INTRODUCTION
The elements of group V have $n^s_2; np^3$ electronic configuration which indicates three singly occupied orbitals. These elements with five valence electrons form bonds which are mainly covalent in character and exhibit $+3$ and $+5$ oxidation states. But for arsenic and bismuth, $+5$ is often less stable than the $+3$ oxidation state. Preference of arsenic for $+3$ state is probably attributed to the poorer shielding of the nucleus afforded by one of the two $4s$ electrons (necessary for oxidation state $+5$).

Because of the availability of d orbitals of fairly low energy, increase of coordination number from five to six is possible whereby the geometry of the molecule changes from the trigonal bipyramidal to octahedral configuration. Consequently their pentahalides have a tendency to act as acceptor molecules. All the 1:1 adducts of pentahalides of group VB elements have an octahedral stereochemistry.

Comparatively a little study has been made with phosphorus(III) halides. Phosphorus trifluoride is a very weak Lewis acid and forms an adduct with trimethylamine at low temperatures only (1). It is also known to form alkylamino-difluorophosphines and bis(alkylamino)difluorophosphines with primary amines. Formation of bis(alkylamino)difluorophosphoranes in this reaction has also been noted (2). Acceptor character of arsenic(III) chloride is readily demonstrated by the formation
of 1:1 complexes with (BuO)$_3$SiNH$_2$ (3) and by the formation of both 1:1 and 1:2 complexes with bipyridyl, 1,10-phenanthroline and o-phenylene-bis-dimethylamine (4). Arsenic(III) chloride and sulphur trioxide form an inseparable mixture which is an adduct AsCl$_3$.SO$_3$ in equilibrium with Cl$_2$AsOSO$_2$Cl (5) but when arsenic(III) chloride is heated with sulphur trioxide at 70°C, a polymeric material of composition (ClAsSO$_4$)$_n$ is obtained which decomposes upon further heating (5). Arsenic(III) chloride in dimethylformamide, on treatment with silver perchlorate, yields the salt of composition [As(DMF)$_5$]$^+3[ClO$_4$]$^-3$ (6). Arsenic trihalides ($X =$ Cl, Br, I) are also known to form adducts with bases such as (BuO)$_3$PO (7), CH$_3$CONMe$_2$ and (Me$_2$N)$_3$PO in dichloroethane solution (8).

A large number of addition compounds of antimony(III) chloride mainly of 1:1 stoichiometric composition have been reported with the hydrocarbons and the organic halogen, oxygen and sulphur containing compounds (9). Malhotra and his coworkers (10) have isolated a number of adducts of antimony(III) chloride with oxygen and nitrogen bases. As compared to trihalides of group (V)B, a large number of adducts of phosphorus(V) halides with donor molecules are known. The adducts of the type $F_5P.B$ where B may be oximes (11-13), amides (14) or nitriles (15) have been reported. Primary amines are known to form adducts of composition $F_5P.NH_2R$ and $F_5P.2NH_2R$ with phosphorus(V) fluoride. While the exact nature of the latter adduct could not
be established, the former \( F_5P.NH_2R \) has been shown to coordinate through nitrogen. The tertiary amines however form compounds of composition \( F_5P.Me_3N \) in fluoroform (16).

The reaction of amines with phosphorus(V) chloride provides an interesting study and the products obtained are quite varied. Phosphorus(V) chloride forms molecular addition compounds of stoichiometric composition 1:1 and 2:1 (2PCl\(_5\cdot A\)) with various donor molecules (17). It also forms an adduct of composition \( PCl_5\cdot 2(CH_3)_3P \) with trimethylphosphine but its structural information is lacking (18). Phosphorus(V) chloride has also a tendency to donate chloride ions in the presence of a chloride ion acceptors to form \( PCl_4^+ \) ions, it combines readily with aluminium(III) chloride (19), boron(III) chloride (20) and antimony(V) chloride (21) to form \( PCl_4^+ \) ion. Phosphorus(V) chloride under suitable conditions may also act as chloride ion acceptor to form \( PCl_6^- \) ion. The ion being formed only when notably weak chloride ion acceptors are involved in the systems and the lattice energy favours its coordination. Iodine(III) chloride is known to form a compound of composition \( ICl_3\cdot PCl_5 \) formulated as \( ICl_2^+\cdot PCl_6^- \). Recently, Malhotra and coworkers (21a) have shown conductometrically the existence of \( PCl_6^- \) ion in the reaction of tetraphenoxy niobium(V) and tantalum(V) chlorides with phosphorus(V) chloride.

