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PHENOXY ANTIMONY(V) TETRACHLORIDE

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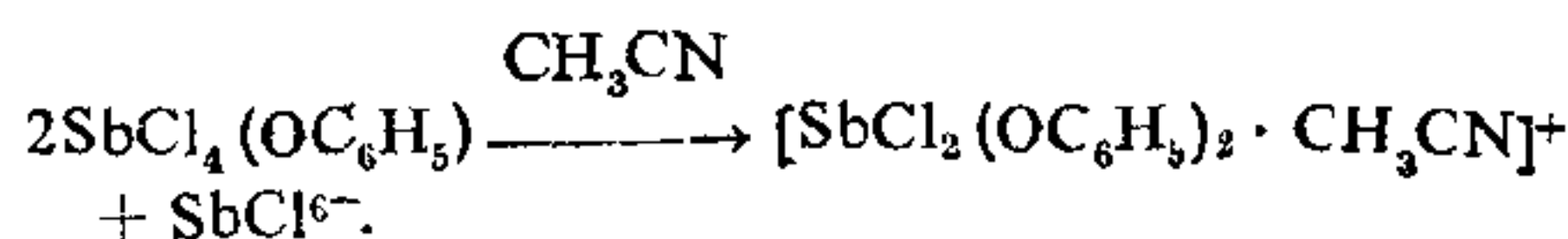
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THE poor acceptor properties of metal alkoxides are mainly due to their polymeric nature¹. Incorporation of an electron withdrawing group in place of alkoxide reduces the degree of polymerisation^{2,3} and enhances their acceptor properties¹. Surprisingly, as compared to the metal alkoxides⁴⁻⁶, very little information is available about the metal phenoxides. Titanium(IV) phenoxide has been found to behave as solvo acid in fused phenol⁷. Lewis acid character of phenoxides of titanium(IV)⁸, niobium(V) and tantalum(V)⁹ has already been established.

Ethoxyantimony(V) tetrachloride is dimeric¹² and its acceptor properties have been established by the formation of addition compounds with a number of donor molecules¹³. A similar study in the case of phenoxides 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°C , a moisture sensitive yellow crystalline compound of composition $\text{SbCl}_4(\text{OC}_6\text{H}_5)$ 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 low (Table I) which suggest it to be a non-electrolyte but the molar conductance value of millimolar solutions in acetonitrile is $26.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ which is very high value for a non-electrolyte. By analogy with the ion $\text{SbCl}_4(\text{CH}_3\text{CN})^+ \cdot \text{SbCl}_6^-$ in acetonitrile¹⁵, possible ions of $\text{SbCl}_4(\text{OC}_6\text{H}_5)$ in acetonitrile may be postulated as



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

Molecular weight determinations of very dilute solution in nitrobenzene give an average value of 690 indicating it to be dimer in this solvent. I.r. spectrum of the compound shows intense bands at 638 and 336 cm^{-1} due to terminal $\nu(\text{Sb}-\text{Cl})$ stretching modes in octahedral environment¹⁶. 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 $540-590 \text{ cm}^{-1}$ 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 $\text{SbCl}_4(\text{OC}_6\text{H}_5)$ takes place through the phenoxy group. Similar observations¹⁸ have been made in the case of the compound $\text{NbCl}_4(\text{OC}_6\text{H}_5)$ wherein polymerisation takes place through the phenoxy group. A possible dimeric structure for the compound $\text{SbCl}_4(\text{OC}_6\text{H}_5)$ where each antimony atom has an octahedral environment may be proposed as

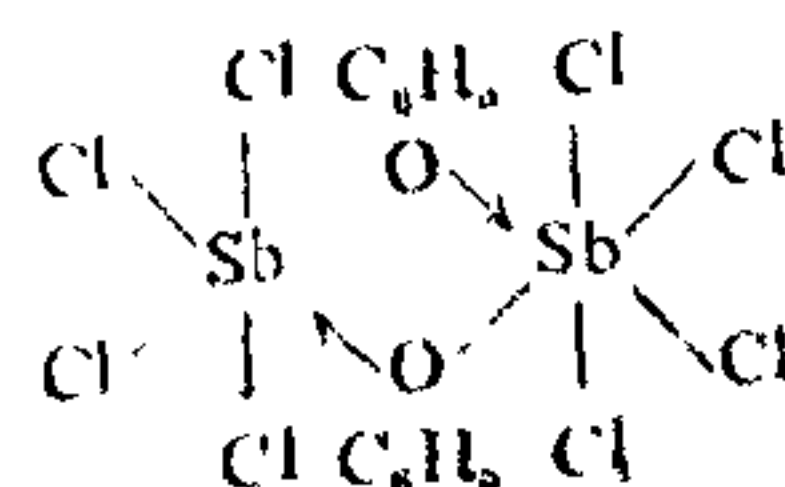


TABLE I
Analytical data of the compounds of phenoxyantimony(V) tetrachloride with bases

