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COMPLEXES OF ANTIMONY(III)

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Abstract

Lewis acidity of antimony(III) halides and their organo substituted derivatives is well known. The molecules SbX_3 are good acceptor and a wide range of neutral complexes have been prepared but it seems antimony trichloride is a weak acceptor as compared to antimony pentachloride. The halide complexes are more interesting because of the part played by the lone pair in determining the stereochemistry where 1:1 complexes have trigonal bipyramidal and 1:2 complexes have square pyramidal configurations. Complexes of antimony trichloride with aromatic hydrocarbon are also known but the presence of organic group in a molecule reduces its capacity to form complexes.

Key words

Antimony(III); acceptor; trichloride; pentachloride; stereochemistry trigonal bipyramidal; Square pyramidal

Introduction

The element antimony has considerable tendency to form complexes specially organo derivatives in its tri and pentavalent where in +3 oxidation state it uses 'ns' electrons due to inert pair effect. As result the Lewis acidity of antimony(III) halides and their organo substituted derivatives is well known (Yadav, 2012: Yadav 2013[a] and Yadav 2013[b]) and anionic derivatives with stoichiometries such as $[SbX_4]^-$, $[SbX_5]^{-2}$, $[SbX_6]^{-3}$, $[Sb_2X_9]^{-3}$ (Fisher & Norman 1994), $[SbPhX_3]^-$, $[SbPhX_4]^{-2}$, $[SbPh_2X_2]^{-2}$ (Hall & Sowerby, 1988) have been isolated. Complexes between the trihalides and neutral donors, such as amines, phosphine oxides and arsine oxides (Smith, 1973) are also well known and crown ether complexes have recently been isolated (Alcock *et al.,* 1990). Complex formation between organoantimony halides and neutral donors is well established (Nunn *et al.,* 1996). Given below is summary of the complex forming tendency of antimony in its trivalent state containing (mainly halide, X) and organic groups R (R = CH_3, C_6H_5, CF, *p*-XC_6H_4; X = CH_3, Cl, Br *etc.*)

Antimony(III) as acceptors

The acceptor strength of a compound is

determined by the nature of the metal, the anionic group attached to it and the strength of the ligand. The stronger the electron attracting power of the substituents, the lesser is the density around the metal, thereby increasing the acceptor strength of the molecules. Thus, when X is an electronegative atom (viz. Cl^- Br^-, etc.) the molecules SbX_3 are good acceptors and a wide range of neutral complexes of the types SbX_3L; SbX_32L (L = Me_2SO; Me_3PO; $POCl_3$, Ph_3AsO etc.) have been prepared (Lindquist, 1963; Trotman-Dickenson, 1973). Detailed thermodynamic data relating to complexes formation are not yet available but it seems clear that to oxygen donors, antimony trichloride is a weak acceptor as compared to antimony pentachloride (Lindquist, 1963). Obviously, the presence of two more electronegative chlorine atoms in antimony pentachloride makes it better acceptor.

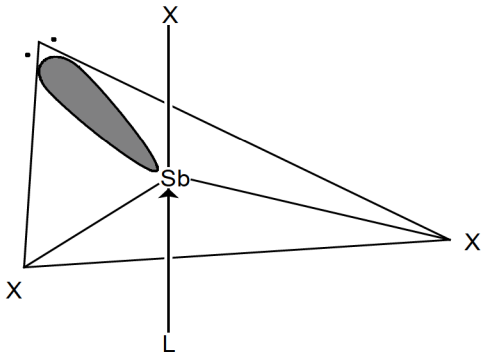

Fig.1 Suggested structure of SbX_3L adduct

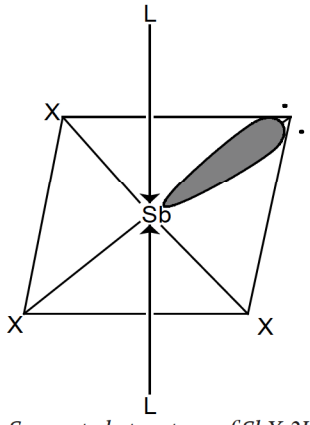

Fig.2 Suggested structure of SbX_32L adduct

Structurally, the halide complexes are of interest because of the part played by the lone pair in determining the stereochemistry. In the 1:1 complexes, the lone pair occupies an equatorial position in a trigonal bipyramidal configuration with the donor L in an axial position (Fig. 1). In 1:2 complexes, the lone pair occupies an equatorial position resulting in distorted square pyramidal environment around the antimony atom (Fig. 2).

Complexes of antimonny trichloride with aromatic hydrocarbon are also known, e.g.; the naphthalene adducts, $2SbCl_3.C_{10}H_8$ (Hulme & Syzmanski, 1969). The hydrocarbon behaves as olefin donating π-electron density to one coordination position at the antimony (Fig. 3).