Arsenic(V) fluoride is relatively a better Lewis acid e.g.
arsenic(V) fluoride forms adducts with acetonitrile and trimethylamine. The latter adduct is non-conducting in solutions while the former forms conducting solutions in acetonitrile with ions such as AsF$_4^-$L$_2$AsF$_6^-$ (22, 23). Significantly arsenic(V) fluoride chemistry is dominated by the use of pentafluoride as a fluoride ion acceptor.

Of all the acceptor molecules of this subgroup elements, antimony(V) chloride has been extensively studied for the formation of molecular addition compounds. Antimony(V) chloride is known to form an adduct of composition SbCl$_5$.CH$_3$CN with acetonitrile which has a possible ionic structure as (SbCl$_4$.2CH$_3$CN)$^+$(SbCl$_6$)$^-$. Similarly the related adduct (SbF$_3$Cl$_2$.CH$_3$CN)$_2$ has been formulated as (SbCl$_4$.2CH$_3$CN)$^+$(SbF$_6$)$^-$ (25). Addition of antimony(V) chloride to phenanthroline in chloroform solution yields 2SbCl$_5$.phen which again may be formulated as [SbCl$_4$.phen]$^+[SbCl$_6$]^-$. Compounds with oxygen donors have also been investigated for molecular adduct formation. Very few adducts of pentahalides of phosphorus with oxygen bases are known, some of which may be formulated as 3PCl$_5$.2(C$_2$H$_5$)$_2$O (26) and PCl$_5$:Phenalenone (27). Phosphorus(V) chloride does not form any solid adduct with carboxylic acids and esters (28) because of the low acceptor-donor strengths of the components.

Two compounds of composition 2SbCl$_3$.CH$_3$COOH and
SbCl$_3$.CH$_3$COOH have been reported in the case of antimony(III) chloride and acetic acid (29). Antimony(III) chloride also forms compounds of composition 2SbCl$_3$.CH$_2$ClCOOH and SbCl$_3$.CH$_2$ClCOOH with monochloroacetic acid (30). Pfeiffer (31) has indicated a compound of antimony(V) chloride and oxalic acid of stoichiometric composition (COOC$_2$H$_5$)$_2$.2SbCl$_5$ as an intermediate which on heating loses ethyl chloride and the resulting compound is an inner complex salt of the formula:

\[
\begin{array}{c}
\text{Cl}_4\text{Sb} \\
\text{O - C = O} \\
\text{SbCl}_4
\end{array}
\]

Antimony(III) chloride yields 1,3 diketonate complexes on reaction with the appropriate sodium salt, and these complexes in which the heavy atom is considered to be in six fold coordination to oxygen, may also be obtained from triethoxystibine and the diketone in benzene (32). Complexes of antimony(V) chloride with aldehydes (33), carboxylic acids (34,35), monoesters (loc cit) and ketones (36) are known in literature. It has been shown by Paul and his coworkers that antimony(V) chloride forms stable adducts with ethyl formate (37), ethyl chloroformate (38) and ethyl acetate (39). Rosenheim and his coworkers (40) have shown the existence of molecular addition compounds of dicarboxylic esters and antimony(V) chloride but concrete evidence is lacking.
Oxy acid halides also form stable 1:1 adducts with antimony(V) chloride. It forms ionic compounds of composition \( \text{NOSbCl}_6 \), \( \text{NO}_2^+\text{SbCl}_6^- \), \( \text{CH}_3\text{COSbCl}_6^- \) and \( \text{C}_6\text{H}_5\text{COSbCl}_6^- \) with nitrosyl chloride (41), nitryl chloride (42), acetyl chloride (39) and benzoyl chloride (43). But in the case of phosphoryl chloride (44), thionyl chloride (45) and selenyl chloride (46), simple addition compounds have been reported. X-ray structures of these adducts show that oxygen atom of these acid chloride acts as the donor atom (47).

