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THE INDUSTRIAL USE OF INORGANIC TIN COMPOUNDS IN COAL CONVERSION PROCESSES AND OTHER SYSTEMS

by

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A THESIS

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ABSTRACT

The chemistry and industrial applications of inorganic tin compounds are reviewed and the use of these derivatives as coal liquefaction catalysts has been investigated. The formation, structure and composition of coal is discussed and a survey of the literature on the use of tin compounds in coal liquefaction carried out.

A series of tin(IV) and tin(II) compounds has been prepared as models for the tin species formed within a range of tin-impregnated coals. These include tin(IV) tetrahalide adducts of aromatic and aliphatic ethers, $SnX_4.nROR^1$, chlorotin(IV) derivatives, $Cl_nSn(OR)_{4-n}$, such as the novel diethylamine adduct $SnCl_2(OSiPh_3)_2.Et_2NH$, tin(II) benzoate, $Sn(O.CO.Ph)_2$ and tin(II) (β -naphthoate), $Sn(O.CO.C_{10}H_7)_2$.

A range of coals from different sources were impregnated with tin(IV) and tin(II) compounds and their Mossbauer spectra compared with the model compounds, in order to determine which species were formed *in-situ*. For each coal, it was found that the uptake of tin reached a saturation level and this was correlated with the moisture content of the coal for tin(IV) chloride and with the ether type groups present for tin(II) chloride.

The use of tin(II) octoate (tin(II) bis(2-ethylhexanoate) as catalyst for the liquefaction of Morwell coal did not improve the yield of liquid products. However, this tin compound was active in the removal of sulphur. Mössbauer studies have shown that in the final residue which remained after the liquefaction, the tin was partially present as tin(II) sulphide. Alumina-supported tin catalysts were found to be active in the hydrocracking of Point of Ayr coal, the yields being comparable with those obtained for a Co-Mo catalyst.

Finally, in view of the recent interest in the Pharmaceutical properties of tin compounds, a number of the model compounds synthesised in these investigations have been evaluated as potential anti-tumour agents, using the P388 Leukaemia and B16 Murine Melanoma test systems.

PUBLICATIONS

1. Spectroscopic (^{119}Sn and ^{13}C NMR, ^{119m}Sn Mossbauer and IR) Studies of Tin(IV) Tetrahalide Adducts of Cyclic and Aromatic Ethers, in the Solid State and in Solution.

   S.J. Blunden, D. Searle and P.J. Smith, Inorg. Chim. Acta, 1985, 98, 185.

2. ^{119}Sn NMR and ^{119m}Sn Mossbauer Studies of Inorganic Tin(IV) Compounds with High Co-ordination Numbers.

   S.J. Blunden, D. Searle and P.J. Smith, Inorg. Chim. Acta, 1986, 116, L31.

3. Structural, Infrared and Mossbauer Studies of Octahedral *cis*-Dichlorobis(diketonate)tin(IV) Complexes Having Anti-tumour Activity.

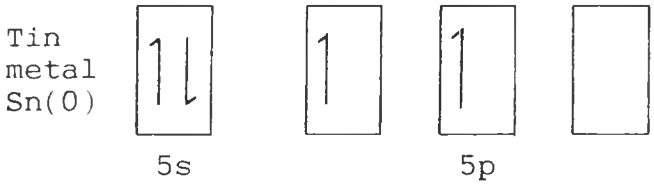
   D. Searle, P.J. Smith, N.A. Bell, L.A. March, I.W. Nowell and J.D. Donaldson Inorg. Chim. Acta, 1989, 162, 143.

CHAPTER 1

INTRODUCTION

1.1 STRUCTURE AND BONDING IN INORGANIC TIN COMPOUNDS

Tin is a Group IV element, which exists in two allotropic forms, α - (or grey) tin, which is stable below 18 ^{o}C and β - (or white) tin, which is stable between 18^{o}C and 232^{o}C. Its electronic configuration is [Kr] $4d^{10}5s^{2}5p^{2}$ and its outer orbitals may be depicted diagrammatically as follows:

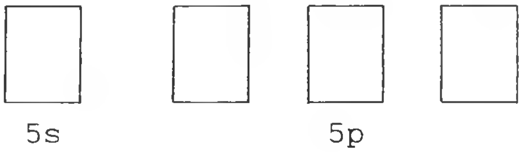


It can exist in $^{+}4$ or $^{+}2$ oxidation states, the valence electrons being used in a variety of ways in bonding.

1.1.1 Tin(IV) Derivatives

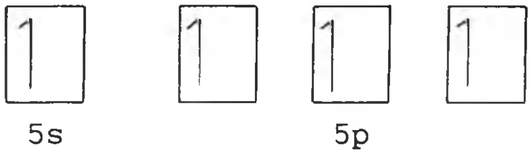
There are three different ways in which Sn(IV) may form derivatives:-

(i) by the loss of all four valence electrons, leading to the formation of the Sn^{4+} ion.



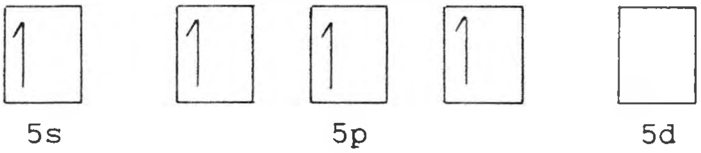
e.g. SnO_2

(ii) by the formation of four equivalent covalent bonds using sp^3 hybrid orbitals, resulting in a tetrahedral configuration.



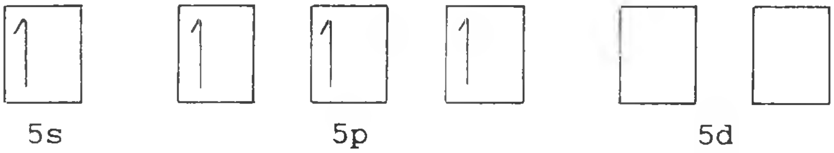
e.g. $SnCl_4$

(iii) by complexation, using vacant 5d orbitals. sp^3d hybridisation leads to the formation of five co-ordinate trigonal bipyramidal or square pyramidal complexes.



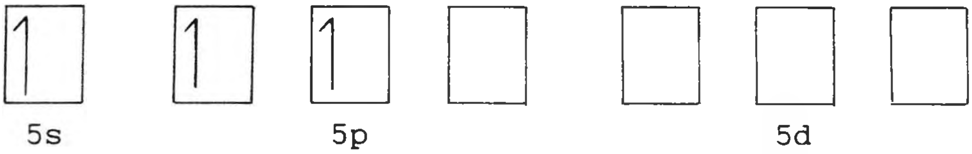
e.g. K_2SnO_3 (square pyramidal); $[Ph_4C_4Cl]^+SnCl_5^-$ (trigonal bipyramidal).

Six co-ordinate octahedral complexes are formed as a result of sp^3d^2 hybridisation.



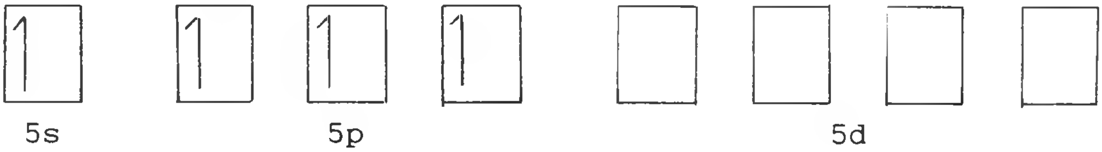
e.g. K_2SnCl_6

sp^3d^3 hybridisation leads to the formation of seven co-ordinate complexes.



e.g. Sn(trop)$_3$OH[tropH = $C_7H_5O_2H$], which has a pentagonal bipyramidal structure.

sp^3d^4 hybridisation leads to the formation of eight co-ordinate complexes which have either dodecahedral or square antiprismatic structures.



e.g. HSn(DTPA).3H_2O(H_5DTPA = diethylenetriaminepentaacetic acid, $(HO.CO.CH_2)_2N(CH_2)_2N(CH_2CO.OH)(CH_2)_2N(CH_2CO.OH)_2$) has a dodecahedral structure.

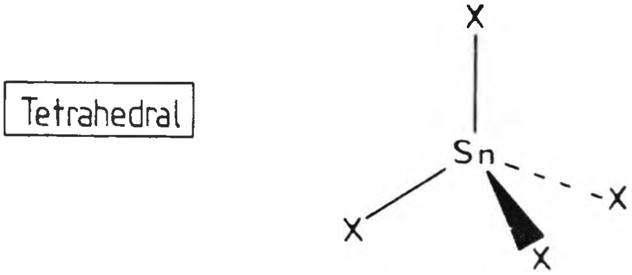
Pc_2Sn(Pc = phthalocyanine) has a square antiprismatic structure.

Six co-ordinate tin(IV) compounds are the most common structures observed and other co-ordination numbers are rare. The common geometries of tin(IV) compounds are shown in Figure 1.1.

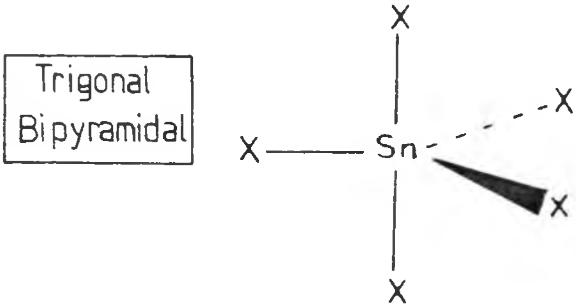
1.1.2 **Tin(II) Derivatives**

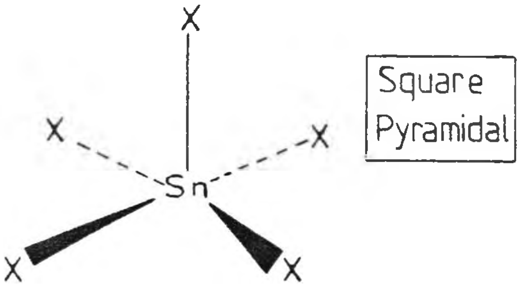
When present in the divalent state, the tin atom is using only two of its four valence electrons in bonding. No promotion of the 5s electron to a 5p orbital occurs, the s

Co-ordination number 4

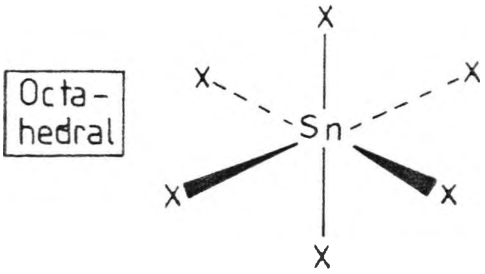


Co-ordination number 5





Co-ordination number 6



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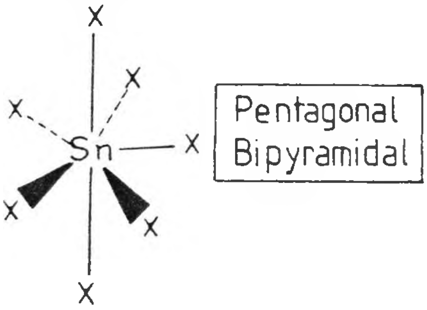

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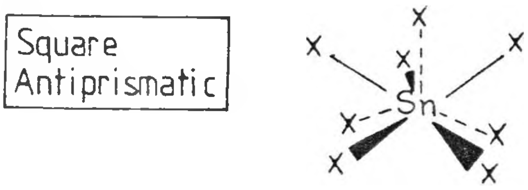


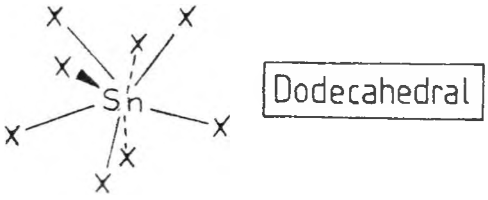


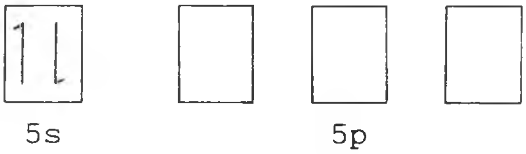
Figure 1-1: The Common Geometries of Inorganic Tin(IV) Compounds

orbital remaining completely filled. The $^{+}2$ oxidation state is less stable than the $^{+}4$ oxidation state, although the divalent state does increase in stability down Group IV.

There are four different ways in which tin(II) may form derivatives:-

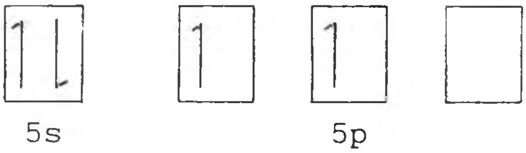
(i) by the loss of the two 5p electrons, leading to the formation of the Sn^{2+} ion.

i.e.



e.g. $SnSO_4$

(ii) by using the two unpaired 5p electrons for the formation of covalent bonds.

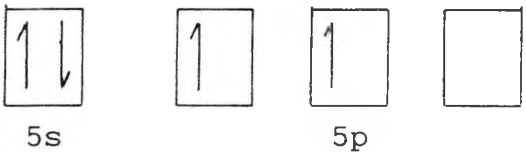


In general, sp^2 hybridisation occurs, leading to the formation of bent molecules (ψ -trigonal) with bond angles approaching 120^{o}C (ψ indicates that a co-ordination position is occupied by a lone pair).

e.g. In the vapour phase, tin(II) halides exhibit this type of bonding.

(iii) Hybridisation including the vacant 5p orbitals, enables complexes to be formed. In each case, one hybrid orbital is occupied by a lone pair of electrons, and this has an important effect on the stereo-chemistry.

Pyramidal molecules are formed on sp^3 hybridisation.



e.g. $SnCl_2.2H_2O$. In this case, each tin atom is situated at the apex of a pyramid containing two chlorine atoms and one co-ordinated water molecule.

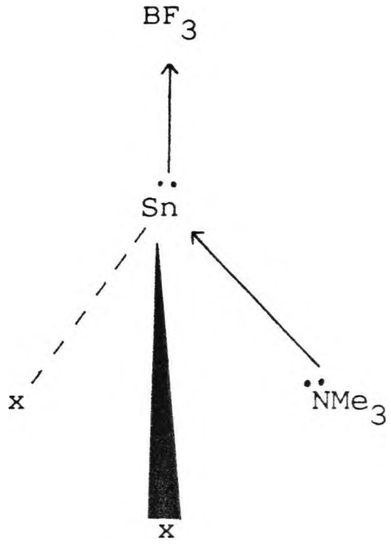
sp^3d and sp^3d^2 hybridisations are possible, but there is no evidence to suggest that they occur in the vapour phase or in solution. In the solid state, sp^3 hybridisation resulting in a trigonal pyramidal structure is most common. The second most common structure is that in which the tin forms two long and two short bonds, e.g. $SnCl_2$.(1,4-dioxan).

(iv) The tin(II) ion may act as a donor, by donating its lone pair to a suitable acceptor.

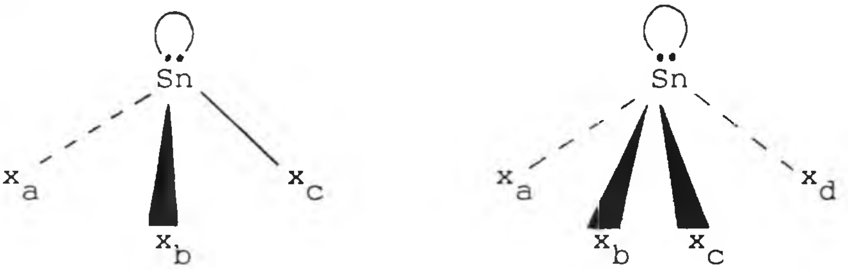
Example: $SnX_2(NMe_3)(BF_3)$ (X = Cl, Br or I) [1]

The tin atom in this compound has accepted a pair of electrons from the trimethylamine ligand and donates its lone pair to the strong Lewis acid, boron trifluoride.

i.e.



The common geometries of tin(II) compounds are shown in Figure 1-2.



Trigonal Pyramidal Pyramidal 4 co-ordinate

Figure 1-2: Common Geometries of Tin(II) Compounds

1.2 THE INDUSTRIAL APPLICATIONS OF INORGANIC TIN COMPOUNDS

1.2.1 Catalysts

Inorganic tin compounds are widely used as catalysts in a variety of industrial processes. The tin catalysts employed may be divided into two groups.

1.2.1.1 Homogeneous Catalysts

In homogeneous catalysis, the tin compound and the reactants are present in the same, i.e. liquid, phase. Inorganic tin compounds are used as homogeneous catalysts in the production of polyurethanes [2, 3, 4], the curing of silicone rubbers [5] and for various organic syntheses, e.g. the transesterification reaction [6], the Friedel-Crafts reaction [7] and in the polymerisation of unsaturated hydrocarbons [8, 9] and epoxides [10].

(a) Polyurethanes

Polyurethanes are manufactured in a variety of forms including rigid and flexible foams. Polyurethanes may be defined as those polymers containing a significant number of urethane linkages, formed as shown in Equation (1-1).

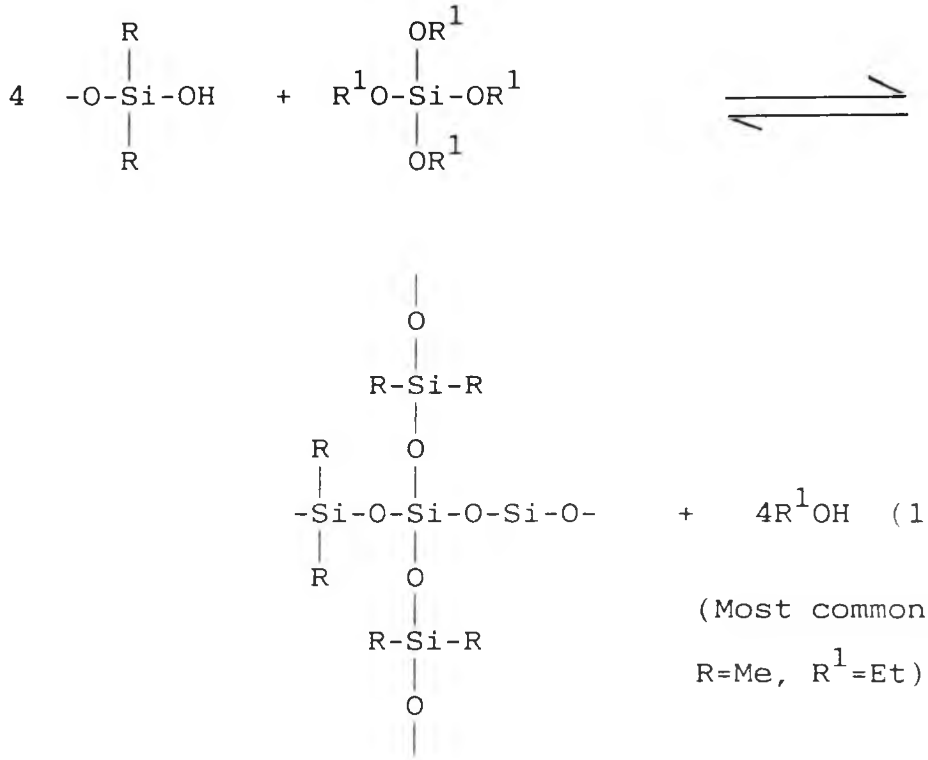
$$RN{=}C{=}O + HOR^1 \longrightarrow RNH{-}C(O)OR^1 \qquad (1\text{-}1)$$

Foaming is produced as a result of trapping of CO_2 gas within the polymer. In order for the reaction of polyurethane foams to be commercially viable, catalysts must be employed to control the relative rates of gas formation and polymerisation. Tin compounds are found to be very effective as catalysts, tin(II) octoate being the most widely used. They are often used in conjunction with tertiary amines, particularly for the manufacture of flexible foams, since a synergistic effect is observed [2]. Attempts have been made to elucidate the mechanism of the tin-catalysed reaction. Britain *et al*. [3] concluded that the metal compound acts as a catalyst by co-ordinating to the isocyanate group. The hydroxyl group then attaches to the metal, and the two functional groups are thus brought into close proximity.

(b) Silicone Crosslinking

Silicone polymeric materials, based on an $(RSi\text{-}O)_n$ grouping, may be produced in many different forms, including resins, gums and elastomers [5]. There are two main types of curing reactions, namely condensation and addition, tin compounds being employed as condensation catalysts.

In condensation crosslinking, a polydialkylsiloxane, having terminal hydroxyl groups, reacts with a tetraalkoxysilane [6] (equation 1-2).



$$4\ -O-\overset{R}{\underset{R}{Si}}-OH + R^1O-\overset{OR^1}{\underset{OR^1}{Si}}-OR^1 \rightleftharpoons -\overset{R}{\underset{R}{Si}}-O-\overset{\overset{|}{\underset{R-Si-R}{O}}}{\underset{\underset{R-Si-R}{O}}{Si}}-O-Si-O- + 4R^1OH$$

(1-2)

(Most commonly, $R=Me$, $R^1=Et$)

The only inorganic tin compound to be used as a catalyst is tin(II) octoate (tin(II)(2-ethylhexanoate)).

(c) <u>Other Systems</u>

The formation of organic esters by the reaction of a carboxylic acid with an alcohol (esterification) or by the reaction of an ester with an alcohol (transesterification) are important industrial processes for the production of moulding resins, cosmetics, PVC plasticisers and packaging for food (equations 1-3 and 1-4).

ESTERIFICATION: $R\ CO.OH + R^1OH \rightarrow R\ CO.OR^1 + H_2O$ (1-3)

TRANSESTERIFICATION: $R\ CO.OR^1 + R^{11}OH \rightarrow R\ CO.OR^{11} + R^1OH$ (1-4)

Tin(II) oxalate $(\overline{\mathrm{SnO.CO.CO.O}})$ is a very effective transesterification catalyst in the formation of phthalates, polyesters and alkyd resins [6].

The Friedel-Crafts alkylation reaction may be represented in general, by equation 1-5.

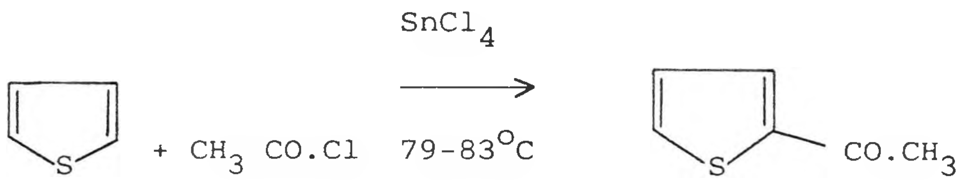
$$\mathrm{Ar{-}H} + \mathrm{RX} \longrightarrow \mathrm{Ar{-}R} + \mathrm{HX} \qquad (1\text{-}5)$$

Although aluminium(III) chloride is most commonly employed to catalyse this reaction, other metal halides, including $SnCl_4$, may be used, especially where more moderate conditions are required.

Friedel-Crafts acylation involves the condensation of an aromatic or aliphatic acid chloride with an aromatic hydrocarbon (equation 1-6).

$$\mathrm{R\,CO.\,Cl} + \mathrm{HAr} \longrightarrow \mathrm{Ar\,CO.R} + \mathrm{HCl} \qquad (1\text{-}6)$$

Tin(IV) chloride may be used as a catalyst for this type of reaction too. For example, on acylating thiophene in the presence of aluminium trichloride, polymerisation occurs [7]. However, if the less active tin(IV) chloride is used, the desired product is obtained [7] (equation 1-7).



(1-7)

Tin(IV) chloride has been used to catalyse polymerisation reactions involving unsaturated hydrocarbons, such as iso-butene and α-methylstyrene. In both cases, a co-catalyst, such as water is required [8, 9].

1.2.1.2 **Heterogeneous Catalysts**

When acting as a heterogeneous catalyst, the solid tin compound is providing a surface on which the specific reaction can occur. In general, the tin compound (most commonly, SnO_2) is used in conjunction with another metal or metal oxide and examples of the types of processes which are catalysed in this way are organic oxidation reactions, the selective methylation of phenol and the cracking, dehydrogenation and cyclisation reactions which are carried out in the petroleum industry.

Table 1-1 shows the principle oxidation reactions for which particular tin-based catalyst systems are used.

CATALYST SYSTEM	OXIDATION REACTION
Tin/vanadium oxides (Sn-V-O)	Vapour phase oxidation and ammoxidation of aromatic hydrocarbons, such as PhMe and xylenes leading to the formation of organic acids, aldehydes and nitriles [11, 12]. Vapour-phase oxidation of aldehydes, such as furfural leading to the formation of acid anhydrides [13].

CATALYST SYSTEM	OXIDATION REACTION
Tin/antimony oxides (Sn-Sb-O)	Oxidation of propene to acrolein [14, 15]. Mechanistic investigations [13, 14] indicated that the acrolein oxygen atom is obtained directly from the catalytic lattice, which is then reoxidised by gas phase oxygen. Oxidation and isomerisation of but-1-ene [16, 17].
Tin/molybolenum oxides (Sn-Mo-O)	Olefinic oxidations, e.g. oxidation of propylene to acetone, but-1-ene and pent-1-ene to methyl ethyl ketone and methyl propyl ketone. It is believed that the mechanism involves an alcoholic intermediate formed by hydration of a carbonium ion [18, 19].
Tin/phosphorus oxides (Sn-P-O)	Dehydrogenation of butenes to butadiene. The activity of the catalyst was increased by steaming at elevated temperatures [20].

Table 1-1: To Show the Uses of Binary Tin Oxide - Metal Oxide Systems

Tin(IV) oxide has been used in conjunction with precious metals to catalyse the oxidation of carbon monoxide. This reaction is important in the removal of toxic CO from exhaust gases, and cigarette filters, although this application is not commercial yet.

The high activity of Pd-SnO_2 catalysts in the oxidation of CO by O_2 has been used to improve the efficiency of carbon dioxide gas lasers [22, 23].

1.2.2 Ceramics

The use of inorganic tin compounds in the pottery and ceramics industry constitutes the oldest application of these compounds. Babylonian and Assyrian wall tiles, decorated with an opaque white glaze based on tin(IV) oxide, have been discovered and are thought to date from the 9th century B.C. [24].

Tin(IV) oxide has been used in two different areas of the pottery industry:-

(i) It has been known to act as an opacifier for many centuries [6] and is one of the most effective opacifying agents, the light being scattered and reflected from the surface of solid particles of SnO_2, suspended in a glaze. In some cases, levels of only 4 - 8% of SnO_2 are necessary in the glaze [25].

(ii) Tin-containing coloured pigments have been known for many years. Tin(IV) oxide has a rutile type structure, the tin atom being octahedrally co-ordinated [26], and its lattice is able to accommodate certain transition metal ions which impart colour to the host matrix, e.g. tin-vanadium yellow [6, 24, 25], chrome-tin pinks [6,27].

Some of the pigments which are used in artists' paints are based on tin, and it was first used in this way in 1300 when a new yellow pigment, lead-tin yellow, appeared. However, it was not until 1941 that it was first analysed and shown to contain tin [28]. The colours produced range from a pale primrose yellow to a golden yellow, depending on the temperature and other conditions of preparation.

Mosaic gold, often used as a substitute for powdered gold pigment from the 14th century to the late 19th century, is synthetically produced tin(IV) sulphide, SnS_2.
During the 19th century, many new pigments for use in artists paints were introduced. These included cerulean blue, a cobalt stannate, $CoO.nSnO_2$, which is a greenish-blue and is still available today [29].

1.2.3 **Pharmaceuticals**

Inorganic tin compounds are used in two main areas in the pharmaceutical industry, that is in dentistry, and as radiopharmaceutical scanning agents.

1.2.3.1 **Dentistry**

Tin(II) fluoride, and to a lesser extent tin(II) pyrophosphate ($Sn_2P_2O_7$) have been used in commercial formulations of toothpastes and mouthwashes and are thought to protect the teeth in the following ways:

(i) tin(II) fluoride controls root hypersensitivity [6].

(ii) tin(II) fluoride, both alone and when used in the presence of acidulated phosphate fluoride (APF), is believed to decrease the solubility of root surfaces in acidic media [30].

(iii) trace amounts of tin(II) fluoride reduce enamel solubility when applied with APF, the APF being administered prior to the SnF_2 [30, 31, 32].

(iv) SnF_2, and SnF_2 with tin(II) pyrophosphate, act as dental plaque inhibitors when applied as toothpastes [33] and mouthwashes [34]. The use of tin(II) fluoride in toothpastes and other dental preparations has declined in recent years because of its hydrolytic instability and ease of oxidation.

1.2.3.2 Radiopharmaceutical Scanning Agents

Radiopharmaceutical scanning agents are used in the diagnosis of disease. Certain nuclei may exist for a finite time in an excited, i.e. metastable, state. On decaying to the ground state, some of these nuclei, such as ^{99m}Tc, emit gamma rays which are highly penetrating. The body has a tendency to concentrate a certain chemical form of these isotopes in a particular organ [35] and, since the gamma rays readily escape from the body, such isotopes are ideal scanning agents.

Although the pertechnetate ion (TcO_4^-) has been used in some nuclear medicine processes, radiopharmaceuticals containing ^{99m}Tc in a lower oxidation state are more useful [6]. An aqueous, acidic solution of tin(II) chloride is the most commonly used reducing agent [35], the reaction being carried out under an inert atmosphere [36].

However, it has been suggested more recently that the tin not only acts as an electron donor, but is actually present in the ^{99m}Tc pharmaceutical, and therefore affects the biodistribution of the technetium complexes [37].

1.2.4 Glass and Plastics Applications

Tin(IV) oxide and other inorganic tin compounds are of great benefit to the glass industry both in the manufacture of certain types of glasses and as surface coatings. In the latter case, the particular property imparted to the glass depends on the thickness of the tin oxide film. In addition, inorganic tin salts are applied to the surface of certain plastics.

1.2.4.1 Inorganic Tin Compounds in the Manufacture of Glass

Tin(IV) oxide electrodes offer a non-reducing and corrosion resistant alternative to molybdenum or graphite electrodes in the manufacture of heavy lead containing glass [38].
An electrode typically contains 98% SnO_2, with small amounts of Sb_2O_5 which enhances conductivity, and CuO, which acts as a shrinking aid during high temperature sintering [39]. Lead glass is used in optical and ophthalmic glass, containing up to 70% Pb, and full lead crystal glass, containing more than 30% Pb. In the U.S.A., glass containing only 24% Pb is called lead crystal and "semi-crystal" glass contains 12% Pb.

1.2.4.2 Inorganic Tin Compounds in Surface Coatings

Tin(II) chloride, in particular, is used in the production of mirrors. The glass surface is sensitised with a solution of $SnCl_2$ and is then immersed in a silver salt (e.g. $AgNO_3$) solution. The Ag^+ ions are reduced to silver metal by the tin(II) ions and a uniform film of silver is produced on the glass [6, 40].

SnO_2 films, too, may be deposited on the surface of glass for various applications [39, 41, 42].

The properties of the resulting coated glass vary depending on the thickness of the SnO_2 film. Films of less than 100nm are used to strengthen glassware [6], e.g. for both returnable and non returnable bottles.

If the thickness of the film is of the order of the wavelength of visible light, i.e. 0.1 - 1.0μm, thin film interference occurs, and an iridescent lustre is observed on the glass surface. This is used in the manufacture of decorative glassware [6].

SnO_2 films of thickness greater than 1μm are electrically conducting, although they are often doped with Sb or F to increase their electrical conductivity [89].

Since these films are transparent, they may be used for de-icing aircraft windscreens [6]. In addition, they are present in fluorescent lamps [39], temperature insensitive resistors and in gas detection devices. SnO_2 is used commercially in gas sensors in Japan [43].

1.2.5 Fire Retardants

Tin chemicals have been investigated as fire retardants for both natural and synthetic polymers.

1.2.5.1 Natural Polymers

(a) Cellulosic Polymers

These are highly flammable and the use of tin chemicals as fire retardants was first investigated in 1859 by Versmann and Oppenheim [44]. Hydrous tin(IV) oxide was precipitated on to the fabric by impregnating it with either tin(II) or tin(IV) chloride, followed by treatment with a basic solution [44]. However, an afterglow was observed with these treatments. This problem was eventually overcome by using a mixture of tin(IV), tungsten(VI) and iron(III) oxides [6]. SnO_2 has often been precipitated on to the fabric by hydrolysis of sodium hydroxystannate, as in the process patented by Kurlychek [45].

(b) Proteinaceous Polymers

Wool is a proteinaceous polymer and although it is relatively fire retardant, more stringent legislation has required that it be rendered more so. The Wool Research Organisation of New Zealand (W.R.O.N.Z.) have formulated a tin containing treatment which may be sprayed on to rugs [46]. It is believed that this treatment (a mixture of tin(IV) chloride, ammonium bifluoride and a polishing agent) acts as a fire retardant for wool by catalysing its thermal breakdown.

