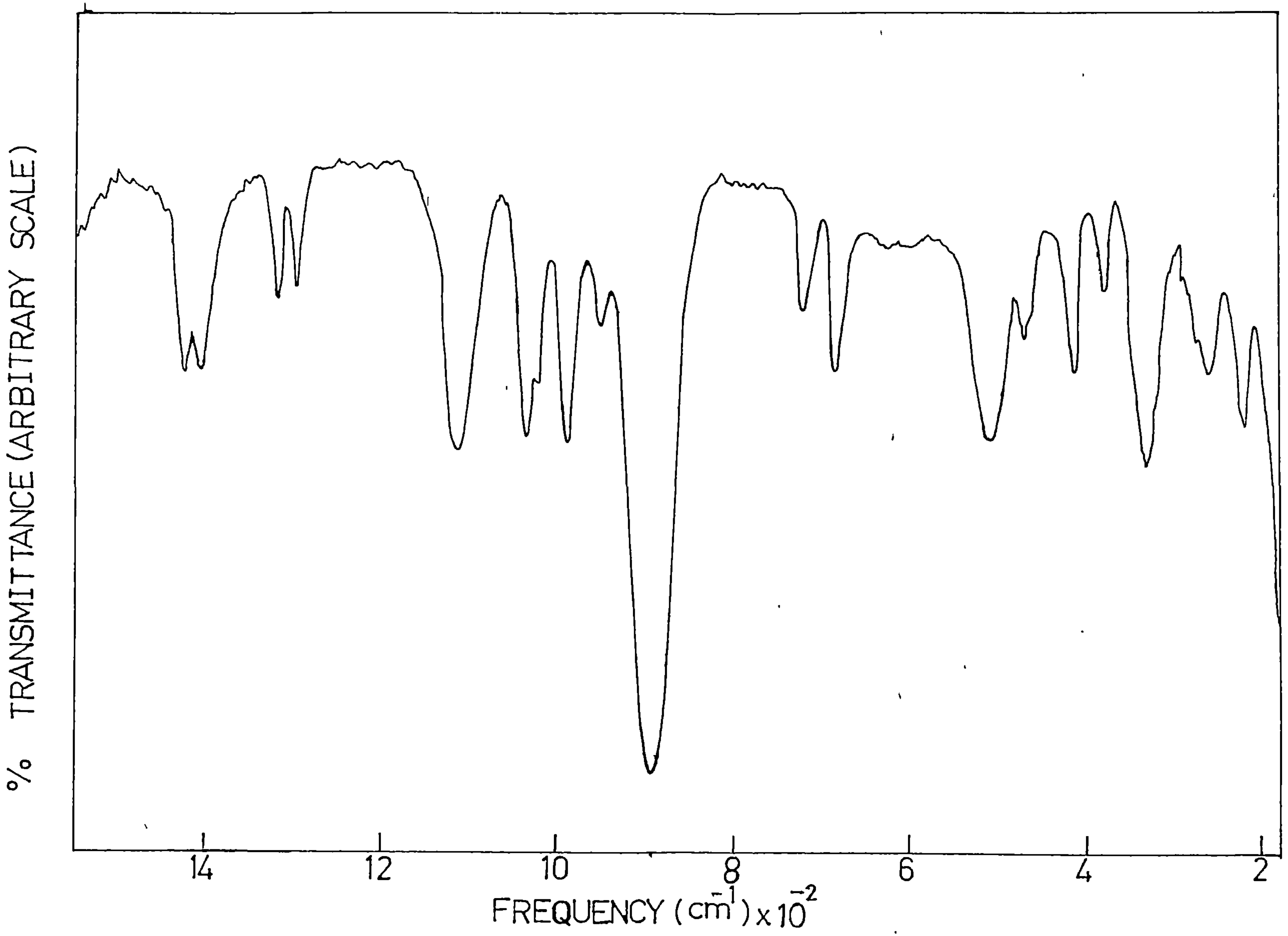

Fig. II. 1 INFRARED SPECTRUM OF $[Ru_2Cl_6(Me_2SO)_4]$ 1

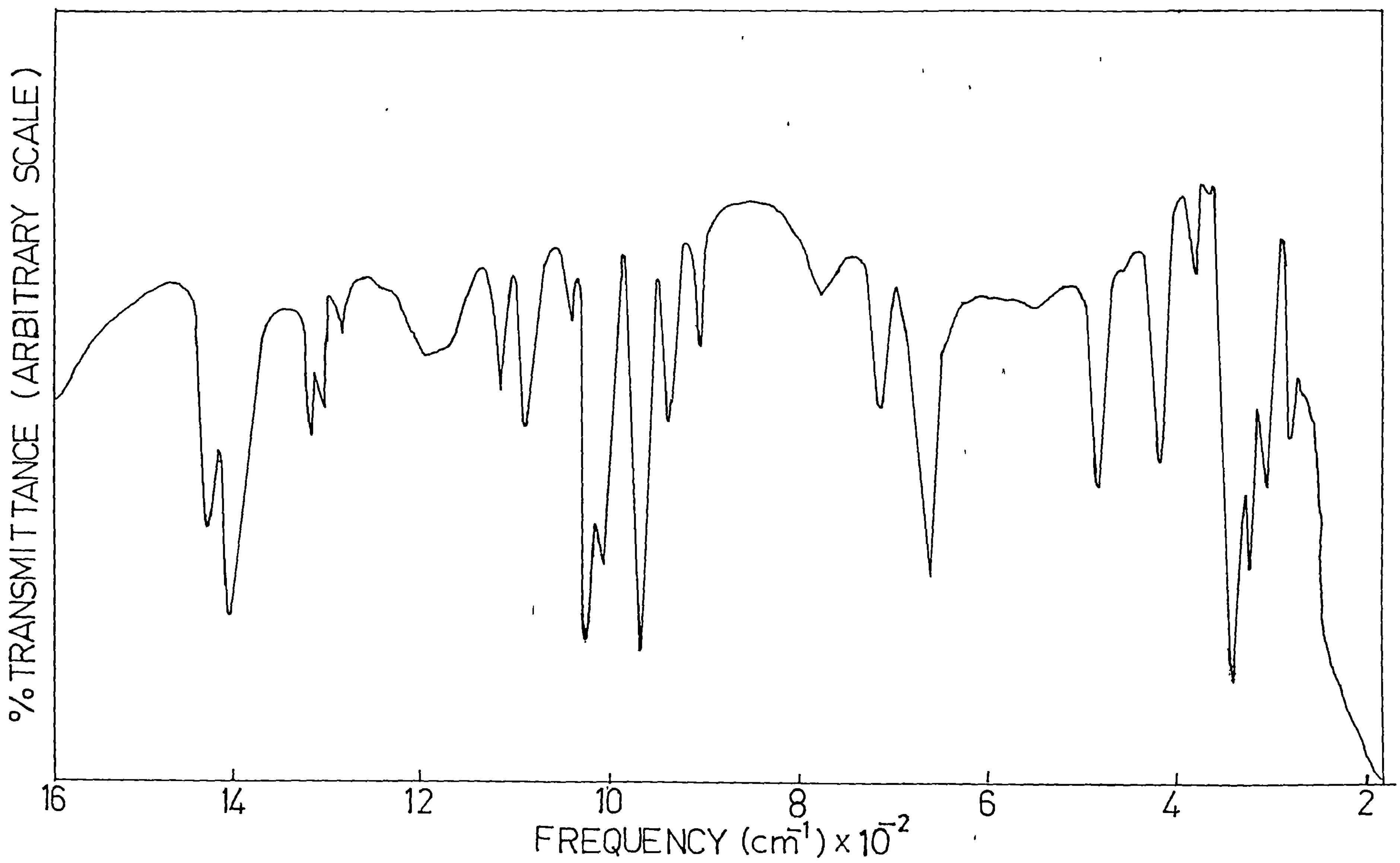

Fig.II.2 INFRARED SPECTRUM OF <u>mer</u>[$RuCl_3(Me_2SO)_3$] <u>2</u>

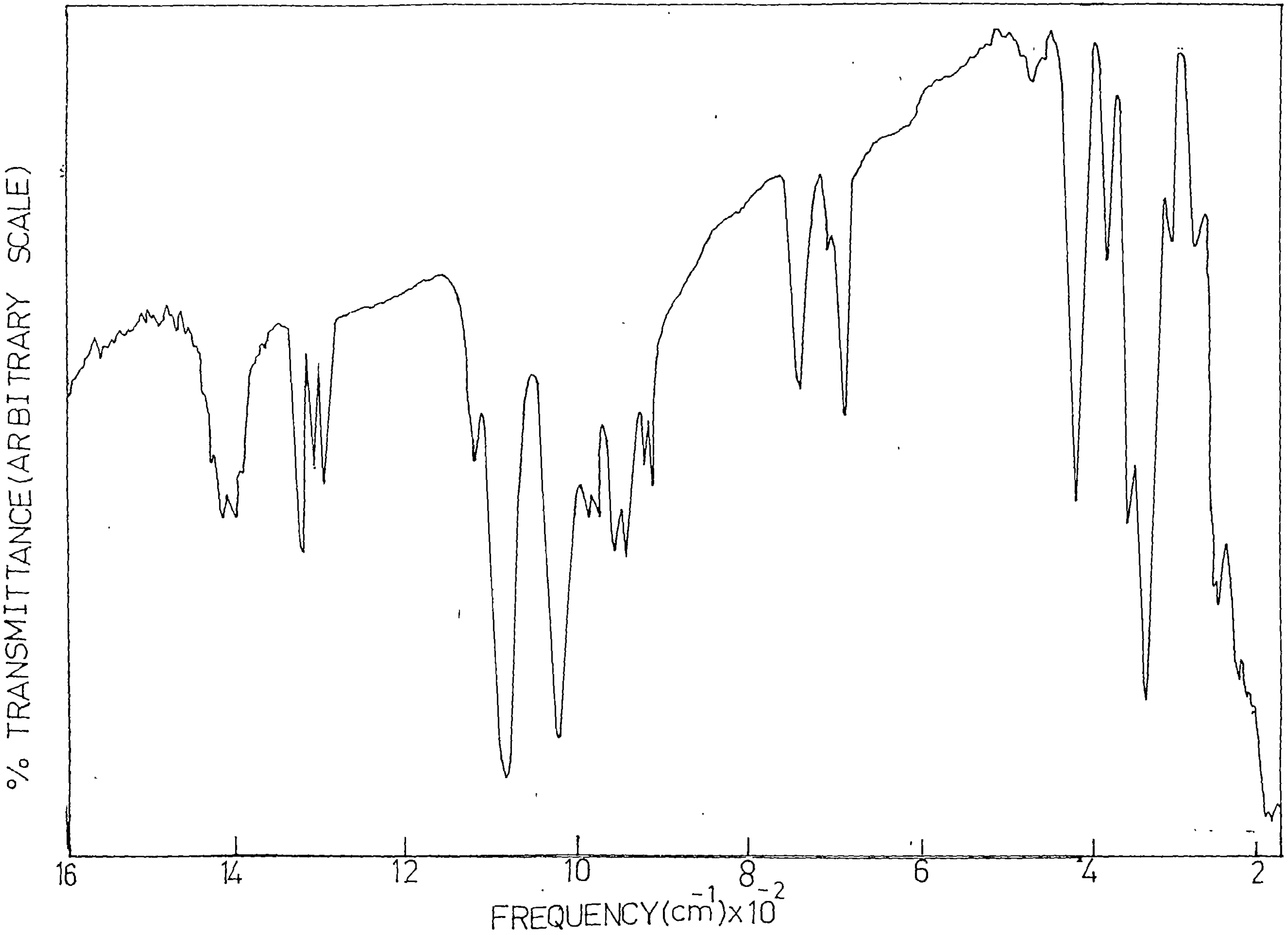

Fig. II.3 INFRARED SPECTRUM OF fac [RuCl$_3$(Me$_2$SO)$_3$] 3 to $\nu_{S=O}$ (S-bonded) and a very strong band at 981 cm^{-1} due to $\nu_{S=O}$ (O-bonded).[2,12] ν_{Ru-O} and ν_{Ru-S} were also observed at 471 and 421 cm^{-1} respectively.[13-16] Comparing the intensities of bands at 981 cm^{-1} and around 1100 cm^{-1}, it may be inferred that compound 2 has two Me_2SO molecules as O-bonded and one as S-bonded. Compound 2 showed bands at 340, 326 and 313 cm^{-1} also, which could be assigned to ν_{Ru-Cl}. The number of ν_{Ru-Cl} bands in the spectrum corresponds to meridional configuration as in $[RhCl_3(Me_2SO)_3]$.[18] Compound 3 seems to be a purely S-bonded isomer, where no strong absorption between 1000 and 850 cm^{-1} were observed, thereby showing the absence of $\nu_{S=O}$ (O-bonded). Bands around 1100 cm^{-1} are assigned to $\nu_{S=O}$ (S-bonded) and a band at 422 cm^{-1} due to ν_{Ru-S}.[13-16] In fact the IR spectral data of 3 have an exact resemblance to that of $[RuCl_3(Me_2SO)_3]$ reported by McMillan et al.[12] The spectrum of this compound showed bands at 343 and 319 cm^{-1}, which may be assigned to ν_{Ru-Cl}. Number and positions of ν_{Ru-Cl} bands conforms to the facial configuration of the complex,[19] as in the case of fac $[RuCl_3(Py)_3]$.[20] The infrared spectra of the compounds 1, 2 and 3 in acetonitrile solutions were similar to that in the solid state (KBr or CsI medium). There was slight deviation (~ 10 to 20 cm^{-1}) of the bands due to ν_{SO} in acetonitrile solution.

MAGNETIC PROPERTIES

The magnetic moment values of the compounds 2 and 3 at room temperature were 1.9 and 1.7 B.M. respectively which are in conformity with the complexes having low-spin ruthenium(III), d^5 system.[21] The room temperature magnetic moment value of compound 1, having composition $[Ru_2Cl_6(Me_2SO)_4]$ is 1.1 B.M. per ruthenium atom which is much lower than expected, for a low spin ruthenium(III), d^5 system and is similar to Antonov's compound.[8] The lowering in the magnetic moment could be due to weak antiferromagnetic interaction of the two ruthenium(III) ions through the bridging chlorides.[22] Proposed structure for the compound 1 is shown in Fig. II.4(a). Lower values of magnetic moment for dimeric ruthenium(III) complexes, viz. $[RuCl_3(Et_2S)_2]_2$ (0.95 BM per ruthenium atom) have been reported earlier.[22]

ELECTRON PARAMAGNETIC RESONANCE SPECTRA

The electron paramagnetic resonance spectrum of compound 3 (Fig II.5) with all three S-bonded Me_2SO groups, in powder form, showed two g values, both at room temperature and at liquid nitrogen temperature. The g values were 2.42 and 1.92, which suggest a facial structure [Fig II.4(C)] with C_{3v} symmetry.[23] The powder EPR spectrum of compound 2 (Fig II.6), at room temperature showed three g values, viz. 2.41, 2.26 and 1.88. This suggest a rhombic geometry around

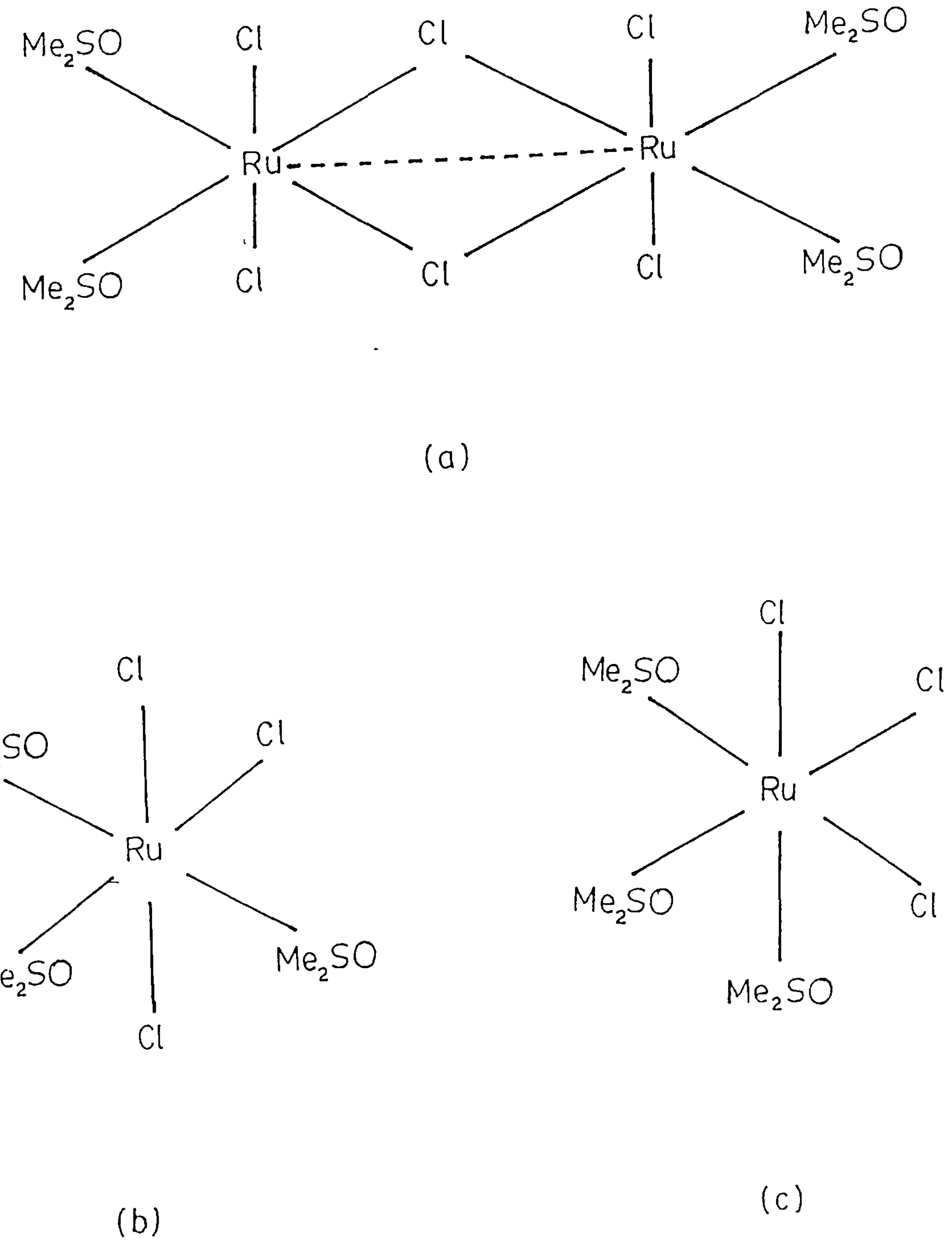

Fig. II 4 a. [$Ru_2(\mu\text{-}Cl)_2\ Cl_4(Me_2SO)_4$], $\underline{1}$
b. *mer*-[$RuCl_3(Me_2SO)_3$], $\underline{2}$
c. *fac*-[$RuCl_3(Me_2SO)_3$], $\underline{3}$

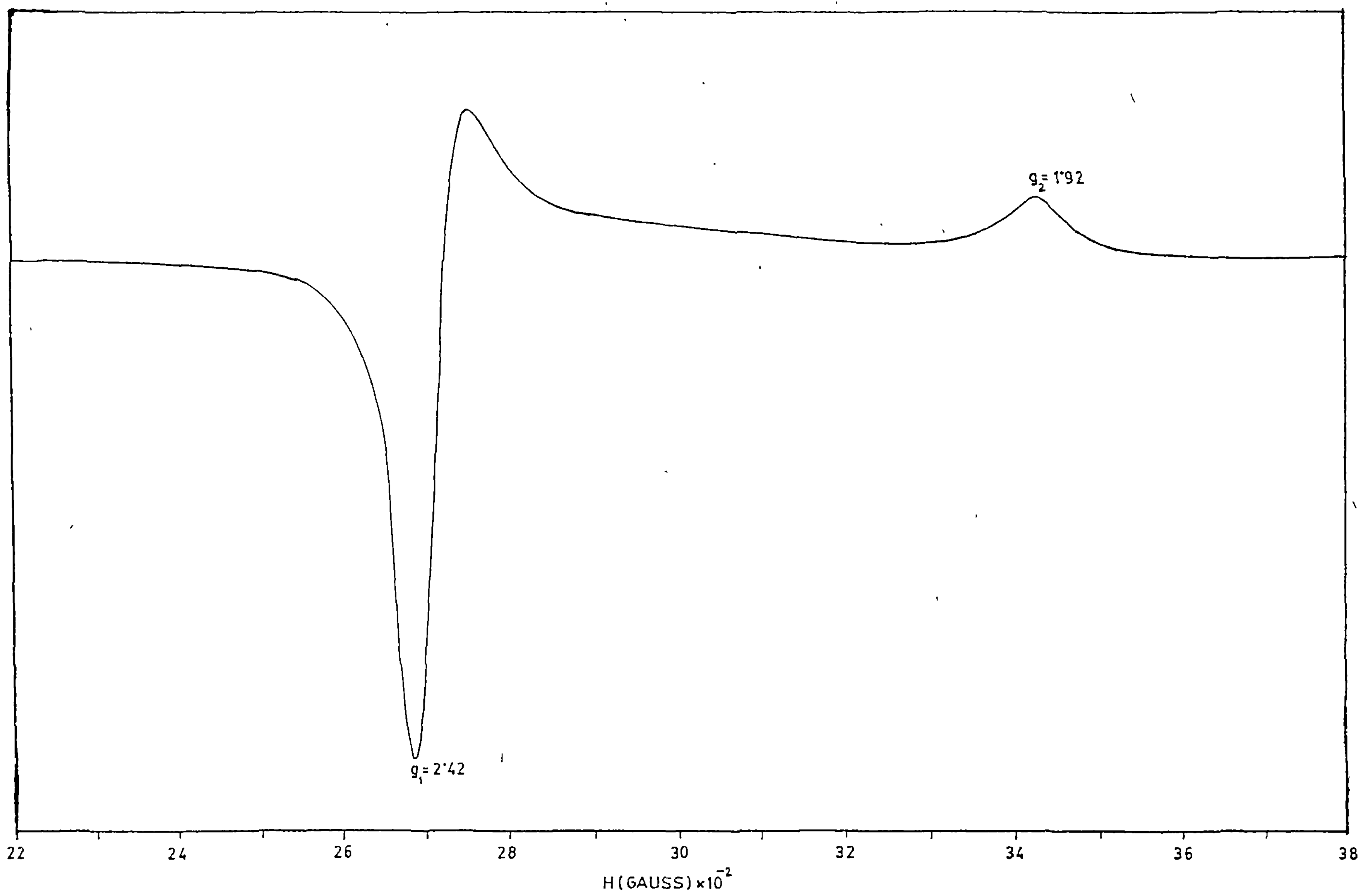

Fig II.5. E P R SPECTRUM OF <u>fac</u>$[RuCl_3(Me_2SO)_3]$ AT R T

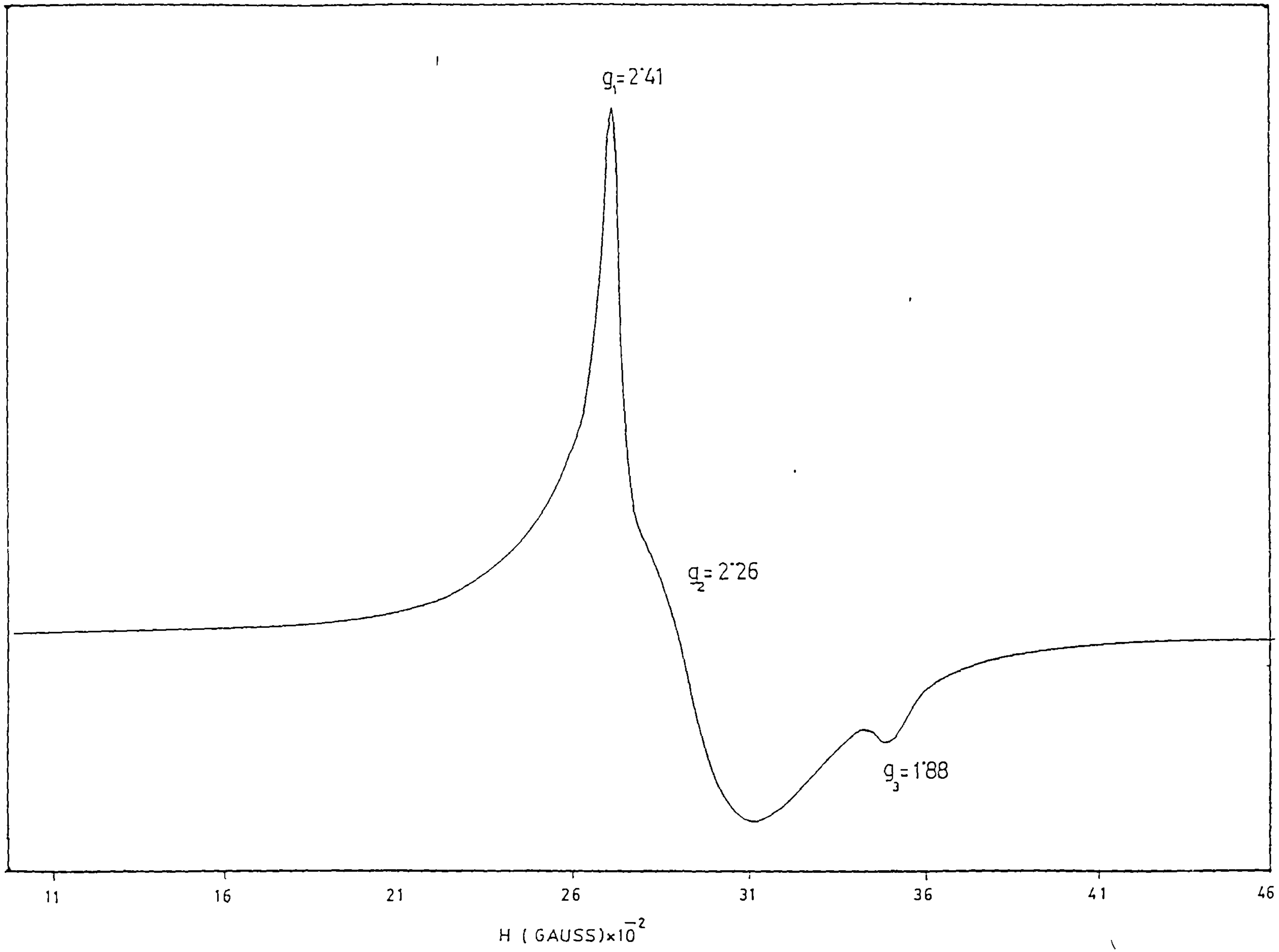

Fig II.6. E P R SPECTRUM OF <u>mer</u> $[RuCl_3(Me_2SO)_3]$ AT R T ruthenium(III). If one presumes the meridional type of structure for compound 2 with a C_{2v} symmetry, the three g values could be explained. Three g values could be obtained also with facial isomer when three Me_2SO groups bonded to ruthenium are not of the same type (O- and S-bonded)(vide supra). However, we prefer a meridional type [Fig II.4(b)], as evidenced from far-IR spectrum. The EPR spectrum of compound 1 (Fig II.7) in the powder form at room temperature, also showed three g values, viz. 2.37, 2.14 and 1.88 which are similar to that of compound 2. Assuming the structure to be dimeric with chloro-bridges, as proposed earlier, if one looks at the symmetry around each of the ruthenium ion, there is a rhombic distortion and the three g values could be explained. A signal corresponding to g = 2.14 in compound 1 is much broader than that of g = 2.26 of compound 2. The broadness of the signal at g = 2.14 may be due to weak interaction among the two neighbouring ruthenium(III) ions, proposed on the basis of lowering of the magnetic moment also. (vide supra).

ELECTRONIC ABSORPTION SPECTRA

The electronic absorption spectral data are given in Table II.3. The electronic absorption spectra of compound 1 and 2 were similar in acetonitrile and in chloroform. Compound 3 has very low solubility in chloroform. The spectrum of compound 1 was similar to that of Antonov's compound except

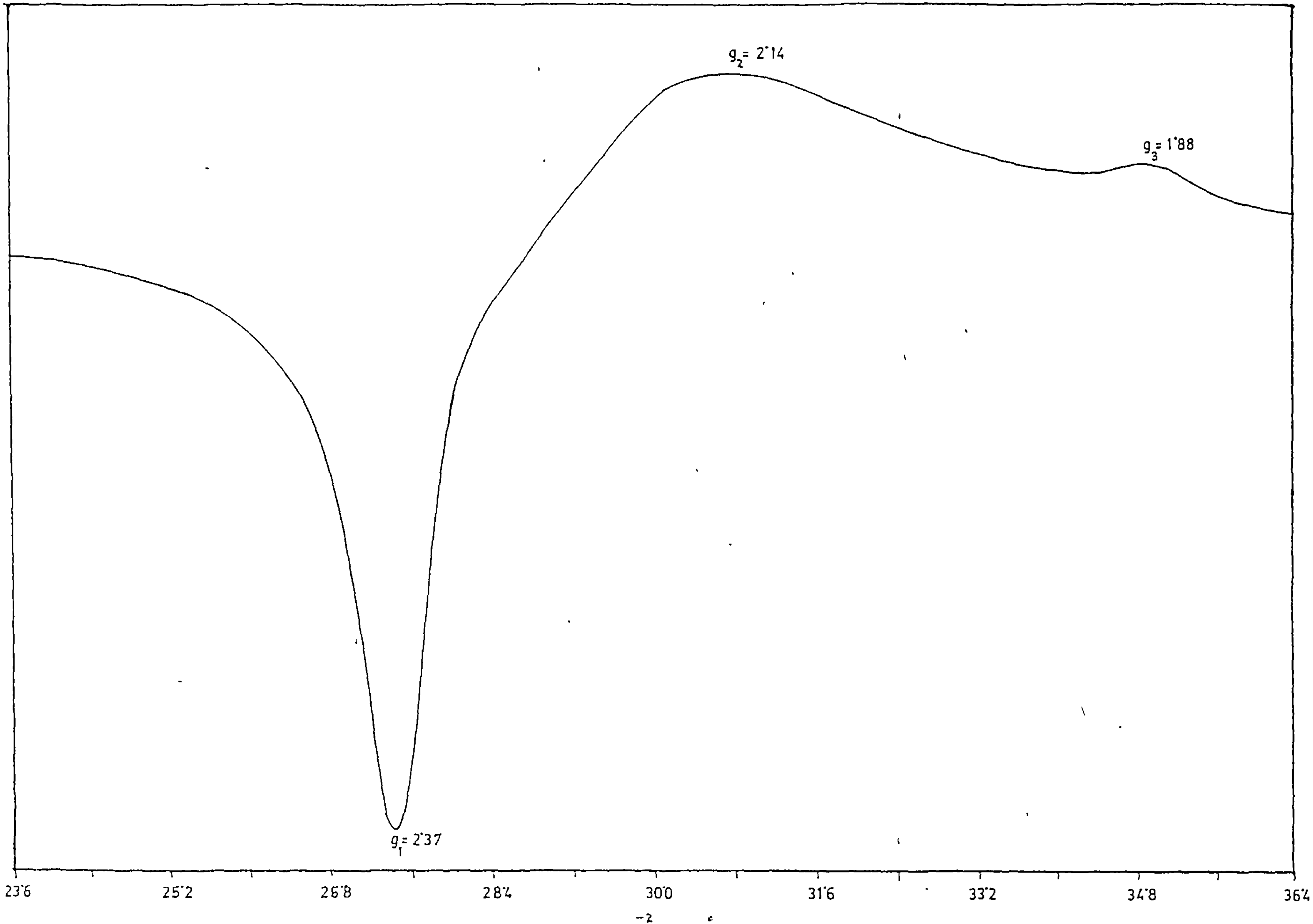

Fig II.7. E P R SPECTRUM OF $[Ru_2Cl_6(Me_2SO)_4]$ AT RT

Table II.3 Electronic absorption spectra of 1, 2 and 3

Compound	λ_{max} in nm (ϵ) in CH_3CN	λ_{max} in nm (ϵ) in $CHCl_3$
1 [$Ru_2Cl_6(Me_2SO)_4$]	455 (11.8×10^3)	457 (10.4×10^3)
	390 (10.5×10^3)	380 (10.6×10^3)
2 mer [$RuCl_3(Me_2SO)_3$]	416 (2.9×10^3)	435 (2.6×10^3)
	385 (3.2×10^3)	380 (2.9×10^3)
3 fac [$RuCl_3(Me_2SO)_3$]	468 (140)	-
	405 (585)	-

that the ϵ value was somewhat larger (assuming the dimeric formula). The compounds 2 and 3 also showed spectra similar to that of compound 1, but with lower ϵ values. The similarity of the electronic absorption spectra of three compounds conforms to a similar type of geometry around the metal in all the cases. Very high value of ϵ (10^3 to 10^4) for compounds 1 and 2 are suggestive that the absorption bands around 450 nm and 400 nm, are having more of charge transfer character than the d-d type absorption band ($^2T_2$ to $^2A_2$, $^2T_1$ or $^2T_2$ transitions). The electronic absorption spectra of these ruthenium(III) complexes have a close similarity to the aqueous solution spectrum of $RuCl_3$ reported by Antonov _et al_.[8]

PROTON MAGNETIC RESONANCE SPECTRA

The ^1H NMR spectra of $[RuCl_3(Me_2SO)_3]$ in $CHCl_3$ and CH_2Cl_2, at room temperature reported by Antonov _et al_[8] had one sharp peak having $\delta = 0.13$ ppm and 0.20 ppm respectively relative to free Me_2SO. In general, the condition for a sharp line ^1H NMR require a short electron spin relaxation time, and a sharp line EPR require a long one. Thus where EPR is observed at room temperature, ^1H NMR is either not observed or is very broad. This is the case with ruthenium(III).[24] In fact sharp line ^1H NMR spectra are not reported for any ruthenium(III) complex. Our efforts too, to get the ^1H NMR spectra of the three compounds synthesized were unsuccessful.

