

SYNTHESIS AND CHARACTERISATION OF SOME ORGANOANTIMONY COMPOUNDS

By

PANKAJ SHARMA

Department of Chemistry

***THESIS SUBMITTED
IN FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY***



INDIAN INSTITUTE OF TECHNOLOGY, DELHI

HAUZ KHAS, NEW DELHI-110016

MAY 1993

Dedicated to
those who like me

ACKNOWLEDGEMENT

With the culmination of the proposed work and compilation in this form, I have an opportunity to accord my sincere thanks to Prof. N.K.JHA for his astute guidance and keen interest in this work. He provided me with necessary manoeuvreability and freedom to work, albeit keeping a watchful eye on the progress, without which this work would have never attained this stage.

I am thankful to CSIR (New Delhi) for financial assistance and Prof.G.N.RAO, Head, Chemistry Department, for providing me the necessary facilities to carry out the research work.

The cooperation and help extended by Rama Shankar, Jalil R.Ugal and Satnam Singh during the course of this work is gratefully acknowledged.

I wish to express my appreciation to my colleagues and friends, especially to Dr.A.K.Mitra, Ramesh Kumari, Kapil Dev, Rajender, Sanjay Balani, R.K.Dubey, Raman Batheja, Surendra Dhingra, Anju Khanna, Abu Khalid, Opendar, Sanjeev Mohanty and Sharad Raizada.

I am also thankful to Mr.Narayan Singh (SLA) and Ved Prakash (JLA) for this cooperation and help in the laboratory and Samsheer Singh Daggar for executing prompt and excellent

typing. The help rendered by the technical staff of the department is duly appreciated.

Last but not the least, I would like to record my deep sense of gratitude to my parents, brother and sister for their moral support in achieving the present objective.



(PANKAJ SHARMA)

May 1993

I.I.T., Delhi

CERTIFICATE

This is to certify that the thesis "SYNTHESIS AND CHARACTERIZATION OF SOME ORGANOANTIMONY COMPOUNDS" being submitted by Mr.Pankaj Sharma to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of a bonafide research work carried out by him. Mr.Sharma 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.



PROF. N.K. JHA
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
NEW DELHI-110 016

ABSTRACT

The thesis contains synthesis and characterisation of monohalodiorganoantimony(V) and triorganoantimony(V) schiff base complexes. All these triorganoantimony(V) and diorganoantimony(V) schiff base complexes were characterised by elemental analysis, vapour pressure osmometry, IR, far IR, ^1H and ^{13}C NMR spectroscopy. The compounds have been formulated as R_2SbXL (where $\text{R} = \text{Me}, \text{Ph}$ or Tolyl and $\text{LH}_2 = \text{SaltmH}_2$ or SalpdH_2) and R_3SbL (where $\text{R} = \text{Me}$ or Ph and $\text{LH}_2 = \text{SaltmH}_2, \text{HacenH}_2, \text{HactmH}_2, \text{GbapH}_2$ or AcacenH_2). Spectroscopic studies indicate the presence of hepta-coordinated antimony in these schiff base complexes, having pentagonal bipyramidal structure.

Present work reports the synthesis and characterisation of a few novel noncyclic catenatristibines containing two Sb-Sb bonds. In these tristibines two antimony atoms have different oxidation states and coordination number than the third antimony atom. The general formula of these compounds are $\text{R}_3'\text{Sb}(\text{SbR}_2)_2$ (where $\text{R}' = \text{Me}, \text{Ph}$ or Tolyl , $\text{R} = \text{Ph}$ or Tolyl). These compounds are moisture and oxygen sensitive. A trigonal bipyramidal structure has been proposed for these tristibines on the basis of IR, ^1H NMR, ^{13}C and ^{121}Sb NMR spectroscopy. On the basis of ^1H NMR and ^{13}C NMR data it is clear that in these compounds the two $-\text{SbR}_2$ groups are in equatorial positions which may be due to the bulkiness of $-\text{SbR}_2$ group whereas one of three R' groups occupies an

equatorial position and the other two occupy the axial positions. Thermogravimetric analysis, in nitrogen atmosphere shows that these tristibines decompose to antimony.

During the present work tertiary stibines containing tetrachloro-4-pyridyl groups namely, tris(tetrachloro-4-pyridyl)stibine, phenylbis(tetrachloro-4-pyridyl)stibine or tolylbis(tetrachloro-4-pyridyl)stibine were synthesised. These stibines were then brominated to get their dibromides. These stibines and their dibromo derivatives were characterised by elemental analysis, vapor pressure osmometry, IR, far IR, ^1H and ^{13}C NMR spectroscopy. Thermogravimetric analysis in nitrogen atmosphere shows that these compounds decompose to antimony which corresponds to the amount of antimony present in these compounds. In static air Sb_2O_3 is the end product of decomposition.