Silk is an insoluble fibrous protein. Tin(IV) chloride has been used for many years for the weighting of silk, but the treatment now used, which involves hydrolysis of $SnCl_4.5H_2O$

by a mixture of $Na_2HPO_4.12H_2O$ and $Na_2SiO_3.9H_2O$ also imparts flame resistance to the fabric. The tin species present in the silk is believed to be hydrous SnO_2 [6].

1.2.5.2 Synthetic Polymers

(a) Non-Oxygenated Polymers

Mixtures of hydrous tin(IV) oxide and iron(III) oxide, tin(II) oxide and zinc oxide, or SnO_2 in the presence of a bromine containing compound, are effective fire retardants for acrylonitrile-butadiene-styrene copolymer [47, 48]. Simultaneous thermal analysis of polypropylene shows that the presence of a halogen compound and tin(IV) oxide increases the formation of excess carbon. The oxide is believed to catalyse char formation, reducing the number of volatile species generated from the polymer [49].

Although P.V.C. is fire resistant, if it does burn, large quantities of smoke are produced. $SnSO_4$, SnO_2 and SnO are moderately good smoke suppressants and are believed to act in the solid phase, interfering with the normal thermal degradation of P.V.C. by promoting the cross-linking of P.V.C. chain segments [50]. A weak synergism has been observed in studies of the SnO_2-MoO_3 system as a smoke retardant for P.V.C. [50]. In addition, tin(II) octoate acts as a smoke suppressant for polystyrene in the presence of a halogen compound [51].

(b) Oxygenated Polymers

Tin bis(2-chloroethyl) phosphate has been found to act as a fire retardant for cellulose acetate fibres when added at a 1% level. The yarn would not burn either as a skein or after being woven into a fabric [52]. Polyacrylate resins may be rendered flame retardant by the addition of 10 - 20% $SnCl_4$ and 0.5 - 5% oxalic acid [53].

Various tin-oxygen compounds have been found to be effective flame retardants for polyamides when used in the presence of halogen [6, 54].

Polyurethane foams used in upholstered furniture constitute a severe fire hazard unless they are effectively flame retarded. Antimony(III) oxide is most widely used for flexible foams, but work has been carried out in which some of the antimony compound is replaced by either SnO or SnO_2 [6].

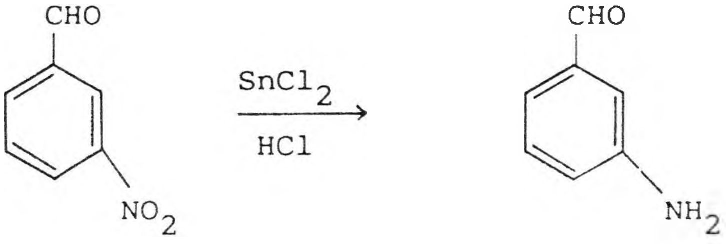
1.2.6 Reducing Agents

Tin(II) compounds are used industrially as reducing agents for both organic and inorganic compounds.

The Stephen aldehyde synthesis which was first discovered in 1925 [55] involves the reduction of an aromatic or aliphatic nitrile to the corresponding aldehyde, the reducing agents being anhydrous $SnCl_2$ and dry gaseous HCl in diethyl ether, or, in later reports, ethyl acetate [56].

Aldehydes may also be synthesised from acid anilides by means of the anhydrous HCl/$SnCl_2$/diethyl ether reduction [57].

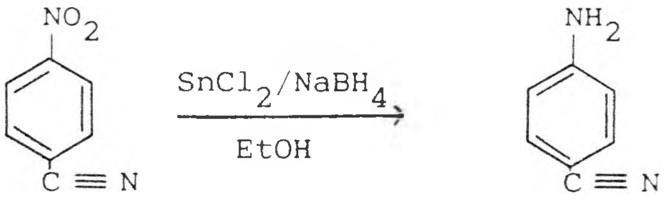
Tin(II) chloride in aqueous hydrochloric acid will selectively reduce a nitro group to an amine. For example, m-nitrobenzaldehyde is reduced to m-aminobenzaldehyde, the aldehyde moiety being unaffected by the reducing agent [57] (equation 1-8).



(1- 8)

The sodium borohydride-$SnCl_2$ system in ethanol also shows high selectivity for aromatic nitro groups even in the presence of other readily reducible functions such as C = O, COR, C⋮N [58] (equation 1-9).

e.g.



(1-9)

Inorganic reductions using tin(II) salts as reducing agents are usually carried out in aqueous media. Those inorganic reductions which are used in industrial processes are as follows:-

(i) reduction of the pertechnetate ion (TcO_4^-) by a tin(II) salt in acidic solution for use in ^{99m}Tc radiopharmaceuticals (see Section 1.2.3.2).

(ii) in the analytical determination of total tin in acid-soluble tin compounds, a quantitative yield of iron(II) ions is produced by reduction of Fe^{3+} to Fe^{2+} in an anion exchange resin, the reducing agent being the tin(II) species [6].

(iii) the pigment "Purple of Cassius" is produced by reduction of gold(III) to gold metal.

(iv) in the production of mirrors, Ag^+ ions are reduced to silver metal by means of Sn^{2+} ions (see Section 1.2.4.2).

1.3 PHYSICAL MEASUREMENTS

1.3.1 Mossbauer Spectroscopy

1.3.1.1 Transmission Mossbauer Spectroscopy

This technique was discovered in 1957 by Mossbauer and involves the resonant absorption of gamma rays. It is a very useful tool for studying the electronic environment of certain atomic nuclei and the three radioactive nuclides which are most often used are ^{57}Co, which decays to give ^{57}Fe, ^{119m}Sn, which decays to give ^{119}Sn and ^{129}I produced by decay of ^{129}Te. The principles of Mossbauer spectroscopy can be most easily explained with reference to ^{57}Fe. On electron capture, ^{57}Co($t_{0.5}$ = 270 days) produces ^{57}Fe in an excited state, denoted ^{57}Fe*. This excited nucleus, known in general as the source, rapidly drops down to the ground state, by emitting a gamma ray of a certain energy. If a second ^{57}Fe nucleus (the absorber) were to be placed in the path of the gamma ray, it would be expected that there would be resonant absorption of that gamma ray, the nucleus being excited into the ^{57}Fe* state. A detector placed behind the second Fe nucleus would shown that this had occurred (Fig. 1-3), since the gamma rays absorbed would be emitted almost immediately in all directions. The absorber is acting as a uniform scatterer and thus a significant proportion of the gamma radiation incident on it is not transmitted through the sample.

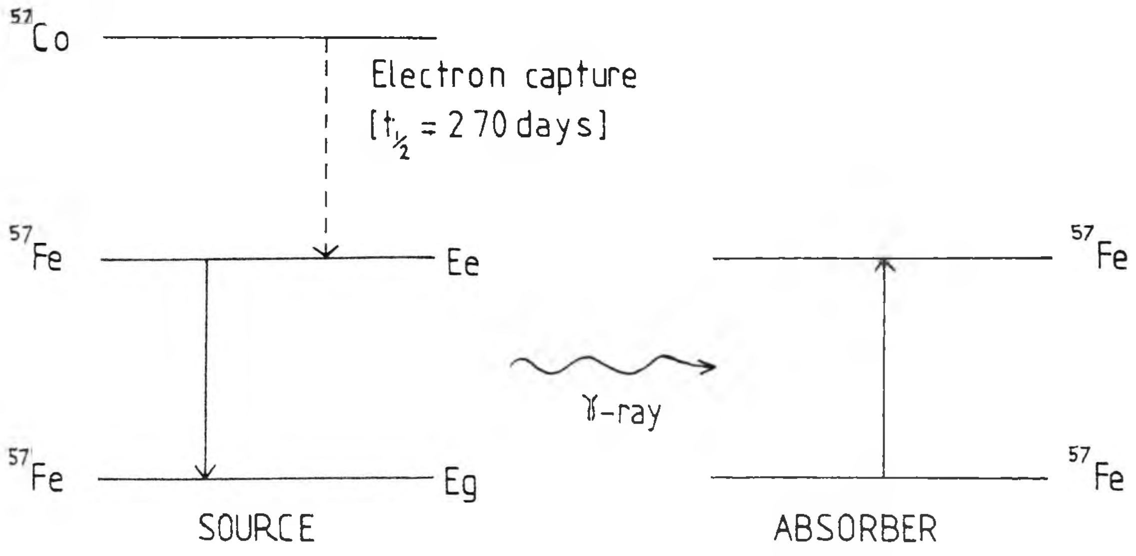


Figure 1-3: **Recoilless Resonance Absorption**

However, in practice, there are a number of factors which must be taken into account in order for resonant absorption to occur.

(i) The emitted gamma rays are not of one energy. They are spread about a mean, i.e. the distribution has a certain natural line width, which is given by the Heisenberg uncertainty principle [59]. For Mossbauer spectroscopy, the uncertainties are very small compared with the energy change involved. In fact, the relative line width is much smaller than that observed in other spectroscopic techniques. Resonance depends on getting the lines of absorber and source to overlap.

(ii) As the source emits the γ -photons, the nuclei will recoil in order to conserve momentum. Therefore, because of the Doppler effect, the frequency of the gamma ray will be shifted and will not match that of the absorber. The effect of recoil may be overcome by the use of a solid crystal lattice for the source, so that the recoil energy is dissipated within the crystal as a whole. The situation is further improved by cooling both the sample and the source to liquid nitrogen temperature (80K) or lower, thus reducing the thermal motion of the lattice atoms.

If these two factors are taken into account, it is possible to obtain resonant absorption of the photons provided that both the source and the absorber nuclei are in identical chemical states. However, if the chemical environments of the source and absorber nuclei are not the same, the energy separations between the ground and excited states will not be identical and absorption will not occur. It is therefore necessary to be able to alter the energy of the emitted gamma ray by means of a scanning device which may be tuned over the entire range of frequencies of interest. If the energy gap in the absorber is greater than the energy gap in the source, then the gamma ray must be given an energy increment, and vice versa. The Doppler effect may be used to increase the frequency of the gamma ray by moving the source towards the absorber and to decrease its frequency by movement of the source away from the absorber. The Doppler Velocity is given by equation 1-10.

$$\text{Doppler velocity} = \frac{\text{Shift in energy gap}}{\text{total transition energy}} \times \text{velocity of light} \qquad (1\text{-}10)$$

In order to achieve this motion, the source is usually mounted on a coil to which an alternating current is applied causing it to oscillate. The Geiger counter output is then fed to a multi channel computer and the results from each point of the source movement are collected and summed over each cycle. The number of counts recorded per second are usually plotted against the velocity in mm s^{-1}, and a fall in the counts/s implies gamma ray absorption by the source. Figure 1-4 is a diagram of a Mossbauer system.

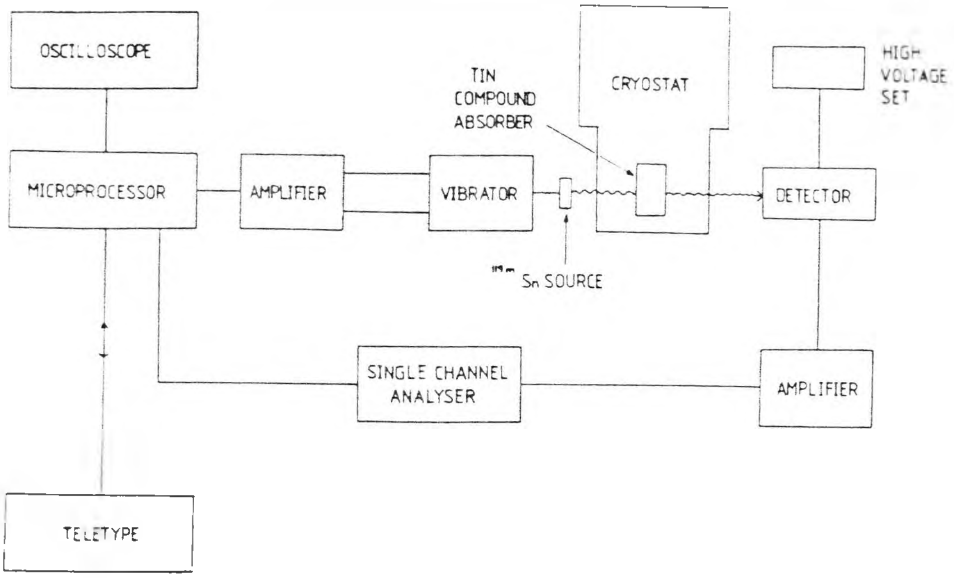


Figure 1-4: **A Typical Mossbauer Spectrometer**

The two most important Mossbauer parameters are the Isomer Shift (δ) and the Quadrupole Splitting (Δ Eq).

(a) **The Isomer Shift (δ)**

This arises because of electrostatic interactions between the charge distribution surrounding the nucleus, and those electrons which have a finite probability of being found in the region of the nucleus. p and d orbitals have zero density at the nucleus and it is therefore the s electron density which is important. It has been shown that the isomer shift is given by equation 1-11.

$$\text{I.S.} = 2KR^2 \frac{\delta R}{R}\left(\left[\Psi_{(0)_s}\right]^2_{a-c}\right) \qquad (1\text{-}11)$$

where K is a constant

R is the radius of the absorber

δR is the difference between the radii of the ground and excited states

and $\left[\Psi_{(0)_s}\right]^2_a$ is the s electron density at the absorber nucleus

For a given nucleus, δR is constant and so the isomer shift is directly proportional to the s electron density. For tin-119, δR is positive and thus an increase in s electron density at the nucleus leads to a more positive isomer shift. Isomer shifts are expressed as shifts of the line from a selected standard. In the case of tin-119 spectroscopy, the standard is usually $CaSnO_3$ or $BaSnO_3$. They can be used to give information about the oxidation state of the tin atom, tin(II) and tin(IV) compounds giving very different isomer shifts (Table 1-2).

TIN SPECIES	ISOMER SHIFT (mm s^{-1})
Sn(II) Example: $SnCl_2$	4.15
Sn(O) Example: α-Sn	2.10
Sn(IV) Example: $SnCl_4$	0.80

Table 1-2: Typical Isomer Shift Values of Tin Compounds in Different Oxidation States [59]

The value of δ also varies with the electronegativity of the atoms which are bonded to Sn, e.g. the isomer shifts of $SnCl_4$, $SnBr_4$ and SnI_4 decrease with increasing electronegativity of the halides (Table 1-3).

TIN COMPOUND	ISOMER SHIFT (mm s^{-1})
$SnCl_4$	0.80
$SnBr_4$	1.10
SnI_4	1.45

Table 1-3: **Isomer Shift Data for Tin(IV) Halides [59]**

(b) The Quadrupole Splitting

The magnitude of the quadrupole splitting parameter gives information about the shape of the distribution of electronic charge around the nucleus. The state of a nucleus is characterised not only by its energy, but also by a spin quantum number. If the nucleus is spherical, and has a uniform charge distribution, then the spin angular momentum (I) is either 0 or 0.5. However, nuclei with a spin angular momentum greater than 0.5, are not spherical, but elongated. The charge density is not uniform and gives rise to a quadrupole moment. It is observed that such nuclei with half-integral quantum numbers greater than 0.5 are often "degenerate", i.e. several states have exactly the same energy when they are placed in a uniform electrostatic field. In a non-uniform field, the quadrupole moment will interact with local electric field gradients, removing the degeneracy of the nuclear energy levels, splitting them into sub-levels corresponding to the number of allowed orientations of the nucleus. The tin-119 ground state has a spin of I = 0.5 and is therefore not affected by an electric field. However, the first excited state, has a spin of I = $^{3}/_{2}$ and it is therefore split into sub-levels ($^{\pm 1}/_{2}$, $^{\pm 3}/_{2}$). In some situations, these states will be degenerate, whereas in others magnetic and electric fields interact with the nucleus to remove the degeneracy. In such a case, the energy gap separating the two levels is called the quadrupole splitting (Figure 1-5).

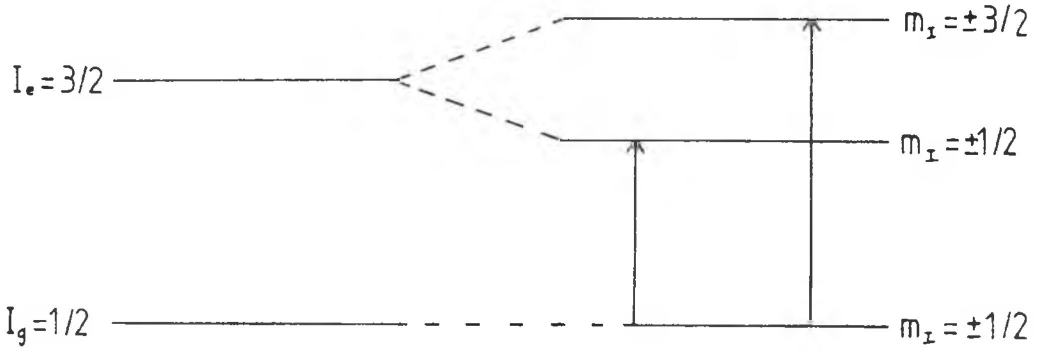


Figure 1-5: **Energy Levels and Mossbauer Transitions for ^{119}Sn Nucleus in an Electric Field Gradient**

The information which can be obtained from the quadrupole splitting may be illustrated by the difference between the spectra obtained for the iron(II) hexacyanide ion $Fe(CN)_6^{4-}$ and the iron(II) nitroprusside ion, $Fe(CN)_5(NO)^{2-}$. In the $Fe(CN)_6^{4-}$ ion, the iron atom is symmetrically bound to six CN^- groups and the Mossbauer spectrum consists of a single sharp line. The $Fe(CN)_5(NO)^{2-}$ ion is not quite symmetrical because one of the cyanide groups has been replaced by a nitrosyl group (NO^+). Its spectrum consists of two lines, since its first excited state is split by the breaking of symmetry.

The tin-119 Mossbauer spectra carried out for this thesis were recorded at 80K using a constant acceleration microprocessor spectrometer. Isomer shifts are relative to $CaSnO_3$. In the present work, Mossbauer spectroscopy has been used to identify and investigate a number of tin(IV) halide/ether adducts, and to study the species formed in impregnating various coals with both tin(II) and tin(IV) compounds. In addition it has given information on the tin species present in residues remaining after coal hydrogenation using tin compounds as catalysts.

1.3.1.2 <u>Conversion Electron Mossbauer Spectroscopy (CEMS)</u>

On absorption of a γ-ray by the absorber, some of the excited tin nuclei drop down to the ground state by emission of a γ-ray, as stated in Section 1.3.1.1. However, some of the excited nuclei decay by internal conversion. In this case, the de-excitation energy of the nucleus is imparted to orbital electrons. However, the binding energy of the K electrons is greater than the de-excitation energy and therefore ejection of the K electrons does not occur. Instead the energy is absorbed by an L electron, which is then ejected with a kinetic energy of 10.6KeV. An electron from the M shell then fills the vacant hole in the L shell and produces a 2.8KeV electron. It is the back scattered internal conversion electrons which are detected in

Conversion Electron Mossbauer Spectroscopy. Only information about the surface of the absorber is obtained because of attenuation of the electrons from within the bulk of the sample.

The spectrometer used for both types of Mossbauer spectroscopy was a Cryophysics MS-102 Mossbauer spectrometer running in a constant acceleration mode. Spectra were accumulated over 512 channels in a multi channel analyser. The detector used was a gas flow proportional counter, detection being achieved by a single tungsten wire anode. The source was mounted vertically on a vibrator over the detector with the sample fixed underneath the source.

1.3.2 **Thermal Analysis**

1.3.2.1 **Differential Thermal Analysis**

This involves heating the sample under investigation and a thermally inert reference material, such as alumina, in a furnace. Any temperature difference between them, known as the differential temperature, ΔT, is continuously recorded as a function of furnace temperature. Any energy gains or losses in the specimen under investigation are then shown on a plot of ΔT against T. If an endothermic change occurs, the temperature of the sample will lag behind that of the reference because of the heat required to carry out the transition. If an exothermic change occurs, the temperature of the sample will be higher than that of the reference. When the physical or chemical change is complete, thermal diffusion brings the sample back to equilibrium, i.e. $\Delta T = 0$. The trace shows a sharp depression (endothermic change) or a peak (exothermic change). Measurements are usually taken of T_{max}, i.e. the temperature of maximum rate of heat change of the sample and T_{onset}, i.e. the temperature at which the heat change begins to occur, which is the point of intersection of the tangent of the leading edge of the peak with the extropolated baseline (Figure 1-6).

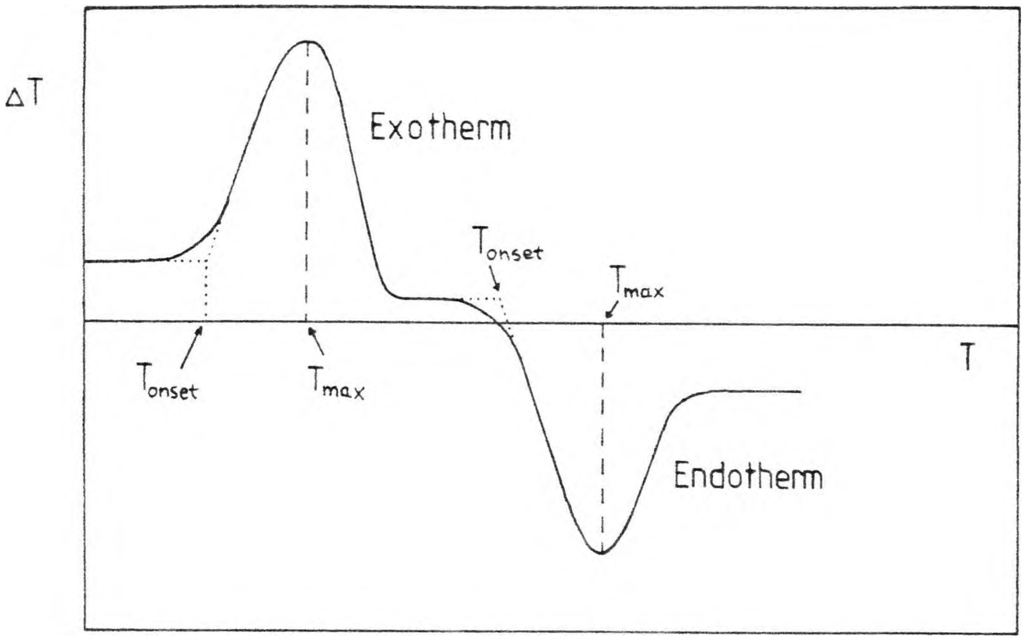


Figure 1-6: <u>Idealised Exothermic and Endothermic Peaks in a DTA Trace and the Measurements Made</u>

1.3.2.2 Thermogravimetric Analysis

In dynamic thermogravimetry, a sample is subjected to a continuous and linear increase in temperature and the change in weight of the sample is recorded as the temperature increases. The weight loss is usually expressed as a percentage of the initial mass of the sample (Figure 1-7).

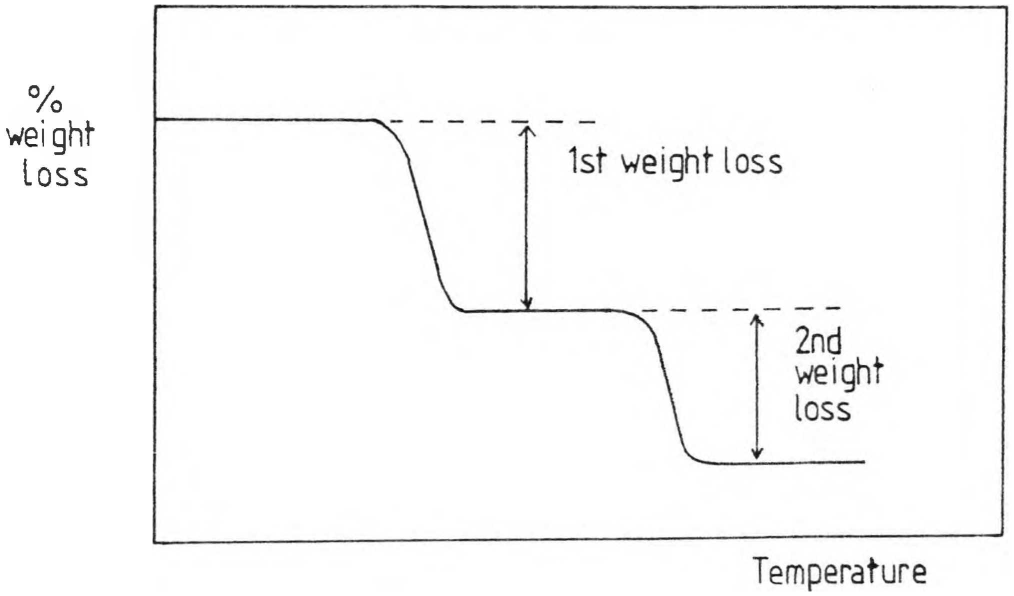


Figure 1-7: **Idealised TGA Trace Showing Two Weight Losses**

Example: TG/DTA analysis of dibromotin(IV) bisdiethyldithiocarbamate has been carried out, both in air and in nitrogen and the results obtained in nitrogen are shown below (Figure 1-8). In the first step, most of the diethylthiocarbamate ligands are lost, the major products of the first stage of decomposition being CS_2, tetraethylthiourea and tin(IV) sulphide. In the second stage, the halogen ligands are lost from the Br_2SnS fragment leaving SnS. As the temperature is increased further, the tin sulphide decomposes leaving metallic tin. The DTA peaks indicate that the first two steps are endothermic due to breakage of bonds and formation of stable products from reactive intermediates [60].

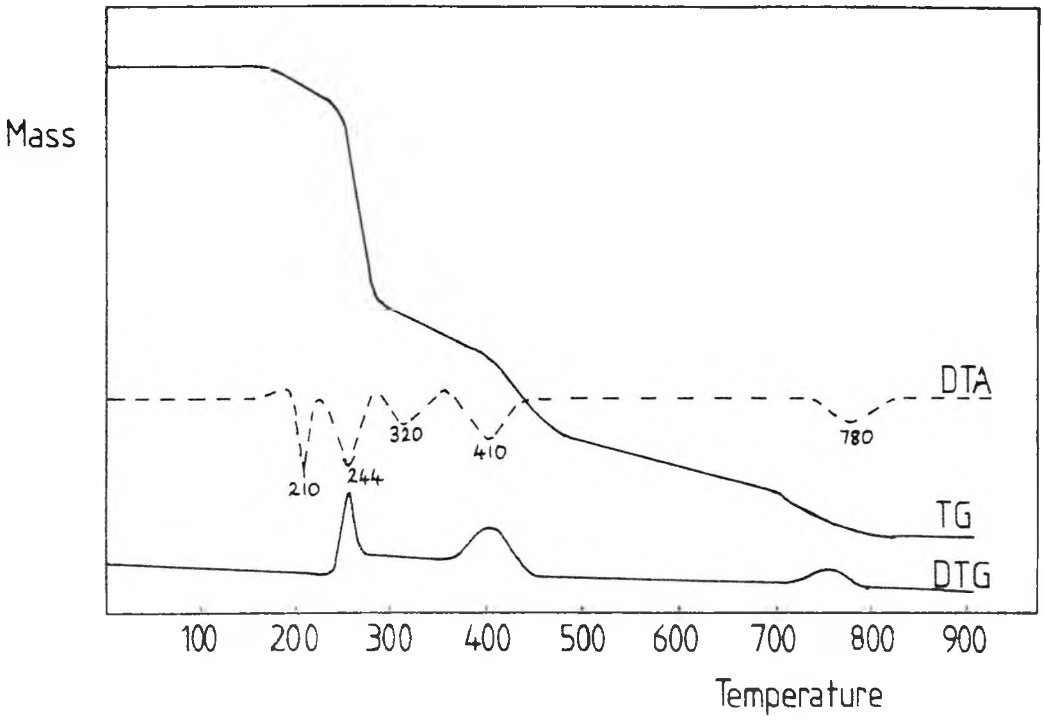


Figure 1-8: **TG/DTA Trace of Dibromotin(IV) bisdiethyldithiocarbamate in nitrogen [60]**

The thermal analyses for this thesis were carried out on a Stanton-Redcroft STA-780 Simultaneous Thermal Analyser using samples of ca. 10mg.

1.3.3 Infrared Spectroscopy

The atoms in a molecule do not remain in fixed positions relative to each other, but are constantly vibrating about some mean position. Vibrations which give rise to a dipole moment change, interact with the electric or magnetic fields associated with infrared radiation and transitions between vibrational energy levels occur. It is these transitions which give rise to infrared spectra. There are two types of normal modes of vibration. Skeletal vibrations, which give bands in the region 1400 - 700 cm^{-1}, involve all the atoms in the molecule. These bands are called the fingerprint bands and are highly typical of the molecule. The group vibrations involve only a small portion of the molecule, and are virtually independent of the structure as a whole.

In this work, the spectra were obtained as KBr discs, Nujol mulls (for solids) or thin films (for liquids) on either a Pye-Unicam SP 2000 or a Perkin-Elmer 1330 Infrared Spectrophotometer.

1.3.4 NMR Spectroscopy

NMR spectra arise because the nuclei of certain atoms, such as ^{1}H, ^{13}C and ^{119}Sn, spin and, when placed in an external magnetic field, their magnetic moment may either be aligned with or against the external field. Alignment with the field is more stable and the energy required to flip the nucleus to the less stable orientation depends on the strength of the external field. In practice, when recording a spectrum, the frequency of the incident radiation is kept constant and the strength of the applied magnetic field is varied. The field strength actually experienced by the nucleus depends on its environment, i.e. the electron density at the nucleus and the presence of nearby nuclei. Thus, in NMR spectroscopy, the applied field strength is measured and is plotted against the absorption. The shifts in position of the NMR absorption because of shielding or deshielding by electrons are known as chemical shifts (δ), expressed in parts per million of the total applied magnetic field. In addition, spin-spin coupling, leading to a splitting of the NMR signal, occurs when two nuclei are sufficiently close together in space, that they exert an appreciable magnetic effect on each other. In this work, both ^{13}C and ^{119}Sn NMR spectroscopy were used in the identification and investigation of tin(IV) halide/ether adducts and various other inorganic tin compounds. The spectra were recorded on a Jeol FX60Q spectrometer. The ^{119}Sn and ^{13}C chemical shifts are relative to Me_4Sn (TMS) respectively.

1.4 SCOPE OF THIS WORK

Chapters 2 - 5 of this thesis describe work which was initiated in order to study the use of inorganic tin compounds as coal liquefaction catalysts. Chapter 2 is a literature survey of previous studies of the use of tin compounds in coal liquefaction. The experimental work described in this thesis has involved studying the interaction of tin(IV) and tin(II) halides with various coals, at room temperature, in order to establish whether these tin compounds react with any of the functional groups present in the coals. This work is described in Chapter 4, the impregnated coals being studied principally by Mossbauer spectroscopy. The Mossbauer parameters of these coal samples are compared with those of model tin compounds whose synthesis and spectroscopic investigation are described in Chapter 3. Chapter 5 gives details of small-scale coal liquefaction experiments which have been carried out using inorganic tin compounds as potential catalysts.

Some of the model compounds which have been synthesised have been tested as potential antitumour agents and the results of in vitro tests are given in Chapter 6. An X-ray crystal structure of one of the compounds has been carried out (at Sheffield Polytechnic) and the results obtained are discussed. A second pharmaceutical use of inorganic tin compounds, the chemoprevention of neonatal jaundice, is investigated in this Chapter.

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CHAPTER 2

COAL STUDIES

2.1 COAL FORMATION, STRUCTURE AND COMPOSITION

Coal may be defined as a combustible rock, which has its origin in the accumulation and partial decomposition of vegetation [1]. It is derived from deposits of peat which have undergone a series of transformations. The particular type, or "rank", of coal formed depends on the severity of the conditions to which the peak has been subjected [2].

Table 2-1 shows the chemical changes which occur in the transition from wood to peat and then through the coal ranks to anthracite.

Class	Moisture in Raw State (%)	% C (d.a.f)[a]	% H (d.a.f)[a]	% O (d.a.f)[a]	Volatile Matter at 900°C (d.a.f)[a]
Wood (typical composition)	20	50	6	42.5	75
Peat (typical composition)	90	60	5.5	32.3	65
Brown Coal	60-40	60-70	*ca.* 5	>25	>50
Lignites	40-20	65-75	*ca.* 5	16-25	40-50
Sub-bituminous	20-10	75-80	4.5-5.5	12-21	*ca.* 45
Bituminous	10	75-90	4.5-5.5	5-20	18-40
Semi-bituminous	<5	90-92	4.0-4.5	4-5	5-20
Anthracite	<5	92-94	3.0-4.0	3.4	15

[a] d.a.f = dry ash-free.

