SYNTHESIS AND CHARACTERISATION OF SOME ANTIMONY(III) DERIVATIVES OF THE SCHIFF BASE DERIVED FROM SALICYLALDEHYDE AND 2-AMINOTHIOPHENOL

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ABSTRACT

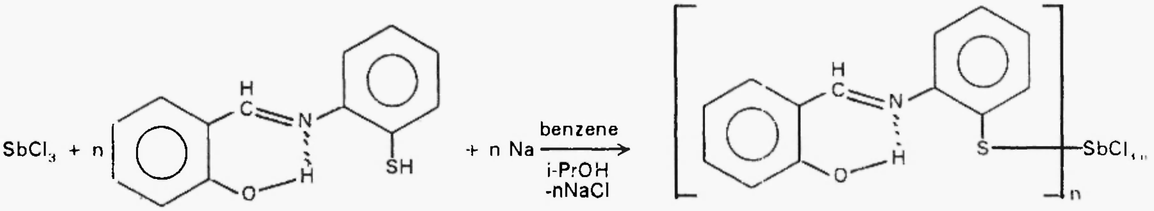
Some antimony(III) derivatives of Schiff base derived from salicylaldehyde and 2-aminothiophenol have been synthesised by the reactions of antimony trichloride with N-(salicylidene) - o - mercaptoaniline in desired molar ratios. These derivatives have been characterised by elemental analysis, molecular weights, conductivity measurements, IR and (^1H and ^{13}C) NMR spectral studies.

INTRODUCTION

Complexes of the title ligand with organotin(IV)[1] have earlier been prepared and characterised from our laboratory. In continuation of our studies on antimony(III) derivatives[2], we report here the synthesis and characterisation of some new complexes of antimony(III).

RESULT AND DISCUSSION

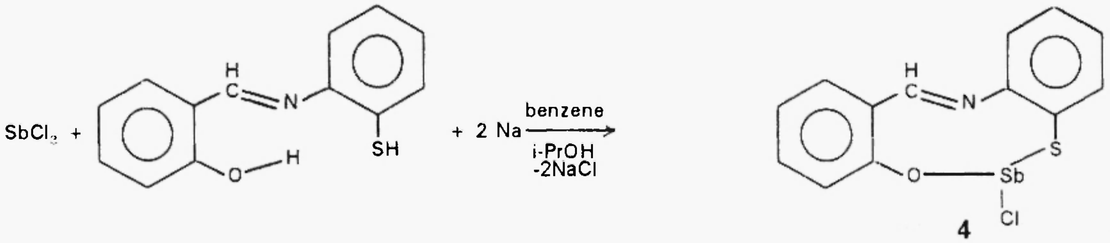
Dichloro, chlorobis and tris antimony(III) derivatives of N-(salicylidene) - o - mercaptoaniline have been synthesised by the reactions of antimony trichloride with the sodium salt of N-(salicylidene) - o - mercaptoaniline in 1:1, 1:2 and 1:3 molar ratios, respectively.



(n = 1,2,3)

1-3

Furthermore, a monochloroantimony(III) derivative of N-(salicylidene) - o - mercaptoaniline has been prepared by the reaction of $SbCl_3$ with the disodium salt of N-(salicylidene) - o - mercaptoaniline in a 1:1 molar ratio.



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This article is dedicated to (late) Dr. R.J. Rao, S.S. in Chemistry, Vikram University, Ujjain.

All these new antimony(III) complexes were prepared by refluxing the reactants in benzene for about 3-4 hours. The desired product could be isolated by evaporation of the solvent under reduced pressure, after filtering off the precipitated sodium chloride. These were further purified by crystallisation from benzene-petroleum ether (40°-60°) mixture. All there compounds are more or less soluble in common organic solvents like $CHCl_3$, CCl_4, C_6H_6, DMF, DMSO etc. Conductive measurements in DMF have been made at room temperature using Digisum Electronic Conductivity Bridge. Molar conductance values (below than 55 ohm^{-1} cm^{-2} mole^{-1}) reveal the non-electrolytic[3] nature of the complexes. Molecular weight determination in $CHCl_3$ solution shows monomeric nature of these complexes.

