STUDIES ON THE COORDINATION CHEMISTRY OF SOME TETRAVALENT AND DIVALENT METALS

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STUDIES ON THE COORDINATION CHEMISTRY OF SOME TETRAVALENT AND DIVALENT METALS

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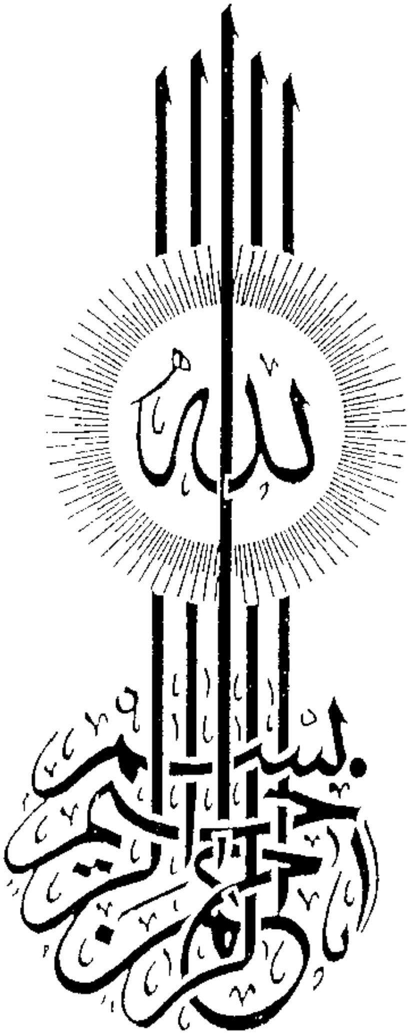

بسم الله الرحمن الرحيم

Dedicated To

My Dear Husband

&

My Parents

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S. Hessein

ABSTRACT

The thesis is divided into two sections:

Section I describes the preparations and properties of some new complex compounds of tin(II) chloride. The ligands contain atoms from Groups V and VI of the periodic Table. Tin(II) exhibits class "A" acceptor behaviour in which the strength of coordination is: $N > P$, $O > S$. In most of the tin(II) complex compounds, water appears to compete in the coordination sphere.

Section II describes the preparations and properties of some new complex compounds of Tin(IV). Some physical measurements, elemental analysis, infrared, ultraviolet and visible spectra and TGA measurements were carried out and the results are discussed.

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Chapter III

Results Of Tin(II) Reactions.

Chapter IV

Discussion Of The Results Of Tin(II) Reactions

Chapter V

Results Of Tin(IV) Reactions

CHAPTER I

INTRODUCTION
AND
AIM OF THE PRESENT WORK

INTRODUCTION

General Chemistry of Tin.-

Occurrence :- Tin is found in nature almost exclusively as the tin(IV) oxide and occasionally with gold in small amounts as tin metal. Many reactions can be performed with the assistance of this element[1], such as the preparations of organometallic tin.

Discoveries of tin in egyptian tombs show that the metal was fairly common in old times. There are several reports on the occurrence of metallic tin in nature in Bohemia, Bolivia, New South Wales, Nigeria- but tin stone or cassiterite is the sole source of commercial tin. This mineral occurs in tetragonal crystals coloured brown or black by impurities, chiefly iron. Cassiterite is stannic oxide, SnO_2, contaminated with more or less arsenical pyrites, copper pyrites, tungstates, and various metallic sulphides.

Extraction of tin is carried out by the reduction of tin(IV) oxide by coal in a reverberatory furance, at high temperature.

$$SnO_2 + 2C \xrightarrow{\Delta H} 2CO + Sn$$

Properties Of The Metal .-

Tin is not attacked either by water or air at ordinary temperatures either separately or together; hence it is used as a protective covering. It takes fire when heated in air between I500 °C and I600 °C , burning with a white flame to stannic oxide. It combines directly with chlorine forming stannic chloride, it reacts slowly with dilute hydrochloric acid and fairly rapidly with the hot concentrated acid, forming solution of stannous chloride[2] .