Compound	Colour and physical state	M.P. °C	Elemental analysis						Molar conductance in nitrobenzene $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$	Molecular weight in nitrobenzene	
			% Found			% Required					
			M	Cl	OPh	M	Cl	OPh			
$\text{SbCl}_4(\text{OC}_6\text{H}_5)$	Brown Solid	132	34.26	39.68	26.28	34.14	39.77	26.82	2.4	356	690
$\text{SbCl}_4(\text{OC}_6\text{H}_5) \cdot \text{C}_8\text{H}_5\text{N}$	Yellow Solid	108	27.18	34.24	20.44	27.32	34.07	20.87	1.8	445.55	438
$\text{SbCl}_4(\text{OC}_6\text{H}_5) \cdot \text{C}_8\text{H}_5\text{NO}$	Yellow Solid	96	26.46	30.64	20.36	26.35	30.72	20.15	0.8	461.55	446
$\text{SbCl}_4(\text{OC}_6\text{H}_5) \cdot \text{C}_{10}\text{H}_9\text{N}_3$	Light Brown Solid	88	23.62	27.82	18.28	23.75	27.66	18.14	1.4	512.55	508
$\text{SbCl}_4(\text{OC}_6\text{H}_5) \cdot \text{C}_8\text{H}_{11}\text{N}_2$	Orange Yellow Solid	126	24.54	28.48	18.56	24.72	28.76	18.88	1.8	485.55	478
$\text{SbCl}_4(\text{OC}_6\text{H}_5) \cdot \text{C}_8\text{H}_7\text{N}$	Yellow Solid	82	24.86	29.46	19.36	25.07	29.62	19.15	2.2	492.55	482

Organic tertiary bases (B) such as pyridine, α -picoline, pyridine N-oxide, 2,2'-bipyridal and 1,10 phenanthroline form addition compounds with $\text{SbCl}_4(\text{OC}_6\text{H}_5)$. 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^{-3} 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 halides¹⁹ and acid halides²⁰ which are typical of the base coordination. In case of pyridine complexes, the $\nu(\text{C}=\text{N})$ observed at 1578 cm^{-1} for free pyridine^{19,21-22} shifts to $1610-1620\text{ cm}^{-1}$ on coordination. The pyridine ring deformation vibrations were also shifted to higher wave numbers¹⁹. In case of α -picoline, the bands present at $1597, 1572, 1479, 1433$ and 996 cm^{-1} due to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ ²³ are shifted to higher regions due to drift of electrons from nitrogen to the metal. In the case of the compound $\text{SbCl}_4(\text{OC}_6\text{H}_5)\cdot\text{C}_5\text{H}_5\text{NO}$, the NO bending vibration at 840 cm^{-1} undergoes a small negative shift. It is also accompanied by the shift of $\nu(\text{NO})$ 1269 and 1249 cm^{-1} (bending) and $\nu(\text{NO})$ 811 and 808 cm^{-1} (stretching) to the lower spectral region which indicates the decrease in the double bond character of the $(\text{N}=\text{O})$ ²⁴. Coordination of pyridine-N-oxide to the acceptor molecule is further supported by the lowering of the ring stretching vibrations²⁴.

The vibrational bands present in the $480-520\text{ cm}^{-1}$ region in the compound $\text{SbCl}_4(\text{OC}_6\text{H}_5)$, assigned to

$\text{Sb} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{---} \end{array} \text{Sb}$ vibrations, has been found to be missing in the spectra of these complexes. This indicates a breakdown of the phenoxy bridging in the parent phenoxide on complex formation. New bands in the region $590-620\text{ cm}^{-1}$, not present in the parent phenoxide, make their appearances which may be assigned to the terminal $\nu(\text{Sb}-\text{O})$ mode. Sb-Cl vibrations ($330-340\text{ cm}^{-1}$) 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 antimony¹⁶. In addition another important band, not present in the spectrum of the pure phenoxide, is observed in the $270-280\text{ cm}^{-1}$ region in these compounds which may be assigned

to $\nu(\text{Sb}-\text{N})$ stretching mode²⁵. It may thus be concluded that phenoxyantimony(V) chloride is a fairly strong acceptor molecule.

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