In fact, in some cases in $CHCl_3$ or CH_2Cl_2 solution, some sharp signals in the S-bonded or O-bonded Me_2SO region were observed at very high resolution. However, a blank run of the solvent showed the signals at the same positions, which may be due to some impurities present in the solvent.

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CHAPTER III

CHAPTER III

USE OF $[Ru_2Cl_6(Me_2SO)_4]$, AND *fac* AND *mer* ISOMERS OF $[RuCl_3(Me_2SO)_3]$ AS VERSATILE STARTING MATERIALS FOR THE SYNTHESIS OF RUTHENIUM(III) COMPLEXES

Some ruthenium(II) complexes, containing monodentate ligands, *viz*., $[RuX_2(Me_2SO)_4]$[1-4], $[RuX_2(PPh_3)_3]$ (X = Cl, Br)[5] and $[RuCl_2(AsPh_3)_2]_2$ are well known, and used extensively as precursors for the synthesis of a wide number of ruthenium(II) complexes.[2,7-14] In case of triphenylphosphine or triphenylarsine complexes, generally, a partial substitution took place, whereas dimethylsulphoxide complexes resulted in both partial and complete substitution of the ligand molecules. In case of ruthenium(III), some complexes with monodentate ligands, *viz*. $[RuX_3(MPh_3)_2(CH_3OH)]$[5] and $[RuX_3(MPh_3)_3]$[15-17] (X = Cl or Br, M = P or As) are used as precursors for the synthesis of many ruthenium(III) complexes. Most of the complexes synthesized, using these complexes, have partial displacement of MPh_3 ligands.[3,13,16-21]

In Chapter II, we have reported the synthesis and characterization of $[Ru_2Cl_6(Me_2SO)_4]$ *1*, *mer* $[RuCl_3(Me_2SO)_3]$ *2* and *fac* $[RuCl_3(Me_2SO)_3]$ *3*. In this Chapter, compounds *1*, *2* and *3* have been used as precursors for the synthesis of many ruthenium(III) complexes containing N, P, As, O and S donor ligands. Depending on the reaction conditions and the nature of the ligands reacted with, complete or partial substitution of dimethylsulphoxide molecules in these compounds are achieved. Only representative ligands containing different donor atoms have been used in this work. However, these complexes will find a much wider horizon as precursors for the synthesis of ruthenium(III) complexes.

EXPERIMENTAL

$[Ru_2Cl_6(Me_2SO)_4]$, *mer* $[RuCl_3(Me_2SO)_3]$ and *fac* $[RuCl_3(Me_2SO)_3]$ were prepared according to the methods described in Chapter II. Analytical data and all physical measurements were obtained as described in Chapter II. Nitrogen analyses of the compounds were obtained from Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. Analytical data, melting point, molar conductance data and magnetic measurement results are presented in Table III.1. Important IR and electronic absorption bands are presented in Table III.2.

Reactions of $[Ru_2Cl_6(Me_2SO)_4]$ 1, mer $[RuCl_3(Me_2SO)_3]$, orange isomer 2, and fac $[RuCl_3(Me_2SO)_3]$, yellow isomer 3 ,

(a) With triphenylphosphine or triphenylarsine

(i) Compound 1, 2 or 3 (0.2g) was dissolved in methanol (20 cm^3) and to which a solution of ligand L ($L = PPh_3$ or $AsPh_3$) in methanol (10 cm^3) was added. Reactions with varying molar ratios of the compounds 1, 2 or 3 and ligand L, viz. 1:1, 1:2, 1:3 and 1:6 were carried out. The reaction mixture was stirred for 30 min to 1 h at room temperature. The compound obtained in each case was centrifuged, washed with little methanol and then with little diethyl ether and dried *in vacuo*. In all the above reactions, even with varying proportions, the final product obtained in each case was of the composition, $[RuCl_3L_2(CH_3OH)]$.

(ii) Reactions similar to that in (i) above were carried out by refluxing the reaction mixture on a water-bath for 30 min. The products obtained were same as in (i).

(b) With pyridine

(i) 0.2g of each of the compounds 1 or 3 was dissolved in minimum quantity of methanol (10 cm^3), to which pyridine (1 cm^3) was added and the mixture was stirred at room temperature for 3-4 h. In case of compound 3, product separated simply on stirring. In case of compound 1, after stirring, the volume of the solution was reduced to about half, at room temperature and diethylether was added, followed by cooling (0°C) for 2-3 h, whereby a green coloured compound separated out. The products were separated by centrifugation, washed with diethyl ether and dried in vacuo. Product obtained from the reaction of 1 was green whereas from 3, it was yellow. These compounds may be isomers, having the composition, $[RuCl_3(Py)_2(Me_2SO)]$.

(ii) Reactions similar to that in (i) above, were carried out by refluxing the reaction mixture on a water-bath for 2 h, concentrated ($\sim 5\ cm^3$) and cooled, when compounds separated out which were centrifuged, washed with diethyl ether and dried in vacuo. The compounds were analysed for $[RuCl_2(Py)_4]$.

(c) With 1,10-phenanthroline

(i) 0.2g of each of the compounds 1, 2 or 3 was dissolved in methanol (20 cm^3) and to which 1,10-phenanthroline (0.1g) in methanol (5 cm^3) was added. The reaction mixture was stirred at room temperature. In case of compound 1 and 2 the products separated after 1-2 h, whereas in case of compound 3, the product separated after 10 min only. The compounds were centrifuged, washed with little methanol followed by diethyl ether and dried in vacuo. The product obtained from the reaction of 1 was brown in colour whereas from 2 and 3 were orange in colour. However, the composition in all three cases was [$RuCl_3$(phen)(Me_2SO)]. Some compound was isolated when the reaction mixture (as above) was refluxed in methanol for 30 min.

(d) With 2,2′-bipyridyl

0.2g of each of the compounds 2 or 3 was dissolved in methanol (20 cm^3) and to which 2,2′-bipyridyl (0.1g) in methanol (5 cm^3) was added. The reaction mixture was stirred at room temperature. In the case of compound 3, the product was separated after 30 min whereas in case of 2 after 2 h. Products obtained were centrifuged, washed first with methanol followed by diethyl ether and were dried in vacuo. The compounds were analysed for [$RuCl_3$(bipy)(Me_2SO)].

(e) With o-phenylenediamine

(i) Compound 2 or 3 (0.2g) was dissolved in ethanol (20 cm^3) and a solution of o-phenylenediamine (0.1g) in ethanol (5 cm^3) was added to it. The reaction mixture was refluxed for 15-20 min, concentrated ($\sim$ 5 cm^3) and the compounds were precipitated by the addition of dry diethyl ether. Products obtained from compounds 2 and 3 were light orange in colour and were analysed for [$RuCl_2$(PDA)$(Me_2SO)_2$].

Reaction of compound 2 with o-phenylenediamine using chloroform as solvent also gave the same product.

(ii) The above reactions were carried out at room temperature with stirring for few hours. Same products were obtained with lower yields.

(f) With acetylacetone

A suspension of compound 3 or a solution of compound 2 (0.2g) was taken in toluene (20 cm^3). Acetylacetone (0.5 cm^3) and triethylamine (1 cm^3) were added to the suspension or solution, and the reaction mixture was refluxed for 2-3 h at 120-130°C, cooled and filtered. The brown coloured mother liquor was concentrated slowly on a water-bath (~ 5 cm^3). Petroleum ether (80-100°C) was added to precipitate a light brown compound. More compound crystallized out from the mother liquor on cooling to 0°C for 2-3 h. The product was centrifuged, washed with little diethyl ether and dried *in vacuo*. The compounds were analysed for $[RuCl_2(acac)(Me_2SO)_2]$.

(g) With acetonitrile

0.2g of each of the compound 1, 2 or 3 was dissolved in acetonitrile (20 cm^3) and was refluxed on a water-bath for 4 h. The reaction mixture was concentrated to small volume (5 cm^3) and dry diethyl ether was added to precipitate a yellowish orange coloured compound. Products obtained were centrifuged, washed with diethyl ether and dried *in vacuo*. These were analysed for $[RuCl_3(CH_3CN)_2(Me_2SO)]$.

(h) With sodium diethyldithiocarbamate or o-aminobenzenethiol

A solution of sodium diethyldithiocarbamate (0.2g) or o-aminobenzenethiol (0.15g) in methanol (10 cm^3) was added to a solution of compound, 1 2 or 3 (0.3g) in methanol (20 cm^3). The reaction mixture in the former case was stirred at room temperature for 2 h and refluxed for 30 min in the latter case. Dark brown and dark-violet crystals separated in the former and the latter cases respectively. The compounds were centrifuged, washed with small quantity of methanol followed by diethyl ether and dried *in vacuo*. The compound in each reaction was of the composition $[Ru(L-L)_3]$ (L-L = diethyldithiocarbamate or o-aminobenzenethiolate).

(i) With carbondisulphide and triphenylphosphine

Compound 2 or 3 (0.2g) was dissolved in carbondisulphide (20-30 cm^3) and triphenylphosphine (0.18g) was added to it and refluxed on a water-bath for 30 min. Dark brown crystals separated out. It was centrifuged, washed with diethyl ether and dried *in vacuo*. The compound in each case was analysed for $[RuCl_3(CS_2)(PPh_3)_2]$.

Preparation of $[Ru(o\text{-aminobenzenethiolate})_3]$ from $RuCl_3.xH_2O$

$RuCl_3.xH_2O$ (0.2g) was dissolved in methanol (10 cm^3) and a solution of o-aminobenzenethiol (0.2g) in methanol

(10 cm^3) was added to it. The mixture was refluxed for 5 min. A compound separated out. It was cooled, centrifuged and washed with methanol and then with ether. It was analysed for $[Ru(abt)_3]$.

RESULTS AND DISCUSSION

$[Ru_2Cl_6(Me_2SO)_4]$ **1**, *mer* $[RuCl_3(Me_2SO)_3]$ **2** and *fac* $[RuCl_3(Me_2SO)_3]$ **3** are soluble in most of the organic solvents, *viz.* methanol, ethanol, acetonitrile and chloroform. Compound **2** is soluble in acetone and benzene also. Hence these compounds are suited for carrying out exchange reactions with other ligands in neutral type organic solvents. In water, however, these complexes dissociate.

The reaction of **1**, **2** and **3** with various donor ligands can be divided into three categories, *viz.* (i) where complete substitution of Me_2SO molecules took place, (ii) where only one Me_2SO molecule was coordinated and (iii) where two Me_2SO molecules were coordinated. The complete or partial substitution of coordinated Me_2SO molecules depend on the reaction conditions and the nature of coordinating molecules, which could be generalised in the following paragraph.

In general, complete substitution of coordinated Me_2SO molecules took place, either when the incoming ligand was stronger coordinating than Me_2SO or when the reaction was carried out at higher temperature, generally at the refluxing condition of the solvent. Examples of complete substitution of Me_2SO molecules due to stronger coordinating ability of ligand is found in case of P, As or S donor ligands at room temperature and at refluxing condition of the solvent. Complete substitution of Me_2SO takes place even in case where there is a nitrogen donor ligand or a nitrogen and sulphur donor chelate, at the refluxing condition of the solvent. Compounds containing one or two Me_2SO molecules are generally obtained when nitrogen or oxygen donor ligands are treated with **1**, **2** or **3** at room temperature conditions. However, in some cases such compounds are obtained under refluxing condition of the solvent also.

Reactions of $[Ru_2Cl_6(Me_2SO)_4]$ **1**, *mer* $[RuCl_3(Me_2SO)_3]$ **2** and *fac* $[RuCl_3(Me_2SO)_3]$ **3** with

Phosphorus, arsenic and sulphur donor ligands

Reactions of **1**, **2** and **3** with triphenylphosphine or triphenylarsine in varying molar ratios (from 1:1 to 1:6, complex : PPh_3 or $AsPh_3$) at room temperature or at methanol refluxing conditions resulted in the formation of $[RuCl_3(MPh_3)_2(CH_3OH)]$ (M = P or As) complexes, which are well characterized and reported by Stephenson and Wilkinson.[5] Complete substitution of Me_2SO is due to the stronger coordinating ability of PPh_3 and $AsPh_3$ compared to Me_2SO. Even when complex : MPh_3 ratio was varied, in all cases, only

/[$RuCl_3(MPh_3)_2(CH_3OH)$]/ was obtained which implies that it is probably the most stable compound of ruthenium(III) with chloro and MPh_3 groups in methanol medium.

Reactions of 1, 2 or 3 with sodium salt of diethyldithiocarbamate at room temperature condition yielded /[$Ru(Et_2NCS_2)_3$]/ which was obtained by the complete substitution of both chloro and Me_2SO groups from these complexes. The product /[$Ru(Et_2NCS_2)_3$]/ is well characterised and studied earlier.[22-23]

A reaction of compound 2 or 3 with carbondisulphide under the refluxing condition of the solvent did not give any substitution of Me_2SO by a thiocarbonyl group or by carbondisulphide. Instead, the starting materials were recovered. However, when a reaction of 2 or 3 with carbondisulphide was carried out in presence of triphenylphosphine under refluxing condition, a dark brown coloured compound separated out, which was analysed for /[$RuCl_3(PPh_3)_2(CS_2)$]/. This compound is same as reported by Ruiz Ramirez and Stephenson,[3] from the reaction of /[$RuCl_3(PPh_3)_2(CH_3OH)$]/ with carbondisulphide. Besides all the bands due to triphenylphosphine, it showed an absorption band at 1505 cm^{-1}, assigned to a linearly bonded carbondisulphide group,[3] and another band at 332 cm^{-1} assigned to ν_{Ru-Cl}. The magnetic moment of the compound measured at room temperature (μ_{eff} = 1.8 B.M.), confirms its behaviour as a low-spin d^5, ruthenium(III)

Table III.1 Some Physical and Analytical Data of New Ruthenium(III) Complexes

Compound	Colour	M.P.°C	μ_{eff} at R.T.(BM)	Λ_M in $\Omega^{-1}cm^2mol^{-1}$	Analysis[a] (%)		
					C	H	N
$[RuCl_3(py)_2(Me_2SO)]$	Yellow	220-25	-	3^b	32.8 (32.5)	4.1 (3.6)	6.0 (6.3)
$[RuCl_3(py)_2(Me_2SO)]$	Green	240^d	-	20^b	32.2 (32.5)	3.9 (3.6)	6.1 (6.3)
$[RuCl_3(phen)(Me_2SO)]$	Orange	240	1.8	3^c	36.2 (36.1)	2.9 (3.0)	5.9 (6.0)
$[RuCl_3(bipy)(Me_2SO)]$	Orange	250	-	6^b	32.2 (32.5)	3.2 (3.2)	6.3 (6.3)
$[Ru(acac)(Me_2SO)_2Cl_2]$	Light brown	215-20	-	3^b	25.6 (25.3)	4.8 (4.4)	-
$[RuCl_3(CS_2)(PPh_3)_2]^e$	Dark brown	$180-85^d$	1.8	-	55.2 (54.9)	4.0 (3.7)	-
$[Ru(abt)_3]$	Violet	-	-	5^c	46.0 (45.3)	4.2 (4.4)	8.8 (8.8)
$[RuCl_3(CH_3CN)_2(Me_2SO)]$	Yellow		1.9	10^c	19.4 (19.5)	3.0 (3.3)	7.3 (7.6)

a, Calculated values are in parentheses; b, in acetonitrile; c, in chloroform;
d, decomposes; e, ref. 3.

Table III.2 Important infrared and electronic absorption bands of Ruthenium(III) complexes containing Me_2SO and other ligands

Compound	Colour	Infrared bands in cm^{-1}	Electronic absorption bands in nm (ϵ)	
			CH_3CN	$CHCl_3$
$[RuCl_3(py)_2(Me_2SO)]$	Yellow	1105s, 1090sh, 1065m, 1015m-s, 423m, 345m, 330m	465 (700) 406 (2200)	470 (740) 408 (2450)
$[RuCl_3(py)_2(Me_2SO)]$	Green	1105s, 1090s, 1065s, 1015m-s, 426m, 380m 351m, 330m.	-	620 (220) 470 (930) 405 (1620)
$[RuCl_3(phen)(Me_2SO)]$	Brown	1090m-s, 423m, 390m, 323m, 254m.	404 (3580) 395 (3770)	404 (4060) 395 (4130)
$[RuCl_3(phen)(Me_2SO)]$	Orange	1090m-s, 430m, 343m, 285m	-	405 (4070) 395 (4280)

Table III.2 continued

Table III.2 continued

Compound	Colour	Infrared bands in cm^{-1}	Electronic absorption bands in nm (ε)	
			CH_3CN	$CHCl_3$
$[RuCl_3(CH_3CN)_2(Me_2SO)]$	Yellow	2315w, 2280m, 1110s, 1090s, 1020s, 331m.	-	-
$[RuCl_3(bipy)(Me_2SO)]$	Dark Orange	1110s, 1015m, 420m, 321m.	408 (5140) 404 (4540)	404 (3530) 395 (3700)
$[Ru(acac)(Me_2SO)_2Cl_2]$	Light Brown	1570m-s, 1510m, 1090s	560 (50)	-

complex. An EPR spectrum of the complex in the powder form at room temperature (Fig III.1) showed three g values, viz. $g_1 = 2.40$, $g_2 = 2.16$ and $g_3 = 1.81$. This confirms once again the presence of ruthenium(III) in low-spin state and signifies rhombic distortion in the complex, which is expected too, due to the presence of three different types of donor sites in the complex.

Reactions of 1, 2 or 3 with o-aminobenzenethiol under refluxing methanol condition gave a completely substituted (both chloro and Me_2SO groups) compound, viz. $[Ru(abt)_3]$. Here, complete substitution may be due to the stronger coordinating ability of the sulphur atom. The IR spectrum of the complex in the region 1100-1000 cm^{-1} showed two weak bands which are due to o-aminobenzenethiolate. Further, no characteristic band due to O-bonded Me_2SO was observed between 1000-900 cm^{-1}. This complex could also be obtained by the direct reaction of ruthenium trichloride with o-aminobenzenethiol in methanol. The IR spectrum of which was superimposable with that of the product obtained by the reaction of 1, 2 or 3 with o-aminobenzenethiol.

Oxygen donor ligands

Reactions of compounds 2 or 3 with acetylacetone in a weakly basic medium under refluxing condition of toluene gave

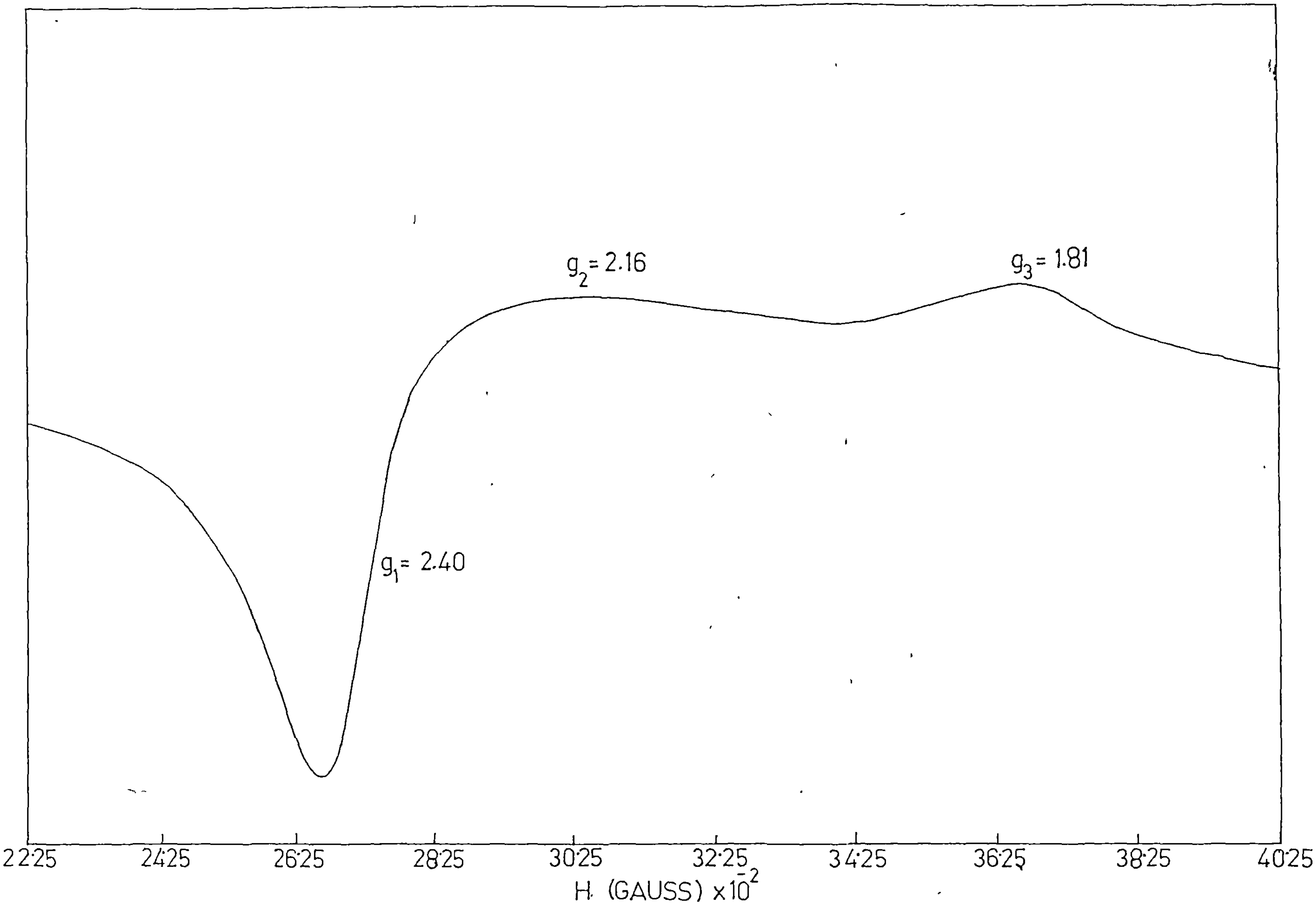

Fig. III.1. E P R SPECTRUM OF $[RuCl_3(CS_2)(PPh_3)_2]$ AT R T a compound of the composition $[RuCl_2(acac)(Me_2SO)_2]$. The IR spectrum showed two strong bands at 1570 and 1510 cm^{-1} which could be assigned to ν_{CO} of the O-bonded type chelating acetylacetonato groups.[24] The presence of Me_2SO molecules was characterised by a very strong band at 1090 cm^{-1}. It is evidently due to S-bonded Me_2SO groups. There were no other bands in the region 1000 to 900 cm^{-1} confirming the absence of any O-bonded Me_2SO group. The IR spectra of the compounds obtained from the reactions of 2 and 3 with acetylacetone were superimposable, thereby confirming that the products obtained from the two isomers, viz. 2 having mostly O-bonded Me_2SO groups and 3 having only S-bonded Me_2SO groups are one and the same, and that the Me_2SO molecules in the product are S-bonded. From the above reactions we may infer that the coordinating behaviour of Me_2SO in the products depend on the incoming ligand and not on the starting compounds. The non-conducting behaviour of the complex in acetonitrile confirms the formula $[RuCl_2(acac)(Me_2SO)_2]$, where chloride ligands are covalently bonded. Reactions of 1, 2 and 3 were carried out with triphenylphosphine oxide and triphenylarsine oxide separately under room temperature and refluxing methanol conditions. In both the cases no substitution of Me_2SO molecules took place and the starting materials were recovered.

Nitrogen donor ligands

(a) *Pyridine* : The products obtained from the reactions of 1, 2 or 3 with pyridine are dependent on the reaction conditions and in some cases on the starting compounds. Reaction of 1 and 3 with pyridine at room temperature, gave different products in each case, whereas reactions of compounds 1, 2 or 3 with pyridine under refluxing condition of methanol for 2 h gave $[RuCl_2(py)_4]$. Reactions of pyridine with other compounds, *viz*. $[RuCl_2(PPh_3)_3]$ or $[RuCl_3(MPh_3)_2(CH_3OH)]$ (M = P or As) under similar conditions were reported to give $[RuCl_2(py)_4]$[3]. Here, besides complete substitution of Me_2SO molecules by pyridine, there is reduction of ruthenium(III) to ruthenium(II) as well. $[RuCl_2(py)_4]$, obtained as above, has a *trans* geometry which is reflected by the far-IR and ^1H NMR spectrum. ^1H NMR spectrum showed a doublet at δ 8.6, and two triplets at δ 7.64 and δ 7.08, which is similar to that reported for trans-$[RuCl_2(py)_4]$[25]. The far-IR spectrum is superimposable with the reported one.[25]

Reactions of compounds 1 or 3 with pyridine at room temperature yielded products which conform to the composition $[RuCl_3(py)_2(Me_2SO)]$. The product from compound 1 was a green isomer whereas from 3, a yellow one. The conductivity measurement showed a very low molar conductance value thereby conforming to the covalently bonded chlorides.

The IR spectra of both the compounds (Fig III.2(a) and Fig III.2(b)) showed strong bands around 1100 cm^{-1} which could be assigned to $\nu_{S=O}$ of the S-bonded Me_2SO groups. A band at 1065 cm^{-1} could be due to pyridine or a combination of pyridine and Me_2SO bands. There were no strong bands in the region 1000 to 900 cm^{-1}, characteristic of O-bonded Me_2SO groups. A band at 1015 cm^{-1} could be assigned to ρ_r CH of the Me_2SO group.[2] Characteristic bands due to coordinated pyridine groups were observed in both the complexes. The IR spectra of the green and yellow isomers showed bands at 426 and 423 cm^{-1} respectively, which could be assigned to ν_{Ru-S} of the S-bonded Me_2SO groups. Further, the green isomer showed three bands at 380, 351 and 330 cm^{-1} which could be assigned to ν_{Ru-Cl}. The presence of three absorption bands for ν_{Ru-Cl}, indicate that two chloride ligands in the complex are arranged in the <u>trans</u> positions and the third ones is <u>cis</u> to both of them as in the case of <u>mer</u> isomer of $[MX_3L_3]$ type system.[26] The yellow isomer has two absorptions at 345 and 330 cm^{-1} assignable to ν_{Ru-Cl}. The presence of two absorption bands for ν_{Ru-Cl} is indicative that the three chlorides in the complex are arranged in the <u>cis</u>- form as in the case of <u>fac</u> isomer of $[MX_3L_3]$ type system.[26]

The EPR spectrum of the yellow and green isomers in powder form at room temperature showed a broad signal at g = 2.25 and 2.21 respectively, which confirms the presence

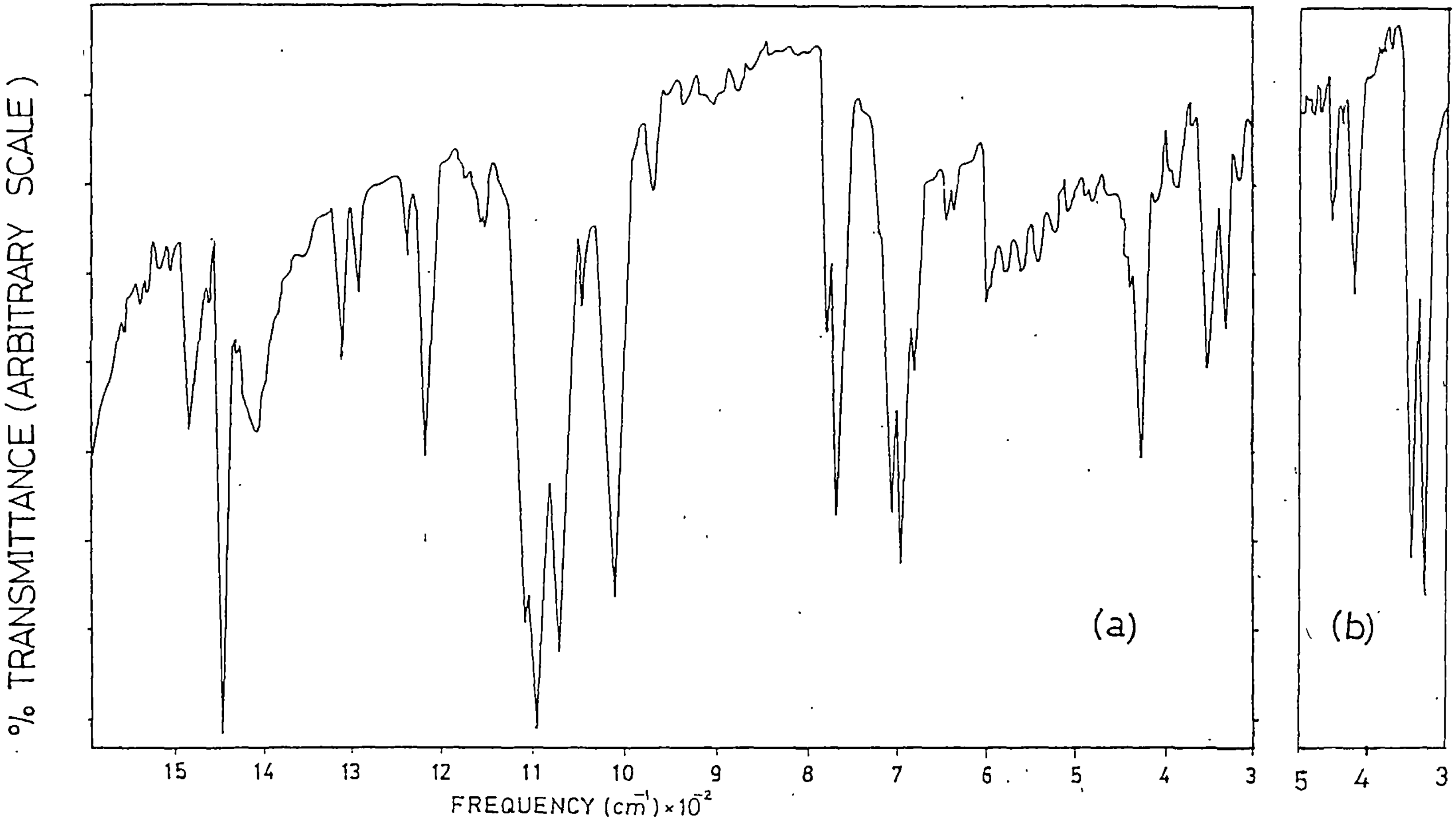

Fig.III.2 INFRARED SPECTRUM OF [RuCl$_3$(Py)$_2$(Me$_2$SO)]-(GREEN) (a)

INFRARED SPECTRUM OF [RuCl$_3$(Py)$_2$(Me$_2$SO)]-(YELLOW) (b) of a low-spin ruthenium(III), d^5 system. The room temperature spectra are not much informative but spectra of the frozen solution of the two compounds in chloroform at liquid nitrogen temperature showed three g values around 2.5, 2.0 and 1.8. Hyperfine coupling due to ruthenium was also observed in these cases. A detailed study of the frozen solution EPR spectra will be taken up later.

(b) 2,2′-Bipyridyl : A reaction of 2 or 3 with 2,2-bipyridyl at room temperature resulted in the partial substitution of Me_2SO molecules leading to the formation of $[RuCl_3(bipy)(Me_2SO)]$ Compounds obtained from 2 or 3 were identical and their IR spectra were superimposable. The compound was non-electrolyte. The IR spectrum of the compound showed a strong band at 1110 cm^{-1} assigned to $\nu_{S=O}$ of the S-bonded Me_2SO group and a band at 1015 cm^{-1} due to ρ_r CH of the Me_2SO molecule. Besides this, all characteristic absorption bands due to bipyridyl were present. However, no band of appreciable intensity in the region 1000-900 cm^{-1} was present confirming the absence of O-bonded Me_2SO groups. Spectrum in the far-IR region showed bands at 420 and 321 cm^{-1} which could be assigned to ν_{Ru-S} and ν_{Ru-Cl} respectively. Thus, IR spectrum confirms the presence of S-bonded molecule. Room temperature EPR measurement of the powder sample showed a broad signal at g = 2.23 which confirms the presence of a low-spin ruthenium(III), d^5 system. However, the spectrum does not say much about the geometry around the metal ion.

