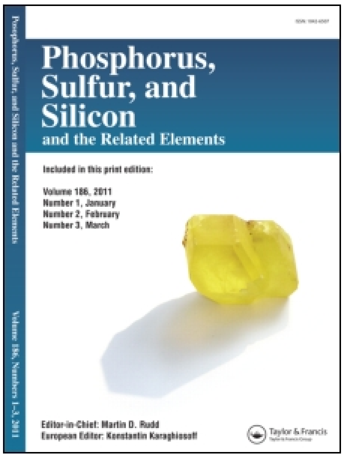

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DIPHENYLANTIMONY(III) DERIVATIVES OF ALKYL XANTHATES

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A few diorganoantimony(III) derivatives, Ph_2SbS_2COR, have been prepared by the interaction of Ph_2SbCl/Ph_2SbOAc with $ROCS_2$ K (where $R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9). These derivatives have been characterized by elemental analyses, molecular weight determinations, IR and NMR (^1H and ^{13}C) spectral data. The monodentate nature of the ligand in these derivatives has been proposed.

Key words: Alkyl xanthates; Diphenylantimony(III) derivatives; Monomers; Spectral data; Monodentate Ligands; Four coordinated antimony.

INTRODUCTION

Xanthate derivatives of a large number of metal and metalloids including those of antimony(III)[1–3] and mono-organoantimony(III) have been synthesized and studied extensively.[4] An exhaustive survey of the literature reveals no mention of the analogous diorganoantimony(III) derivatives. In the present communication, we report the synthesis and characterization of diphenylantimony(III) derivatives of some alkyl xanthates. A noteworthy feature of these derivatives is the monodentate behaviour of the ligands which is in contrast to the earlier reports on corresponding monoorgano[5]- and tris[6]-antimony(III) derivatives in which the bidentate nature of the ligands has been reported.

RESULTS AND DISCUSSION

The interaction of Ph_2SbCl/Ph_2SbOAc and potassium alkyl xanthates in 1:1 molar ratio yield the corresponding diorgano-antimony derivatives.

$$Ph_2SbCl + ROCS_2K \rightarrow Ph_2SbS_2COR + KCl \downarrow$$

$$Ph_2SbOOCCH_3 + ROCS_2K \rightarrow Ph_2SbS_2COR + CH_3COOK \downarrow$$

(where $R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9).

All these derivatives are yellow coloured viscous liquids, fairly soluble in common organic solvents and purified by $CHCl_3$/pet.ether solution. The vapour pressure osmometric molecular weight measurement in chloroform solution at 45°C as well as in freezing benzene solution show the monomeric nature of these derivatives. The molecular weights of these derivatives are found to be independent of the concentration.

IR SPECTRA

IR spectra of the complexes have been recorded in the region 4000–200 $\mathrm{cm^{-1}}$.

All diphenylantimony xanthates show a strong intensity absorption band in the range 1208–1255 $\mathrm{cm^{-1}}$ which may be attributed to $\nu\,\mathrm{C{-}O{-}C}$ which characterizes[7] the $\mathrm{C{-}O{-}\overset{\overset{S}{\|}}{C}}$ group, and another band in the range 1126–1192 $\mathrm{cm^{-1}}$ may be assigned to $\nu\,\mathrm{O{-}\overset{\|}{C}}$ group.[7] The absorption band near ~1040 $\mathrm{cm^{-1}}$ may be assigned to ν CSS. In all cases this absorption band is either split into two close bands or has well defined shoulders. These two close bands may be assigned to $\nu\,\mathrm{S{-}C{=}(S)}$ and $\nu\mathrm{(S){-}C{=}S}$. The appearance of these bands for ν CSS indicate the monodentate nature of the xanthate moiety. Similar observations have been reported by earlier workers in the case of metal dithiocarbamate,[8,9] dithiocarbazate[10,11] and 2-alkylaminocyclopentene-1-carbodithioate[12,13] complexes.

The band observed in the range 446–458 $\mathrm{cm^{-1}}$ may be assigned to ν Sb-C,[14,15] this is basically a phenyl deformation mode incorporating some Sb-C deformation. A band appearing in the region 325–378 $\mathrm{cm^{-1}}$ is being assigned to $\nu\,\mathrm{Sb{-}S}$.[16]

NMR SPECTRA

The ^{1}H NMR spectra of the complexes display the characteristic proton resonances due to alkyl, alkoxy and aromatic protons. The aromatic protons appear in the region δ 6.86–7.66 ppm. The complex, $\mathrm{CH_3OCS_2SbPh_2}$ exhibits a singlet for the methyl protons at δ 4.3 ppm, while the complex $\mathrm{CH_3CH_2OCS_2SbPh_2}$ display a quartet at δ 4.3 ppm and a triplet at δ 1.5 ppm, respectively for the $\mathrm{{-}CH_2}$ and $\mathrm{{-}CH_3}$ protons. In i-$\mathrm{C_3H_7OCS_2SbPh_2}$, a doublet is obtained for the six $\mathrm{({-}CH_3)_2}$ protons at δ 1.3 ppm, whereas a multiplet has been observed for the —CH proton. The rest of the complexes also exhibit the expected signals for the corresponding protons.