CONTENTS

Abstract	i
Abbreviations	iii
List of Tables	iv
List of Figures	vi

CHAPTER 1 INTRODUCTION

1.1	ORGANOANTIMONY COMPOUNDS	1
1.2	ORGANOANTIMONY SCHIFF BASE COMPLEXES	2
1.3	DI OR POLYSTIBINES CONTAINING Sb-Sb BOND	12
1.3.1	Distibines	12
1.3.2	Reactions of Distibines	13
1.3.3	General Properties	15
1.3.4	Polystibines	18
1.4	TERTIARY STIBINES CONTAINING HETEROCYCLIC RING	21
1.5	SCOPE OF THE WORK	25

CHAPTER 2 MATERIALS AND METHODS

2.1	INTRODUCTION	27
2.2	SOLVENTS AND REAGENTS	27
2.3	PREPARATION OF ANTIMONY AND OTHER ORGANOANTIMONY COMPOUNDS	28
2.3.1	Antimony tribromide	28
2.3.2	Triphenyl stibine	28
2.3.3	Triphenyl antimony dibromide	29
2.3.4	Tri(p-tolyl)stibine	30

2.3.5	Trimethyl stibine dibromide	30
2.3.6	Phenyl antimony(III) dibromide	31
2.3.7	Dimethyl antimony(V) dibromide	31
2.3.8	Diphenyl antimony(V) tribromide	32
2.3.9	Diphenyl antimony(V) trichloride	32
2.4	PREPARATION OF SCHIFF BASES	33
2.4.1	N,N-bis(Salicylidene)-o-phenylene- diamine (salpdH ₂)	33
2.4.2	N,N-bis(Salicylidene)-o-1, 3-propylene-diamine (saltmH ₂)	33
2.4.3	N,N-bis(o-hydroxyacetophenone)-1, 3-propylene-diamine (hactmH ₂)	33
2.4.4	N,N-bis(o-hydroxyacetophenone)- ethylenediamine (hacenH ₂)	34
2.4.5	Bis(acetylacetone)ethylenediamine (AcacenH ₂)	34
2.4.6	Glyoxalbis(o-aminophenol) (GbapH ₂)	34
2.5	PHYSIOCHEMICAL STUDIES	35
2.5.1	Elemental analysis	35
2.5.2	Melting point	36
2.5.3	Molar Conductance	36
2.5.4	Molecular weight determination	37
2.5.5	Infrared and far-infrared spectra	37
2.5.6	UV-vis spectra	38

2.5.7 Nuclear magnetic resonance spectra	38
2.5.8 Thermogravimetric analysis	38
2.5.9 Mass Spectrum	38

CHAPTER 3 MONOHALODIORGANOANTIMONY(V) AND TRIORGANO- ANTIMONY(V) SCHIFF BASE COMPLEXES

3.1 INTRODUCTION	39
3.2 SECTION A: MONOHALODIORGANOANTIMONY(V) SCHIFF BASE COMPLEXES	40
3.2.1 Experimental	40
3.2.2 Results and discusson	41
3.3 SECTION B: TRIORGANOANTIMONY(V) SCHIFF BASE COMPLEXES	49
3.3.1 Experimental	49
3.3.2 Results and Discussion	50

CHAPTER 4 NONCYCLIC CATENA TRISTIBINES

4.1 INTRODUCTION	76
4.2 EXPERIMENTAL	77
4.2.1 Preparation	77
4.2.2 Characterisation	80
4.3 RESULTS AND DISCUSSION	80
4.3.1 IR and FAR IR Spectra	81
4.3.2 UV-Visible Spectra	82
4.3.3 ¹ H NMR Spectra	82

4.3.4	^{13}C NMR Spectra	84
4.3.5	^{121}Sb NMR Spectra	85
4.3.6	Mass Spectrum	87
4.3.7	Thermogravimetric Analysis	87
4.4	THIN LAYER CHROMATROGRAPHY AND ^1H NMR RESULTS OF THE BROMINATION PRODUCTS OF $\text{Tolyl}_3\text{Sb}(\text{SbPh}_2)_2$	88
 CHAPTER 5 TETRACHLORO-4-PYRIDYL STIBINES		
5.1	INTRODUCTION	110
5.2	EXPERIMENTAL	110
5.2.1	Preparation	111
5.2.2	Characterisation	114
5.3	RESULTS AND DISCUSSION	115
5.3.1	Molecular Weight Determination	116
5.3.2	IR and FAR IR Spectra	116
5.3.3	UV-Visible spectra	120
5.3.4	^1H NMR Spectra	120
5.3.5	$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra	121
5.3.6	Thermogravimetric Analysis	124
 CHAPTER 6 SUMMARY AND FURTHER SCOPE		
6.1	SUMMARY	140
6.2	FURTHER SCOPE	143
 REFERENCES		144