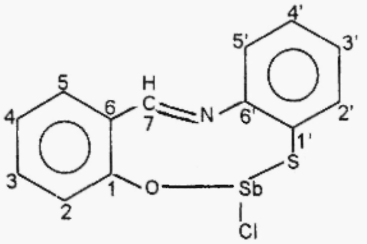
IR Spectral Data

The infrared spectra of these complexes have been recorded in the 4000-200 cm^{-1} range on a Perkin-Elmer 377 spectrophotometer, using KBr pellets.

The ligand exhibits a ν(OH) band at 3100 cm^{-1} of the intramolecularly hydrogen bonded phenolic OH. The complex 4 do not show this band indicating a deprotonation of the hydroxy group. The Schiff base exhibits a ν(SH) band around 2500 cm^{-1}.[4,5] This band disappears in all the complexes indicating deprotonation and consequent coordination of the sulphur atom to antimony.[6-9] A ν(C=N) (azomethine) band is found around 1620-1640 cm^{-1} in the ligand. In the complexes this band shifts by 35 cm^{-1} to lower wave numbers indicating coordination of the azomethine nitrogen to the central metal atom.[10] The ligand exhibits a band between 1295 and 1305 cm^{-1} due to (C-C-O).[11 12] In the complex 4, this band shifts to higher energy by 5-15 cm^{-1} indicating the coordination of the phenolic oxygen.[13] The ν(C-S) in the ligand occurs between 700-790 cm^{-1}. In the complexes, this band shifts to higher energy by 30-40 cm^{-1} which is indicative of coordination of the sulphur.[9 14] Bands of medium and weak intensities in the region 600-440 cm^{-1} may be due to Sb-O stretching vibrations. Bands observed at ~ 330 cm^{-1} can be ascribed to Sb-S.[6]

NMR Spectral Data

The ^1H NMR spectra of these complexes have been recorded in $CDCl_3$ and the values of observed chemical shifts are listed in the experimental section. The ^1H NMR spectra show characteristic resonance of corresponding ligand protons. The ^1H NMR spectra of all the complexes except 4 show a signal at δ 11.5 ppm of the -OH proton of salicylaldehyde group. The spectrum of the complex 4 does not exhibit this signal suggesting deprotonation of this -OH group.[10] A complex pattern due to the protons of the phenyl group has been observed in the region at δ 6.4-8.0 ppm. The signal due to the azomethine proton appears at δ 4.25 ppm.[10]



^{13}C NMR spectra of all the compounds have been recorded in $CDCl_3$. The aromatic carbon resonances of these derivatives were assigned by using incremental rules for aromatic substitution.[15] The C-1 and C-1' carbons exhibit signals in the characteristic region downfield at δ 163.17 and δ 162.53 ppm respectively. This is in agreement with the earlier work on corresponding derivative of organotin(IV)[1]. The azomethine carbon also absorbs as expected at δ 151.77 ppm, like the other Schiff base derivatives of antimony(III).[6, 10]

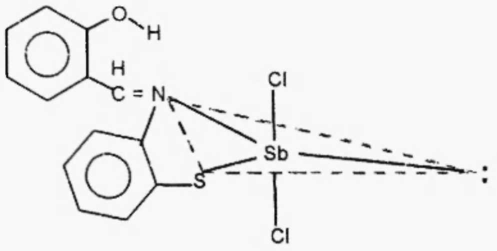
Compound 1. Sb [$SC_6H_4N=C(H)C_6H_4OH$] Cl_2
151.48, C-7; 117.72, C-6; 131.83, C-5; 122.37, C-4; 132.47, C-3; 119.83, C-2; 162.69, C-1; 119.47, C-6'; 133.35, C-5'; 121.43, C-4'; 133.73, C-3'; 119.48, C-2'; 161.27, C-1'.