(c) <u>1,10-phenanthroline</u> : The products obtained from the reaction of compound <u>1</u> with 1,10-phenanthroline at room temperature and methanol refluxing conditions were same, having brown colour and composition, $[RuCl_3(phen)(Me_2SO)]$. The products obtained from the reaction of compound <u>2</u> or <u>3</u> with 1,10-phenanthroline under similar conditions were same having orange-yellow colour and composition, $[RuCl_3(phen)(Me_2SO)]$. The brown and orange-yellow compounds may be isomers. Non-ionic nature of the compounds was confirmed by their molar conductivity measurements. IR spectra of both the compounds showed strong bands around 1090 cm^{-1}, which could be assigned to $\nu_{S=O}$ of the S-bonded Me_2SO molecule. In the far-IR region, the brown compound showed absorptions at 423, 390, 323 and 254 cm^{-1}. The first band may be due to ν_{Ru-S} whereas the rest three bands due to ν_{Ru-Cl}. The orange yellow compound showed absorptions at 430, 343 and 285 cm^{-1}. Here again, the absorption at 430 cm^{-1} could be due to ν_{Ru-S} whereas the bands at 343 and 285 cm^{-1} due to ν_{Ru-Cl}. The presence of three absorption bands due to ν_{Ru-Cl} in case of brown compound may be assigned to its structure where two of the chloride ligands are <u>trans</u> to each other and the third one <u>cis</u> to them, and presence of two absorption bands due to ν_{Ru-Cl} in case of orange-yellow compound, may be due to the presence of all three chloride ligands in the cis position.[26] (similar to green and yellow isomers of $[RuCl_3(py)_2(Me_2SO)]$). The magnetic moment of the orange yellow compound observed at room temperature was, μ_{eff} = 1.9 B.M., a value expected for low-spin d^5, ruthenium(III) complexes. Its EPR spectrum in powder form at room temperature showed two g values at 2.50 and 2.12. The structure proposed for this compound on the basis of far-IR would be in conformity with the EPR result, if one assumes that ligand field due to Me_2SO is similar to that of nitrogen donor 1,10-phenanthroline, hence two g values. Room temperature EPR spectrum of brown compound in powder form showed a broad signal at g = 2.27, confirming the presence of low-spin d^5 system.

(d) <u>o-Phenylenediamine</u> : Reactions of <u>2</u> or <u>3</u> with <u>o</u>-phenylenediamine, under refluxing condition of methanol gave a light orange compound, of the composition, $[RuCl_2(PDA)(Me_2SO)_2]$. It is diamagnetic and showed IR absorption at 1065 cm^{-1}, assignable to $\nu_{S=O}$ of the S-bonded Me_2SO. There was no absorption of appreciable intensity in the region 1000-900 cm^{-1}, confirming the absence of any O-bonded Me_2SO group. The ^1H NMR spectrum of the compound in $(CD_3)_2SO$ (Fig III.3) showed two broad singlets at δ 7.48 and δ 7.33, one singlet at δ 6.1 and a sharp singlet at δ 3.25. The signals at δ 7.48 and δ 7.33 may be assigned due to the <u>o</u>- and <u>p</u>-protons in <u>o</u>-phenylenediamine.[27] The signals

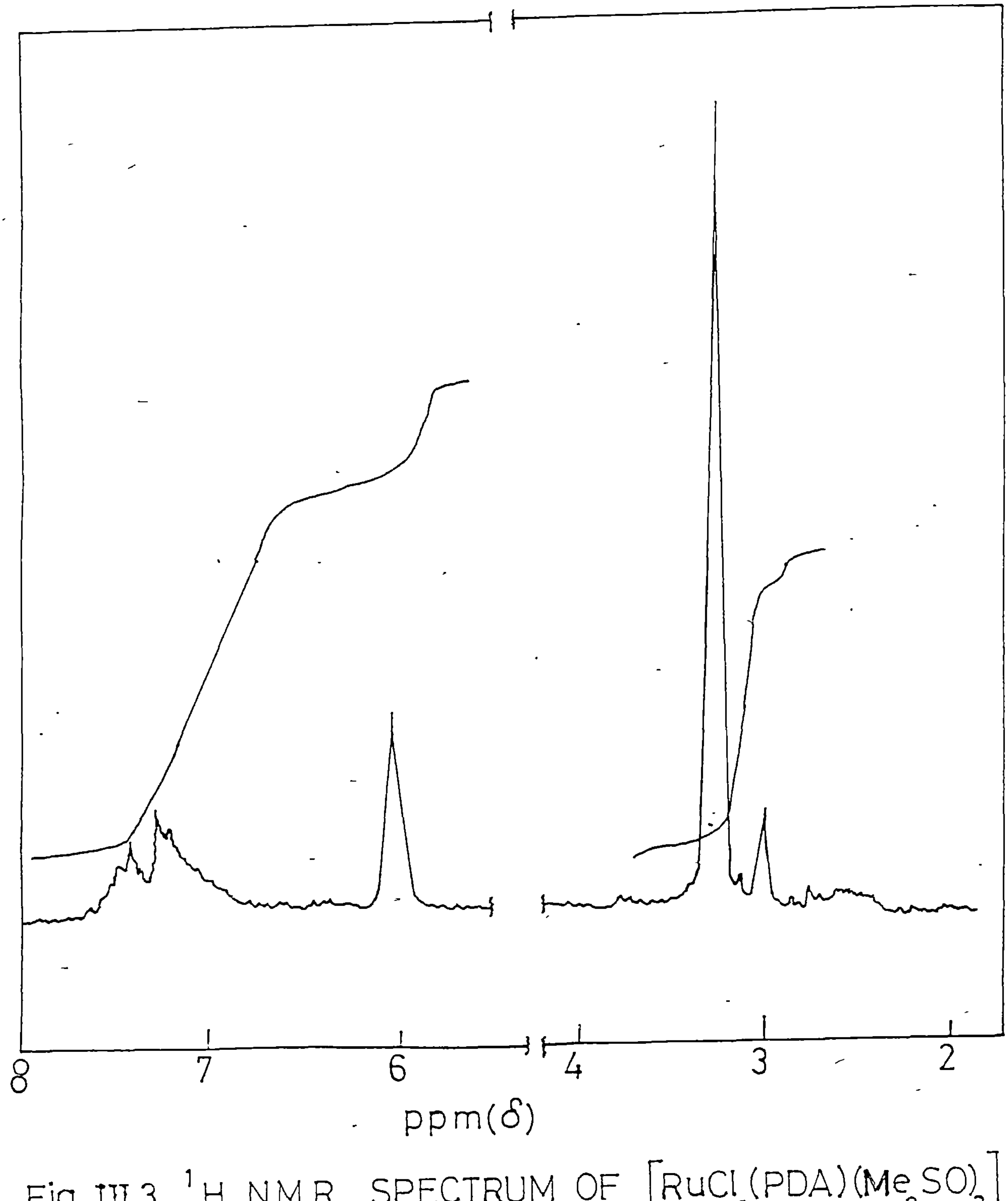

Fig III.3 ^{1}H NMR SPECTRUM OF $[RuCl_2(PDA)(Me_2SO)_2]$ IN $(CD_3)_2SO$

at δ 6.1 may be due to the four protons attached to the two nitrogen atoms of the amino groups. In case, where the o-amino groups are not coordinated, the aromatic amino protons are expected in the range δ 3.6 - 4.7.[27] However, due to the coordination of the nitrogen atoms to the metal, the electron density around the nitrogen atoms are reduced, thereby decreasing shielding of the protons at the nitrogen atoms and leading to a signal at lower field i.e. at a higher δ value (δ 6.1). The signal at δ 3.25 is indicative of the S bonded Me_2SO groups. The ratio of the protons under δ 3.25 and δ 6.1 is 3:1, confirming the presence of twelve protons of two Me_2SO groups (S-bonded) compared to four protons of the two amino groups of one o-phenylenediamine molecule. The presence of a singlet for two Me_2SO groups at δ 3.25 is indicative of the presence of six methylprotons on each Me_2SO group in equivalent environments. Hence a structure for $[RuCl_2(PDA)(Me_2SO)_2]$ with two S-bonded Me_2SO groups in trans positions, two chloride ligands in cis positions and two amino-groups of o-phenylenediamine in cis-positions, is most probable. Preparation of a compound of the composition $[RuCl_2(PDA)(Me_2SO)_2]$, was reported by Evans et al.,[2] by the reaction of o-phenylenediamine with $[RuCl_2(Me_2SO)_4]$. However, no physical measurements were reported.

(e) Acetonitrile : Reaction of 1, 2 or 3 with acetonitrile (as solvent) at refluxing condition gave, in all cases a compound of the composition $[RuCl_3(CH_3CN)_2(Me_2SO)]$. The products obtained from all these compounds are same and are confirmed with superimposable IR and visible spectra, melting points and the analytical data. Here complete substitution of the Me_2SO molecules do not take place probably due to the weak coordinating ability of acetonitrile compared to Me_2SO. The molar conductance measurements of the complex showed a very low molar conductance value, confirming thereby the presence of all covalently bonded chloride ligands. IR absorption bands at 2315 and 2280 cm^{-1} could be assigned to ν_{CN} of the coordinated CH_3CN molecules preferably in the cis positions.[12] Two bands around 1100 cm^{-1} can be assigned to $\nu_{S=O}$ of the S-bonded Me_2SO group. There were no bands of appreciable intensity in the region 1000-900 cm^{-1} which could be due to O-bonded Me_2SO. A band at 331 cm^{-1} was observed, which could be assigned to ν_{Ru-Cl} in the complex. All other bands due to Me_2SO and CH_3CN were also present in the spectra. Thus, the complex contains only S-bonded Me_2SO group.

ELECTRONIC SPECTRA

The electronic absorption spectral data of the new ruthenium(III) complexes are presented in Table III.2.

The spectra showed similar features in chloroform and acetonitrile solution. Generally, all the ruthenium(III) complexes have absorption around 500 nm and 400 nm with molar extinction coefficients of the order of 10^3. High values of ϵ for all these complexes are suggestive that these absorptions have more of charge-transfer character than the d - d type. In case of the green isomer of $[RuCl_3(py)_2(Me_2SO)]$, an absorption band at 620 nm with $\epsilon = 220$ and in case of $[RuCl_2(acac)(Me_2SO)_2]$, a band at 560 nm with $\epsilon = 50$ was observed. These bands have relatively low value of ϵ and hence may be due to d - d transition ($^2T_2$ to $^2A_2$, $^2T_1$ or $^2T_2$ type). The electronic absorption bands for the ruthenium compounds are similar to other ruthenium(III) complexes.[28] All the compounds, for which electronic absorption bands are presented in Table III.2 have six coordination around ruthenium(III). However, there is considerable lowering of symmetry from O_h due to the presence of different mono or bidentate ligands. Absorption bands with high value of ϵ for such low symmetry ruthenium(III) complexes, cannot be assigned to d → d transitions alone, which may be obscured by charge-transfer bands in these regions.[28]

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CHAPTER IV

CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF $[RuBr_3(Me_2SO)_3]$ AND $[RuBr_2(Me_2SO)_3]$ AND THEIR USE AS PRECURSORS FOR THE SYNTHESIS OF RUTHENIUM(III) AND RUTHENIUM(II) BROMO COMPLEXES

INTRODUCTION

Synthesis and study of the complexes of ruthenium(II) and ruthenium(III) containing chloride as one of the ligands and other mono- or multidentate ligands have been carried out in greater detail due to the easy availability of the source material, viz. commercial ruthenium trichloride, $RuCl_3.xH_2O$. Similar to ruthenium trichloride, its bromo-analogue, viz. ruthenium tribromide is not available commercially. Hence, synthesis and study of the complexes of ruthenium(II) and ruthenium(III) containing bromide as one of the ligands and other mono or multidentate ligands have not been carried out in detail.[1]

Complexes of ruthenium(II) and ruthenium(III) containing chloride and Me_2SO ligands studied, are cis $[RuCl_2(Me_2SO)_4]$[2,3], fac and mer $[RuCl_3(Me_2SO)_3]$[4,5], $[Ru_2Cl_6(Me_2SO)_4]$[5],

$[Ru_2Cl_4(Me_2SO)_5]$,[6] $[NMe_2H_2][RuCl_3(Me_2SO)_3]$[7], and M $[RuCl_4(Me_2SO)_2]$[8] (where M = Na or Bu_4N). Some of the above mentioned compounds have been used as precursors for the synthesis of other ruthenium(II) and ruthenium(III) complexes.[3,6,9-11] The only ruthenium(II) or ruthenium(III) complex containing bromide and Me_2SO ligands, reported is <u>trans</u> $[RuBr_2(Me_2SO)_4]$,[2,12-14] having all S-bonded Me_2SO groups. No report is available on ruthenium(III) complexes containing bromo and Me_2SO ligands. $[RuBr_2(Me_2SO)_4]$ has been used as precursor for the synthesis of some ruthenium(II) bromo complexes of the type, $[RuBr_2(Me_2SO)_3L]$, (L = PPh_3, $AsPh_3$, PBu_3 or $P(OBu)_3$, $[RuBr_2L_4]$ (L = py or CH_3CN) and $[RuBr_2(Me_2SO)_2(diphos)]$.[15] $[RuBr_2(Me_2SO)_4]$ has been found to have better activity compared to <u>cis</u> $[RuCl_2(Me_2SO)_4]$, as molecular oxygen oxidation catalyst towards thioethers to give sulphoxides.[15,16]

The synthesis of complexes containing bromide as one of the ligands is achieved by one of the following methods: (i) reaction of $RuBr_3$ (obtained from the reaction of ruthenium oxide with HBr also) with the ligand,[2,13,17] (ii) generating $RuBr_3$ or bromoruthenate(III) in situ using $RuCl_3$ or chlororuthenate(III) and LiBr, NaBr or HBr and treating with the ligand,[18-23] (iii) metathesis of the chloro, hydroxo or hydrido group to bromo group using LiBr, NaBr, KBr, HBr or Br_2[21,22,24-30] in the complex, (iv) reaction of a complex containing oxalato group with HBr,[31-33], and (v) substitution of one or more ligand (L) molecules in a bromo complex of the type, $[RuBr_3L_3]$, $[RuBr_3L_2(MeOH)]$ (where L = PPh_3 or $AsPh_3$), $[RuBr_2L_3]$ (L = PPh_3) or $[RuBr_2L_4]$ (where L = Me_2SO) by other ligands.[12,15,34] Table IV.1 describes different preparative methods for the complexes of ruthenium(III) and ruthenium(II) containing bromide and other mono- or bidentate ligands.

Out of the above mentioned five methods, method (ii), (iii) and (v) are more frequently used. In method (v), the ligand L substituted in the complexes are PPh_3, $AsPh_3$ or Me_2SO. Complete substitution of PPh_3 or $AsPh_3$ by weak donor ligands is generally not successful. However, Me_2SO containing complexes may be good for such purposes. In this Chapter, we have described the synthesis and characterization of one ruthenium(III) complex, viz. $[RuBr_3(Me_2SO)_3]$ and other ruthenium(II) complex, viz. $[RuBr_2(Me_2SO)_3]$. These two complexes have been used as precursors for the synthesis of other ruthenium(III) and ruthenium(II) complexes. $[RuBr_2(Me_2SO)_3]$ is a potential molecular oxygen oxidative catalyst also, as $[RuBr_2(Me_2SO)_4]$.[15,16]

Table IV.1 Complexes of Ruthenium(II) and Ruthenium(III) containing Bromide and other Monodentate or Bidentate Ligands

Sl.No	Complex	Preparation	Physical Properties	References
1.	trans $[RuBr_2(Me_2SO)_4]$	(i) $RuBr_3 + Me_2SO + H_2$	IR, UV-VIS,	2,14
		(ii) $Ru_2O_3.xH_2O + HBr + Me_2SO$	X ray, ^1H NMR	13
		(iii) $[RuBr_3(AsPh_3)_2MeOH] + Me_2SO$	CV	12
2.	trans $[RuBr_2(py)_4]$	(i) $RuBr_3 + H_2 + py$	IR	17
		(ii) $[RuBr_2(PPh_3)_3] + py$	IR, ^1H NMR	12
		(iii) $[RuBr_2(Me_2SO)_4] + py$	IR, UV-VIS, CV	15
3.	cis $[RuBr_2(py)_4]$	$[Ru(py)_4(ox)]H_2O + HBr$	far IR, Raman ^1H NMR	31
4.	$[RuBr_2(PPh_3)_n]$ (n = 3,4)	$RuCl_3.xH_2O + LiBr + PPh_3$	MW	18

Table IV.1 continued

Table IV.1 continued

Sl.No	Complex	Preparation	Physical properties	Reference
5.	$[RuBr_3(AsPh_3)_3]$	$RuCl_3.xH_2O + HBr + LiBr + AsPh_3$	Λ_M, μ, M, IR, UV-VIS	19
6.	$[Ru(NH_3)_5Br]Br_2$	$RuCl_3.xH_2O + HBr + NH_2NH_2.H_2O$	IR	20
7.	$[RuBr_2(L-L)_2]$ (L-L = diars, dmpe or depe)	$RuCl_3 + NaBr + L-L$	μ	21,22
8.	$[RuBr_3(AsMePh_2)_3]$	$K_2[RuCl_5(H_2O)] + HBr + AsMePh_2$		23
9.	mer $[RuBr_3L_3]$ (L = PMe_2Ph, PEt_2Ph)	$[RuCl_3L_3] + LiBr$	IR	24,25
10.	$[RuBr_3(PPh_3)_2(H_2O)]H_2O$	$Me_4N[RuCl_4(PPh_3)_2] + LiBr$	μ, IR	26

Table IV.1 continued..

Table IV.1 continued

Sl.No	Complex	Preparation	Physical Properties	References
11.	$[RuBr_3(PhSR)_3]$ (R = Me, Et, n-propyl)	$[RuCl_3(PhSR)_3]$ + LiBr	IR, UV-VIS, ^1H NMR, EPR	27
12.	$[Ru(diars)_2Br_2]ClO_4$	$[Ru(diars)_2Cl_2]+HClO_4+Br_2$	μ	21
13.	$[Ru(L-L)_2Br_2]$ (L-L = dmpe, depe)	$[Ru(L-L)_2Cl_2]$ + KBr	μ	22
14.	$[RuBr_2(QAS)]$	$[RuCl_2(QAS)]$ + NaBr	χ_M, UV-VIS	28
15.	cis $[Ru(CO)_4Br_2]$	$[Ru(CO)_4H_2]$ + Br_2	IR	29
16.	$[RuBr_2(NH_3)_4]Br.H_2O$	$[Ru(OH)Cl(NH_3)_4]Cl.H_2O+HBr+KBr$		30
17.	A $[RuBr_4(aniline)_2]$ A = Me_4N, $C_6H_5NH_3$, C_5H_6N	A $[Ru(OX)_2(aniline)_2]$ + HBr	IR, VIS, μ	32

Table IV.1 continued....

Table IV.1 continued..

Sl No	Complex	Preparation	Physical Properties	Reference
18.	<u>cis</u> $[RuBr_2(en)_2]Br.H_2O$	$[Ru.OX(en)_2][Ru(OX)_2en].2H_2O$ + HBr	UV-VIS, IR	33
19.	$[RuBr_3(AsPh_3)_2]$	$[RuBr_3(AsPh_3)_2(MeOH)]$ + C_6H_6	far-IR, μ, ^1H NMR, EPR,	12
20.	$[RuBr_3(MPh_3)_2L]$ (M = P, As (L = CH_3CN, $PhCH_2CN$, PhCN, CH_2CHCN, Me_2SO, Et_2S,CS,THF)	$[RuBr_3(MPh_3)_2(MeOH)]$ + L	VIS, IR, ^1H NMR	12
21.	$[RuBr_3(MPh_3)L_2]$ (M=P, As (L_2= $(py)_2$, $(Me_2S)_2$, phen, bipy)	$[RuBr_3(MPh_3)_2(MeOH)]$ + L_2	VIS, IR, ^1H NMR	12

Table IV.1 continued...

Table IV.1 continued

Sl-No	Complex	Preparation	Physical Properties	References
22.	$[RuBr_2(MPh_3)_2(bdk)]$ MPh_3 = PPh_3, $AsPh_3$ bdk = acac, dbm, ba	(i) $[RuBr_3(AsPh_3)_3]$ + bdk (ii) $[RuBr_3(MPh_3)_2(MeOH)]$ + bdk M = P or As	IR, VIS, μ.	34
23.	$[RuBr_2(Me_2SO)_3L]$ (L = PPh_3, $AsPh_3$, PBu_3 and $P(OBu)_3$)	$[RuBr_2(Me_2SO)_4]$ + L	IR, UV-VIS, ^1H NMR, CV	15
24.	$[RuBr_2(Me_2SO)_2(diphos)]$	$[RuBr_2(Me_2SO)_4]$ + diphos	IR, UV-VIS, ^1H NMR, CV	15
25.	<u>trans</u> $[RuBr_2(CH_3CN)_4]$	$[RuBr_2(Me_2SO)_4]$ + CH_3CN	IR, UV-VIS ^1H NMR, CV	15

EXPERIMENTAL

All the solvents were distilled before use. Ruthenium trichloride trihydrate was obtained from Aurora Matthey Ltd, Calcutta. Analytical data and all physical measurements were obtained as described in Chapter II and Chapter III. Analytical data, melting point, molar conductance data and magnetic measurement results are presented in Table IV.2. Important IR and electronic absorption bands are presented in Table IV.3. ^{1}H NMR spectral data are given in Table IV.4. The analysis for bromide was carried out by the standard method,[35] the details of which are described below.

ESTIMATION OF BROMIDE

An accurately weighed amount of the complex was decomposed by heating with a melt of KNO_3 and KOH mixture (1:8) at around ~800°C. It was cooled and extracted with distilled water and then acidified with dilute HNO_3. It was then digested on a water-bath for about 30 min and filtered. Silver nitrate solution (0.1M) was added to precipitate silver bromide. The mixture was digested slowly on a water-bath for about 30 min for coagulation of the precipitate keeping away from light. The precipitate was filtered through a sintered glass crucible (G-4), washed with very dilute HNO_3 (1:100) to free from silver nitrate and dried to a constant weight at 120°C. The precipitate was weighed as silver bromide. Analytical data are presented in Table IV.2.

1. Preparation of $[RuBr_3(Me_2SO)_3]$

Hydrated ruthenium trichloride (0.25g, 1 mmol) was dissolved in conc. HBr (5 cm^3), to which LiBr (1g) was added. The mixture was warmed on a water bath to get a clear solution. The solution was centrifuged and dimethylsulphoxide (1.5 cm^3) was added to the clear solution and refluxed in an oil-bath (130-140°C) for 5 min (longer time refluxation results in the separation of an insoluble compound). Dark violet crystals separated out. The product was cooled, centrifuged and the compound was washed 2-3 times with water followed by ethanol and dried *in vacuo*. It was analysed for $[RuBr_3(Me_2SO)_3]$. Yield, 0.45g (80%).

2. Preparation of $[RuBr_2(Me_2SO)_3]$

Hydrated ruthenium trichloride (0.25g, 1 mmol) was dissolved in ethanol (20 cm^3), to which LiBr (2g) was added and refluxed for 30 min. To the clear solution dimethylsulphoxide (1.5 cm^3) was added and refluxed for another 2 h. The solution was concentrated to small volume (5 cm^3) on a water bath and cooled to 0°C. A yellow compound separated out. The mother liquor, on concentration and on addition of acetone gave more of the yellow compound. The compound was washed 2-3 times with ethanol, then with ether and dried *in vacuo*. It was analysed for $[RuBr_2(Me_2SO)_3]$. Yield, 0.35g (75%).

Reaction of $[RuBr_3(Me_2SO)_3]$

(i) With triphenylphosphine and triphenylarsine

(a) To a solution of $[RuBr_3(Me_2SO)_3]$ (0.3g, 0.5 mmol) in ethanol (10 cm^3), triphenylphosphine or triphenylarsine (0.4 to 0.5g, 1.5 mmol) in ethanol (10 cm^3) was added and stirred at room temperature for 3 h. Dark purple compound separated out. It was centrifuged, washed with little ethanol and then with ether and dried *in vacuo*. The compound was analysed for $[RuBr_3(MPh_3)_2(Me_2SO)]$ (M = P or As).

(b) A reaction similar to above (a) was carried out under refluxing condition of the solvent, when $[RuBr_3(MPh_3)_3]$ (M = P or As) was obtained.

(ii) With pyridine

(a) To a clear solution of $[RuBr_3(Me_2SO)_3]$ (0.3g) in toluene (10 cm^3), pyridine (0.5 cm^3) was added and stirred at room temperature for 1 h. The solution was cooled to 0°C for 2-3 h, when violet compound separated out. It was centrifuged, washed with ether and dried *in vacuo*. The compound was analysed for $[RuBr_3(py)(Me_2SO)_2]$. Yield, 0.24g (80%).

(b) A reaction similar to (a) above, using methanol as solvent was carried out where solution was refluxed for 1 h. Light brown crystals separated out and collected as in (a) above. It was analysed for $[RuBr_3(py)_3]$. Yield 0.25g (83%).

(c) A reaction similar to (a) above, using methanol as solvent with excess pyridine (~ 5 cm^3) was refluxed for 3 h. Dark brown crystals separated out and collected as above. It was analysed for $[RuBr_2(py)_4]$. Yield, 0.2g (66%).

(iii) With 2-methyl pyridine

2-methyl pyridine (0.5 cm^3) was added to $[RuBr_3(Me_2SO)_3]$ (0.3g) and the mixture was warmed on a water-bath for 30 min to get a clear solution. It was cooled and diethyl ether was added to precipitate a green compound. It was centrifuged, washed with ether and dried *in vacuo* and was analysed for $[RuBr_3(C_6H_7N)(Me_2SO)_2]$. Yield, 0.22g (73%).

(iv) With 2,2'-bipyridyl

$[RuBr_3(Me_2SO)_3]$ (0.3g, 0.5 mmol) was dissolved in ethanol (20 cm^3), to which 2,2'-bipyridyl (0.1g, 0.6 mmol) was added and refluxed on a water bath for 10 min. The solution was concentrated to small volume (~ 5 cm^3) when crystalline compound separated out. It was centrifuged, washed first with ethanol and then with diethyl ether and dried *in vacuo*. It was analysed for $[RuBr_3(bipy)(Me_2SO)]$. Yield, 0.18g (60%).

(v) With o-phenylenediamine

(a) To a clear solution of $[RuBr_3(Me_2SO)_3]$ (0.3g, 0.5 mmol) in toluene (10 cm^3), o-phenylenediamine (0.12g, 1 mmol) was added. The mixture was warmed on water bath for 10 min. Reddish brown compound separated, which was centrifuged, washed with ethanol-ether mixture and dried *in vacuo*. It was analysed for $[RuBr_2(PDA)(Me_2SO)_2]$. Yield, 0.2g (74%).

(b) A reaction similar to (a) above was carried out by taking $[RuBr_3(Me_2SO)_3]$ and PDA in molar ratio 1:1, when a dark red compound separated out. The compound is soluble in most of the organic solvents. It was washed carefully with a small quantity of ethanol and dried *in vacuo*. It was analysed for $[RuBr_2(PDA)_2(Me_2SO)_2]Br$. Yield, 0.3g, (80%).

(vi) With sodium diethyl dithiocarbamate

(a) To a clear solution of $[RuBr_3(Me_2SO)_3]$ (0.3g, 0.5 mmol) in toluene (15 cm^3) sodium diethyldithiocarbamate (0.12g, 0.5 mmol) was added and the mixture was refluxed on an oil-bath for 30 min (110-15 °C). The solution was cooled, centrifuged and concentrated to small volume ($\sim$5 cm^3) on water bath. Petroleum ether (60-100°C) was added when brown complex precipitated. The mixture was cooled to 0°C for 6 h. It was centrifuged, washed with ether and dried *in vacuo*. The compound was analysed for $[Ru(Et_2NCS_2)(Me_2SO)_2Br_2]$.

(b) A reaction similar to the above (a) was carried out by taking $[RuBr_3(Me_2SO)_3]$ and sodium diethyldithiocarbamate in the molar ratio (1:3) and refluxing the solution for 2h. The compound obtained was analysed for $[Ru(Et_2NCS_2)_3]$.

(vii) With carbon disulphide and triphenylphosphine

To a clear solution of $[RuBr_3(Me_2SO)_3]$ (0.3g, 0.5 mmol) in carbon disulphide (20 cm^3), triphenylphosphine (0.4g, 1.5 mmol) was added and refluxed for 1 h. Dark reddish brown crystals separated. It was cooled, centrifuged, washed with ether and dried *in vacuo*. The compound was analysed for $[RuBr_2(CS_2)(PPh_3)_3]Br$.

(viii) With acetylacetone

A solution of $[RuBr_3(Me_2SO)_3]$ (0.3g) was made in toluene (20 cm^3). Acetylacetone (0.5 cm^3) and triethylamine (0.5 cm^3) were added to the solution and refluxed in an oil bath for 2 h. The solution was cooled, filtered and concentrated slowly to about 2 cm^3. Light petroleum ether (40-60°C) was added to precipitate a purple compound. It was centrifuged, washed with ether and dried *in vacuo*. The compound was analysed for $[Ru(acac)_3]$.

Reactions of $[RuBr_2(Me_2SO)_3]$

(i) With triphenylphosphine

(a) To a solution of $[RuBr_2(Me_2SO)_3]$ (0.2g) in methanol (10 cm^3), a solution of PPh_3 (0.2g) in methanol (5 cm^3) was added and the mixture was stirred at room temperature for 2 h. A reddish brown compound separated out. It was centrifuged, washed with ether and dried <u>in vacuo</u>. The compound was analysed for $[RuBr_2(PPh_3)_4]$. Yield 0.45g (85%).

(b) A reaction similar to the above reaction (a) was carried out, where the solution was refluxed for 10 min. When a compound, same as in reaction (a) separated out.

(ii) <u>With pyridine</u>

(a) Pyridine (0.5 cm^3) was added to a solution of $[RuBr_2(Me_2SO)_3]$ (0.2g) in methanol (10 cm^3) and the mixture was stirred at room temperature for 3 h. A yellow compound separated out which was isolated as in above (i). The compound was analysed for the composition, $[RuBr_2(py)_2(Me_2SO)_2]$. Yield 0.2g (90%).

(b) Pyridine (0.5 cm^3) was added to a solution of $[RuBr_2(Me_2SO)_3]$ (0.2g) in methanol (10 cm^3) and the solution was refluxed for 1 h. The solution on concentration ($\sim$ 5 cm^3) and cooling to room temperature, resulted in the separation of a brown crystalline compound of the composition, $[RuBr_2(py)_4]$. This was centrifuged, washed with methanol and then with diethyl ether and dried <u>in vacuo</u>. Yield 0.18g (85%).

(iii) With 1,10-phenanthroline

(a) $[RuBr_2(Me_2SO)_3]$ (0.2g) was dissolved in methanol (10 cm^3) and a solution of 1,10-phenanthroline (0.12g) in methanol (5 cm^3) was added to it. The solution was stirred at room temperature for 10 min. Dark yellow coloured compound separated out. This was centrifuged, washed with methanol and ether and dried in vacuo. The compound was analysed for $[RuBr_2(phen)(Me_2SO)_2]$. Yield 0.16g (68%).

(b) A reaction similar to (a) above with excess of 1,10-phenanthroline (0.24g) was carried out by refluxing on a water-bath for 1 h. Dark orange solution was obtained which was concentrated to small volume ($\sim$2 cm^3). Diethyl ether was added to precipitate a dark orange coloured compound. It was centrifuged, washed with methanol and then with diethyl ether and dried in vacuo. The compound was analysed for $[Ru(phen)_2Br_2]$. Yield 0.18g ($\sim$70%).

(iv) With 2,2'-bipyridyl

To a solution of $[RuBr_2(Me_2SO)_3]$, (0.2g) in methanol (10 cm^3), 2,2'-bipyridyl (0.1g) in methanol (5 cm^3) was added and the mixture was stirred at room-temperature for 2 h. The volume of the solution was reduced ($\sim$1 cm^3), at room temperature, and diethyl ether was added to precipitate a dark brown coloured compound. The compound was centrifuged, washed with methanol followed by diethyl ether and dried in vacuo. The compound was analysed for [$RuBr_2(bipy)(Me_2SO)_2$]. Yield 0.16g (70%).

(b) A reaction similar to the above, was carried out by taking [$RuBr_2(Me_2SO)_3$] and 2,2'-bipyridyl in the molar ratio 1:2, and refluxing on a water-bath for 2 h. The orange coloured compound was precipitated by adding diethyl ether to concentrated (~2 cm^3) solution. It was analysed for [$Ru(bipy)_2Br_2$]. Yield 0.15g (~65%).

RESULTS AND DISCUSSION

The only reported bromide complex containing dimethylsulphoxide ligand is [$RuBr_2(Me_2SO)_4$].[2,12-14] We report here, two new complexes, viz. [$RuBr_3(Me_2SO)_3$] and [$RuBr_2(Me_2SO)_3$], a ruthenium(III) and ruthenium(II) complex respectively.

