Chapter 7
SUMMARY AND CONCLUSION

The work described in this thesis was planned by keeping in view the three main objectives, namely, (i) to investigate systematically chemistry of \( N^1 \)-substituted thiosemicarbazones \( \{(R^1R^2C^2=\text{N}^3-N^2(H)-C^1=\text{S})N^1HR^3, H_\text{n}L\} \) by changing the substituents at \( C^2 (R^1, R^2) \) and \( N^1 (R^3) \) atoms, (ii) to correlate stoichiometry and nuclearity of complexes with the variation in substituents, and (iii) to investigate the effect of co-ligands on donor properties of thiosemicarbazones as well as on spectral properties and packing interactions of complexes. For this purpose, 35 thiosemicarbazones have been synthesized by systematic variation of substituents at \( C^2 (R^1, R^2) \) and \( N^1 (R^3) \) atoms and their interactions with Ni\(^{II}\), Pd\(^{II}\), Cu\(^{II}\) and Co\(^{II}\) metals have been carried out. The work was carried out initially on Ni\(^{II}\) and then to Cu\(^{II}\), Co\(^{II}\) and Pd\(^{II}\) metal ions. A large number of Ni\(^{II}\) complexes with variable geometry and nuclearity have been obtained. Also with Cu\(^{II}\), Cu\(^{I}\), Pd\(^{II}\) and Co\(^{III}\) several complexes have been obtained. Pd\(^{II}\) has shown cyclopalladation reactions. In case of Co\(^{II}\) oxidation occurred to Co\(^{III}\).

In this thesis, 77 new complexes of Ni\(^{II}\), Pd\(^{II}\), Cu\(^{I, II}\) and Co\(^{III}\) with thiosemicarbazones have been obtained and their chemistry is described. Complexes have been characterized using analytical and spectroscopic techniques (IR, UV-Vis, NMR). The crystal structure of 59 complexes has been obtained using X-ray crystallography. Fluorescence studies for some complexes have been carried out. Ni\(^{II}\) has formed mono-, di- and tetra- nuclear complexes. Mononuclear complexes involve bis-square planar, square planar, square pyramidal and octahedral geometries. Dinuclear complexes have square planar-square planar (4 : 4), square planar-trigonal bipyramidal (4 : 5), square planar-octahedral (4 : 6) and octahedral-octahedral (6 : 6) coordination pairs. Tetranuclear complexes involve square planar-octahedral-octahedral-square planar (4 : 6 : 6 : 4) coordination pair. Pd\(^{II}\) has formed mono- and one tri- nuclear complexes. Mononuclear complexes involve C–H and N–H bond activations. Trinuclear complex involves the loss of furan ring of thio- ligand during complexation. Copper\(^{II}\) has formed mononuclear complexes with square planar and square pyramidal geometries and one dinuclear complex with 4 : 5 coordination pair. Cobalt\(^{III}\) has formed only octahedral complexes.

Some important conclusions are drawn from this study, which are enumerated below.
1. Keeping $R^2 = H$, for $R^1 = \text{furan, thiophene, pyrrole and phenyl substituents}$, nickel(II) has formed trans square planar complexes ($I$–$7, 11, 12$). Interestingly, $R^1 = \text{furan}$ and $R^3 = \text{Ph}$ has favored a cis square planar complex $3$. Further, for $R^1 = \text{pyridyl group at } C^2$ carbon, octahedral complexes $8$–$10$ have been obtained.

2. Introduction of a methyl group at $C^2$ carbon ($R^2 = \text{Me}$) has induced unprecedented furan ring coordination in complexes $13$–$15$. However, thiophene ring remained pendant and merely formed square planar complexes $16$–$17$.

3. Thiosemicarbazones having 2-hydroxyphenyl groups at $C^2$ carbon, {$(5-\text{R}-2-\text{OH}-\text{C}_6\text{H}_3)-C^2(R^2)=N^3-N^2\text{H}^-\text{C}^-\text{S}-\text{N}^1\text{HR}^3, \text{H}_2\text{L}$}, generally lose $-\text{OH}$ and $-\text{N}^2\text{H}^-$ protons and coordinate as tridentate donors (O, N, S). Their interaction with nickel(II) resulted in the formation of $\{\text{NiL}\}$, which has yielded:

(a) Square planar complexes with py, PPh$_3$, 2-Phpy co-ligands ($19$–$23$).

