Abstract

This thesis describes the physico-chemical studies of metal complexes with nitrogen and sulphur donor ligands. Emphasis has been given to the synthesis and characterization of polyazamacrocycles and dithiocarbamato complexes of transition metal ions and Sn(IV). They have been characterized by FT-IR, NMR (\(^1\)H, \(^{13}\)C and \(^{119}\)Sn), mass spectrometry and X-ray crystallography. In some cases they have been studied by TGA/DSC. Some of the ligands and their complexes have been tested for their antibacterial and antifungal activity. The thesis is divided into six chapters.

The first chapter highlights the major advances in the area of transition metal ions and Sn(IV) with polyazamacrocycles and dithiocarbanates. It explores various chemical and biological applications of polyazamacrocycles and dithiocarbanates in general.

Chapter 2 describes the synthesis of fourteen membered hexaza macrocyclic complexes of the type \([\text{CuL}]X_2\) and \([\text{CuL}^1]X_2\) [where \(L = 3,10\text{-bisbenzyl-1,3,5,8,10,12-hexaazacyclotetradecane}\) and \(L^1 = 3,10\text{-bisbenzyl-6,13-dimethyl-1,3,5,8,10,12-hexaaza-cyclotetradecane}\) and \(X = \text{ClO}_4^- (1, 4) \text{SCN}^- (2) \text{ and PF}_6^- (3, 5))\]. These air stable monometallic complexes have been synthesized by template assisted condensation reaction and characterized by spectral and X-ray crystallographic techniques. An attempt has been made to study the effect of anions on the gross geometry and chemical properties of the Cu(II) ion. Their crystal structure show axially elongated octahedral geometry with weakly coordinated anions. The macrocyclic cyclam adopts trans-III configuration with six- and five-membered chelate rings in chair and gauche conformation, respectively. It was also observed that in the solid state the arrangement of the coordination sphere is distorted octahedral whereas in solution, a square-planar structure is predominant. The molar conductance
of the complexes indicates that the axially bonded anions are almost entirely
dissociated in acetonitrile solution. The EPR spectra of complexes 1-4 are axial and
consistent with a $d_{x^2-y^2}$ ground state.

In chapter 3, the synthesis and spectral characterization of azido derivative of
Cu(II) complexes with macrocyclic ligands of the type $[\text{CuL}(\text{N}_3)(\text{ClO}_4)\cdot\text{3/2O}]_n$ (1),
$[\text{CuL}(\text{N}_3)_2]$ (2) and $[\text{CuL}^1(\text{N}_3)(\text{ClO}_4)]_n$ (3) have been described. On the basis of
single-crystal X-ray diffraction studies 1 and 3 have been found to adopt a 1D infinite
polymeric chain structure where Cu(II) ions are bridged by single azide ligands in $\mu$-
1,3 (end-to-end) bridging mode in a trans-position with respect to the azide unit.
When $[\text{CuL}(\text{N}_3)(\text{ClO}_4)\cdot\text{3/2O}]_n$ was recrystallized from acetone, non-polymeric
polymorph 2 was obtained, where the Cu(II) ion is in a tetragonally distorted
equatorial environment with four equatorial N atoms of the macrocycle and two
monodentate azide ligand in trans axial position. The chains of
$[\text{CuL}(\text{N}_3)(\text{ClO}_4)\cdot\text{3/2O}]_n$ and $[\text{CuL}^1(\text{N}_3)(\text{ClO}_4)]_n$ propagate parallel to the
crystallographic b-axis and are stacked one over the other along the c-axis by
hydrogen bonding. The 1D chains of 1 are in hexagonal close packing arrangement.
The azido groups exhibited asymmetric coordination behaviour for 1 and 2 while that
of 3 was found to be symmetrical. The ClO$_4^-$ ions fill up the channel formed between
the strings of octahedra and are held by hydrogen bonds leading to the formation of
3D network.

