Summary

The coordination chemistry of pyridinecarboxamide derivatives is quite extensive and their complexes exhibit different geometries and coordination numbers. While extensive studies have been directed to elucidate the structures of complexes of N-pyridinecarboxamides and \( \text{N,N'-pyridinedicarboxamides} \) and their modified multifunctional ligands, only a limited number of investigations have been reported so far for the complexes of pyridinedithiocarboxamides. The primary objective of the present work was aimed at:

1) The preparation and characterization of various \( \text{N,N,N',N'-tetraalkylpyridine-2,6-dithiocarboxamide} \) derivatives (R = Me, Et, \( \text{^t} \text{Pr, } \text{^t} \text{Bu and Ph} \)) and their complexes with the transition elements namely Cu(II), Co(II) and Ni(II).

2) To ascertain the degree of magnetic coupling between metal centre in case of polynuclear complexes.

3) To study the effect of steric congestion caused by the introduction of bulky groups on the side arms on the solid state geometry of these complexes.

The work presented in this thesis has been apportioned into three parts. The first chapter reviews primarily the structural diversity, exhibited by the pyridinecarboxamides in their complexes with various transition metals. This chapter also briefly spells out the scope of the work presented in this dissertation.

The second chapter deals with the experiments carried out to prepare and purify the starting materials either by known literature methods or by improvised procedures, together with the preparation of hitherto unknown pyridine- dithiocarboxamides and their complexes with salts of Cu(II), Co(II) and Ni(II). The complexes were identified and characterized with melting points, elemental analyses, \(^1\text{H-NMR}, \) vibrational spectroscopy, electronic spectroscopy and X-ray crystallography. Magnetic measurements were carried out for a few complexes. These measurements give important
information about the presence of magnetic exchanges taking place in polynuclear complexes. For mononuclear complexes these studies indicate the presence of orbital coupling in the complexes. ESR studies have been reported for some complexes to know the value of zero field splitting parameter. The results have been discussed in three sections:

The first section deals with the preparation and characterization of Cu$_2$Cl$_4$.S-dapt (S-dapt = S-dmpt, S-dept, S-dpp, S-dhp, S-mppt and S-mmpt), CuBr$_2$.S-dapt (S-dapt = S-dmpt, S-dept, S-dpp and S-dhpt), CuCl. ClO$_4$.S-dapt (S-dapt = S-dept, S-dp and S-dbpt), [Cu(S-dept)$_2$](X)$_2$, (X= BF$_4$' , ClO$_4$' and PF$_6$'). These compounds were prepared by reacting anhydrous Cu(II) salts with appropriate ligands in 1:1 or 2:1 molar ratios using suitable anhydrous solvents.

The 2:1 complexes Cu$_2$Cl$_4$(S-dapt) (R= Me, Et, 'Pr, 'Bu and Ph) have been shown to consist of anionic dimer [Cu$_2$(μ-Cl)$_2$Cl$_2$]$^2$ and a cationic moiety which can be monomeric [Cu.CI.(S-dept)]$^+$ or dimeric [(Cu.CI.(S-dept))]$^2$. These observations are well supported by elemental analyses and molar conductance values and are authenticated by X-ray crystal structure determination of Cu$_2$Cl$_4$.S-dept 2, Cu$_2$Cl$_4$.S-dept.EtOH 3, Cu$_2$Cl$_4$.S-dpp 4 and Cu$_2$Cl$_4$.S-dbpt 5. Their X-ray crystal structures reveal that these complexes are composed of anionic and cationic dimers, that in both cases contain the metal centers which interact via coulombic and/or hydrogen bonding interactions. In both cases the Cu centers in the anionic moieties adopt a slightly distorted tetrahedral geometry whereas for the cationic moieties they adopt square-pyramidal type of geometry. Magnetic susceptibility data show that compounds 2 and 3 present an overall antiferromagnetic behavior arising from the contribution of both anionic and cationic moieties. For 2, the best fit obtained gave $J_1 = -2.62±0.19$ cm$^{-1}$, $J_2 = -19.54±0.47$ cm$^{-1}$ and $g_2 = 2.164±0.004$ cm$^{-1}$ ($R = 8.28 \times 10^{-5}$) whereas for 3 it gave $J_1 = 4.48±2.73$ cm$^{-1}$, $g_1 = 2.20±0.03$, $J_2 = -11.26±2.01$ cm$^{-1}$ and $g_2 = 2.10±0.03$ ($R = 1.15 \times 10^{-4}$).

