RESUME AND FURTHER

SCOPE OF THE WORK
5.1 RESUME

The organic chemistry of tellurium has been making great strides both in basic and applied research as evident from the number of research articles appearing in the literature. Tellurium and its organic derivatives in recent years have attracted considerable interest in the field of organic synthesis, ligand chemistry, organic superconductors, photoimaging agents, radio-pharmaceuticals for diagnostic purposes and precursors for semiconducting materials etc.

The ligand chemistry of tellurium which acts as soft donor was little explored until 1970s, probably due to commercial non-availability of a wide-variety of organotellurium ligands and the misconception that they are air-sensitive, foul-smelling and toxic. However, in recent years the coordination chemistry of organochalcogen ligands containing hard donor-atoms (such as N & O) alongwith soft tellurium, has become quite an interesting and active area of inorganic research since such ligand framework can provide insight into competitive coordination behaviour between the hard and soft donors towards a metal centre and also stabilise low as well high oxidation states of a metal atom. Such molecular systems may be important in transition metal catalysed asymmetric synthesis and as single source precursors in MOCVD processes.

Transition metal complexes of macrocyclic ligands have been studied for several years. Recently interest has drawn by their catalytic properties which led to their industrial application. Also, synthetic tetraazamacrocycles are considered typically good models for oxygen carrier due to the presence of four N-donor sites, appropriate for metal ligand binding.

Over recent years, considerable effort has been directed towards the design and synthesis of tellurium containing macrocyclic ligands. Macrocycles that contain different ring sizes and which contain mixed donor functionalities are capable of rich coordination chemistry.

The present work has therefore been undertaken to synthesize metal complexes with tellurium containing 10-membered and 12-membered
tetraazamacrocycles (Te$_2$N$_4$M system) by condensation reactions of diaryltellurium dichlorides and ethylenediamine/1,3-diaminopropane with hard and soft divalent transition metal chlorides.

The thesis entitled, "INVESTIGATIONS ON METAL COMPLEXES WITH ORGANOTELLURIUM LIGANDS" has been divided into four coherent chapters.

The first chapter ‘Introduction’ is a review of literature on various aspects of chemistry of organotellurium compounds. A brief survey of literature of different types of tellurium ligands is compiled in this chapter. A special emphasis has been given on tellurium containing macrocycles – their classification and complexation behaviour with the metal ions. An objective of the present work has also been discussed in this chapter.

The second chapter ‘Synthesis and Physical Properties of Metal Complexes of Tellurium Containing Macrocycles’ deals with the synthesis and physical properties of metal complexes with macrocyclic ligands.

The diaryltellurium(IV) dichlorides, R$_2$TeCl$_2$ (R = p-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, p-methoxyphenyl) are prepared by direct reaction of tellurium tetrachloride with phenol, o-cresol and anisole, respectively.

The divalent metal ions (Mn$^{II}$, Co$^{II}$, Ni$^{II}$, Pd$^{II}$, Pt$^{II}$, Cu$^{II}$, Zn$^{II}$, Cd$^{II}$, Hg$^{II}$) complexes with 10-membered tellurium containing tetraazamacrocycles (Te$_2$N$_4$M) have been prepared by template condensation of diaryltellurium dichloride and ethylenediamine with metal dichlorides in 2 : 2 : 1 molar ratio. The corresponding complexes with 12-membered tellurium containing tetraazamacrocycles are obtained by condensation of diaryltellurium dichlorides and 1,3-diaminopropane with metal chlorides.

A total of 54 complexes have been synthesized during this course of study, which are:
Where, $M = Mn^{II}$, $Co^{II}$, $Ni^{II}$, $Cu^{II}$, $Zn^{II}$, $Cd^{II}$ and $Hg^{II}$

Where,

$M' = Pd^{II}$ and $Pt^{II}$

$n = 2$ or $3$

$R = p$-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, $p$-methoxyphenyl.
These complexes are generally coloured, crystalline solids which are fairly stable in dry air. They possess only limited solubility and dissolve only in more polar donor solvents such as DMSO and DMF. There are only slightly soluble in acetone, acetonitrile, methanol, ethanol and insoluble in non-polar organic solvents like petroleum ether, benzene, carbon tetrachloride and chloroform.

These new complexes have been characterized by conductance and magnetic measurements, electronic absorption, infrared and proton magnetic resonance spectral techniques.

The results of ‘Conductance, Magnetic and Electronic Spectral Studies’ are discussed in the third chapter of the thesis.

The solution behaviour of divalent metal ion complexes with tellurium containing tetraazamacrocycles has been investigated by conductance measurements in dimethylsulphoxide and acetonitrile. The molar conductance data predict these complexes to be weak to 1 : 1 electrolytes (beyond 1 : 1 electrolytes in some cases as well) in solution presumably due to the likely formation of $[\text{MLCl}]^+ \& \text{Cl}^- \text{ or } [\text{MLCl(DMSO)}]^+ \& \text{Cl}^-$ ions in solution. Four complexes namely $\text{HgL}_3\text{Cl}_2$, $\text{CdL}_6\text{Cl}_2$, $\text{HgL}_2\text{Cl}_2$, $\text{CoL}_3\text{Cl}_2$ which behave as 1 : 1 electrolytes in acetonitrile have been subjected to Onsager law and a comparison of $(A + \omega BA^2)$ found to calculated made. This also confirms their 1 : 1 electrolyte type behaviour.

