A Review on Diorganoantimony compounds

M. Santhana raj prabhu
Assistant Professor, PG and Research Department of Chemistry,
Muthurangam Government Arts College, Vellore 632 002, Tamilnadu, India.

Received: March 28, 2018 Accepted: May 10, 2018

ABSTRACT *The chemistry of di-organometallic compounds of antimony has been reviewed. Synthesis and structure of their compounds have been described. This review summarizes the β-diketones derivatives, Schiff base derivatives and the biological activity of organoantimony compounds. This survey encourages to synthesis various organoantimony compounds further in this field for various applications.*

Keywords: *Synthesis, Structure, Biological activity and Organoantimony compounds.*

INTRODUCTION:

Antimony complexes have been used in the field of medicine and cosmetics [1,2]. For the treatment of various parasitic diseases antimony containing compounds are commonly used. For example, sodium antimony(V) gluconate is being used as a drug [3]. Due to the fascinating structural diversity varying from discrete monomeric molecular species to supramolecular assemblies the chemistry of organoantimony(V) complexes has attracted significant attention in recent times [4]. Similar to that of *cis*-platin, organoantimony derivatives also exhibit significant antimicrobial properties as well as antitumor activities [5] which is associated with cytostatic activity. The biological toxicity of Sb is less than Pt and Pd based anticancer substances. In addition, organoantimony derivatives also show important functions as biocides, fungicides, catalyst components and antioxidants. Antimony in the oxidation state of +5 is interesting considering its hypervalent nature [6]. In organic synthesis organoantimony(V) compounds have been used either as reagents or as catalysts extensively [7].

BIOLOGICAL ACTIVITY:

Antimonials Since 1913, has been used in the field of therapeutic agent with the introduction of Sb(III) potassium tartarate in the treatment of leishmaniasis. Pentavalent antimonials have replaced trivalent antimonials due to less toxic nature of Sb(V) compounds such as meglumine antimoniate for treating diseases. Meglumine antimoniate is recommended by WHO as a first choice medicine for leishmaniasis therapy [8]. Bayer in 1915 introduced the first organometallic fungicides Upsulun which is an organomercurial compound. Since organomecurial compounds are environment unfriendly, Beiter and Leebrick 1963 chose a series of tri and pentavalent organoantimony and organobismuth compounds and examined their activity against fungicides. It was found that organoantimony are moderately fungitoxic and more effective than organobismuth compounds. Burrell and Corke in 1980 studied the fungitoxicity of organo antimony compounds and found that fungal toxicity activity increased with increasing the molecular weight of organic compound attached to group VA element [9].

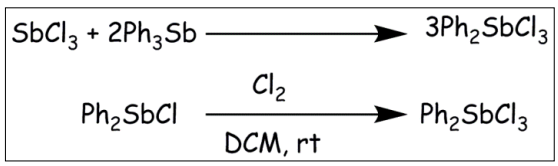
Cristian Silvestru *et al* investigated the organoantimony(III) derivatives of dithiophosphorus ligand which were found to shows antitumor properties in both *in vitro* and *in vivo* studies [10]. Cytotoxic activity to vascular endothelical cell was diminished when they replaced the bismuth atom by antimony atom in 2-(N,N-dimethylaminomethyl)phenylbis(4-methyl phenyl)bismuthane (DAPBi) [11]. $(C_6F_5)_2SbPh$ shows antifungal, antibacterial and insecticidal activities. This compound has also been used as pesticide and insecticide for plant diseases as reported by R. Kant *et al*. Later the group also synthesized the diaryl antimony(III) amide which exhibits antitumor activity against mammary cancer cell line and human breast adenocarcinoma cell line. In addition it also shows antibacterial activity against *Pseudomonas aeruginosa, Staphylococcus aureus, and Klebsiela pneumonia.* It exhibits significant antifungal properties against *Aspergillus flavus and Aspergillus niger* [12].

Organoantimony(V) derivatives from Schiff bases exhibits higher antimicrobial activity than organoantimony(III) derivatives against *Aspergillus flavus and Escherichia coli* [13]. Potent antimicrobial properties are revealed in three discrete organoantimony(III) containing heteropolytungstates which was recently documented by U. Kortz *et al* [14]. Organostibonic acids have also been used as potential anticancer agents, which inhibits the DNA binding [15] group of B-ZIP proteins at micromolar concentration have been recently reported by Vinson *et al* [16].

