The present work incorporates the donor-acceptor behaviour of organoxy/organo-organoxy silicon and germanium derivatives containing M–N bond(s). Firstly, the reactions of N-fluorophenyl-1,1,1-tris(2,2,2-trifluoroethoxy)-silanamines and germanamines with titanium(IV)chloride are described. This results in the isolation of some new sila and germapolyamines adducts. Secondly the synthesis and characterization of some new penta and hexacoordinated silicon and germanium compounds of diverse compositions containing NCS group(s) in the structural framework have been undertaken. The whole work in the dissertation is presented as Chapter II and Chapter III. The contents of these chapters are given below.

**Chapter - II:** Synthesis of organoxy/organo-organoxy silanamines and germanamines and their reactivity towards titanium(IV)chloride.

**Chapter - III:** Synthesis of organoxy/organo-organoxy isothiocyanatosilanes and germanes and their reactivity towards triethanolamine and 1,3-diketones.

**Chapter - II:** Some hitherto unknown N-(2)fluoro/(2,4)difluoro/(2,4,6)trifluoro/(2,3,5,6)-tetrafluoro and (2,3,4,5,6)pentafluorophenyl-1,1,1-tris(2,2,2-trifluoroethoxy)silanamines as well as germanamines have been prepared by the reaction of the chlorosilane/germane with corresponding fluoroaniline or its lithium salt. All these silanamines and germanamines are colourless hygroscopic liquids and therefore, require careful handling in an all-glass vacuum line. These compounds have been characterized by elemental analyses, infrared, $^1$H, and $^{19}$F NMR spectral data. Infrared spectra show characteristic absorptions due to $\nu$ NH, $\nu$ Si/Ge-O(C) and benzene ring vibrations at 3480-3470, 3380-3360; 1070-1050 and 740, 720 and 690 cm$^{-1}$ respectively. Since the compounds formed are of good purity, therefore, $^{13}$C and $^{29}$Si NMR spectra of only (CF$_3$CH$_2$O)$_3$SiNHC$_6$H$_3$F$_2$ have been studied as a
representative member in this series of compounds. Multinuclear magnetic resonance data of these silanamines and germanamines are summarized below.

**Silanamines**: \( ^1H \) NMR, NH 3.6-3.7; OCH\(_2\) 4.2-4.3; phenyl ring 6.8-7.0 ppm, \( ^19F \) NMR, CF\(_3\) 77.0-78.0; ring fluorine 120.0-175.0 ppm, \( ^13C \) NMR (fluorine coupled) [of \((\text{CF}_3\text{CH}_2\text{O})_3\text{SiNHCO}_2\text{F}_2\) only]; OCH\(_2\) (62.56, 62.27, 61.97, 61.61); CF\(_3\) (126.55, 124.35, 122.14, 119.93); ring carbons 130.73, 156.30, 154.47, 103.92, 103.73, 103.54, 152.01, 150.09, 110.94, 110.77, 119.93 ppm and \( ^29Si \) NMR [of \((\text{CF}_3\text{CH}_2\text{O})_3\text{SiNHCO}_2\text{F}_2\) only]; -51.7 ppm.

**Germanamines**: \( ^1H \) NMR, NH 3.6-3.7; OCH\(_2\) 4.1-4.3; phenyl ring 6.8-7.0 ppm; \( ^19F \) NMR, CF\(_3\) 78.0-79.0; ring fluorine 120.0-175.0 ppm respectively.

All the data are in agreement with the compositions of the compounds \((\text{CF}_3\text{CH}_2\text{O})_3\text{MNHR}\) [where \( M = \text{Si or Ge} \) and \( R = \text{C}_6\text{H}_4\text{F}, \text{C}_6\text{H}_3\text{F}_2, \text{C}_6\text{H}_2\text{F}_3, \text{C}_6\text{HF}_4 \) or \( \text{C}_6\text{F}_5\)].

