SUMMARY AND CONCLUSION

The chemistry of transition metal complexes of thiosemicarbazones has been receiving considerable attention largely because of their pharmacological properties. Due to their interesting biological activities, such as antibacterial, anti-convulsant and antiproliferative-antitumor, thiosemicarbazones have attracted great attention in the recent years. The biological activity and the medicinal properties of thiosemicarbazones depend upon the chemical nature of the moiety attached to the C=S carbon atom. The structure diversity of thiosemicarbazide based compounds is considerably increased not only due to the condensation of the different carbonyls but also due to the alkylation of the different part of the thiosemicarbazide. Thiosemicarbazone usually act as chelating ligands with transition metal ion, bonding through the sulfur and hydrazine nitrogen atom. Thiosemicarbazones can coordinate to metal as neutral molecules or after deprotonation, as anionic ligands and can adopt variety different coordination modes. The possibility of their being able to transmit electronic effects between a reduce unit and metal centre is suggested by the delocalization of the π bonds in the thiosemicarbazone chain.

Thiosemicarbazones \( (R^1R^2C^{\equiv}=N^3\cdots-N^2(H)\cdots-C^1(=S)N^1R^3R^4) \) constitute an important class of N, S-donor ligands, and their coordination chemistry
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was initially explored during the early sixties. The synthesis of thiosemicarbazones involves condensation of a ketone, or an aldehyde with a thiosemicarbazide under ambient conditions. They are represented by the general formula $R^1R^2C=N–NH–C(S)–NH_2$. In the solid state, these thiosemicarbazones exist in the thione form. In solution, however, they are known to tautomerize into the thiol form. Complexation usually takes place via dissociation of the acidic proton, resulting in the formation of a five membered chelate ring. When an additional donor site D is incorporated in such ligands, linked to the carbonylic carbon via one or two intervening atoms, D,N,S tricoordination usually takes place.

Objectives of the present work

Thiosemicarbazones have emerged as an important class of ligands over a period of time, for a variety of reasons, such as variable donor properties, structural diversity and biological applications. In order to pursue the interesting coordinating properties of thiosemicarbazones, complexes with different types of ligand environments are essential. With this knowledge taken from the literature, we undertook the present study by taking two different NNS and ONS donor types thiosemicarbazones as principal ligands. Introduction of heterocyclic bases like 1,10-phenanthroline, 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine and 5,5′-dimethyl-2,2′-bipyridine, and anions like azide, chloride, dicyanamide, thiocyanate etc., the classical $N,N$ donor ligands leads to the syntheses of mixed-ligand complexes which can cause different bonding, spectral properties and geometries in coordination compounds.
We have synthesized the following two new and two earlier reported ligands using 4-benzyloxsalicylaldehyde, 5-bromosalicylaldehyde, 2-benzoypyridine 4-phenylthiosemicarbazide, 4-ethylthiosemicarbazide, 4-methylthiosemicarbazide and N,N-dimethylthiosemicarbazide.

- 4-Benzyloxsalicylaldehyde–N^4–phenylthiosemicarbazone (H_2bspt)
- 5-Bromosalicylaldehyde –N^4-ethylthiosemicarbazone (H_2brset)
- 2-Benzoylpyridine –N^4-ethylthiosemicarbazone (Hbpet)
- 2-Benzoylpyridine –N^4,N^4-dimethylthiosemicarbazone (Hbpdt)

Summary of the thesis:
The thesis is divided into seven chapters.

Chapter 1

Chapter 1 involves a brief overview to thiosemicarbazones and their metal complexes, bonding and coordination nature of thiosemicarbazones and their various applications. The objectives of the present work and the various physicochemical methods adopted for the characterization of the thiosemicarbazones and their complexes are also discussed in this chapter.