Table 2-1 Composition of Wood, Peat and Coal Types [3]

It can be seen from this table that the carbon content increases and the oxygen content decreases on moving to higher coal ranks.

For many years there was some controversy as to whether coals have a primarily graphite-like or diamond-like structure. Indeed, evidence has been found to suggest that coal can have both aromatic and aliphatic character using various techniques eg. oxidative degradation [5,6], UV visible spectroscopy [5,7] and NMR [8-14]. It can be concluded that the more sophisticated methods of studying coal structure largely support the classical view that all coals are at least partially aromatic and that the aromaticity increases with rank.

In addition to carbon, coals also contain various heteroatoms, the most important of which is oxygen. It is generally agreed that the oxygen content decreases with rank. The oxygen functional groups found in coals are hydroxyl, carboxyl, carbonyl, ether and methoxy.

Work carried out up to 1961 has been reviewed by Van Krevelen [4] who came to the following conclusions:

i) the -OH groups present in coals are predominantly phenolic, or weakly acidic in nature.
ii) brown coals may contain up to ca. 9% oxygen as hydroxyl groups.

The hydroxyl content then decreases only slightly with increasing carbon content until 80% carbon coals, after which a more rapid decrease is observed. A hydroxyl content of less than 1% is associated with coals containing 90% carbon.

Abdel-Baset [17,18] found that the amount of oxygen present in the form of -OH groups (but not other forms of oxygen) in sub-bituminous or high volatile bituminous coals is a rank parameter, decreasing with coalification. Whitehurst [5] however, suggested that oxygen functionalities varied systematically with rank.

All coals contain some carbonyl groups but carboxyl and methoxy groups are reported to be present only in brown coals and lignites. Early work [4] indicated that brown coals contain ca. 5.5% carboxyl oxygen. More recently, a study of the chemical characteristics of Victorian Brown coal has been carried out [19] and oxygen found to be one of the major elements (>25%) present in the organic matter of this coal. Approximately 50% of this oxygen is present in the form of acidic groups, ie. phenolic hydroxyls or free carboxylic acids, whereas the rest is found in carbonyl groups, ether linkages or heterocyclic ring structures.

Blom et al. [15] obtained the distribution of oxygen functionalities for various coals, lignites containing ca. 7% OH groups, 1% carbonyl groups and between 0.2-5% carboxyl groups. Other coals were found to contain only hydroxyl groups (0.6-5.6%) and carbonyl groups (<1%). After subtracting the methoxy, hydroxyl, carbonyl and carboxyl oxygen contents from the total oxygen, some residual oxygen still remains and this is believed to be present as ether oxygen.

Ruberto et al. [20] have further concluded that a significant portion of the oxygen in sub-bituminous coals occurs in saturated ether functional groups, α- or β- to the aromatic moieties or as furan systems.

Much less is known about the sulphur functional groups present in coal. The total ratio of inorganic and organic sulphur can vary within the range 0.2 to 10 weight % (wt. %) although most coals contain between 1.0 and 4.0 wt. %.

Organic sulphur has been found to occur in various forms in coal: -SH [16,22], -S-S- [22], R-S-R [22], thiophenic and aryl sulphur [22,23] and dibenzothiophene [21].

Very little has been reported on the form of organic nitrogen in coals. Hayatsu et al. [21] found that lignite coal contained a small amount of pyridine. The most abundant heteroaromatic in anthracite coal is acridine or benzoquinoline but bituminous coal contains less nitrogenous heteroaromatics than the anthracite coal. However it does contain some acridone.

2.2 COAL LIQUEFACTION

2.2.1 The Importance of Coal Liquefaction

Interest in the conversion of coals to liquid fuels is usually controlled by access to petroleum. Coal liquefaction *via* hydrogenation was first reported by Bertholet in 1869 [24]. However, in the United States, petroleum became the preferred energy source after its discovery in Pennsylvania in 1859 and later in Texas. Other countries which did not have their own oil supply continued to study coal liquefaction and of these, it was in Germany that most of the early work from which present-day techniques have evolved was carried out. During World War II, twenty-seven synthetic fuel plants were built in Germany.

The discovery of massive petroleum reserves in the Middle East in the mid-1940s again precluded the need for coal liquefaction until recently, when due to unrest in this area, coupled with continual petroleum depletion and rapidly increasing costs of imported petroleum, coal liquefaction is again being considered as a major source of liquid fuels.

2.2.2 The Mechanism of Coal Liquefaction

The structure of coal is very different from that of the hydrocarbons found in petroleum. In particular, coals have high heteroatom and low hydrogen contents. Thus, two of the main objectives in the conversion of coal to liquid products are to increase the hydrogen content and eliminate the heteroatoms.

Many studies aimed at elucidating the mechanism of coal liquefaction have been carried out, and it is generally believed [25,26] that there is initial thermal cleavage of the coal molecule, in which the connecting links between clusters of condensed aromatics and hydroaromatics are thermally ruptured and free radicals are formed. This is followed by competition between stabilisation of the free radicals by hydrogen (from the coal itself) and repolymerisation of the radicals, leading to the formation of high molecular weight products. During the next stage of the reaction, benzene solubles are slowly formed [26]. The hydrogen required for this reaction is supplemented by hydrogen gas.

In the coal hydrogenation stage, reactions yielding liquid products are usually carried out at temperatures between 300°C and 500°C, under a hydrogen pressure of 6MPa to 10MPa in an autoclave. The reaction may be carried out in the presence or absence of solvent, in a batch autoclave or in a continuous reactor.

This reaction results in the formation of a solid residue, a liquid product and a gaseous effluent. The liquid product may be separated into various fractions, known as oils (hexane/petroleum soluble material), asphaltenes (petroleum/hexane insoluble, toluene soluble material) and asphaltols (toluene insoluble, THF soluble material).

2.2.3 Tin Catalysts in Coal Liquefaction Processes

Many investigations have been initiated in an attempt to find an effective catalyst for the coal liquefaction process. The literature indicates that tin compounds are effective coal liquefaction catalysts. Reviews on the hydrogenation of coal and tar have appeared covering the subject up to 1945 [27] and up to 1963 [28] and, although a few papers published before 1963 have been included, the following literature survey concentrates on the work which has been carried out since that time. Many different tin compounds have been investigated as catalysts and work has been carried out on both tin(IV) (Section 2.2.3.1) and tin (II) (Section 2.2.3.2) derivatives and on tin metal (Section 2.2.3.3). The possible promotion of the catalytic activity of tin by other species has been investigated as have different methods of applying the catalysts and the effect of varying the reaction conditions.

2.2.3.1 Tin(IV) Compounds

(a) Tin(IV) Halides

Only one investigation on the use of anhydrous $SnCl_4$ has been reported [29], the coal used being Montana sub-bituminous coal. The workers found that all of the tin (IV) tetrahalide was lost at temperatures below 450°C, whereas if tin(II) chloride was used, only approximately one half of this compound was volatilised. Hence, tin(IV) chloride was not studied further.

Wood et al. [30] studied both hydrated tin(IV) and tin(II) chloride ($SnCl_4.5H_2O$ and $SnCl_2.2H_2O$) as catalysts for Last Chance, Utah coal, and this work is discussed further in Section 2.2.3.2 (a). The hydrated tin(IV) chloride was less active than either the tin(II) chloride or the zinc halides tested, although it gave higher conversions than the other metal halides studied.

$SnCl_4.5H_2O$ has been studied as a catalyst for Victorian Brown coal by Cashion et al. [31] who incorporated the tin compound by means of ion exchange. Since Victorian Brown coal contains carboxylate ions in association with various metal cations, these cations may be readily displaced by ion exchange with, for example, tin or iron [32].

Using this method, it is possible to achieve a high dispersion of the catalyst within the coal. Cashion et al. [31] studied the 119^mSn Mössbauer spectrum of the tin-impregnated coal and found that, after ion exchange, the tin was present as SnO_2, which was believed to be formed as the result of hydrolysis of an unstable intermediate tin(IV) carboxylate species. After liquefaction, β-Sn and SnS were found in the residue, in addition to SnO_2. The performance of the tin catalyst was comparable with that of a commercial cobalt-molybdenum catalyst and exceeded that of an iron-based catalyst. Similar results were obtained by Cook and Cashion [33], the β-Sn appearing at temperatures above 380°C.

(b) Tin(IV) Oxide

Extensive work on the use of tin catalysts was carried out by the U.S. Bureau of Mines between 1944 and 1956 [34] and, for these experiments, a high volatile bituminous coal from Pittsburgh was used. These studies included an investigation of SnO_2 in the presence of ammonium chloride. The yield of liquid products obtained indicated that this is a highly active system.

The use of tin(IV) oxide in the presence of another species which might enhance its activity was also investigated by the Amoco Oil Company [35]. Several tin oxide-molybdenum trioxide mixtures, eg. SnO_2-MoO_3/Al_2O_3 were tested, and it was found that the tin-molybdenum catalysts were superior to pure SnO_2 or to molybdenum trioxide supported on alumina. It was concluded that mixed Sn-Mo catalysts act bifunctionally, the MoO_3 catalysing coal cracking reactions and the SnO_2 catalysing the hydrogenation of the cracked products.

In 1985, Mahoney et al. [36] patented a process for the recovery of upgraded liquid products from coal and coke using similar catalysts. The results obained, with and without the SnO_X promoter, are shown in Table 2-2 (the actual value of x in the catalysts containing SnO_X was not given). The catalyst performances were compared with the results obtained using a reference catalyst (Table 2-2).

Catalyst Concentration (wt. %)								
SnO_x	MoO_3	Al_2O_3	%C	R.A [a]	%S	R.S [b]	%N	R.N [c]
0	15.8	82.7	58.65	0.99	1.92	1.23	2.38	1.32
4	15	81	60.21	1.03	1.52	0.97	1.34	0.74
10	14	76	60.45	1.04	1.47	0.94	1.59	0.91
22	12	66	62.09	1.08	1.49	0.95	1.69	1.10

[a] R.A = relative activity as compared with reference catalyst.

[b] R.S = relative sulphur content as compared with %S for reference catalyst.

[c] R.N = relative nitrogen content as compared with %N for reference catalyst.

Table 2-2 Results Obtained by Mahoney et al. Using Sn-Mo Catalysts [36]

The authors again showed that catalysts containing both tin and molybdenum were more active than catalysts which did not contain any tin and they discovered that the Sn/Mo catalysts were superior to the reference catalyst. In addition, tin-containing catalysts had higher desulphurisation and denitrogenation activities than the reference catalyst.

Yamaguchi et al. [37] used single and multicomponent metal oxide catalysts in their studies and tested the potential of these materials for the cracking of a sub-bituminous coal by means of high pressure differential thermal analysis (D.T.A).

The order of total conversion was:-

$MoO_3(94.8\%) > Fe_2O_3-SnO_2-ZrO_2(88.3\%) > MoO_3-SnO_2-ZrO_2(87.7\%) > MoO_3-SnO_2(83.7\%)$.

This is in disagreement with the results obtained by Mahoney et al. [35] who found that the mixed molybdenum-tin catalyst gave a higher conversion than the individual catalysts. An increase in the catalytic activity of the Fe_2O_3-ZrO_2 catalyst was observed [37] on addition of SnO_2. Since tin(IV) oxide was present in the three catalysts which gave the highest conversion to liquid products, Yamaguchi et al. [37] concluded that tin-containing catalysts show the highest selectivity towards the production of liquid products.

When using a bituminous coal, Yamaguchi and Hattori [38] found that the catalysts which gave the highest percentage conversions were:-

$Fe_2O_3+SO_4^{2-}>MoO_3-TiO_2>MoO_3-Fe_2O_3-SnO_2$.

Again, the tin-containing catalyst showed the greatest selectivity towards oil formation. Tin(IV) oxide gave the highest oil yield of the catalysts tested by Mizumoto et al. [39] and, on studying the liquefaction of various coals in the presence of this catalyst, they found that the highest conversion was obtained for the coal with the greatest volatiles content. X-ray diffraction analysis of the coal residue indicated that the tin(IV) oxide had been reduced to tin metal. These workers used the model compound, dibenzyl ether, to show that tin(IV) oxide increased the yield of liquid products by catalysing the hydrogenation, rather than the recombination, reactions believed to occur during liquefaction.

Mizumoto et al. extended these studies to the effects of reaction temperature and pressure, as well as coal type [40], on tin(IV) oxide catalysed reactions. They found that increasing the temperature led to a decrease in the asphaltene yield but an increase in the overall conversion. The conversion decreased sharply on lowering the pressure. Thus, they [40] concluded that the overall conversion is strongly affected by pressure, whereas changing the temperature has more effect on the yield of asphaltenes and little effect on the total yield.

Stenberg and Srinivas [41] used the model compounds, diphenyl ether and diphenylmethane, to test the effectiveness of MoO_3-SnO_2, Fe_2O_3-SiO_2, Fe_2O_3-TiO_2, Fe_2O_3 and commercially available MoO_3-CoO, as catalysts for the cleavage of carbon-carbon and carbon-oxygen bonds found in coals. CO-H_2O or H_2 were used as reducing agents, under conditions similar to those of a typical coal liquefaction experiment. For diphenylmethane, the order of activity of the catalysts when using H_2 as the reducing agent was as follows:

$Fe_2O_3\text{-}SiO_2 \approx MoO_3\text{-}SnO_2 > CoO\text{-}MoO_3 > Fe_2O_3\text{-}ZrO_2 \approx Fe_2O_3\text{-}TiO_2$.

However, when using CO-H_2O, MoO_3-SnO_2 was much more active than Fe_2O_3-SiO_2. The water gas shift reaction (Equation 2-1) is believed to control the activity.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2\text{-}1)$$

Only MoO_3-SnO_2 and CoO-MoO_3 catalysts were effective in promoting the cracking of diphenyl ether in the presence of either H_2 or CO-H_2O. The percentage conversion in the hydrocracking of diphenyl ether with H_2 was found to be lower than that in the hydrocracking of diphenylmethane [41]. This result contradicts the conclusions of Takemura [42] that ether cleavage is more favourable than carbon-carbon bond cleavage and implies that the relative ease of cleavage of these bonds depends on the reaction conditions and nature of the catalyst.

Cochran et al. [43] were interested in discovering the role of tin catalysts in the coal liquefaction process and their studies included an investigation of SnO_2. Table 2-3 shows the results obtained for the various catalysts used in a series of liquefaction experiments and indicates that SnO_2 gave the highest conversion.

Catalyst	Conversion (wt. % Dry Ash Free Coal)
None	69
CoO, MoO_3/Al_2O_3	76
Sulphided CoO, MoO_3/Al_2O_3[a]	92
Sulphided Ni, $W/SiO_2Al_2O_3$[a]	75
SnO_2	100
$SnCl_2.2H_2O$	98
Sn	90

[a] Cobalt-molybdenum and nickel-tungsten catalysts sulphided by exposure to a stream of hydrogen sulphide in hydrogen.

Table 2-3 Effect of Catalysts on the Conversion of Victorian Brown Coal [43]

Cook *et al.* [33] found that SnO_2, added in powdered form, reacted more slowly and gave lower yields than $SnCl_4$ and $SnCl_2$, even though these catalysts are believed to be present in the form of $SnO_2.xH_2O$. This was thought to be due to the fact that the catalyst was more finely dispersed on being introduced from an aqueous solution (the hydration state of SnO_2 was found to vary [33] and no indication of the value of x is given).

(c) Organotin Compounds

Tetraphenyltin was tested for use in coal liquefaction by the U.S. Bureau of Mines [34] and was found to be highly active when used in the presence of ammonium chloride, giving 88% conversion of Pittsburgh Seam coal.

The distribution of a catalyst has been found to have an effect on its activity. Sharma *et al.* [44] and Suzuki *et al.* [45,46] postulated that organometallic compounds might be more readily dispersed within the coal because of their compatability with the organic vehicle used to slurry coal in many liquefaction reactions. Sharma [44] studied the effectiveness of several organometallics as catalysts for the liquefaction of both a sub-bituminous (Navajo) coal and a bituminous (York Canyon) coal. Some of the results obtained are shown in Table 2-4. The organotin compounds only showed a high catalytic activity for the sub-bituminous coal.

Catalyst	% Conversion	
	Navajo	York Canyon
None	61	44
$Mo(CO)_6$	79	73
Ph_4Sn	73	58
Ph_3SnH	67	--
$Pd(acac)_2$	84	72
$Ir(CO)_3Cl$	83	77

Table 2-4 Results of Hydrogenation of Navajo Mine and York Canyon Coals [44]

Suzuki et al. [45] used an Australian Brown coal for their studies and found that the conversion and yield of oils increased in the presence of the organotins, these compounds decomposing to metallic tin during the course of the reaction. Increasing the amount of catalyst increased the coal conversion, but had no effect on the oil yield, indicating that these compounds do not catalyse the degradation of the heavier oil fractions. However, increasing the hydrogen pressure did have an effect on the oil yield. Addition of a large excess of sulphur to the tin catalyst decreased its catalytic ability, whereas addition of $Fe(CO)_5$ increased it slightly and addition of sulphur to this binary catalyst led to a further improvement. These authors, like Mizumoto et al. [39], concluded that the tin acted as a catalyst by stabilising the coal radicals.

In a second paper, Suzuki et al. [46] suggest several possible reaction schemes for the conversion of coal to liquid products and they studied three different coals - a brown coal, a sub-bituminous coal and a bituminous coal - to test their proposals. Direct early depolymerisation, as opposed to consecutive depolymerisation of preasphaltenes and asphaltenes, was believed to occur in the case of the brown coal in the presence of Bu_4Sn. The sub-bituminous coal was largely cracked via direct processes, rather than sequential depolymerisation, although some consecutive hydrogenation did occur. Unlike, $Fe(CO)_5$ however, Bu_4Sn did not promote the hydrogenation of condensed aromatic rings.

Sequential processes were favoured for the bituminous coal, as predicted, since this coal contains fewer ether linkages and more condensed aromatic rings.

Boucher [48,49] addressed the problem of upgrading coal liquids by means of heteroatom removal and, to investigate this, he used both supported and unsupported metallophthalocyanines as catalysts, including those of Sn(IV), Mg(II), Cr(III), Fe(II) and Ru(II), and nitrogen-containing model compounds, eg. quinoline and isoquinoline. The ruthenium(II) phthalocyanine was found to be the most effective supported catalyst for the hydrogenation of quinoline followed by dichlorophthalocyaninotin(IV). The order of activity of the unsupported catalysts, $Sn(pc)X_2$ (pc = phthalocyanine), was reported to be I>Cl>Br>OH, the hydroxyl derivative showing no activity. Sn(pc) and $Sn(pc)_2$ were inactive and the authors therefore concluded that the presence of halogen is necessary for the tin phthalocyanine derivative to be effective in the hydrogenation of nitrogen-containing compounds.

2.2.3.2 Tin(II) Compounds

(a) Tin(II) Halides

Many workers have used tin(II) chloride as a coal liquefaction catalyst, probably because of its ready availability and ease of handling. In particular, the group at Monash University, Victoria, Australia have carried out a series of investigations using Victorian Brown coal and, as mentioned in Section 2.2.3.1 (a), tin compounds may be added to this coal by means of ion exchange. Tin(II) chloride was found by Hatswell et al. [32] to be readily incorporated into this coal and, in fact, it exchanged more effectively than iron(III) sulphate or iron(III) chloride.

Hydrogenation of Sn- and Fe- exchanged coals showed that the tin-exchanged coal was more readily converted than iron-exchanged coal [32,50]. X-ray diffraction [32] and ^{119m}Sn Mossbauer data [31] indicated that, after the hydrogenation, the tin was present as tin(II) sulphide, tin(IV) oxide and tin metal (β-Sn). The amount of SnO_2 present decreased as the reaction proceeded, whereas β-Sn appeared after ca. 20 minutes' reaction time and SnS after 1 hour.

This work was extended by Cook et al. [51], who studied the hydrogenation of this coal at various temperatures using a tin catalyst. Some reduction by hydrogen gas of $SnO_2.xH_2O$ occurred, even at temperatures as low as 205°C, with hydrated tin(II) oxide being formed. Tin(II) sulphide first appeared at temperatures between 250°C and 300°C, but as more β-Sn was formed, the amount of tin(II) sulphide decreased. β-Sn was only detected at temperatures above 300°C.

The major catalytic activity of the tin was observed at temperatures above 345°C and the authors concluded that the tin species formed at lower temperatures do not catalyse the degradation of coal. β-Sn first appeared at 350°C and it was concluded that the Sn(O) oxidation state is active during the liquefaction process [51].

Cashion et al. [31,33] believe that the first stage in the process involves the reduction of the tin to tin metal, which, being a liquid at the temperature of the reaction, is readily dispersed. It is then thought to react with sulphur and oxygen from the coal.

The use of Mossbauer spectroscopy to investigate the form of the tin catalyst after liquefaction has been studied by Vaishnava et al. [52]. They used both coal which had been impregnated with $SnCl_2$, and coal which had been dry-mixed with $SnCl_2.2H_2O$. In the former case, the tin was present as SnO_2 after impregnation, whereas it was necessary to heat the dry-mixed sample to 200°C before SnO_2 was observed. Vaishnava et al. [52] concluded that the oxide was formed as the result of cleavage of ether linkages. After hydrogenation and subsequent cooling, both SnO_2 and SnS were present, in agreement with other workers [31,33,51]. The mechanism of the reaction is believed [52] to involve, initially, the reduction of tin(IV) oxide to tin metal, which then acts as a catalyst. In addition, it is believed to react with coal oxygen or sulphur, in the latter case forming tin(II) sulphide. This is in disagreement with the conclusions of other workers [51] who found that the tin(II) sulphide was formed prior to the β-Sn.

The findings of Shibaoka et al. [53] are in agreement with those of Vaishnava et al. [52], in that the tin(II) chloride used as catalyst is believed to be reduced to β-Sn very early on in the hydrogenation process. They additionally noted the formation of tin(II) sulphide and, like Vaishnava [52], believe that it is formed as a result of scavenging of sulphur from the coal.

Weller et al. [54] came to the conclusion that the most stable form of tin under liquefaction conditions is tin(II) sulphide, after carrying out a series of reactions in which tin(II) chloride, metallic tin and tin(IV) oxide were reacted with either hydrogen sulphide and hydrogen or sulphur and hydrogen under coal liquefaction conditions. In each case, more than 90% of the tin was present as tin(II) sulphide, indicating that this species is both kinetically and thermodynamically stable.

The catalytic ability of hydrated tin(II) chloride for the hydrogenation of Victorian Brown coal has been noted by Cochran et al. [43]. Dry-mixed $SnCl_2.2H_2O$ was studied and the conversion obtained was 98% (Table 2-7), indicating a highly active catalyst. The conclusions drawn are detailed in Section 2.2.3.1 (b).

Kawa et al. [55], found that $SnCl_2$ is more active for coal liquefaction than other metal catalysts studied, including $ZnCl_2$, but the product formed was high in asphaltene. SnI_2 and $SnCl_2.2H_2O$ were not as effective as some of the catalysts studied for reducing the asphaltene content. All of the metal halides studied were active in sulphur and nitrogen removal.

In further studies, Kawa et al. investigated the Synthoil Process [56], which involved the hydrodesulphurisation (HDS) of coal. Several commercial catalysts were tested for this process, in addition to some which were prepared by impregnating commercial supports with various metal compounds.

The high surface area catalysts were all supported on alumina and contained a small amount of silica, as well as the metal being tested. Tin was the most active catalyst for the conversion of coal to oil, but it was inferior to molybdenum and nickel for the removal of sulphur. In addition, the desulphurisation activity of tin decreased as the tin concentration increased. For the low surface area catalysts, the support surface was completely covered with the metal compound used in the impregnation and could therefore have no catalytic or promotional effect. At a 5% metal level, desulphurisation was poor, but high oil yields were obtained with the Mo, Sn and Ni catalysts. This implied that the yield of oil did not depend on the presence of a high surface area or the availability of the support surface, whereas desulphurisation requires either or both of these conditions.

The structural parameters of the liquid products were of interest to Tanner et al. [57], who used either benzene or cyclohexane as extraction solvents for SRC (solvent refined coal) after hydrogenation. Of the metal chlorides studied, only $ZnCl_2$ and $SnCl_2$ gave solubilities in benzene as good as, or better than, those obtained in the absence of catalysts and their products were characterised by high $^{H}/_{C}$ and aliphatic hydrogen to aromatic hydrogen ($^{Hal}/_{Har}$) ratios. A marked improvement in the solubility of SRC in cyclohexane was observed in the presence of $ZnCl_2$ and $SnCl_2$. Increasing the temperature of the hydrogenation increased the yield of liquid products and their $^{H}/_{C}$ ratio.

From this work, it was concluded [57] that the effectiveness of a catalyst depends strongly on its acidity, with only the mildly acidic compounds enhancing solubility. The mild Lewis acids are believed to promote SRC liquefaction by catalysing the cleavage of aliphatic linkages and the hydrogenation of the aromatic groups present in the SRC. Strongly acidic Lewis acids do not catalyse the liquefaction because they also catalyse a reaction, known as the Scholl condensation of aromatic groups, which leads to the formation of direct aryl-aryl bonds. These are very stable and are not readily broken.

$SnCl_2$ (and $ZnCl_2$) may be used as coal liquefaction catalysts in the molten form and the results obtained by Nomura et al. [58], when using such catalysts to liquefy an Australian bituminous coal, are shown in Table 2-5. The $SnCl_2$ melt gave higher oil (hexane-soluble) yields than $ZnCl_2$. $SnCl_2$ is believed to be a weaker Lewis acid than $ZnCl_2$, and, in agreement with Tanner et al. [57], the authors believed that this decrease in Lewis acidity is advantageous in increasing the hexane-soluble yield. The catalytic activity of $SnCl_2$ was enhanced by the presence of KCl.

Catalyst	Gas Yield (wt. %)	Hexane-Soluble Yield (wt. %)	Benzene-Soluble Yield (wt. %)	Benzene-Insoluble Yield (wt. %)
None	8.3	8.9	7.5	75.3
$ZnCl_2$	27.3	21.0	0.7	51.0
$ZnCl_2$-KCl-NaCl	17.1	33.3	1.4	48.2
$SnCl_2$	13.3	36.9	7.1	42.9
$SnCl_2$-KCl	12.8	43.4	13.4	30.4

Table 2-5 Hydrogenation of Big Ben Coal with Molten Salt Catalysts [58]

Unlike $ZnCl_2$, the $SnCl_2$-containing catalysts also increased the yield of benzene soluble product.

Nomura et al. continued their studies of the use of molten salt catalysts by extending their investigations to three different lithotypes (defined by Van Krevelen [4]) of an oxygen-rich brown coal [59]. The lithotypes were designated: pale, medium light (M-l) and medium-dark (M-d).

The catalysts studied included: $SnCl_2$, $SnCl_2$-KCl, $ZnCl_2$-$SnCl_2$, and $SnCl_2$-$ZnCl_2$-KCl, and the results showed that, in general, higher yields were obtained for the pale lithotype than for the other two materials.

The solvent used as vehicle for a coal liquefaction experiment is believed by Kershaw et al. [60] to have an effect on the yield. The conversions obtained in the absence of solvent and in the presence of a donor solvent (decalin) and non-donor solvents (tetralin and mesitylene), using $SnCl_2$ as catalyst, were studied. Higher yields of asphaltene were obtained in the presence, rather than in the absence of solvents, tetralin giving the best results. The liquid product was more aromatic in the absence of solvent. Increasing the temperature led to an increase in yield in the presence of solvents.

Kershaw et al. [60] believe that their results can be explained by means of a dual mechanism involving both donor hydrogen from the coal-derived products or the donor solvent and direct hydrogenation. Cochran et al. [43], however, concluded that transfer of hydrogen does not occur via the solvent, which is not in accord with Kershaw et al. [60].

Tin catalysts are expensive and several investigations have been carried out in an attempt to reduce the cost, or improve the activity, by using them in the presence of another component.

The U.S. Bureau of Mines have studied $SnCl_2$ on its own and in the presence of additives, such as ammonium chloride and Fuller's earth [34,61]. Similar results of ca. 85% conversion were obtained in both cases. Tin added either as $SnCl_2$ or as metallic powder, was found to be active, even at concentrations as low as 0.1%. However, at these low levels of addition, the activity appears to be dependent on the mode of addition of the tin(II) chloride catalyst, solution impregnation being the most effective method.

In addition to studying an SnO_2-MoO_3 catalyst [Section 2.2.3.1 (b)], Mahoney et al [35] investigated $SnCl_2$-MoO_3 catalysts for the H-coal process, which was being tested at pilot plant level. The optimum loading of $SnCl_2$ on the MoO_3/Al_2O_3 was 5%, further increases in tin concentration giving only a slight increase in activity. The $SnCl_2$-MoO_3/Al_2O_3 catalyst was still giving a good yield (ca. 89%) of THF-soluble products even after 250 hours in a continuous reactor, despite the fact that a considerable amount of Cl-ion were lost. This indicated that only a small amount of chloride-ions were necessary to maintain activity. The conversion to benzene-soluble material was greater than that obtained for a commercial Co-Mo catalyst, whereas conversion to hexane-soluble material was lower.

The use of the $SnCl_2$-MoO_3/Al_2O_3 catalyst was discussed by Mahoney et al. [36] in a patent, the results again indicating that the activity of a tin-Al_2O_3 catalyst is improved by the presence of molybdenum. Sulphided catalysts were also active.

McCandless et al. [29] tested whether the presence of hydrogen chloride gas had an effect on the yields and products formed from the liquefaction of Montana sub-bituminous coal. Preliminary screening, using a 5% HCl-H_2 atmosphere, indicated that the most effective catalysts included $SnCl_2$, $CoCl_2$, $CuCl_2$ and $ZnCl_2$. The presence of HCl in the feed gas led to a striking improvement in the oil yield. A further advantage of the use of the H_2/HCl system is that it facilitates the recovery of the catalyst, since, in the presence of excess hydrogen chloride, the metal is not poisoned by nitrogen and sulphur.

Victorian Brown coal may contain up to 66 weight % water when mined and, before hydrogenation, it is usually dried. However, drying is expensive and, to overcome this problem, some investigators [62,63] have studied the possibility of using carbon monoxide and water in the direct liquefaction of coal, thus generating hydrogen by means of the water-gas shift reaction. Cassidy et al. [64] have recently investigated the effect of water on the catalytic activity of a range of elements in the presence of H_2, synthesis gas (50:50 v/v CO/H_2) and CO. Tin was amongst the metals studied and was introduced into the Morwell Victorian Brown coal by means of ion exchange. Table 2-6 shows the conversions obtained from both wet and dry coal.

Transition metals, together with tin and lead, promoted the liquefaction in the presence and absence of water, but the tin lost some of its activity in the wet coal reaction. The authors were able to show that the presence of water prevented the utilisation of hydrogen from the hydrogen donor solvent.

On replacing hydrogen with carbon monoxide, the catalysts, including tin, which were active in the presence of hydrogen, became completely inactive in the wet coal reaction (Table 2-6). The results obtained when using synthesis gas were, as expected, midway between those obtained when using pure hydrogen and pure carbon monoxide (Table 2-6). Thus, it appears that the presence of water has a detrimental effect on coal liquefaction.

Catalyst	wt. % Conversion of Dry Coal in H_2	wt. % Conversion of Wet Coal in H_2	wt. % Conversion of Wet Coal in CO	wt. % Conversion of Wet Coal in Synthesis Gas
None	64	57	57	56
Na_2CO_3	--	55	58	57
Mg	--	54	60	58
Ca	--	53	55	54
Mn	66	55	58	59
Ni	80	76	51	64
Zn	75	75	51	66
Mo	79	--	--	--
Sn	87	72	50	62
Pb	71	76	55	61

Table 2-6 The Effect of Metal Promoters on the Liquefaction of Dry and Wet Coal Using Various Feed Gases [64]

Marshall et al. [50,64,65] investigated the possibility of developing a cheaper catalyst for Victorian Brown coal by using a mixed iron-tin system. In addition, single component catalysts containing either tin or iron were tested.

As found previously [32], the tin gave higher conversions than the iron catalyst, and, in addition, the total conversion increased with the tin concentration. A synergistic effect was observed when the mixed iron-tin catalyst was used, a higher total conversion and asphaltene yield being obtained for the mixed tin/iron catalysts than for either of the two metals used separately. The exact reason for this synergism is not known, but Marshall et al. [50] have suggested that the iron and tin promoted different steps in the hydrogenation sequence.

Mixed tin-iron catalysts for Victorian Brown coal were studied in more detail by looking at the effect of varying the reaction conditions [66,67]. Cassidy et al. [66,67] found that the tin and iron-tin catalysts behaved similarly at temperatures below 385°C, the conversion increasing with temperature for both catalyst systems. At higher temperatures, a more gradual increase was observed for the tin-exchanged coal. However, in the case of the Fe-Sn catalyst, there was a more marked temperature dependence and higher yields were obtained. The tin-catalysed reactions showed the most marked pressure dependence, conversion increasing with pressure.