The reactions of these silanamines and germanamines with titanium(IV) chloride in 1:1 molar ratio in dry petroleum ether (40-60°C) at 0 to -10°C give orange red to yellow solid compounds immediately. These compounds are extremely hygroscopic and insoluble in most of the common organic solvents except in nitromethane, nitrobenzene or acetonitrile. Elemental analyses suggest the composition of silanamine adducts to be \( \text{Si(NHR)}_4.3\text{TiCl}_4 \) (Where \( R = \text{C}_6\text{H}_3\text{F}_2 \) or \( \text{C}_6\text{H}_2\text{F}_3\)); \( \text{Si(NHR)}^1_4.4\text{TiCl}_4 \) (Where \( R^1 = \text{C}_6\text{HF}_4 \) or \( \text{C}_6\text{F}_5\)) and germanamine adducts to be \((\text{CF}_3\text{CH}_2\text{O})_2\text{Ge(NHR)}_2.2\text{TiCl}_4 \) and \( \text{CF}_3\text{CH}_2\text{OGe(NHR)}_3.2\text{TiCl}_4 \) (Where \( R = \text{C}_6\text{H}_4\text{F}, \text{C}_6\text{H}_3\text{F}_2, \text{C}_6\text{H}_2\text{F}_3, \text{C}_6\text{HF}_4 \) or \( \text{C}_6\text{F}_5\)). These compounds have also been characterized by infrared, \( ^1H \), and \( ^19F \) NMR spectral data. Infrared spectra reveal that \( v \) NH modes (3390-3380, 3220-3210 cm\(^{-1}\)) experience negative spectral shifts indicating coordination through nitrogen atom. \( ^1H \) NMR of silanamines adducts show phenyl ring protons between 7.00-7.20 ppm only. \( ^19F \) NMR spectra of these adducts show ring fluorine at 121.0-175.0 ppm. However, the peaks at 77.0-78.0 ppm due to CF\(_3\) group in the starting compounds are absent in these adducts. \( ^13C \) NMR of
Si(NHC₆H₃F₂)₄·3TiCl₄, ring carbons at 167.78, 165.77, 160.68, 158.68, 132.54, 116.55, 109.04 ppm reveals that ortho and para substituted fluorine containing carbon atoms undergo a marked downfield chemical shift of about 8-10 ppm as compared to the parent silanamine. This shift reveals a direct drag of electron density from C–F bonds, thereby deshielding these carbon atoms. However, all the above mentioned data are consistent with the proposed composition of the compounds.

Germanamine adducts of TiCl₄ show δ¹H NMR, NH 3.6-3.7, OCH₂ 4.2-4.3, phenyl ring protons 6.8-7.0 ppm; δ¹⁹F NMR, CF₃ 77.0-78.0, ring fluorine 120.0-175.0 ppm. All these data are also in accordance with compositions of the compounds given above.

A comparative assessment of the reactivity of analogous silanamines and germanamines towards titanium(IV)chloride reveal that disproportionation is more facile in the case of silanamines. For example the reactions of N-(2,4)difluoro/(2,4,6)trifluorophenyl-1,1,1-tris(2,2,2-trifluoroethoxy)silanamines with titanium(IV)chloride show complete disproportionation of 2,2,2-trifluoroethoxy group, while analogous germanamines on reactions with the same Lewis acid show incomplete disproportionation of 2,2,2-trifluoroethoxy group. The difference in the reactivity of silanamines and germanamines has been explained keeping in view the competitive πr–dτ bonding between M–N and M–O bonds (M = Si or Ge).

These adducts form further addition compounds even with weak basic solvents such as nitromethane and acetonitrile. The compositions of these adducts are Si(NHR)₄·3TiCl₄·3L; Si(NHR¹)₄·4TiCl₄·4L; (where R = C₆H₃F₂ or C₆H₂F₃ and R¹ = C₆H₄F or C₆F₅) and (CF₃CH₂O)₂Ge(NHR)₂·2TiCl₄·2L; CF₃CH₂OGe(NHR)₂·2TiCl₄·2L (where R = C₆H₄F, C₆H₃F₂, C₆H₂F₃, C₆HF₄ or C₆F₅ and L = CH₃NO₂ or CH₃CN). It is apparent from these compositions that the number of solvent molecules is the same as the number of TiCl₄ molecules attached in a complex. This may signify that the Lewis acid molecule is coordinatively unsaturated in these complexes. Since these double adducts formed are insoluble in most of the common organic solvents, their detailed structural investigations through
multinuclei NMR spectral studies in solution state or single crystal X-ray studies in solid state have not been possible. With a view to have some insight into the structure of these addition compounds, their infrared spectra have been carefully recorded. The special feature of these spectra is the variation of $\nu$ CH bands between 2610-2580 cm$^{-1}$. In literature such bands are assigned to interactions between CH and transition metals. This is known as 'agostic' interactions. However, it is too early to comment on the nature of these bands in the present compounds and the final word of the structure of these compounds will come from single crystal X-ray data only.