(b) Dinuclear complexes with $4:4; 4:5; 4:6$ and $6:6$ coordination pairs with N, N- donor as co-ligands (bipy, dmbipy, 4,4'-bipy, phen). The bridging by $N^2$ donor atom in the nickel(II) dinuclear complexes remained unaltered for $R^3 = \text{H, Me}$; $R^2 = \text{H}; R^3 = \text{H, Me, Et, Ph}$. The expected $4:5$ coordination pattern is observed in $26a$ and $27$. But nickel showed tendency to absorb $\text{H}_2\text{O}$ ($24, 38$–$42$) or methanol ($25, 26b, 28, 29, 43$ and $44$) from the reaction medium or atmosphere and coordination pattern changed from $4:5$ to $4:6$ pairs. However, the presence of a electron withdrawing group in 2-hydroxyphenyl ring ($R = \text{NO}_2$) and electron releasing group at $C^2$ carbon ($R^2 = \text{Me}$) has changed the coordination pattern. The presence of a methyl group at $C^2$ carbon ($R^2 = \text{Me in place of H}$) has changed the nuclearity of complexes as well as the donor properties of the thio- ligands and has formed mononuclear octahedral ($32, 33$) and unusual tetranuclear complexes ($45, 46$; $4:6:6:4$ coordination pair). For $R = \text{NO}_2$, sulfur bridging is favored for $R^3 = \text{Me}$ ($30; 6:6$ coordination pair) and inhibited by $R^3 = \text{Et}$ ($31$; square pyramidal).

(c) Octahedral complexes ($47$–$49$) with terpydine co-ligand.

(d) Diphosphines (dppm) have displayed two type of coordination behavior, depending on the thio- ligand used. For $R^2 = \text{H}$, in dinuclear complexes, $50$–$52$, dppm bridges two metal centers and for $R^2 = \text{Me}$, in mononuclear complexes, $53, 54$, one P atom of the dppm is coordinating to nickel center while the other P atom is pendant.
The introduction of a methyl group at C\(^2\) carbon (R\(^2\) = Me), induced C–H bond activation of thiophene ring (R\(^1\)) in palladium(II) complexes, 56 and 57. Similarly for R\(^2\) = Me, Ph, complexes 58–61, involve C–H bond activation of phenyl rings (R\(^1\)).

For R\(^2\) = Me, pyrrole ring (R\(^1\)) undergoes N–H bond activation in complexes, 62 and 63.

2-acetylfuran-N-methyl thiosemicarbazone with a methyl group (R\(^2\)) at C\(^2\) carbon has formed unusual trinuclear complex, [Pd\(_3\)(atscN-Me)\(_2\)Cl\(_2\)PPh\(_3\)]\(_2\) (64). During complex formation, 2-acetylfuran-N-methylthiosemicarbaone (HaftscN-Me, aftscN-Me\(^-\) anion) has changed to 2-hydroxyacetaldehyde-N-methyl thiosemicarbazone (H\(_2\)atscN-Me, atscN-Me\(^-\) anion).

Copper(II) with monodentate co-ligand, py, has formed square planar complexes, 65 and 66 and with bipy it has formed a square pyramidal complex, 67. However, introduction of an ethyl group in place of methyl (R\(^2\)) at N\(^1\) atom, has yielded unprecedented N\(^2\)-bridged dinuclear complex, 68 (4 : 5 coordination pair).

Copper(II) chloride with thio- ligands (R\(^1\) = furan or thiophene rings) has formed sulfur bridged copper(I) complexes, 73 and 74.

Cobalt(II) chloride with thiophene- and furan-2-carbaldehyde-N\(^1\)-methyl thiosemicarbazones involved slow aerial oxidation and formed tris-octahedral complexes, [CoL\(_3\)] (76 and 77).

In short the substituents at C\(^2\)/N\(^1\) atoms have led to the formation of a variety of complexes with various metal ions. A variety of coordination pairs have been isolated, along with several reactions involving C–H, N–H and C–C bond activations. It provides the impetus to pursue chemistry in systematic way.