The tin catalyst was superior to the iron and the mixed iron-tin systems for oxygen removal, but the order of ability for the transfer of hydrogen was:

iron-tin>tin>>iron>untreated coal.

From these experiments, Cassidy et al. [66] concluded that the iron-tin catalyst was superior to the other systems, since it gave good conversions at relatively low pressures and temperatures. However, they noted that the tin catalyst gave lower oxygen content products, but that it had the disadvantage of producing a higher yield of hydrocarbon gases.

Qader et al. [68] studied the effect of temperature and pressure on the first step of a two-stage coal hydrogenation process and came to similar conclusions to other workers [66,67] on their effect. They believe that the higher activity of $SnCl_2$, compared to other catalysts, such as ammonium molybdate, nickel(II) chloride and iron(II) chloride, is due to its higher thermodynamic stability towards decomposition. However, an excess of tin salt was required for the coal hydrogenation and this implies that a proportion of the tin salt vapourised and decomposed thereby becoming catalytically inactive.

Wood et al. [69] studied the effect of reaction variables on the liquefaction of bituminous coals in a continuous short residence time reactor. The optimum yield of liquid products when using $SnCl_2.2H_2O$ was obtained at a feed rate of 5g/min and a temperature of 575°C. $ZnCl_2$ was tested as a catalyst too and offered some advantages over the tin compound, although the overall conversion was lower.

After modifying the reactor to prevent the build-up of solids in the reaction zone, Wood [30] carried out a survey of different catalysts, including $SnCl_2.2H_2O$ and $SnCl_4.5H_2O$ [Section 2.2.3.1 (a)].

The zinc halides and tin(II) chloride were the most active catalysts tested, but the zinc chloride had the advantage of being much cheaper and was, therefore, used in further tests.

When carrying out the hydrogenation of coal under high pressures and temperatures in the absence of solvent, the process is known as hydropyrolysis. Barrass et al. [70] studied the effect of various catalysts, including tin(II) chloride, on this reaction using South African coal. The tin(II) halides and zinc halides were found to be particularly effective and, on increasing their concentration, the proportion of "heavier" products and the heteroatom content of the oil were reduced. On increasing the pressure of the reaction, similar results to those obtained by Cassidy et al. [67] were obtained. Increasing the temperature also led to an increase in the total conversion and, for temperatures below 500°C, to an increase in the yield of oil. The yield of asphaltene decreased with temperature.

This work was extended [71,72] to study the actual chemical composition of the oil produced from a fixed bed of tin(II) chloride-impregnated coal.

Kershaw et al. [71,72] found that, increasing the concentration from 1 to 15% tin increased the amount of oil formed. The proportion of polar compounds decreased, with mainly an increase in the percentage of aromatic hydrocarbons.

From these results, Kershaw et al. [71,72] concluded that increasing the catalyst concentration has a beneficial effect on the quality of the oil obtained, reducing its viscosity and heteroatom content. However, they stated that it was unlikely that high catalyst concentrations would be used, for economic reasons. Increasing the temperature was beneficial, since it produced an oil of lower molecular weight and viscosity, but it also increased aromaticity and hence $^{H}/_{C}$ ratios were less favourable. Increasing the residence time decreased the heteroatom content, but again led to an increase in aromaticity.

Although Sharma et al. [44] were mainly concerned with the effect of organometallic compounds on coal liquefaction [Section 2.2.3.1 (c)], their studies also included the use of tin(II) chloride. This compound was found to be an excellent catalyst for the conversion of York Canyon Mine, and Navajo Mine coals, in particular, producing more asphaltene than was formed in the uncatalysed reaction.

On studying the effect of reaction time, [44] it was found that the catalysts, including $SnCl_2$, assisted in the conversion of asphaltenes to oils and gases. However, the amount of oil and asphaltene decreased as the temperature increased, implying that more gaseous product was being formed at higher temperatures.

Sulimma et al. [73] studied the hydropyrolysis of a coal using thermogravimetric analysis (TGA) in the presence of several different catalysts. Some of the results obtained are shown in Table 2-7.

Catalyst	$r^1{}_{max}{}^a$ (%/min)	Tat $r^1{}_{max}{}^b$ (°C)	$X_{600}{}^c$ (%)
None	0.98	450	54.0
$SnCl_2.2H_2O$	2.37	480	76.8
$ZnCl_2$	2.55	480	78.1
$AlCl_3$	1.84	490	72.0
Sn	1.97	470	68.0
SnO	2.05	475	67.8
SnO_2	2.11	475	71.5

$^a r^1{}_{max}$ = maximum reaction rate.
^{b}Tat $r^1{}_{max}$ = temperature of maximum rate.
$^c X_{600}$ = degree of conversion to tar and gas up to 600°C.

Table 2-7 Hydropyrolysis of Westerholt Coal (5% Catalyst Loading) [73]

The dichlorides of tin and zinc had the most pronounced effect on the reaction and these compounds were employed for a more detailed study of the process.

On studying the effect of pressure, the authors found that the first stage of the reaction does not involve hydrogen and is probably a thermally induced cleavage. Increasing the heating rate led to an increase in the rate of reaction, but a decrease in the total percentage conversion. This is because a higher heating rate leads to a higher concentration of free radicals, a situation which favours recombination reactions.

Figure 2-1 illustrates the effect of catalyst loading on the total conversion for temperatures up to 600°C. $SnCl_2$ showed catalytic activity at very low catalyst concentrations, eg. 0.1%. It was active, even during the very first stage of the reaction, which is believed to involve the cleavage of ether linkages [73]. The second stage of the reaction was concluded to be a catalytic stabilisation of the radicals by hydrogen.

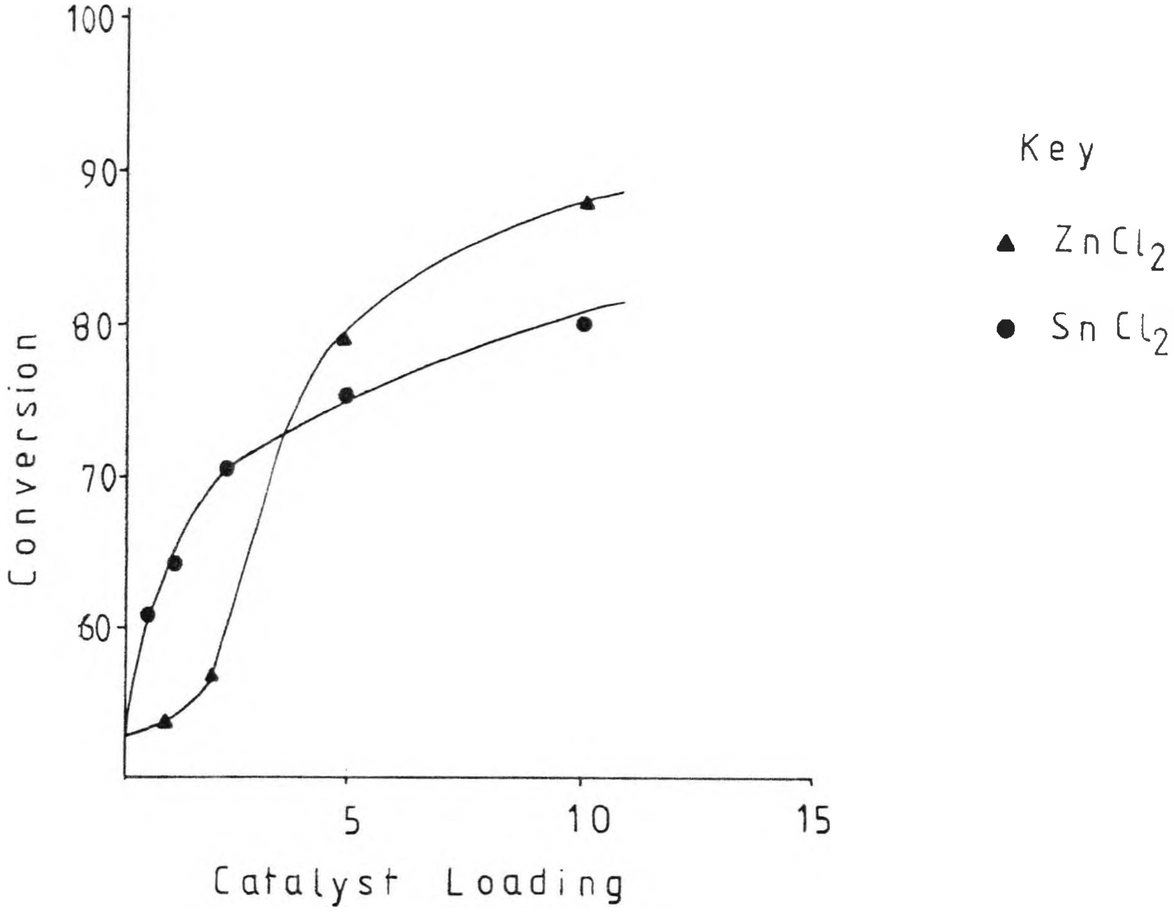

Figure 2-1 The Effect of Catalyst Loading on Conversion Obtained on Hydropyrolysing Westerholt Coal [73]

Zielke et al. [74] studied the effectiveness of molten metal halide catalysts for the hydrocracking of polynuclear aromatics using either a coal residue (obtained by hydrocracking a coal extract in the presence of a nickel molybdate catalyst) or a model compound, pyrene. $SnCl_2$, unlike $ZnCl_2$, was found to be ineffective as a hydrocracking catalyst for either pyrene or the hydrocracked coal extract.

Thus, it is believed that the activity of the tin catalysts for the hydrogenation of coal and coal extracts must be related to their activity with respect to scission of specific weak bonds.

The ash present in coals is thought to have an effect on the yield of products obtained on liquefaction. Therefore, in their investigations, Lovetro et al. [77] used solvent-refined coal (SRC), which is essentially ash-free, rather than coal itself. They compared the yields obtained in the absence of catalyst, in the presence of $SnCl_2.2H_2O$ as catalyst and in the presence of a commercial $Co/Mo/SiO_2-Al_2O_3$ catalyst. Although liquefaction was high in all cases, it was highest for the $SnCl_2.2H_2O$ catalyst. However, oil production was hardly affected by the presence of the tin catalyst. Hydrogen consumption was greatest for the $SnCl_2.2H_2O$ catalyst and this was thought to be due to the formation of low-boiling liquid products which are lost during distillation. The tin catalyst was also superior to the commercial catalyst for the removal of nitrogen and oxygen.

The activity of supported tin catalysts for the hydrogenation of bitumen was found to depend on the method of preparation. Four different catalysts were prepared by Kriz et al. [78] (Table 2-8).

Catalyst	Method of Preparation
A	Calcined extrudates impregnated with $SnCl_2$ in methanol.
B	As for catalyst A but the extrudates were sulphided using H_2S/H_2 mixture.
C	Aqueous solution of $SnCl_2$, added to α-alumina monohydrate and milled. Resulting paste extruded, dried and calcined.
D	Aluminium tris(iso-propoxide) and $SnCl_2$ in iso-propanol, co-precipitated by hydrolysis. Precipitate extruded, dried and calcined.

Table 2-8 Method of Preparation of Catalysts [78]

Only catalysts C and D improved the quality of the products. The reason for this was thought to be that very little of the tin was exposed to the bitumen in catalysts A and B, since it sintered within the cracks. A study of the catalysts after the reaction indicated that the tin is then present as tin(II) sulphide, as observed by other workers [33, 51-53].

The use of tin(II) salts for the upgrading of coal liquids with particular reference to the hydrogenation of nitrogen-containing compounds was investigated by Boucher [49]. Results obtained when using phthalocyanine complexes have already been described in Section 2.2.3.1 (c).

On preparing SiO_2-supported $SnCl_2$ catalysts, all of the chlorine volatilised as the catalyst dried and, in this case, the tin is believed to be present in the form, "SnO". However, for the Al_2O_3/SiO_2 and Al_2O_3 supports, the chlorine was retained. The supported tin(II) halides were found to be active in the hydrogenation of quinoline, the order of activity being: I>Br>Cl. In addition, they were shown to be more active than the tin(II) halides when used as homogenous catalysts. $NaSnCl_3$ was tested as a catalyst too and was more active than tin(II) chloride. The order of stability of the catalysts was: $SnO > SnCl_2 > NaSnCl_3$. In addition, their stability was affected by the temperature of the reaction, more tin being lost at higher temperatures.

The metal salts were, in general, more stable than the phthalocyanines [Section 2.2.3.1 (c)].

In addition to studies of coal itself, Larkins et al. [79,80] studied the hydrogenation of coal-derived materials which had been produced using an Fe-Sn catalyst. Thus, these still contained some iron and tin when used for the subsequent reactions. These investigators compared the results obtained in the absence of any additional catalyst and in the presence of $Ni/Mo/Al_2O_3$ as catalyst. This catalyst did not increase the conversion of the parent coal or of THF insolubles, since, in these cases, there was sufficient iron and tin already present to catalyse the reaction. A complete range of products, from THF insolubles to oils, was obtained on hydrogenating the asphaltenes and asphaltols, and the $Ni/Mo/Al_2O_3$ catalyst did increase the oil yield for these starting materials, whereas addition of more iron or tin did not.

(b) Tin(II) Sulphide

The U.S. Bureau of Mines, in particular, published several papers which studied the potential of this compound as a coal liquefaction catalyst [34,60,81]. The tin(II) sulphide was found to promote the liquefaction of Pittsburgh Seam coal and its activity was further increased in the presence of ammonium chloride. In addition, the workers tried to elucidate the origin of the asphaltene fraction formed from Bruceton coal [81], by carrying out the hydrogenations for various lengths of time. They found that the asphaltene content of the product decreased with time, whilst the oil content increased. They therefore concluded that the asphaltenes were not formed as the result of condensation or polymerisation of the oil product, but that they were intermediate products which were then further hydrogenated to give oils (thus agreeing with the conclusions of Suzuki et al. [49]).

Tin(II) sulphide was also found to be active as a catalyst for the hydrogenation of Victorian Brown coal [33]. As mentioned previously [31,51,53], tin(II) sulphide was formed during tin-catalysed liquefaction experiments and these studies indicated that it may still have been involved in the catalytic process in this form. However, this does not imply that SnS itself is catalytic. Cook et al. [33] believed that elemental tin, formed by reduction of SnS, may have been the active species.

(c) Tin(II) Oxide

In addition to studying supported catalysts containing the tin(II) halides [Section 2.2.3.2 (a)], Boucher et al. [49] considered supported tin(II) oxide as a possible catalyst for the hydrogenation of the model compound, quinoline. The catalyst was prepared by reaction of an $SnCl_2$ catalyst with NH_4OH prior to drying. The SnO/SiO_2 catalyst was more active than SnI_2 for this reaction. As mentioned previously [Section 2.2.3.2 (a)], the $SnCl_2/SiO_2$ catalyst prepared by Boucher et al. lost its chloride ion on drying and the tin was believed to be present in the form SnO . This catalyst was more active than the SnO formed by hydrolysis of $SnCl_2$ at room temperature. Boucher et al. [48] believed that the dispersion of the tin may have been greater in the first case, implying that the activity of the catalyst was sensitive to its method of preparation.

Tin(II) oxide was included as one of the compounds studied by Cook et al. [33] and the conversion obtained was comparable to that obtained by them for other tin compounds. On hydrogenating the Victorian Brown coal, in the presence of SnO, the tin species present were: $SnO.yH_2O$ and SnS. At 380°C, β-Sn was also observed.

2.2.3.3 Tin Metal

Several studies on the use of tin metal as a coal liquefaction catalyst, both alone and in the presence of additives, have been carried out.

It is believed [20,82] that sub-bituminous coals consist of two- and three-ring condensed aromatic structures, linked mainly by oxygen atoms. Mobley and Bell [83] have suggested that the presence of a catalyst accelerates the cleavage of ether linkages present in the coal. Matsuura et al. [84] tested this hypothesis by studying the liquefying activity of molten metals, including tin, and plotting the conversions obtained against the heats of oxide formation of these metals. A volcano-shaped relationship was observed (Figure 2-2). (No indication of which oxides are referred to is given in the literature).

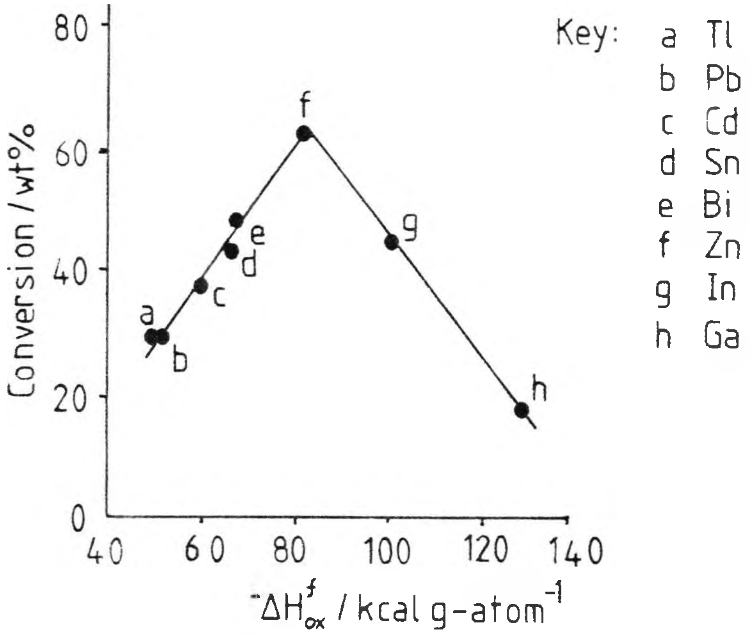

Figure 2-2 Relationship Between Coal Liquefaction Activities of Molten Metals and Heats of Oxide Formation [84]

All of the metals studied were active as coal liquefaction catalysts. Matsuura et al. [84,85] put forward the theory that this indicates that the molten metals were reacting with oxygen links within the coal. Thus, a metal with small $-\Delta H_{ox}^{f}$ would have a lower catalytic activity, since there would only be weak interaction between the metal and the oxygen atoms and vice versa. However, if the heat of oxide formation was too large, a stable complex would be formed between the metal and the oxygen moiety in the coal and, again, liquefaction would be retarded.

On studying the effect of reaction conditions on the liquefaction of a coal, in the presence of a molten tin catalyst [86], the same authors found that the overall degree of liquefaction (C_L) and the degree of conversion to asphaltenes (C_A) were increased in the presence of catalysts at all temperatures. A maximum was observed in both cases at 400°C. However, the catalyst had little effect on the conversion to oils.

Asphaltene formation increased but conversion to oils was constant over the whole range of values, 0-10g:1 of catalyst :coal ratio studied, again implying that the tin catalyst is not involved in the formation of oils.

In further work, Ozawa, Matsuura et al [87] studied the kinetics of liquefaction using the molten tin catalyst. The second oil fraction (oil-2) was believed to be formed as a result of successive reactions and the preasphaltenes were believed to be intermediate products.

Their suggested reaction scheme is shown in Figure 2-3.

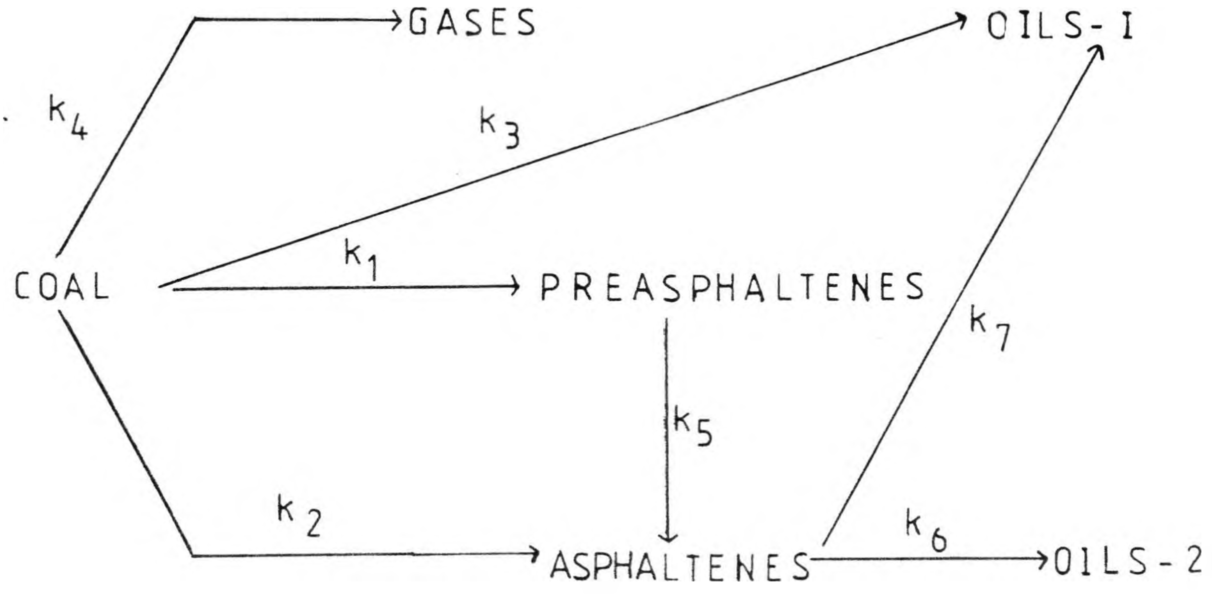

Figure 2-3 Reaction Scheme Postulated by Ozawa et al. [87]

The rate constants calculated indicate that the tin was catalysing the formation of the higher molecular weight products. By contrast, little effect was seen in the formation of the lower molecular weight products. This disagreed with the conclusions of Weller *et al*. [75], who believed that the formation of oil from reactive coal fragments was catalysed by tin.

In order to study the mechanism of coal liquefaction further, Ozawa *et al* [88] subjected model ether compounds, *eg*. benzyl phenyl ether, to coal liquefaction conditions in the presence of molten tin.

They found [88] that the ether cleavage was not affected by the presence of the molten tin catalyst. However, a rearrangement reaction showed a clear catalytic effect, and it was concluded that the molten tin provides adjacent adsorption sites for the phenoxy and benzyl radicals.

Asphaltenes and model ethers have also been used by Cassidy et al. [66,76] to study tin metal as a promoter. Neither the β-Sn nor the iron compounds studied increased the production of oils from asphaltenes. Like Ozawa et al. [88], they found that ethers such as diphenyl ether, were not affected by the presence of tin [76], and the reaction of dibenzyl ether was in fact suppressed.

Tin metal as a coal liquefaction catalyst was included as part of the Mossbauer study carried out by Cook et al [33], which showed that most of the tin catalyst was still in the form of β-Sn at 380°C. The tin metal was an active catalyst, giving high conversions.

The use of tin metal in the presence of additives has been investigated by several groups of workers. Pelipetz et al [81] studied powdered metal catalysts, such as tin, zinc, arsenic and antimony, in the presence of ammonium chloride, as catalysts for Bruceton coal. The tin increased the degree of coal liquefaction to the greatest extent without decreasing the asphaltene content at 400°C. Increasing the temperature to 415°C increased the yield further and decreased the asphaltene content.

On studying several alloys, including tin-zinc, as potential catalysts, these workers found that the presence of zinc lowered the activity of tin as a hydrocracking agent for coal.

A tertiary tin-zinc-antimony catalyst was tested and was found to enhance the hydrogenation of asphaltenes to a greater degree than a Zn-Sb catalyst. In addition, there was no adverse effect on the coal cracking ability of the tin.

Table 2-9 shows the results of tests carried out by the U.S. Bureau of Mines [34,61] using different forms of tin metal, both alone and in the presence of additives. It can be seen that the activity of the tin is influenced by its distribution within the coal, since, when added as metal shot or as a single piece, the conversions to liquid products were low. The addition of ammonium chloride or certain acidic compounds, such as HCl, HBr and HI, increased the activity of the metal, whereas neutral sodium chloride did not have this effect, and neither did sulphuric acid. Hawk et al. [34] concluded that, when any of the three halogens, chlorine, bromine or iodine is present in a form which is or can become acidic, it will promote the catalytic ability of tin.

Catalyst	Weight % maf Coal	
	Conversion	Asphaltenes
Sn (metal powder)	70	30
Sn (metal powder) + NH_4Cl	88	29
Sn (metal, 20 mesh) + NH_4Cl	39	17
Sn (metal shot, 8 mesh) + NH_4Cl	59	23
Sn (metal, single piece) + NH_4Cl	53	23
Sn (metal powder) + CCl_4	87	24
Sn (metal powder) + NaCl	65	36
Sn (metal powder) + HCl	86	22
Sn (metal powder) + H_2SO_4	70	48

Table 2-9 Hydrogenation of Pittsburgh Seam Coal Using Tin Metal and Additives as Catalysts [34]

Investigations using an asphaltene obtained from a previous coal hydrogenation, and Bruceton coal, have been carried out by Weller et al. [75], in order to formulate a theory of coal hydrogenation. The asphaltene was further hydrogenated in the presence of either HCl, Sn, Sn + NH_4Cl or Ni + HCl. The Sn + NH_4Cl catalyst was superior to the others. However, tin, in the absence of NH_4Cl, did not catalyse this reaction. A reaction scheme was proposed [75] in which the asphaltene is split into reactive fragments by the HCl. In the presence of tin, the reactive fragments are converted to oil. This is in disagreement with the conclusions of Cassidy et al [66,76].

The Bruceton coal was hydrogenated in the presence of either Sn, NH_4Cl or Sn + NH_4Cl. The results indicated that the reaction scheme postulated for asphaltenes is also applicable to coal.

2.3 CONCLUSIONS

(i) In general, tin compounds were found to be active as catalysts for the liquefaction of any coal type, whether using a batch autoclave or a continuous reactor. They were comparable with commercial cobalt-molybdenum catalysts and were not deactivated by continued use [31,40].

(ii) In particular, the tin compounds promote the yield of oil [38-40,56,57,58] and Tanner et al [57] and Weller et al [75] believe that this increase is due to an increase in the conversion of asphaltenes to oil. By contrast, other investigators found [55,67] that tin does not have the same effect on the hydrogenation of asphaltenes as on coal itself. The oil yield was also increased by:

i) increasing the temperature [57,68,70].
ii) including HCl in the gas feed [29].

and the quality of the oil was improved by increasing the catalyst concentration [70-72].

(iii) Increasing the pressure was found to increase the overall conversion [40,66-68,70] and showed that the tin catalysts were only active at higher pressures [73].

(iv) Tin compounds were, in addition, found to be effective in the removal of heteroatoms from the liquid products [77].

(v) Tin catalysts may be improved by the presence of additives such as NH_4Cl [34] or KCl [58] and, for the phthalocyanines, the presence of halogen was required [48], although this was not found to be the case for organotin compounds [45].

(vi) After liquefaction, the tin was converted to β-Sn and SnS [31,33,51-53] and, in some cases, SnO was observed [31,33,51]. SnS is believed by some workers to be the most stable form of the catalyst [54]. β-Sn is stated to be the active species by some investigators [33,51,75,76], whereas others concluded that either $SnCl_2$ itself [68,74] or an intermediate formed from the decomposition of organotin compounds catalysed the reaction [47].

(vii) The mechanism of the liquefaction process is believed to involve thermal rupture of the coal, forming radicals which are stabilised by the presence of tin [79].

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CHAPTER 3

MODEL COMPOUND STUDIES

3.1 TIN(IV) COMPOUNDS

These tin(IV) compounds were prepared so that their Mossbauer spectra could be compared with the Mossbauer spectra of a series of tin-impregnated coals (Chapter 4), in order to determine which species were being formed within the coal. Other data, such as infrared and NMR parameters, were determined to complete the characterisation. The compounds are discussed in order of decreasing number of halide groups attached to the tin atom.

3.1.1 Tin(IV) Tetrahalide Adducts of Aromatic and Aliphatic Ethers, $SnX_4.nROR^1$ (n = 1 or 2)

Tin(IV) compounds have been shown to be effective as coal liquefaction catalysts [1 - 3] but the mechanism of their catalytic action is not fully understood. The structure of coal, as discussed in Chapter 2, Section 2.1, indicates that ether linkages may be important in at least some coals. Mobley and Bell [4] believe that coal liquefaction catalysts accelerate the cleavage of the ether linkages and several other groups of workers [5 - 9] have claimed that tin may catalyse coal liquefaction in this way and have given evidence to support their claim. Mobley and Bell [4] studied the reaction of model ethers in the presence of zinc chloride under coal liquefaction conditions and found that both cyclic and non-cyclic ethers react readily in the presence of $ZnCl_2$, provided that the ether oxygen atom is adjacent to at least one methylene group.

Tin(IV) chloride is also known to react with monofunctional ethers, forming 1:2 adducts, and with difunctional ethers, forming 1:1 adducts. It was therefore decided, initially, to study complexes of this type using ethers similar to those investigated by Mobley and Bell [4] and, subsequently, to determine whether a similar species would be formed in various coals under similar conditions. The ethers chosen for study were: tetrahydrofuran (THF),tetrahydropyran (THP), 2-methyltetrahydrofuran (2-Me-THF), 3-methyltetrahydrofuran (3-Me-THF), 2,5-dimethyltetrahydrofuran (2,5-Me_2-THF), 2,2,5,5,-tetramethyltetrahydrofuran (2,2,5,5-Me_4-THF), dihydrobenzofuran (DHBF), dibenzyl ether (Bz_2O), diphenyl ether (Ph_2O), benzyl phenyl ether (BzPhO), furan (Fur), and 1,4-dioxan (diox).

Microanalytical data and melting points of those adducts which were sufficiently stable to be isolated are shown in Table 3-1, together with the literature values for those adducts reported previously.

From the microanalytical data, it appears that, in most cases, a 1:2 adduct has been formed, in accordance with the literature [10 - 14]. Dioxan forms a 1:1 adduct, as reported previously [13], each dioxan molecule acting as a bridging ligand between two tin atoms, resulting in a linear polymeric structure. In addition, the ether, 2,2,5,5-Me_4-THF, formed a 1:1 adduct with $SnCl_4$ and this is believed to be due to steric hindrance, 2,2,5,5-Me_4-THF being a bulky ligand.

Compound	Solvent	M.p.(°C)	Analysis:Found (Calc.)		
			C	H	Hal
$SnCl_4$.2THF	Petroleum ether	168-170 (165-175)[a]	23.22 (23.70)	3.83 (3.95)	34.92 (35.06)
$SnBr_4$.2THF	Petroleum ether	110-113 (120)[b]	16.46 (16.47)	2.75 (2.74)	55.66 (54.89)
$SnCl_4$.2THP	$CHCl_3$	159-165 (subl.)	25.20 (27.71)	4.33 (4.62)	32.77 (37.79)
$SnBr_4$.2THP	Petroleum ether	107-115 (subl.)	19.59 (19.64)	3.31 (3.27)	53.38 (52.37)
$SnCl_4$.2 (2-Me-THF)	Petroleum ether	c	25.56 (25.62)	4.81 (5.16)	31.49 (30.25)
$SnCl_4$.2 (3-Me-THF)	Petroleum ether	111-113	26.13 (27.75)	4.41 (4.66)	31.65 (28.53)
$SnCl_4$.diox	Petroleum ether	200-203 (175-195)[a] 187[d]	14.64 (13.80)	3.51 (2.31)	39.75 (40.68)
$SnCl_4$.(2,2,5,5-Me_4-THF)	$CHCl_3$	c	24.76 (24.72)	4.89 (4.15)	33.84 (36.48)

[a] Ref. 13 [b] Ref. 14
[c] M.p. not recorded, due to instability of the compound
[d] Ref. 15

Table 3-1: **Melting Point and Analytical Data for Tin(IV) Halide Adducts**

It was not possible to isolate solid products from the following ethers: dihydrobenzofuran, dibenzyl ether, diphenyl ether, benzyl phenyl ether and furan. In the cases of dibenzyl ether and furan, solid products were observed, initially, but these were so hygroscopic that satisfactory analytical data could not be obtained.