In chapter 4, a fascinating molecule $[\text{NiL}](\text{ClO}_4)_2$ has been explored {where L
= 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo-(3.3.1)nonane}. The heterobimetallic
$[\text{Ni}(\text{L})][\text{CoCl}_4]$ was synthesized in high yield by a facile reaction between
$[\text{Ni}(\text{L})](\text{ClO}_4)_2$ and $[\text{CoCl}_2(\text{PPh}_3)_2]$. The X-ray crystal structure of $[\text{Ni}(\text{L})][\text{CoCl}_4]$
clearly establishes the cationic-anionic interaction. A square-planar geometry is evident for the \([\text{Ni(L)}]^2+\) cation while the anion is found to be tetrahedral. A two step thermolytic pattern is observed in the pyrolysis of the bimetallic complex. In another setup \(\text{Ni(dtc)}_2\) \([\text{dtc} = \text{diethyldithiocarbamate}]\) was synthesized by the interaction of \(\text{NiL(ClO}_4)_2\) with sodium diethyldithiocarbamate. Although the crystal structure of \(\text{Ni(dtc)}_2\) has already been reported \((R=10.6\%)\) we have refined its crystal structure up to \(R = 2.99\%\). We have also observed the rare \(\text{C--H---Ni}\) anagostic interactions, generally exhibited by \(d^8\) complexes which were previously overlooked. To investigate the structure of \(\text{Ni(dtc)}_2\) in solution, variable temperature NMR spectra have also been recorded between 25 °C to minus 50 °C.

In chapter 5, the interaction of potassium bis(2,2-dithiopiperazinato-2,2-diamino-diethylamine \((K_2L)\) with \(R_2\text{SnCl}_2\) leading to the formation of bimetallic complexes of the type \(R_4\text{Sn}_2L_2\) \(\{\text{where } R = \text{CH}_3 (2), \text{C}_4\text{H}_9 (3), \text{C}_6\text{H}_5 (4)\}\) and \(\text{Sn}_2\text{L}_2\text{Cl}_4\) \((5)\) \([L = \text{bis(2,2’-dithiopiperazinato-2,2’-diaminodiethylamine) dithiocarbamate}]\) have been reported. They have been characterized by FT-IR, UV-vis, \(^1\text{H NMR}, ^{119}\text{Sn NMR}, \text{ESI-MS}, \text{TGA/DSC}, \text{microanalysis and molar conductivity data}. On the basis of FT-IR spectral studies, a symmetrical bidentate coordination has been proposed for all the complexes while the absence of any higher peak in the ESI-MS suggests the formation of binuclear complexes. On the basis of \(^{119}\text{Sn NMR} \)spectra, six-coordinate geometry has been observed for the Sn-atom in all the complexes. The TGA/DSC profile of the complexes implies their higher stability than its precursor. However, on the basis of IDT values the stability of the organotin complexes was found to follow the order \(4 > 3 > 2\). The molar conductivity value of 1 mM solution of the complexes suggests their non-ionic nature.
In chapter 6, the synthesis of a mononuclear precursor complex, \([(\text{CH}_3)_2\text{Sn(tpdtc)}]\) and several heterobimetallic derivatives of the type, \([(\text{CH}_3)_2\text{Sn(tpdtc)}]M\text{Cl}_2\) have been synthesized by simple addition of transition metal chlorides, where tpdtc = tetraethylenepentamine bis(dithiocarbamate), M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). They have been characterized by physicochemical and spectral techniques. A square-pyramidal geometry has been proposed for all the complexes with one chloride ion occupying the axial while the three nitrogen atoms and second chloride occupying the equatorial positions. A symmetrical bidentate coordination leads to the formation of 18 member cavity. The thermal studies reveal that the mononuclear complex decomposes in three stages while its heterobimetallic analog exhibits a simple two-stage profile. The conductivity measurement data (1 mM solution) implies a non-electrolytic behavior for them which is evident by their low conductivity values measured at room temperature. The heterobimetallic complexes have also been tested for their antibacterial (Escherichia coli and Pseudomonas aeruginosa) and antifungal activity (Aspergillus niger and Fusarium oxysporum). All the complexes were found to be active against the test organisms and maximum activity was found for \([(\text{CH}_3)_2\text{Sn(tpdtc)}]\)CuCl_2.