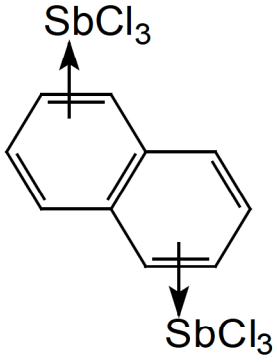

Fig.3 Suggested Structure of $2SbCl_3.C_{10}H_8$ adduct

A considerable distortion of naphthalene skeleton occurs with a shortening of the complexed C–C bond. SbX_3 also exhibits acceptor behavior towards electro negatively charged donors, for *e.g.* it forms $[SbX_4]^{-1}$, $[SbX_5]^{-2}$, *etc.* (Trotman-Dickenson, 1973; Hall & Sowerby, 1986).

Some organoderivatives of trivalent antimony also act as halides acceptor to form anions of the type $[RSbX_3]^{-1}$, $[RSbX_4]^{-2}$ or $[R_2SbX_2]^{-1}$ by successive addition of halogen atom(s), with consequent delocalization of the ionic charge and stabilization of the system (Fig. 4 to 6) (Hall & Sowerby, 1988).

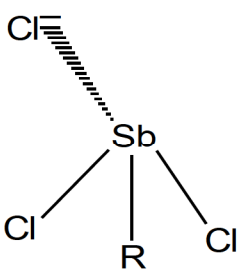

Fig.4 Suggested structure of $[RSbCl_3]^{-1}$ anion

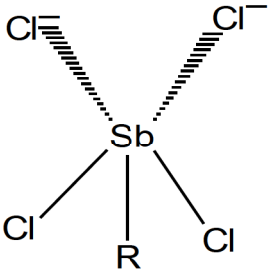

Fig.5 Suggested structure of $[RSbCl_4]^{-2}$ anion

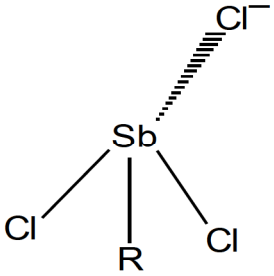

Fig.6 Suggested structure of $[RSbCl_3]^{-1}$ anion

The presence of organic group, in a molecule reduces its capacity to form complexes. Thus, trialkylstibine do not appear to form complexes with electron donors. The effects of electronegative trifluoromethyl group is shown in the formation of the weak complex between tris(trifluoromethyl)antimony and pyridine (Dale *et al.*,1957).

Nottingham group (Nunn *et al.*, 1996) reported the complex formation between $SbPhX_2$, $SbPh_2X$ and $SbPh_2X_3$ where X = Cl or Br and the nitrogen donors pyridine, 2,2'-bipyridyl and 1,10-phenanthroline. Both 1:1 and 1:2 complexes were formed between $PhSbCl_2$ and pyridine but with Ph_2SbCl only 1:1 compounds were obtained. 2,2'-bipyridine and 1,10-Phenanthroline afforded 1:1 complexes with both mono and diphenyl halides. On the basis of spectroscopic studies, $PhSbX_2$.Py and Ph_2SbX.Py have been assigned Pseudo-trigonal bipyramidal structure with a halogen and nitrogen donor in axial positions (Fig. 7 & 8).

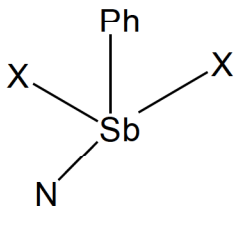

Fig.7 Suggested structure of PhSbX2.Py

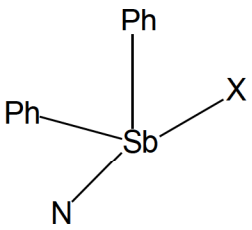

Fig.8 Suggested structure of $Ph_2SbX.Py$

A square pyramidal structure with axial phenyl group has been proposed for $PhSbX_2.2Py$ (Fig. 9).

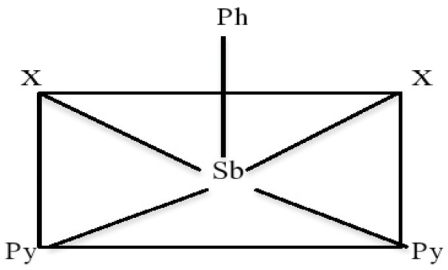

Fig: 9

Fig.9 Suggested structure of $PhSbX_2.2Py$

With bidentate ligands, $PhSbCl_2$ was again found to possess square pyramidal structure (Fig. 10).

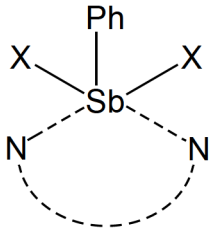

Fig.10 Suggested structure of $PhSbCl_2.bipy$

X-ray crystallographic data of $PhSbCl_2$.biby, confirms the figure (10), and the solid consists of discrete $PhSbCl_2$.bipy molecules. The antimony atom, which is on a mirror plane, is

surrounded in the basal plane by two chlorine atoms and the phenyl group occupies the apical position (Nunn *et al.,* 1996).

Conclusion

Complex formation tendency of antimony plays important role as result of this voluminous amount of work done on organoderivatives of antimony(III) such as anionic, cationic complexes and molecular adducts. However, a perusal of literature reveals that complex forming tendency of antimony(III) halides is yet to be accomplished.

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