(a) Infrared Studies

The most important peak in the spectra of the adducts is attributable to the C-O-C stretching frequency, which is lower than that in the parent ligand, because of donation of the oxygen lone pair to the tin atom. Table 3-2 gives the values of ν(C-O-C) and $\Delta\nu$ (i.e. the difference between (C-O-C) in the parent ether and in the complex) for each adduct. The largest shift of the ν(C-O-C) band would be expected to result from the strongest donor ligand, there being a greater weakening of the C-O-C bonds with stronger donating ability of the ether. Based on the $\Delta\nu$ values, the order of donor strength is as follows:

THP $\approx$ diox $\approx$ 3-Me-THF>THF>2-Me-THF>$2_1$5-Me_2-THF

Compound	IR Data ν(C-O-C)[a] (cm^{-1})	$\Delta\nu$(C-O-C) (cm^{-1})	^{119m}Sn Mossbauer Parameters δ (mms^{-1})	ΔEq (mms^{-1})
$SnCl_4$.2THF	1005	65	0.41	1.23
$SnCl_4$.2THF	-	-	0.43[b]	1.14[b]
$SnCl_4$.2THF	-	-	0.43[c]	1.29[c]
$SnCl_4$.2THF	-	-	0.47[d]	1.23[d]
$SnCl_4$.2THF	-	-	0.43[e]	1.26[e]
$SnBr_4$.2THF	1005	65	0.70	1.27
$SnBr_4$.2THF	-	-	0.76[e]	1.34[e]
$SnCl_4$.2THP	1005	90	0.45	1.36
$SnBr_4$.2THP	1000	100	0.76	1.46
$SnCl_4$.2(2-Me-THF)	1040	60	0.49	1.26
$SnCl_4$.2(3-Me-THF)	1015	85	0.44	1.12
$SnCl_4$.2(2,5-Me-THF)	1060	45	0.54	1.19

(cont'd)

	IR Data		^{119m}Sn Mossbauer Parameters	
Compound	ν(C-O-C)[a] (cm^{-1})	$\Delta\nu$(C-O-C) (cm^{-1})	δ (mms^{-1})	ΔEq (mms^{-1})
$SnCl_4$.(2,2,5,5-Me_4-THF)	-	-	0.62	0.00
$SnCl_4$.diox	1055	85	0.41	0.90
$SnCl_4$.diox	-	-	0.49[f]	1.48[f]
$SnCl_4$.2diox	-	-	0.45[b]	1.10[b]
$SnCl_4(H_2O)_2$ 2diox	-	-	0.26[g]	0.00[g]

[a] ν(C-O-C) in free ethers:THF (1070cm^{-1}), THP (1095cm^{-1}), 2-Me-THF (1100cm^{-1}), 3-Me-THF (1100cm^{-1}), 2,5-Me_2-THF (1105cm^{-1}), diox (1130cm^{-1}).

[b] Ref. 16. [c] Ref. 17. [d] Ref. 18. [e] Ref. 19.

[f] Ref. 15. [g] Ref. 20.

Table 3-2: IR and Mossbauer Data for the Adducts

(b) Mossbauer Studies

The Mossbauer parameters for the complexes are shown in Table 3-2, together with the relevant literature values. Good agreement is observed in general with the literature values.

The isomer shifts are all lower than those of the parent tin(IV) halides ($SnCl_4$, δ = 0.78mms^{-1}; $SnBr_4$, δ = 1.06mms^{-1} [21]). Since the isomer shift is a measure of the s electron density at the tin nucleus, this implies that complexation of tin tetrahalides with oxygen-containing donor compounds leads to a reduction in the s electron density. This reduction has been observed previously [16, 15, 22]. In the parent tetrahalide, the tin atom is sp^3 hybridised but, on complexation, sp^3d^2 hybrid orbitals are formed, leading to an octahedral complex [16, 23]. Another reason for this decrease is the increased polarity of the bonds to the tin atom with increasing co-ordination number from 4 to 6, in the sense $Sn^{\delta+} - X^{\delta-}$, these bonds being longer at higher co-ordination numbers [24]. However, X-ray spectroscopy data obtained by Poleshchuk et al. [25] indicated that the total electron density on the Cl atoms decreases slightly on complex formation with such complexes as THF and dioxan compared with $SnCl_4$ itself.

It has been suggested [16] that the most strongly interacting ligands give the greatest diminution of isomer shift. In agreement with this, Poleshchuk et al. [25] found that, when studying the octahedral complexes of $SnCl_4$ with donor ligands, the electron density of the Cl atoms increases as donor strength increases.

On this basis, the following approximate donor order may be established.

THF $\simeq$ diox>3-Me-THF $\simeq$ THP>2-Me-THF>2,5-Me_2-THF.

Previous workers [26, 27] have also found that THF is a stronger donor than 2,5-Me_2THF in benzene solution and it is believed that the lower base strength of 2,5-Me_2-THF compared with THF is due to steric effects. This is in agreement with the results obtained here, where, in addition, the monosubstituted tetrahydrofuran derivatives, 2-Me-THF and 3-Me-THF, were found to have intermediate isomer shifts and, thus, intermediate basicities. However, it should be noted that a slightly different order of donor strengths was obtained from the infrared results, THF and

THP being in reversed positions. It is possible that the ν(C-O-C) bands assigned for the THP adducts (Table 3-2), although the strongest in the C-O-C stretching region, could consist of two overlapping absorptions, and may, therefore, have given rise to an error in the quoted value of ν .

Tin(IV) chloride formed a 1:1 adduct with the sterically hindered, 2,2,5,5-Me_4-THF, even in the presence of an excess of the ligand, and the significantly higher value of δ(0.62mms^{-1}) is indicative of a pentaco-ordinate trigonal bipyramidal structure. No quadrupole splitting was observed in the Mossbauer spectrum of this complex, and, in accord with this, it has been found that other five co-ordinate complexes, e.g. $SnCl_4.Ph_3PO$ (δ = 0.53mms^{-1}, ΔEq = O) [16] and $SnCl_4.NMe_3$ (δ = 0.70mms^{-1}, Δ Eq = 0) [28] show single Mossbauer resonances.

The isomer shift is also affected by the electronegativity of the halogen atoms. $SnCl_4$.2THF and $SnCl_4$.2THP have lower isomer shifts than $SnBr_4$.2THF and $SnBr_4$.2THP respectively. This is consistent with greater electrostatic character in Sn-Cl bonds [24, 28].

The quadrupole splitting values for the 1:2 complexes (Table 3-2) fall in the range 1.12 - 1.46mms^{-1}. It has been observed [29] that octahedral tin(IV) halide adducts with O-donor ligands, which were assigned a trans configuration on the basis of IR information, were found to exhibit Mossbauer quadrupole splittings of ca. 1mms^{-1}, whereas there were no resolvable quadrupole splittings for cis complexes.

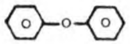
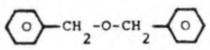
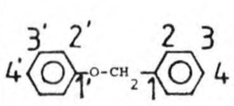
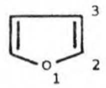
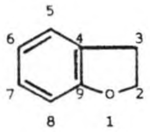
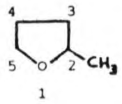
Hence, it seems likely that the ether molecules are occupying trans positions in the octahedral $SnX_4.2L$ adducts. However, inconsistent results have been reported in the literature regarding the configuration of such complexes [30 - 33].

The Mossbauer parameters for the 1:1 adduct of tin(IV) chloride with dioxan are similar to those observed for the 1:2 complexes and suggest that, in this case, the trans octahedral tin atom geometry is maintained by a polymeric structure in which the difunctional ether ligand bridges planar $SnCl_4$ units, as noted earlier [15, 34]. Ichiba et al. reported [16] Mossbauer data for a 1:2 adduct, $SnCl_4$.2diox (although the microanalyses were not quoted for this compound) but its parameters (Table 3-2) are similar to those which were found in this work for the 1:1 adduct. It is of interest to note that the hydrolysis product $SnCl_4(H_2O)_2$.2diox, which is known by X-ray crystallography [35] to contain an octahedral tin atom geometry, with the two water molecules occupying cis positions, shows a single line Mossbauer spectrum. No quadrupole splitting was observed for $SnCl_4$.2,2,5,5-Me_4-THF, this being in agreement with the results obtained for other five coordinate complexes [15, 28].

(c) ^{119}Sn and ^{13}C NMR Studies

The interactions of $SnCl_4$ and $SnBr_4$ with the cyclic and aromatic ethers, in CCl_4 solution, were studied by ^{119}Sn and ^{13}C NMR spectroscopy. Solutions of the appropriate reagents were mixed at room temperature and their ^{119}Sn and ^{13}C chemical shifts recorded (Table 3-3).

^{119}Sn NMR chemical shifts are indicative of co-ordination number, an increase of which is accompanied by a change in $\delta(^{119}Sn)$ to low frequency [36]. In CCl_4 solution, $SnCl_4$ and $SnBr_4$ presumably exist as discrete four co-ordinate monomers and have $\delta(^{119}Sn)$ values of -149 ppm and -637 ppm respectively. These shifts should be compared to those obtained from the same compounds in methanol solution (-600.5 ppm and -1307.0 ppm respectively), in which the species present is the 6-co-ordinate neutral adduct, $SnX_4.2MeOH$ [13], the increase in co-ordination number being reflected by the change in $\delta(^{119}Sn)$. From Table 3-3, it may be seen that, in some cases, addition of the ether to a solution of the inorganic tin(IV) halide produces a shift in $\delta(^{119}Sn)$ to low frequency. However, the change in frequency is not as great as that observed for the $SnX_4.2MeOH$ complexes. This is due to the fact that it represents an average chemical shift having a value between that of free and complexed SnX_4, as the tin compound spends some of the time in the free and some in the complexed form. If the mole ratio of the ether to tin halide is increased, $\delta(^{119}Sn)$ moves to lower frequency, indicating that SnX_4 exists for a longer period of time in the complexed form. In fact, in

Ether	SnX_4	Ether: SnX_4	$\delta(^{119}Sn)$ (ppm)	$\delta(^{13}C)$ (ppm)				
	$SnCl_4$		- 149					
	$SnBr_4$		- 637					
				157.2(C-1)	129.4(C-3)	122.8(C-4)	118.8(C-2)	
	$SnCl_4$	1:1	- 150	157.2	129.4	122.8	118.8	
	$SnBr_4$	1:1	- 637.6	157.2	129.4	122.8	118.8	
				138.3(C-1)	128.0(C-3)	127.3(C-2/4)	127.2(C-2/4)	71.6(CH_2)
	$SnCl_4$	1:1	- 181	136.8	128.2	128.0	127.8	71.2
		10:1	- 602	136.6	128.2	128.0	127.8	71.2
	$SnBr_4$	1:1	- 696	138.1	128.1	127.4	127.3	71.6
		10:1	- 835	138.1	128.1	127.4	127.3	71.6
				158.6(C-1)	137.0(C-1^1)	129.2(C-3)	128.3(C-3^1)	69.5(CH_2)
				127.5(C-4^1)	127.0(C-2^1)	120.7(C-4)	114.7(C-2)	
	$SnCl_4$	1:1	- 153	158.7	137.1	129.2	128.2	69.4
				127.5	127.0	120.6	114.7	
				142.1(C-2)	109.2(C-3)			
	$SnCl_4$	1:1	- 149	142.1	109.2			
	$SnBr_4$	1:1	- 637	142.1	109.2			
				159.7(C-9)	127.7	126.2(C-4)	124.4[a]	
				120.1	109.4(C-8)	70.4(C-2)	29.7(C-3)	
	$SnCl_4$	1:1	- 163	160.0	127.7	126.2	124.4	
				119.9	109.3	70.2	29.7	
	$SnBr_4$	1:1	- 641.4	159.9	127.7	126.2	124.4	
				120.1	109.4	70.3	29.7	
				74.6(C-5)	67.1(C-2)	33.2(C-4)	25.9(C-3)	21.0(CH_3)
	$SnCl_4$	1:1	- 334	80.9	70.4	32.0	24.3	21.1
		10:1	- 604	80.9	70.4	32.0	24.3	21.1
	$SnBr_4$	1:1	- 755	76.1	67.7	32.7	25.2	21.3
		10:1	-1317	76.1	67.7	32.7	25.2	21.3

[a] Assignment of this resonance was uncertain.

Table 3-3: ^{119}Sn and ^{13}C NMR Chemical Shifts of Tin(IV) Halide Ether Adducts the case of $SnCl_4$ with Bz_2O or 2-Me-THF, and $SnBr_4$ with the latter compound, when the ether was present in a 10:1 molar excess, $\delta(^{119}Sn)$ values were obtained which are consistent with the presence, in solution, of a 6-co-ordinate adduct, $SnX_4.2L$.

Since the formation of a donor complex results in a change in $\delta(^{119}Sn)$, the magnitude of this change gives a direct indication of the relative strength of the interaction from each individual ether. Thus, by comparing values obtained (Table 3-3) from solutions containing 1:1 mole ratios of SnX_4 to ether, it may be seen that, of the compounds studied, 2-Me-THF has the strongest interaction, whereas Ph_2O and Fur do not co-ordinate significantly to the tin atom. The relative strength of the donor interactions may therefore be summarised as follows:

2-Me-THF>DHBF>Bz_2O>BzPhO>Ph_2O $\approx$ Fur.

^{13}C chemical shift measurements (Table 3-3) are in accord with the results discussed above. Where the ether forms a strong donor complex with the tin halide, the $\delta(^{13}C)$ values are significantly different from those of the free ether. It might be expected that electron donation to tin would result in a deshielding of the carbon atoms adjacent to oxygen and a high frequency shift of $\delta(^{13}C)$ would occur. However, this is not always observed and, with Bz_2O, and C-2 of DHBF, complexation results in a low frequency shift of $\delta(^{13}C)$ for the carbon adjacent to oxygen, as has been noted previously in related systems [37]. Comparison of $\delta(^{13}C)$ values for complexes formed with $SnCl_4$ and $SnBr_4$ with those of the free ether, shows that the largest change occurs with the former tin halide, indicating, as would be expected on the grounds of Lewis acidity, that the stronger interactions occur with $SnCl_4$.

Attempts to study the reaction of the tin tetrahalides with THF and THP in solution were precluded by the immediate precipitation of the adduct on mixing.

3.1.2 Chlorotin(IV) Derivatives, $Cl_nSn(OR)_{4-n}$ $(n = 1 - 3)$

It is possible that tin(IV) chloride could interact with hydroxyl groups within the coal structure. The compound, $SnCl_3(OEt).EtOH$, has been prepared previously by Ichiba *et al.* [16] simply by mixing $SnCl_4$ and ethanol, and thus it is possible that tin(IV) chloride could interact at room temperature with the hydroxyl groups present within coals to form a tin alkoxy-chloro species. The synthesis and spectroscopy of $SnCl_3(OMe).MeOH$, which has been prepared previously [38], is described in this section.

On reaction of $SnCl_4$ with methanol, it appears that $SnCl_4.2MeOH$ is formed initially at room temperature and, on refluxing, $SnCl_3(OMe).MeOH$ results.

However, even after refluxing, not all of the $SnCl_4.2MeOH$ had reacted, since some of this complex crystallised on cooling the solution and was identified by microanalysis (Section 3.3.2). $SnCl_3(OMe).MeOH$ was insoluble in hot toluene and was filtered off from the hot solution.

The complex, $SnCl_2(acac)_2$ (Hacac = acetylacetone, Me CO.CH_2CO.Me), is reported in the literature [39, 40] and the analogous compounds, $SnCl_2(bzac)_2$ (Hbzac = benzoylacetone, PhCO.CH_2CO.Me) and $SnCl_2(bzbz)_2$ (Hbzbz = dibenzoylmethane, PhCO.CH_2CO.Ph) are dealt with in Chapter 6 of this thesis, since they have also been tested as antitumour agents.

The complex, $SnCl_2(OSiPh_3)_2.2Et_2NH$, is believed to be a new compound. The actual product which was hoped for was $SnCl_2(OSiPh_3)_2$. Initially, the method of Audichya et al. [41] for the formation of dichlorotin(IV) diphenoxide was employed, the tin(IV) chloride and triphenylsilanol being stirred together at room temperature for several hours. However, infrared studies indicated that no reaction had occurred. It was therefore decided to carry out the reaction in the presence of base, which it was hoped would assist in the cleaving of the tin-chlorine bond. Thus, tin(IV) chloride and triphenylsilanol were stirred together at room temperature in the presence of excess diethylamine (Equation 3-4).

$$SnCl_4 + 2Ph_3SiOH + 4Et_2NH \xrightarrow[rt]{toluene} SnCl_2(OSiPh_3)_2.2Et_2NH + 2Et_2NH_2^+Cl^- \qquad (3\text{-}4)$$

Attempts were made to form similar complexes with other amines, but these proved to be unsuccessful.

The tin(IV) ethoxides, $Cl_nSn(OEt)_{4-n}$, where n = 1 - 3, studied were supplied by Dr. D. Shibuta, Mitsubishi Metal Corporation, Japan, as was $Sn(OEt)_4$ (Section 3.1.3).

(a) Infrared Studies

Table 3-4 shows a selection of the bands in the infrared spectra of $SnCl_3(OMe).MeOH$ and $SnCl_3(OEt)$.

$SnCl_3(OMe).MeOH$	$SnCl_3(OEt)$
3450 w	
3320 m	3300 w
3200 w	3240 w
	3160 w
2700 w	2720 w
	2670 w
2500 vw	
2380 w	
1600 m	1570 w
1440 sh	1450 sh
1355 sh	1365 sh
	1340 sh
	1300 w
1280 vw	1275 m
	1210 vw
1125 m	1160 m
1080 m	1090 m
	1010 m
970 s	990 m
	885 m
	860 m
	765 w
730 m	720 s
545 s	530 m
520 sh	
510 sh	
480 w	455 w
425 sh	
405 sh	405 w
400 sh	
385 s	

Table 3-4: **Selected Infrared Bands of Trichlorotin Compounds**

The methoxy [38] compound is known by X-ray crystallography to exist as a dimeric species in the solid state with bridging alkoxide groups. The analogous ethoxy compound, $SnCl_3(OEt).EtOH$, is also dimeric [42]. The band at $545cm^{-1}$ in the methoxy compound may be due to vibration of the 4-membered Sn-O-Sn-O ring present in this species [43, 44].

However, this band has also been assigned to the Sn-O stretching vibration by other workers [45]. A band is present at 530cm^{-1} in the spectrum of $SnCl_3(OEt)$, but the stoichiometry of this compound and the Mossbauer data discussed in Section 3.1.2(b) imply that there is no 4-membered Sn-O ring present in $SnCl_3(OEt)$ and this band must be due to the ν(Sn-O-Sn) stretch.

The bands at 970cm^{-1} and 990cm^{-1} have been assigned to the ν(Me-O) and ν(Et-O) stretching frequencies respectively, in agreement with the conclusions of Kawasaki _et_ _al_. [44].

The bands at 1080cm^{-1} and 1090cm^{-1} in the spectra of $SnCl_3(OMe).MeOH$ and $SnCl_3(OEt)$ are assigned to the Sn-O-C stretch [45].

As expected, the infrared spectra of $SnCl_2(OEt)_2$ and $SnCl(OEt)_3$ were largely similar to that of $SnCl_3(OEt)$ and similar assignments of the bands were made.

The spectrum of $SnCl_2(acac)_2$ (Table 3-5) was in good agreement with that reported by Jones and Fay [40] who assigned the bands. On complexation, the carbonyl stretching frequency was reduced from 1620cm^{-1} to 1545cm^{-1}. The νs(Sn-O) and νas(Sn-O) stretches are assigned to the bands at 468 and 595cm^{-1} respectively. The infrared studies of $SnCl_2(bzac)_2$ and $SnCl_2(bzbz)_2$ are described in Chapter 6 of this thesis and many of the details discussed there are applicable to $SnCl_2(acac)_2$.

IR bands (cm^{-1})	$SnCl_2(acac)_2$		
This work	Literature[a]		Assignment[a]
Nujol	Nujol	Solution	
		1572	} ν_s(C—O)
1545 s		1554	}
1530 sh		1532	ν_{as}(C—C)
1425 m		1425	CH_3 def.
		1362	CH_3 sym. def.
1345 s		1345	ν_{as}(C—O)
1285 s	1282	1282	ν_s(C—C)
1200 vw	1202		
	1195	1193	δ(C-H)
1030 s	1024	1025	CH_3 rock
940 s	936	938	Complex vibration
815 s	809	800	π(C-H)
690 vw	684	685	Ring def.
650 vw	649	647	π(C—C—C)
595w	591	590	Some (Sn-O)
	554		
468 w	461	457	ν(Sn-O)
428 w	422	419	Ring def?
	416		

[a] Ref. 40

Table 3-5: <u>Infrared Assignments for $SnCl_2(acac)_2$</u>

The infrared data for $SnCl_2(OSiPh_3)_2.2Et_2NH$ are given in Table 3-6. The high frequency band at 3230cm^{-1} is believed to be due to the N-H stretch of the diethylamine group which is co-ordinated to the tin atom. Such a band has been observed by Sumarokova <u>et al</u>. [46] for $SnCl_4.2Et_2NH$ (ν_{as}(N-H) = 3200cm^{-1}) and, as observed for the ether adducts, the tin compound is acting as a Lewis acid by accepting electrons from the ligand.

IR bands $SnCl_2(OSiPh_3)_2.2Et_2NH$ (cm^{-1})	Assignment
3230 s	ν(N-H)
2380 w	
1430 s	ν(Si-Ph)
1120 vs	ν(Si-Ph)
1110 s	Ring in-plane deformation
1060 m	ν(Si-Ph)
1035 w	ν(Si-Ph)
980 vs	ν_{as}(Si-O-Sn)
755 m	Bending C-H vib.
750 m	Bending C-H vib.
715 vs	Out of place C-H def.
540 w	
520 vs	
480	
440	
330	ν_{as}(Sn-Cl)
310	ν_s(Sn-Cl)
289	
262	
237	

Table 3-6: **Infrared Assignments for $SnCl_2(OSiPh_3)_2.2Et_2NH$**

The spectra of stannosiloxanes are characterised by an intense Si-O-Sn vibration in the region 950-980cm^{-1} and this band is observed at 980cm^{-1} in the spectrum of $SnCl_2(OSiPh_3)_2.2Et_2NH$. Literature values for various stannosiloxanes range from 909 to 980cm^{-1} [47, 48, 49].

In studies of Si-phenyl vibrations, resonances at 1430cm^{-1} and near 1100cm^{-1} have been investigated most thoroughly [50]. The band at 1430cm^{-1} is typical of monosubstituted aromatics. The band at 1110cm^{-1} is due to an in-plane deformation of the ring having some contribution from the Si-C stretch. The resonances at 1120cm^{-1}, 1060cm^{-1} and 1030cm^{-1} in the spectrum of $SnCl_2(OSiPh_3)_2.2Et_2NH$ have been assigned to Si-Ph vibrations, on the basis of the conclusions made by Zeitler et al. [51] in their studies of $Ti(OSiPh_3)_4$. Other assignments made were based on the work of Zeitler et al. [51].

The far infrared spectrum of this complex was investigated. The number of infrared active Sn-Cl bands is known to indicate whether the Cl atoms are cis or trans. Two peaks were present in the spectrum of $SnCl_2(OSiPh_3)_2.2Et_2NH$ at 330cm^{-1} and 310cm^{-1}, the latter being stronger than the former, and it is probable that these bands are due to ν_{as}(Sn-Cl) and ν_s(Sn-Cl) respectively, the implication being that the Cl atoms are cis.

(b) Mossbauer Studies

Table 3-7 shows the Mossbauer parameters of the chlorotin(IV) derivatives studied for this work and those of similar compounds studied in the literature.

$SnCl_3(OMe).MeOH$ has a similar isomer shift to those of $SnCl_3(OEt).EtOH$ [16] and $SnCl_3ox.oxH$ [52]. This is expected for the compounds, $SnCl_3(OEt).EtOH$ and $SnCl_3(OMe).MeOH$, which are known to have a similar dimeric structure [16, 38, 42, 53], the small value of the quadrupole splitting indicating a cis configuration [16]. The isomer shift of $SnCl_3(OMe).MeOH$ is lower than those of the ether adducts discussed in Section 3.1.1. This indicates a lower s electron density at the tin nucleus. The structure of this

Tin Derivative	Mossbauer Parameters δ(mm s^{-1})	 ΔEq(mm s^{-1})
$SnCl_3(OMe).MeOH$	0.31	0.70
$SnCl_3(OEt)$	0.31	0.46
$SnCl_3(OEt).EtOH^a$	0.33	small
$SnCl_3ox.oxH^b$	0.37	0.0
$SnCl_3ox^b$	0.34	0.0
$SnCl_2(OEt)_2$	0.28	0.56
$SnCl_2(acac)_2$	0.21	0.0
$SnCl_2(OSiPh_3)_2.2Et_2NH$	0.27	0.77
$SnCl_2ox_2{}^b$	0.32	0.0
$SnCl(OEt)_3$	0.26	0.74

[a] Ref. 16
[b] oxH = 8-hydroxyquinoline, Ref. 52

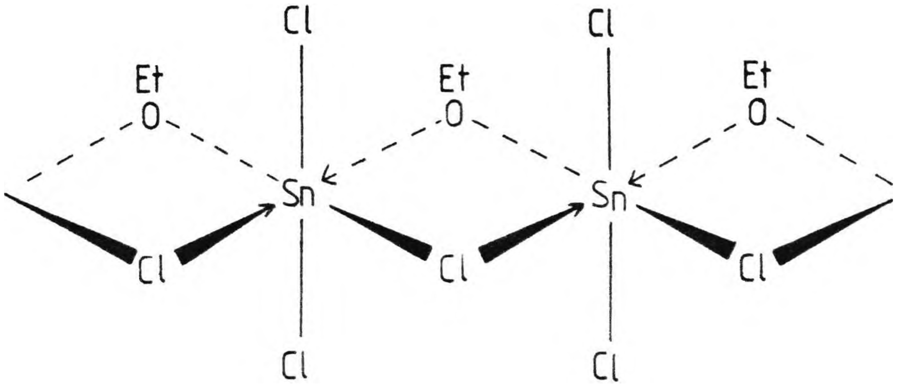
Table 3-7: **^{119m}Sn Mossbauer Parameters of Chlorotin(IV) Derivatives**

complex is analogous to that of the ether adducts, with the exception that one of the chlorines in the co-ordination sphere of the tin atom has been replaced by an alkoxy group. (and R_2O replaced by ROH) Thus, it can be concluded that the alkoxy groups are more electronegative than the chlorine atom [24]. The Sn-OR bond is more ionic than the Sn-Cl bond and the tin atom is more electropositive. The dependence of isomer shift on the number of halogen atoms attached to the tin atom has been noted previously by Ali et al. [52].

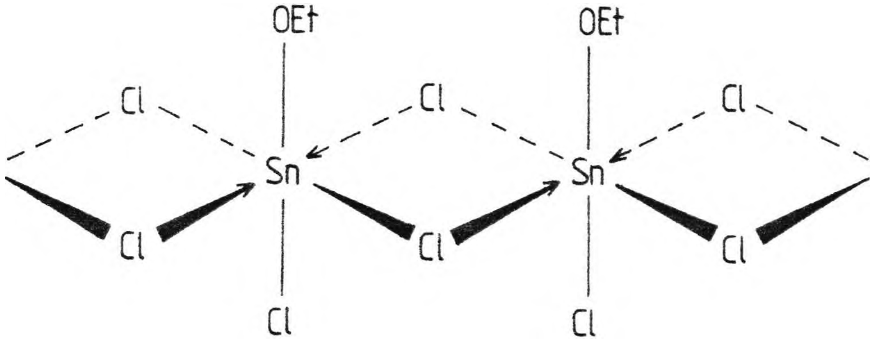
However, these workers indicate that changes in co-ordination of the tin atom have a much greater effect on chemical shift than does ligand replacement. The fact that $SnCl_3(OEt)$ has a similar isomer shift to $SnCl_3(OEt).EtOH$ implies that it too is six co-ordinate and thus suggests that this complex has a polymeric structure. This reasoning has been used to suggest a polymeric structure for $SnCl_3ox$ [52], whose isomer shift was close to that of $SnCl_3ox.oxH$ (Table 3-7). However, a polymeric structure for $SnCl_3ox$ and $SnCl_3(OEt)$ requires that at least four of the positions in the co-ordination sphere of the tin atom are occupied by Cl atoms (Figure 3-1), whereas only three are occupied by Cl atoms in $SnCl_3(OEt).EtOH$ and $SnCl_3(ox).oxH$. This increase in the number of Cl atoms in the co-ordination sphere may explain why the isomer shifts of $SnCl_3(OEt)$ and $SnCl_3ox$ are slightly lower than those of $SnCl_3(OEt).EtOH$ and $SnCl_3(ox).oxH$ respectively (Table 3-7).

The isomer shift of $SnCl_2(OEt)_2$ lies within the range of values observed for six co-ordinate dichlorotin(IV) compounds and this would imply that $SnCl_2(OEt)_2$ has a six co-ordinate polymeric structure. Figure 3-2 shows the possibilities. In structure II, the tin atom is in an environment of 3Cl and 3 oxygen atoms, and thus is in a different environment from the tin atom in $SnCl_2(acac)_2$. The value of the isomer shift obtained does not rule out this possibility.

The complex $SnCl(OEt)_3$, has a lower isomer shift than $SnCl_2(OEt)_2$, which is believed to be six co-ordinate. This lower isomer shift is expected if both complexes have a

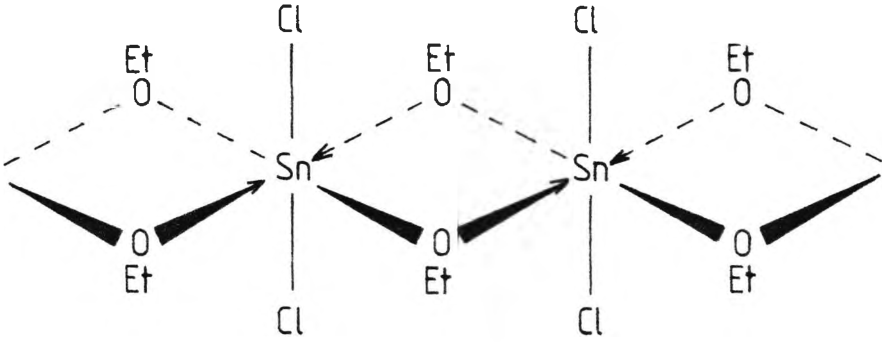


(I) 1 Cl bridge, 1 alkoxy bridge

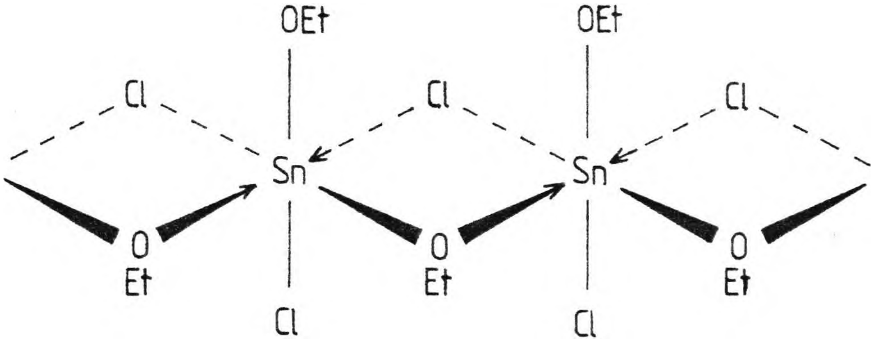


(II) 2 Cl bridges

Figure 3-1: <u>Possible Polymeric Structures for $SnCl_3(OEt)$</u>



(I) 2 alkoxy bridges



(II) 1 alkoxy bridge, 1 Cl bridge

Figure 3-2: Possible Polymeric Structures of $SnCl_2(OEt)_2$

similar structure, i.e. if the tin atom has the same co-ordination number in each case, because of the greater electronegativity of the ethoxide group than that of the chloro group.

The low value of the quadrupole splitting indicates a symmetrical electronic environment about the tin atom.

The Mossbauer parameters obtained for $SnCl_2(bzac)_2$ and $SnCl_2(bzbz)_2$ are given in Chapter 6 and are in good agreement with those of $SnCl_2(acac)_2$, which is also discussed in more detail in that Chapter.

The isomer shift of $SnCl_2(OSiPh_3)_2.2Et_2NH$ is significantly higher than that of $SnCl_2(acac)_2$, indicating a higher s electron density at the tin atom. Compounds of the type, $SnCl_4.2L$ (L = N-containing ligand, e.g. trimethylamine or pyridine), have isomer shifts in the region, $\delta = 0.5 - 0.6 mm\ s^{-1}$ [54]. These are higher than those of the ether adducts, since the effectiveness of the donor atom decreases in the order

$$O>N>S>P$$

Comparison of the isomer shifts of $SnCl_4.2L$ (L = N-containing ligand) with that of $SnCl_2(OSiPh_3)_2.2Et_2NH$ again indicates that a reduction in the number of halogen atoms leads to a decrease in the isomer shift when the halogen atoms are replaced by oxygen-containing groups [52].