Like the elements of group V, the elements of group VI show essentially non-metallic covalent character except for polonium and to a very slight extent by tellurium. In addition to the formation of divalent species, the elements form compounds in formal +4 and +6 oxidation states. Tellurium is also known to form an eight coordinate ion \( \text{TeF}_8^2^- \).

Tellurium(II) chloride forms a complex of composition \( \text{TeCl}_2\cdot2\text{pyridine} \) with pyridine. Bromine reacts with tellurium(II) chloride to form yellow dichlorodibromide \( \text{TeCl}_2\cdot\text{Br}_2 \). More stable complexes are formed with thiourea and substituted thioureas of composition \( \text{Te(tu)}_2\cdot\text{Cl}_2 \) and \( \text{Te(tu)}_4\cdot\text{Cl}_2\cdot2\text{H}_2\text{O} \). Most of the nitrogen donor adducts of the chalcogen tetrahalides have the composition \( \text{XY}_4\cdot2\text{L} \) with monodentate ligand (\( X = \text{Se} \) or \( \text{Te} \), \( Y = \text{Cl} \)) but adducts of selenium or tellurium(IV) halides with four molecules of ammonia or two molecules of ethylene diamine are
also known (48). Interestingly, some of these compounds have been proposed six coordination for the metal e.g. \((\text{SeCl}_2\text{en}_2)\text{Cl}_2\). Mono- and bidentate nitrogen donor complexes of composition \(\text{TeF}_4\cdot\text{L}\) and \(2\text{TeF}_4\cdot\text{L}\) respectively with ions such as \(\left[\text{L}_2\text{TeF}_3\right]^+\left[\text{TeF}_5\right]^-\) or \(\left[\text{L}\text{TeF}_3\right]^+\left[\text{TeF}_5\right]^-\) (49) which is supported by conductance studies (50). Tellurium(VI) fluoride is known to form amine complexes of the type \(\text{TeF}_6\cdot2\text{R}_3\text{N}\) which appear to be eight coordinate species (51), but no structural data is available.

The 1:1 complexes of selenium(IV) chloride with bases are similar to the 1:1 complexes with tellurium(IV) fluoride. However, it has been suggested (52) that 1:2 complexes of composition \(\text{SeCl}_4\cdot2\text{py}\), on the contrary, contain octahedral \(\left[\text{SeCl}_3\cdot2\text{py}\right]^+\cdot\text{Cl}^-\) ions. Hygroscopic addition compounds with sulphur trioxide of composition \(\text{TeCl}_4\cdot\text{SO}_3\), \(\text{TeCl}_4\cdot2\text{SO}_3\), phosphorus oxychloride (\(\text{TeCl}_4\cdot\text{POCl}_3\)) and phosphorus pentachloride (\(\text{TeCl}_4\cdot2\text{PCl}_5\)) and with a number of other chlorides such as tin(IV) chloride, antimony(V) chloride, vanadium(IV) chloride, titanium(IV) chloride and aluminium(III) chloride have been established. Compounds of composition \(\text{TeCl}_4\cdot2\text{tu}, \text{TeCl}_4\cdot6\text{tu}\) with thiourea, \(\text{TeCl}_4\cdot2\text{py}\) with pyridine, \(\text{TeCl}_4\cdot2\text{tmtu}\) with tetramethylthiourea, \(\text{TeCl}_4\cdot2\text{en}\) with ethylenediamine and with other ligands have been isolated (53). These halides are also known to form compounds with alkyl amides. Substituted dimethylformamidyl tellurium(IV) chloride \(\text{TeCl}_3\text{CON}(\text{CH}_3)_2\cdot\text{DMF}\)
and monodimethylformamidyl selenium(IV) chloride SeCl₃ CON(CH₃)₂ have been isolated.

