Alkylxanthates of Phenylantimony(III)

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Synthesis and characterization of PhSb(S$_2$COR)$_2$ (where R = alkyl group) are reported. The resulting derivatives are white crystalline solids and monomers in refluxing benzene. IR and PMR data reveal pseudo-octahedral geometry for these chelates, with sulphur atoms occupying the equatorial position and the phenyl group and lone pair of electrons occupying two axial positions.

Antimony(III) halides have been reported$^{1-5}$ to interact with organic ligands and form a variety of complexes, the geometries of which depend on the nature of the ligands used. Similar studies with alkyl- or aryl-antimony(III) halides are very limited. In the present note, we report the synthesis and physicochemical studies of some alkylxanthates of phenylantimony(III).

Phenyldichlorostibine$^6$ and potassium alkylxanthates$^7$ were prepared by the literature methods. Phenyldialkoxystibines were prepared by the reactions of sodium alkoxides with phenyldichlorostibine.

Alkylxanthates of phenylantimony(III) were prepared by the following general procedure: Phenyl dichlorostibine (0.63 g, 2.33 mmol) in CS$_2$ was added to a suspension of potassium ethylxanthate (0.76 g, 4.72 mmol) in CS$_2$ and the reaction mixture stirred for 2 hr at the room temperature. Potassium chloride formed was filtered off and the filtrate dried in vacuo to afford bis-derivatives (Eq. 1).

These bis-chelates can also be prepared by the insertion of CS$_2$ across Sb-O bond (Eq. 2) by refluxing for 1 hr the corresponding phenyldialkoxystibines in excess CS$_2$ and removing excess solvent in vacuo.

PhSb(OR)$_2$ $\rightarrow$ PhSb(S$_2$COR)$_2$ 

(R = Me, Et and Pr$^i$)

These chelates are white crystalline solids, soluble in common organic solvents and are monomeric in refluxing benzene. These are nonvolatile and tend to decompose on heating to yield PhSbS finally. The TG and DTA of a representative compound, PhSb(S$_2$COMe)$_2$, have been carried out to illustrate the mode of decomposition in these chelates. The DTA shows an endothermic peak at 125°C indicating the simultaneous fusion and decomposition of the complex. The TG reveals rapid decomposition of the complex with a 43% mass loss at 125°C, yielding finally PhSbS and volatile products which appear to be COS, CS$_2$, hydrocarbons and thionester etc.$^{8,9}$

The coordinate analyses in Ni(II) xanthates$^{10}$ have shown that the bands are highly coupled in the IR spectra of such complexes. However, the following assignments can be made for the absorptions observed in the IR spectra of the presently synthesized complexes: (i) vC=O−C$\approx$1200; (ii) vC−O$\approx$1150; (iii)
\( vC=S \sim 1020; \) (iv) \( vSb=S^{11} \) in the region 325-400 cm\(^{-1}\).

The appearance of only one strong band \( \sim 1020 \) cm\(^{-1}\) (for \( vC=S \)) indicates the bidentate nature of the ligand\(^{12}\). The IR data reveal bidentate nature of the ligands. In these monomeric chelates the central antimony atom appears to acquire a coordination number of five. These pentacoordinated compounds may have either a trigonal bipyramidal or square pyramidal geometry. The presence of a stereochemically active lone pair of electrons in antimony (III) complexes is well established\(^{13}\).

The PMR spectra of some of the derivatives have been recorded in CDCl\(_3\). The PMR spectrum of the simplest derivative, PhSb(S\(_2\)COMe\(_2\)), displays a six-proton singlet at \( \delta 4.05 \) due to protons of two methyl groups, while the aromatic protons appear as a multiplet in the region \( \delta 7.10 \) to \( 8.05 \). The appearance of a six-proton singlet for two methyl group indicates that the protons of both the methyl groups are magnetically equivalent. Similarly in the spectrum of PhSb(S\(_2\)COEt\(_2\)), the methyl protons appear as a triplet at \( \delta 1.43 \), and methylene protons as a quartet at \( \delta 4.52 \). The aromatic protons appear as a multiplet in the region \( \delta 7.20-8.10 \). In the spectrum of PhSb(S\(_2\)COPr\(_2\)), a six-proton doublet at \( \delta 1.45 \) has been assigned to protons of two methyl groups and one-proton multiplet at \( \delta 5.5 \) to \( CH \) of isopropyl. As usual the aromatic protons are seen as a multiplet in the region \( \delta 7.20-8.20 \). Therefore, the most plausible geometry for these derivatives appears to be a pseudo-octahedral with the sulphur atoms occupying the equatorial positions and the phenyl group and lone pair of electrons occupying the two axial positions.

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References