Compound 2. Sb [$SC_6H_4N=C(H)C_6H_4OH$]$_2$ Cl
151.61, C-7; 117.66, C-6; 131.94, C-5; 122.42, C-4; 132.51, C-3; 119.72, C-2; 162.45, C-1; 119.42, C-6'; 133.20, C-5'; 121.12, C-4'; 133.54, C-3'; 119.27, C-2'; 161.33, C-1'.

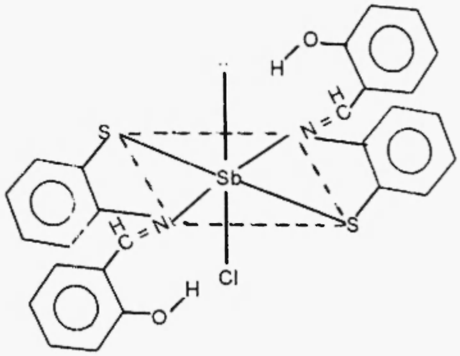
Compound 3. Sb [$SC_6H_4N=C(H)C_6H_4OH$]$_3$
151.77, C-7; 117.80, C-6; 131.60, C-5; 122.10, C-4; 132.64, C-3; 119.64, C-2; 162.75, C-1; 119.21, C-6'; 133.47, C-5'; 121.51, C-4'; 133.64, C-3'; 119.53, C-2'; 161.12, C-1'.

Compound 4. Sb [$SC_6H_4N=C(H)C_6H_4O$] Cl
151.57, C-7; 117.58, C-6; 132.16, C-5; 122.57, C-4; 132.30, C-3; 119.96, C-2; 163.17, C-1; 119.23, C-6'; 130.21, C-5'; 121.22, C-4'; 131.35, C-3'; 119.96, C-2'; 162.53, C-1'.

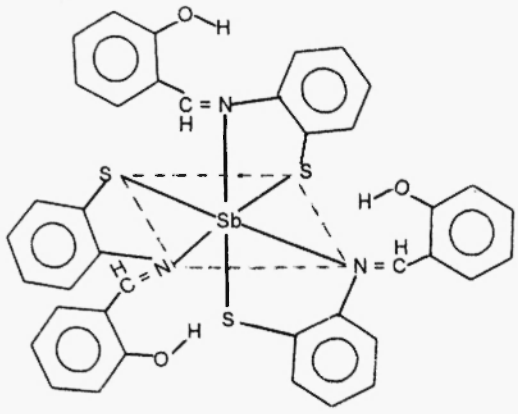
Thus above studies indicate a bidentate mode of attachment of the ligand to the metal atom, which leads to a distorted octahedral geometry if the presence of the stereochemically active lone pair is also considered in the capping position in tris derivative (c)[16], while bis derivative have octahedral geometry with the lone pair occupying an axial position (b)[17] and monoderivatives possess trigonal bipyramidal geometry with the lone pair in equatorial position (a,d).[18]



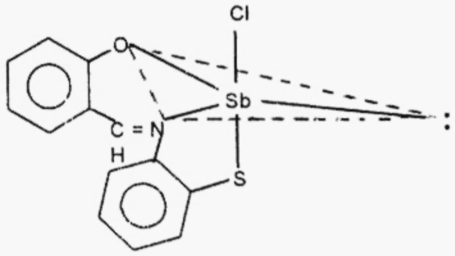
(a)



(b)



(c)



(d)

EXPERIMENTAL

Precautions were taken to exclude moisture throughout the experiments. All the chemicals used were of reagent grade. All the solvents used were dried by standard methods.[19] $SbCl_3$ was purified by distillation (78°/10mm). The ligand was synthesised as reported earlier.[1] Antimony, sulphur and nitrogen were determined iodometrically, gravimetrically and by Kjeldahl's method, respectively.[19] IR spectra were recorded on a Perkin-Elmer model 377 spectrophotometer. The ^{1}H NMR spectra were recorded on a Perkin-Elmer R-32 using TMS as an internal reference and ^{13}C NMR on JEOL FX-90 using TMS as an external standard.