Infrared spectral studies of 1:1 complexes of tellurium(IV) fluoride with dioxane and pyridine N-oxide support their ionic formulation as [(dioxane)₂TeF₃]⁺[TeF₅]⁻ and [(PyNO)₂TeCl₃]⁺[TeCl₅]⁻ (49,50). Selenium, tellurium and polonium(IV) halides react with \( \beta \) -diketones with the elimination of hydrogen halide, either by displacement of hydrogen from the methylene group between the two carbonyl groups or from one or both of the terminal methyl groups (54). Selenium(IV) chloride reacts with acetylacetone or its copper derivative to yield dimeric selenium acetylacetonate Se₂(C₅H₇O₂)₂ as the main product which has the ring structure (55,56). This explains the failure of the compound to enolize and supports the reactivity of \( \alpha \) -carbon atom. Tellurium(IV) chloride is known to react with an excess of acetylacetone to form a compound of composition (C₅H₇O₂)TeCl₂. Hydrogen chloride is eliminated if the \( \beta \) -diketone is not in excess (56).

As compared to tellurium, the chemistry of tungsten is quite varied, covering nine oxidation states ranging from -2 to +6. Gaseous ammonia forms a nitride of composition W₂N₃ with tungsten hexachloride at room temperature but with liquid ammonia at -33°C two solvates of composition WCl₆·6NH₃ and WCl₆·4NH₃ are reported, which on heating give a compound
supposed to be $\text{WCl}_2(\text{NH}_2)_2$. Aminolysis with primary amines, however, yields tetraamidodervatives of composition $\text{WCl}_2(\text{NHR})_4$. The use of secondary and tertiary amines leads to its reduction giving $\text{WCl}_6^{2-}$ ions which may then be aminolyzed to yield $\text{WCl}_3^3\text{NR}_2\cdot 2\text{NHR}_2$. Tungsten(VI) chloride yields a compound of composition $[\text{W(NMe}_2]_3]_x$ when reacted with dialkyl lithium amide (57). A compound of composition $\text{W}_2(\text{NMe}_2)_10$ is formed by the disproportionation of $[\text{W(NMe}_2]_3]_x$ (58).

Acetylacetonates of molybdenum and tungsten have received little attention. Goan and his coworkers (59) formulated the species obtained from photochemical interaction of acetylacetone with tungsten hexacarbonyl as dimer having composition $[\text{WO}_2(\text{OH})(\text{ac.ac})]_2$ or $[\text{WO}_2(\text{ac.ac})_2]$. The preparation of dioxomolybdenum(VI) acetylacetonate, $\text{MoO}_2(\text{ac.ac})_2$ was reported by Jones (60) and Fernelius (61). Oxyligands such as triphenylphosphine oxide or pyridine N-oxide react with tungsten oxytetrachloride or (VI) chloride to give oxygenated products of composition $\text{WO}_2\text{Cl}_2\text{L}_2$ \((L = \text{Ph}_3\text{PO, C}_5\text{H}_5\text{NO})\) (62). The reaction of tungsten(VI) fluoride with dimethyl ether yields oxotetrafluoro(dimethyl ether) tungsten(VI) of composition $\text{WO}_4\cdot \text{Me}_2\text{O}$ (63).

Like ethers, oxygen atom in alcohols can form a wide variety of addition compounds with various metal halides. Inspite of the widespread use of lower alcohols as preparative
media and their sure existence as coordinated alcoholic species in solutions, only a very few well characterised simple addition compounds of alcohols are known in the solid state. Flint and Goodgame (64) have reported some alcohol complexes of transition metal thiocyanates of composition \( [\text{ROH}]_2 (\text{NCS})_2 \) where \( M = \text{Mn(II), Co(II), Ni(II)} \) and \( R = \text{Me or Et} \). A lowering of the \( O-H \) stretching frequency in the i.r. spectra is due to coordination of alcohol to the metal as well as to hydrogen bonding of the hydroxyl group in these adducts.

There are two possible modes of coordination in alcohols, one in which the hydroxyl proton is retained and the coordination of the alcoholic oxygen to the metal results in the formation of an adduct having the bond formation of the type \( R-O-M \). There are only a few examples of the above type of metal halide adducts of alcohols (65,66).