The nature of the superexchange pathways in 2 and 3 is discussed based on structural, magnetic and molecular orbital considerations. Theoretical calculations have been performed at Extended Hückel level in order to obtain their molecular orbitals and energies using their crystallographic data.
The compound 4 contains two cationic units, \([\{\text{Cu}(\text{S-dppt})\text{Cl}\}^+]\) and an anionic dimer with the formula \([\text{Cu}_2\text{Cl}_4(\mu-\text{Cl})_2]^{2-}\). It is noticeable that the cationic fragments present no Cu...Cu interaction owing to the intervening presence of the dinuclear anionic unit. The coordination geometry around each Cu(II) ion is slightly distorted square planar which is bonded by the pyridylic N atom and the two S atoms of S-dppt ligand and also by a terminal chloro ligand. The anionic fragment in compound 4, \([\text{Cu}_2\text{Cl}_4(\mu-\text{Cl})_2]^{2-}\), consists of two tetra-coordinated Cu metal centers bridged by two chloro ligands. The coordination environment of each Cu(II) atom is completed with two terminal Cl atoms, determining a tetrahedrally distorted geometry around the metal. Complex 5 consists of a cationic binuclear moiety, \([\text{Cu}_2(\text{S-dbpt})_2(\mu-\text{Cl})_2]^{2+}\), and anionic species with formula \([\text{Cu}_2(\mu-\text{Cl})_2\text{Cl}_4]^{2-}\). The anionic fragment in 5 consists of two tetra-coordinated Cu metal centers bridged by two chlorine ligands. The coordination environment of each Cu atom is completed with two terminal Cl ligands, determining a distorted tetrahedral geometry around the metal. In the cationic fragment, each copper atom is penta-coordinated by the pyridilic N atom and the two S atoms of the S-dept ligand, as well as by two chlorine atoms acting as bridging ligands. Each metal center presents a distorted square pyramidal geometry. Both square pyramids in the dimeric unit share a basal-to-apical edge in such a way that the corresponding basal planes are disposed in a parallel fashion and are related by a \(C_2\) symmetry axis.

Magnetic susceptibility measurements suggest an antiferromagnetic interactions for compounds 2 and 3. The fit of the data for 2, suggests two contributions towards magnetic susceptibility: one arising from the super exchange interaction within the dimeric anionic complex and another one from the two \([\text{CuCl}(\text{S-dept})]^+\) units bridged through the S atoms of the S-dept ligand \([\chi_M T = (\chi_M T)_{\text{dimer1}} + (\chi_M T)_{\text{dimer2}}]\). For compound 3 case, the overall magnetic coupling throughout the compound is weakly antiferromagnetic in nature, with a \(J\) value around -11 cm\(^{-1}\). It is not obvious to decide whether this coupling is due primarily to a super exchange pathway taking place through the chloro bridges in the cationic moiety (first approach described), or if it is due to the
hydrogen bonding between monomeric anions (second approach), since a good fit is obtained regardless of the approach utilized.

Compounds of copper(II) bromide with S-dapt (R= Me, Et, iPr and iBu) corresponds to composition CuBr₂·S-dapt and the copper ion appears to be five coordinated. Complexes [Cu(S-dept)₂](X)₂, (X= BF₄⁻, ClO₄⁻ and PF₆⁻) behave as 1:2 electrolytes and geometry around copper ion in [Cu(S-dept)₂]²⁺ appears to be octahedral.

In the second section, synthesis and structural investigations on the following compounds of Co(II) salts with S-dapt ligands have been discussed: Co₂Cl₄·S-dapt (S-dapt = S-dmpt, S-dept, S-dppt, S-dbpt, S-dphpt) were prepared by reaction between anhydrous CoCl₂ and appropriate ligand. The crystal and molecular structure of a 2:1 complex of CoCl₂ with S-dept [Co₂Cl₄(S-dept)], has been determined. The compound is built up of {Co(S-dept)Cl}⁺ and [Co₂Cl₄(µ₂-Cl)₂]²⁻ groups. The cobalt atom in the cation is bonded to two sulphur atoms, a pyridilic nitrogen atom of the S-dept ligand, and a chlorine atom in a distorted square planar geometry. The {Co(S-dept)Cl}⁺ units are stacked over each other in a staggered manner so that each cobalt atom interacts weakly with a sulphur atom of a unit above and below it. The anionic cobalt is present as the centrosymmetric [Co₂Cl₄(µ₂-Cl)₂]²⁻ ion in which two chlorine bridges complete tetrahedral coordination about the cobalt atoms. Based on the composition similar geometry can be expected for other complexes.

