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Antimony(III) Complexes of Bifunctional Tridentate *Schiff* Bases

By

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With 1 Figure

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Several new *Schiff* base derivatives of antimony(III) have been synthesized by the reaction of antimony(III) isopropoxide with the *Schiff* bases having the donor system, O—N—O. The reactions in 1 : 1 and 2 : 3 molar ratios [$Sb(O{-}i{-}C_3H_7)_3$: : *Schiff* base] have yielded $Sb(O{-}i{-}C_3H_7)$ (*SB*) and Sb_2 (*SB*)$_3$ type of derivatives (where *SB* represents the anion of the *Schiff* base and *SB*H_2 = o-hydroxyacetophenone-2-hydroxy-1-propylimine, o-hydroxycetophenone-3-hydroxy-1-propylimine, salicylidene-2-hydroxyethylamine, salicylidene-2-hydroxy-1-propylamine and 2-hydroxy-1-naphthylidene-2-hydroxyethylamine) resp. In the resulting *Schiff* base derivatives, the central antimony atom appears to be tetracoordinated as indicated by their monomeric state determined ebullioscopically. The infrared spectra of the resulting complexes have been recorded and tentative structures indicated. The thermogravimetric analysis of antimony-monoisopropoxysalicylidene-2-hydroxy-1-propylamine has also been carried out.

Introduction

In recent years, reactions of antimony(III) ethoxide with oxygen[1–3] and nitrogen[4] donor ligands have been investigated. Communications[5, 6] from these laboratories related to the preparation and characterisation of several antimony(III) complexes with monofunctional bidentate *Schiff* bases have been reported. However, reactions of antimony(III) isopropoxide with bifunctional tridentate *Schiff* bases derived from o-hydroxyacetophenone, salicylaldehyde and 2-hydroxynaphthaldehyde with hydroxyalkylamines having the donor system, O—N—O do not

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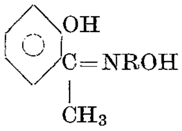
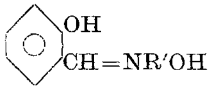
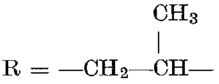
seem to have been studied so far. In the present paper, reactions of antimony(III) isopropoxide with these *Schiff* bases as shown below have been described.

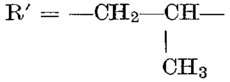


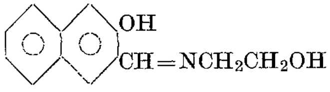


I:

$R = -CH_2-CH(CH_3)-$

II: $R = -(CH_2)_3-$

III: $R' = -(CH_2)_2-$

IV:

$R' = -CH_2-CH(CH_3)-$



V

In general, these reactions in 1 : 1 and 2 : 3 molar ratios may be represented as follows:

$$Sb(O-i\text{-}C_3H_7)_3 + SBH_2 \rightarrow Sb(O-i\text{-}C_3H_7)(SB) + 2\, i\text{-}C_3H_7OH$$
$$2\, Sb(O-i\text{-}C_3H_7)_3 + 3\, SBH_2 \rightarrow Sb_2(SB)_3 + 6\, i\text{-}C_3H_7OH$$

Experimental

The reactions were carried out under strictly anhydrous conditions. $Sb(i\text{-}C_3H_7O)_3$ was prepared by the Null method[7] and was destilled (105 °C/14 mm) before use.

2-Propanol (BDH) was dried over Na wire and then fractionated over $Al(i\text{-}C_3H_7O)_3$. Benzene (BDH) was dried in the same manner, followed by azeotropic fractionation in presence of ethanol.

Schiff bases[8] were synthesized as usual.

The experimental technique of the azeotropic removal of 2-propanol is the same as described in earlier papers[5, 6] and special care was taken to avoid hydrolysis. The course of the reactions was assured by estimating the alcohol in the azeotrope due to the replacement with the ligand. The experimental details of all these reactions are summarized in Table 1.

Sb was estimated as antimonous pyrogallate[9], while the nitrogen by *Kjeldahl*'s method. 2-Propanol was estimated by the oxidimetric method[10] using $K_2Cr_2O_7$ in 12.5% H_2SO_4.

The values found were satisfactory.

Molecular weights were determined ebullioscopically in boiling benzene IR spectra were recorded in the range of 4000–400 cm^{-1} with a Perkin-Elmer 337 grating infrared spectrophotometer.