Chapter 2

Chapter 2 describes the syntheses of four tridentate thiosemicarbazones and their characterization by elemental analyses, mass, FT-IR, UV-Vis and ¹H NMR spectral studies. Among the four ligands two are ONS and remaining are NNS ligands. X-ray quality single crystals of these two ligands were grown and their molecular structures were established by single crystal X-ray diffraction studies.
The thiosemicarbazones synthesized are

- 4-Benzylloxsalicylaldehyde–$N^4$-phenylthiosemicarbazone ($H_2$bspt)
- 5-Bromosalicylaldehyde –$N^4$-ethylthiosemicarbazone ($H_2$brset)
- 2-Benzoylpyridine –$N^4$-ethylthiosemicarbazone (Hbpet)
- 2-Benzoylpyridine –$N^4,N^4$-dimethylthiosemicarbazone (Hbpdt)

**Chapter 3**

This chapter deals with the coordination chemistry of four oxidovanadium(IV) complexes derived from 4-benzylloxsalicylaldehyde–$N^4$-phenyl thiosemicarbazone and a dioxidovanadium(V) complex derived from 2-benzoylpyridine–$N^4,N^4$-dimethyl thiosemicarbazone.

All complexes except the dioxidovanadium complex are mononuclear with heterocyclic bases 1,10-phenanthroline, 2,2’-bipyridine, 4,4’-dimethyl-2,2’-bipyridine and 5,5’-dimethyl-2,2’-bipyridine as coligands. All the complexes are characterized by various techniques such as elemental analyses, molar conductivity and magnetic susceptibility measurements, FTIR, UV-vis and EPR spectral studies. The observed molar conductivity values in $10^{-3}$ M DMF solution confirm that all the complexes are non-electrolytic in nature. Magnetic susceptibility measurements clearly indicate that all the complexes except the dioxidovanadium complex are paramagnetic in nature with vanadium in $+4$ oxidation state. In all the complexes except the dioxidovanadium complex, thiosemicarbazones are coordinated to the metal centre in the thioiminolate form and act as dideprotonated tridentate ligands. In the EPR spectra, $g$ values are found to be less than the free electron value.
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and in DMF at 77 K, they displayed well resolved axial anisotropy with two sets of eight line pattern with $g_\parallel < g_\perp$ and $A_\parallel > A_\perp$ relationship characteristic of an axially compressed $d^{1}_{xy}$ configuration. We could isolate X-ray quality single crystals for the dioxidovanadium complex by the slow evaporation of the mother liquor. The molecule exhibited distorted square pyramidal geometry with N, N and S atoms of the principal ligand and one of the oxo group occupying the square plane and the other oxo group occupying the axial position. There are no intra and intermolecular hydrogen bonds in the molecule. The neighbouring molecules are interconnected by $\pi \cdots \pi$ and C–H···π interactions.

Chapter 4

Chapter 4 deals with the syntheses and characterization of six nickel complexes of the thiosemicarbazones by CHNS analyses, conductivity and magnetic susceptibility measurements, infrared and electronic spectral studies. All the complexes are found to be non-electrolytic in nature. The five-coordinate complexes are found to be paramagnetic with two unpaired electrons. In all of them, thiosemicarbazone moiety coordinates to the metal in the thioiminolate form as evidenced from the infrared spectra. We could isolate X-ray quality single crystal for one of the nickel complex by the slow evaporation of the mother liquor. The nickel(II) atom has square-planar geometry surrounded by one sulfur atom and three nitrogen atoms. In the crystal packing three molecules are linked through hydrogen bonding i.e., two molecules are bridged by a third one. Further, crystal packing is reinforced by very weak $\pi \cdots \pi$ and metal···π interactions.
Chapter 5

This chapter describes the syntheses and characterization of nine copper(II) complexes. The characterization techniques include elemental analyses, molar conductivity studies and magnetic susceptibility measurements, FTIR, UV-Vis and EPR spectral studies. Heterocyclic bases like 1,10-phenanthroline, 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine and 5,5'-dimethyl-2,2'-bipyridine were used as coligands and iodide and azide as anions. In all the complexes, the ONS donor thiosemicarbazones (H₂bspt and H₂brset) exist in thioiminolate form and coordinates to the metal through azomethine nitrogen, thioiminolate sulfur and phenolate oxygen. For NNS donor thiosemicarbazones, the ligands coordinate to the metal through azomethine nitrogen, thioiminolate sulfur and pyridyl nitrogen. The molar conductivity values obtained for all the complexes confirmed their non-electrolytic nature. The magnetic susceptibility measurements reveal that all the complexes are paramagnetic and for mononuclear complexes the effective magnetic moment values are found to be close to the spin only value which corresponds to a single unpaired electron. The low magnetic moment values for two complexes may be due to considerable antiferromagnetic interaction between the metal centers. EPR spectra in polycrystalline state at 298 K show that some of the compounds are isotropic and some are axial. In DMF at 77 K, some complexes are found to be axial with hyperfine lines in the parallel and perpendicular regions. Superhyperfine splittings give clear evidence for the coordination of azomethine nitrogen and that of heterocyclic bases to the metal. The g values calculated indicate that in most of the complexes the unpaired electron in
Cu(II) resides in the $d_{x^2-y^2}$ orbital. The complexes in which $g_{||} > g_\perp > 2.0023$ suggest a distorted square pyramidal structure and rules out the possibility of a trigonal bipyramidal structure which would be expected to have $g_{||} < g_\perp$.