The other mode of coordination involves substitution of the proton by the metal ion resulting in the bond formation of the type \( R-O-M \). Such type of compounds are known as alkoxides, which have been widely investigated and characterised (67-69). The most significant advances have involved the chemistry of the transition metal alkoxides (70) with emphasis on the ligand aspects of the alkoxo group. These alkoxides are insoluble, nonvolatile polymeric solids and some of them are monomeric ligands.
During the past two decades, there has been a noticeable increase in the industrial applications of metal alkoxides (71-75), possibly because of their use in the development of new useful polymeric material. A number of insoluble beryllium alkoxides of composition BeCl_{2-n}(OPh)_n have been synthesized by the metathetic reactions of beryllium(II) chloride with lithium alkoxide and by the alcoholysis of beryllium methoxide (76). Three alkoxides namely, methoxide, ethoxide and isopropoxide of bismuth(III) have been reported in the case of bismuth(III) chloride (77). Chlorides of niobium(V) and tantalum(V) are known to form alkoxides of composition M(OR)_{5} when refluxed in dry parent alcohol in the presence of ammonia (78,79). Niobium(V) alkoxides are thermally less stable than tantalum(V) alkoxides. Stability decreases with increasing length of the alkyl chain. NMR studies and molecular weight measurements show that normal (V) alkoxides are dimer in boiling benzene solution but when dissolved in the parent alcohol, the molecular complexity of (V) alkoxide changes.

Chlorides of non-metals such as boron (80-82), silicon (83-88) and phosphorus (89,90) undergo solvolysis readily with the replacement of all the halogen by the alkoxo groups to form alkoxides of composition B(OR)_{3}, Si(OR)_{4} and P(OR)_{3}. The alkoxide derivatives of sulphur, selenium, tellurium, arsenic, antimony (91-96) and bismuth are highly volatile products and generally show monomeric behaviour. Alkoxides of arsenic (90),
antimony (94,95-97), bismuth (98), selenium (97,99), tellurium (97,100,101) and tungsten (70,102) have also been synthesised and characterised.

A characteristic feature of these alkoxides is that their alkoxy groups are labile and can be replaced by other alkoxy groups. This alcohol exchange reaction has been widely used for the preparation of organo oxygen compounds, the -OR groups being replaceable by simple esters (103,104), \( \beta \)-diketones (105), \( \beta \)-ketoesters (106,107) and glycols (108,109). Kumar and coworkers (110) studied the reactions of antimony(III) ethoxide with a number of \( \beta \)-diketones and \( \beta \)-ketoesters in different molar ratios and mono, bis and tris derivatives were easily obtained. The reactions of antimony(III) ethoxide (111) with various glycols in 1:1, 1:2, 2:3 molar ratios yield monoethoxide monoglycolates, bis(glycolates) and di-antimony tris(glycolates) respectively. The solubility of these derivatives increases with increasing branching of the alkylene group of glycols.

Metal alkoxides readily combine with hydrogen halides and acyl halides and the alkoxy groups are replaced by halogens. In the case of the alkoxides of titanium(IV) and zirconium(IV), it has been shown by Mehrotra (112) that the reaction of hydrogen chloride results in the formation of substantially the same product as obtained by the reaction involving the metal chloride and alcohol. These workers have also isolated compounds of
composition $\text{AlX(OR)}_2$, $\text{AlX}_2(\text{OR})\cdot0.5\text{CH}_3\text{COOR}$ and $\text{AlX}_3\cdot1.5\text{CH}_3\text{COOR}$
by the action of aluminium(III) alkoxide and acetyl chloride in
predetermined molar ratios (113).

Reactions of germanium(IV) alkoxides (114) and tin(IV) alkoxides
with acetyl chloride yield mixed chloride-alkoxide
derivatives (115). Bradley and his coworkers (116) have
isolated compounds of composition $\text{TiCl}_3\cdot\text{CH}_3\text{COOEt}$,
$\text{TiCl}_3(\text{OEt})\cdot\text{CH}_3\text{COOEt}$ and $\text{TiCl}_3(\text{OPr})\cdot\text{CH}_3\text{COOEt}$ by the action of
titanium(IV) alkoxide and acetyl chloride in predetermined
molar ratios. Similar studies have been carried out in the
case of zirconium(IV) alkoxide. Interestingly, in several of
the above reactions involving acetyl chloride, the resultant
metal chloride-alkoxide was obtained as a stable addition
compound with alkyl acetate (117,118).