$$Sn + 2HCl \xrightarrow{\Delta H} SnCl_2 + H_2 .$$

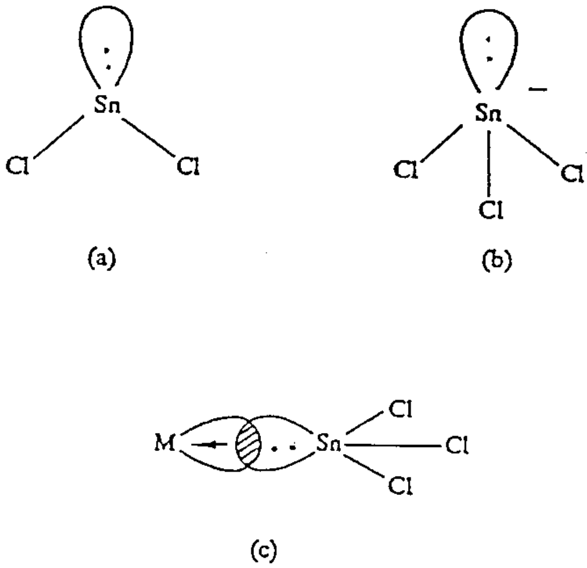
Uses Of Tin And Its Compounds.-

Tin is often used as a heteroatom in organic chemistry as well as in organometallic or molecular inorganic chemistry. Tin is used as tinplate, solder, bronze, tinning, alloys and chemicals. In addition to this extensive use of the metal itself and its alloys, various compounds of tin are used in industry and commerce. Tin(IV) oxide is used in ceramic glazes and as a polishing powder. Tin chlorides are used to weigh natural silk, stabilize soap perfumes, silver glass mirrors and as chemical reducing agents. Tin(II) fluoride finds extensive use as an additive to dentifrices[3] . Monobutyltin compounds stabilize plastic films, and dibutyl and other organo-tins are used as stabilizers[4]. Tributyltin compounds are used in industrial fungicides, insecticides, anti-fouling paints and disinfectants, and triphenyltin derivatives are used in agricultural pesticile purposes[5].

Recently, new results of studies on the structure of tin compounds have been collected and discussed[6-8] , and the syntheses and reactions of some organic derivatives of tin(II) have been compared[9,IO] .

The Chemistry Of The Different Oxidation States Of Tin·-

With a ground state configuration for tin of $5s^2 5p^2$, it can form covalent tin(II) compounds with the use of two unpaired p-electrons. When the $5s^2$ electrons take no part in compound formation, the bond angle in such an SnX_2 molecule would be 90°. Normally, however, the s-electrons are incorporated into an sp^2 hybridized bond situation, and the resultant bond angle is about I20° . Thus, for example, tin (II) chloride in the gas phase has the structure illustrated in Fig. I (a)[11], with two sp^2 orbitals forming covalent bonds to halogen and one directional lone pair of electrons.



(a)

(b)

(c)

Fig. I. (a) $SnCl_2$ (gaseous), (b) $SnCl_3^-$, (c) $M \leftarrow SnCl_3$ complex, illustrating the directional lone pair of electrons in each case .

Figure I (b) shows the $SnCl_3^-$ ion in which tin(II) may be regarded as sp^3 hybridized, with the two tin chlorine bonds and the directional lone pair of $SnCl_2$, but with the coordination of a chloride ion into the vacant sp^3 orbital. Fig. I (c) shows how the directional lone pair of $SnCl_3^-$ behaves as a donor ligand to metals, etc. In this latter case it is possible for the tin atom to act simultaneously as a π-electron acceptor, thus increasing the overall strength of the tin- acceptor atom bond[11] .

The large size of the Sn^{2+} ion gives it, usually, an octahedral environment in materials containing smaller ions such as fluoride and oxide; and maximum distortion is to be expected in such compounds of tin(II). The extra stabilization, and hence the extent of distortion, will, however, fall rapidly with increasing tin-anion distances.

Hybridization of the available 5s and 5p orbitals of tin produces a suitable situation for the formation of four tetrahedral covalent bonds. Many tin compounds such as tin(IV) halides (except fluoride) and the organotin compounds have this covalent mode of bonding.

Whereas tin(II) compounds do not appear to utilize the 5d orbitals except in the possible cases of π-bonding in donor-acceptor complexes, tin(IV) compounds make extensive use of 5d orbitals. Thus, for example, in complexes such as $(CH_3)_3SnCl.C_5H_5N$, the five-coordinate tin atom is sp^3d hybridized in a trigonal bipyramidal envir-