[$RuBr_3(Me_2SO)_3$]

The analytical data (Table IV.2) of a dark violet compound, obtained by treating ruthenium trichloride with dimethylsulphoxide in presence of lithium bromide and hydrogen bromide conform to the composition [$RuBr_3(Me_2SO)_3$]. It showed very low molar conductance ($5\,\Omega^{-1}cm^2mol^{-1}$) in acetonitrile conforming all covalently bonded bromide. The IR spectrum of the compound (Fig. IV.1) throws light on the nature of coordination of Me_2SO with ruthenium. The spectrum showed a band of

Table IV.2 Some analytical and physical data of some Ruthenium(III) and Ruthenium(II) bromo complexes

Compounds	Colour	M.P. °C	Analysis^a (%)				Conductance in $\Omega^{-1}cm^2mol^{-1}$	μ_{eff} at RT (BM)
			C	H	N	Br		
1. $[RuBr_3(Me_2SO)_3]$	Dark violet	250	12.4 (12.5)	3.0 (3.1)	-	40.8 (41.7)	5^b	2.1
2. $[RuBr_3(py)_3]$	Light brown		31.1 (31.1)	3.0 (2.6)	7.0 (7.3)	41.1 (41.5)	3^c	-
3. $[RuBr_3(py)(Me_2SO)_2]$	Violet	140	19.0 (18.8)	3.0 (3.0)	2.3 (2.4)	-	-	2.0
4. $[RuBr_3(Me\text{-}py)(Me_2SO)_2]$	Green	180-185	19.5 (19.4)	3.0 (3.1)	2.4 (2.3)	-	-	1.92
5. $[Ru(bipy)(Me_2SO)Br_3]$	Dark brown	240	25.2 (25.0)	2.5 (2.4)	4.5 (4.9)	-	10^b	-
6. $[RuBr_2(PDA)_2(Me_2SO)_2]Br$	Reddish brown	190-195	27.2 (27.0)	3.8 (3.9)	7.6 (7.8)	-	128^b	-

Table IV.2 continued...

Table IV.2 continued

Compound	Colour	M.P. °C	Analysis^a (%)				Conductance in $\Omega^{-1}cm^2mol^{-1}$	μ_{eff} at RT (BM)
			C	H	N	Br		
7. $[RuBr_2(PDA)(Me_2SO)_2]$	Light pink	200-205	22.9 (22.8)	4.0 (3.8)	5.1 (5.3)		6^b	D
8. $[Ru(Et_2NCS_2)(Me_2SO)_2Br_2]$	Brown	250	18.7 (19.1)	3.4 (3.9)	2.7 (2.5)		2.5^b	
9. $[RuBr_2(CS_2)(PPh_3)_3]Br$	Reddish brown	195-200	54.7 (54.9)	3.7 (3.7)	-		112^b 80^c	1.65
10. $[RuBr_2(Me_2SO)_3]$	Yellow	220-225	14.3 (14.5)	3.5 (3.6)		31.8 (32.3)	8^b	D
11. $[RuBr_2(py)_2(Me_2SO)_2]$	Dark yellow	185-190 (d)	29.0 (29.2)	3.5 (3.8)	4.6 (4.9)		5^b	D
12. $[RuBr_2(phen)(Me_2SO)_2]$	Yellow	230-235 (d)	31.8 (32.1)	3.0 (3.3)	4.3 (4.7)		8^b	D

Table IV.2 continued

Table IV. 2 continued

Compound	Colour	M.P. °C	Analysis[a] (%)				Conductance in $\Omega^{-1}cm^2mol^{-1}$	μ_{eff} at RT (BM)
			C	H	N	Br		
13. $[RuBr_2(bipy)(Me_2SO)_2]$	Dark brown	200-205 (d)	29.0 (29.3)	3.0 (3.5)	4.5 (4.9)		3^b	D
14. $[RuBr_2(phen)_2]$	Dark Orange	–	45.8 (46.3)	2.4 (2.6)	8.6 (9.0)		10^b	
15. $[RuBr_2(bipy)_2]$	Orange	–	41.4 (41.9)	2.5 (2.8)	9.3 (9.8)		12^b	

a, Calculated values are in parentheses

b, in acetonitrile; c, in chloroform;

d, decomposes ; D, diamagnetic

Table IV.3 Important IR and electronic absorption bands of Ruthenium(III) and Ruthenium(II) complexes containing Me_2SO and other ligands

Compounds	IR bands in cm^{-1}	Electronic absorption bands λ_{max} in nm (ϵ_{max})	
		CH_3CN	$CHCl_3$
$[RuBr_3(Me_2SO)_3]$	1030m-s, 970s, 468m, 295w	602(1150) 520(2900) 490(2500) 395(950)	620(1200) 540(2300) 500(2150) 395(800)
$[RuBr_3(py)(Me_2SO)_2]$	965m, 447w, 292w, 245w	-	588(1270) 526(1700) 476(2900) 400(950)
$[RuBr_3(Me\text{-}py)(Me_2SO)_2]$	990s, 970s, 478m,	440(990)	-

Table IV.3 continued

Table IV.3 continued

Compound	IR bands in cm^{-1}	Electronic absorption bands λ_{max} in nm (ϵ_{max})	
		CH_3CN	$CHCl_3$
$[RuBr_3(bipy)(Me_2SO)]$	970s, 479m-s, 458, 292w, 275w	570 (700) 500 (2500) 425 (1800)	575 (1050) 500 (2600) 481 (2750) 420 sh
$[RuBr_2(PDA)_2(Me_2SO)_2]Br$	1120s	-	495
$[Ru(Et_2NCS_2)(Me_2SO)_2Br_2]$	1080s, 1530m-s	-	465 (1350)
$[Ru(CS_2)(PPh_3)_3Br_2]Br$	1510m-s	656 (210) 485 (2850)	510 (3900) 390 (1850)
$[RuBr_2(Me_2SO)_3]$	1097s, 1030m 423m, 247w	365 (330) 220 (37000)	
$[RuBr_2(PDA)(Me_2SO)_2]$	1130s		

Table IV.3 continued...

Table IV.3 continued

Compounds	IR bands in cm^{-1}	Electronic absorption bands λ_{max} in nm (ϵ_{max})	
		CH_3CN	$CHCl_3$
$[RuBr_2(py)_2(Me_2SO)_2]$	1180s, 1060s		
$[RuBr_2(phen)(Me_2SO)_2]$	1075s, 1060s 425m		
$[RuBr_2(bipy)(Me_2SO)_2]$	1080s, 1060s		

s, strong;
m, medium;
w, weak

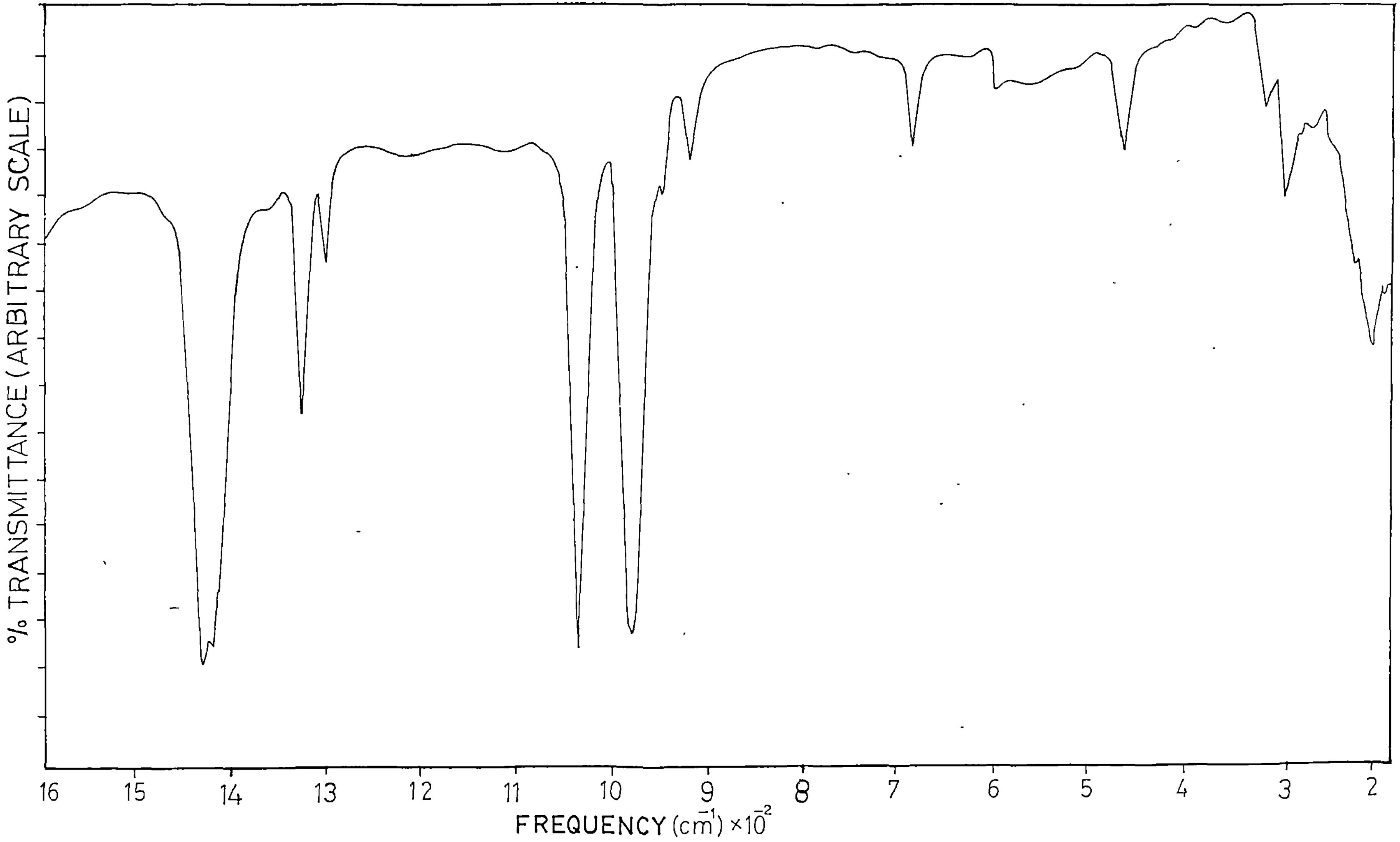

Fig IV.1 INFRARED SPECTRUM OF $[RuBr_3(Me_2SO)_3]$

medium intensity at 1030 cm^{-1} and a strong band at 970 cm^{-1}. The former can be assigned to ρ_r(CH), whereas the latter to $\nu_{S=O}$ (O-bonded) of the Me_2SO groups.[3] Bands at 468 cm^{-1} and 295 cm^{-1} in the far IR region may be assigned to ν_{Ru-O}[36,37] and ν_{Ru-Br}[38] respectively. The room temperature magnetic moment value of the complex (μ_{eff}) observed, was 2.1 B M., confirming the presence of a low-spin d^5 Ru(III) system. The room temperature EPR measurement of the compound in the powder form showed a broad signal at g = 2.2. A frozen solution EPR spectrum in dichloromethane at liquid nitrogen temperature also showed a broad signal at g = 2.12 which means that the symmetry around ruthenium(III) is close to that of a cubical one, which is possible if one assumes that the O-bonded Me_2SO groups and the bromides have similar ligand fields. With these information, it is not possible to clearly assign a facial or a meridional geometry to the complex. With the help of above measurements it is inferred that $[RuBr_3(Me_2SO)_3]$ is the first example of ruthenium complex containing bromide and dimethylsulphoxide having all three O-bonded Me_2SO groups. Other reported compounds viz., two isomers of $[RuBr_2(Me_2SO)_4]$ have either completely S-bonded[12] or both S- and O-bonded[13] Me_2SO groups.

Reactions of $[RuBr_3(Me_2SO)_3]$

With Phosphorus and Arsenic donor ligands

Reactions of $[RuBr_3(Me_2SO)_3]$ with triphenylphosphine or triphenylarsine gave either complete or partial substitution of dimethylsulphoxide depending on the reaction conditions. Reactions at room temperature resulted in the formation of $[RuBr_3(MPh_3)_2(Me_2SO)]$ (M = P or As) whereas at refluxing condition of ethanol yielded completely substituted complexes, viz. $[RuBr_3(MPh_3)_3]$. The IR spectra of $[RuBr_3(MPh_3)_3]$ (M = P or As) showed all absorption bands characteristics of PPh_3 or $AsPh_3$. No band characteristic of S- or O-bonded Me_2SO were observed. For $[RuBr_3(MPh_3)_2(Me_2SO)]$ all the bands due to PPh_3 or $AsPh_3$ and one band of medium intensity at 975 cm^{-1} was observed, which could be assigned to $\nu_{S=O}$ of O-bonded Me_2SO group.[12] Similar compounds were reported by the reaction of $[RuBr_3(MPh_3)_2(MeOH)]$ (M = P or As) with dimethylsulphoxide.[12]

With Sulphur and Oxygen donor ligands

Reactions of $[RuBr_3(Me_2SO)_3]$ with sodium diethyl dithiocarbamate in the molar ratio 1:1 resulted in the partial substitution of Me_2SO leading to the formation of a non-electrolyte complex $[RuBr_2(Et_2NCS_2)(Me_2SO)_2]$ ($\Lambda_M = 2.5\ \Omega^{-1}cm^2mol^{-1}$). However, a reaction in the molar ratio 1:3 resulted in the complete substitution of Me_2SO and bromide leading to

$[Ru(Et_2NCS_2)_3]$.[39,40] The IR spectrum of $[RuBr_2(Et_2NCS_2)(Me_2SO)_2]$ (Fig IV.2) showed strong bands at 1080 cm^{-1} and 1530 cm^{-1}, besides all other bands due to diethyl dithiocarbamate. The former may be assigned to $\nu_{S=O}$ (S-bonded) of the Me_2SO group whereas the latter one to ν_{CN} of a chelating diethyl dithiocarbamate group. ν_{CN} for unidentate diethyl dithiocarbamate group is generally observed at a lower frequency (1470 cm^{-1}).[41] Hence $[RuBr_2(Et_2NCS_2)(Me_2SO)_2]$ is expected to have six coordination having a chelating diethyl dithiocarbamate group.

A reaction of $[RuBr_3(Me_2SO)_3]$ with PPh_3 in carbon disulphide medium resulted in the formation of $[RuBr_2(CS_2)(PPh_3)_3]$ Br. However, CS_2 did not react and coordinate to the metal if PPh_3 was not used, and the starting compound was isolated. The compound, $[RuBr_2(CS_2)(PPh_3)_3]$Br showed a molar conductance of 112 $\Omega^{-1}cm^2mol^{-1}$ in acetonitrile, which is close to the 1:1 electrolytic behaviour of the compound. The IR spectrum showed a band of strong intensity at 1510 cm^{-1} besides all bands due to PPh_3. The absorption at 1510 cm^{-1} may be assigned to a linearly bonded CS_2 group to the metal.[12] The μ_{eff}, of the complex at room temperature was 1.65 B M., which is close to the value for one unpaired electron in a low-spin d^5 octahedral complexes of ruthenium(III).

A reaction of $[RuBr_3(Me_2SO)_3]$ with acetylacetone resulted in the complete substitution of the bromo and Me_2SO groups leading to the formation of $[Ru(acac)_3]$. In this case no partial substi-

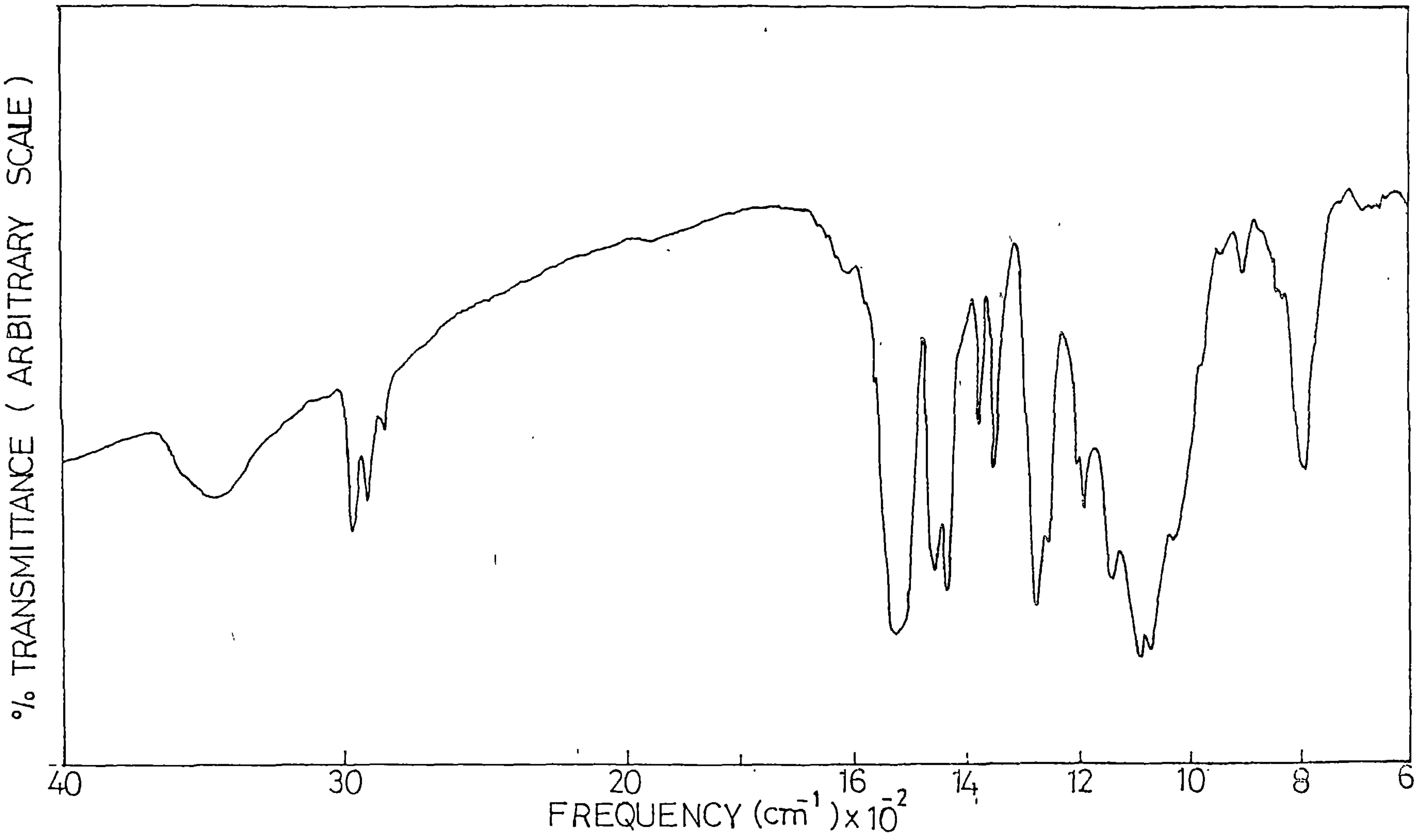

Fig.IV,2 INFRARED SPECTRUM OF $[Ru(Et_2NCS_2)(Me_2SO)_2Br_2]$

tution product could be isolated as in the case of the chloro-analogues, reported in Chapter III. $[Ru(acac)_3]$ showed IR absorptions at 1560 and 1515 cm^{-1} which are characteristics of chelating O-bonded acetylacetonate group, assigned to $\nu_{(C\overset{\cdots}{=}O)}$ and $\nu_{(C\overset{\cdots}{=}C)}$ respectively.[38] It is the same compound as reported by Endo <u>et</u> <u>al</u>.[42] An attempt to substitute Me_2SO in $[RuBr_3(Me_2SO)_3]$ with $OPPh_3$ was unsuccessful and $[RuBr_3(Me_2SO)_3]$ was recovered after the reaction.

<u>With Nitrogen donor ligands</u>

<u>Pyridine</u> : Reaction of $[RuBr_3(Me_2SO)_3]$ with pyridine at room temperature yielded a dark violet compound of the composition $[RuBr_3(py)(Me_2SO)_2]$ where only one Me_2SO molecule was substituted by pyridine. The IR spectrum showed a band at 965 cm^{-1} which could be assigned to $\nu_{S=O}$ (O-bonded) and a band at 447 cm^{-1} could be due to ν_{Ru-O}. Besides these, characteristic bands due to pyridine were also observed. Bands at 292 cm^{-1} and 245 cm^{-1} may be assigned to ν_{Ru-Br}. The room temperature magnetic moment value, μ_{eff}, was 2.0 B M , thereby confirming the oxidation state of ruthenium as 3+. Dimethylsulphoxide groups in $[RuBr_3(py)(Me_2SO)_2]$ are O-bonded as in the parent compound.

Complete substitution of Me_2SO molecules took place when slightly stronger reaction condition was employed, leading to the formation of a brown crystalline compound of the composition $[RuBr_3(py)_3]$. The IR spectrum of the compound showed all the bands due to pyridine. The room temperature EPR spectrum (Fig IV.3) of the compound in powder form showed two signals corresponding to g values 2.65 and 1.95. If, one presumes a facial type of structure for $[RuBr_3(py)_3]$ with a C_{3v} symmetry, two g values can be explained.[43]

Reaction of $[RuBr_3(Me_2SO)_3]$ with pyridine under much stronger condition (large excess of pyridine and refluxing for longer time) resulted in the formation of $[RuBr_2(py)_4]$. Besides complete substitution of Me_2SO, reduction of ruthenium(III) to ruthenium(II) was also achieved. The far IR spectrum of this compound in the region 500-250 cm^{-1} is superimposable with that of trans $[RuBr_2(py)_4]$ reported by Raichart and Taube.[31] The ^1H NMR spectrum of the compound in $CDCl_3$ showed a doublet at δ 8.73 and triplets at δ 7.63 and δ 7.04, similar to trans $[RuBr_2(py)_4]$, reported earlier.[31] $[RuBr_2(py)_4]$, obtained from $[RuBr_3(Me_2SO)_3]$, thus, has a trans geometry.

2-Methyl pyridine : A reaction of $[RuBr_3(Me_2SO)_3]$ with 2-methyl pyridine on slight warming gave a dark green compound of the composition, $[RuBr_3(Me\text{-}py)(Me_2SO)_2]$. The IR spectrum of the compound showed strong bands at 990 and 970 cm^{-1} characteristic of $\nu_{S=O}$ (O-bonded) of the Me_2SO groups. A band at 478 cm^{-1} may be due to ν_{Ru-O}. The room temperature magnetic moment value, μ_{eff} was 1.92 B.M., thereby confirming the oxidation state of ruthenium as 3+. The partially substituted product

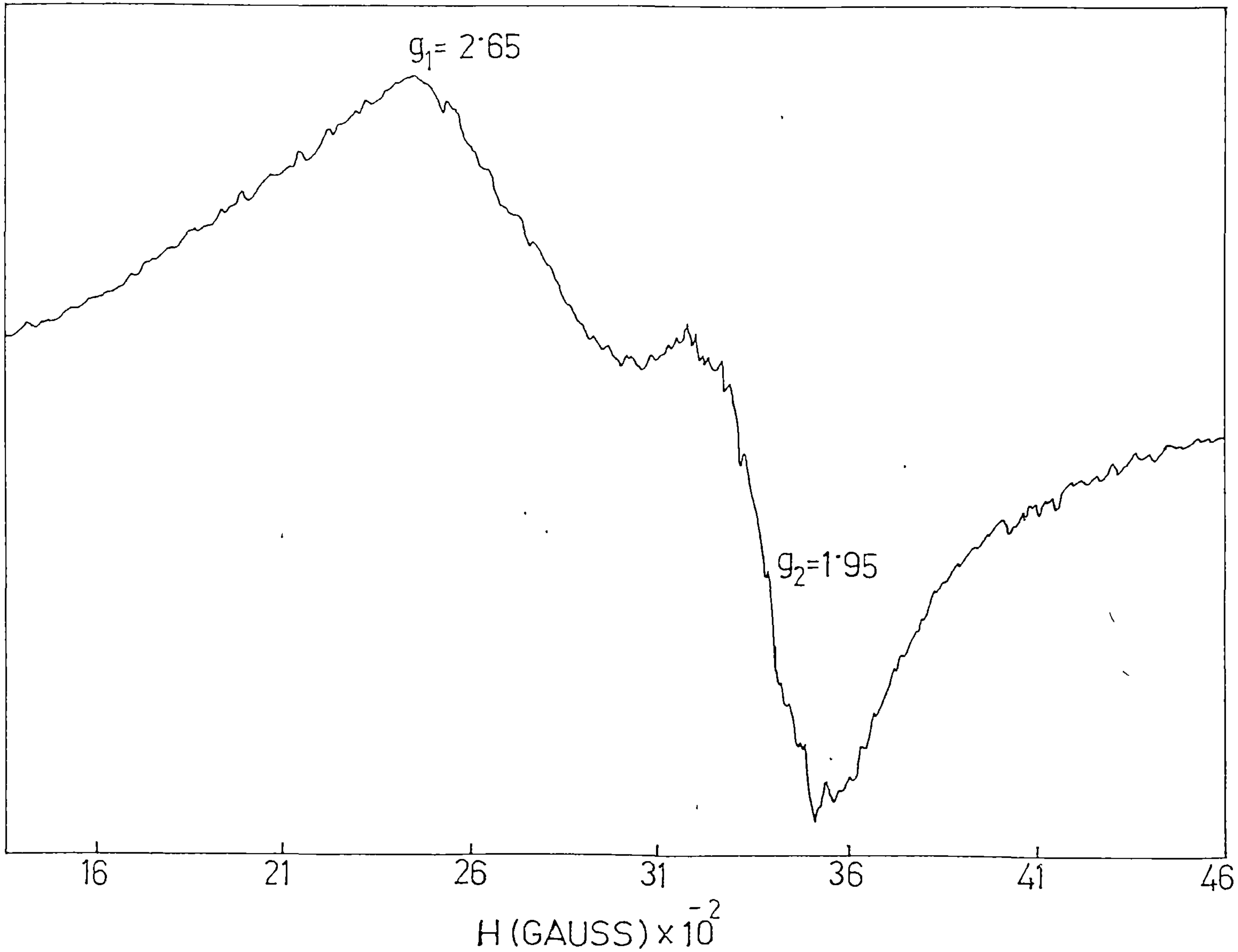

Fig IV.3. E P R SPECTRUM OF $[RuBr_3(py)_3]$ AT R T.

with 2-methyl pyridine is similar to that of pyridine reaction. Attempts to obtain completely substituted product were unsuccessful.

<u>2,2'-bipyridyl</u> : A reaction of $[RuBr_3(Me_2SO)_3]$, with 2,2'-bipyridyl (1:1 ratio) results in a partially substituted complex of the composition $[Ru(bipy)(Me_2SO)Br_3]$. Conductivity measurements in acetonitrile showed negligible molar conductance thereby confirming the covalent bonding of all bromide ligands. The IR spectrum showed a strong band at 970 cm^{-1} assigned to $\nu_{S=O}$ of the O-bonded Me_2SO groups. All the bands due to bipyridyl are also present. Besides, weak bands at 479 and 458 cm^{-1} may be due to ν_{Ru-O} and bands at 292 and 275 cm^{-1} due to ν_{Ru-Br}. Room temperature EPR spectrum of the powdered sample showed a broad signal at g = 2.19, which is indicative of one unpaired electron in a low-spin d^5 ruthenium(III) complex.

<u>*o*-phenylenediamine</u> : Reaction of $[RuBr_3(Me_2SO)_3]$ with *o*-phenylenediamine in the molar ratio 1:1 resulted in the formation of a reddish brown compound of the composition, $[RuBr_2(PDA)_2(Me_2SO)_2]Br$. The conductance measurement in acetonitrile showed a molar conductance value of 128 $\Omega^{-1}cm^2mol^{-1}$, thereby confirming the 1:1 electrolytic nature of the complex. IR spectrum showed one strong band at 1120 cm^{-1} besides all other bands due to *o*-phenylenediamine, which may be assigned to $\nu_{S=O}$ of S-bonded Me_2SO groups. EPR spectrum of the complex in

the powder form at room temperature showed a broad signal at $g = 2.60$ which may confirm the 3+ nature of ruthenium in this complex.

When a reaction of $[RuBr_3(Me_2SO)_3]$ with o-phenylenediamine in the molar ratio 1:2 was carried out, reduction of ruthenium(III) to ruthenium(II) took place leading to the formation of a complex of the composition $[RuBr_2(PDA)(Me_2SO)_2]$. Very low value of molar conductance (6 $\Omega^{-1}cm^2mol^{-1}$) in acetonitrile confirms that bromide is covalently bonded in the complex. It is a diamagnetic compound confirming its oxidation state as 2+. The IR spectrum showed a strong band at 1130 cm^{-1} which may be assigned to $\nu_{S=O}$ (S-bonded). There was no band of appreciable intensity in the region 1000-900 cm^{-1} which confirms the absence of O-bonded Me_2SO groups. ^1H NMR spectrum of $[RuBr_2(PDA)(Me_2SO)_2]$ in $(CD_3)_2SO$ (Fig. IV.4) showed two broad singlets at δ 7.4 and δ 7.2, one singlet at δ 6.2 and a sharp singlet at δ 3.3. The ^1H NMR spectrum of $[RuBr_2(PDA)(Me_2SO)_2]$ is similar to that of $[RuCl_2(PDA)(Me_2SO)_2]$, described in Chapter III. Besides the features of the ^1H NMR spectrum discussed in Chapter III, the ratio of proton area under the curve at δ 6.2 and under the curve at δ 7.4 and δ 7.2 (taken together) is 1:1, which confirms that the number of amino protons and the aromatic protons are same, i.e. four in each case. On the basis of IR and ^1H NMR results a structure with the two S-bonded Me_2SO groups in the trans position, the two bromide ligands in the cis positions and

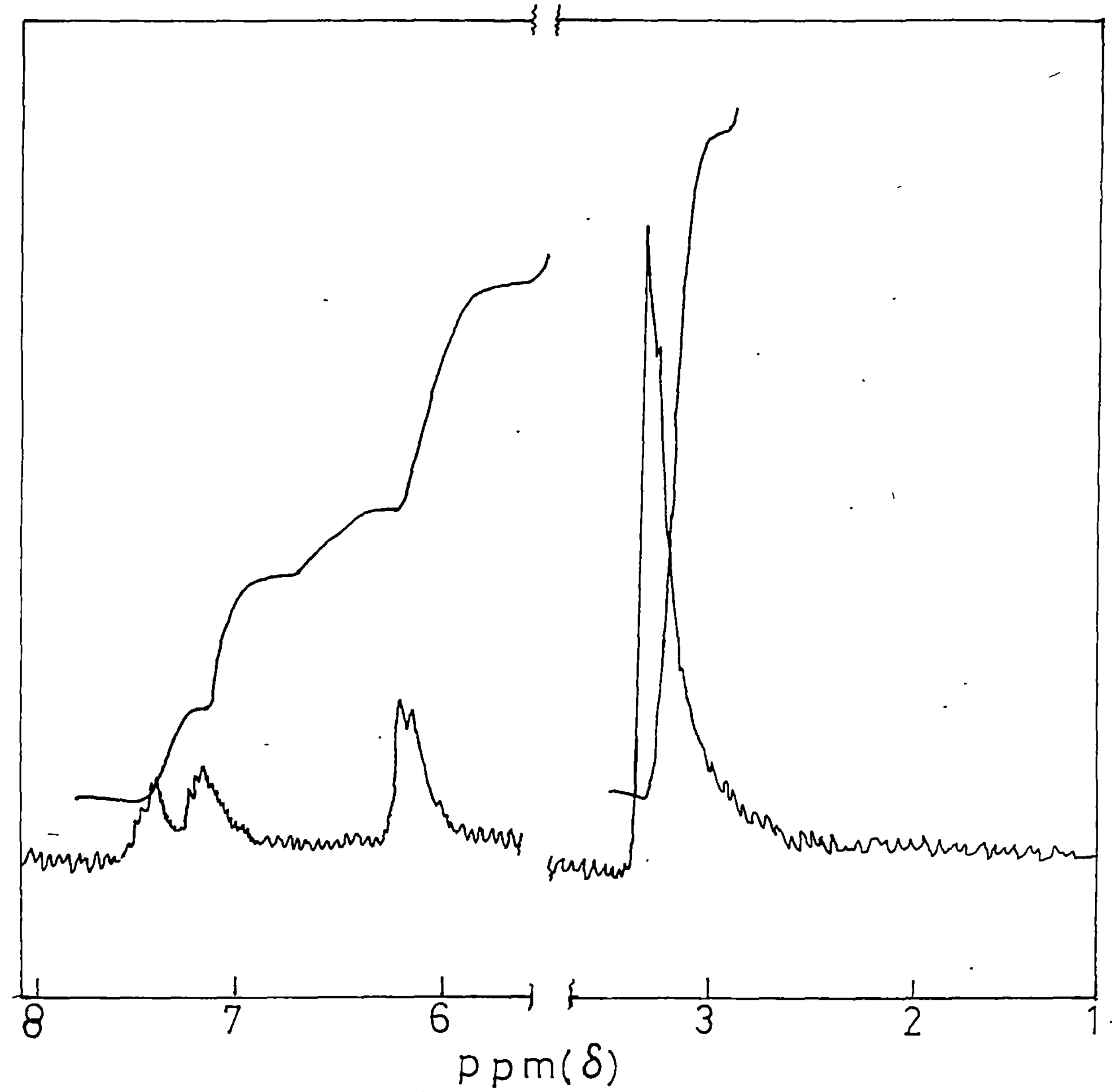

Fig. IV.4. ^{1}H NMR SPECTRUM OF $[RuBr_2(PDA)(Me_2SO)_2]$ IN $(CD_3)_2SO$

the two amino groups of PDA in the cis positions is proposed.