Reactions of (V) alkoxides of niobium and tantalum
with acetyl chloride also result in the formation of addition
compound of metal(V) chloride-alkyl acetate (119,120).
Tellurium(IV) alkoxides also react with acetyl chloride in
equimolar and bimolar ratios to form simple derivatives of
composition $\text{Te(OR)}_3\text{Cl}$ and $\text{Te(OR)}_2\text{Cl}_2$ respectively (121). However,
the reaction products obtained using three and four moles of
acetyl chloride are coordinated with 0.5 moles of ester and
correspond to the formulae $\text{Te(OR)}\text{Cl}_3\cdot(0.5\text{CH}_3\text{COOR})$ and
$\text{TeCl}_4(0.5\text{CH}_3\text{COOR})$ respectively (loc cit).
Like alkoxides, metal phenoxides find many industrial applications (122-125), but it is very surprising that very little attention has been focussed on the metal phenoxides. In contrast to alcohols, phenols have less tendency to form addition compounds with neutral ligands; the formation of phenolate complexes is greatly favoured due to their Bronsted acidity. A large number of bi- and multi-dentate ligands containing \( \text{C}_6\text{H}_5\text{O}^- \) e.g. the Schiff's base derived from salicylaldehyde complexes of monofunctional phenolate anions are less well characterised. In the dimeric \( N,N' \)-dimethyl-salicylaldimine nickel(II) complex which contains one molecule of the catechol, oxygen acts as a bridge between two metal atoms (126). Stable complexes of composition \( \text{ML}_2 \) and \( \text{ML}_2 \cdot \text{H}_2\text{O} \) where \( L = 2\text{-methoxyphenol and some of its derivatives with nickel(II), copper(II) and zinc(II) have also been reported (127).}

Beryllium(II) chloride forms a phenoxide of composition \( \text{Be(OC}_6\text{H}_5)^2 \) with phenol (128). Diethyl beryllium on reacting with highly hindered 2,6-di-t-butyl phenol results into a colourless air sensitive monomeric compound where beryllium is two coordinate only (129). Substituted phenoxides of magnesium, silver and lead are also reported but their structural information is missing (130). Alkoxy and aryloxy derivatives of magnesium hydride of composition \( \text{HMgOR} \) (where \( R \) is alkyl or phenyl group) are also known (131). Preparation of metallic phenates by the reaction of anhydrous acetates with phenol has
already been attempted (132). Phenoxides of manganese(II) have been reported by Prasad and his coworkers (133).

A number of workers have investigated the reaction of iron(III) chloride with phenols (134-137). Thermometric and conductance titration curves (138) of iron(III) chloride and phenol show two breaks corresponding to Fe$^{3+}$/phenol ratio of 1:3 and 1:6. But spectroscopic evidence shows the presence of a compound of composition Fe[Fe(OFh)$_6$]. Moeller and his coworkers (139) have suggested a possibility of the formation of a compound of composition Fe(OFh)$_3$. Robinson and his coworkers (140) have shown that between pH 1.4-2.0, there is a reduction of Fe$^{3+}$ to Fe$^{2+}$ and it is accompanied by the formation of phenolic oxide. A series of bis(aryloxo) iron(II) and bis(alkoxo) iron(II) complexes of the type Fe(OC$_6$H$_4$X)$_2$(bipy)$_n$ and Fe(OR)$_2$(bipy)$_n$ with 2,2'-bipyridine have been prepared by the reaction of diethyl bis(2,2'-bipyridine) iron(II) and corresponding substituted phenols or alcohols respectively (X = NO$_2$, CN, Cl, C$_6$H$_5$, H) and their i.r. and n.m.r. studies suggest that the phenoxo ligand is normally bonded to iron through oxygen (141) unlike the $\pi$-bonding between ruthenium and phenoxy ligand in RuH(OC$_6$H$_5$)(FPh$_3$)$_2$ as observed by Wilkinson and his coworkers (142). A compound of composition B(OFh)$_3$ is obtained when boron(III) chloride reacts with phenol at -70°C. Boron(III) phenoxyde, unlike boron(III)
alkoxide has acceptor properties as it forms 1:1 addition compound with organic tertiary bases (80).