The mechanism of the Lewis acid aided disproportionation reactions of silanamines has been proposed by Narula et al.\textsuperscript{92,94} The tentative mechanism is shown in the Scheme I.

\begin{enumerate}
  \item (RO)$_3$SiNHR$^1$ + MCl$_4$ $\rightarrow$ (RO)$_3$SiNHR$^1$.MCl$_4$
  \item (RO)$_3$SiNHR$^1$.MCl$_4$ + (RO)$_3$SiNHR$^1$ $\rightarrow$ (RO)$_2$Si(NHR$^1$)$_2$.MCl$_4$ + (RO)$_4$Si
  \item (RO)$_2$Si(NHR$^1$)$_2$.MCl$_4$ + MCl$_4$ $\rightarrow$ (RO)$_2$Si(NHR$^1$)$_2$.2MCl$_4$
  \item (RO)$_2$Si(NHR$^1$)$_2$.2MCl$_4$ + (RO)$_3$SiNHR$^1$ $\rightarrow$ ROSi(NHR$^1$)$_3$.2MCl$_4$ + (RO)$_4$Si
  \item ROSi(NHR$^1$)$_3$.2MCl$_4$ + MCl$_4$ $\rightarrow$ ROSi(NHR$^1$)$_3$.3MCl$_4$
  \item ROSi(NHR$^1$)$_3$.3MCl$_4$ + (RO)$_3$SiNHR$^1$ $\rightarrow$ Si(NHR$^1$)$_4$.3MCl$_4$ + (RO)$_4$Si
\end{enumerate}

\textbf{SCHEME I}

There are many intermediates which are still not isolated. There is a general observation that lowering of temperature may help in isolating the missing products in the reaction sequence of the disproportionation of organoxy/organo-organoxy silanamines. Earlier report by Narula et al.\textsuperscript{92} reveal that the compounds like N-benzyl/phenyl/(o)-chlorophenyl-1,1,1-triethoxy/ tri n-propoxy silanamines on reaction with Lewis acids show incomplete disproportionation yielding compounds of compositions, ROSi(NHR$^1$)$_3$.2MCl$_4$ and (RO)$_2$Si(NHR$^1$)$_2$.2MCl$_4$ [where $R = C_2H_5$, $n$-C$_4$H$_9$; $R^1 = C_6H_5CH_2$, $C_6H_5$, (o)-C$_6$H$_4$ and $M = Ti$ or Sn]. The intermediate addition compounds such as (RO)$_3$SiNHR$^1$.MCl$_4$ and (RO)$_2$Si(NHR$^1$)$_2$.MCl$_4$ etc., have still not been isolated.
With a view to isolate these adducts, these reactions were carried out at -55 to -60°C. and yellow to orange coloured solids were obtained. However, the elemental analyses and spectroscopic data of the products obtained show that, contrary to the expectations, the silanamines undergo complete disproportionation to produce 1,1,1,1-tetrakis(organoamino)silanes.3TiCl$_4$. Infact, lower temperature has accelerated the disproportionation reactions.

There are many germanium polyamine adducts such as Ge(NHR)$_4$.3TiCl$_4$ and Ge(NHR)$_4$.4TiCl$_4$ which have also not yet been isolated. Considering that low temperature accelerated mechanism holds good for germanamines also, the low temperature reactions were also carried out for these germanamines. Therefore, N-(2)fluoro/(2,4)difluorophenyl-1,1,1-tris(2,2,2-trifluoroethoxy)germanamines were reacted with titanium(IV)chloride at -55 to -60°C. The analytical and spectroscopic data of the products thus obtained have revealed complete disproportionation of the above germanamines and 1,1,1,1-tetrakis(organoamino)germanes. Lewis acid adducts, [Ge(NHR)$_4$.3TiCl$_4$] were isolated. However, the adduct Ge(NHR)$_4$.4TiCl$_4$ is not formed. It is well known that thermodynamic parameters such as enthalpy change ($\Delta H$), entropy change ($\Delta S$) etc. are important to understand the path of a reaction. Since this disproportionation reaction is spontaneous, the estimation of these parameters is rendered difficult and hence no light could be thrown on the nature of these reactions.