$[RuBr_2(Me_2SO)_3]$

The analytical data (Table IV.2) of a yellow compound obtained by the reaction of ruthenium trichloride with lithium bromide and dimethylsulphoxide in ethanol medium conforms to the composition $[RuBr_2(Me_2SO)_3]$. The compound is diamagnetic, thereby confirming it to be a d^6 low-spin ruthenium(II) complex. The IR spectrum (Fig IV.5) showed a strong absorption band at 1097 cm^{-1} which could be assigned to $\nu_{S=O}$ (S-bonded).[3] Bands at 423 cm^{-1} and 245 cm^{-1} may be assigned to ν_{Ru-S}[36,37] and ν_{Ru-Br}[38] respectively. There was no strong absorption in the region 1000-900 cm^{-1} indicative of the absence of any O-bonded Me_2SO groups. The ^1H NMR spectrum of a freshly prepared solution of $[RuBr_2(Me_2SO)_3]$ in $(CD_3)_2SO$ showed a sharp signal at δ 3.3 which is weak field by δ 0.7 from free Me_2SO (δ 2.6) indicative of S-bonded Me_2SO groups.[3,7] The other signal observed is at δ 2.6 which could be due to the residual protons of $(CD_3)_2SO$. There are no signals in the range δ 2.6 to 3.3 indicative of the absence of O-bonded Me_2SO groups. Further, signal at δ 3.3 is a sharp singlet indicative of all the three Me_2SO groups in equivalent positions[7] which is possible only if the structure is a trigonal bipyrimidal with the three Me_2SO groups in the equatorial positions and the two bromides in the axial positions. The ^1H NMR spectrum of $[RuBr_2(Me_2SO)_3]$ in $(CD_3)_2SO$ after keeping

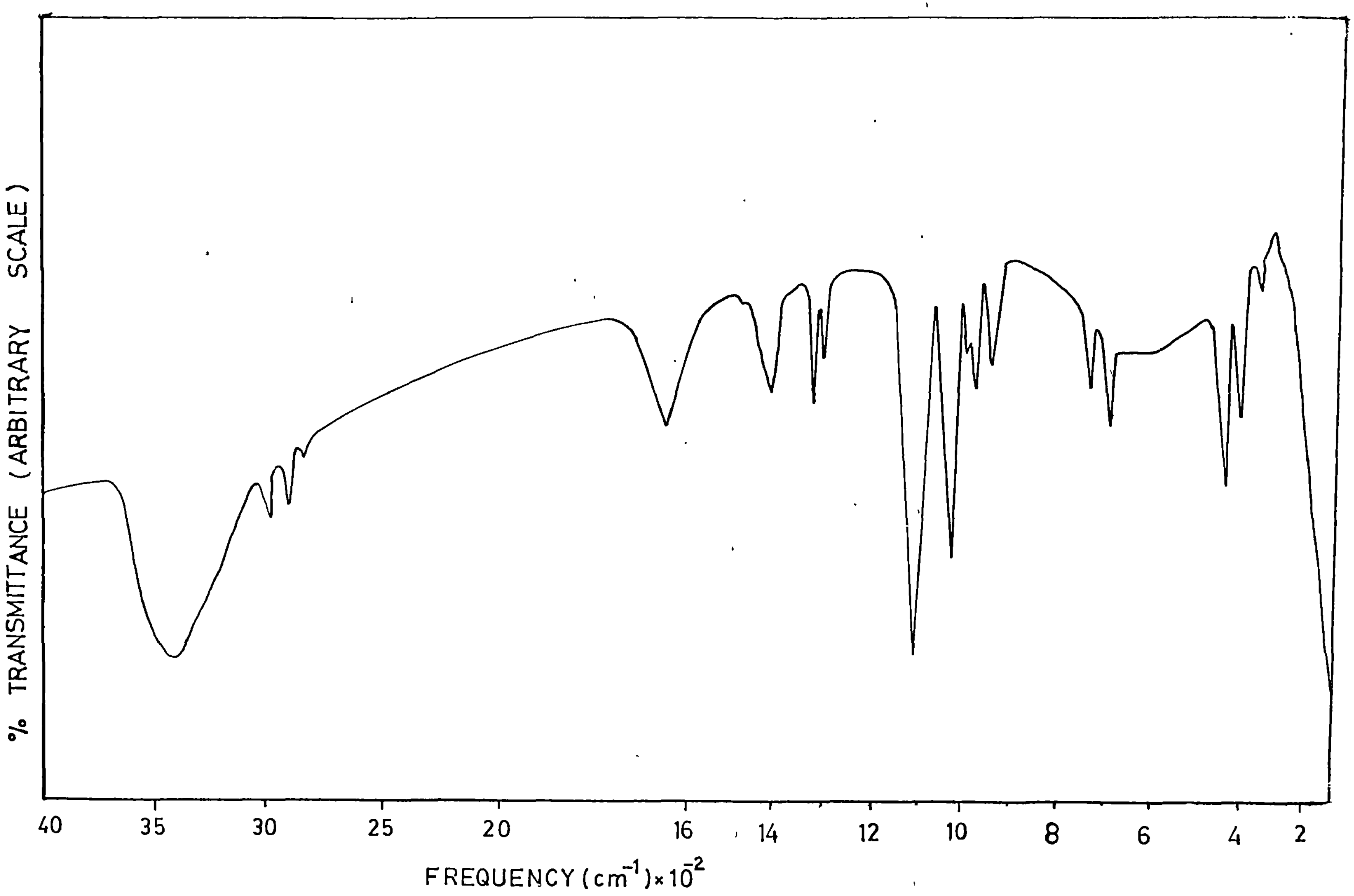

Fig. IV.5 INFRARED SPECTRUM OF $[RuBr_2(Me_2SO)_3]$

the solution for 100 h at room temperature or by warming on water bath for 3 h; does not show any change with respect to the spectrum of a freshly prepared solution. The intensity of the signal at δ 3.3 is practically not reduced. This shows that an exchange of $(CH_3)_2SO$ molecules coordinated to the metal, with the solvent $(CD_3)_2SO$ molecules, does not take place under the conditions mentioned above.

Some preliminary reactions were carried out to examine the potentiality of $[RuBr_2(Me_2SO)_3]$ as precursor for the synthesis of ruthenium(II) bromo complexes. Reactions carried out at room temperature in methanol, resulted in partial or complete substitution of Me_2SO groups. Reaction of $[RuBr_2(Me_2SO)_3]$ with PPh_3 at room temperature or by refluxing in methanol resulted in a completely substituted (Me_2SO) compound. The product, has a composition $[RuBr_2(PPh_3)_4]$. The IR spectrum clearly showed the presence of PPh_3 and absence of any Me_2SO group. The compound is same as reported by Stephenson and Wilkinson.[18]

Reactions of $[RuBr_2(Me_2SO)_3]$ with ligands like pyridine, 1,10-phenanthroline and 2,2'-bipyridyl at room temperature led to partially substituted compounds having composition, $[RuBr_2(py)_2(Me_2SO)_2]$ or $[RuBr_2(L\text{-}L)(Me_2SO)_2]$, (L-L = phen or bipy). The molar conductance values of these compounds was found to be 5-12 $\Omega^{-1}cm^2mol^{-1}$ which indicate the covalent nature of bromides. The IR spectra of these compounds clearly showed the presence of S-bonded Me_2SO molecules, besides the presence of respective amines. Two strong absorption bands in the region 1080-1060 cm^{-1} were observed for these complexes which could be assigned to ν_{SO} of S-bonded Me_2SO groups. A band of medium intensity at 425 cm^{-1} in case of $[RuBr_2(phen)(Me_2SO)_2]$ could be assigned to ν_{Ru-S}. Reactions of $[RuBr_2(Me_2SO)_3]$ with pyridine, 1,10-phenanthroline and 2,2'-bipyridyl carried out by refluxing in methanol resulted in the complete substitution of Me_2SO molecules by the ligands. The compounds, thus obtained, were analysed for the composition, $[RuBr_2(py)_4]$ or $[RuBr_2(L-L)_2]$ (L-L = phen or bipy). The IR spectra of these compounds showed no characteristic absorption in the region where ν_{SO} for S-bonded or O-bonded Me_2SO could be observed.

The presence of S-bonded Me_2SO molecules in case of partially substituted compounds and absence of any Me_2SO molecules in case of completely substituted compounds, was further confirmed with the help of ^1H NMR spectra. ^1H NMR spectrum of $[RuBr_2(py)_4]$ in $CDCl_3$ showed a doublet at δ 8.74 and two triplets at δ 7.63 and δ 7.06 and no signal was observed in the region δ 2-4. Absence of any signal in the region δ 2-4, confirms the absence of any Me_2SO molecules. Presence of two triplets and one doublet in the region δ 7-9 is due to the pyridine molecules in <u>trans</u> $[RuBr_2(py)_4]$.[31] The ^1H NMR spectrum of $[RuBr_2(py)_2(Me_2SO)_2]$ in $CDCl_3$ (Fig.IV.6) showed a sharp singlet at δ 3.44,

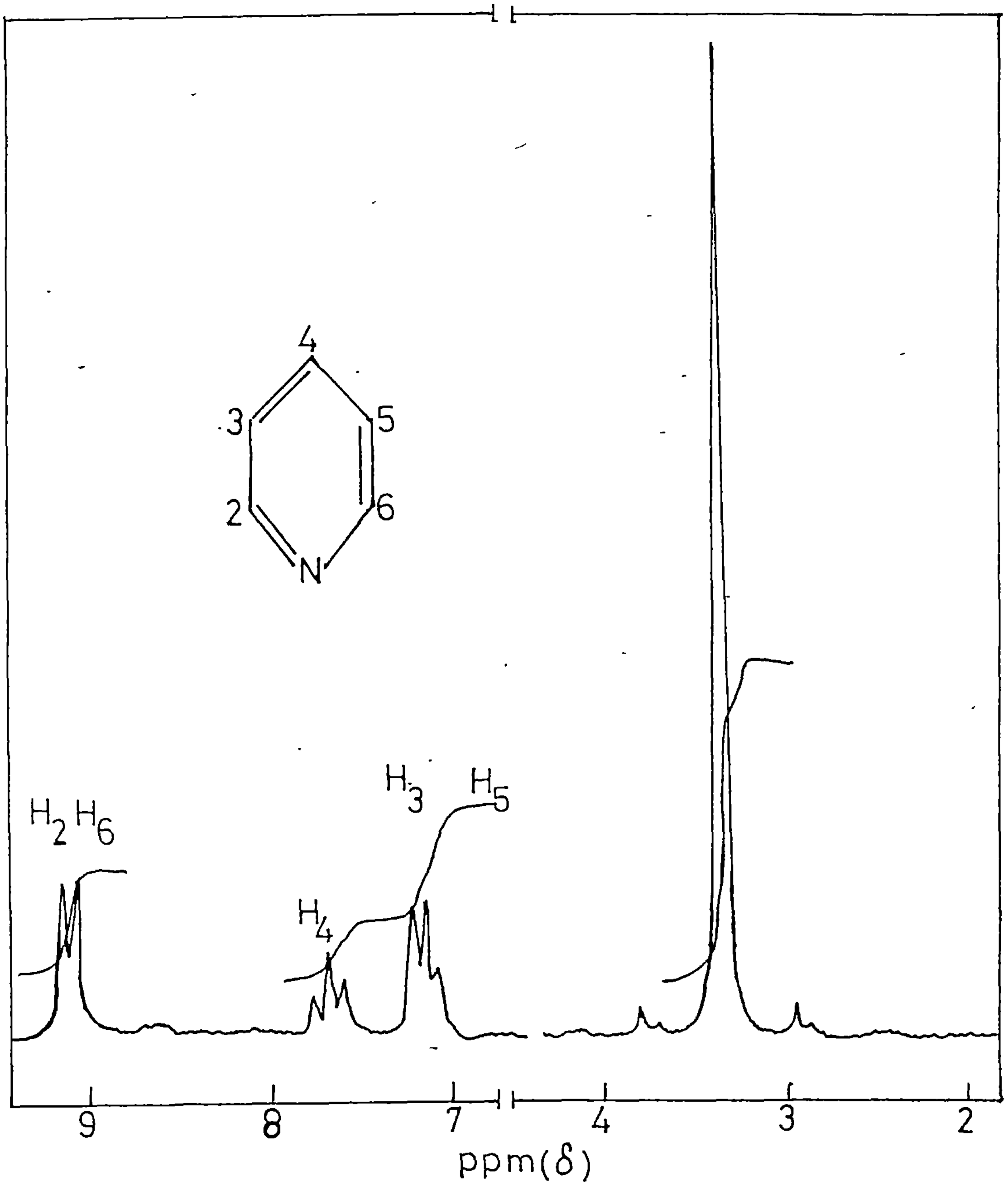

Fig.IV.6 ^1H NMR SPECTRUM OF trans $[RuBr_2(py)_2(Me_2SO)_2]$ IN $CDCl_3$

two triplets at δ 7.2 and δ 7.75, and one doublet at δ 9.12. The singlet at δ 3.44 could be assigned due to the methyl protons of S-bonded Me_2SO molecules. The pattern of the signals in the region δ 7.20 - 9.12 is characteristic where the pyridine molecules are coordinated in the trans positions.[31] Further, only one sharp signal at δ 3.44 is indicative that the two Me_2SO molecules are in equivalent environments, which is possible only if a trans structure for $[RuBr_2(py)_2(Me_2SO)_2]$ is envisaged. The ratio of the areas of the signals due to the protons of the pyridine and Me_2SO is 5:6, thereby confirming the presence of equal number of pyridine and Me_2SO molecules in the complex.

The ^1H NMR spectrum of $[Ru(bipy)_2Br_2]$ in $(CD_3)_2SO$ (Fig IV.7(a)) showed a doublet at δ 8.95, a triplet at δ 8.18 and a multiplet (an asymmetrical quintet) at δ 7.70 and no signals in the region δ 2-4. Signals in the region δ 7.5 - 9.0 are characteristic of aromatic protons of 2,2'-bipyridyl. The structure proposed for $[Ru(bipy)_2Br_2]$, on the basis of ^1H NMR is a trans one. For trans isomer, the four pyridine rings of the two bipyridyl molecules have equivalent environments, whereas for the cis isomer, the pyridine of each ligand are inequivalent, but each is equivalent to one pyridine ring of the other bipyridyl. Thus the aromatic region in the spectrum of the trans isomer should contain four multiplets, while that of the cis isomers should consists of signals from eight distinguishable hydrogens.[44] The spectrum of $[Ru(bipy)_2Br_2]$ has one

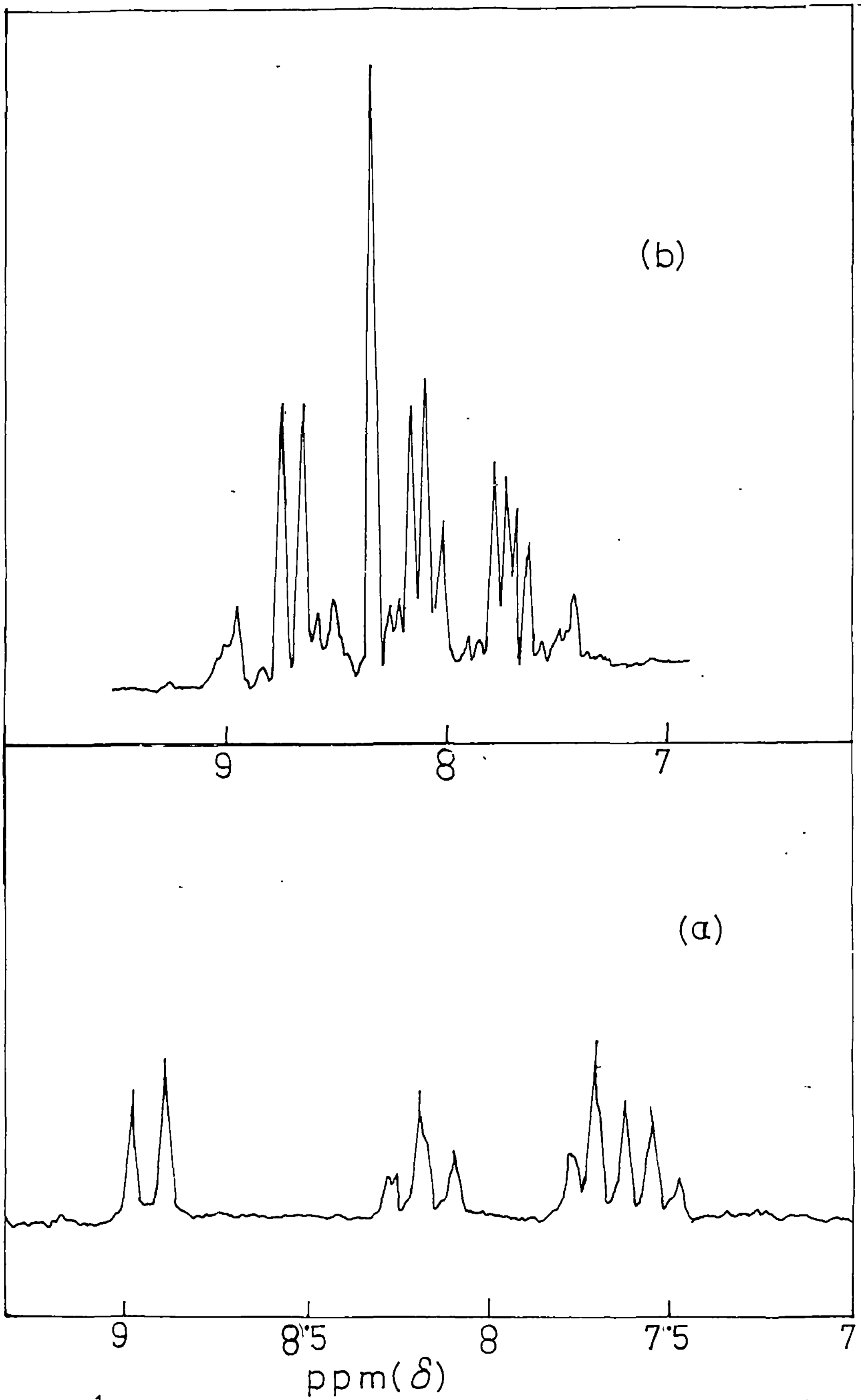

Fig IV.7 ^1H NMR SPECTRUM OF trans $[Ru(bipy)_2Br_2]$ (a) IN $(CD_3)_2SO$

trans $[Ru(phen)_2Br_2]$ (b) IN CD_3CN

doublet, one triplet and one asymmetrical quintet (may be due to the combination of a doublet and a triplet), thus, in all four multiplets as expected for <u>trans</u> $[Ru(bipy)_2Br_2]$. The ^1H NMR spectrum of $[Ru(phen)_2Br_2]$ in CD_3CN (Fig IV.7(b)) showed a doublet at δ 8.65, a singlet at δ 8.28, a doublet at δ 8.07 and a quartet at δ 7.67. The presence of four sets of signals in the aromatic region for 1,10-phenanthroline is expected only for a <u>trans</u> isomer similar to that of <u>trans</u> $[Ru(bipy)_2Br_2]$ discussed above. Hence a <u>trans</u> geometry for $[Ru(phen)_2Br_2]$ is also proposed.

The ^1H NMR spectrum of $[Ru(bipy)(Me_2SO)_2Br_2]$ in $(CD_3)_2SO$, showed a sharp singlet at δ 3.30 and multiplets at δ 7.66, δ 8.12, δ 8.66 and δ 9.82. The signal at δ 3.30 could be assigned due to the methyl protons of S-bonded Me_2SO molecules. The spectrum in the aromatic region is not well resolved. However, the signals in the region δ 7.5 - 10, could be assigned due to the protons of bipyridyl. The ratio of the area under the signals in the aromatic region to the area of the signal at δ 3.30 is 2:3, corresponding to 8 protons due to one bipyridyl molecule : 12 protons due to two Me_2SO molecules in the complex. The ^1H NMR spectrum of $[Ru(phen)(Me_2SO)_2Br_2]$ in CD_3CN, showed a sharp singlet at δ 3.7, a singlet at δ 8.03, a doublet at δ 8.50, another doublet at δ 10.1, and few weak signals in the region δ 7.6 - 8. The singlet at δ 3.7 could be assigned due to the

Table IV.4 ^1H NMR spectral data of some Ruthenium(II) complexes

Compounds	δ (ppm)	Solvent
$[RuBr_2(PDA)(Me_2SO)_2]$	3.3s, 6.2s, 7.2s, 7.4s	$(CD_3)_2SO$
<u>trans</u> $[RuBr_2(py)_4]$	7.04t, 7.63t, 8.73d	$CDCl_3$
$[RuBr_2(Me_2SO_3)_3]$	3.3s	$(CD_3)_2SO$
<u>trans</u> $[RuBr_2(py)_2(Me_2SO)_2]$	3.44s, 7.2t, 7.75t, 9.12d	$CDCl_3$
$[RuBr_2(bipy)(Me_2SO)_2]$	3.3s, 7.66m, 8.12m, 8.66m, 9.82m	$(CD_3)_2SO$
$[RuBr_2(phen)(Me_2SO)_2]$	3.7s, (7.6-8)m, 8.03s, 8.5d, 10.1d	CD_3CN
<u>trans</u> $[Ru(bipy)_2Br_2]$	7.7m, 8.18t, 8.95d	$(CD_3)_2SO$
<u>trans</u> $[Ru(phen)_2Br_2]$	7.75q, 8.07d, 8.39s, 8.82d	$(CD_3)_2SO$
	7.67q, 8.07d 8.28s, 8.65d	CD_3CN

s, singlet; d, doublet; t, triplet
q, quartet; m, multiplet

methyl protons of S-bonded Me_2SO molecules and all the signals in the aromatic region (between δ 7.6 - 10.1) due to the protons of 1,10-phenanthroline. Further, the ratio of the areas under the signal at δ 3.7 and the signals in the aromatic region confirm the composition of the complex as $[Ru(phen)(Me_2SO)_2Br_2]$.

Electronic Spectra

Electronic spectral data of new ruthenium(III) complexes are given in Table IV.3. The spectra shows similar features in chloroform and acetonitrile solutions. Generally, all ruthenium(III) complexes have two absorptions around 400 nm and 500 nm with molar extinction coefficients of the order of 10^3. High value of ϵ for all these complexes is suggestive of a greater contribution due to charge-transfer rather than d-d transitions. In some cases, one band at lower frequency with slightly lower ϵ value is also observed, viz for $[RuBr_3(bipy)(Me_2SO)]$ at 570 nm (ϵ = 700) and for $[Ru(CS_2)(PPh_3)_3Br_2]Br$ at 656 nm (ϵ = 210). These bands may have more of d-d character (transitions from $^2T_2$ to $^2A_2$, $^2T_1$ or $^2T_2$ type) than the charge-transfer. Electronic absorption bands for ruthenium(III) complexes are similar to other ruthenium(III) complexes.[25,45] All the ruthenium(III) complexes described in Table IV.2 have six coordination around ruthenium(III). However, the symmetry is lowered considerably from O_h due to the presence of two or three different type of ligands, monodentate

and bidentate ones. Absorption bands with high value of ϵ for such low symmetry ruthenium(III) complexes, can not be assigned to *d-d* transitions alone, which may be obscured by charge-transfer transitions in those regions.[45] The electronic spectrum of $[RuBr_2(Me_2SO)_3]$ in acetonitrile shows one band at 365 nm with $\epsilon = 330$. If the complex is assumed to have a trigonal bipyrimidal geometry, it will have a D_{3h} symmetry. Due to lowering in symmetry the absorptions bands due to *d-d* transitions are expected to have slightly higher ϵ values (10^2). Thus the band at 365 nm can be assigned to one of the *d-d* transitions ($^1A_1$ to $^1A_2$, ^1E or $^1B_2$).[46] The other band at 220 nm is due to charge-transfer only.

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CHAPTER V

CHAPTER V

SYNTHESIS AND CHARACTERIZATION OF [RuI_2L_4] (L = Me_2SO, CH_3CN or py) AND USE OF [RuI_2L_4], (L = Me_2SO and CH_3CN) AS PRECURSORS FOR THE SYNTHESIS OF RUTHENIUM(II) IODO COMPLEXES

Synthesis and study of the complexes of ruthenium(II) and ruthenium(III) containing iodide as one of the ligands and other mono or multidentate ligands has not been carried out in much detail compared to its chloro analogues. It is probably due to (i) the non-availability of ruthenium triiodide commercially and (ii) lack of solubility of ruthenium triiodide obtained by the metathesis of ruthenium trichloride and potassium iodide or sodium iodide in non-coordinating solvents.

The synthesis of ruthenium(II) or ruthenium(III) complexes containing iodide as one of the ligands is achieved by one of the following methods:

(i) metathesis of the chloro, hydroxo or hydrido groups in the complexes to iodo using KI, NaI or HI,[1-13]

(ii) substitution of a ligand L, viz. py or N_2 in the complex by iodide,[14-16]

(iii) reaction of a complex containing oxalato group/groups with HI,[17-19] and

(iv) reaction of ruthenium triiodide (generated in situ also, by treating ruthenium trichloride and KI, NaI or HI) with the ligand.[2,6,20-22] Table V.1 describes different preparative methods for the complexes of ruthenium(III) and ruthenium(II) containing iodide and other mono or bidentate ligands.

Among the above mentioned four methods, method (i) is used most frequently for the synthesis of ruthenium(II) or ruthenium(III) complexes containing iodide and other ligands. There are no examples in literature where an iodide containing ruthenium(II) or ruthenium(III) complex is used as precursor for the synthesis of iodo complexes by substituting the coordinated ligand with new ligands.

In the present chapter, attempt has been made to use ruthenium triiodide as the source material for the synthesis of ruthenium(II) complexes containing iodo and other ligands, viz. Me_2SO, CH_3CN, pyridine or triphenylphosphine. Ruthenium triiodide was dissolved in coordinating solvents, viz. Me_2SO, CH_3CN or py for this purpose. Complexes thus synthesized were characterised and some of them were used as precursors for the synthesis of other ruthenium(II) complexes containing iodide as one of the ligands.

Table V.1 Complexes of Ruthenium(III) and Ruthenium(II) containing Iodide and Other Mono or Bidentate Ligands

Sl. No	Complex	Preparation	Physical properties	Reference
1.	$[Ru(OH)I(NH_3)_4]I$	$[Ru(OH)Cl(NH_3)_4]Cl.H_2O$ + KI + HI		1
2.	$[RuI_2(NH_3)_4]I$	$[Ru(OH)I(NH_3)_4]$ + HI		1
3.	$[Ru(L-L)_2I_2]$ (L-L : dmpe, depe)	i) $[Ru(L-L)Cl_2]$ + KI ii) $RuCl_3$ + NaI + (L-L)	DM	2
4.	$[Ru(phen)_2I_2]$	$[Ru(phen)_2Cl_2]$ + NaI	UV-VIS	3
5.	$[RuI_3(PPh_3)_2]$	$[H_2Ru(PPh_3)_4]$ + I_2 (1:2 molar ratio)	IR	4
6.	$[RuHI(PPh_3)_3]$	$[H_2Ru(PPh_3)_4]$ + I_2 (1:1 molar ratio)	IR	4
7.	<u>trans</u> $[Ru(PPh_2H)_4HI]$	$[RuH_2(HPPh_2)_4]$ + NaI	IR ^1H NMR	5

Table V.1 continued

Table V.1 continued

Sl.No	Complex	Preparation	Physical properties	Reference
8.	$Cs_2[RuI_4(CO)_2]$	$Cs_2[RuCl_4(CO)_2]$ + HI	IR Raman	6,7,8
9.	<u>cis</u> $[RuI_2(CO)_4]$	$[Ru(CO)_4H_2]$ + I_2	IR	9
10.	$[RuI_2(QAS)]$	$[RuCl_2(QAS)]$ + NaI	μ, Λ_M, UV-VIS	10
11.	$[RuI_2(CO)_2(PPr_2Ph)_2]$	$[RuCl_2(CO)_2(PPr_2Ph)_2]$+ NaI	IR ^1H NMR	11
12.	$[RuHI(CO)(PPr_2Ph)_3]$	$[RuHCl(CO)(PPr_2Ph)_3]$+ NaI	IR ^1H NMR	11
13.	$[Ru(EDA)_2I_2]$	$[Ru(EDA)_2Cl_2]$ + NaI	μ, UV-VIS, IR	12
14.	$[RuI_2(P(OPh)_3)_4]$	$[RuCl_2(P(OPh)_3)_4]$ + NaI	IR	13

Table V.1 continued

Table V.1 continued

Sl.No	Complex	Preparation	Physical Properties	References
15.	$[Ru(phen)_2I(py)]ClO_4$	<u>cis</u> $[Ru(phen)_2(py)_2]Cl_2$ + LiI + $NaClO_4$		14
16.	$[Ru(bipy)(py)_2I_2]$	$[Ru(bipy)(py)_4]$ + KI		15
17.	$[Ru(NH_3)_5I]I_2$	$[Ru(NH_3)_5(N_2)]I_2$ + HI	IR	16
18.	$PhNH_3\ [RuI_4(aniline)_2]$	$PhNH_3\ [Ru(OX)_2(aniline)_2]$ + HI	IR UV-VIS μ, Λ_M	17
19.	<u>cis</u> or <u>trans</u> $[RuI_2(py)_4]$	$[Ru(py)_4(OX)]H_2O$ + HI	far-IR, Raman ^{1}H NMR	18
20.	$[RuI_2(en)_2]I$	$[Ru(OX)(en)_2][Ru(OX)_2en]$ + HI	UV-VIS	19
21.	$[RuI_2(CO)_2]$	RuI_3 + HI + HCOOH	IR Raman	6,7, 8
22.	$[RuI_2(Me_2SO)_4]$	RuI_3 + Me_2SO	IR	20

Table V.1 continued

Table V.1 continued

Sl.No.	Complex	Preparation	Physical Properties	References
23.	*trans* $[Ru(diars)_2I_2]$	$RuCl_3 + NaI +$ diars	μ	21
24.	$[Ru(diars)_2I_2](ClO_4)$	$[Ru(diars)_2I_2] + HClO_4 + Br_2$	μ	21
25.	$[RuI_3(AsMePh_2)_3]$	$K_2[RuCl_5(H_2O)] + KI + AsMePh_2$		22

EXPERIMENTAL

Ruthenium trichloride trihydrate was obtained from Aurora Matthey Ltd., Calcutta. Ruthenium triiodide was prepared by a modification of the reported methods.[23-25] Analytical data and other physical measurements, viz. IR, ^{1}H NMR, EPR, μ_{eff} etc were obtained as described in Chapters II and III. Analytical data, melting point and molar conductance data are presented in Table V.2. Important IR and electronic absorption bands are given in Table V.3. ^{1}H NMR spectral data are reported in Table V.4. Iodide was estimated by the standard method,[26] the details of which are described below.

ESTIMATION OF IODIDE

An accurately weighed amount of the complex was decomposed by heating with a melt of KNO_3 and KOH mixture (1:8) at around ~800 °C. It was cooled and extracted with distilled water. The solution was acidified with dilute HNO_3 and then made ammoniacal and digested slowly on a water-bath for about 30 min. It was filtered through a quantitative filter paper. Precipitation of silver iodide was made by adding a very dilute solution of silver nitrate (~ 0.05 M) slowly and with constant stirring to the ammoniacal solution, until precipitation was complete. The solution was made acidic by adding dilute HNO_3 (1 percent by volume). The solution was digested on a water-bath for about 15 min. The precipitate was filtered through a pre-weighed sintered glass (G-4) crucible and was washed with one percent nitric acid, and finally with a little water. The crucible with the precipitate was dried in an air-oven at about 120°C for about 2 h to get constant weight. The precipitate was weighed as silver iodide.

PREPARATIONS

(i) Ruthenium Iodide, $RuI_3.xH_2O$

To a solution of hydrated ruthenium trichloride (1g) in water (20 cm^3), hydroiodic acid (5 cm^3) and potassium iodide (5g) were added. The reaction mixture was stirred at room temperature (for 2 h), when a black compound separated out. The compound was centrifuged, washed 2-3 times with water, then with acetone and dried *in vacuo*. (Yield, 1.7g, 85%). It was analysed for its iodide content. Iodide, Found: 70.5%, Calcd for $RuI_3.3H_2O$: 70.1%.

(ii) $[RuI_2(Me_2SO)_4]$

Method A : To a suspension of finely powdered $RuI_3.xH_2O$ (0.5g) in acetone (25 cm^3), dimethylsulphoxide (5 cm^3) was added. The mixture was refluxed on a water-bath for about 2 h. The colour of the solution changed from black to green and then to brown, and a reddish brown compound separated out. The compound after centrifugation was washed successively with acetone and ether. It was dried <u>in vacuo</u> and was analysed for $[RuI_2(Me_2SO)_4]$. Yield, 0.55g (85%).

<u>Method B</u> : A mixture of $RuI_3.xH_2O$ (0.5g) and dimethylsulphoxide (5 cm^3) was refluxed in an oil bath (130-140°C) for 5 min, when a clear solution was obtained. The volume was reduced to 2 cm^3, cooled and acetone was added to it with stirring. The compound separated after 30 min, was obtained as in method A. Yield, 0.55g, (85%).