CoX₂·(S-dapt) [X = Br, I, NCS and NCSe and (S-dapt = S-dmpt, S-dept, S-dppt, S-dbpt, S-dphpt] were prepared by reaction between anhydrous Co(II) salt and the appropriate ligand. Mononuclear cobalt(II) complexes, [Co(S-dept)X₂] [X = Br(25), I(30) and NCS(35)] and [Co(S-dphpt)Br₂] 28 were characterised by conductivity, spectral and single crystal X-ray diffraction studies. These studies reveal that the compounds consist of discrete monomeric molecules in which the cobalt atoms are five-coordinated in an environment that is best described as being distorted square pyramidal. In dimethylformamide the iodo complexes show significant ionic dissociation (1:1 electrolytes) and their crystal field absorption spectra are interpretable in
terms of octahedral structure \[\text{[Co(S-dapt)(DMF)\_2]}^+\]. Magnetic susceptibility measurements suggest an antiferromagnetic interactions for these compounds. The temperature dependence of the magnetic susceptibility data on compounds are indicative of high-spin compounds with a important zero-field splitting. The best fit was obtained with \(|D| = 20.5 \text{ cm}^{-1}\) and \(g = 2.53\) for 25, \(|D| = 14.2 \text{ cm}^{-1}\) and \(g = 2.38\) for 30 and \(|D| = 17.7 \text{ cm}^{-1}\) and \(g = 2.35\) for 35. The X-band EPR spectra at low temperature is also characteristic of an \(S = 3/2\) with important zero-field splitting. The most important band appears at low fields \((\sim 1200 \text{ G})\). In all cases, the coordination polyhedron of the Co(II) ion is a distorted square pyramid, with an electronic configuration of high-spin. Although there is no correlation between the angle of rotation of thioamide groups and the pyridine ring, but the conformation of the ligand is dependent on the size of the anion. The compounds show major distortion in the geometry with large out-of-plane displacement of the Co(II) ion, of \(\sim 0.6\) to \(0.74 \text{ Å}\). The distortion of the geometry, due to the S-dept ligand with voluminous donor atoms, could explain the stabilization of the \(S = 3/2\) than the \(S = 1/2\) state.

Important zero-field splitting is observed, as it could be expected for high-spin Co(II) compounds. The \(D\) value seems to be very sensitive to the nature of the ligand. The compounds reported in the literature, with CoO\(_2\)N\(_2\) core show larger \(|D|\) values than compounds 25, 30 and 35, with a CoNS\(_2\)X\(_2\) core. The smallest value corresponds to compound 30 containing more diffuse donor atoms (CoNS\(_2\)I\(_2\) core) with maximum covalence of the Co-L bonds. The EPR spectra at low temperature show two bands, at low fields, characteristic of systems with a ground state \(S = 3/2\) and an important zero-field splitting as is the case for Co(II) compounds. Complexes \([\text{Co(S-dept)\_2}]^+(X)\) \((X = \text{BF}_4^-, \text{ClO}_4^-\text{ and PF}_6^-)\) behave as 1:2 electrolytes and geometry around cobalt ion in \([\text{Co(S-dept)\_2}]^{2+}\) appears to be octahedral.

In the third section, syntheses and structural investigations of the following compounds of Ni(II) salts have been discussed: Ni\(_2\)Cl\(_4\).S-dept and Ni(SCN)\(_2\).S-dept (S-dept = S-dept, S-dppt, S-dbpt) were prepared by reaction between anhydrous Ni(II) salt and the appropriate ligand. Complex
Ni(SCN)$_2$(S-dept), 44 shows two distinct $v$(CN) modes for the NCS$^-$ group, at 2087 and 2007 cm$^{-1}$. The higher frequency band is assigned to the N-bonded terminal thiocyanate group and the lower frequency band at 2007 cm$^{-1}$ strongly indicates the presence of N-bridging thiocyanate ligand joining the two nickel centres. This unusual bridging mode of thiocyanate ligand has been observed for a very limited number of complexes. The peaks attributed to NCS are not perturbed in its solution spectrum thus suggesting that the solid state structure is retained in CHCl$_3$ solution. In the crystal lattice, complex 44 exists as a centrosymmetric dimer in which the dinuclear core is bridged by two N-bonded thiocyanate groups. The near octahedral geometry of the nickel atom is achieved through the two bridging N atoms of the thiocyanate groups, three SNS donor atoms of the ligand S-dept and through the terminal nitrogen atom of a nonbridging thiocyanate moiety. To the best of our knowledge, complex 44 presents the first example in literature with the highest asymmetry in N-bridging thiocyanato ligands. Magnetic susceptibility measurements suggest weak antiferromagnetic interactions for this compound.