Table 1. *Synthesis and Characteristics of Antimony(III) Schiff Base Complexes*

$Sb(i\text{-}C_3H_7O)_3$, g	*Schiff* base, g	Molar ratio	Refl. time, h	Compound, yield (g), nature
1.18	$C_{11}H_{15}NO_2$ 0.76	1 : 1	3	$Sb(O—i\text{-}C_3H_7)(C_{11}H_{13}NO_2)$ (1.43), yellow semisolid
0.86	$C_{11}H_{15}NO_2$ 0.84	2 : 3	4½	$Sb_2(C_{11}H_{13}NO_2)_3$ (1.15), yellow semisolid
1.59	$C_{11}H_{15}NO_2$* 1.03	1 : 1	3	$Sb(O—i\text{-}C_3H_7)(C_{11}H_{13}NO_2)$ * (1.97), yellow semisolid
0.77	$C_{11}H_{15}NO_2$* 0.75	2 : 3	5	$Sb_2(C_{11}H_{13}NO_2)_3$ * (1.05), yellow semisolid
1.22	$C_9H_{11}NO_2$ 0.68	1 : 1	2	$Sb(O—i\text{-}C_3H_7)(C_9H_9NO_2)$ (1.32), yellow solid
1.37	$C_9H_{11}NO_2$ 1.14	2 : 3	4	$Sb_2(C_9H_9NO_2)_3$ (1.67), yellow solid
1.38	$C_{10}H_{13}NO_2$ 0.83	1 : 1	2½	$Sb(O—i\text{-}C_3H_7)(C_{10}H_{11}NO_2)$ (1.63), yellow solid
0.86	$C_{10}H_{13}NO_2$ 0.78	2 : 3	5	$Sb_2(C_{10}H_{11}NO_2)_3$ (1.10), yellow solid
1.43	$C_{13}H_{13}NO_2$ 1.03	1 : 1	3	$Sb(O—i\text{-}C_3H_7)(C_{13}H_{11}NO_2)$ (1.88), yellow solid
0.80	$C_{13}H_{13}NO_2$ 0.87	2 : 3	5	$Sb_2(C_{13}H_{11}NO_2)_3$ (1.12), yellow solid

* Has been used to distinguish between the compounds of same molecular formula.

Thermogravimetric analysis was carried out on a Stanton (Massflow type) Automatic Recording Thermogravimetric Balance under a controlled rate of heating (4 °C/min).

Results and Discussion

The reactions of Sb(III) isopropoxide with the *Schiff* bases in 1 : 1 and 2 : 3 molar ratios liberated 2 and 6 moles of 2-propanol respectively and resulted in the synthesis of the corresponding 2-propoxy Sb(III) *Schiff* base and diSb(III) tris *Schiff* base derivatives. The resulting complexes have been isolated as yellow semisolids or solids and are non volatile. They are soluble in benzene except the derivatives of 2-hydroxy-1-naphthylidene-2-hydroxyethylamine, which are only sparingly soluble. Generally these were found to be susceptible to hydrolysis except the derivatives of 2-hydroxy-1-naphthylidene-2-hydroxyethylamine.

The ebullioscopic determination of molecular weights in boiling benzene shows them to be monomeric and the central metal atom

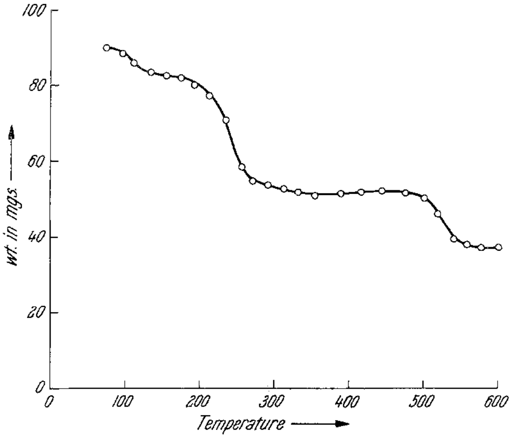
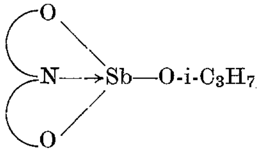
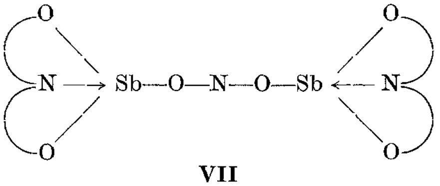


Fig. 1. Thermolysis curve: $Sb(O—i\text{-}C_3H_7)(OC_6H_4CH:NCH_2CHOCH_3)$; wt of the compound taken = 90 mg, wt left = 37 mg, Calcd. wt for Sb_2O_3 = 35.6 mg

in these complexes may probably be in the tetra[11] coordinated environment (VI and VII):



VI



VII

On comparing the infrared spectra of the *Schiff* bases as well as their metal complexes it can be concluded that the chelate formation takes place through the oxygen (phenolic and alcoholic) and nitrogen of the >C=N-group of the ligands. This is supported by the disappearance of the OH frequency bands in the 3400–3100 cm^{-1} region and appearance of the bands in the region 610–570 cm^{-1}, which may probably be attributed to ν (Sb—O) vibrations.

A strong band in the region 1640–1601 cm^{-1} in the *Schiff* bases is the characteristic absorption band of the >C=N-group. This remains almost unaltered in the resulting derivatives probably due to the stronger force existing in the >C=N-group. A similar observation has been made by other workers[12] as well.

Thermogravimetric analysis of Sb(III) monoisopropoxysalicylidene-2-hydroxy-1-propylamine, $Sb(O—i\text{-}C_3H_7)(OC_6H_4CH:NCH_2CHOCH_3)$ has also been carried out. The product appears to be stable upto 90 °C and, thereafter, a loss in weight upto 210 °C probably due to the dealkoxylation is recorded. Another intermediate product remains stable upto 350 °C and it finally gets converted into Sb_2O_3 at 580 °C (Fig. 1).

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