Aryloxy derivatives of sulphur(IV) and sulphur(VI) have been prepared by the reaction of aryl silyl ethers with sulphur(IV) fluoride and thionyl tetrafluoride respectively (143, 144). The products obtained depend upon the nature of aryl group and also on the relative strength of the reactants. Attempts to prepare the corresponding alkoxy derivatives of sulphur(IV) fluoride have been unsuccessful (145). The greater stability of aryloxy sulphur tetrafluorides over the alkoxy derivatives is comparable with that of phosphorus derivatives (146). From $^{19}$F n.m.r. studies, it is inferred that in the case of arylxysulphur(IV) fluorides, there are doublet and triplet corresponding to the axial and equatorial fluorines, while bis(aryloxy)sulphur difluoride shows only one $^{19}$F signal but the chemical shift of these signals indicates that they are equatorial as well which is quite unexpected because there are only a few examples where the steric effects of bridging groups leave an equatorial fluorine in preference to an axial fluorine (147). It is possible that the entire geometry of tris(aryloxy) thionyl fluorine molecules has been altered, i.e. to a polymer or a square pyramidal configuration so that conventional distinction between equatorial and axial fluorides are no longer meaningful. Morgan and Burstall (148) while reacting selenium oxychloride with phenol observed that despite the acidic nature
of the hydroxyl proton, proton of the phenyl ring participates in the liberation of hydrogen chloride in these reactions and compounds of composition $(ArOH)_3SeCl$ and $(ArOH)_2Se$ have been isolated. Similar behaviour has been observed in the reaction of thionyl chloride and phenol which results in the formation of compounds of composition $(C_6H_5OH)SCl$ and $(C_6H_5OH)_2S$ (149). However, phenol esters of amido and diaminophosphoric acids have been prepared by the action of phosphorus oxychloride and phenol in the presence of a base (150). Iodine monobromide however is known to brominate phenol (151).

Reactions of halides of titanium(IV), zirconium(IV) and thorium(IV) with phenols have been studied in detail by a number of workers. Compounds of composition $Ti(OPh)_4$.PhOH, $Zr(OPh)_4$.PhOH, $ZrCl(OPh)_3$.PhOH and $ThCl_2(OPh)_2$ have been isolated in the case of titanium, zirconium and thorium respectively (129). Recently, Malhotra and his coworkers (152) have assigned polymeric structures to the phenoxides of zirconium(IV). Some substituted phenoxides of tin(IV) are known which have been prepared by a number of synthetic routes (153, 154). Sandhu and his coworkers (155) have synthesized dibutyl tin(IV) phenoxides. From cryoscopic, n.m.r. and i.r. studies, a dimeric structure for the compound $[(OPh)Bu_2Sn]_2O$ based on the analogy with a structure of the compound $[R_2SnX]_2$ C (156) has been proposed as:
Uranium(IV) chloride forms a compound of composition \( \text{U(OPh)}_4 \cdot 2\text{PhOH} \cdot \text{NH}_3 \) when refluxed with phenol and ammonia in benzene \((157)\). Bagnall and his coworkers \((158)\) obtained a phenoxide of composition \( \text{U(OPh)}_4(\text{OEt}) \) when excess of phenol was refluxed with \( \text{U(OEt)}_5 \) for nine hours. When refluxed for shorter periods, a mixture of \( \text{U(OPh)}_4(\text{OEt}) \) and \( \text{U(OPh)}_3(\text{OEt})_2 \) was obtained. A brown paste of composition \( \text{U(OPh)}_4\text{Cl} \cdot 2\text{DMF} \) was obtained when \( \text{CsUCl}_6 \) was added to a suspension of sodium phenoxide in benzene followed by extraction with \( \text{N,N}'\text{-dimethylformamide} \).