Magnetic moment measurements in conjunction with electronic spectra have been used to gain information about the oxidation state and stereochemistry of central metal ion in these complexes. Complexes of Mn$^{II}$ (5.40 – 5.92 B.M., 5 unpaired electrons), Co$^{II}$ (4.40 – 5.17 B.M., 3 unpaired electrons), Ni$^{II}$ (2.90 – 3.44 B.M., 2 unpaired electrons) and Cu$^{II}$ (1.77 – 2.15 B.M., 1 unpaired electron) are observed to be paramagnetic, whereas those of Pd$^{II}$, Pt$^{II}$, Zn$^{II}$, Cd$^{II}$ and Hg$^{II}$ are found to be diamagnetic in nature. The solution electron absorption spectra in DMSO, alongwith magnetic studies suggest the distorted octahedral or tetragonal geometry for Mn$^{II}$, Co$^{II}$, Ni$^{II}$, Zn$^{II}$, Cd$^{II}$ and Hg$^{II}$ complexes and a square planar geometry for Pd$^{II}$ and Pt$^{II}$ complexes.
The infrared and proton magnetic resonance spectral studies on the metal complexes with tellurium containing tetraazamacrocycles have been presented in Chapter – IV ‘Characterization of Metal Complexes with Tellurium Containing Tetraazamacrocycle – Part B’.

The metal complexes with tellurium containing tetraazamacrocycles have been studied by infrared and proton magnetic resonance spectroscopy.

The infrared spectra of these complexes have been recorded in the region 4000-400 cm$^{-1}$. The spectra are quite complex and an attempt has therefore been made to identify the donor sites of the macrocyclic ligand by comparing the spectra of metal complexes with those of parent diaryl tellurium dichloride and diamine. All the complexes show bonds pertaining of this group in bonding with the metal or diamine. The IR spectra of metal complexes with 10-membered and 12-membered macrocycles do not show bands characteristics of free amino group, instead a single sharp absorption band at 3270-3150 cm$^{-1}$ assignable to coordinated secondary amino group have been observed. This observation confirms the formation of proposed macrocyclic skeleton. Further support to this is extended by appearance of bands of medium to strong intensity at around 1640 cm$^{-1}$ and 880-825 cm$^{-1}$ which may be assigned as N - H deformation coupled with N-H out of the plane bending vibrations. The C–N stretching vibration in these macrocyclic complexes appear at 1200-1160 cm$^{-1}$. Evidences for skeleton of macrocyclic moiety and its coordination through the N-atoms are also provided by appearance of new weak to medium intensity band in the region 480-400 cm$^{-1}$ due to Te - N and M - N stretching vibrations. However, the heavy M – N and M - Cl vibrations could not be ascertained due to non-availability of far infrared data.

A few representative metal complexes with tetraazamacrocycles have also been studied by $^1$H NMR spectroscopy. A comparison of spectra of the complexes with the constituent diarytellurium dichloride and ethylene diamine/1,3-diaminopropane has been made to draw conclusion regarding structure and bonding in these complexes. The phenyl protons in these complexes resonate at a slightly upfield side 6.87 – 7.88 $\delta$ ppm, which may indicate the substitution of two chlorine atoms of diarytellurium moiety by two N-atoms of the amine and hence the
formation of proposed tetraazamacrocyclic skeleton. This gets further support from changes in the proton NMR spectra of ethylenediamine/1,3-diaminopropane. The free amino protons which resonate at 1.19 and 1.15 $\delta$ ppm in ethylenediamine and 1,3-diaminopropane respectively, disappear in the complexes. Instead a broad singlet at relatively downfield side (1.40 – 2.05 $\delta$ ppm) assignable to coordinated secondary amino group appears. This points towards the formation of tellurium containing tetraazamacrocycle and subsequently coordination through the N-atoms of tetraazamacrocycle. The possibility of linkage of Te to the divalent metal ion is also ruled out on the basis of aryl protons chemical shift data.

The infrared and proton magnetic resonance alongwith other studies reveal the tetracoordination of central metal ion in Pd$^{II}$ and Pt$^{II}$ and hexacoordination in Mn$^{II}$, Co$^{II}$, Ni$^{II}$, Cu$^{II}$, Zn$^{II}$, Cd$^{II}$ and Hg$^{II}$ in their respective complexes with square planar or distorted octahedral or tetragonal geometries respectively.

A part of the work has been communicated for publication / presentation and some more research papers are in the process of communication.

5.2 FURTHER SCOPE OF THE WORK

Now since the complexes of divalent metal ions with tellurium containing 10-membered and 12-membered tetraazamacrocycles have been prepared and characterized in the solution as well as in the solid state, attempts may be made to prepare and characterize similar complexes with other metal ions in different oxidation states. This could help in extending the complexation behaviour of these macrocycles and hence in better understanding of their structures.

Structures of these new complexes need further investigation by techniques as far infrared, Raman, X-Ray, Mossbauer, $^{13}$C and $^{125}$Te NMR, Photoelectron and ESR spectroscopy, which would help in confirming the skeleton of Te containing macrocycles and its interaction with the metal ions.
The present work has been confined only to the synthesis of tellurium containing 10-membered and 12-membered tetraazamacrocycles. One may think of designing and synthesis of new tellurium containing large macrocycles with donor atoms other than nitrogen (oxygen or sulphur). Such macrocycles which contain different ring sizes and mixed donor functionalities would be able of providing rich coordination chemistry. Also, these molecular systems may find applications in transition metal catalysed asymmetric synthesis and also as single source precursors in MOCVD processes and hence may be investigated towards such applications.

Also, synthetic tetraazamacrocyle molecules are considered typically good models for oxygen carrier due to the presence of four N-donor sites appropriate for metal-ligand binding. In line with the various bioinorganic applications in nucleic acid chemistry like foot-printing and sequence specific binding agents for modelling the restriction enzymes in genomic research, and as structural probes for therapeutic applications in cancer treatment, these tellurium containing macrocycles may also be investigated for.

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