(iii) <u>$[RuI_2(py)_4]$</u>

A mixture of finely powdered $RuI_3.xH_2O$ (0.2g) and pyridine (1 cm^3) was heated on a water-bath for about 2 h. A green coloured solution was obtained. Brown crystalline compound separated from the solution, on cooling. It was centrifuged, washed with acetone and ether, and dried <u>in vacuo</u>. It was analysed for $[RuI_2(py)_4]$. Yield 0.22g, (86%).

(iv) $[RuI_2(CH_3CN)_4]$

A suspension of $RuI_3.xH_2O$ (0.2g) in acetonitrile (10 cm^3) was refluxed on a water-bath for about 4 h, when a clear solution was obtained. The solution was concentrated and cooled to room temperature, when a reddish brown crystalline compound separated out. It was centrifuged, washed with ether and dried *in vacuo*. The compound was analysed for $[RuI_2(CH_3CN)_4]$. Yield 0.14g (74%).

(v) $[RuI_2(CH_3CN)_2(PPh_3)_2]$

To a solution of $RuI_3.xH_2O$ (0·2g) in acetonitrile (20 cm^3) triphenylphosphine (0.5g) was added. The mixture was refluxed for 4 h. A yellow solution was obtained which on concentration, yielded yellow crystalline compound. The compound was washed with ether and dried *in vacuo*. It was analysed for the composition, $[RuI_2(CH_3CN)_2(PPh_3)_2]$. Yield 0.25g (70%).

(vi) $[RuI_2(CS)(PPh_3)_3]$

To a suspension of finely powdered $RuI_3.xH_2O$ (0.2g) in carbondisulphide (20 cm^3), triphenylphosphine (0.5g) was added. The mixture was refluxed on a water-bath for 2 h. It was kept overnight at room temperature when most of the solvent evaporated and a brownish-red compound separated out. The compound was first washed with water followed by ether and dried in vacuo. It was analysed for [$RuI_2(CS)(PPh_3)_3$]. Yield 0.28g (65%).

Reactions of [$RuI_2(Me_2SO)_4$]

(i) With triphenylphosphine. To a solution of [$RuI_2(Me_2SO)_4$] (0.2g) in methanol (20 cm^3), triphenylphosphine (0.35g) (molar ratio 1:4) was added. The reaction mixture was refluxed for 5 min and cooled to room temperature, when a dark brown compound crystallised out. It was centrifuged, washed with ether and dried in vacuo. The compound was analysed for [$RuI_2(PPh_3)_2(Me_2SO)$].

[$RuI_2(PPh_3)_2(Me_2SO)$] was obtained also when a reaction similar to above was carried out at room temperature by stirring the reaction mixture for about 1 h.

(ii) With pyridine.

(a) To a solution of [$RuI_2(Me_2SO)_4$] (0.2g) in methanol (10 cm^3), pyridine (1 cm^3) was added and stirred at room temperature for 3 h. A reddish brown compound separated out, which was centrifuged, washed with ether, and dried in vacuo. The compound obtained was analysed for [$RuI_2(py)_2(Me_2SO)_2$].

(b) A reaction similar to condition (a) was carried out under refluxing condition of solvent for 2 h, and cooled.

A dark-brown crystalline compound separated. It was washed with ether and dried *in vacuo*. The compound was analysed for $[RuI_2(py)_4]$.

(iii) *With 2,2'-bipyridyl or 1,10-phenanthroline*

(a) To a solution of $[RuI_2(Me_2SO)_4]$(0.2g) in methanol (20 cm^3), a methanolic solution of 2,2'-bipyridyl or 1,10-phenanthroline (0.2g in 5 cm^3) was added. The solution was stirred at room temperature for about 3 h. Orange coloured compound separated out in each case, which was washed with acetone and dried *in vacuo*. The compounds had the composition, $[RuI_2(L\text{-}L)(Me_2SO)_2]$ (L-L = bipy or phen).

(b) A reaction similar to above (a) using 2,2'-bipyridyl was carried out by refluxing the mixture on a water-bath for 3 h. The solution was concentrated and cooled, and the products isolated as in (a) above. It was analysed for $[RuI_2(bipy)_2]$.

(iv) *With acetonitrile*. $[RuI_2(Me_2SO)_4]$ (0.2g) was dissolved in acetonitrile (20 cm^3). The solution was refluxed for about 1 h, concentrated (2 cm^3) and cooled to room temperature. A yellow crystalline compound separated out which was washed with ether and dried *in vacuo*. The compound had the composition, $[RuI_2(CH_3CN)_3(Me_2SO)]$.

(v) *With sodium diethyldithiocarbamate*. $[RuI_2(Me_2SO)_4]$ (0.2g) was suspended in toluene (20 cm^3) and sodium diethyldithiocarbamate (0.15g) was added. The suspension was refluxed for

30 min to give a dark-green coloured solution. The solution was concentrated (5 cm^3). Addition of light petroleum ether (bp. 80-100°C)followed by cooling in ice-salt mixture yielded green needle shaped crystals. The compound had the composition $[Ru(Et_2NCS_2)_2(Me_2SO)_2]$

Reaction of $[RuI_2(CH_3CN)_4]$ with Me_2SO

A clear solution of $[RuI_2(CH_3CN)_4]$ (0.2g) in dimethylsulphoxide (2 cm^3) was obtained by heating the mixture on a water-bath for 5 min. The solution was cooled and acetone was added with constant stirring. The solution was stirred for 15 min. A yellow crystalline compound separated out. The compound was centrifuged, washed with diethyl ether and dried in vacuo. The compound was analysed for $[RuI_2(CH_3CN)_3(Me_2SO)]$.

RESULTS AND DISCUSSION

The preparation of ruthenium triiodide had been reported either by the metathetic reaction between $RuCl_3.xH_2O$ and KI in aqueous solution[23-25] or by the action of HI on RuO_4.[27] We have synthesised $RuI_3.3H_2O$ by the metathetic reaction between $RuCl_3.xH_2O$ and KI in the presence of HI. The compound has μ_{eff} = 2.1 B.M. at room temperature. The room temperature EPR spectrum showed a broad signal at $g = 2.05$.

$[RuI_2S_4]$ (S = py, CH_3CN or Me_2SO)

In the literature there are very few reports[6,20] of the use of RuI_3 as a starting compound for the syntheses of ruthenium(II) iodo compounds. Hence in the present work we have explored the possibility of synthesising ruthenium iodo compounds using RuI_3 as the source material. RuI_3 is generally insoluble in non-coordinating solvents. Hence reactions have been carried out using a solvent (S) which coordinates to ruthenium, viz. dimethylsulphoxide, acetonitrile or pyridine. Normally, when a reaction was carried out between RuI_3 and the solvent (S) under refluxing condition, products of the composition, $[RuI_2S_4]$, were obtained. Solvent, being present in excess, acts both as a coordinating agent and reducing agent [reducing ruthenium(III) to ruthenium(II)]. $[RuI_2S_4]$ (S = py, MeCN, Me_2SO) are diamagnetic, thereby confirming that the metal is in 2+ state having a d^6 low-spin configuration. Conductivity measurements in acetonitrile or methanol showed low molar conductance values (10-15 $\Omega^{-1}cm^2mol^{-1}$) indicative of covalently bonded iodide to ruthenium(II).

The IR spectrum of $[RuI_2(py)_4]$ showed the presence of all bands due to coordinated pyridine. The spectrum in the far-IR region showed bands of medium to weak intensities at 465, 408, and 290 cm^{-1}. The ^1H NMR spectrum in $CDCl_3$ (Table V.4) showed triplets at δ 7.03 and δ 7.63 and a doublet at δ 9.01. The far-IR and the ^1H NMR spectra were similar to the

Table V.2 Some analytical and physical data of some new Ruthenium(II)-iodo complexes

Compounds	colour	M.P.°C	Analysis[a] (%)			Molar Conductance, Λ_M in $\Omega^{-1}cm^2mol^{-1}$
			C	H	N	
$[RuI_2(Me_2SO)_4]$	Brown	255-60 (d)	14.5 (14.4)	3.7 (3.6)	38.0* (38.1)	9[b]
$[RuI_2(CH_3CN)_4]$	Reddish brown	> 250	18.3 (18.5)	2.2 (2.3)	10.8 (10.8)	15[b]
$[RuI_2(py)_2(Me_2SO)_2]$	Reddish brown	210-15 (d)	25.0 (25.1)	3.1 (3.3)	4.1 (4.2)	3[c]
$[RuI_2(PPh_3)_2(Me_2SO)]$	Dark Brown	145-50	47.7 (47.6)	3.5 (3.8)	-	5[f]
$[RuI_2(PPh_3)_2(CH_3CN)_2]$	Light yellow	190-95	49.8 (49.9)	3.7 (3.7)	3.2 (3.0)	14[b]
$[RuI_2(CH_3CN)_3(Me_2SO)]$	Yellow	160-62	16.9 (17.3)	3.0 (2.7)	7.4 (7.6)	5[f]

Table V.2 continued

Table V.2 continued

Compounds	Colour	M.P.°C	Analysis[a] (%)			Molar Conductance, Λ_M in $\Omega^{-1}cm^2mol^{-1}$
			C	H	N	
$[RuI_2(CS)(PPh_3)_3]$	Brownish red	200-05	55.4 (55.7)	3.6 (3.8)	-	5^b
$[RuI_2(bipy)(Me_2SO)_2]$	Orange	>250	25.4 (25.2)	3.0 (3.0)	4.0 (4.2)	5^f
$[RuI_2(phen)(Me_2SO)_2]$	Orange	165-70	28.0 (27.7)	3.0 (2.9)	3.8 (4.1)	3^f

a, Calculated values are in parentheses; b, in methanol;

c, in acetonitrile; d, decomposes; f, in chloroform; , * % iodide

Table V.3 Important infrared and UV-visible bands of some new Ruthenium(II) complexes

Compounds	infrared bands in cm^{-1}	λ_{max} in nm (ϵ)
$[RuI_2(Me_2SO)_4]$	1079s, 1026, 976, 930, 420, 383, 246	480sh (400)^a
$[RuI_2(CH_3CN)_4]$	2275m	360 (11,000)^b
$[RuI_2(py)_2(Me_2SO)_2]$	1085s, 1070s	
$[RuI_2(PPh_3)_2(Me_2SO)]$	1120s	
$[RuI_2(PPh_3)_2(CH_3CN)_2]$	2270m	420sh^b
$[RuI_2(CH_3CN)_3(Me_2SO)]$	2310m, 2275m, 1120s, 1100s	360 (410)^b
$[RuI_2(CS)(PPh_3)_3]$	1270s	535 (1470)^b 370sh
$[RuI_2(bipy)(Me_2SO)_2]$	1085s, 418s	375 (3100)^b 280 (26700) 235 (70600)
$[RuI_2(phen)(Me_2SO)_2]$	1105s, 1070s, 425m	

a, in CH_3OH; b, in CH_3CN; m, medium; s, strong

Table V.4 ^1H NMR spectral data of some Ruthenium(II) complexes

Compounds	δ ppm	solvent
$[RuI_2(py)_4]$	7.03t, 7.63t, 9.01d	$CDCl_3$
$[RuI_2(PPh_3)_2(Me_2SO)]$	3.6s, (7.3-7.6)b,m	$CDCl_3$
$[RuI_2(py)_2(Me_2SO)_2]$	3.7s, 7.15t, 7.74t, 9.25d	$CDCl_3$
$[RuI_2(CH_3CN)_3(Me_2SO)]$	2.5, 3.55	$CDCl_3$
$[RuI_2(bipy)(Me_2SO)_2]$	3.37, 3.42, 3.53, (7.25-8.7)m, 10.1d	CD_3CN
$[RuI_2(phen)(Me_2SO)_2]$	3.45s, (7.35-8.3)m	CD_3CN

s, singlet; d, doublets; t, triplets;

b, broad; m, multiplets.

one reported for trans $[RuI_2(py)_4]^{18}$ and hence a trans structure for the synthesised $[RuI_2(py)_4]$ is proposed.

The IR spectrum of $[RuI_2(CH_3CN)_4]$ showed a band of medium intensity at 2275 cm^{-1}, besides other bands due to CH_3CN. This band may be assigned to ν_{CN} of coordinated CH_3CN group.[28] The presence of only one band around 2275 cm^{-1} indicate that all the four CH_3CN groups are in equivalent position, which is possible only in the case of trans $[RuI_2(CH_3CN)_4]$ and hence a trans geometry for $[RuI_2(CH_3CN)_4]$ is proposed.

The IR spectrum of $[RuI_2(Me_2SO)_4]$ (Fig V.1) showed a band at 1079 cm^{-1} (strong) which is characteristic of ν_{SO} (S-bonded) of the Me_2SO groups. Besides this, bands of medium intensities at 1026, 976 and 930 cm^{-1} were also observed which may be assigned to ρ_r CH.[29] The IR spectral pattern in the region 1100-900 cm^{-1} was identical to that of $[RuBr_2(Me_2SO)_4]$,[29] which was reported to have a trans geometry, with all S-bonded Me_2SO. This confirms the presence of all the Me_2SO groups in S-bonded fashion. Bora and Singh[20] reported the preparation of $[RuI_2(Me_2SO)_4]$ by a slightly different method and characterised it using the IR spectrum as having both S-bonded and O-bonded Me_2SO. The IR spectrum of $[RuI_2(Me_2SO)_4]$ in the region 600-350 cm^{-1} was similar to that of $[NMe_2H_2][RuCl_3(Me_2SO)_3]$, a ruthenium(II) compound containing all S-bonded Me_2SO groups.[30]

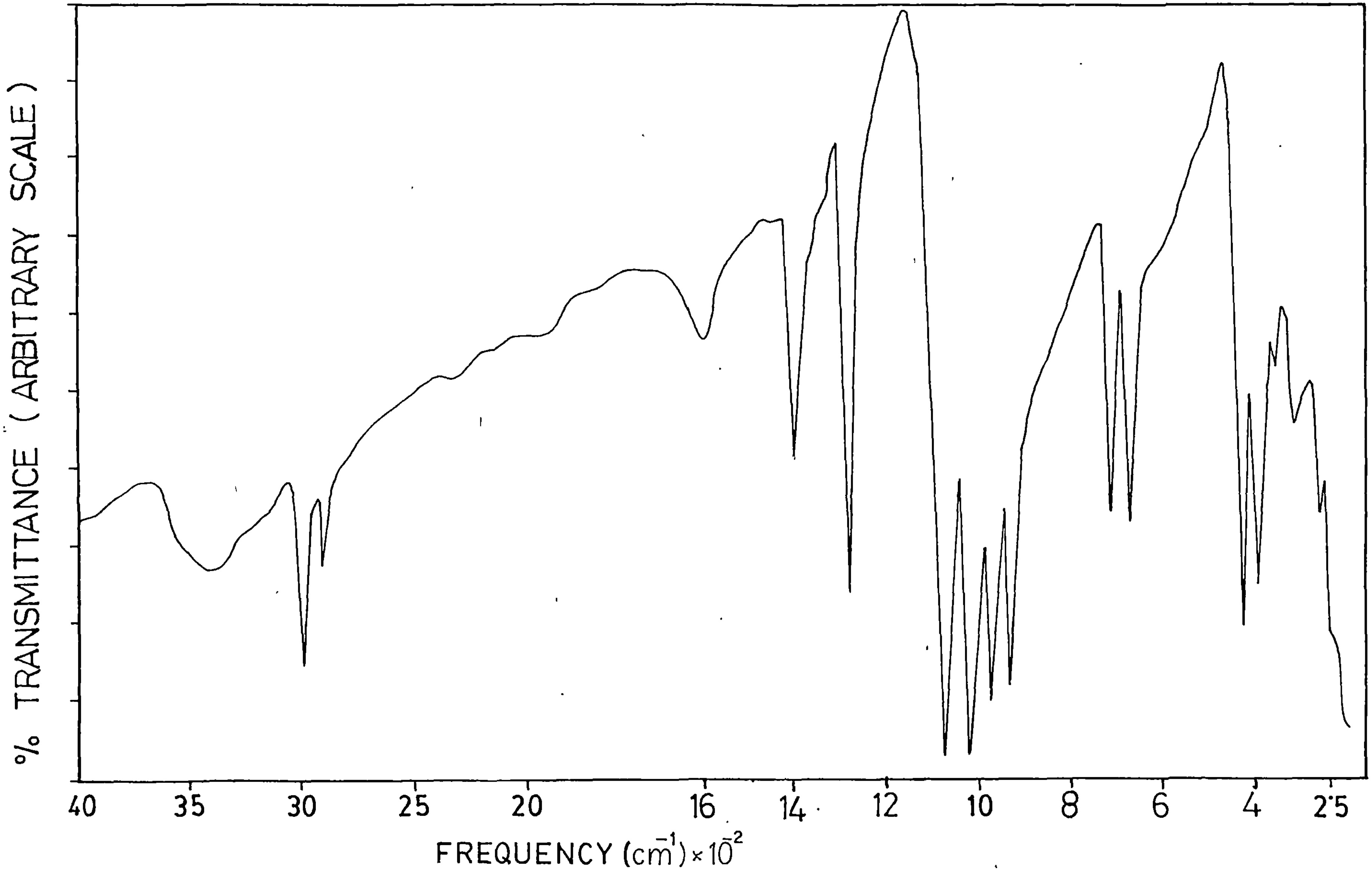

Fig. V.1 INFRARED SPECTRUM OF $[RuI_2(Me_2SO)_4]$

It showed a strong absorption at 420 cm^{-1} and a medium band at 383 cm^{-1}. Absorption at 420 cm^{-1} may be due to the combination of ν_{Ru-S} and $\delta_{S(CSO)}$, whereas 383 cm^{-1} band may be due to $\delta_{a(CSO)}$. Further, one band at 246 cm^{-1}, may tentatively be assigned to ν_{Ru-I}.[31]

Ruthenium(II) Iodo complexes containing PPh_3 and other groups

Reaction of RuI_3 with PPh_3 in a non-coordinating solvent or a weakly coordinating solvent like acetone under refluxing condition, did not result in the formation of ruthenium iodo triphenylphosphine complex. Reaction of RuI_3, using melt of PPh_3 as a solvent at its boiling point also, did not lead to the coordination of PPh_3, instead RuI_3 separated unreacted. However, when RuI_3 was treated with PPh_3, in a coordinating solvent like acetonitrile, a compound of the composition $[RuI_2(CH_3CN)_2(PPh_3)_2]$ was obtained. It was non-conducting and diamagnetic in nature. The IR spectrum showed a band of medium intensity at 2270 cm^{-1} besides other bands due to acetonitrile and PPh_3. One band at 2270 cm^{-1} is characteristic of ν_{CN} of acetonitrile groups coordinated to ruthenium in the <u>trans</u> position,[28] A reaction of RuI_3 with PPh_3 in CS_2 medium resulted in the formation of a compound of the composition $[RuI_2(CS)(PPh_3)_3]$. It was diamagnetic in nature, thereby confirming ruthenium to be in 2+ state. The low value of the molar conductance in CH_3OH ($5\,\Omega^{-1}cm^2mol^{-1}$) is indicative of covalently bonded iodides. Besides the presence of all the bands due to PPh_3, the IR spectrum showed a strong band at 1270 cm^{-1} which may be assigned to ν_{CS} of the thiocarbonyl group.[32]

Reactions of $[RuI_2(Me_2SO)_4]$

With triphenylphosphine. Reaction of $[RuI_2(Me_2SO)_4]$ with PPh_3 at room temperature and under refluxing condition of methanol gave $[RuI_2(PPh_3)_2(Me_2SO)]$ only. The compound was diamagnetic confirming the oxidation state of ruthenium as 2+. It was non-conducting in nature, confirming the covalent nature of the iodides. The IR spectrum of the complex showed all the bands due to PPh_3 and a strong band at 1120 cm^{-1}, which is characteristic of ν_{SO} (S - bonded) of the Me_2SO group. The ^1H NMR spectrum of $[RuI_2(PPh_3)_2(Me_2SO)]$ in $CDCl_3$ at room temperature showed a sharp signal at δ 3.6 and broad signals in the region δ 7.3 to δ 7.6. The former one is due to the methyl protons of Me_2SO (S-bonded) and the latter due to the phenyl protons of PPh_3 groups. The ratio of the area under the two signals is 1:5 confirming the presence of one Me_2SO and two PPh_3 molecules (6:30 protons) in the complex.

<u>With pyridine</u>. A reaction of $[RuI_2(Me_2SO)_4]$ with pyridine at room temperature led to the formation of a partially substituted $[RuI_2(py)_2(Me_2SO)_2]$ complex. The IR spectrum showed all the bands due to pyridine and two strong bands at 1070 and 1085 cm^{-1} due to ν_{SO} (S-bonded) of the Me_2SO molecules. ^1H NMR *spectrum of the complex in* $CDCl_3$ (*Fig.* V.2) showed a sharp signal at δ 3.7 characteristic of the methyl proton of the S-bonded Me_2SO groups. Other signals observed were a doublet at δ 9.25 and triplets at δ 7.74 and δ 7.15. The ^1H NMR spectral pattern in the region δ 7.1-9.25 is characteristic where the pyridine molecules are coordinated in the <u>trans</u> position.[18] Further, only one sharp signal at δ 3.7 is indicative that two Me_2SO molecules are also in equivalent environments, which is possible if a <u>trans</u> structure is present in $[RuI_2(py)_2(Me_2SO)_2]$. The ratio of the areas of the signals due to the protons of pyridine and Me_2SO is 5:6, thereby confirming the presence of equal numbers of pyridine and Me_2SO molecules in the complex. Reactions of $[RuI_2(Me_2SO)_4]$ with pyridine in refluxing methanol gave a completely substituted product, <u>viz</u>. $[RuI_2(py)_4]$. The IR and ^1H NMR spectra of this compound were superimposable with that of $[RuI_2(py)_4]$ obtained by a reaction of RuI_3 and pyridine, discussed earlier in this chapter. Hence a <u>trans</u> geometry for $[RuI_2(py)_4]$ is proposed.

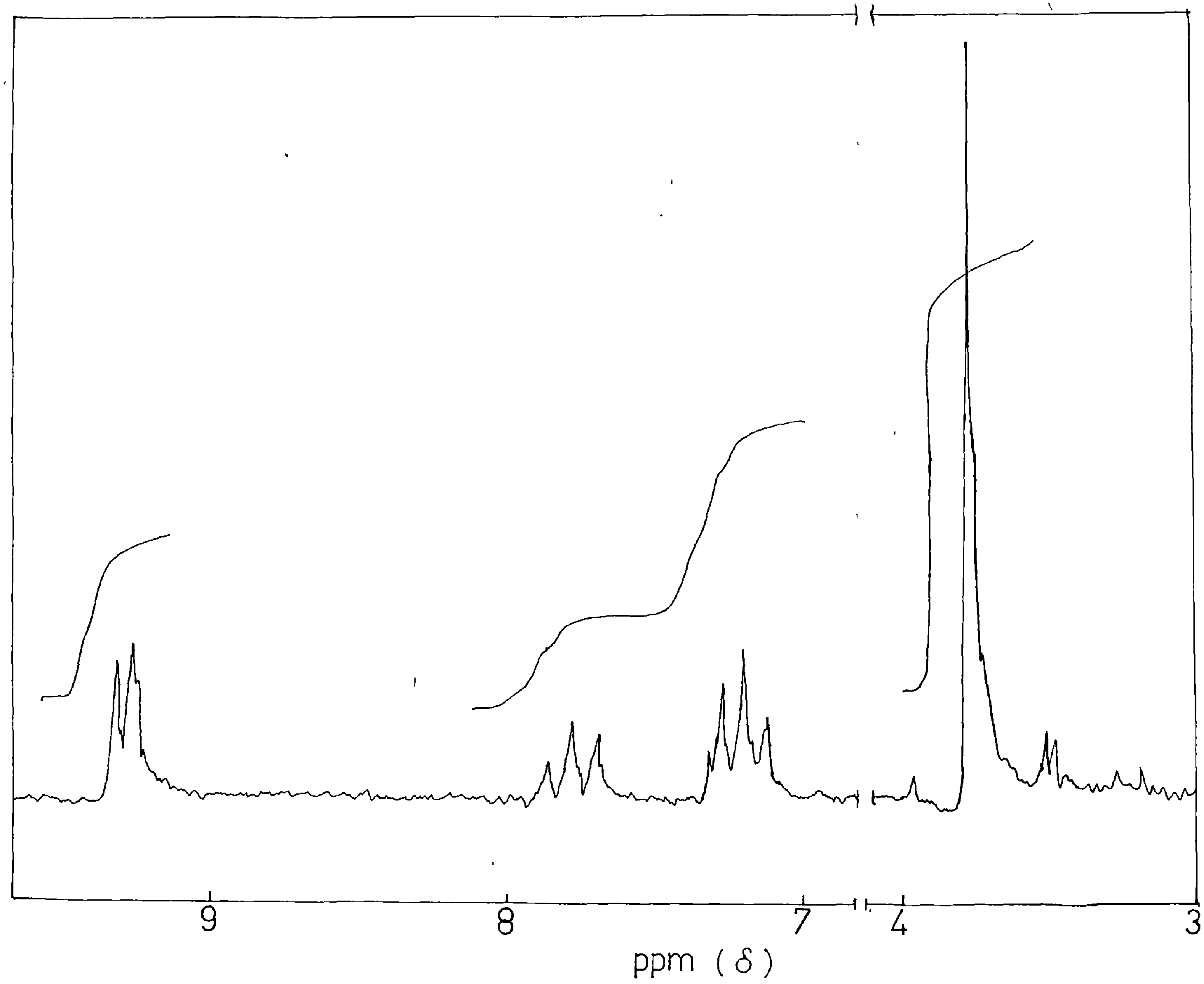

Fig. V.2 ^{1}H NMR SPECTRUM OF <u>trans</u> $[RuI_2(py)_2(MeSO)_2]$ IN $CDCl_3$

<u>With 2,2'-bipyridine and 1,10-phenanthroline</u>. Room temperature reaction products of $[RuI_2(Me_2SO)_4]$ with 2,2'-bipyridine and 1,10-phenanthroline were of the composition, $[RuI_2(L-L)(Me_2SO)_2]$ (L-L = bipy or phen). The compounds were diamagnetic and had very low molar conductance, confirming ruthenium(II) complexes, having covalent iodide. The IR spectrum of the bipyridyl containing complex showed strong bands at 1085 and 418 cm^{-1} which could be assigned to ν_{SO} (S-bonded) of the Me_2SO and ν_{Ru-S} respectively. Similarly, in case of the complex containing 1,10-phenanthroline, bands at 1105 and 1070 cm^{-1} could be assigned to $\nu_{S=O}$ (S-bonded) of the Me_2SO groups and at 425 cm^{-1} due to ν_{Ru-S}. The ^1H NMR spectrum of the two complexes in CD_3CN, further confirm the composition of the complexes and the bonding mode of Me_2SO groups. The ^1H NMR spectrum of $[RuI_2(bipy)(Me_2SO)_2]$ in CD_3CN showed signals at δ 3.53, δ 3.42 and δ 3.37 which are characteristic of the methyl protons of the S-bonded Me_2SO. A doublet at δ 10.1 and multiplet in the region δ 7.25-8.7 were observed due to the protons of the coordinated bipyridyl group.[33] A doublet at δ 10.1 is due to the two protons present next to the coordinated nitrogen atoms,[33] and multiplets in the region δ 7.25-8.7 are due to the rest of the protons in bipyridyl. The ratio of the signals around δ 10.1 and around δ 3.4 was 1:6, thereby confirming the presence of two protons from one bipyridyl and twelve protons

from the two Me_2SO molecules. The ^1H NMR spectrum of $[RuI_2(phen)(Me_2SO)_2]$ in CD_3CN showed one signal at δ 3.45 assigned to the methyl protons of S-bonded Me_2SO groups and multiplets in the region δ 7.35-8.3 assigned to the protons due to 1,10-phenanthroline.[34]

Reaction of $[RuI_2(Me_2SO)_4]$ with 2,2'-bipyridine in refluxing methanol led to the formation of $[RuI_2(bipy)_2]$. The compound is the same as that of Fergusson and Harris[35] obtained by the metathesis of $[Ru(bipy)_2Cl_2]$ with iodide. The UV-visible spectrum of the compound showed absorptions similar to that of the reported one .[35,36]

With acetonitrile. Reactions of $[RuI_2(Me_2SO)_4]$ with acetonitrile under refluxing condition substituted only three of the four Me_2SO molecules leading to the formation of $[RuI_2(CH_3CN)_3(Me_2SO)]$. A compound of the same composition was obtained when $[RuI_2(CH_3CN)_4]$ was reacted with dimethylsulphoxide. The IR spectra of the compounds obtained by both the methods were superimposable confirming that the compounds obtained are one and the same. The IR spectrum of $[RuI_2(CH_3CN)_3(Me_2SO)]$ showed two bands of medium intensity at 2310 and 2275 cm^{-1}, assigned to ν_{CN} of coordinated CH_3CN. It shows that at least two of the acetonitrile molecules are bonded in the cis position to ruthenium.[28] The strong bands at 1120 and 1100 cm^{-1} in the complex may be assigned to $\nu_{S=O}$ (S-bonded) of the Me_2SO

molecule. The ^{1}H NMR spectrum of the complex in $CDCl_3$ showed signals at δ 2.5 and δ 3.55. The signals at δ 2.5 may be assigned to the methyl protons of the coordinated CH_3CN. Protons due to free acetonitrile are observed around δ 2.2. However, upon coordination, the methyl protons of CH_3CN shift downfield by δ 0.3 (to δ 2.5). A signal at δ 3.55 could be assigned to methyl protons of S-bonded Me_2SO molecules. The ratio of the areas under the two signals is 3:2 thereby conforming the presence of three acetonitrile (9 H) and one Me_2SO (6 H) molecule in the complex.

With sodium diethyldithiocarbamate. The reaction of $[RuI_2(Me_2SO)_4]$ with sodium diethyldithiocarbamate led to the formation of $[Ru(Et_2NCS_2)_2(Me_2SO)_2]$. This compound was obtained by Evans et al[37] by the reaction of $[RuCl_2(Me_2SO)_4]$ with the ligand. The compound showed a strong band at 1490 cm^{-1} characteristic of ν_{CS} for the bidentate diethyldithiocarbamate groups.[38] Another strong band at 1075 cm^{-1} is due the ν_{SO} (S-bonded) of the Me_2SO groups.

Electronic Spectra

Electronic absorption spectra of all the complexes Table V.3)showedsome absorptions in the 350-500 nm region. Absorption bands with high ϵ value (10^3-10^4) are largely due to charge-transfer transitions whereas bands with lower ϵ value (10^2-10^3) may be of the d-d type ($^1A_{1g} \longrightarrow {}^1E_g$ or $^1A_2$).[39]

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CHAPTER VI

CHAPTER VI

CATIONIC AND ANIONIC COMPLEXES OF RUTHENIUM(III) : $[Ru(Me_2SO)_6]X_3$ ($X = ClO_4$ or BPh_4), $Me_4N\ [RuCl_4(Me_2SO)_2]$ AND $Et_4N\ [RuBr_4(Me_2SO)_2]$.

Hexakis-dimethylsulphoxide ruthenium(II) cation is reported in the literature by different groups of workers,[1-3] and has been characterized using various physical methods including X-ray crystallography.[3] The cation is found to have three Me_2SO molecules coordinated to ruthenium(II) via the oxygen atoms and the rest three Me_2SO molecules, via the sulphur atoms to give the facial isomer of irregular octahedral geometry.[3] Synthesis of $[Ru(Me_2SO)_6]^{2+}$ has been achieved either from cis $[RuCl_2(Me_2SO)_4]$ or from $[Ru(cod)(Me_2SO)_4]^{2+}$. Similar cation of ruthenium(III), viz. $[Ru(Me_2SO)_6]^{3+}$ has been reported by Bora and Singh.[4,5] However, these are not well characterised and our attempts to repeat the preparation according to Bora and Singh were unsucessful. The compounds reported by Bora and Singh are $[Ru(Me_2SO)_6]X_3$ (X = Cl, Br or ClO_4). The synthesis reported by them make use of $RuCl_3$ or $RuBr_3$. In this chapter, we report the synthesis and characterization of $[Ru(Me_2SO)_6]X_3$ ($X = ClO_4$ or BPh_4) using fac or mer $[RuCl_3(Me_2SO)_3]$ or $[Ru_2Cl_6(Me_2SO)_4]$. The ruthenium(III) cationic complex has been characterized using various physical methods and seems to have a structure similar to that of its ruthenium(II) analogue.

The reports on the synthesis and characterization of ruthenium(II) and ruthenium(III) complex anions containing halide and Me_2SO ligands are very scarce. Such compound reported for ruthenium(II) is $[NMe_2H_2][RuCl_3(Me_2SO)_3]$.[6] X-ray crystallographic studies and other physical measurements reveal that the complex ion has a facial structure and has all S-bonded Me_2SO groups.[6] The compounds reported for ruthenium(III), *viz*. $M[RuCl_4(Me_2SO)_2]$ (where M = Na, NBu_4), are very poorly characterised,[4] and their syntheses are not reproducible. In this chapter, synthesis and characterization of some ruthenium(III) anions, *viz*. $[RuX_4(Me_2SO)_2]^-$ are described. Use of *fac* or *mer* $[RuCl_3(Me_2SO)_3]$ or $[Ru_2Cl_6(Me_2SO)_4]$ or $[RuBr_3(Me_2SO)_3]$ has been made to synthesize them.