DIORGANOANTIMONY COMPOUNDS:

Synthesis of diphenylantimony trichloride:

Diorganoantimony(V) halides have been synthesized by treating antimony(III) chlorides with diazonium salts or by halogenations of diorganoantimony(III) halides R_2SbX with X_2 (X = Cl, Br) (Scheme 1) [17, 18].



Scheme 1

Some of the reducing agents like stannous chloride, sulfur dioxide are used to reduce diorganoantimony(V) halides to diorganoantimony(III) halides.

Dimeric structure of diphenylantimony trichloride:

Michaelis and Reese first synthesized diphenylantimony trichloride where they obtained it as a monohydrate. When heating the monohydrated compound to 100 ˚C they readily obtained the anhydrous compound. Initially there was uncertainty about the structure of Ph_2SbCl_3. Bordner *et al* resolved the ambiguity by examining the single-crystal X-ray diffraction data of the anhydrous Ph_2SbCl_3 and found that it exists as a dimer with chlorine bridges and geometry around antimony was found to be octahedral (Figure 1) [19].

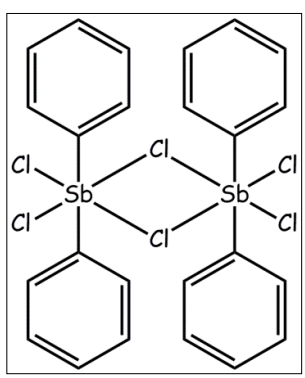


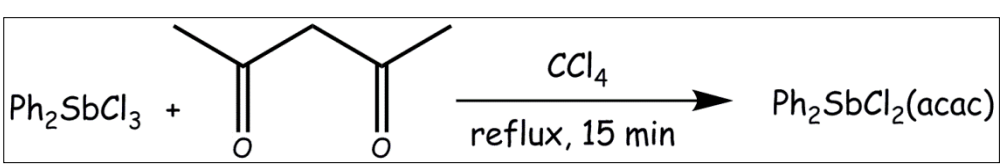
Figure 1: Dimeric structure of diphenylantimony trichloride.

Bone and Sowerby synthesized diarylantimony(V) tribromide (Ph_2SbBr_3) and the two mixed halides Ph_2SbBr_2Cl and $Ph_2SbBrCl_2$ [18]. These compounds are monomeric in solid state and geometry around antimony was found to be trigonal-bipyramidal with two phenyl groups and a bromine atom occupying the equatorial positions. Due to weak intermolecular interactions arising between axial halogen atom and antimony, these units are linked to form infinite chains in solid state. On the other hand when compared with above mentioned compounds Ph_2SbCl_3 shows a dimeric nature in solid state.

With various oxygen donor ligands such as DMSO and HMPA diorganoantimony(V) halides forms monomeric covalent adducts ($R_2SbX_3.L$). Octahedral geometry has been proposed on the basis of IR and NMR spectra.

Diorganoantimony *β*-diketone derivatives:

Diorganoantimony trihalide when treated with acetylacetone under reflux condition gave rise to diorganoantimony(V) *β*-diketones, $Ph_2Sb(CH_3COCHCOCH_3)Cl_2$ (Scheme 2) which are monomeric in nature (Figure 2) [20].



Scheme 2

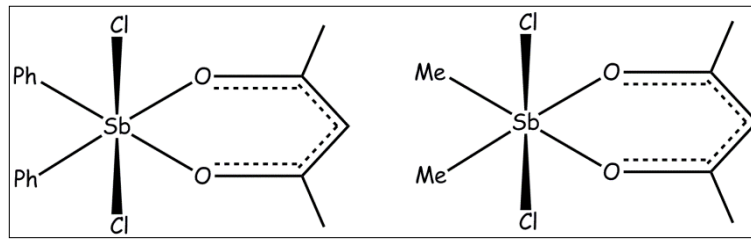
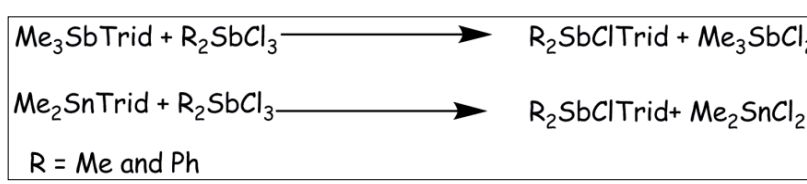


Figure 2: Diphenyldichloro(acetylacetonato)antimony & Dimethyldichloro(acetylacetonato)antimony.