3.1.3 Non-Halogen Containing Tin(IV) Derivatives

Tetrakis(triphenylsiloxy)stannane was prepared as the result of an investigation of the reaction of tin(IV) chloride with triphenylsilanol in the presence of other bases, besides diethylamine (Section 3.1.2). On substituting this amine with either triethylamine or dipropylamine, all four chlorine atoms were replaced, leading to the formation of $Sn(OSiPh_3)_4$ (Equation 3-6).

$$SnCl_4 + 4Ph_3SiOH + 4R_2R^1N \longrightarrow Sn(OSiPh_3)_4 + 4R_2R^1NH^+Cl^- \qquad (3\text{-}6)$$

$R = R^1 = Et$ or $R = Pr$, $R^1 = H$

This compound has been prepared previously from tin(IV) chloride and sodium triphenylsilanolate, $NaOSiPh_3$ [55]. Following the literature method for the preparation of $Sn(trop)_4$ [56] (Equation 3-7), the resulting product was found to be the monohydrate, $Sn(trop)_4.H_2O$.

$$SnCl_4 + 4Na^+(trop)^- \xrightarrow[\text{MeOH}]{\text{Reflux 2 days}} Sn(trop)_4 + 4NaCl \qquad (3\text{-}7)$$

$HSn(DTPA).3H_2O$ and $Sn(EDTA).H_2O$ were also prepared, according to the literature methods [57, 58] (Equations 3-8 and 3-9).

$$Na_3H_2(DTPA) + SnCl_4 \xrightarrow[\text{20 mins}]{90^\circ C} HSn(DTPA).3H_2O + 3NaCl + HCl \qquad (3\text{-}8)$$

$$Na_2H_2(EDTA).2H_2O + SnCl_4 \xrightarrow{\text{hot } H_2O} Sn(EDTA).H_2O + 2NaCl + 2HCl \qquad (3\text{-}9)$$

High co-ordination number 7- and 8- co-ordinate inorganic tin(IV) complexes are known and several of these have been synthesised as possible model compounds for the tin-coal species. The compounds, tin(IV) tetraacetate, $Sn(OAc)_4$ (AcOH = Me.COOH) tin(IV) tetratropolonate monohydrate, $Sn(trop)_4.H_2O$, (trop = $C_7H_5O_2^-$), monohydrodiethylenetriaminepentaacetatotin(IV) trihydrate, $HSn(DTPA).3H_2O$, and tin(IV) ethylenediaminetetraacetate monohydrate, $Sn(EDTA).H_2O$, were chosen for study, since their 7- and 8-co-ordinate structures have been established by X-ray crystallography or related techniques [57, 59-63]. ^{119}Sn NMR spectroscopic investigations on organotin compounds indicate that the ^{119}Sn chemical shift, (^{119}Sn), moves progressively to lower frequencies as the co-ordination number of the metal increases from 4 to 7 [36, 64] and the following study showed that the same is true for inorganic tin(IV) complexes [see Section 3.1.3(c)].

Tin(IV) tetraacetate has been prepared previously by Sawyer and Frey [65] from tetraphenyltin and excess acetic acid in the presence of acetic anhydride (Equation 3-10).

$$SnPh_4 + 4AcOH \xrightarrow[\text{Reflux 21 hours}]{\text{Acetic anhydride}} Sn(OAc)_4 + 4PhH \qquad (3\text{-}10)$$

The purpose of the acetic anhydride is to remove any moisture, the product being very hygroscopic. Infrared, ^{119m}Sn Mossbauer and ^{119}Sn NMR spectra were obtained for the above complexes, as well as the TGA/DTA for $Sn(trop)_4.H_2O$.

(a) **Thermogravimetric and Differential Thermal Analysis (TGA/DTA) of Sn(trop)$_4$.H$_2$O**

Table 3-8 shows the TGA/DTA results for Sn(trop)$_4$.H$_2$O, the heating of the sample being carried out in an atmosphere of dry nitrogen.

Degradation Stage	T_i [a] (°C)	T_f [b] (°C)	T_{max} [c] (°C)	Weight Loss(%)	H
1	32	51	50	2.8	ENDOTHERMIC
2	218	403	368	73.0	ENDOTHERMIC
3[d]	403	438	407	3.6	ENDOTHERMIC
4[e]	438	e	f	4.4	-

[a] T_i = Onset Temperature *i.e.* temperature at which the sample begins to lose weight.

[b] T_f = Offset Temperature *i.e.* temperature at which the sample stops losing weight.

[c] T_{max} = Temperature of Maximum Rate of Weight Loss.

[d] Residue at offset temperature, 438°C = 20.6% by weight.

[e] Residue at 600°C = 16.0% by weight.

[f] Gradual weight loss until final temperature of 600°C.

Table 3-8: **TGA/DTA Results for Sn(trop)$_4$.H$_2$O**

After the heating process had been completed, a black residue remained. The first weight loss of 2.8% (degradation stage 1) corresponded to the loss of the water of hydration, 1 mole of H$_2$O being lost per molecule of complex (calculated = 3.2%). This process gave rise to an endothermic peak in the DTA plot. Although the sample had been dried in an oven at 90°C prior to this experiment, it had apparently picked up moisture again. The very low temperature at which the water is removed indicates that it is only loosely held.

The second and third degradation stages correspond to loss of the organic part of the molecule, leaving a residue of tin metal.

(b) Infrared Studies

The infrared spectrum of $Sn(OEt)_4$ resembled those of the chloroethoxides and the same assignments have been made.

The infrared spectra of the triphenylsiloxy products obtained when using either triethylamine or dipropylamine were identical. The strong Sn-O-Si band was present at $945cm^{-1}$, a slightly lower value than that observed in $SnCl_2(OSiPh_3)_2.2Et_2NH$. Other bands observed in these spectra were similar to those observed in the dichloro complex (apart from the absence of the N-H stretching band) and were given the same assignment. A very weak band was observed in the spectrum in the region of $850cm^{-1}$. The Si-OH band in Ph_3SiOH occurs in this part of the spectrum and Bedford et al. [55] comment on the ease of hydrolysis of the Sn-O-Si bond. Thus, this band may result from a small degree of hydrolysis of the product, $Sn(OSiPh_3)_4$.

The infrared spectrum of $Sn(OAc)_4$ run by Alcock et al. [66] showed two ν_{as} (C - O) at $1635cm^{-1}$ and $1575cm^{-1}$ and two ν_s(C-O) at $1400cm^{-1}$ and $1315cm^{-1}$. However, in the spectrum run for this thesis, the band at $1635cm^{-1}$ was not observed and the band at $1400cm^{-1}$ was very weak, a stronger band being observed at $1420cm^{-1}$. The X-ray crystal structure of this complex [59] throws some light on to the reason why two antisymmetric and two symmetric C-O stretching frequencies are observed, since it showed that the Sn-O bond lengths were irregular.

The infrared spectrum of $Sn(trop)_4.H_2O$ was largely similar to that of tropolone itself. The band at 1620cm^{-1} in the parent compound is due to the carbonyl stretching vibration. This relatively low value may result from hydrogen bonding to the hydroxyl group which is also present in the molecule, but an alternative theory has been put forward by Koch [67]. He believes that the presence of a 7-membered ring results in the weakening of the C=O bond and a strengthening of the ring. On complexing to the tin atom, the carbonyl frequency is reduced further to 1600cm^{-1}.

The band at 1560cm^{-1} appears to have been shifted to 1530cm^{-1} on complexation and is believed to be characteristic of a 7-membered ring [50].

The infrared spectrum of $Sn(EDTA).H_2O$ contains the bands shown in Table 3-9. The X-ray crystal structure of this complex [63] indicates that this is a 7 co-ordinate complex in which both of the nitrogen atoms and 4 carboxylate oxygen atoms and the water molecule bind to the tin atom. Bands are visible in the spectrum at 1700 cm^{-1} and 1655cm^{-1} and are in close agreement with bands observed for this complex by Langer et al. [58]. It is possible that two antisymmetric C-O stretching vibrations are observed because of hydrogen bonding of two carboxyl groups in each molecule to the water molecule, which leads to a lowering of the stretching frequency.

$\nu(cm^{-1})$	Assignment
1700 s	$\nu_{as}(C-O)$
1655 s	$\nu_{as}(C-O)$ (H bonded)
1370 sh	$\nu_{s}(C-O)$
1350 m	$\nu_{s}(C-O)$
1110 w	
1085 m	$\nu(C-N)$

Table 3-9: **Assignment of a Selection of Peaks in the Infrared Spectrum of Sn(EDTA).H_2O**

The infrared spectrum of HSnDTPA.$3H_2O$ has been studied previously [57], and the bands observed for this thesis are in close agreement with those of Krishna Iyer *et al.* [57]. Some of these bands are shown in Table 3-10.

$\nu(cm^{-1})$	Band observed by Krishna Iyer *et al.*[57]	Assignment
3550 m	3540 m	
3420 m	3310 m	$\nu_{as}(OH)$
1655 s	1650 vs	$\nu_{as}(C=O)$
1635 s		
1370 sh		
1355 m	1350 s	$\nu_{s}(C-O)$
1090 m		$\nu(C-N)$

Table 3-10: **Infrared Assignments of HSnDTPA.$3H_2O$**

Comparison of the spectrum of $HSnDTPA.3H_2O$ with that of H_5DTPA indicated that most of the other bands were present in both spectra. The free acid shows $\nu(C=O)$ stretching bands at 1735cm^{-1} and 1695cm^{-1}, and the absence of bands in this region in the product indicates that there are no free carboxyl groups. From the spectrum, it appears that the carbonyl stretching frequency has been split into a doublet, although this was not observed by previous workers [57]. The X-ray crystal structure determination indicates that the tin atom in this complex is co-ordinated to 3 nitrogen atoms and 5 oxygen atoms of the carboxyl groups. Thus, each carboxyl group is acting as a unidentate ligand.

(c) Mossbauer Studies

The Mossbauer results for the compounds studied are shown in Table 3-11.

The effect of the electronegativity of the ligands directly bonded to the tin atom on the Mossbauer isomer shift has already been discussed in Section 3.1.2(b). The decrease in isomer shift, indicating an increase in electronegativity as the number of ethoxy groups increases in the series, $SnCl_{4-n}(OEt)_n$ (n = 1-4), may be plotted graphically (Figure 3-3). A linear relationship is observed, indicating that

Tin Derivative	Mossbauer Parameters(mms^{-1}) δ(mms^{-1})	 ΔEq	Co-ordination Number
$Sn(OEt)_4$	0.23	0.62	Not known
$Sn(OSiPh_3)_4$	0.14	0.0	Not known
$Sn(OAc)_4$	0.08[a]	0.2	8[b]
$Sn(NO_3)_4$	-0.04[c]	0.4[c]	8[d]
$Sn(trop)_4.H_2O$	-0.02	0.0	8[e]
$Sn(ox)_4$[f]	-0.05[g]	0.0[g]	8[g, h]
$HSn(DTPA).3H_2O$	0.21	0.0	8[i]
$Sn(EDTA).H_2O$	0.16	0.0	7[j]

[a] Ref. 21
[b] Ref. 59
[c] Ref. 68
[d] Ref. 69
[e] Ref. 60 (reported as anhydrous material)
[f] $Sn(ox)_4$ = tetra-8-oxyquinolinatotin(IV)
[g] Ref. 61
[h] Ref. 62
[i] Ref. 57
[j] Ref. 63

Table 3-11: <u>^{119m}Sn Mossbauer Data for Non-halogen Containing Tin Complexes</u>

these chloro-ethoxy compounds have a similar structure. It has already been suggested that $SnCl_3(OEt)$ and $SnCl_2(OEt)_2$ have six co-ordinate structures (Section 3.1.2(b)) and the implication is that $Sn(OEt)_4$ is six co-ordinate too.

The eight co-ordinate compounds, $Sn(NO_3)_4$, $Sn(trop)_4.H_2O$ and $Sn(ox)_4$, have a low isomer shift, as anticipated. The isomer shift of $HSn(DTPA).3H_2O$ is higher and is consistent with an increase of the s electron density at the tin nucleus on forming the anion.

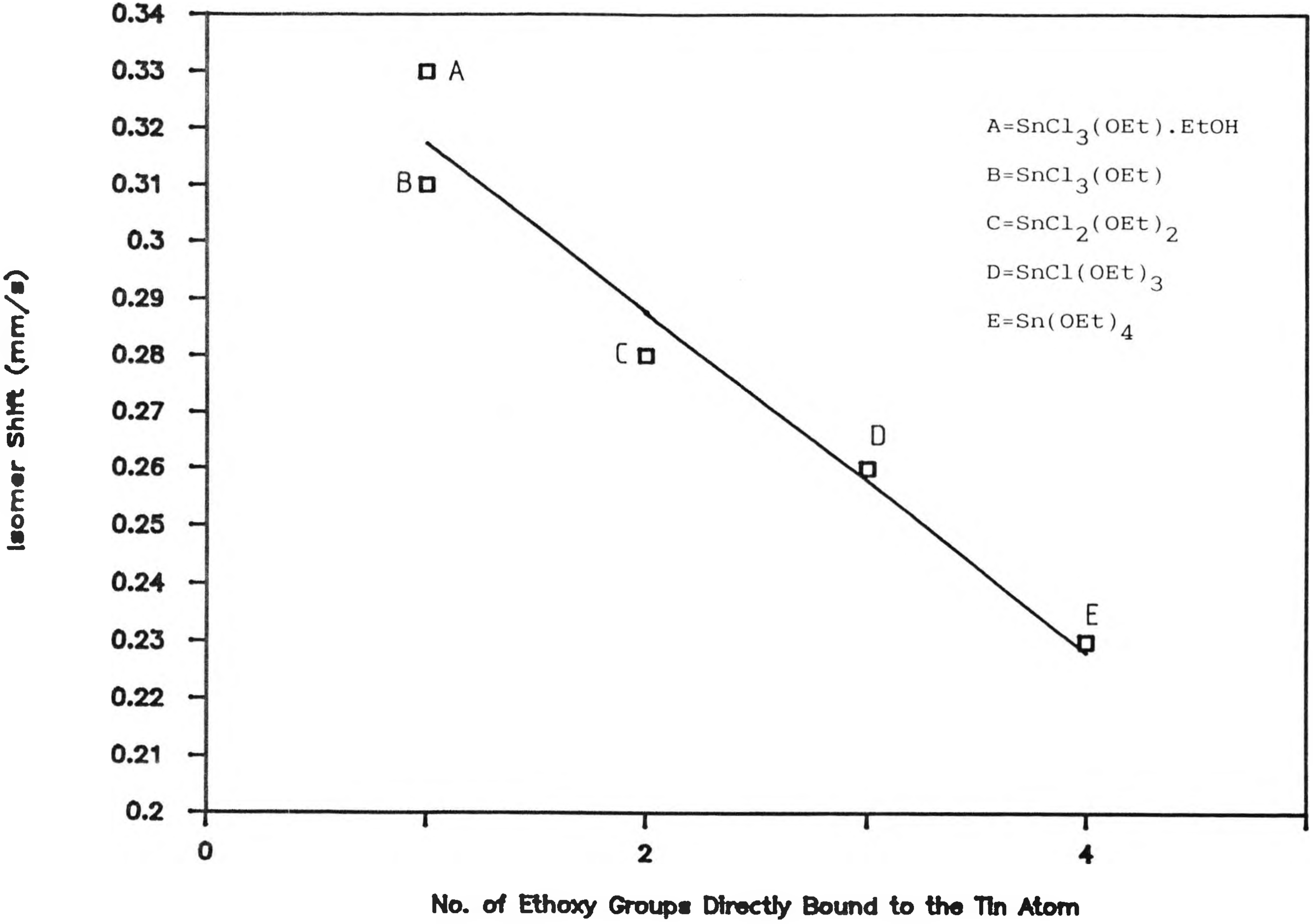


Figure 3-3: Variation of ^{119m}Sn Mossbauer Isomer Shift with Electronegativity

(c) ^{119}Sn NMR Studies

The results obtained for the ^{119}Sn NMR studies carried out for this thesis and those found in the literature are shown in Table 3-12.

Compound	Coord-ination Number	Solution NMR		δ(^{119}Sn) (ppm)	Solid State NMR δ(^{119}Sn) (ppm)
		Solvent	Concn.		
1. $Sn(OAc)_4$	8	toluene/ acetic acid	10%w/v	-858.2	-
2. $Sn(NO_3)_4$	8	CH_2Cl_2	1.1M	-1033[a]	-
		$CDCl_2$	1.1M	-1033[a]	-
3. $Sn(trop)_4 . H_2O$	8	$CDCl_3$	1%w/v (sat'd)	-793	-
4. $HSn(DTPA) . 3H_2O$	8	H_2O	1-2%w/v (sat'd)	-783.5	-
5. $Sn(EDTA) . H_2O$	7	H_2O	1-2%w/v (sat'd)	-673.8	-
6. $Sn(O^nBu)_4$	6	$CDCl_3$	0.2M	-612[b]	-
7. $Na_2Sn(OH)_6$	6	H_2O	sat'd	-592[c]	{-563.4[d] {-564.4[d]
8. SnO_2	6	-	-	-	{-603.4[d] {-604.3[e]
9. $SnCl_4 . 2MeOH$	6	CD_3OD	30%w/v	-600.5[f]	-
10. $Cl_2Sn(acac)_2$	6	$CDCl_3$	10%w/v	-646.2	-642[g]
11. Na_2SnO_3	5	-	-	-	-480.3[e]
12. $Sn(O^tBu)_4$	4	$CDCl_3$	-	-373[h]	-

(cont'd)

Compound	Coord-ination Number	Solution NMR Solvent	Concn.	$\delta(^{119}Sn)$ (ppm)	Solid State NMR $\delta(^{119}Sn)$ (ppm)
13. $Sn(OSiPh_3)_4$	not known	-	-	-	-429.7
14. $SnCl_4$	4	neat CCl_4	- 10%w/v	-150[c] -149[j]	- -

[a] Ref. 70
[b] Ref. 71
[c] Ref. 72
[d] Ref. 73
[e] Ref. 74
[f] Ref. 75
[g] Ref. 76
[h] Ref. 77
[j] Ref. 78

Table 3-12: **^{119}Sn NMR Chemical Shifts of Inorganic Tin(IV) Compounds**

The Table shows that, as for organotin compounds, the ^{119}Sn NMR chemical shift increases as the co-ordination number of the tin atom increases. The (^{119}Sn) of the 4 co-ordinate compound, $SnCl_4$, increases to -600ppm in methanol, where the 6 co-ordinate neutral adduct $SnCl_4.2MeOH$ is present. The five co-ordinate Na_2SnO_3 has an intermediate value. Values of ca. -600ppm are observed for the 6 co-ordinate compounds, $Na_2Sn(OH)_6$, $K_2Sn(OH)_6$ and $Sn(O^nBu)_4$, in which there are at least 4 directly bound oxygen constituents. The 8 co-ordinate species (compounds 1-4) studied all show chemical shift values in the range -784 to -1033ppm, whilst the 7 co-ordinate complex, $Sn(EDTA).H_2O$, has an intermediate value.

The actual structure of $Sn(OSiPh_3)_4$ is not known. However, the value of the solid state NMR chemical shift (Figure 3-4) obtained is similar to the solution value of $Sn(O^tBu)_4$ implying a 4 co-ordinate configuration. Both derivatives

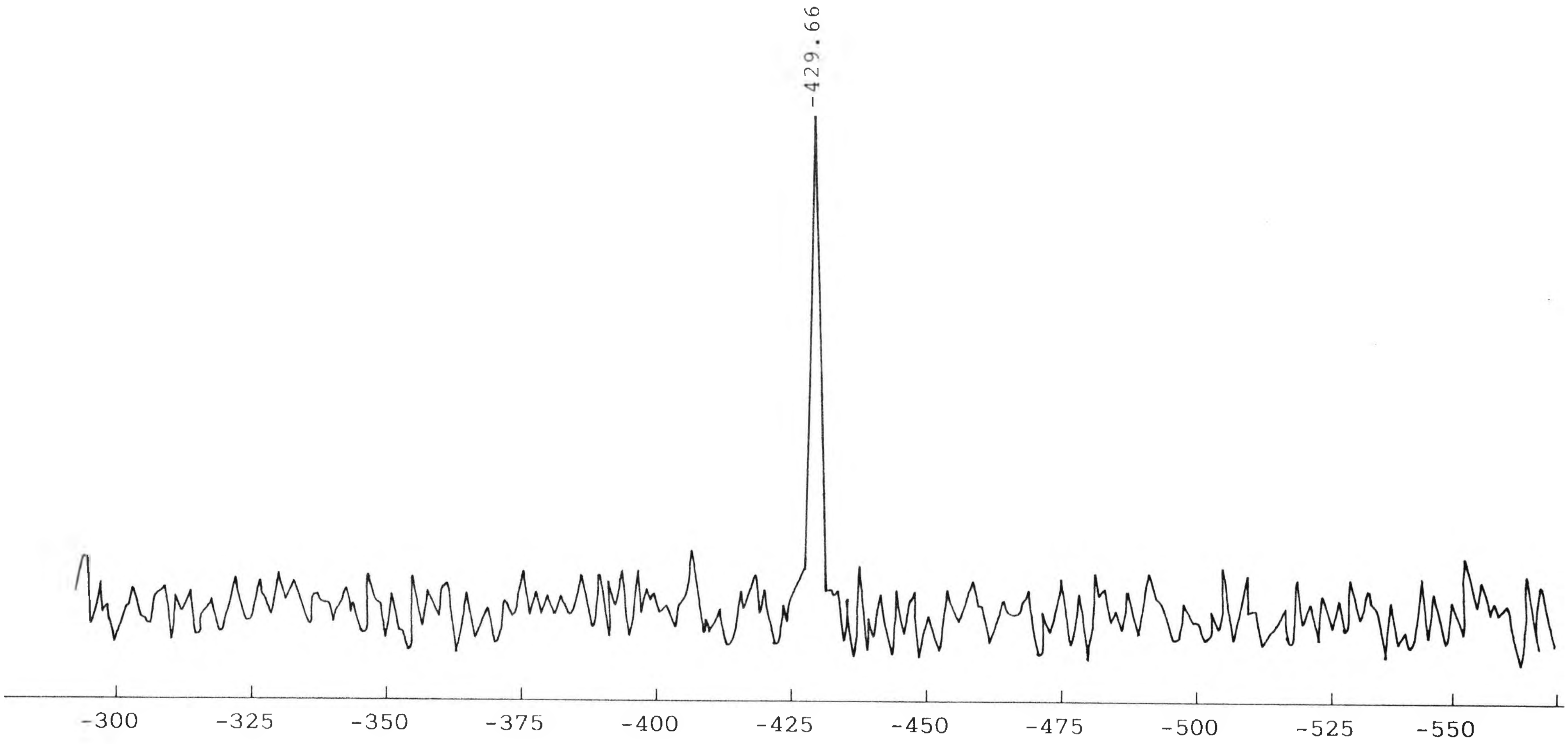


Figure 3-4: **Solid State ^{119}Sn NMR Spectrum of $Sn(OSiPh_3)_4$**

contain bulky organic ligands and tetrahedral rather than octahedral configurations may have been adopted for steric reasons. The information given in Table 3-12 is shown graphically in Figure 3-5.

3.1.4 Tetrakis(cyclohexanethio)stannane

The ^{119m}Sn Mossbauer spectrum of the residue obtained from the coal liquefaction experiments carried out at North Staffordshire Polytechnic, using Morwell coal with tin(II) octoate as catalyst, is discussed in detail in Chapter 5. One of the peaks observed in this spectrum has an isomer shift of 1.53mm s^{-1}. Such a resonance has been observed previously by Cook et al. [79], who suggested that it is due to the presence of an organotin(IV) compound or a metal alloy. However, compounds of the type, $Sn(SR)_4$, are known to have isomer shifts in the range, $\delta = 1.2 - 1.5$ mm s^{-1} [21]. It was therefore decided to synthesise the complex, tetrakis(cyclohexanethio)stannane, $Sn(SC_6H_{11})_4$, since, being saturated, this would be a good model for the products obtained from a coal hydrogenation experiment. Moieties in which a sulphur atom is attached to a 6 membered ring are a feature of the Wiser model for a bituminous coal [80] and it is possible that such species could be present in the coal studied here.

$Sn(SC_6H_{11})_4$ was prepared by the method used by Mehrotra et al. [84] for the preparation of $Sn(S^nBu)_4$, $Sn(S^nHex)_4$ and $Sn(S.CO.Et)_4$ (Equation 3-11).

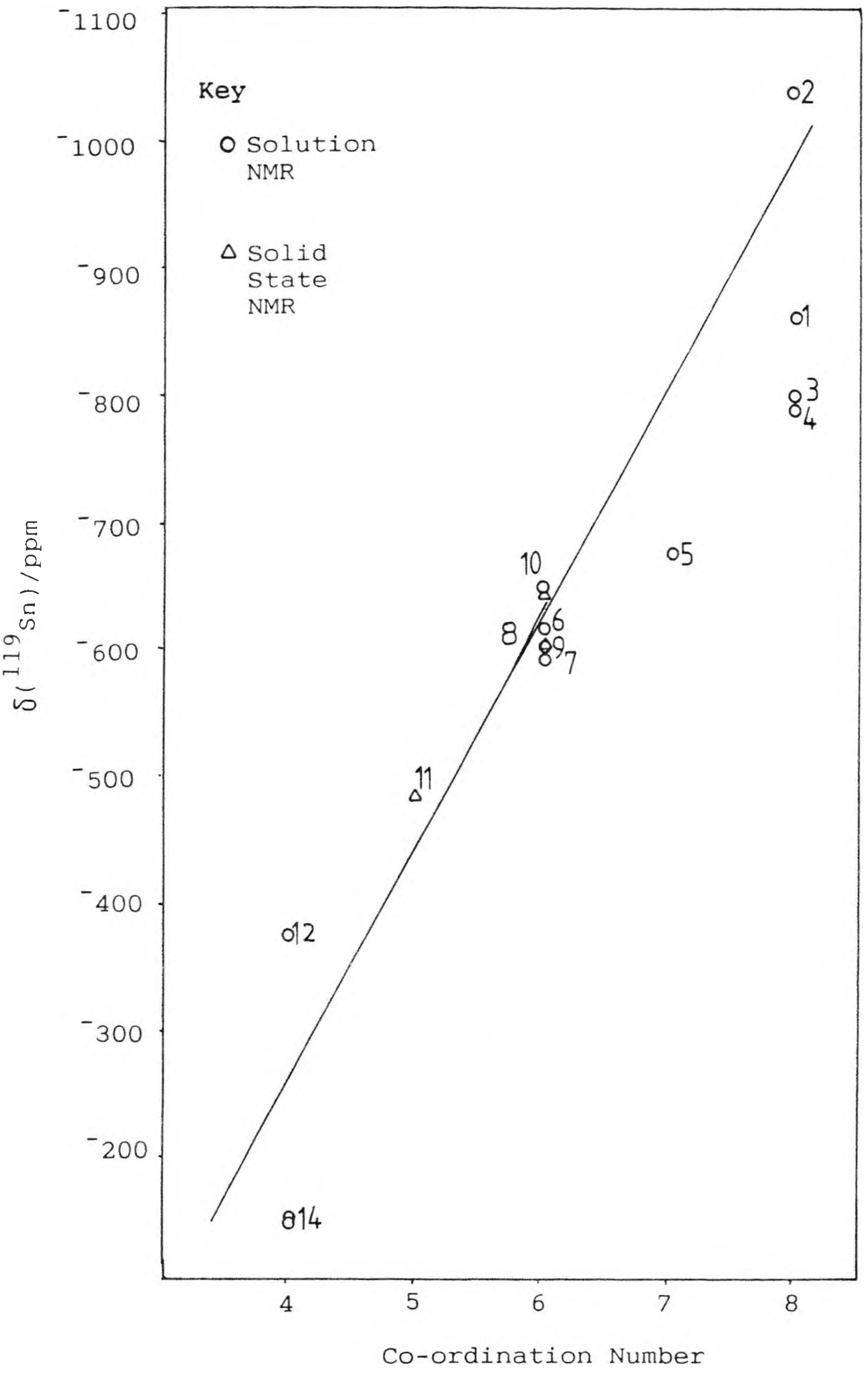


Figure 3-5: Variation of Chemical Shift with Co-ordination Number

$$Sn(OAc)_4 + 4C_6H_{11}SH \xrightarrow[r.t.]{CHCl_3} Sn(SC_6H_{11})_4 + 4\ AcOH \qquad (3\text{-}11)$$

(a) ^{119m}Sn Mossbauer Studies

The ^{119m}Sn Mossbauer parameters of $Sn(SC_6H_{11})_4$ and of other tetrathiolato-tin compounds studied in the literature are shown in Table 3-13.

Compound	Mossbauer Parameters δ (mm s^{-1})	 ΔEq(mm s^{-1})
$Sn(SC_6H_{11})_4$	1.31	0.0
$Sn(SPh)_4$	1.47[a]	0.0[a]
$Sn(edt)_2$[b]	1.34[c]	0.98[c]
	1.44[a]	1.07[a]
$Sn(p2dt)_2$[d]	1.43[a]	0.96[a]
$Sn(tdt)_2$[e]	1.21[e]	1.52[c]

[a] Ref. 83
[b] edt = ethane-1,2-dithiolato.
[c] Ref. 83
[d] p2dt = propane-1,2-dithiolato.
[e] tdt = toluene-3,4-dithiolato.

Table 3-13: ^{119m}Sn Mossbauer Parameters for Tetrathiolato-tin Compounds

Poller *et al.* [82] concluded that $Sn(SPh)_4$ is a monomeric tetrahedral compound, partly because of the absence of a quadrupole splitting in the ^{119m}Sn Mossbauer spectrum. $Sn(SC_6H_{11})_4$ showed a singlet Mossbauer peak and this, in addition to its low melting point, indicates that it is, in all probability, a monomeric species. The reason for the lower isomer shift observed for $Sn(SC_6H_{11})_4$ than for $Sn(SPh)_4$ is not known. It is expected that, as the electronegativity of the ligand increases, the bonds to the tin atom become more ionic and the tin atom itself becomes more positive. The loss of valence shell electron density, particularly from the s shells, would be expected to lead to a decrease in isomer shift. This is observed for the compounds, $SnMe_4$ and $SnPh_4$ [24], the former having a higher isomer shift than the latter. The opposite trend is observed for the compounds, $Sn(SPh)_4$ and $Sn(SC_6H_{11})_4$.

As stated previously, increasing the co-ordination number of the tin atom leads to a decrease in isomer shift [24]. $Sn(tdt)_2$ is believed [82] to be polymeric, the tin atoms being six co-ordinate and, as expected, it has a significantly lower isomer shift than either $Sn(SC_6H_{11})_4$ or $Sn(SPh)_4$.

3.2 TIN(II) COMPOUNDS

It has been suggested that the uptake of tin from tin(II) chloride in aqueous solution can be correlated with the carboxylic acid content of a wide range of low-rank, sub-bituminous and bituminous coals [84]. It is therefore possible that a tin(II) carboxylate species may be formed on impregnating at least some of the coals studied in this thesis, with tin(II) chloride (Chapter 4). Thus, the tin(II) carboxylates, tin(II) benzoate, $Sn(O.CO.Ph)_2$, and tin(II) β-naphthoate, $Sn(O.CO.C_{10}H_7)_2$, were synthesised as possible model compounds, in order that their ^{119m}Sn Mossbauer isomer shifts could be compared with those of the tin-impregnated coals (Chapter 4). The ^{119m}Sn Mossbauer parameters of the tin-containing coals are compared with other tin(II) species in Chapter 4, but these model compounds have not been prepared, the comparisons being made using literature values.

The tin(II) benzoate and β-naphthoate were synthesised from tin(II) chloride, <u>via</u> tin(II) methoxide (Equations 3-12 and 3-13 [85]).

$$SnCl_2 + 2MeOH + 2R_2R^1N \xrightarrow{r.t.} Sn(OMe)_2 + 2R_2R^1NH^+Cl \qquad (3\text{-}12)$$

$R = Et,\ R^1 = Et \text{ or } H$

$$Sn(OMe)_2 + 2ArCOOH \xrightarrow[\text{toluene}]{\text{Reflux}} Sn(O.CO.Ar)_2 + 2MeOH \qquad (3\text{-}13)$$

$Ar = Ph \text{ or } C_{10}H_7$

3.2.1 Tin(II) Carboxylates

Although a pure sample of the β-naphthoate was formed, it was not possible to obtain $Sn(\alpha\text{-}O.CO.C_{10}H_7)_2$ from the reaction of tin(II) methoxide with α-naphthoic acid.

(a) Infrared Studies

The infrared spectra of both tin(II) benzoate and tin(II) naphthoate have been studied previously by Ewings et al. [85]. The most characteristic band in the spectra of $Sn(O.CO.Ph)_2$ and $Sn(O.CO.C_{10}H_7)_2$ is $\nu_{as}(CO)$ and the values obtained for this band are $1510cm^{-1}$ and $1530cm^{-1}$. These values are lower than the frequencies observed in the parent acids [$\nu(CO)$ = $1685cm^{-1}$ in benzoic acid and $1680cm^{-1}$ in β-naphthoic acid). It is of interest to compare these bands with the $\nu_{as}(CO)$ frequency observed for $Sn(O.CO.H)_2$ $1563cm^{-1}$) [86], which is known [87] by x-ray crystallography to contain a 4 co-ordinate tin atom geometry, with each tin atom bonded intermolecularly to four different formate group carbonyl oxygen atoms.

