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Monothio-β-Diketonates of Antimony(III)

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The coordination complexes of sulfur donor ligands have aroused considerable interest during the past 15 years. The donor sulfur atom in such complexes confers properties which are sometimes highly novel and differ markedly from those of the analogous oxygen derivatives. Replacement of one of the oxygen atoms by sulfur atom gives rise to monothio-β-diketones, which have also attracted considerable attention as chelating agents [1]. In continuation to our studies on the chemistry of antimony(III) β-diketonates [2], we report in this communication the synthesis and structures of the corresponding monothio-β-diketonates.

Experimental

Monothio-β-diketones were synthesised by Claisen type condensation of ketones with thionic ester [3]. Ethylthioacetoacetate and ethylthiobenzoylacetate were also prepared by reported methods [4, 5]. Antimony isopropoxide was prepared by ammonia method [6]. All reactions were carried out under anhydrous conditions.

IR spectra were measured in nujol mulls or neat between CsI Optics in the range of 4000–200 cm^{-1} with a Perkin Elmer model 577 spectrophotometer. PMR spectra were determined by Perkin Elmer R12B spectrometer (60 MHz) in CCl_4 solutions using TMS as an external standard. Molecular weights were determined cryoscopically.

Reaction of Antimony Isopropoxide with Ethylthioacetoacetate in 1:3 Molar Ratio

A mixture of antimony isopropoxide (1.19 g) and ethylthioacetoacetate (1.75 g) in anhydrous benzene was kept overnight. Benzene and librated isopropanol were removed under vacuum (40 °C/0.1 mm) giving a yellow coloured viscous liquid. *Anal.* Found: Sb, 21.95 and S, 16.84%. Calcd. for $Sb(MeCSCHCOOEt)_3$: Sb, 21.85 and S, 17.26%.

Reaction of Antimonytrichloride with Sodium Salt of Monothiobenzoylacetone in 1:3 Molar Ratio

A chloroform solution of antimonytrichloride (0.72 g) was added to the suspension of sodium salt of monothiobenzoylacetone (prepared from 0.23 g sodium and 1.69 g ligand) in chloroform. Reaction mixture was refluxed for 2 hours. Sodium chloride formed during the reaction was filtered off. Filtrate was evaporated under vacuum (40 °C/0.1 mm) giving a brown red sticky solid. *Anal.* Found: Sb, 17.50 and S, 14.70%. Calcd. for $Sb(PhCSCHCOMe)_3$: Sb, 18.58 and S, 14.68%.

Results and Discussion

Reaction of antimony isopropoxide with monothio-β-diketones and monothio-β-ketoesters in 1:3 molar ratios at ambient temperature yields tris-derivatives of the type SbL_3:

$$\mathrm{Sb(OPr^i)_3 + 3HL \xrightarrow{Benzene} SbL_3 + 3Pr^iOH}$$

[where HL = $PhCSCH_2COMe$ (BzacSH), $PhCSCH_2CO$-Ph (DbzmSH), $PHCSCH_2COC_6H_4Cl$-*p* (*p*-ClDbzmSH), $PHCSCH_2COC_6H_4Br$-*p* (*p*-BrDbzmSH), $MeCSCH_2CO$-OEt (EAASH) and $PhCSCH_2COOEt$ (EBASH)].

Compared to reactions of antimonyisopropoxide with β-diketones, the above reactions are faster and all the three moles of isopropanol could be librated even at ambient temperature. However, only two moles of alcohol could be replaced under similar conditions in the case of the reactions with β-diketones [2].

SbL_3 may also be obtained by the reaction of antimonytrichloride and sodium salt of the ligand in 1:3 molar ratio in refluxing chloroform:

$$\mathrm{SbCl_3 + 3NaL \xrightarrow{chloroform} SbL_3 + 3NaCl}$$

(where L = BzacS and DbzmS).

All these chelates are hydrolytically unstable, monomeric in freezing benzene and are coloured. The intense colour of some of these complexes might be due to the π–π* transitions in the $\mathrm{S{-}\overset{|}{C}{=}\overset{|}{C}{-}\overset{|}{C}{=}O}$ [7] chromophore.