β-diketonate ligand acts as bidentate ligand in both the complexes and the oxygen atoms from acetylacetone bonds to antimony atom. Interpretations drawn from ^{1}H NMR spectral studies have been confirmed by single crystal X-ray diffraction analysis of $Me_2Sb(acac)Cl_2$ and $Ph_2Sb(acac)Cl_2$ [21]. $Me_2Sb(acac)Cl_2$ compound possess a slightly distorted octahedral geometry around antimony in which methyl groups occupy equatorial positions and are bent towards the planar acetylacetonato group. In compound $Ph_2Sb(acac)Cl_2$ the geometry around antimony was distorted octahedral in which the two chlorine are arranged trans to each other (Figure 2).

Schiff base derivative of diorganoantimony:

Diorganoantimony(V) complexes with planar tridentate schiff base ligands (Trid) have been prepared by the exchange reactions of diorganoantimony(V) chlorides with corresponding schiff bases of trimethylantimony(V) or dimethyltin(IV) compounds (Scheme 3). These reactions proceed due to greater Lewis acidity of $R_2Sb(V)$ compared to $Me_3Sb(V)$ or $Me_2Sn(IV)$ [22]. Planar tridentate ligands (Trid) coordinate to antimony in ONO fashion, the chelating ONO atoms assumed to be arranged in a *meridional* fashion and a linear C-Sb-C skeleton has been proposed based on IR and ^{1}H NMR studies. Certain compounds such as $Me_2Sb(Sah)Cl$, $Me_2Sb(Bah)Cl$, $Ph_2Sb(Bah)Cl$ and $Ph_2Sb(Aah)Cl$ shows octahedral geometry with *meridional* arrangement as proven by Mössbauer spectroscopy (Figure 3) [23].



Scheme 3

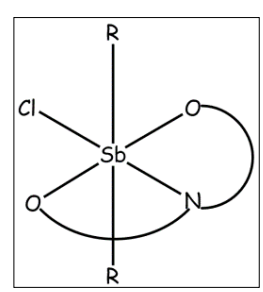
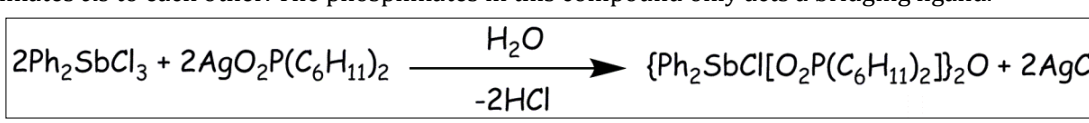


Figure 3: Meridional arrangement of tridentate Schiff base ligand around antimony.

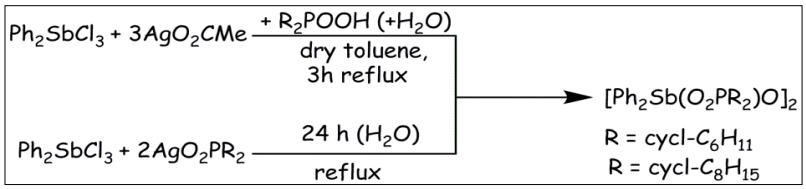
Reaction with Silver salt of phosphinates:

Diphenylantimony trichloride when treated with two equivalents of silver salts of phosphinates leads to the isolation of partially hydrolyzed product $\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$ (Scheme 4). Single crystal X-ray diffraction studies reveals that antimony atoms are in octahedral coordination with bridging phophinates *cis* to each other. The phosphinates in this compound only acts a bridging ligand.