(b) ^{119m}Sn Mossbauer Studies

The ^{119m}Sn Mossbauer parameters for $Sn(O.CO.Ph)_2$ and $Sn(O.CO.C_{10}H_7)_2$ are given in Table 3-14, together with the literature values in parentheses.

Compound	Mossbauer Parameters	
	δ(mm s^{-1})	ΔEq(mm s^{-1})
$Sn(O.CO.Ph)_2$	3.36	2.10
	$(3.17)^a$	$(1.69)^a$
$Sn(O.CO.C_{10}H_7)_2$	3.52	1.62
	$(3.35)^a$	$(2.00)^a$

[a] Ref. 85

Table 3-14: Mossbauer Data for Tin(II) Carboxylates

The isomer shifts obtained are similar to those of the tin(II) carboxylates studied by Donaldson *et al.* [88] and to the value obtained by Harrison *et al.* [87] for tin(II) formate, for which a crystal structure determination has been carried out.

3.3 EXPERIMENTAL

3.3.1 Tin(IV) Tetrahalide Adducts, $SnX_4.2L$ and $SnX_4.L$

The adducts of $SnCl_4$ with the ethers were prepared by adding the appropriate ether (0.017 moles) in petroleum ether, toluene or chloroform, to a stirred solution of anhydrous tin(IV) chloride (2.26g, $1cm^3$, 0.008 moles) in the same solvent, the reaction being carried out under dry nitrogen. An immediate precipitate formed for each ether ligand and this was removed by filtration, dried in vacuo and stored in a sealed tube.

The $SnBr_4$ adducts of tetrahydrofuran and tetrahydropyran were prepared similarly and, in both cases, an immediate pale yellow precipitate was formed.

Microanalyses, melting points, infrared, Mossbauer and NMR spectra were determined and these are listed in Tables 3-1, 3-2 and 3-3.

3.3.2 Trichlorotin(IV) methoxide methanol (1:1) and Tetrachlorotin(IV)-methanol (1:2)

$SnCl_4$ (0.03 moles, 9.04g, $4cm^3$) was added to an excess of methanol (0.15 moles, 4.71g, $5.93cm^3$). An initial exothermic reaction took place, white fumes being observed. After this initial reaction had subsided, the solution became orange-coloured. Toluene was added and the mixture was refluxed for half an hour, after which time, a white precipitate was visible. This precipitate was filtered off from the hot toluene and dried in vacuo. On cooling the solution, a further precipitate was formed and this too was separated by filtration and dried in vacuo. Microanalytical data and melting points of both products were obtained and are given below. In addition, infrared and Mossbauer spectra were run and the results obtained are listed in Tables 3-4 and 3-7.

$SnCl_4.2MeOH$. M.p. 199-201°C (subl.). Found: C, 7.70; H, 2.58; Cl, 41.99. Calculated for $C_2H_8O_2Cl_4Sn$: C, 7.40; H, 2.48; Cl, 43.69.

$SnCl_3(OMe).MeOH$ M.p. 197 - 204°C (subl.). Found: C, 8.22; H, 2.32; Cl, 35.99. Calculated for $C_2H_7O_2Cl_3Sn$: C, 8.34; H, 2.45; Cl, 36.91.

3.3.3 Dichlorotin(IV) Derivatives

(a) Bis(acetylacetonate-O,O)dichlorotin(IV)

$SnCl_2(acac)_2$ has been prepared previously by several groups of workers [40, 89 - 91]. A chloroform solution of $SnCl_4$ (2.26g, $1cm_3$, 0.009 moles) was added slowly dropwise to an excess of acetylacetone (3.8g, $4cm_3$, 0.04 moles). The solution was refluxed for one hour. Colourless crystals formed on cooling and these were filtered off, washed with isopropanol and ice-cold petroleum ether and dried in air. Infrared and Mossbauer data were obtained, M.p. 193 - 195°C (lit. m.p. 203 - 205°C [46]). Found: C, 30.85; H, 3.52; Cl, 18.64. Calculated for $C_{10}H_{14}O_4Cl_2Sn$: C, 30.97; H, 3.64; Cl, 18.28.

(b) Dichlorobis(triphenylsiloxy)tin(IV)-diethylamine (1:2)

Triphenylsilanol, Ph_3SiOH (4.80g, 0.02 moles) and $SnCl_4$ (2.26g, 1cm^3 0.009 moles) were dissolved in toluene. An excess of diethylamine, Et_2NH (3.54g, 5cm^3, 0.05 moles), was then added slowly dropwise with stirring, the reaction being carried out under dry nitrogen. An immediate white precipitate was formed and this was filtered off and dried *in vacuo*. This product was then stirred in methanol for several minutes in order to remove the $Et_2NH_2^+Cl^-$ by-product. The remaining white solid was again dried *in vacuo*. Infrared and Mossbauer data were obtained. M.p. 220°C (dec.). Found: C,59.40; H, 6.00; N, 3.08; Cl, 8.22. Calculated for $C_{40}H_{42}O_2N_2Cl_2Sn$; C, 59.60; H, 5.91; N, 3.16; Cl, 8.00.

3.3.4 Non-Halogen Containing Tin(IV) Derivatives

(a) Tetrakis(triphenylsiloxy)stannane : $Sn(OSiPh_3)_4$

$SnCl_4$ (1.13g, 0.5cm^3, 0.004 moles) and Ph_3SiOH (2.40g, 0.009 moles) were dissolved in toluene. Et_3N (1.76g, 2.43cm^3, 0.02 moles) was added slowly dropwise with stirring. As a precaution, the reaction was carried out in an atmosphere of dry nitrogen. A white solid formed immediately. The $SnCl_2(OSiPh_3)_2.2Et_2NH$ was insoluble in methanol and had been stirred in this solvent to remove the Et_2NH_2Cl salt. However, the siloxy product obtained from this reaction appeared to be soluble in methanol. The reaction was, therefore, repeated and the resulting white precipitate was stirred briefly in water. The remaining solid was filtered off and the filtrate gave a positive chloride ion test with silver nitrate solution. Microanalytical, infrared, ^{119m}Sn Mossbauer and solid state ^{119}Sn NMR data were obtained for the product.

In a second experiment, the triethylamine was replaced by dipropylamine (1.76g, 2.38cm^3, 0.02 moles).

M.p. 200°C (dec.) Found, using Et_3N as base: C, 70.38; H, 5.15.

Found, using Pr_2NH as base: C, 70.11; H, 4.94. Calculated for $C_{72}H_{60}O_4Si_4Sn$: C, 70.87; H, 4.96.

(b) Tetraacetatotin(IV) : $Sn(OAc)_4$

Tetraphenyltin, Ph_4Sn (5g, 0.01 moles), was added to acetic acid (13.36cm^3), and acetic anhydride (22.53cm^3). The mixture was allowed to reflux under an inert atmosphere overnight (ca. 21 hours), after which time a clear solution was observed. A colourless crystalline solid formed on cooling. The infrared, Mossbauer and ^{119}Sn NMR spectra were run.

Found: C, 26.13; H, 3.28. Calculated for $C_8H_{12}O_8Sn$: C, 27.08; H, 3.41.

(c) Tetratropolonatotin(IV) monohydrate : $Sn(trop)_4 . H_2O$

It was necessary to firstly synthesise sodium tropolonate, $Na^+(trop)^-$, from sodium metal and tropolone. The starting materials were not purified before use.

The sodium (0.5g, 0.02 moles) was dissolved in dry methanol and tropolone (2.67g, 0.02 moles) was then added. An immediate yellow precipitate formed. The mixture was refluxed for 3 hours, but no further visible changes were observed. The reaction was carried out under an inert atmosphere. The product was submitted for analysis to ensure that sodium tropolonate had, in fact, been formed. Found: C, 57.98; H, 3.53. Calculated for $C_7H_5O_2Na$; C, 58.34; H, 3.50.

Tin(IV) tetratropolonate was then synthesised in accordance with the literature method [56]. A solution of tin(IV) tetrachloride (0.99g, 0.44cm^3, 0.004 moles) in 0.44cm^3 methanol was added to a slurry of sodium tropolonate (2.19g, 0.015 moles) in methanol. Acetonitrile (88cm^3) was added. The mixture was refluxed for two days, during which time the solid present appeared to become paler in colour. The solution was filtered while hot and the product dried *in vacuo*.

It was submitted for microanalysis and, in addition, thermogravimetric and differential thermal analysis of a sample (4.89mg) of the complex were obtained. The TGA/DTA traces were recorded within the range 22 - 600° C at a heating rate of 10° C per minute. The sensitivity was 200V and heating was carried out in a nitrogen atmosphere. Infrared, ^{119m}Sn Mossbauer and ^{119}Sn NMR spectra were obtained.

Found: C, 53.70; H, 3.16; Sn, 18.9. Calculated for $C_{28}H_{22}O_3Sn$: C, 54.14; H, 3.57; Sn, 18.11

(d) Monohydrodiethylenetriaminepentaacetatotin(IV) trihydrate : HSn(DTPA).3H_2O

This product was prepared following the method of Krishna Iyer *et al*. [63]. The sodium salt was synthesised initially in accordance with Equation (3-14).

$$3NaOH + H_5DTPA \longrightarrow Na_3H_2DTPA + 3H_2O \qquad (3\text{-}14)$$

The starting materials were commercially available and were not purified before use. A sodium hydroxide solution (2.40g, 0.06 moles, 50cm^3 water) was added dropwise to a stirred slurry of diethylenetriaminepentaacetic acid, (7.87g in 50cm^3 H_2O). A clear solution (0.2M) of Na_3H_2DTPA was formed. This solution was then heated to 90°C and a solution of tin(IV) chloride (5.21g, 2.31cm^3, 0.02 moles in 4.6cm^3 H_2O) was added dropwise with stirring. Turbidity was observed with each addition. This increased during the course of the addition and subsequently decreased. The solution was kept at 90°C for *ca*. 20 mins., after which time it was filtered and allowed to cool. A colourless solid crystallised and this was separated by filtration, washed with a small amount of cold water and allowed to dry in air.

Microanalysis, IR, Mossbauer and ^{119}Sn NMR parameters were obtained.

Found: C, 29.81; H, 4.40; N, 7.39; Sn, 20.8. Calculated for $C_{14}H_{25}N_3O_{13}Sn$: C, 29.92; H, 4.48; N, 7.48; Sn, 21.12.

(e) Ethylenediamenetetraacetatotin(IV) monohydrate $Sn(EDTA).H_2O$

All starting materials were commercially available and were not purified before use. $Sn(EDTA).H_2O$ has been prepared previously [58]. A solution of $SnCl_4$ (2.26g, 1.0cm^3, 0.009 moles) was prepared in ice-cold water (*ca.* 3cm^3) and this was added dropwise with stirring to a solution of $Na_2H_2EDTA.2H_2O$ (3.72g, 0.01 moles). A clear solution was observed initially but, after *ca.* 10 minutes, a white precipitate formed. This was separated by filtration, washed with a small amount of water and allowed to dry. The product was submitted for microanalysis and IR, Mossbauer and ^{119}Sn NMR spectra were obtained.

Found: C, 28.18; H, 3.34; N, 6.53. Calculated for $C_{10}H_{18}N_2O_9Sn$: C, 28.27; H, 3.32; N, 6.59.

3.3.5 Tetrakis(cyclohexanethio)stannane : $Sn(SC_6H_{11})_4$

This was prepared from tetraacetatotin(IV) which was synthesised as previously (Section 3.3.4(b)) using tetraphenyltin (5g, 0.01 moles) and an excess of acetic acid (13.4cm^3) in the presence of acetic anhydride (22.5cm^3).

After refluxing, the acetic acid and acetic anhydride were removed under reduced pressure and the tin(IV) tetraacetate was dissolved in degassed chloroform. A solution of cyclohexanethiol (5.44g, 5.74cm^3, 0.05 moles) in chloroform was then added slowly dropwise with stirring, under an atmosphere of dry nitrogen. A clear solution was obtained, i.e. no change was observed. The solution was allowed to stand for ca. 1 hour and the solvent was then removed under reduced pressure. The white solid formed was recrystallised from methanol.

Microanalytical and Mossbauer data were obtained. No infrared studies were carried out on this complex.

M.p. (sealed tube): 55 - 56°C. Found: C, 50.56; H, 7.43; S, 21.69; Sn, 21.4. Calculated for $C_{24}H_{44}S_4Sn$: C, 49.74; H, 7.65; S, 22.13; Sn, 20.48.

3.3.6 **Tin(II) Carboxylates** : $Sn(O.CO.R)_2$

Tin(II) methoxide was prepared initially. Excess base (Et_2NH or Et_3N) (8cm^3) was added slowly dropwise, with stirring, to a solution of $SnCl_2$ (5g, 0.03 moles) in dried methanol (150cm^3). The reaction was carried out in an atmosphere of dry nitrogen. The white solid which precipitated was filtered off rapidly and dried in vacuo. The carboxylic acid (0.06 moles) and the tin(II) methoxide were refluxed in dried, degassed toluene overnight under an inert atmosphere.

Both solids dissolved in the toluene initially, giving a clear solution. The tin(II) benzoate, a colourless solid, separated on cooling, but the tin(II) β-naphthoate appeared to be insoluble in the hot toluene. Microanalytical data and melting points are given below.

Tin(II) benzoate: M.p. 145 - 150°C (lit. 190°C [85]). Found: C, 46.72; H, 2.91; Sn, 32.6. Calculated for $C_{14}H_{10}O_4Sn$: C, 46.59; H, 2.79; Sn, 32.89.

Tin(II) β-naphthoate: M.p. 209 - 211°C (lit. 157 - 159°C [85]). Found: C, 56.97; H, 3.08; Sn, 25.2. Calculated for $C_{22}H_{14}O_4Sn$: C, 57.31; H, 3.06; Sn, 25.74.

3.4 CONCLUSIONS

(i) From these studies, it can be concluded that the chloroethoxy compounds, $SnCl_{4-n}(OEt)_n$ (n = 1 - 4), are six co-ordinate, whereas tetrakis(cyclohexanethio)stannane is a tetrahedral monomeric species. A trigonal pyramidal structure is predicted by ^{119m}Sn Mossbauer spectroscopy for tin(II) benzoate and tin(II) β-naphthoate.

(ii) The overall order of donor ability of the various ethers studied towards the tin(IV) halides has been established as follows:

THF ≃ diox>3-Me-THF ≃ THP>2-Me-THF>2,5-Me_2-THF>
DHBF>Bz_2O>BzPhO>Ph_2O ≃ Fur

(iii) It appears that, as for organotin compounds, the ^{119}Sn chemical shift of inorganic tin complexes is affected by the co-ordination number of the tin atom, moving to lower frequencies as the co-ordination number increases.

In addition, the 8 co-ordinate complexes, $Sn(NO_3)_4$, $Sn(trop)_4.H_2O$ and $Sn(OX)_4$, had low ^{119m}Sn Mossbauer isomer shifts, indicating that this parameter too is affected by co-ordination number.

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CHAPTER 4

INTERACTION OF TIN COMPOUNDS WITH COAL

4.1 INTRODUCTION

In this Chapter the interaction of both tin(IV) and tin(II) chloride with several different coal types has been studied. The uptake of tin by the various coals was investigated and the tin species present was studied using $119^{m}Sn$ Mossbauer spectroscopy.

The parameters obtained were compared with those of the model compounds discussed in the previous Chapter.

In addition, the effect of drying the coal samples on the tin uptake was studied.

4.2 COAL TYPES STUDIED

Samples of several coals of different ranks were obtained from various sources and Table 4-1 gives their analyses on a Dry Mineral Matter Free (dmmf) or a Dry Mineral Matter and Inorganics Free (dmif) basis. In addition, where these are known, the nature and amounts of the oxygen functional groups present have been included. The coals are arranged in order of increasing oxygen content.

Coal Type	Elemental Microanalytical Data (%)					Oxygen Functional Groups Present	Moisture Content %
	C	H	O	N	S		
Schuylkill[a]	94.8	1.85	1.0	0.9	b	All oxygen is present in the form of ether groups	0.5
Cortonwood[a] Silkstone	87.2	5.6	3.9	1.7	0.7	ca. 66% present as -OH groups ca. 34% present as ether groups	1.0
Cresswell[a]	84.5	5.5	5.9	1.9	1.3	ca. 58% present as -OH groups ca. 42% present as ether groups	2.4
Gedling[a]	81.6	5.2	9.4	1.7	1.0	ca. 54% present as -OH groups ca. 46% present as ether groups	10.0
Herrin No.6[a]	81.9	5.3	11.2	1.6	2.2	ca. 50% present as -OH groups ca. 10% present as ester groups ca. 40% present as ether groups	
Milmerran[a]	79.0	6.3	12.6	b	b	b	
Callide[a]	79.3	3.8	15.4	b	b	b	
Wyodak[a]	76.3	5.5	19.4	1.1	b	Carboxylic, carbonylic; alcoholic, phenolic -OH groups present	18.2
Hagel[c]	71.5	4.4	23.3	0.8	0.3	ca. 40% present as -OH groups ca. 40% present as -COOH groups ca. 12% present as ether groups ca. 4% present as -C=O groups	
Morwell[c]	69.2	4.8	25.2	0.5	0.3	ca. 33% present as -OH groups ca. 30% present as -COOH groups	

[a] Microanalysis determined on a dmmf basis.
[b] Values not known.
[c] Microanalysis determined on a dmif basis.

Table 4-1 Microanalytical Data and Oxygen Functional Groups Present in the Coals Studied

Table 4-1 indicates that coals with a wide range of oxygen contents were studied.

Mass (g) of Tin Added per g Coal	Tin Content After Impregnation (%)						
	Schuylkill	Cortonwood Silkstone	Cresswell	Gedling	Wyodak	Morwell	Hagel
0.06	1.81	1.8, 2.5[a]	2.8	5.5, 2.5[a], 5.8[a]	6.1	6.1, 5.8[a]	8.0
0.13	3.76	2.5, 2.0[a]	4.0	7.7, 9.9[a],	6.6	11.5, 10.2[a]	12.2
0.22	2.82	2.9, 2.0[a]	5.1	7.2	6.8	12.6, 12.2[a]	15.4
0.36	4.94	2.3, 2.9[a], 2.2[a]	4.0	8.2	8.7	13.7, 9.7[a]	21.0
0.56	3.22	2.9	6.1	7.9, 12.8[a]	7.8	17.0, 13.8[a]	20.0
0.88	3.09	4.6, 3.6[a]	7.1	8.5	9.5	18.1, 10.8[a]	21.0
1.51	3.48	3.7, 6.0[a]	6.7	8.6	12.1	17.6	24.0

[a] Repeat experiment of impregnation of coal with $SnCl_4$ (Section 4.6.1)

Table 4-2 Results of Concentration Study of Uptake of Tin, as Tin(IV) Chloride, by Various Coals

4.3 INTERACTION OF TIN(IV) CHLORIDE WITH COALS

4.3.1 Concentration Studies

The uptake of tin, by Schuylkill, Cortonwood, Cresswell, Gedling, Wyodak, Morwell and Hagel coals, was investigated, the coals being impregnated at room temperature from a solution of tin(IV) chloride (anhydrous) in petroleum ether. For these studies, the coals were not dried before use. Table 4-2 shows the amounts of tin taken up by each of the coals at various levels of tin addition. Figure 4-1 is a graphical representation of these results. The Figure indicates that there is a saturation level of tin uptake which varies with the coal type; this may result from either the tin interacting with (a) certain functional groups present within the coal or (b) the moisture which is present within the various coals, the moisture content also varying with rank. In order to investigate possibility (a), the tin saturation level for each coal was plotted against its oxygen content (Table 4-3 and Figure 4-2) and a possible correlation was observed.

Coal Type	Oxygen Content (%)	Tin Present at Saturation Level (%)
Schuylkill	1.0	3.8
Cortonwood Silkstone	3.9	5.6
Cresswell	5.9	7.9
Gedling	9.4	8.5
Wyodak	19.4	10.0
Morwell	23.3	17.8
Hagel	25.2	22.2

Table 4-3 Table of Percentage Tin at Saturation Level for Coals of Different Oxygen Contents

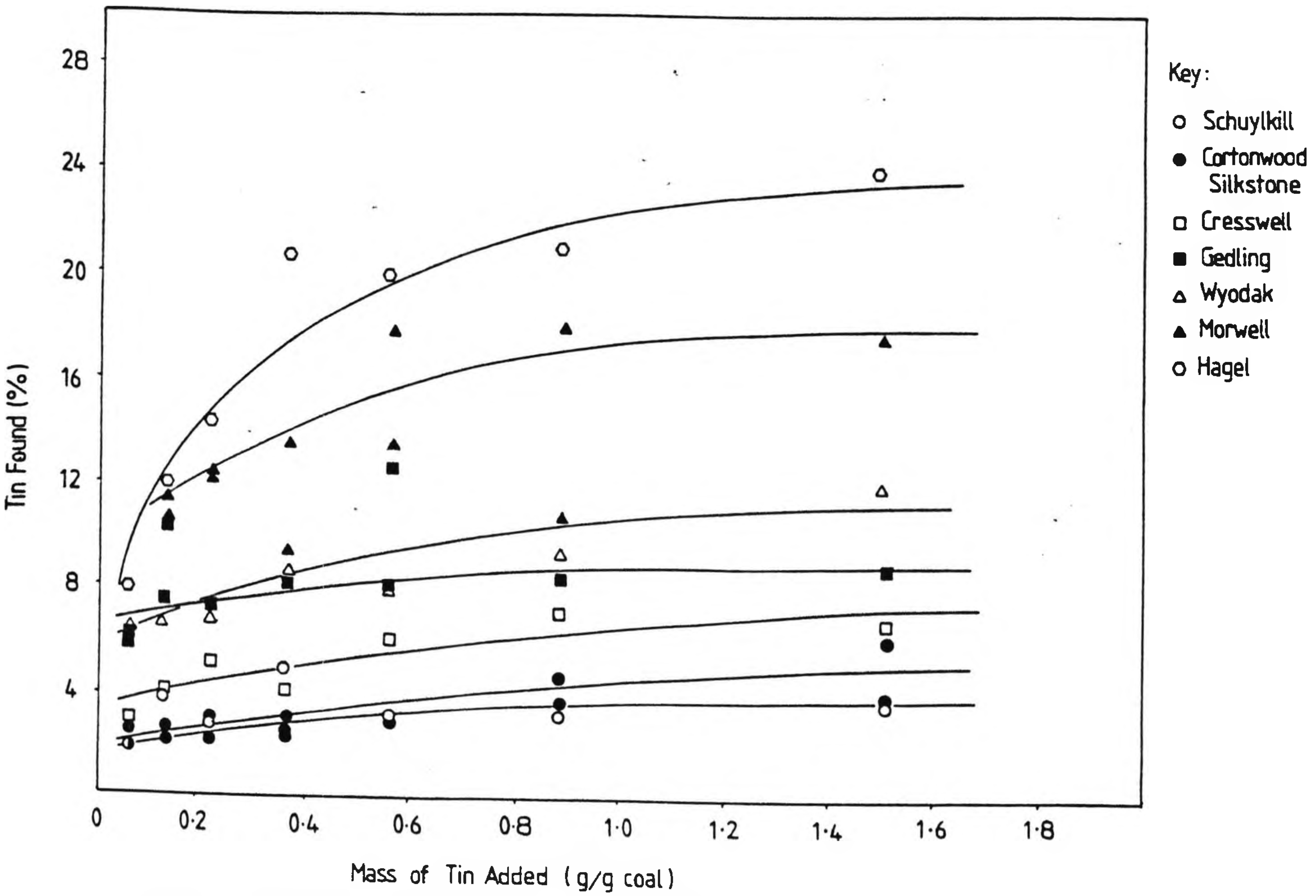


Figure 4-1: Uptake of Tin by Various Undried Coals

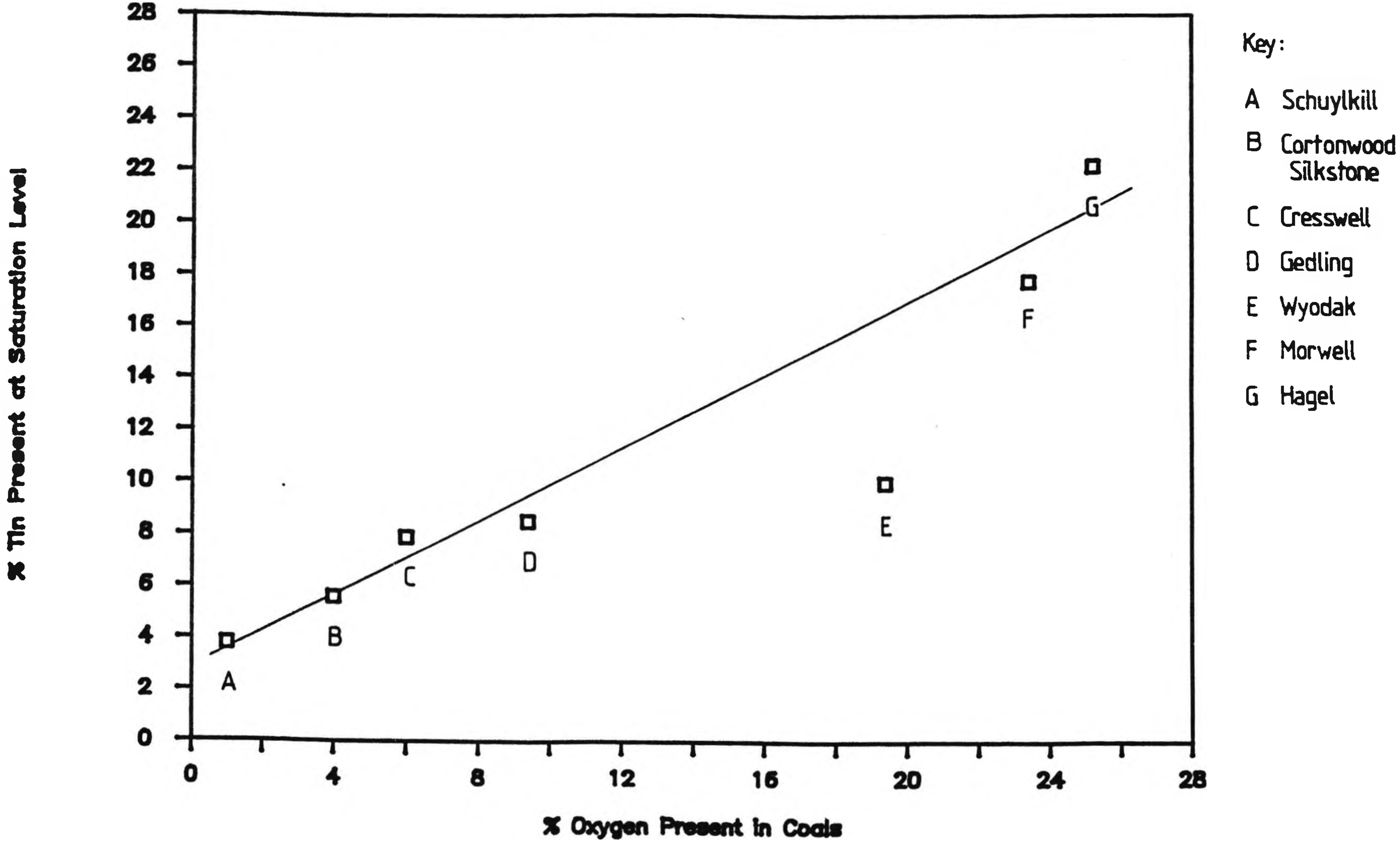


Fig.4-2: Graph of Percentage Tin Uptake Saturation Level as a Function of Amount of Oxygen Present in Coals

The interaction of tin(IV) chloride with a particular oxygen functional group was then investigated by plotting graphs of the percentage tin saturation levels as a function of the percentage oxygen present in the forms of hydroxyl and ether groups within the coals (where these values are known). These are shown in Figure 4-3 and Figure 4-4. It was not possible to draw a similar graph for the carboxyl content, since information on this functional group was only available for the Morwell and Hagel coals. Figures 4-3 and 4-4 indicate a strong correlation with the hydroxyl oxygen, but this is less pronounced with the ether oxygen. These results indicate that the tin(IV) chloride may be interacting with either or possibly both of these functional groups. As described in Chapter 3, tin(IV) chloride reacts readily at room temperature with certain ethers, such as tetrahydrofuran and tetrahydropyran (Section 3.1.1), which are believed [1] to model ether species found in coals.

In addition, the literature and Chapter 3 give evidence to show that tin(IV) chloride will react with certain alcohols at room temperature. Tin(IV) chloride was found to react with methanol forming the adduct $SnCl_4.2MeOH$, as described in Chapter 3, Section 3.1.2. Thus, a room temperature interaction of tin(IV) chloride with hydroxyl-containing species is not unprecedented. However, the results obtained here are specific to the coals studied and an investigation of a larger number of coals would be required for firmer conclusions to be drawn.

