ACCEPTOR DONOR PROPERTIES OF ORGANOANTIMONY(III) COMPOUNDS

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CERTIFICATE

This is to certify that the thesis entitled "ACCEPTOR DONOR PROPERTIES OF ORGANOANTIMONY(III) COMPOUNDS" being submitted by Mr. Jalil Rhaif Ugal to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Jalil has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which, to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

[Signature]

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JALIL RHAIF UGAL
DEDICATED TO

NAWAL

THE WOMAN THAT I LOVE

THE NAME THAT I KEEP
ABSTRACT

In the present investigation three kinds of compounds have been synthesized and characterized. These are:

i) Mixed trihalophenylantimonates(III)
ii) Mixed dihalodiphenylantimonates(III)
iii) Complexes of HgX₂(X = Cl, Br, I, SCN) with arylstibines.

A series of mixed trihalophenylantimonates(III) with the general formula $R₄N[PhSbX₂Y]$ ($R = Me, Et, Bu$; $X = Cl, Br$; $Y = Br, I$ and $X \neq Y$) were prepared by the reaction of $R₄NY$ and $PhSbX₂$ in the 1:1 molar ratio in ethanol or methanol. These compounds were characterized by elemental analysis, conductance measurements, IR, far IR and $¹H$ NMR spectroscopy. Some of these compounds were subjected to thermogravimetric analysis in a nitrogen atmosphere. Molecular structure of one of these compounds ($Et₄N[PhSbCl₂Br]$) was also determined by single crystal X-ray diffraction which showed that the anion in this compound is present as a dimer in which antimony atoms are bridged through bromine atoms.

The second series consisted of the mixed dihalodiphenylantimonates(III) of the general formula $R₄N[Ph₂SbXY]$. These compounds were synthesized by the reaction of $R₄NY$ and $Ph₂SbX$ in ethanol or methanol in 1:1 molar ratio. The characterization of these compounds was
carried out by the same methods as in the mixed trihalophenylantimonates(III).

In addition to these two series of mixed haloorganooantimonates, an attempt was made to synthesize mixed tetrahaloantimonates(III) by the reaction of $R_4NY$ and $\text{PhSbX}_2$ in 2:1 molar ratio, however, only the 1:1 compounds were obtained. In one particular case the reaction of $\text{PhSbCl}_2$ with $\text{Me}_4\text{NCl}$, $\text{Me}_4\text{NBr}$ in 1:1:1 molar ratio gave mixed tetrahalophenylantimonate(III) $[\text{Me}_4\text{N}]_2[\text{PhSbCl}_3\text{Br}]$.

For the third kind of compounds, trimesitylstibine and triphenetylstibine were used as ligands in an attempt to synthesize some transition metal complexes.

i) Reactions of $\text{MX}_2$ ($\text{M} = \text{Co(II)}, \text{Ni(II)}, \text{Cd(II)}$; $\text{X} = \text{Cl, Br, I, SCN}$) were carried out with $\text{Sb(MeS)}_3$ in 1:1 molar ratio in non aqueous solvents did not yield the desired complexes.

ii) Reactions of $\text{HgX}_2$ ($\text{X} = \text{Cl, Br, I, SCN}$) with $\text{Sb(Mes)}_3$:

These reactions were carried out in the 1:1 and 1:2 molar ratios in THF. From the 1:1 molar reactions, the 1:1 $\text{HgX}_2.S\text{b(Mes)}_3$ complexes could be isolated. However, the 1:2 molar reactions yielded the same 1:1 complexes, that is $\text{HgX}_2.S\text{b(Mes)}_3$ instead of the desired 1:2 complexes.

These complexes were characterized by elemental analysis, conductance measurements, IR, far IR and $^1\text{H}$ NMR
spectroscopy. Thermogravimetric analyses of three of these complexes were carried out in a nitrogen atmosphere.

iii) Reactions of HgX₂ with Sb(Phenetyl)₃.

These reactions were carried out in the 1:1 and 1:2 molar ratios. However, no complex of definite composition could be obtained in any reaction except in the case of HgI₂. Both 1:1 and 1:2 complexes, i.e. HgI₂·Sb(Phenetyl)₃ and HgI₂[Sb(Phenetyl)₃]₂ were isolated. These complexes were characterized by elemental analysis, conductance measurements, IR, far IR and ¹H NMR spectroscopy.
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