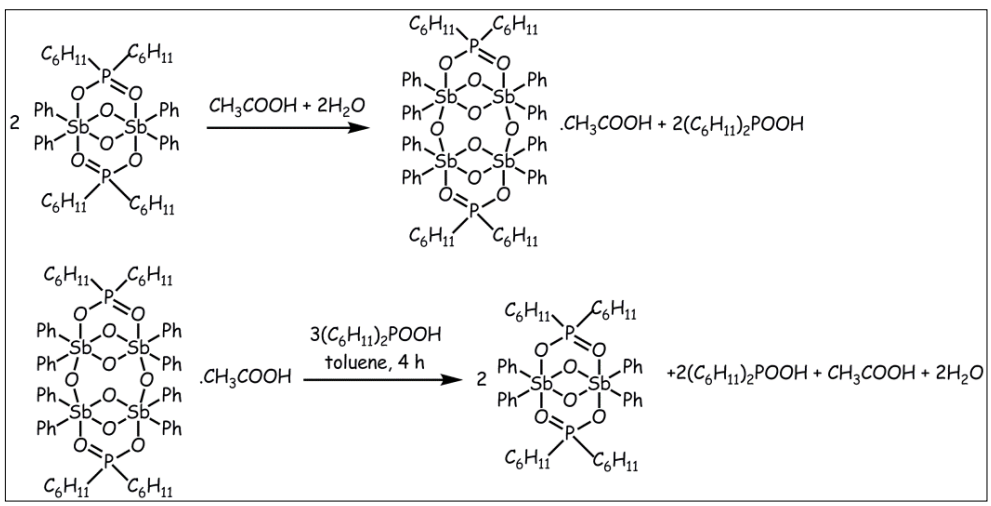


Scheme 4

Kumara Swamy and co-workers reported antimony(V) phosphinates by reacting diphenylantimony trichloride with three equivalence of silver acetate followed by one equivalence of phosphinic acid leading to the isolation of dimeric compounds of formula $[Ph_2Sb(O_2PR_2)O]_2$. Interestingly when the dimer was reacted with acetic acid / water gives the tetra nuclear cage of formula $Ph_8Sb_4O_4(OH)_2(O_2P(C_6H_{11})_2)_2$ (Scheme 5) [24].



Scheme 5

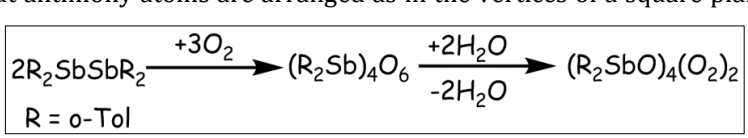


Scheme 6

All the compounds are structurally characterized by single crystal X-ray diffraction analysis. In the di and the tetra nuclear clusters, the antimony atoms are octahedral coordinated with four membered Sb_2O_2 rings. In tetranuclear cluster two Sb_2O_2 rings are linked by oxo bridges on two sides to give a Sb_4O_6 cage (Scheme 6).

Diorganoantimony based μ_4-peroxo complex:

The first main group element μ_4-peroxo complex of antimony was synthesized by treating tetra-*o*-tolyldistibane in air and subsequent reaction with H_2O_2 and the intermediate $(o\text{-}Tol_2Sb_4)O_6$ (Scheme 7) was identified by mass spectrometry. The complex is stable in solution state. Single crystal X-ray diffraction studies reveal that antimony atoms are arranged as in the vertices of a square planar arrangement (Figure 4) [25].



Scheme 7

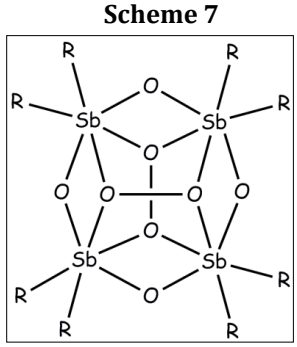


Figure 4: μ_4-peroxo Complex of Antimony

Synthesis of Quadruply bridged diorganoantimony compound:

Quadruply bridged diorganoantimony compounds $[(SbPh_2)_2(\mu\text{-}O)_2(\mu\text{-}O_2AsR_2)_2]$ [26] where R = Me or Ph have been synthesized by reacting $[(SbPh_2BrO)_2]$ with 2 moles of either $Na(O_2AsMe_2)$ or $Na(O_2AsPh_2)$ in DCM and the mixture was refluxed for 24 h. The compounds have been characterized by a various spectroscopic methods and analytical methods (Figure 5).

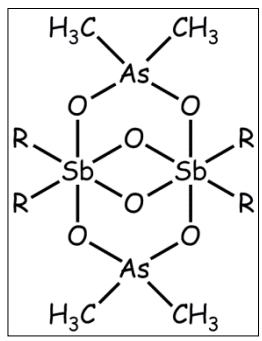


Figure 5: Quadruply bridged diorganoantimony compounds.

