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

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TO

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Dedicated

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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.

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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

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

A B S T R A C T

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

S-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-phenylene-diamine) are treated with compounds 1, 2 or 3 at room temperature condition. However, in some cases, such compounds are obtained even at higher temperature ($\sim$ 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 fac or mer $[RuCl_3(Me_2SO)_3]$ and characterized to have the Me_2SO molecules bonded through the S-atom and seems to have a cis 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 cis geometry.

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