The ^{13}C NMR of two representative compounds along with $\mathrm{PhSbL_2}$ and $\mathrm{SbL_3}$ (where L = i-$\mathrm{C_3H_7OCSS^-}$) were recorded and are summarized in Table I. The signals for the alkyl and alkoxy carbons were observed at their usual positions. The CSS carbon has been observed at δ 214.3 ppm in i-$\mathrm{C_3H_7OCS_2SbPh_2}$. This signal has been observed at δ 220.13 and 221.05 ppm in the corresponding monoorganoantimony(III), $\mathrm{PhSbL_2}$ and antimony(III), $\mathrm{SbL_3}$, derivatives, respectively, where the ligand is reported to behave as a bidentate moiety.[1,5] Had the ligand been a bidentate moiety in these diorganoantimony(III) derivatives too, this signal should have been deshielded. This upfield chemical shift in CSS carbon signal indicates the monodentate behaviour of the ligands in these derivatives.

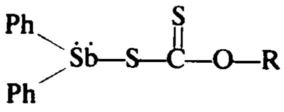
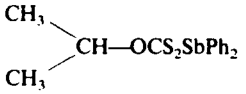
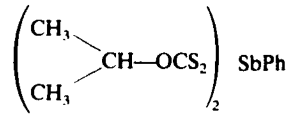
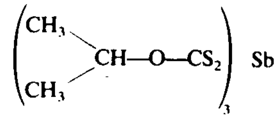


TABLE I

^{13}C NMR spectral data for antimony(III)- and organoantimony(III) alkyl xanthates

S. No.	Complex	Types of C atoms $-CH_3$	$>CH_2$	$>C-O$	CSS	C(s)	C(o)	C(m)	C(p)	δ'
1.	$CH_3CH_2CH_2OCS_2SbPh_2$	10.37	21.7	77.4	215.3	140.4	129.1	138.5	129.4	-9.1
2.	 $(CH_3)_2CH-OCS_2SbPh_2$	21.2	—	79.9	214.3	140.5	129.1	135.7	129.4	-6.3
3.	 $[(CH_3)_2CH-OCS_2]_2SbPh$	21.30	—	80.46	220.13	145.85	129.22	135.19	128.56	-6.63
4.	 $[(CH_3)_2CH-O-CS_2]_3Sb$	21.3	—	80.84	221.05	—	—	—	—	—

The appearance of only one set of signals for the carbon atoms of the two phenyl groups indicates their equivalent nature. The corrected chemical shift values, δ'[17,18] defined as δ' = δ Cp − δ Cm (where δ Cp and δ Cm are the chemical shift values of para- and meta-carbon atoms of the phenyl ring, respectively) are found to be negative (Table I) in these derivatives. This negative value is an indicative of an electron release from metal atom towards phenyl ring through p_π-p_π conjugation.

EXPERIMENTAL

Moisture was carefully excluded throughout experimental manipulations. The chemicals used were of reagent grade. Antimony trichloride (Fluka, 80°/10 mm) was distilled before use. The diphenylantimony chloride[19] and potassium alkyl xanthates[4] have been synthesized by the literature methods. Antimony[20] and sulphur[20] were estimated iodometrically and gravimetrically, respectively. Molecular weights were determined on Knauer Vapour Pressure Osmometer in chloroform solution at 45°C and cryoscopically in benzene solution. IR spectra of the compounds have been recorded as neat films on Nicolet DX FT IR spectrophotometer using caesium iodide plates. ^1H NMR spectra were recorded on a JEOL FX-90Q spectrometer in $CDCl_3$ solution using TMS as an internal reference. ^{13}C NMR spectra were recorded on 270 MHz BRUKER spectrometer.

All derivatives have been synthesized by the reaction of Ph_2SbCl/Ph_2SbOAc with the corresponding ligands in 1:1 molar ratio in benzene solution. Since same procedure has been employed for synthesizing these derivatives, the preparation of only one derivative is being described and the results of the rest are being summarized.

Synthesis of n-$C_3H_7OCS(S)SbPh_2$. Weighed amount of n-$C_3H_7OCS_2K$ (0.54 g, 3.10 mM) was added to a benzene suspension of corresponding amount of Ph_2SbCl (0.96 g, 3.09 mM). The reaction mixture was refluxed for ~2 hours. The NaCl thus formed was filtered off and the excess solvent was removed under reduced pressure to yield a yellow coloured, viscous liquid in quantitative yield. The product was purified by redissolving it in chloroform and recovered by adding excess of pet. ether (40–60°). The product on analysis was found to have Sb = 29.22%, S = 15.05%; calculated Sb = 29.51%, S = 15.61%.

Using the above experimental procedure, the following five complexes have also been synthesized and characterized.

	obs (%)		calc (%)	
(i) $CH_3OCS_2SbPh_2$	31.15	16.31	31.68	16.75
(ii) $C_2H_5OCS_2SbPh_2$	30.08	15.69	30.55	16.16
(iii) i-$C_3H_7OCS_2SbPh_2$	29.41	14.98	29.51	15.61
(iv) n-$C_4H_9OCS_2SbPh_2$	28.09	14.91	28.54	15.09
(v) i-$C_4H_9OCS_2SbPh_2$	28.23	14.79	28.54	15.09

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