CONCLUSION: This review describes the synthesis, spectroscopic and structure aspects of diorgano antimony compounds. But still there is a need to explore the chemistry on organoantimony compound for more applications.

REFERENCES:

1. Krebs, R. E., (2004) "The History and Use of our Earth's Chemical Elements", GreenwoodPress, Westport, Conn, 219.
2. Ulrich, N., (2003), "Antimony, Chemical and Engineering News", 81, 126.
3. Rais, S., Perianin, A., Lenoir, M., Sadak, A., Rivollet, D., Paul, M., Deniau, M., (2004), Antimicrob. Agents Chemother, 44, 2406.
4. Quan, L., Yin, H. D., Cui, J. C., Hong, M., (2009), J. Organomet. Chem. 2009, 694, 3683.
5. Silvestru, C., Socaciu, C., Baba, A., Haiduc, I., (1990), Anticancer Res, 10, 803.
6. Sharma, P., Perez, D., Vazquez, J., Toscano, A., Gutierrez, R., (2007), Inorg. Chem. Commun, 10, 389.
7. Huang, Y. Z., (1992), Acc. Chem. Res, 25, 182.
8. WHO (World Health Organization), Leishmaniasis: disease information, 2007. Available from: http://www.who.int/tdr/diseases/leish/diseaseinfo.htm.
9. Burrell, R. E., Corke, C. T., Goel. R. G., (1983), J. Agric. Food Chem, 31, 85.
10. Socaciu, C., Pasca, L., Silvestru, C., Bara, A. Haiduc. I., (1994), Metal-based drugs, 1, 291.
11. Kohri, K., Yoshida, E., Yasuike, S., Fujie, T., Yamamoto, C., Kaji. T., (2015), J. Toxicol. Sci, 40, 321.
12. Kant, R., Chandrashekar, A. K., Anil. K. S., (2008), Phosphorus, Sulfur and Silicon, 183, 1410.
13. Agrawaly, R., Sharmay, J., Nandaniz, D., Batraz, A., Singh. Y., (2011), J. Coord. Chem, 64, 554.
14. Barsukova-Stuckart, M., Piedra-Garza, L. F., Gautam, B., Alfaro-Espinoza, G., Izarova, N. V., Banerjee, A., Bassil, B. S., Ulrich, M. S., Breunig, H. J., Silvestru, C., Kortz, U., (2012), Inorg. Chem, 51, 12015.
15. Seiple, L.A., Cardellina, J. H., Akee, R., Stivers, J. T., (2008), Mol. Pharmacol, 73, 669.
16. Zhao, J., Jason, R., Stagno, J. R., Varticovski, L., Nimako, E., Rishi, V., McKinnon, K., Akee, R., Shoemaker, R. H., Ji, X., Vinson. C., (2012), Mol. Pharmacol, 82, 814.
17. Bamgboye, T. T., Begley, M. J., Sowerby, D. B., (1989), J. Organomet. Chem, 362, 77.
18. Bone, S. P., Sowerby, D. B., (1979), J. Chem. Soc. Dalton Trans, 715.
19. Bordner, J., Doak, G. O., Peters, Jr. J. R., (1974), J. Am. Chem. Soc, 96, 6763.
20. Meinema, H. A., Noltes, J. G., (1969), J. Organometal. Chem, 16, 257.
21. Kanehisa, N., (1978), Bull. Chem. Soc, 51, 2222.
22. Meinema, H. A., (1976), J. Organometal. Chem, 107, 249.
23. Bertazzi, N., Bianca, F. D., Gibb, T. C., Greenwood, N. N., Meinema, H. A., Noltes, J. G., (1977), J .Chem. Soc. Dalton Trans, 957.
24. Said, M. A., Kumara Swamy, K. C., Poojary, D. M., Clearfield, A., Veith, M., Huch, V., (1966), Inorg. Chem, 35, 3235.
25. Breunig, H. J., Kruger, T., Lork. E., (2003), Angew. Chem. Int. Ed. Engl, 36, 615.
26. Gibbons, M. N., Sowerby. D. B., (1997), J. Chem. Soc., Dalton Trans, 2785.