Reaction between antimony trichloride and sodium salt of N-(salicylidine) - o - mercaptoaniline in a 1:1 molar ratio :

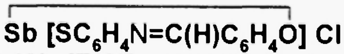
0.11g, (4.60 m mole) of sodium metal and 15 ml of isopropanol were taken in a round bottom flask (fitted with a dried and cooled water condenser and guard tube) and refluxed for about half an hour till a clear solution of sodium isopropoxide was obtained. After cooling, 1.06 g. (4.60 m mole) of N-(salicylidine) - o - mercaptoaniline was added and the mixtur was refluxed for an hour again. 1.00 g, (4.60 m mole) of antimony trichloride in benzene was added and the mixture was further refluxed for 2-3 hours to ensure the completion of the reaction. The desired product 1.5 g (88%) was isolated by evaporation of the solvent under reduced pressure, after filtering off the precipitated sodium chloride. The product was further purified by crystallisation using a benzene-petroleum ether (40°-60°) mixture.

All other antimony(III) derivatives of N-(salicylidine) - o - mercaptoaniline were synthesised similarly. The pertinent data for this compound and other derivatives are listed below.

Compound 1. $Sb[SC_6H_4N{=}C(H)C_6H_4OH]Cl_2$
Yield 88%; Mol. Wt. [F(C)] : 436(421); Orange solid; M.P. 177-179°C.
Analysis [% F(C)] : Sb, 28.26 (29.05); N, 3.10(3.34); S, 7.32(7.09); Cl, 16.00 (16.95).
IR (cm^{-1}) : νOH, 3160; νC=N, 1590; νSb-S, 332; νSb-N, 435.
^{1}H NMR (δppm) 11.5, S, 1H (OH); 6.8-8.0, m, 8H (Ph); 4.25, S, 1H (=CH).

Compound 2. $Sb[SC_6H_4N{=}C(H)C_6H_4OH]_2Cl$
Yield 81%; Mol. Wt. [F(C)] : 627(613.5); Orange solid; M.P. 164-166°C.
Analysis [% F(C)] : Sb, 17.59 (19.84); N, 4.23(4.56); S, 10.16(10.43); Cl, 5.59 (5.79).
IR (cm^{-1}) : νOH, 3140; νC=N, 1580; νSb-S, 335; νSb-N, 440.
^{1}H NMR (δppm) 11.5, S, 2H (OH); 6.75-7.90, m, 8H (Ph); 4.26, S, 1H (=CH).

Compound 3. $Sb[SC_6H_4N{=}C(H)C_6H_4OH]_3$
Yield 85%; Mol. Wt. [F(C)] : 821(806); Orange solid; M.P. 158-160°C.
Analysis [% F(C)] : Sb, 14.65 (15.10); N, 4.89(5.21); S, 11.18(11.92)
IR (cm^{-1}) : νOH, 3020; νC=N, 1610; νSb-S, 330; νSb-N, 415.
^{1}H NMR (δppm) 11.4, S, 3H (OH); 6.5-7.8, m, 8H (Ph); 4.25, S, 1H (=CH).

Compound 4.

$Sb[SC_6H_4N{=}C(H)C_6H_4O]Cl$
Yield 78%; Mol. Wt. [F(C)] : 395(384.5); Orange solid; M.P. 194-196°C.
Analysis [% F(C)] : Sb, 28.98(31.68); N, 3.10(3.63); S, 8.10(8.32); Cl, 8.91 (9.23).
IR (cm^{-1}) : νC=N, 1610; νSb-S, 328; νSb-O, 600-440; νSb-N ~ 450.
^{1}H NMR (δppm) : 6.6-7.5, m, 8H (Ph); 4.24, S, 1H (=CH).

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