Naphthols like phenols are known to react with metal salts and form metal naphthoxides. Anhydrous manganese(II) chloride reacts with 1 and 2-naphthol to yield respective naphthoxides \((133)\). Two series of naphthoxides of aluminium have been reported by Parasad and his coworkers \((159)\). Funk and his coworkers \((160,161)\) obtained naphthoxides of niobium(V) and tantalum(V) by the reaction of metal chlorides and 2-naphthol. Tungsten(VI) chloride forms naphthoxides of composition \( \text{WCl}_2(\text{OC}_{10}H_7)_4 \) and \( \text{W(OC}_{10}H_7)_6 \) with 2-naphthol \((161)\), whereas tungsten(V) bromide forms naphthoxides of composition \( \text{WBr}_3(1-\text{C}_{10}H_7\text{O}) \) and \( \text{WBr}_2(2-\text{C}_{10}H_7\text{O})_3 \cdot 2\text{C}_{10}H_7\text{OH} \) with 1- and 2-naphthols \((162)\). Similarly naphthoxides of composition
WO(1-C_{10}H_{7}O)_{4} and WO(2-C_{10}H_{7}O)_{4} have been obtained by the reaction of tungsten oxytetrachloride with naphthols (163-165). Malhotra and his coworkers (166) have isolated and characterised the naphthoxides of niobium(V) and tantalum(V) which are dimers. A series of chloronaphthoxides of titanium(IV) have been isolated only recently and they have been assigned polymeric structure involving naphthoxy rather than chloro group for polymerisation (167). Acceptor properties of naphthoxides of titanium(IV) have also been established (168).

Survey of literature thus reveals that the alkoxide derivatives of sulphur, selenium, tellurium, phosphorus, arsenic and antimony are highly volatile products and generally show monomeric behaviour and can be readily distilled without decomposition. This has been attributed to the electronegativity of the central atom and also due to extensive intramolecular \( p\pi - d\pi \) bonding with predominantly covalent character prevailing in these alkoxides. Apparently as the size of the central atom increases, the extent of \( p\pi - d\pi \) bonding decreases. In view of these interesting observations and increasing industrial use of phenoxides of metals and non-metals, it is worthwhile to prepare such phenoxides e.g. those of phosphorus, arsenic, antimony, tellurium and tungsten and to observe the effect of ring on the reactivity of the M-O-C moiety. The present work has been divided into three chapters.
The first chapter includes the preparation and characterisation of phenoxides of phosphorus(V), arsenic(III), antimony(III) and antimony(V). Solvo base character of phosphorus(V) phenoxide has been established in the solvo system fused phenol and acid-base neutralisation reactions have been carried out. Formation of double phenoxides of alkali metal phenoxides and those of phosphorus(V) and arsenic(III) have been predicted and they have been isolated and characterised. Reactions with acetyl chloride and hydrogen chloride to get back the original phosphorus chlorides have also been attempted. From the conductance and i.r. studies, an attempt has been made to elucidate the structure of these compounds.

The second chapter deals with the Lewis acid character of these phenoxides. Addition compounds of these phenoxides with various nitrogen and oxygen donors which include pyridine, piperidine, α-picoline, 2,2'-bipyridyl, 1,10-phenanthroline, pyridine N-oxide, α-picoline N-oxide and triphenylphosphine oxide, amides like N-methylformamide, N,N'-dimethylformamide, N-methylacetamide, N,N'-dimethylacetamide, hexamethyl phosphoramide etc. have been isolated. An attempt has also been made to study the behaviour of monochloro-phosphorus(V) phenoxide in the presence of chloride ion acceptor molecules such as antimony(V), iron(III) and aluminium(III) chlorides.
The third chapter includes the preparation of phenoxides of tellurium(IV) and tungsten(VI). An attempt has been made to establish the Lewis acid character of these phenoxides. Reaction products of phenoxides of tellurium(IV) with diketones, which include benzoin, acetylacetone, 2-hydroxyacetophenone, dibenzoylmethane and ethyl acetoacetate, with aliphatic and aromatic aldehydes viz. acetophenone, ethyl methyl ketone, salicylaldehyde etc. have been isolated and characterised. Based upon elemental analysis, conductance, i.r. and cryoscopic studies, an attempt has been made to elucidate the structure of these chelated compounds.