EXPERIMENTAL

All the solvents were freshly distilled before use. *fac* and *mer* $[RuCl_3(Me_2SO)_3]$, $[Ru_2Cl_6(Me_2SO)_4]$ and $[RuBr_3(Me_2SO)_3]$ were prepared as described in Chapters II and IV. Analytical data and all physical measurements were obtained as described in Chapters II and III. Analytical data, molar conductance values and magnetic moment of the complexes are presented in Table VI.1. Important IR and electronic absorption bands are given in Table VI.2.

PREPARATIONS

(a) $[Ru(Me_2SO)_6][ClO_4]_3$

To a solution/suspension of $[Ru_2Cl_6(Me_2SO)_4]$ or *fac* or *mer* $[RuCl_3(Me_2SO)_3]$ (0.5g) in ethanol (30 cm^3), a solution of $AgClO_4$ in ethanol (10 cm^3) (molar ratio 1:4) was added. The mixture was stirred at room temperature for 10-12 h and then refluxed on a water-bath for 1 h. The solution was cooled to room temperature and centrifuged out the precipitated AgCl. To the light violet mother liquor, dimethylsulphoxide (1 cm^3) was added and stirred at room temperature for 2-3 h. The solution was concentrated on a water-bath to a small volume (~ 2cm^3). It was cooled in ice and methanol was added to precipitate the violet compound. The compound was recrystallized from acetone and dried *in vacuo*. Yield 0.82g (~75%). It was analysed for $[Ru(Me_2SO)_6][ClO_4]_3$.

(b) $[Ru(Me_2SO)_6][BPh_4]_3$

$[Ru(Me_2SO)_6][ClO_4]_3$ (0.2g), was dissolved in acetone (10 cm^3) and a solution of $NaBPh_4$ (0.25g) in acetone (10 cm^3) was added to it. The reaction mixture was stirred at room temperature for 1 h, when the colour changed from violet to green. The green solution was concentrated at room temperature, to small volume (~ 2 cm^3). Methanol was added to precipitate the light green compound. The compound was centrifuged, washed with little acetone and dried in vacuo. It was analysed for $[Ru(Me_2SO)_6][BPh_4]_3$.

(c) $Me_4N\,[RuCl_4(Me_2SO)_2]$

$[Ru_2Cl_6(Me_2SO)_4]$, or fac or mer $[RuCl_3(Me_2SO)_3]$ (0.5g) was dissolved in methanol (20 cm^3). A solution of tetramethylammonium chloride (0.2g) in methanol (5 cm^3) was added to it and the reaction mixture was refluxed on a water bath for 1 h. After concentrating and cooling the solution to room temperature, orange crystals separated out. The compound was centrifuged, washed with diethyl ether and dried in vacuo. Yield 0.4g ($\sim$ 75%). It was analysed for $Me_4N\,[RuCl_4(Me_2SO)_2]$.

(d) $Et_4N\,[RuBr_4(Me_2SO)_2]$

$[RuBr_3(Me_2SO)_3]$ (0.3g) was dissolved in methanol (20 cm^3) and a solution of tetraethylammonium bromide (0.15g) in methanol (10 cm^3) was added to it. The reaction mixture was refluxed for 10 min, concentrated and cooled to room temperature. Violet crystals separated out which were centrifuged, washed with methanol and dried in vacuo. Yield 0.3g ($\sim$ 80%). It was analysed for $Et_4N\,[RuBr_4(Me_2SO)_2]$.

RESULTS AND DISCUSSION

$[Ru(Me_2SO)_6]X_3$ (X = Cl, Br or ClO_4) were reported by Bora and Singh,[4,5] $[Ru(Me_2SO)_6]X_3$ (X = Cl or Br) were synthesized by them using $RuCl_3.xH_2O$ or $RuBr_3.xH_2O$. However, our attempts to synthesize these compounds according to Bora and Singh were unsuccessful. $[Ru(Me_2SO)_6](ClO_4)_3$ was reported by the metathesis of $[Ru(Me_2SO)_6]Cl_3$ with silver perchlorate.[4] We have synthesized $[Ru(Me_2SO)_6](ClO_4)_3$ by the reaction of $[Ru_2Cl_6(Me_2SO)4]$ or *fac* or *mer* $[RuCl_3(Me_2SO)_3]$ with silver perchlorate in presence of excess dimethylsulphoxide. A metathetic reaction of $[Ru(Me_2SO)_6](ClO_4)_3$ with $NaBPh_4$ resulted in $[Ru(Me_2SO)_6](BPh_4)_3$.

The compositions of $[Ru(Me_2SO)_6]X_3$ (X = ClO_4 or BPh_4) were confirmed with the help of analytical data (Table VI.1). The molar conductance values for these complexes in acetonitrile was about 350 $\Omega^{-1}cm^2mol^{-1}$ which is nearly the expected value for a 1:3 electrolyte.[7] The IR spectra of these complexes are similar to those of the reported ruthenium(II) complexes, *viz.* $[Ru(Me_2SO)_6]X_2$ (X = BF_4 or BPh_4).[2,3] The IR spectrum of $[Ru(Me_2SO)_6](ClO_4)_3$ (Fig VI.1a) was superimposable with that of $[Ru(Me_2SO)_6](ClO_4)_2$, prepared according to Evans *et al.*[1] The IR spectrum of the compound $[Ru(Me_2SO)_6](ClO_4)_3$, showed strong absorption at 1140, 1120 and 1090 cm^{-1} in the region 1150 - 1050 cm^{-1}. These bands may be due to ν_{SO} of S-bonded

Table VI.1 Analytical and Physical data of some Cationic and Anionic Complexes of Ruthenium(III)

Compounds	Colour	M.P. °C	Analysis[a] (%)			Conductance in $\Omega^{-1} cm^2 mol^{-1}$ in CH_3CN	μ_{eff} at RT in B.M.
			C	H	N		
$[Ru(Me_2SO)_6](ClO_4)_3$	Violet	120	16.2 (16.2)	4.2 (4.2)		350	1.9
$[Ru(Me_2SO)_6](BPh_4)_3$	Light green	170	65.2 (65.8)	6.0 (6.3)		340	-
$Me_4N\,[RuCl_4(Me_2SO)_2]$	Orange yellow	260(d)	20.1 (20.3)	5.3 (5.1)	2.7 (2.9)	128	1.8
$Et_4N\,[RuBr_4(Me_2SO)_2]$	Violet	205-208	20.8 (20.4)	4.9 (4.5)	1.8 (2.0)	115[b]	1.92

a, Calculated values are in parentheses

b, in methanol

d, decomposes

Table VI.2 Important IR and electronic absorption bands of cationic and anionic complexes of Ruthenium(III)

Compounds	IR bands in cm^{-1}	Electronic absorption bands λ_{max} in n.m (ϵ) in CH_3CN
$[Ru(Me_2SO)_6](ClO_4)_3$	1140s, 1120s, 1090s, 925m, 480m-w, 429m-w	575 (320)
$[Ru(Me_2SO)_6](BPh_4)_3$	1570m, 1470m, 1120s, 920s, 700s, 480m-w, 430m	-
$Me_4N\ [RuCl_4(Me_2SO)_2]$	1120s, 955m-w, 415m, 345s, 330s, 265m, 225m	475 (350) 405 (4520) 292 (1220)
$Et_4N\ [RuBr_4(Me_2SO)_2]$	1080w, 1060w, 1030m-s, 997m-s, 977m-s, 290m, 235m, 208m, 195m	535 (1260) 490 (1180) 440 (1880) 385 sh

s, strong; m, medium; w, weak;

sh, shoulder

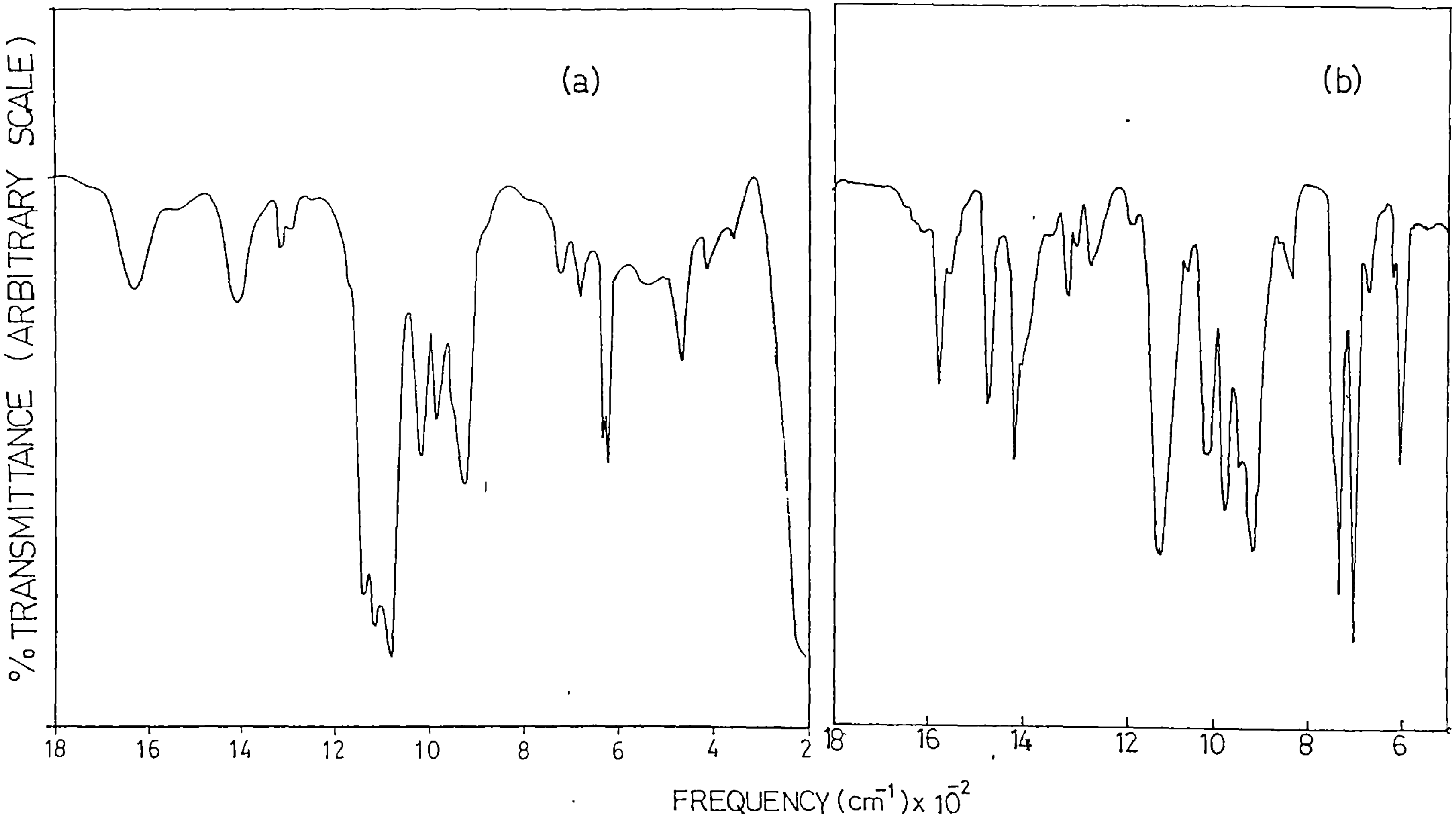

Fig. VI.1 INFRARED SPECTRUM OF (a) $[Ru(Me_2SO)_6](ClO_4)_3$

(b) $[Ru(Me_2SO)_6](BPh_4)_3$

Me_2SO and due to ionic ClO_4^-.[8] The IR spectrum of $[Ru(Me_2SO)_6](BPh_4)_3$ (Fig VI.1b) showed only one absorption in that region at 1120 cm^{-1} which can unambiguously be assigned to ν_{SO} of S-bonded Me_2SO groups. Thus, for $[Ru(Me_2SO)_6](ClO_4)_3$, the absorption at 1120 cm^{-1} can be assigned to ν_{SO} of S-bonded Me_2SO and the absorption at 1140 and 1090 cm^{-1} to ionic perchlorate. Further one band at 925 cm^{-1} of medium intensity was observed for $[Ru(Me_2SO)_6]X_3$ ($X = ClO_4$ or BPh_4), which could be assigned to ν_{SO} of the O-bonded Me_2SO groups. The positions of IR bands due to ν_{SO} (S-bonded) and ν_{SO} (O-bonded) observed for $[Ru(Me_2SO)_6]X_3$ are same as reported for the ruthenium(II) analogues, *viz* $[Ru(Me_2SO)_6]X_2$ ($X = BPh_4$ or BF_4).[2,3] In the far IR region, bands of weak to medium intensity were observed at 480 and 429 cm^{-1} which may be assigned to ν_{Ru-O} and ν_{Ru-S} respectively.[9,10] Besides the bands described above IR spectrum of $[Ru(Me_2SO)_6](BPh_4)_3$, showed bands at 1570, 1470, and 700 cm^{-1} also, which are characteristic of the presence of BPh_4^- anion.[2] An X-ray crystal study of BF_4^- salt of $[Ru(Me_2SO)_6]^{2+}$ revealed[3] that the ruthenium(II) was coordinated to three Me_2SO molecules, *via* the oxygen atom and to the rest three Me_2SO molecules, *via* the sulphur atom, to give the facial isomer having C_{3v} symmetry. As the IR spectrum of $[Ru(Me_2SO)_6]^{3+}$ is superimposable to that of $[Ru(Me_2SO)_6]^{2+}$, we also propose a structure for the ruthenium(III) cationic complex, same as for the ruthenium(II) cationic complex. EPR spectral observation (discussed later) also support the same.

The magnetic moment value observed at room temperature for $[Ru(Me_2SO)_6](ClO_4)_3$ was 1.9 B.M., characteristic of a low-spin d^5, ruthenium(III) system. The EPR spectrum of $[Ru(Me_2SO)_6](ClO_4)_3$ in powder form at room temperature, (Fig VI.2) showed two signals at g = 2.31 and 1.88. If one presumes, three S-bonded Me_2SO and three O-bonded Me_2SO groups bonded to the metal to give a facial isomer (vide supra) a C_{3v} symmetry is expected. For such ruthenium(III) compounds having facial geometry, generally a two line spectrum is observed.[11,12] The electronic absorption spectrum of $[Ru(Me_2SO)_6](ClO_4)_3$ in acetonitrile in the visible region showed a broad band at 575 nm having molar extinction coefficient (ϵ), 320. Absorption in ruthenium(III) system with $\epsilon = 10^2$ could normally be assigned due to spin allowed d-d transition.[13] Thus 575 nm band may be assigned to one of the d-d transition, viz. $^2T_2 \longrightarrow {}^2A_2, {}^2T_1$ or $^2T_2$. Thus, with the help of the above studies, a facial structure with three S-bonded and three O-bonded Me_2SO groups, for $[Ru(Me_2SO)_6]^{3+}$ is proposed.

The complex ion $[RuCl_4(Me_2SO)_2]^-$ was reported by Bora and Singh from $[Ru(Me_2SO)_6]Cl_3$.[4] As described earlier, synthesis of $[Ru(Me_2SO)_6]Cl_3$ according to Bora and Singh was not reproducible, hence the synthesis of $[RuCl_4(Me_2SO)_2]^-$ could not be reproduced. We have achieved the synthesis of $Me_4N\,[RuCl_4(Me_2SO)_2]$, using $[Ru_2Cl_6(Me_2SO)_4]$, fac or mer $[RuCl_3(Me_2SO)_3]$. $Et_4N\,[RuBr_4(Me_2SO)_2]$ has been synthesized using $[RuBr_3Me_2SO)_3]$.

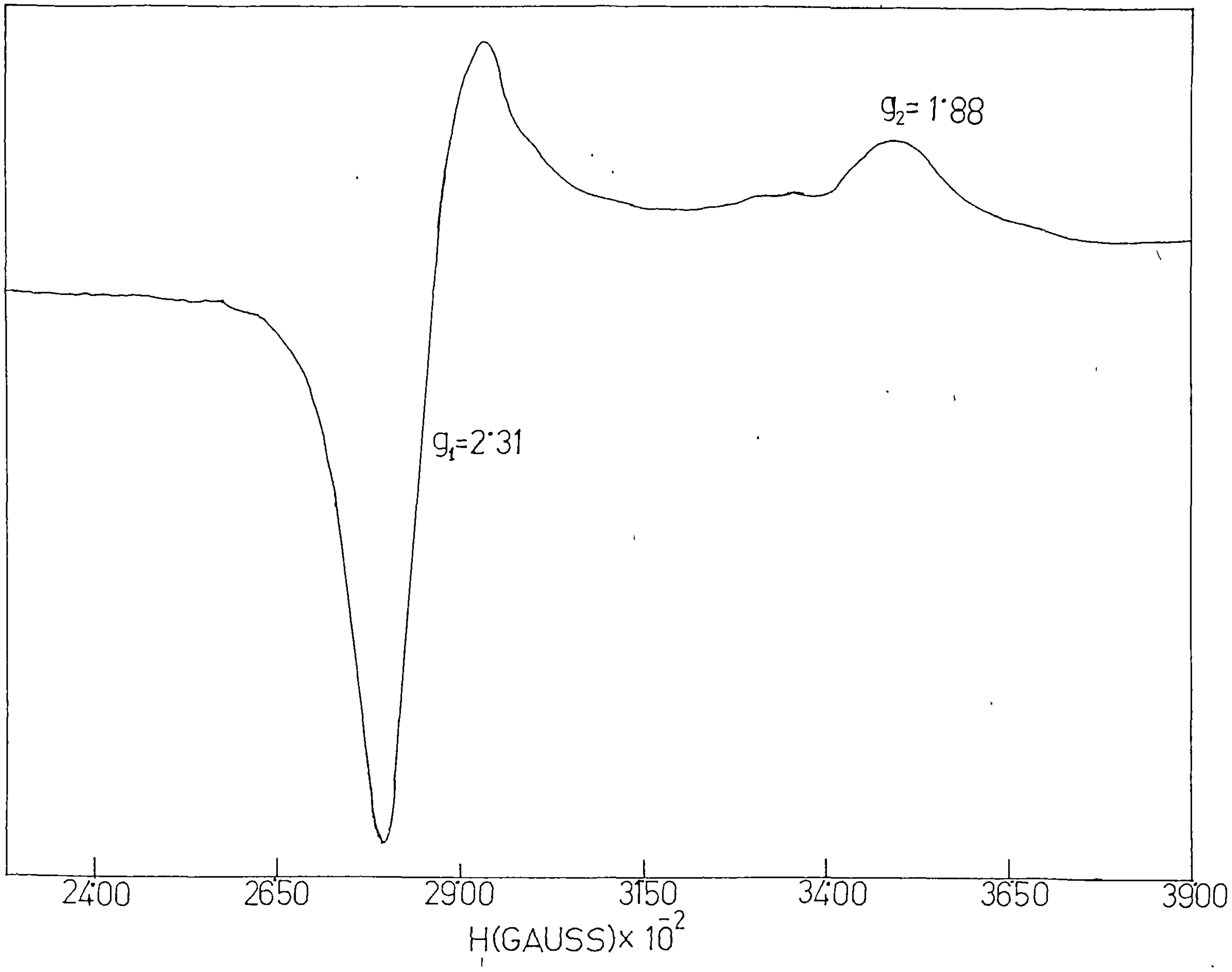

Fig. VI.2 E P R SPECTRUM OF $[Ru(Me_2SO)_6](ClO_4)_3$ AT R T.

The compositions of Me_4N [$RuCl_4(Me_2SO)_2$] and Et_4N [$RuBr_4(Me_2SO)_2$] were confirmed with the help of analytical data (Table VI.1). The molar conductance values for the compounds in acetonitrile were about 120 $\Omega^{-1}cm^2mol^{-1}$ which is characteristic of their 1:1 electrolytic behaviour.

The IR spectra of Me_4N [$RuCl_4(Me_2SO)_2$] (Fig VI.3) obtained from [$Ru_2Cl_6(Me_2SO)_4$] or fac or mer [$RuCl_3(Me_2SO)_3$] were superimposable, which means the mode of coordination of Me_2SO to ruthenium in [$RuCl_4(Me_2SO)_2$]$^-$ is independent of the starting compounds (having either completely S-bonded Me_2SO molecules or both S and O-bonded Me_2SO molecules). The complex anion has only S-bonded Me_2SO groups, evident from the presence of a strong band at 1120 cm^{-1} due to ν_{SO}, (S-bonded Me_2SO). A band of medium to weak intensity was observed at 955 cm^{-1} which is due to the presence of Me_4N^+ cation. The possibility of the presence of this band due to ν_{SO} of O-bonded Me_2SO cannot be ruled out. However, looking at its intensity (medium to weak) and comparing with that of 1120 cm^{-1} band, it seems unlikely that the band is due to ν_{SO} of O-bonded Me_2SO. Further, an absorption at 415 cm^{-1} could be assigned due to ν_{Ru-S}.[9,10] Four bands at 345(s), 330(s), 265(m) and 225(m)cm^{-1} were observed in the region 350 - 200 cm^{-1}. If one presumes a

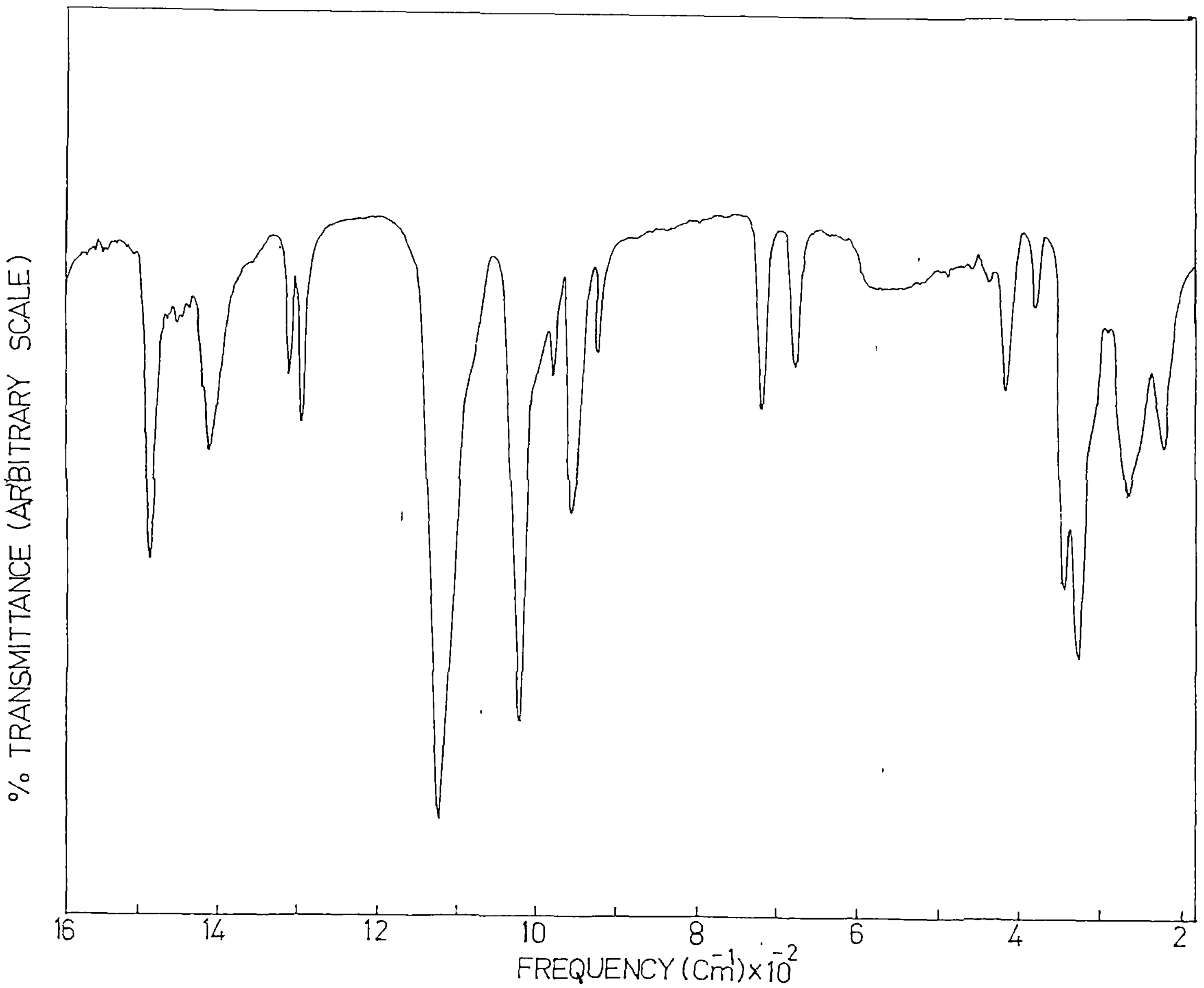

Fig VI.3. INFRARED SPECTRUM OF $Me_4N[RuCl_4(Me_2SO)_2]$

trans geometry for the complex leading to D_{4h} symmetry, according to group theory, only one absorption band due to ν_{Ru-Cl} is expected, whereas for a cis complex four ν_{Ru-Cl} are expected. Thus the four absorptions in the region 350 - 200 cm^{-1} may be assigned due to ν_{Ru-Cl} of the cis $[RuCl_4(Me_2SO)_2]^-$, similar to four ν_{Pt-Cl} at 353, 344, 330 and 206 cm^{-1} for cis $[PtCl_4(NH_3)_2]$.[14] Hence a cis geometry for $[RuCl_4(Me_2SO)_2]^-$ is proposed.

The IR spectrum of $Et_4N[RuBr_4(Me_2SO)_2]$ (Fig VI.4), showed two weak bands at 1080 and 1060 cm^{-1} and three bands of medium to strong intensity at 1030, 997 and 977 cm^{-1} in the region 1100 - 900 cm^{-1}. The bands at 1080 and 1060 cm^{-1} are present in Et_4NBr. A band at 1030 cm^{-1} could be due to $\rho_r(CH_3)$ of Me_2SO. The bands at 997 and 977 cm^{-1} may be assigned due to ν_{SO} of O-bonded Me_2SO molecules. Thus in $[RuBr_4(Me_2SO)_2]^-$, the mode of coordination of Me_2SO to ruthenium most probably remains O-bonded, same as that of the starting compound, viz. $[RuBr_3(Me_2SO)_3]$. The spectrum in the region 350 - 180 cm^{-1} showed medium intensity bands at 290, 235, 208 and 195 cm^{-1}. These bands may be assigned due to ν_{Ru-Br}. Presence of four bands due to ν_{Ru-Br} is indicative of a cis geometry, for $[RuBr_4(Me_2SO)_2]$, similar to $[RuCl_4(Me_2SO)_2]^-$ (vide supra).

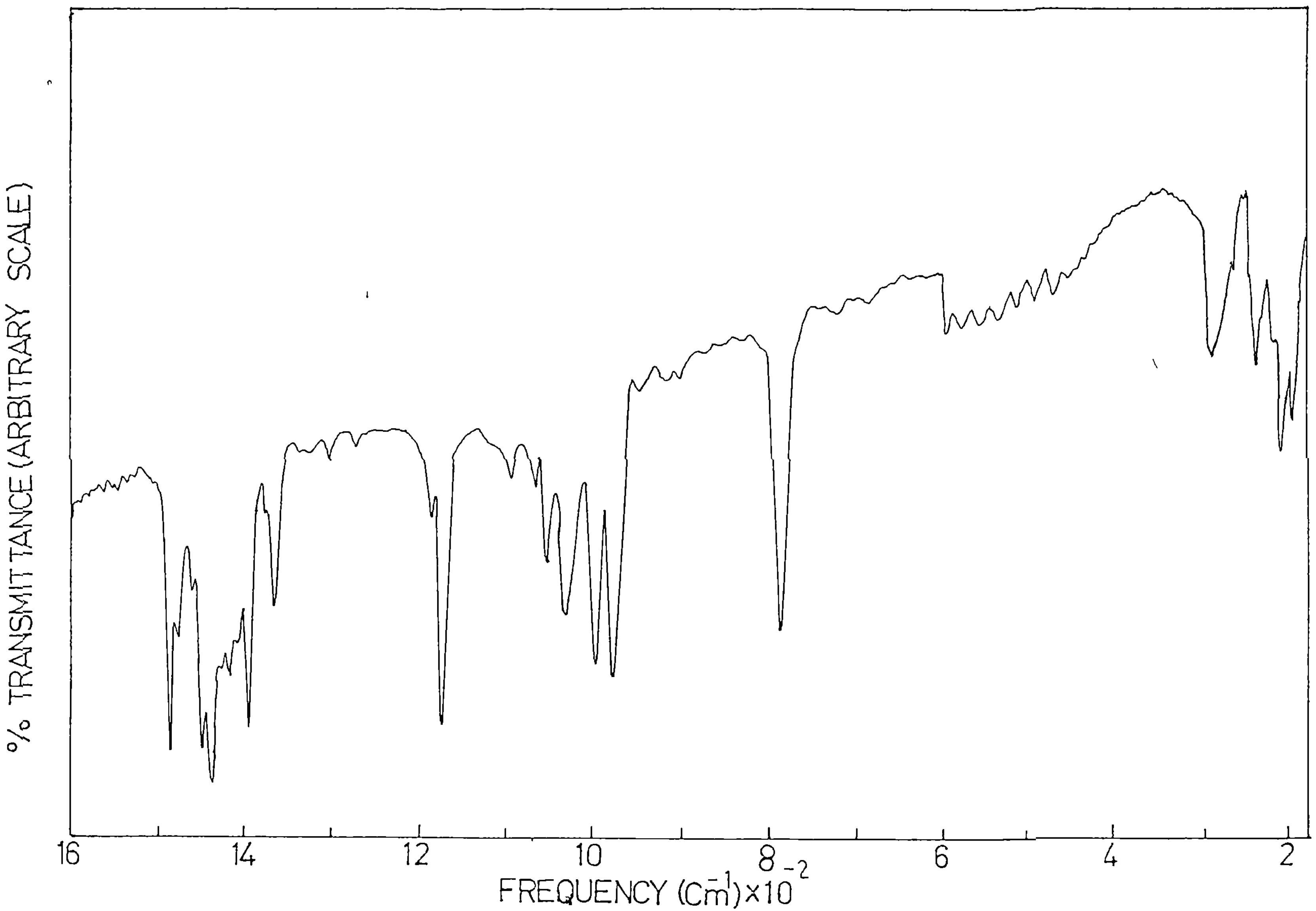

Fig VI 4 INFRARED SPECTRUM OF $Et_4N[RuBr_4(Me_2SO)_2]$

The magnetic moment values, μ_{eff}, for the two anionic complexes are 1.8 and 1.9 BM, thereby confirming that the complexes contain low-spin, d^5 ruthenium(III). The EPR spectrum of $Et_4N\ [RuBr_4(Me_2SO)_2]$ in powder form at room temperature showed a broad signal at g = 2.17. However, for a cis geometry of the complex (vide supra) one expects $g_x \neq g_y \neq g_z$ and hence three g values are expected. The presence of one broad signal at g = 2.17 means that the symmetry around ruthenium(III) is close to cubic which is possible if one assumes that the O-bonded Me_2SO groups and the bromides have similar ligand field. Similar observations were made for $[RuBr_3(Me_2SO)_3]$ (discussed in Chapter IV). The electronic absorption spectrum of $[RuCl_4(Me_2SO)_2]^-$ in CH_3CN (Fig. VI.5a) showed one band of low intensity at 475 nm (ϵ = 350) and two bands of higher intensities, viz. at 405 nm (ϵ = 4520) and at 292 nm (ϵ = 1220). The band at 475 nm may be assigned due to one of the d-d transition of the type $^2T_2 \rightarrow {}^2A_2$, $^2T_1$ or $^2T_2$. Other bands may be mostly due to charge-transfer type of transitions from ligand to the metal. The electronic absorption spectrum of $[RuBr_4(Me_2SO)_2]^-$ in methanol (Fig.VI.5b) showed bands at 535 nm (ϵ = 1260), 490 nm (ϵ = 1180), 440 nm (ϵ = 1880) and a shoulder at 385 nm. Since all these bands have ϵ values around 10^3, these may be assigned to charge transfer type of transition from ligand to the metal as in the case of its chloro-analogue.