With a view to have added support about the composition of these adducts, base exchange reactions using the stronger electron donors such as 2,2'-bipyridyl, pyridine and ethylenediamine in carbontetrachloride separately were attempted. The solids obtained in these reactions as identified by $^1$H NMR spectral data in DMSO(d$_6$) correspond to TiCl$_4$ adducts of the bases used. From the filtrates tetrakis(organoamino)silanes/germanes were isolated. It may be mentioned here that the present approach offers a new method for the formation of such sila and germapolyamines though it is admitted that an efficient base exchange is needed for the isolation of these amines in reasonably good quantities.
Chapter - III:

This chapter incorporates the synthesis and reactivity of organoxy/organo-organoxy isothiocyanatosilanes and germanes towards triethanolamine and 1,3-diketones. The prime object is the isolation and characterization of hypervalent silicon and germanium compounds of diverse composition containing NCS group(s) in the structural framework.

Firstly the synthesis of 1-isothiocyanatogermatrane has been undertaken by a simple and facile route. For this triethoxyisothiocyanatogermane was thought to be the likely precursor to achieve the objective. Triethoxychlorogermane has been prepared by the reaction of germaniumtetrachloride with the sodium salt of ethanol. Triethoxyisothiocyanatogermane has been prepared by the reaction of triethoxychlorogermane with potassium thiocyanate in dry acetonitrile medium. This is a hygroscopic and distillable liquid and is characterized by elemental analyses, infrared, $^1$H and $^{13}$C NMR spectral data. Infrared spectrum reveals characteristic absorptions $\nu$ NCS, $\nu$ Ge-O(C) and $\delta$ NCS modes at 2080, 1050-1040 and 460 cm$^{-1}$ respectively. $^1$H and $^{13}$C NMR spectra of triethoxyisothiocyanatogermane has been recorded in CDCl$_3$. The identity of various groups has been checked on the basis of chemical shift values. $\delta$ $^1$H NMR CH$_3$ 0.9; OCH$_2$ 3.8 ppm, $\delta$ $^{13}$C NMR, CH$_3$ 10.2; and OCH$_2$ 58.4 ppm. These spectral data are in agreement with the composition [(EtO)$_3$GeNCS] of the compound.

The reaction of equimolar quantities of triethoxyisothiocyanatogermane and triethanolamine in dichloromethane results in the formation of a white solid. Elemental analyses of the compound correspond to the composition of 1-isothiocyanatogermatrane. This compound is soluble in acetonitrile, tetrahydrofuran and nitrobenzene etc. This white crystalline solid is characterized by infrared, $^1$H, $^{13}$C NMR spectral data and mass spectrum as well as single crystal x-ray studies. The diagnostic absorptions in the infrared spectrum include $\nu$ NCS, $\nu$ Ge-O(C) and $\delta$ NCS at 2110, 1050-1040 and 470 cm$^{-1}$ respectively. A positive spectral shift of about 25-30 cm$^{-1}$ has been observed in $\nu$ NCS mode. This change
may probably be attributed to the increased $-N\equiv C-S^-$ character in the pentacoordinated germatrane molecule. The $\delta^1$H NMR spectrum in CD$_3$CN shows two triplets at 3.88 and 3.06 ppm due to OCH$_2$ and NCH$_2$ protons. The $\delta^{13}$C NMR spectrum in CD$_3$CN shows some interesting features e.g. a 'triplet' observed at 139.23, 139.02 and 138.81 ppm. This triplet is due to the $^{13}$C-$^{14}$N coupling. \[J(\text{BC-14N}) = 21.0 \text{ Hz.}\]

In the molecule, it is the first example in a pentacoordinated organo/organoxy germanium compounds which has shown this kind of coupling.

Mass spectrum of 1-isothiocyanatogermatrane shows molecular ion peak $[M]^+$ of intensity 37.2% at m/z 278 according to $^{74}$Ge labelling. The base peak $[\text{M}]^+ - \text{NCS}$ having intensity 100% is observed at m/z 220. This step is followed by the consecutive loss of OCH$_2$ fragments. The schematic path is shown as follows:

<table>
<thead>
<tr>
<th>m/z</th>
<th>% Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>278</td>
<td>37.2%</td>
</tr>
<tr>
<td>220</td>
<td>100%</td>
</tr>
<tr>
<td>190</td>
<td>26.1%</td>
</tr>
<tr>
<td>160</td>
<td>35.2%</td>
</tr>
<tr>
<td>130</td>
<td>7.5%</td>
</tr>
</tbody>
</table>

The fragmentation pattern of the germatranyl skeleton is in line with those reported in literature.

X-ray crystal structure reveals that the three oxygen atoms are equatorially placed in a conventional fashion whereas the transannular nitrogen atom and the NCS group are placed axially in the molecule. This is a first observation in metallatranes of group 14 elements where two nitrogen atoms apically face each other. A salient feature of the X-ray is the Ge$_1$ $\equiv N$ bond distance [2.081(5) Å] in the present compound is the shortest ever reported so far in germatranes.
Interestingly the N–C(S) bond distance [1.133(8) Å] is appreciably shortened and compares to C≡N bond distance [1.135(6) Å] found in germylecyanides.

