The poor acceptor properties of metal alkoxides are mainly due to their polymeric nature. Incorporation of an electron withdrawing group in place of alkoxide reduces the degree of polymerisation and enhances their acceptor properties. Surprisingly, as compared to the metal alkoxides, very little information is available about the metal phenoxydes. Titanium(IV) phenoxydes has been found to behave as a Lewis acid in fused phenol. Lewis acid character of the phenoxydes of titanium(IV), niobium(V) and tantalum(V) has already been established.

Ethoxyantimony(V) tetrachloride is dimeric and its acceptor properties have been established by the formation of addition compounds with a number of donor molecules. A similar study in the case of phenoxydes of antimony is lacking. Accordingly phenoxyantimony(V) tetrachloride has been prepared for the first time and its acceptor properties have been established by isolating a number of addition compounds with bases.

When equimolar solutions of antimony(V) chloride and phenol in carbon tetrachloride were mixed at $-10^\circ C$, a moisture sensitive yellow crystalline compound of composition $\text{SbCl}_4(\text{OC}_6\text{H}_5\text{Cl})$ separates out which turns brown when brought to room temperature. Compound of similar composition was obtained when $\text{SbCl}_4(\text{OEt})$ and phenol were mixed in equimolar ratio in carbon tetrachloride suggesting low reactivity of Sb-Cl bond as compared to Sb-O bond. Molar conductance values of $10^{-3}$ molar solution in nitrobenzene is 1.4 (Table I) suggest it to be a non-electrolyte but the molar conductance value of millimolar solutions in acetonitrile is 26.4 ohm$^{-1}$ cm$^2$ mol$^{-1}$ which is very high value for a non-electrolyte. By analogy with the ion $\text{SbCl}_4(\text{CH}_3\text{CN})^-$, $\text{SbCl}_4^-$ in acetonitrile, possible ions of $\text{SbCl}_4(\text{OC}_6\text{H}_5\text{Cl})$ in acetonitrile may be postulated as

$$\text{CH}_3\text{CN}$$

$$2\text{SbCl}_4(\text{OC}_6\text{H}_5\text{Cl}) \rightarrow [\text{SbCl}_2(\text{OC}_6\text{H}_5\text{Cl})_2 \cdot \text{CH}_3\text{CN}]^+ + \text{SbCl}_4^-.$$

Other possible ions such as $[\text{SbCl}_2(\text{OC}_6\text{H}_5\text{Cl}) \cdot \text{CH}_3\text{CN}]^+$, $[\text{SbCl}_6(\text{OC}_6\text{H}_5\text{Cl})]$ etc. cannot be ruled out.

Molecular weight determinations of very dilute solution in nitrobenzene give an average value of 693 indicating it to be dimer in this solvent. IR, spectrum of the compound shows intense bands at 638 and 336 cm$^{-1}$ due to terminal $\nu$(Sb-Cl) stretching modes in octahedral environment$^{36}$. No band has been observed below 300 cm$^{-1}$ where bridging $\text{Sb}^-$-$\text{Cl}^-$-$\text{Sb}$ stretching modes are expected to lie and thus excludes the possibility of dimerisation through chlorine bridging. Terminal antimony-oxygen stretching modes are expected to lie between 540-590 cm$^{-1}$ but no band has been observed in this region. Instead a sharp band at 520 cm$^{-1}$ with a shoulder at 495 cm$^{-1}$ has been observed which has been assigned to $\text{Sb}^-$-$\text{O}^-$-$\text{Sb}$ stretching modes$^{12,17}$ suggesting that dimerisation of $\text{SbCl}_4(\text{OC}_6\text{H}_5\text{Cl})$ takes place through the phenoxy group. Similar observations$^{13}$ have been made in the case of the compound $\text{NbCl}_4(\text{OC}_6\text{H}_5\text{Cl})$ wherein polymerisation takes place through the phenoxy group. A possible dimeric structure for the compound $\text{SbCl}_4(\text{OC}_6\text{H}_5\text{Cl})$ where each antimony atom has an octahedral environment may be proposed as
Table 1