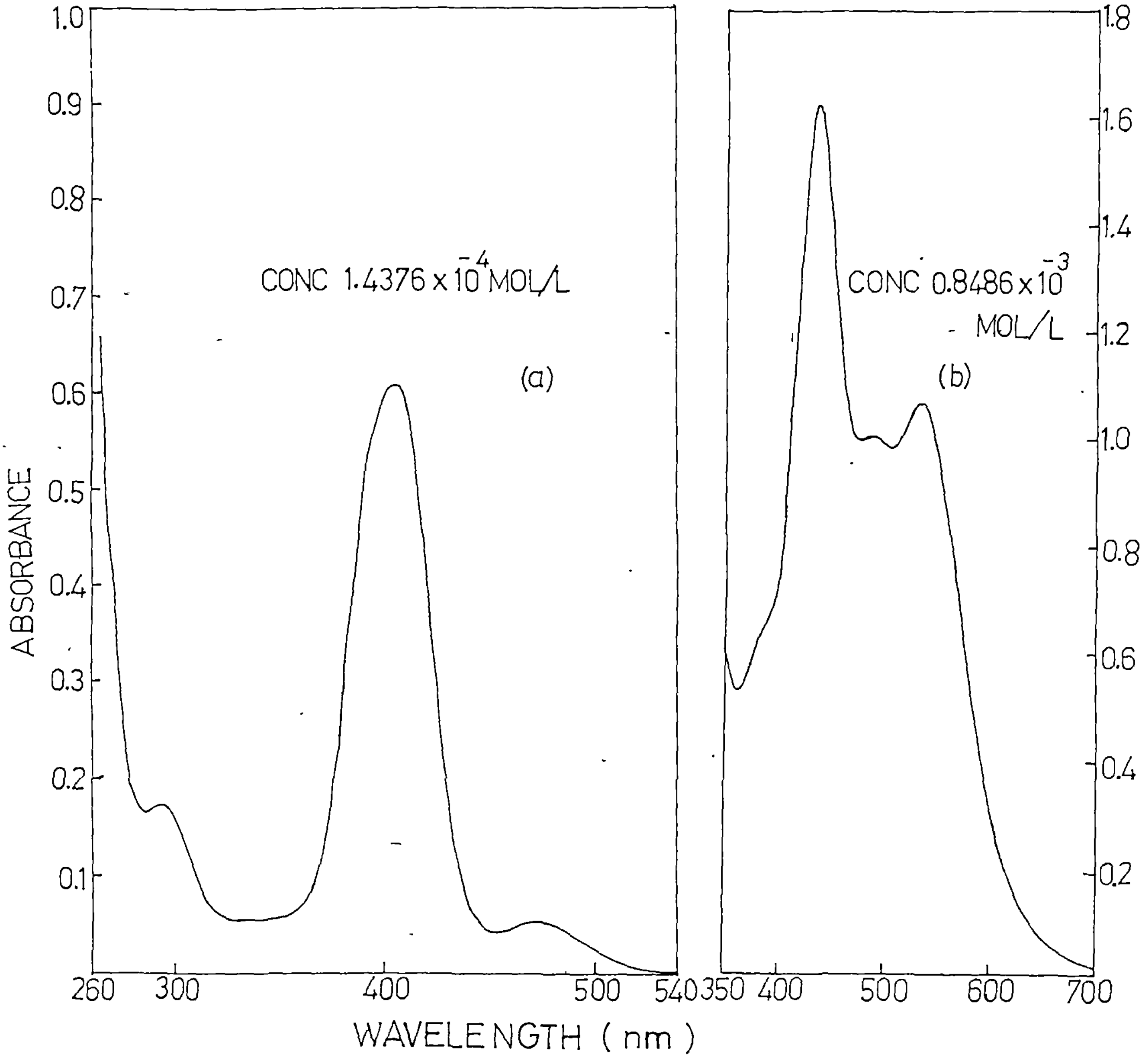

Fig VI.5. ELECTRONIC SPECTRA OF (a) $Me_4N[RuCl_4(Me_2SO)_2]$ IN CH_3CN

(b) $Et_4N[RuBr_4(Me_2SO)_2]$ IN CH_3OH

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CHAPTER VII

CHAPTER VII

CONVENIENT SYNTHESIS OF BIS(2,2'-BIPYRIDYL) COMPLEXES OF RUTHENIUM(III) AND TRIS(2,2'-BIPYRIDYL) OR (1,10-PHENANTHROLINE) COMPLEXES OF RUTHENIUM(II)

AND

NOVEL SYNTHESIS OF $[\text{Ru(1,10-PHENANTHROLINE)}_2\text{Br}_2]\text{X}$ ($\text{X} = \text{Br}, \text{ClO}_4, \text{BPh}_4$)

The chemistry of diimine complexes of ruthenium(II) and ruthenium(III) is interesting because of their physical, chemical and structural properties. The attention of inorganic chemists during the past decade has been focussed on the chemistry of $[\text{Ru(bipy)}_3]^{2+}$ and its derivatives due to a unique combination of chemical stability, redox properties, excited state reactivity, luminescence emission and excited state life time. In particular, the ruthenium(II) diimine complexes have played and are still playing a key role in the development of photochemistry, photophysics, photocatalysis, electrochemistry, photo electrochemistry, chemi- and electrochemi- luminescence and electron and energy transfer.[1]

As a result of which, such complexes are being considered as promising candidates for the role of ideal photocatalysts for the visible light photoinduced decomposition of water into dihydrogen and oxygen. The interest in evolving easy methods of synthesizing these compounds continues, besides studying their physical, chemical and photocatalytic behaviours in detail.

Synthesis of ruthenium(III) complexes containing (mono, bis or tris) 2,2'-bipyridyl or 1,10-phenanthroline is generally achieved by the oxidation of their ruthenium(II) analogues with (i) chlorine,[2-5] (ii) a cerium(IV) compound,[6-10] (iii) lead(IV) oxide[11,12] or (iv) silver nitrate.[6] Recently $K[RuCl_4(bipy)]$ and $[RuCl_3(bipy)]$ were reported from $RuCl_3.xH_2O$.[13-15] The synthesis of $[Ru(bipy)_2Cl_2]Cl.2H_2O$ was first described by Bailer <u>et</u> <u>al</u>.[4] by the oxidation of $[Ru(bipy)_2(C_2O_4)]$ with chlorine. Latter, Fergusson and Harris[5] obtained this compound by the oxidation of $[Ru(bipy)_2Cl_2]$ with chlorine. Syntheses of $[Ru(bipy)_2Cl_2]Cl.2H_2O$, described above, involve two steps, (i) preparation of a ruthenium(II) complex containing 2,2'-bipyridyl and (ii) its oxidation using chlorine. Recently Bottomley and Mukaida[16] have reported a one pot synthesis of the ruthenium(III) complex described above. In this chapter, we describe a very simple method of synthesising

$[Ru(bipy)_2Cl_2]Cl.2H_2O$, by the metathesis of Me_2SO groups in an easily synthesised ruthenium(III) compound, viz. fac- or mer- $[RuCl_3(Me_2SO)_3]$.[17]

Reports on the synthesis of ruthenium(III) complexes containing (mono or bis) 2,2'-bipyridyl or 1,10-phenanthroline and bromide ligands are very few. $[RuBr_2(py)_2(bipy)]ClO_4$ and $[RuBr(py)_3(bipy)][ClO_4]_2$ were reported by the oxidation of their ruthenium(II) analogues with cerium(IV) ammonium sulphate.[2] $NH_4[RuBr_4(bipy)]$ was reported by the metathesis and reduction of $[RuCl_4(bipy)]$ with HBr and NH_4Br.[2] $[Phen\ H][RuBr_4(phen)]H_2O$ was reported by the metathesis of $K_2[RuCl_5(H_2O)]$ with HBr and NH_4Br in situ and reaction with 1,10-phenanthroline. In this chapter, we report the synthesis of a new ruthenium(III) complex, viz $[Ru(phen)_2Br_2]Br$, by a simple substitution of Me_2SO with 1,10-phenanthroline in $[RuBr_3(Me_2SO)_3]$[18]. This is the first example of a bis(1,10-phenanthroline) ruthenium(III) complex containing bromide ligands. Chloro-analogue of this ruthenium(III) complex is known.[3]

Various methods have been described for the synthesis of ruthenium(II) complexes of the type, $[Ru(L\text{-}L)_3]X_2.nH_2O$ (L-L = bipy or phen, X = Cl, Br, I, ClO_4 etc).[19] Most of the methods make use of commercial $RuCl_3.xH_2O$; a ruthenium(III) compound, viz. $K_2[RuCl_5(H_2O)]$; or ruthenium(IV) compounds, viz. K_2 $[RuCl_6]$ or K_4 $[Ru_2OCl_{10}]$. In most cases, excess of the ligand acts as a reducing agent to give the ruthenium(II) compounds, $[Ru(L-L)_3]X_2.nH_2O$. We report here a simple method of complete substitution of chloro and Me_2SO groups from fac or mer $[RuCl_3(Me_2SO)_3]$ by 2,2'-bipyridyl or 1,10-phenanthroline to give $[Ru(L-L)_3]X_2.nH_2O$. Substitution reactions of $[RuCl_2(Me_2SO)_4]$ with 2,2'-bipyridyl or 1,10-phenanthroline were reported to give partially substituted products only.[20]

EXPERIMENTAL

All the solvents were freshly distilled before use. fac and mer $[RuCl_3(Me_2SO)_3]$ and $[RuBr_3(Me_2SO)_3]$ were prepared as described in Chapter II and Chapter IV respectively. Analytical data and other physical measurements, viz. IR, ^{1}HNMR, EPR, μ_{eff} were obtained as described in Chapters II and III. Analytical data and molar conductance data are reported in Table VII.1. Electronic absorption spectral data are given in Table VII.2.

PREPARATIONS

(a) $[Ru(bipy)_2Cl_2]Cl.2H_2O$

To a solution of fac or mer $[RuCl_3(Me_2SO)_3]$ (0.2g) in methanol (10 cm^3), 2,2'-bipyridyl (0.11g) (molar ratio, 1:1.5) was added and refluxed on a water-bath for 30 min. In case of <u>mer</u> $[RuCl_3(Me_2SO)_3]$, the product separated out on cooling, whereas in case of <u>fac</u> $[RuCl_3(Me_2SO)_3]$, diethyl ether was added to precipitate the orange coloured compound. It was centrifuged, washed with ether and dried <u>in vacuo</u>. Yield 0.18g, (75%).

(b) $[Ru(bipy)_2Cl_2]ClO_4$

To a solution of $[Ru(bipy)_2Cl_2]Cl.2H_2O$ (0.2g) in methanol (10 cm^3), a solution of NH_4ClO_4 (0.05g) in methanol (5 cm^3) was added and the mixture was refluxed on a water-bath for 15 min, concentrated and cooled to room temperature. Brown crystalline compound separated out. It was centrifuged, washed with ether and dried <u>in vacuo</u>.

(c) $[Ru(phen)_2Br_2]Br$

To a solution of $[RuBr_3(Me_2SO)_3]$ (0.2g), in toluene (10 cm^3), 1,10-phenanthroline (0.1g) (molar ratio 1:1.5) was added and warmed on a water-bath for 10 min. A compound separated, which was centrifuged, washed with ethanol and then with ether and dried <u>in vacuo</u>. Yield 0.16g, (66%).

(d) $[Ru(phen)_2Br_2]X$, ($X = ClO_4$, BPh_4)

$[Ru(phen)_2Br_2]Br$ (0.2g), was dissolved in methanol (20 cm^3) and a methanolic solution of NH_4ClO_4 or $NaBPh_4$

(molar ratio of the complex : X = 1:1.5) was added to it. In case of $NaBPh_4$ an orange compound separated on mixing at room temperature, whereas in case of NH_4ClO_4, refluxing of the mixture for 30 min and cooling to room temperature yielded a brown crystalline compound. The compounds were centrifuged, washed with ether and dried in vacuo.

(e) $[Ru(bipy)_3]Cl_2.H_2O$

To a solution of fac or mer $[RuCl_3(Me_2SO)_3]$ (0.2g) in ethanol (20 cm^3), 2,2'-bipyridyl (0.22g) (molar ratio 1:3) was added and refluxed the mixture for 2 h, when a dark orange solution was obtained. The solution was concentrated to ~ 5cm^3, cooled to room temperature and diethyl ether was added to precipitate the compound. The compound was centrifuged, washed with ether and dried in vacuo. Yield 0.2g, (65%).

(f) $[Ru(bipy)_3]Br_2$

$[RuBr_3(Me_2SO)_3]$ (0.2g) was dissolved in ethanol (20 cm^3) and a solution of 2,2'-bipyridyl (0.2g) (molar ratio ~1:4) in ethanol was added to it. The mixture was refluxed for 2 h when an orange coloured solution was obtained. The solution was concentrated, cooled, and diethyl ether was added to precipitate a yellow orange compound. It was centrifuged, washed with ether and dried in vacuo. Yield 0.18g, (~72%).

(g) $[Ru(bipy)_3]X_2H_2O$ ($X = ClO_4$, BPh_4)

To the orange coloured solution obtained in reaction (e) or in reaction (f) above, an ethanolic solution of NH_4ClO_4 or $NaBPh_4$ (molar ratio of the complex : X = 1:3) was added. In case of $NaBPh_4$, the mixture on stirring at room temperature for 5 min. yielded an orange coloured compound, whereas in case of NH_4ClO_4, refluxing of the mixture for 15 min and cooling to room temperature yielded the red crystalline compound. The compounds were separated as in (e) above.

(h) $[Ru(phen)_3]X_2.nH_2O$ ($X = ClO_4$, $n = 2$; $X = BPh_4$, $n = 6$)

fac or *mer* $[RuCl_3(Me_2SO)_3]$ (0.2g) was dissolved in ethanol (5 cm^3) and 1,10-phenanthroline (0.28g) (molar ratio 1:3) was added to the solution. To the above reaction mixture, toluene (10 cm^3) was added and heated on a water-bath for 2 h. The solution was concentrated ($\sim$ 5 cm^3) and an ethanolic solution of NH_4ClO_4 or $NaBPh_4$ (molar ratio of the complex : X = 1:3) was added. Complexes separated in similar way as in reaction (g) above.

RESULTS AND DISCUSSION

Synthesis of ruthenium(III) complexes containing 2,2'-bipyridyl or 1,10-phenanthroline were generally reported by the oxidation of their ruthenium(II) analogues.[2-12] Only, in case of mono diimine complexes, direct reactions of commercial $RuCl_3 \cdot xH_2O$ with the diimines were reported.[13-15] We have been able to achieve the synthesis of bis diimine ruthenium(III) complexes using easily synthesizable compounds, viz. fac or mer $[RuCl_3(Me_2SO)_3]$ and $[RuBr_3(Me_2SO)_3]$. Reaction between the Me_2SO complexes and the diimines, resulted under suitable condition, complete substitution of Me_2SO and resulted in the formation of $[Ru(bipy)_2Cl_2]Cl \cdot 2H_2O$ and $[Ru(phen)_2Br_2]Br$ respectively.

$[Ru(bipy)_2Cl_2]Cl \cdot 2H_2O$, synthesised by the substitution of Me_2SO molecules from fac or mer $[RuCl_3(Me_2SO)_3]$, were characterised by the elemental analysis (Table VII.1) and various physical methods. Similarly, $[Ru(bipy)_2Cl_2]ClO_4$, synthesised by the metathesis of the chloro-compound, was also characterised. The electronic absorption spectra of these compounds in acetonitrile were similar to the ones reported earlier.[4-6,16] The IR spectrum showed complete substitution of Me_2SO groups. All characteristic IR bands due to bipyridyl were observed. Far IR spectra showed two bands at 340 and 320 cm^{-1} which may be due to ν_{Ru-Cl}, similar to those reported earlier.[4] Presence of two bands due to ν_{Ru-Cl} conforms to the cis geometry of the complex in solid state.[4] In case of $[Ru(bipy)_2Cl_2]ClO_4$, a very strong band at 1090 cm^{-1} was also observed, which is characteristic of the ClO_4^- group present in the ionic fashion.[21] An EPR spectrum of $[Ru(bipy)_2Cl_2]Cl \cdot 2H_2O$

Table VII.1 Analytical and Physical data of Ruthenium(III) and Ruthenium(II) *Complexes containing 2,2'-Bipyridyl or 1,10-Phenanthroline*

	Compounds	Colour	Λ_M in $\Omega^{-1}cm^2mol^{-1}$ in CH_3CN	Analytical data[a] (%)		
				C	H	N
1.	$[Ru(bipy)_2Cl_2]Cl.2H_2O$	Orange	120	43.1 (43.2)	3.8 (3.6)	9.9 (10.1)
2.	$[Ru(bipy)_2Cl_2]ClO_4$	Brown	130	41.0 (41.1)	2.9 (2.7)	9.4 (9.6)
3.	$[Ru(phen)_2Br_2]Br$	Brown	118	41.0 (41.1)	2.6 (2.3)	7.7 (8.0)
4.	$[Ru(phen)_2Br_2]ClO_4$	Reddish brown	120	39.6 (39.9)	2.0 (2.2)	7.6 (7.8)
5.	$[Ru(phen)_2Br_2]BPh_4$	Orange	120	61.0 (61.2)	3.6 (3.8)	5.6 (5.9)
6.	$[Ru(bipy)_3]Cl_2.H_2O$	Orange	220	54.3 (54.7)	3.6 (3.9)	12.5 (12.8)
7.	$[Ru(bipy)_3]Br_2.2H_2O$	Yellow orange	260	42.4 (42.6)	3.8 (3.3)	9.7 (9.9)
8.	$[Ru(bipy)_3](ClO_4)_2H_2O$	Red	230	45.9 (45.8)	3.2 (3.3)	10.6 (10.7)

Table VII.1 continued

Table VII.1 continued

Compounds	Colour	Λ_M in $\Omega^{-1}cm^2mol^{-1}$ in CH_3CN	Analytical data[a] (%)		
			C	H	N
9. $[Ru(bipy)_3](BPh_4)_2H_2O$	Orange	220	76.0 (76.3)	5.6 (5.5)	6.7 (6.9)
10. $[Ru(phen)_3](ClO_4)_2.2H_2O$	Brown	210	46.2 (46.4)	3.0 (3.0)	8.8 (9.0)
11. $[Ru(phen)_3](BPh_4)_26H_2O$	Yellow orange	220	72.3 (72.6)	5.1 (5.4)	6.0 (6.1)

a : Calculated values are in parentheses

Table VII.2 Electronic Absorption Spectral Data of the Complexes

Compounds	λ_{max} nm (ϵ) in CH_3CN
1. $[Ru(bipy)_2Cl_2]Cl.2H_2O$	420sh; 380 (6.3×10^3); 310sh 295 (2.4×10^4)
2. $[Ru(bipy)_2Cl_2]ClO_4$	425sh; 382 (6.5×10^3); 310sh 295 (2.7×10^4)
3. $[Ru(phen)_2Br_2]Br$	560 (1.36×10^3); 490 (4.30×10^3); 395 (3.25×10^3); 360 (2.93×10^3); 292sh; 267 (4.2×10^4)
4. $[Ru(bipy)_3]Cl_2.2H_2O$	450 (1.15×10^4); 420sh; 390sh 350sh; 288 (6.76×10^4); 254sh; 242 (2.07×10^4)
5. $[Ru(bipy)_3][ClO_4]_2.H_2O$	450 (1.12×10^4); 430sh; 392sh; 325sh; 284 (7.5×10^4); 255sh 240sh
6. $[Ru(bipy)_3][BPh_4]_2.H_2O$	450 (1.32×10^4); 430sh; 395sh; 323sh; 286 (7.8×10^4); 255sh 240sh
7. $[Ru(phen)_3][BPh_4]_2.6H_2O$	442 (1.64×10^4); 418 (1.62×10^4); 315sh; 285sh; 262 (10.2×10^4)

in powder form at room temperature showed only one broad signal around $g = 2.15$. However, a frozen solution EPR spectrum in chloroform at liquid nitrogen temperature (Fig. VII.1) gave two g values, $g_1 = 2.62$ and $g_2 = 2.43$. If one assumes a <u>trans</u> structure in solution, distortion from cubic geometry is expected along the Cl - Ru - Cl axis. Hence two g values are expected.

A reaction of $[RuBr_3(Me_2SO)_3]$ with 1,10-phenanthroline yielded a brown compound of the composition, $[Ru(phen)_2Br_2]Br$. Reactions of $[Ru(phen)_2Br_2]Br$ with NH_4ClO_4 or $NaBPh_4$ in methanolic solution yielded $[Ru(phen)_2Br_2]X$, (X = ClO_4, BPh_4). All these compounds, <u>viz</u>. $[Ru(phen)_2Br_2]X$ (X = Br, ClO_4 or BPh_4) showed molar conductance value in acetonitrile in the range 100 - 110 $\Omega^{-1}cm^2mol^{-1}$, confirming that these are 1:1 electrolytes. The IR spectra of these compounds showed the presence of all the bands due to 1,10-phenanthroline and absence of any Me_2SO groups present. In case of complexes containing ClO_4^- and BPh_4^- anions, IR absorptions at 1085 and 1580 cm^{-1} respectively were also observed which are characteristic of the ionic nature of the respective anionic groups.[21,22] The magnetic moment (μ_{eff}) values at room temperature for $[Ru(phen)_2Br_2]Br$ and $[Ru(phen)_2Br_2]ClO_4$ were 2.2 B.M. and 1.8 B.M respectively, which is characteristic of a low-spin d^5, ruthenium(III) complex. A room temperature EPR spectrum of $[Ru(phen)_2Br_2]Br$ showed a broad signal at $g = 2.18$ which

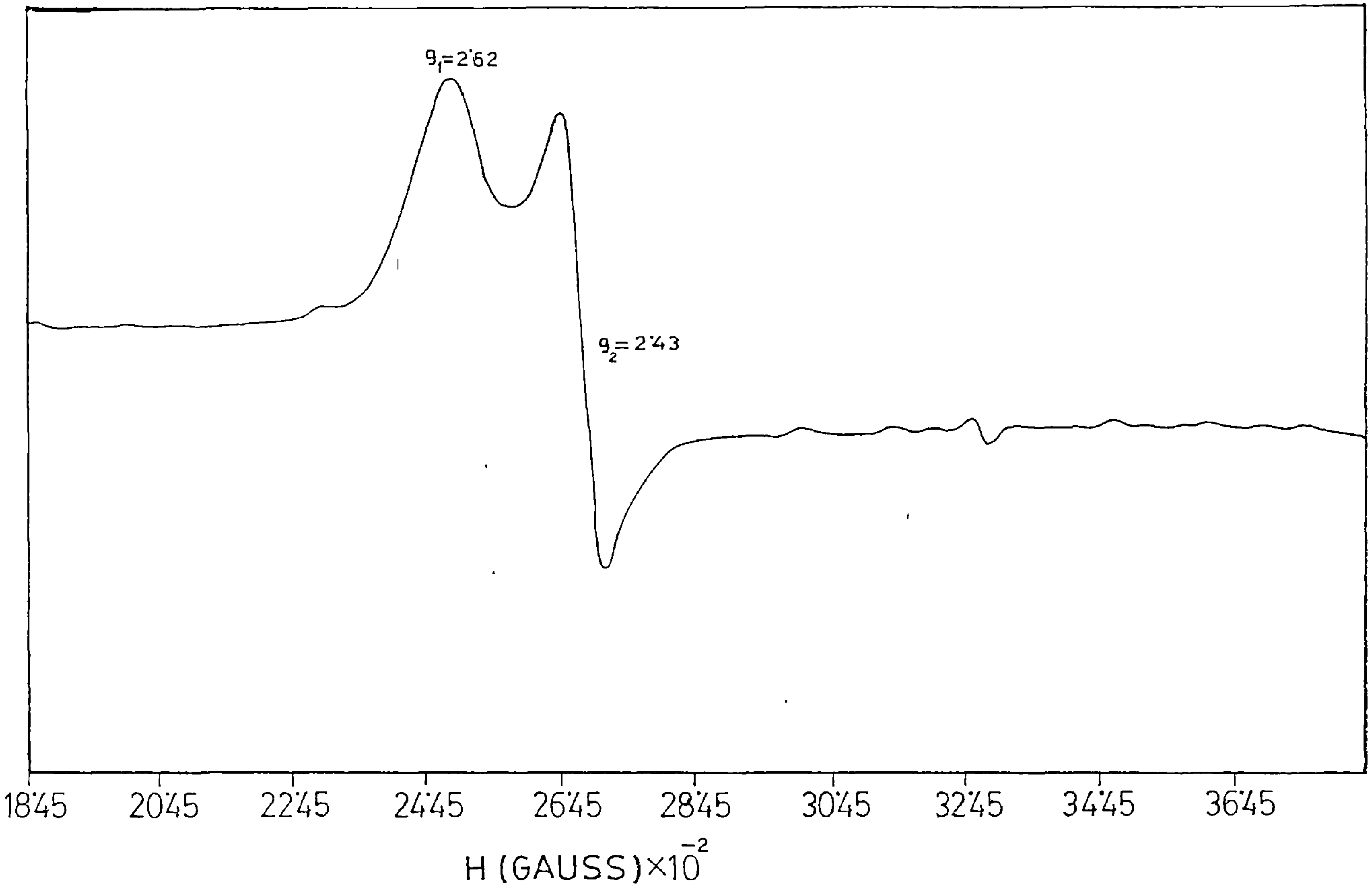

Fig VII.1 E P R SPECTRUM OF FROZEN SOLUTION OF [Ru(bipy)$_2$Cl$_2$] Cl.2H$_2$O IN CHCl$_3$ AT 77°K further confirms the low-spin d^5 configuration for this complex. The electronic spectrum of the complex (Fig VII.2) in CH_3CN showed absorption at 560, 490, 395 and 360 nm in the visible region. These absorptions having ϵ of the order of 10^3 are mostly of the charge transfer type. These bands may be assigned to the charge-transfer from Br^- to the empty orbital on the metal viz. (e_g^*). Similar observations were reported for $[Ru(bipy)_2Cl_2]Cl.2H_2O$.[5] Electronic absorptions in the UV-region were observed at 292 and 265 nm with ϵ of the order of 10^4. These bands may be assigned to $\pi - \pi^*$ type of transitions in 1,10-phenanthroline.[5,23]

$[Ru(bipy)_3]Cl_2$ and $[Ru(L-L)_3]X_2.nH_2O$ (X = ClO_4, BPh_4, L-L = bipy or phen) were obtained by the reaction of fac or mer $[RuCl_3(Me_2SO)_3]$ with excess of the diimines and metathesis of the chloro analogue (obtained in situ), with ClO_4^- or BPh_4^- respectively. $[Ru(bipy)_3]Br_2.2H_2O$ was obtained by the reaction of $[RuBr_3(Me_2SO)_3]$ with excess of 2,2'-bipyridyl. These complexes are diamagnetic in nature, thereby confirming that ruthenium is present in 2+ oxidation state. The reduction of ruthenium(III) in $[RuX_3(Me_2SO)_3]$ (X = Cl or Br) to ruthenium(II) in these compounds is achieved by the diimines, which act both as the ligand and the reducing agents, in these reactions. In fact, most of the methods of preparation of these complexes make use of the reaction of ruthenium(III) or ruthenium(IV) compounds with the diimines.[19] $[Ru(bipy)_3]X_2.H_2O$ (X = ClO_4

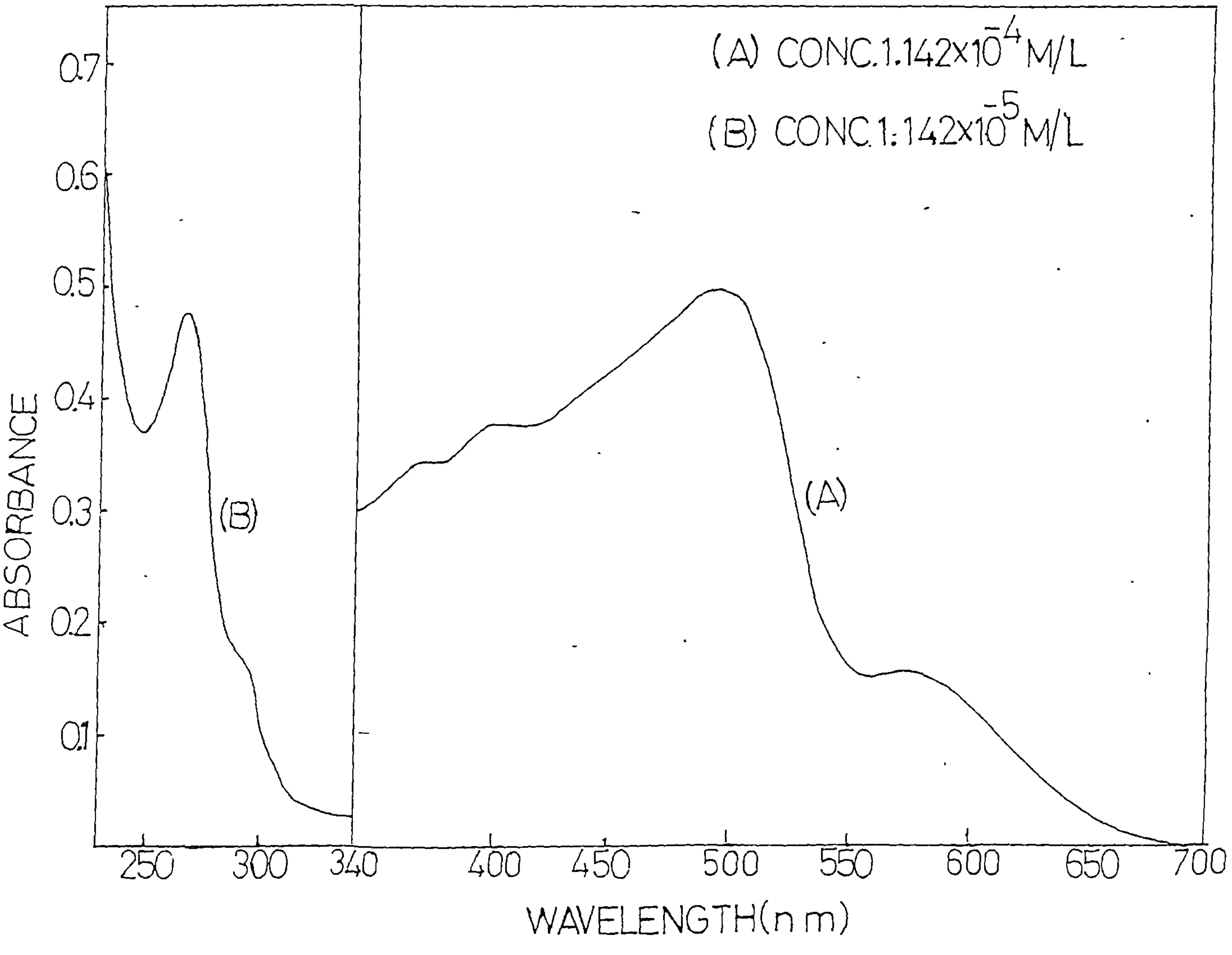

Fig VII.2 ELECTRONIC SPECTRUM OF $[Ru(phen)_2Br_2]Br$ IN CH_3CN

or BPh_4) obtained either from fac or mer $[RuCl_3(Me_2SO)_3]$ or from $[RuBr_3(Me_2SO)_3]$ are same as evidenced from the overlapping IR and ^1H NMR spectra.

The characterization of these complexes was made with the help of analytical data (Table VII.1) and various physical methods. The UV-visible spectra of these complexes were superimposable with those of the reported ones earlier[23-25] (Table VII.2). The IR spectra of all these complexes did not show absorption bands due to Me_2SO groups. All IR absorption bands due to 2,2'-bipyridyl or 1,10-phenanthroline were present. The IR spectra of these complexes in the region 350-200 cm^{-1}, showed no absorption bands, thereby confirming the absence of any covalently bonded terminal chloro groups. Presence of ionic ClO_4^- groups was confirmed by the appearance of a strong and broad band at 1085 cm^{-1}.[21] Presence of BPh_4^- groups in the complexes was confirmed by the appearance of bands at 1575 and 1480 cm^{-1}.[22]

The ^1H NMR spectra of $[Ru(bipy)_3]X_2$ (X = Cl, ClO_4) in $(CD_3)_2SO$ showed a doublet at δ 8.9, a triplet at δ 8.2, and a quintet at δ 7.7. The signals were same as reported for $[Ru(bipy)_3]^{2+}$ systems.[26] The ^1H NMR spectrum of the compound $[Ru(bipy)_3](BPh_4)_2.H_2O$ showed all the signals as mentioned above and more signals in the region δ 6.7 to δ 7.3 which could be assigned due to the phenyl protons of BPh_4^- groups.

The ^1H NMR spectrum of $[Ru(phen)_3](ClO_4)_2$ showed signals in the region δ 7.3 - 8.6. The signals are similar to the ones reported earlier.[27]

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APPENDIX

APPENDIX

LIST OF PUBLICATIONS

1. Ruthenium(II) complexes with triphenylphosphine or triphenylarsine and other monodentate ligands.
   Raj K. Poddar, K.P. Sarma and U.C. Sarma,
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2. Complexes of Ruthenium(III) with dimethylsulphoxide-I. $[Ru_2Cl_6(Me_2SO)_4]$, *fac* and *mer* isomers of $[RuCl_3(Me_2SO)_3]$: Versatile starting materials for the synthesis of Ruthenium(III) complexes.
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   Polyhedron, 1988, **7**,

3. Complexes of Ruthenium(III) and Ruthenium(II) with dimethylsulphoxide-II. $[RuBr_3(Me_2SO)_3]$ and $[RuBr_2(Me_2SO)_3]$: Versatile starting materials for the syntheses of Ruthenium bromo complexes.
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