**Chapter 6**

Chapter 6 explains the syntheses and characterization of eight zinc complexes of the thiosemicarbazones by CHNS analyses, conductivity and magnetic susceptibility measurements, infrared and electronic spectral studies. The observed molar conductivity values in $10^{-3}$ M DMF solution confirm that all the complexes are non-electrolytes. The tridentate character of the thiosemicarbazones is inferred from IR spectra. The structure of two of the complexes $[\text{Zn(bpet)(dca)}]_n$ and $[\text{Zn(Hbpet)}](\text{NO}_3)_2\cdot\text{H}_2\text{O}$ has been resolved using single crystal X-ray diffraction studies. The crystal structure revealed a monoclinic space group $P2_1$ for complex $[\text{Zn(bpet)(dca)}]_n$ and orthorhombic space group $Pca\overline{2}_1$ for $[\text{Zn(Hbpet)}](\text{NO}_3)_2\cdot\text{H}_2\text{O}$. The compound $[\text{Zn(bpet)(dca)}]_n$ adopts a distorted square pyramidal geometry. Basal plane consist of azomethine N, pyridine N and S atom from ligand and N atom from dicynamide ligand and the axial site is occupied by a N atom of dicynamide ligand of the next unit. The dicyanamide ligand employed the $\mu_{1,5}$ bridge mode linking the adjacent Zn atom to produce one dimensional zig-zag chains. In compound $[\text{Zn(Hbpet)}](\text{NO}_3)_2\cdot\text{H}_2\text{O}$, Zn centre displays a distorted octahedral geometry and the ligand is coordinated in the neutral form. The zinc in the complex is hexacoordinated through two thioamide sulfur atoms, two azomethine nitrogen and two pyridyl nitrogen atoms.
The basal plane consist of two pyridyl nitrogen and two thioamide sulfur atoms and the apical positions are occupied by azomethine nitrogen atoms. Three-dimensional (3D) polymeric network arrangement was built via weak N–O····π and CH····π interactions between [Zn(Hbpet)] moieties.

The $^1$H NMR spectral data of the ligand Hbpet and its complex [Zn(Hbpet)](NO$_3$)$_2$·H$_2$O were recorded in DMSO-d$_6$ with tetramethylsilane as an internal standard. In the case of [Zn(Hbpet)](NO$_3$)$_2$·H$_2$O complex, the spectrum is only slightly modified, with the same multiplicity of the signals and some slight changes in the chemical shifts with respect to the ligand. The singlet which integrate as a single hydrogen present in the spectra of the ligand at 13.6 ppm is not disappeared in the spectra of the complex. This provides an evidence for the coordination of the ligand in the thioiminol form.

Chapter 7

Eight cadmium complexes have been synthesized and physico-chemically characterized by CHNS analyses, conductivity and magnetic susceptibility measurements, infrared and electronic spectral studies. Heterocyclic bases like 1,10-phenanthroline, 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 5,5′-dimethyl-2,2′-bipyridine and anions like thiocyanate, azide and chloride act as coligands. The molar conductivity measurements in DMF (10^{-3} M) indicate that all the complexes are non-electrolytes. The IR spectral studies show that the thiosemicarbazones coordinate in thioiminolate form in all the complexes and act as dideprotonated tridentate ligands. We could isolate X-ray quality single
crystals for one of the cadmium complex by the slow evaporation of the mother liquor. This compound is a sulfur-bridged cadmium box-dimer in which the environment of each Cd(II) atom can be described as distorted square pyramidal. The intermolecular hydrogen bonding interaction links two dimer units in the crystal cell giving rise to a 2D laminar packed structure. Further, crystal packing is reinforced by very weak C–H⋯π and metal⋯π interactions.