Analytical data of the compounds of phenoxyantimony(V) tetrachloride with bases

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour and physical state</th>
<th>M.P. °C</th>
<th>Elemental analysis</th>
<th>Molar conductance in nitrobenzene ohm⁻¹ cm³ mole⁻¹</th>
<th>Molecular weight in nitrobenzene Required</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbCl₄(OC₆H₅)</td>
<td>Brown Solid</td>
<td>132</td>
<td>M</td>
<td>34.26</td>
<td>39.68</td>
<td>26.28</td>
</tr>
<tr>
<td>SbCl₄(OC₆H₅)·C₆H₅N</td>
<td>Yellow Solid</td>
<td>108</td>
<td>Cl</td>
<td>27.18</td>
<td>24.24</td>
<td>20.44</td>
</tr>
<tr>
<td>SbCl₄(OC₆H₅)·C₆H₅NO</td>
<td>Yellow Solid</td>
<td>96</td>
<td>OPh</td>
<td>20.36</td>
<td>26.04</td>
<td>20.36</td>
</tr>
<tr>
<td>SbCl₄(OC₆H₅)·C₆H₄N₃</td>
<td>Light Brown Solid</td>
<td>88</td>
<td>OPh</td>
<td>23.62</td>
<td>27.82</td>
<td>18.28</td>
</tr>
<tr>
<td>SbCl₄(OC₆H₅)·C₆H₄N₂</td>
<td>Orange Yellow Solid</td>
<td>126</td>
<td>M</td>
<td>24.54</td>
<td>28.48</td>
<td>18.56</td>
</tr>
<tr>
<td>SbCl₄(OC₆H₅)·C₆H₅N</td>
<td>Yellow Solid</td>
<td>82</td>
<td>Cl</td>
<td>24.96</td>
<td>29.46</td>
<td>19.36</td>
</tr>
</tbody>
</table>
Organic tertiary bases (B) such as pyridine, a-picoline, pyridine N-oxide, 2,2'-bipyridal and 1,10 phenantraclidine form addition compounds with SbCl₅ (OC₆H₅). Stoichiometric composition of these compounds has been established by elemental analyses which agrees well with the calculated values within the limits of the experimental errors (Table I). They are all moisture sensitive and change their colours on exposure to moisture. They are soluble in most of the polar organic solvents and the molar conductance values of 10⁻⁴ M solutions show them to be non-ionic. Molecular weight determinations of very dilute solutions in nitrobenzene (Table I) show them to be monomers.

Infrared spectra of these compounds especially in the lower spectral region is very informative. Shift of electrons from nitrogen or oxygen atom of the base to the acceptor molecule results in the perturbation of their bands in the lower or higher spectral region identical to those observed in the complexes of these bases with metal halides and acid halides which are typical of the base coordination. In case of pyridine complexes, the ν(C=N) observed at 1578 cm⁻¹ for free pyridine shifts to 1610-1620 cm⁻¹ on coordination. The pyridine ring deformation vibrations were also shifted to higher wave numbers. In case of a-picoline, the bands present at 1597, 1572, 1479, 1433 and 996 cm⁻¹ due to ν(C=C) and ν(C=N) were shifted to higher regions due to drift of electrons from nitrogen to the metal. In the case of the compound SbCl₅(OC₆H₅)₂C₆H₅NO, the NO bending vibration at 840 cm⁻¹ undergoes a small negative shift. It is also accompanied by the shift of ν(NO) 1269 and 1249 cm⁻¹ (bending) and ν(NO) 811 and 808 cm⁻¹ (stretching) to the lower spectral region which indicates the decrease in the double bond character of the (N=O) bond. Coordination of pyridine-N-oxide to the acceptor molecule is further supported by the lowering of the ring stretching vibrations.

The vibrational bands present in the 480-520 cm⁻¹ region in the compound SbCl₅ (OC₆H₅)₂, assigned to Sb-O-Sb vibrations, has been found to be missing in the spectra of these complexes. This indicates a breakdown of the phenoxy bridging in the parent phenoxy on complex formation. New bands in the region 599-620 cm⁻¹, not present in the parent phenoxy, make their appearances which may be assigned to the terminal ν(Sb-O) mode. Sb-Cl vibrations (330-340 cm⁻¹) in the spectra of the most of the complexes are observed at the same position as observed in the parent molecule, i.e., at the position of the six coordinated antimony. In addition another important band, not present in the spectrum of the pure phenoxy, is observed in the 270-280 cm⁻¹ region in these compounds which may be assigned to ν(Sb N) stretching mode. It may thus be concluded that phenoxyantimony(V) chloride is a fairly strong acceptor molecule.

December 13, 1979.