Preliminary observations have been made on the reactivity of germatrane molecule. The reactions of equimolar quantities of 1-isothiocyanatogermatrane and titanium(IV) or tin(IV)chlorides in dichloromethane result in the formation of an orange yellow or white solid respectively. Elemental analyses correspond to the 1:1 composition of germatrane molecule with TiCl₄/SnCl₄. These compounds are very hygroscopic and soluble in polar organic solvents such as acetonitrile and nitrobenzene. These adducts have been characterized by infrared and ¹H NMR spectral data. Infrared spectra reveal ν NCS modes as a doublet at 2000-1920 and 1990-1910 cm⁻¹ respectively in the cases of TiCl₄/SnCl₄ adducts and suffers a negative spectral shift of 180-200 cm⁻¹ as compared to that of parent 1-isothiocyanatogermatrane. ¹H NMR spectra also confirm the presence of germatranyl skeleton in the molecules. Further observations such as ¹³C, ¹⁵N and ⁷³Ge NMR spectral studies are in progress to unequivocally decide the structure and nature of bonding in these compounds. Infact reactivity of 1-isothiocyanatogermatrane constitutes the future plan of the project.

Neutral hexacoordinated bis(1,3-diketonato)isothiocyanatosilanes and germanes have been prepared by the reaction of isothiocyanatosilanes and germanes with acetylacetone, benzoylaceton and trifluoroacetylacetone. These white to pale yellow compounds are stable solids soluble in chloroform, acetonitrile and tetrahydrofuran etc. The structures of these compounds have been elucidated with the help of infrared, ¹H, ¹³C and ²⁹Si NMR (wherever applicable) spectral data. The diagnostic absorptions in the infrared spectra include the vibrational bands of ν NCS and ν CO at 2110-2100 and 1550-1530 cm⁻¹ respectively. A comparison of the infrared spectra of these compounds with those of the pure 1,3-diketones and precursor organoxy/organo-organoxy isothiocyanatosilanes and germanes show some interesting features. A negative spectral shift (75-95 cm⁻¹) of ν CO band and a positive spectral shift of (20-30 cm⁻¹) ν NCS mode have been observed in the
spectra of these compounds. The former absorption clearly suggests chelation with the ligands acting as bidentate monoanionic species while the later, i.e., change of ν NCS band, is interpreted in terms of increased $\equiv$C–S character developed in the compounds. The stereochemistry of these compounds has been satisfactorily elucidated by $^1$H NMR spectra. These spectra reveal that bis(β-diketonato)isothiocyanatosilanes and germanes are stereochemically labile in solution. However, a point of difference is observed between the silicon and germanium analogs. The cis $\rightarrow$ trans equilibria in the case of silicon compounds is attained much faster than in the germanium compound. e.g., the cis isomer of (acac)$_2$Si(NCS)$_2$ starts equilibrating to its trans isomer after 30 minutes and finally takes 24 hours for the equilibrium to be complete in the cis/trans ratio (1.6:1). The germanium cis analog (acac)$_2$Ge(NCS)$_2$ changes its identity after 24 hours and a complete equilibrium is established after 72 hours. The substitution of one CH$_3$ group by an electron withdrawing group such as C$_6$H$_5$ or CF$_3$ in the ligand tends to change the stereochemistry from cis to trans isomer. Thus bis(benzoylacetonato)-diisothiocyanatosilane exists initially as an isomeric mixture of cis and trans (4.8:1) forms in solution but completely transforms to trans isomer in 48 hours. Contrary to this, bis(benzoylacetonato)diisothiocyanatogermaine exists predominantly as a non-rigid trans product. bis(trifluoroacetylacetonato)diisothiocyanato silane adopts an isomer free trans structure. Similarly phenyl bis(acetylacetonato)/(benzoylacetonato)isothiocyanatosilanes and germanes exist as trans isomers in solution and these molecules retain their geometry even after 5 to 6 days.

It must be mentioned here that the mechanism of stereochemical lability in the metal β-diketonates have been studied previously on the basis of kinetic data. Since isomerization process in case of present β-diketonates of silicon and germanium is slow enough to be detected on NMR scale, the kinetic measurements by NMR remain a desired objective. This constitutes the future plan of the project.