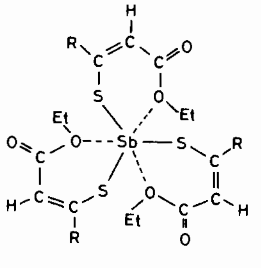
A broad band (2700–2100 cm^{-1}) attributable to the intramolecularly hydrogen bonded thiol group [8–10] in the free ligand is absent in the IR spectra of these complexes. The absence of free carbonyl absorptions in the IR spectra of antimony(III) tris-(monothio-β-diketonates) and the presence of absorptions due to coordinated carbonyl group ($\nu\mathrm{C}\overset{\cdots}{-}\mathrm{O}$) in the region 1565–1600 cm^{-1} may indicate that ligand moieties are chelated [10, 12].

Contrary to monothio-β-diketone complexes of antimony(III) corresponding monothio-β-ketoester derivatives show absorption bands at ~ 1710 and ~ 1640 cm^{-1}. The presence of these IR bands in the latter complexes provide good evidence of the free

TABLE I. Reactions of Antimony Isopropoxide with Monothio-β-diketones.

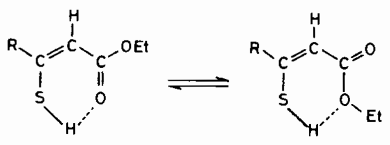
Reactants (g)			Product	Nature of the product	Analysis (%) Found (Calcd.)		$\nu C\overset{\cdots}{=}O$ (cm^{-1})
Sb(OPr^i)$_3$	RCSCH$_2$ R	COR′ R′			Sb	S	
0.85	Ph 1.53	Me	Sb(PhCSCHCOMe)$_3$	Sticky brown solid	18.18 (18.58)	14.27 (14.68)	1560–70
1.18	Ph 2.84	Ph	Sb(PhCSCHCOPh)$_3$	Orange red solid	14.52 (14.50)	10.76 (11.46)	1595
0.61	Ph 1.69	p-ClC$_6$H$_4$	Sb(PhCSCHCOC$_6$H$_4$Cl-p)$_3$	Orange red solid	12.80 (12.91)	9.58 (10.20)	1585
0.70	Ph 2.23	p-BrC$_6$H$_4$	Sb(PhCSCHCOC$_6$H$_4$Br-p)$_3$	Orange red solid	11.28 (11.31)	9.41 (8.94)	1581
1.19	Me 1.75	OEt	Sb(MeCSCHCOOEt)$_3$	Yellow coloured viscous liquid	21.95 (21.85)	16.84 (17.26)	1700–10 1640
1.38	Ph 2.88	OEt	Sb(PhCSCHCOOEt)$_3$	Yellow pasty mass	16.30 (16.38)	12.86 (12.94)	1710 1640

carbonyl group [11]. By analogy, these monothio-β-ketoester derivatives of antimony(III) may also have chelated structure in which etheral oxygen is coordinated (I):



I

This structure may get support from the studies made by Doyle and Tobias [13] and by Duus [14]. The former workers suggested that in β-ketoesters, the keto and etheral oxygens are of comparable donor strengths. Similarly Duus [14] studied the β-thioketoesters and concluded that steric overcrowding is considerably more pronounced in the normal intramolecularly hydrogen bonded *cis*-enethiol structure II, than it is in the structure III:

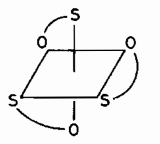


II III

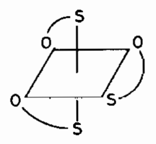
The bands in the region 540–612 cm^{-1} for all these complexes may be assigned to the ν(Sb–O) vibrations [6]. The Sb–S [6] symmetric and antisymmetric stretchings and $\nu C\overset{\cdots}{=}S$ [15] have been observed in the region 338–400 cm^{-1} and 1270–1190 cm^{-1} respectively.

From the IR studies of these complexes it appears that antimony atom in these derivatives is six coordinated. However, the presence of the stereochemically active lone pair of electrons of antimony should lead to a distorted octahedral geometry [2].

The PMR spectra of Sb(BzacS)$_3$ show singlets at δ 2.32 and 6.80 due to methyl and methine protons respectively. Such tris chelates with unsymmetrical bidentate ligands may exhibit two geometrical isomers, *i.e. cis* (*facial*) IV and *trans* (*meridional*) V [16, 17]. The PMR spectra of *cis* isomer exhibit single resonances due to three fold axis of symmetry while *trans* isomer exhibit three resonances. The presence of one methyl and methine signal for Sb(BzacS)$_3$ at room temperature may suggest that it exists exclusively in the *cis* form.



cis - IV



trans - V

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