The moisture contents of the coals, after air-drying, ie. as received, were provided by the suppliers of Schuylkill, Cortonwood Silkstone, Cresswell, Gedling and Wyodak coals (Table 4-1), and this has been determined empirically for Morwell coal (Section 4.3.3). The possibility that tin may be interacting with the moisture within the coal was investigated by plotting the percentage tin present at saturation level as a function of the moisture content of the coals (Figure 4-5). The results obtained for coals with a high moisture content were very scattered, but those with a lower moisture content did show an increase in uptake as the

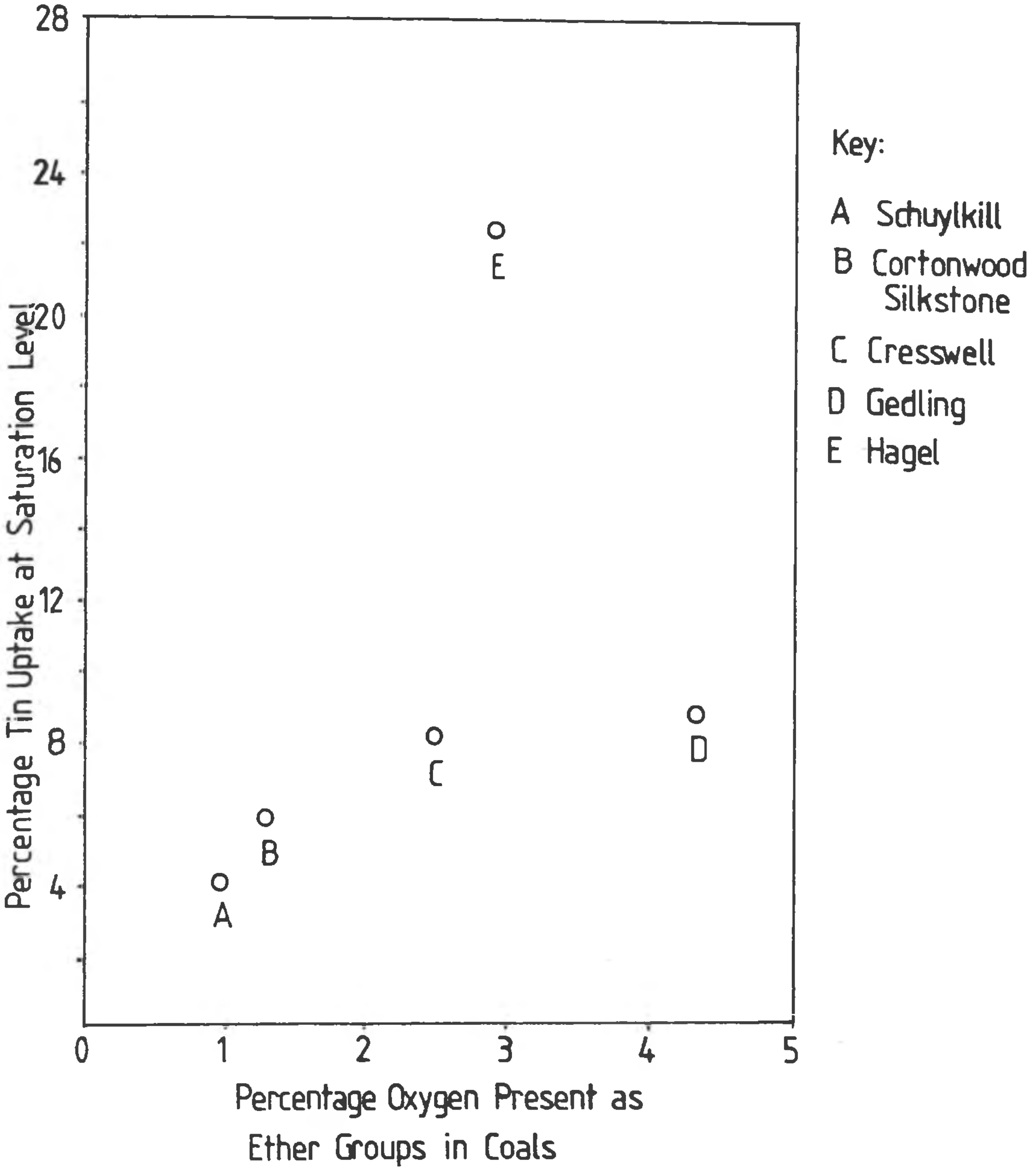


Fig. 4-3: Graph of Percentage Tin Uptake at Saturation Level as a Function of Percentage Oxygen Present in Ether Groups

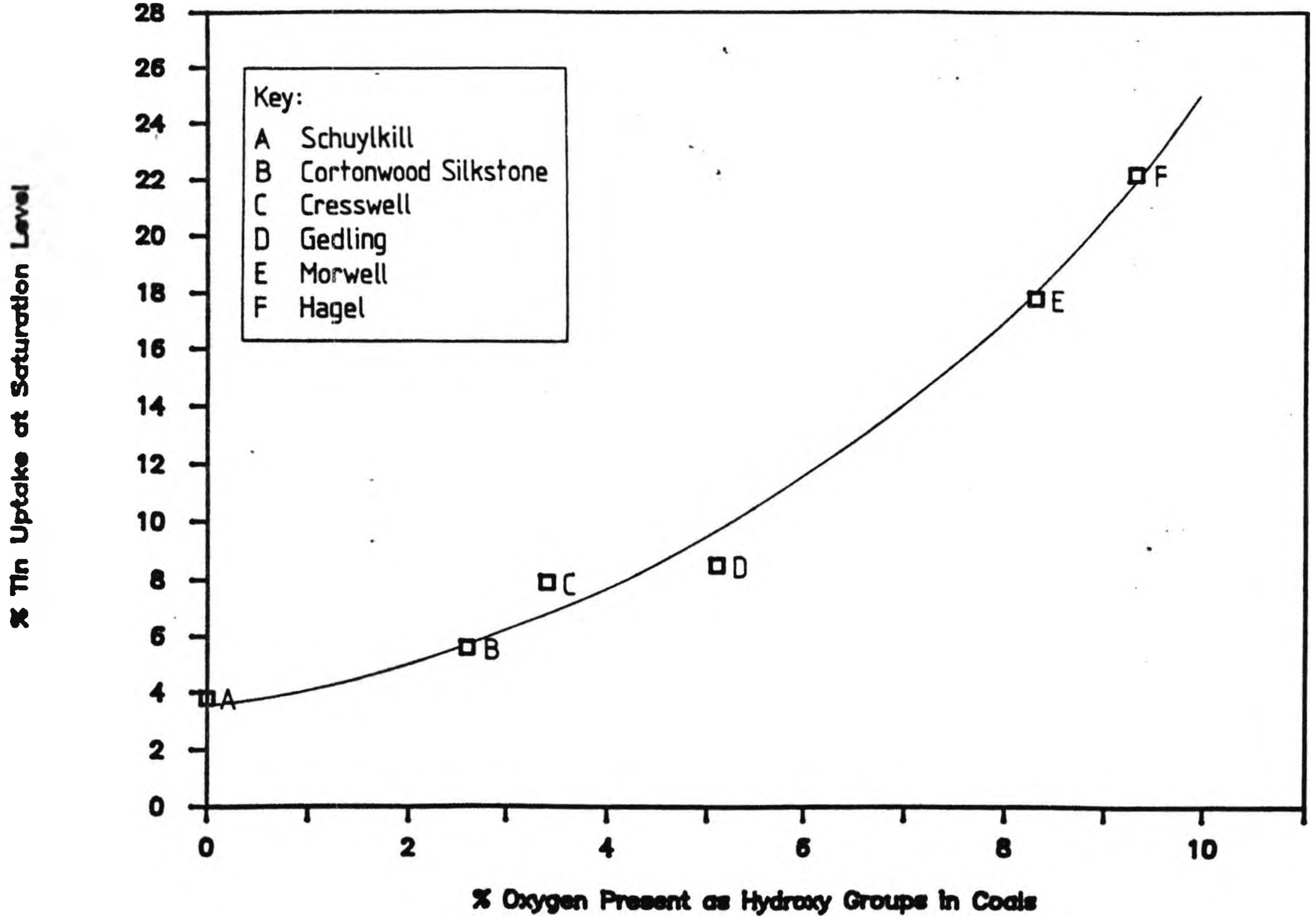


Figure 4-4: Graph of percentage Tin Uptake at Saturation Level as a Function of Percentage Oxygen Present in Hydroxyl Groups

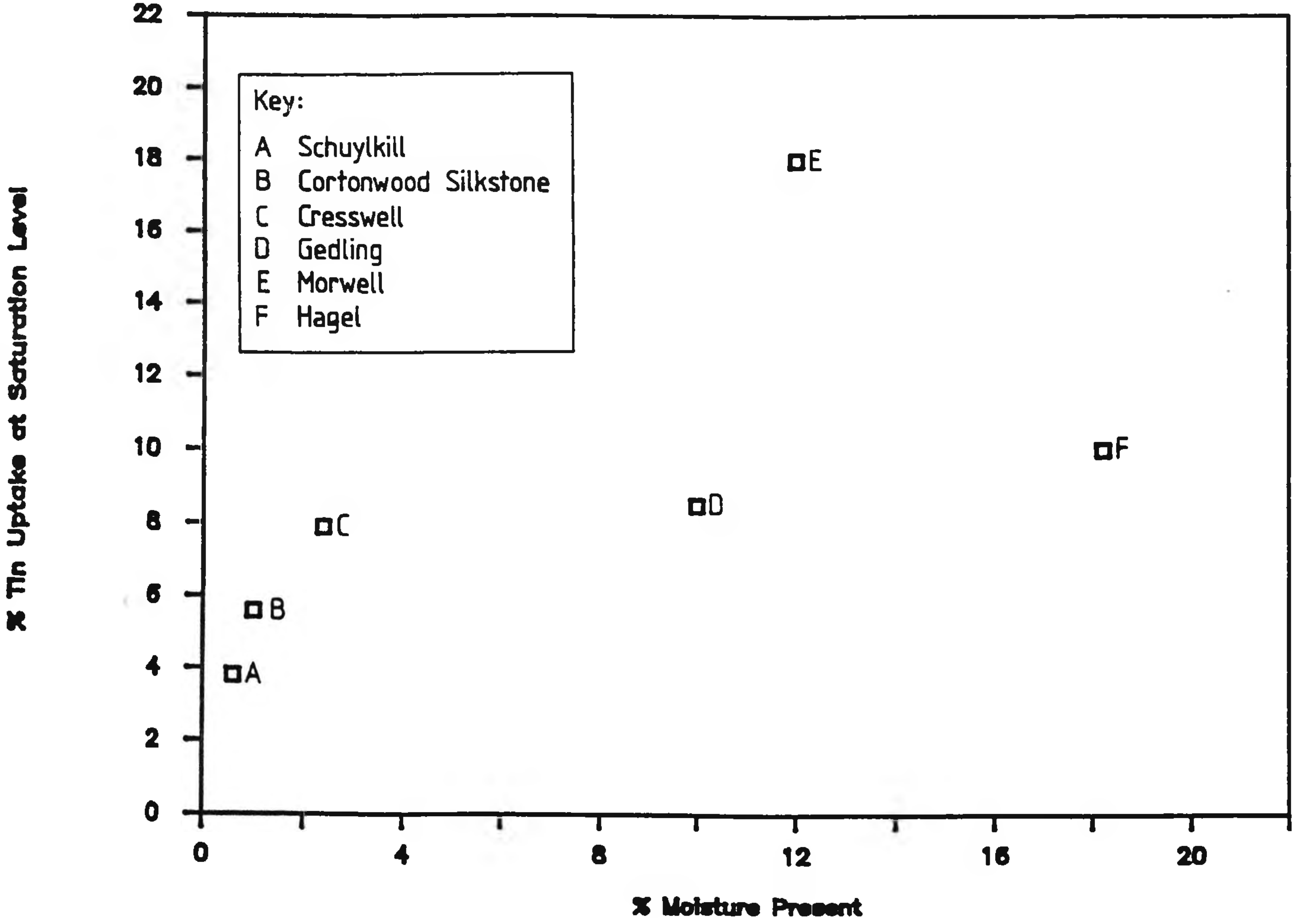


Figure 4-5: Graph of Percentage Tin Uptake at Saturation Level as a Function of Percentage Moisture in Coals

moisture content increased. In order to test the effect of moisture further, Morwell coal was dried by heating to 105°C under a nitrogen atmosphere, the dry coal being impregnated with tin(IV) chloride using the same procedure as that used previously (Section 4.3.1 and Section 4.6.3). The results of these investigations are given in the following section.

4.3.2 Effect of Coal Drying on Tin Uptake

The Morwell coal was dried by heating to 105°C under a nitrogen atmosphere (Section 4.6.2). Table 4-4 shows the tin uptake obtained for different levels of tin added to the dried coal using petroleum ether as solvent. In addition, a small number of experiments were carried out using toluene as solvent, since it has been suggested [3] that the acidic sites within the Morwell coal might be more readily accessed with this solvent. The results obtained are represented graphically in Figure 4-6 and the tin uptakes obtained for the undried Morwell coal are shown for comparison.

Tin Added (g/g Coal)	% Tin Found After Impregnation [a]	% Tin Found After Impregnation [b]
0.06	1.3	1.9
0.13	1.5	2.3
0.22	3.0	-
0.56	1.5	-
0.88	1.3	2.4

[a] solvent: petroleum ether.
[b] solvent: toluene.

Table 4-4 Uptake of Tin(IV) Chloride by Dried Morwell Coal

There does not appear to be a significant increase in the tin uptake when using toluene rather than petroleum ether as solvent. However, the percentage tin found in the dried coal samples was significantly less than that obtained for the coal containing 12% water. These results could indicate that

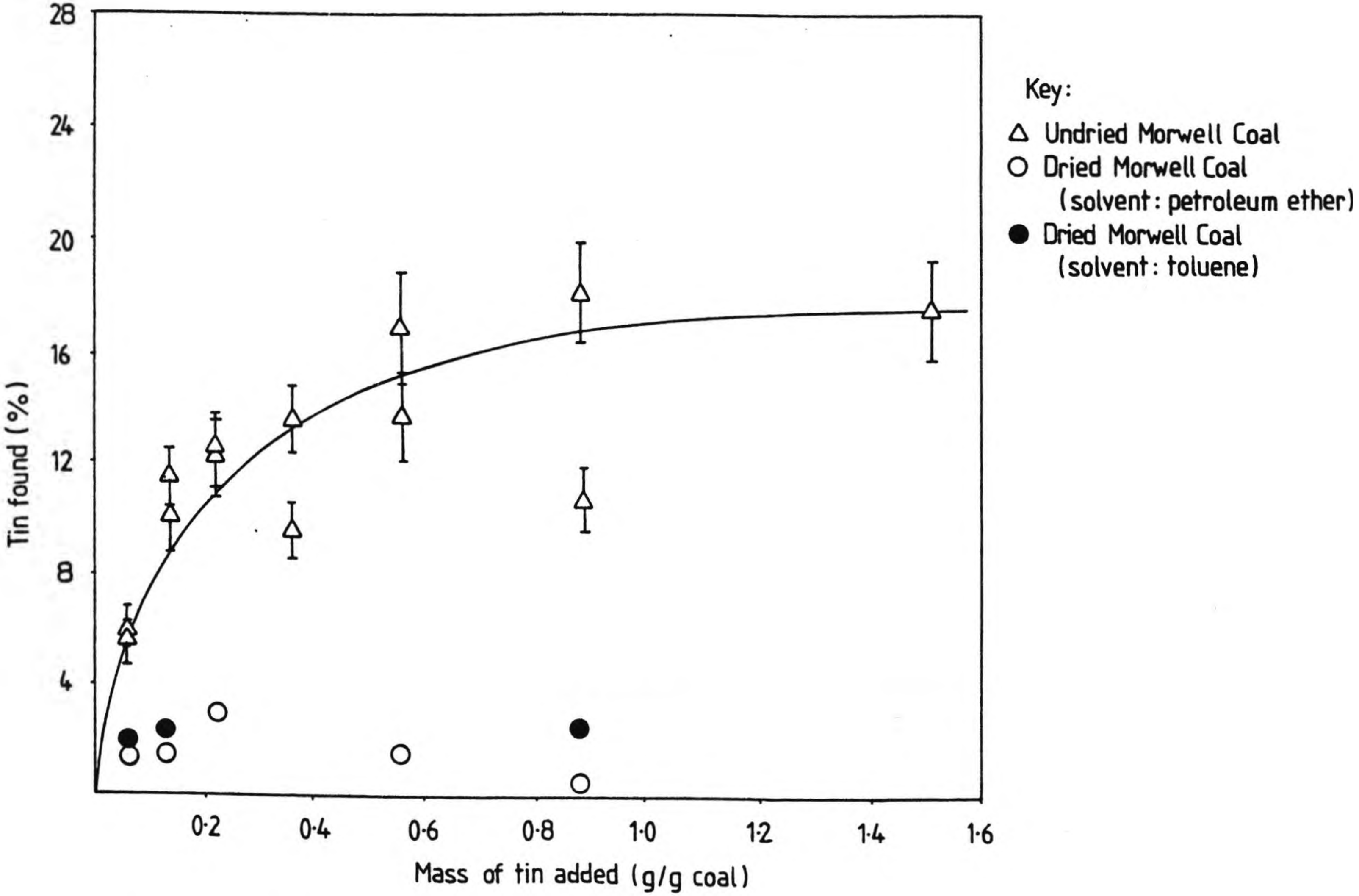


Figure 4-6: Graph of Percentage Tin Uptake for Dried and Undried Morwell Coal

the tin(IV) chloride was reacting with water rather than the coal structure itself. However, it is possible that the drying of the coal has chemically altered the structure of the coal, thus preventing tin uptake. If the tin were reacting with the moisture within the coal, it would be expected that the tin uptake would increase with moisture content for a given coal. An investigation was therefore carried out in which the tin uptake by Morwell coal, to which various amounts of water had been added, was monitored.

4.3.3 Addition of Water to Morwell Coal

A series of Morwell coal samples having different moisture contents was prepared by adding water to "air dried" Morwell coal samples. This was done by placing a coal-water mixture in a vessel under reduced pressure, the vacuum being applied until the required amount of moisture, by weight, was present. The air-dried coal already contains some moisture as explained previously (Section 4.3.1) and the amount present was determined by drying samples of Morwell coal at 105°C, the average value of water content then being calculated. Table 4-5 gives the weights of the coal samples, both before and after drying, and the percentage moisture contents.

Mass of Wet Coal (g)	Mass of Dry Coal (g)	Percentage Moisture Present (wet coal basis)
3.63	3.22	11.3
5.42	4.73	12.7
4.81	4.20	12.7
2.59	2.20	15.1
3.04	2.66	12.5
4.85	4.31	11.1
3.12	2.73	12.5
3.38	3.01	10.9
3.77	3.28	13.0
2.30	2.03	11.7
2.14	1.88	12.1
2.33	2.07	11.2
2.50	2.24	10.4
	Average Value = 12.1	

Table 4-5 Moisture Contents of Samples of Morwell Coal

The Morwell coal samples, to which water had been added, were impregnated with tin from a solution of tin(IV) chloride in petroleum ether and Table 4-6 gives the weight percentage of water contents of the coal samples, and wt. % Sn and, in some cases, chlorine, found after impregnation. Figure 4-7 is a graphical representation of these data. Similar results were obtained for both levels of tin addition, ie. 0.88g Sn/g of coal and 3.28g Sn/g coal and, thus, it appears that, provided there is an excess of tin present, the tin uptake is independent of the amount of tin added to the coal initially. The results also indicate that the tin uptake does increase with the moisture content of the coals, and this appears to be independent of whether toluene or petroleum ether is used as a solvent.

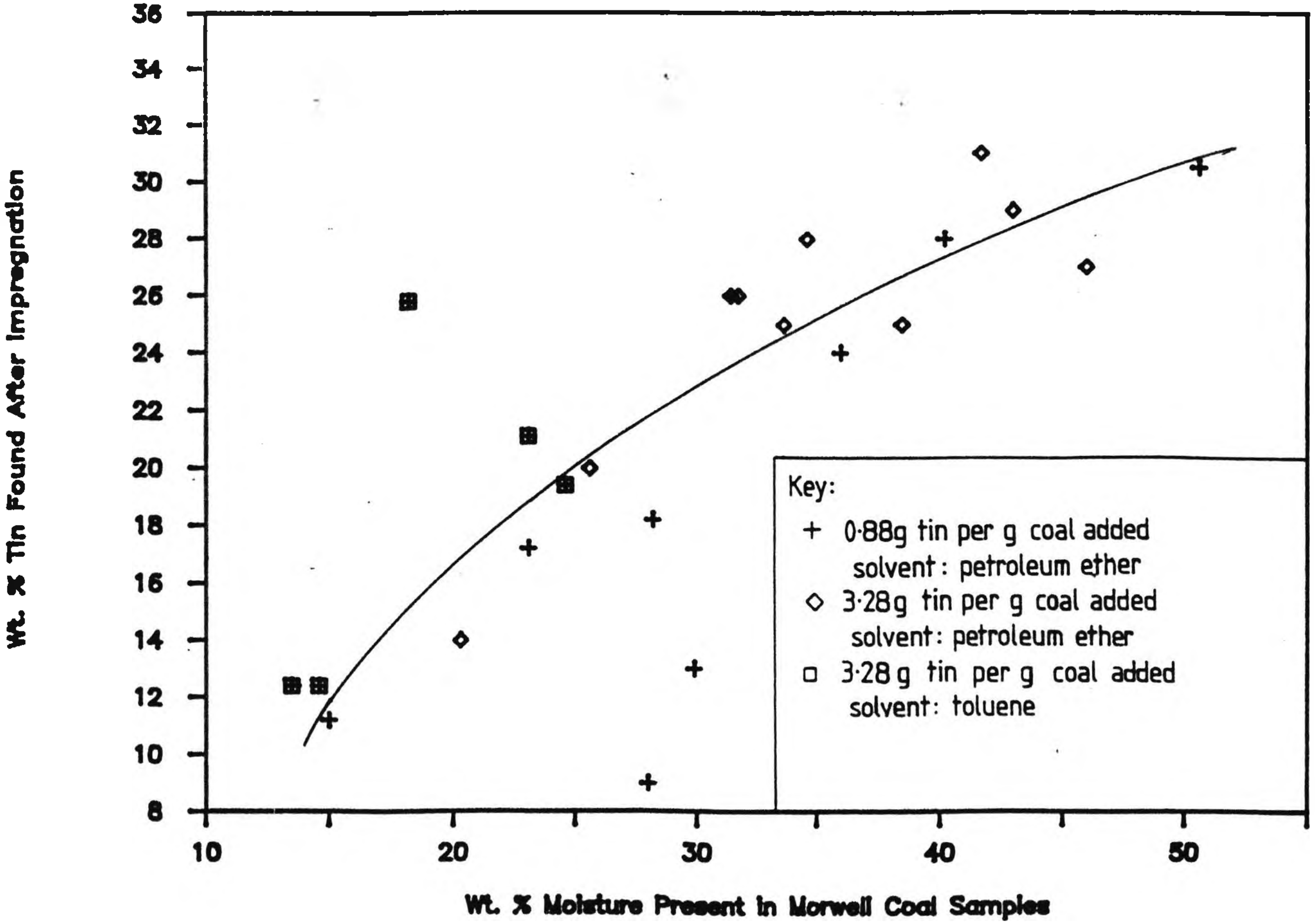


Figure 4-7: Uptake of Tin by Morwell Coal to which Water has been Added

Experiment Number	wt. % H_2O Present (wet coal basis)	wt. % Tin Found After Impregnation	wt. % Chlorine Found After Impregnation
1	31.4	26.0	n.d. [a]
2	41.6	31.0	n.d.
3	20.3	14.0	n.d.
4	33.7	25.0 [b]	n.d.
5	25.6	20.0	n.d.
6	46.1	27.0	n.d.
7	38.5	25.0	n.d.
8	34.6	28.0	n.d.
9	42.9	29.0	n.d.
10	31.5	26.0	n.d.
11	28.2	18.2	24.9
12	23.1	17.3	19.9
13	15.0	11.2	12.7
14	50.5	30.5 [c]	n.d.
15	36.0	24.0	24.5
16	40.2	28.0	30.8
17	29.9	13.0	n.d.
18	28.0	9.0	14.4
19	24.6	19.4	20.1
20	13.5	12.4	15.2
21	18.1	25.8	26.8
22	14.6	12.4	13.3
23	23.1	21.1	21.9

[a] n.d. = not determined.

[b] average of two values: 21.0 and 29.0.

[c] average of two values: 31.0 and 30.0.

Table 4-6 Uptake of Tin by Morwell Coal Samples Having Different Moisture Contents

This implies that the tin is interacting with the water present in the coal.

4.3.4 Mossbauer Studies of Impregnated Coals

4.3.4.1 Transmission ^{119m}Sn Mossbauer Spectra of Impregnated Coals

^{119m}Sn Mossbauer spectroscopy was found to be a very convenient method of studying the coal samples which had been impregnated with tin(IV) chloride.

Table 4-7 shows the Mossbauer results obtained for various coals at low levels of tin addition. The Table also gives Mossbauer data for various inorganic model compounds. The synthesis and Mossbauer spectra of most of these model compounds are discussed in Chapter 3 of this thesis.

It is of interest to note that, for all of the coals studied, an isomer shift of ca. 0.2mm s^{-1} was obtained. As stated previously (Chapter 1), the isomer shift provides information on the chemical environment of the tin atom, since it varies with the co-ordination number of the metal and with the electronegativities of the ligands attached to it. Table 4-8 shows the immediate environment of the tin atoms in some of the model compounds, Mossbauer parameters of which are listed in Table 4-7.

Coal Type/ Model Compound	% Tin Present	Mossbauer Parameters			
		δ (mm s^{-1})	ΔEq (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})
Schuylkill	1.81	0.22	0.0	1.33	-
Cortonwood	{ 2.40	0.12	0.0	1.26	-
Silkstone	{ 1.42	0.20	0.0	1.24	-
Cresswell	n.d.	0.21	0.0	0.80	-
Gedling	5.4	0.21	0.0	1.46	-
Herrin No. 6	5.5	0.22	0.0	1.37	-
Wyodak	6.1	0.21	0.0	1.43	-
Hagel	8.0	0.19	0.0	1.57	-
Morwell	6.0	0.18	0.0	1.41	-
$SnCl_4$ [a]		0.78	0.0	-	-
$SnCl_4.2THF$		0.41	1.23	1.08	1.02
$SnCl_4.2THP$		0.45	1.36	1.00	1.00
$SnCl_4.2(2\text{-}Me\text{-}THF)$		0.49	1.26	1.14	1.23
$SnCl_4.2(3\text{-}Me\text{-}THF)$		0.44	1.12	1.35	1.17
$SnCl_4.diox$		0.41	0.90	1.19	1.26
$SnCl_4.5H_2O$ [b]		0.30	0.0	-	-
$SnCl_3(OMe).MeOH$		0.31	0.70	1.21	1.30
$SnCl_3(OEt)$		0.31	0.46	1.15	1.21
$SnCl_2(OEt)_2$		0.28	0.56	1.04	1.08
$SnCl_2(acac)_2$		0.21	0.0	1.36	-
$SnCl_2(bzac)_2$					
$SnCl_2(bzbz)_2$					
$SnCl(OEt)_3$		0.26	0.74	1.13	1.19
SnO_2 [c]		0.00	0.00	-	-
$Sn(OEt)_4$		0.23	0.62	1.18	1.11
$Sn(OSiPh_3)_4$		0.14	0.0	1.21	-
$Sn(OAc)_4$		0.08	0.2	-	-
$Sn(trop)_4.H_2O$		-0.02	0.0	1.28	-

[a] ref. 4.
[b] ref. 5.
[c] ref. 6.

Table 4-7 ^{119m}Sn Mossbauer Results for Tin(IV) Chloride Impregnated Coals and Model Compounds

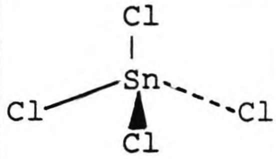
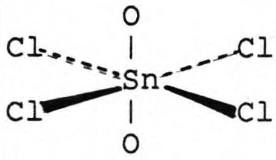
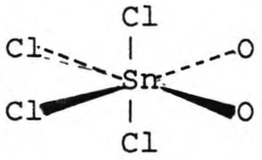
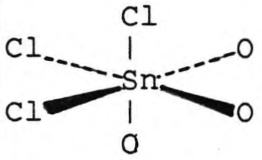
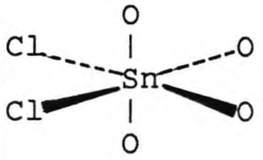
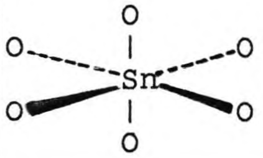
Complex	Sn Environment
$SnCl_4$	
$SnCl_4.2THF$ $SnCl_4.2THP$ $SnCl_4.2(2\text{-}Me\text{-}THF)$ $SnCl_4.2(3\text{-}Me\text{-}THF)$ $SnCl_4.diox$	
$SnCl_4.5H_2O$	
$SnCl_3(OMe).MeOH$	
$SnCl_2(acac)_2$ $SnCl_2(bzac)_2$ $SnCl_2(bzbz)_2$	
SnO_2	

Table 4-8 Table to Show the Environments of the Tin Atoms in Various Inorganic Tin Complexes

The isomer shifts obtained for the coals indicate that the tin is not present as starting material, tin(IV) chloride, the isomer shifts in the coals being much lower than 0.78mm s^{-1} observed for the pure tin(IV) tetrahalide. In addition, it appears that a tin(IV) halide-ether adduct has not been formed, the model complexes of this type all having isomer shifts within the range 0.4-0.5mm s^{-1}. The observed isomer shifts are, in fact, very similar to those obtained for dichlorotin(IV) species, such as $SnCl_2(acac)_2$, $SnCl_2(bzac)_2$ and $SnCl_2(bzbz)_2$, in which the tin atom is in an environment of 2 chlorine and 4 oxygen atoms (X-ray structure of $SnCl_2(bzbz)_2$ is given in Chapter 6).

However, it cannot necessarily be concluded that the tin(IV) species present within the coal is in such an environment, since it is possible that a mixture of tin compounds has been formed, the line widths observed in the coal being, in general, broader than those of the pure model compounds and thus the actual isomer shift observed may result from several overlapping peaks. In order to illustrate this, an investigation of the Mossbauer spectra of mixtures of various amounts of SnO_2 and $SnCl_4.5H_2O$ in graphite was carried out. These two compounds were chosen for study since the isomer shifts obtained for the tin-containing coal species was intermediate between those of these two compounds. The results obtained are shown in Table 4-9.

Mass of SnO_2 (g)	Mass of $SnCl_4.5H_2O$ (g)	% Sn Present as SnO_2	% Sn Present as $SnCl_4.5H_2O$	Mossbauer Parameters δ(mm s^{-1})	Γ (mm s^{-1})
1.51	0	100.0	0	0.05	1.68
1.36	0.36	89.9	10.1	0.06	1.50
1.21	0.71	79.8	20.2	0.07	1.46
1.05	1.06	69.5	30.5	0.09	1.54
0.90	1.41	59.7	40.3	0.09	1.42
0.75	1.76	49.6	50.4	0.12	1.45
0.61	2.11	40.3	59.7	0.15	1.41
0.45	2.46	29.7	70.3	0.18	1.42
0.30	2.81	20.2	79.8	0.22	1.36
0.15	3.16	10.1	89.9	0.26	1.21
0	3.51	0	100.0	0.33	1.17

Table 4-9 Table Showing the Variation in Mossbauer Parameters with Variation in the Amount of SnO_2 and $SnCl_4.5H_2O$ in a Mixture

Figure 4-8 is a graph showing the change in isomer shift as the percent of tin present in the form of SnO_2 decreases. The results obtained indicate that it is possible to obtain a broad Mossbauer resonance similar to that obtained for the tin-impregnated coals from a mixture of tin species. On averaging the isomer shifts obtained for the various tin containing coals, a value of 0.21 is obtained. Such a value would be observed for the $SnCl_4.5H_2O/SnO_2$ mixtures when the amount of tin present in the form of SnO_2 is 22.6%.

It is therefore clear that, although some hydrolysis of the tin(IV) chloride to a species in which the oxygen is in an environment of six oxygen atoms may have occurred, the value of isomer shift obtained within the coals indicates the presence of tin species with mixed chlorine-oxygen environments. Recent ^{119}Sn NMR studies of $SnCl_4.5H_2O$ and $SnCl_6^{2-}$ aqueous solutions [7,8] in both the presence and

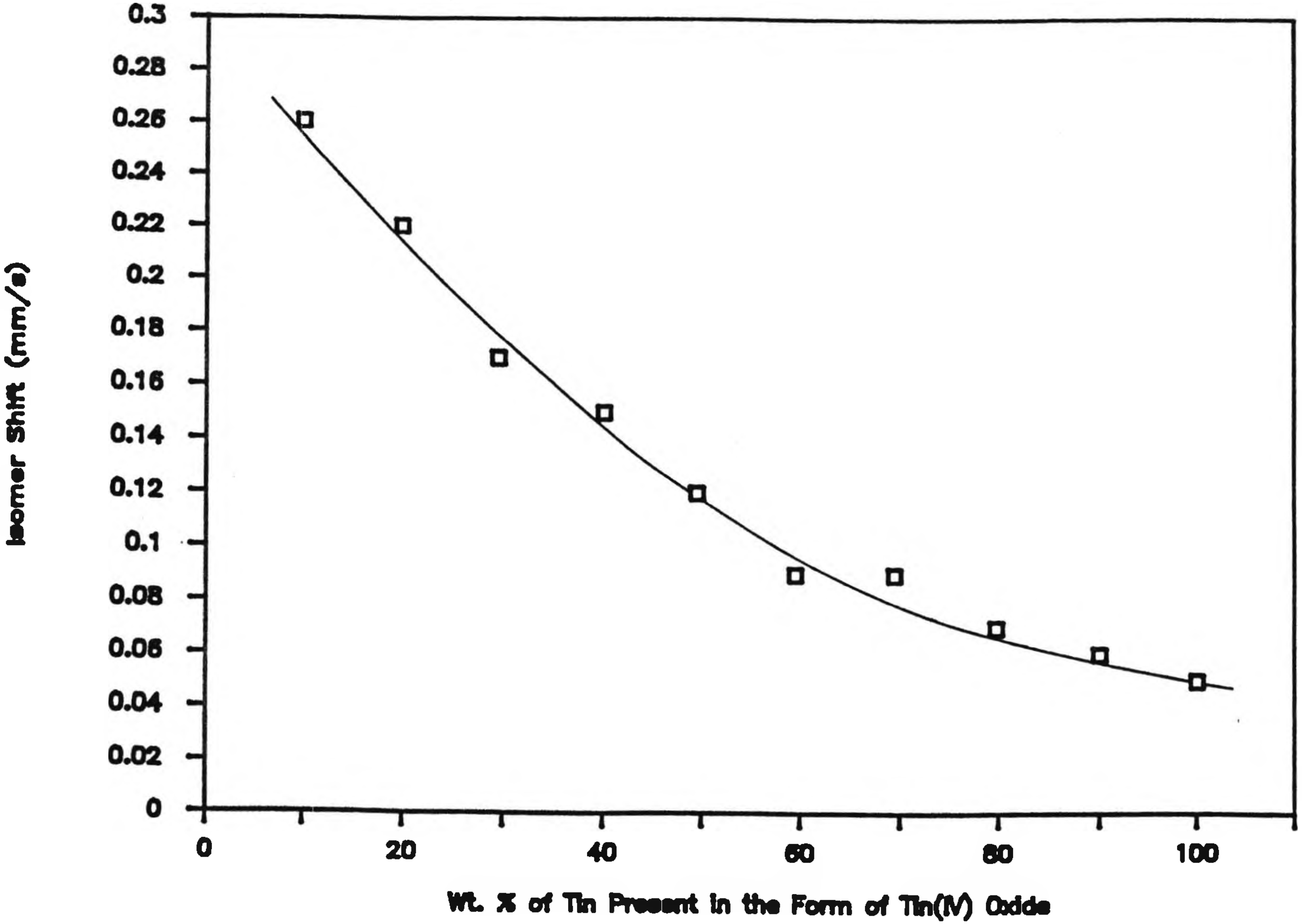


Figure 4-8: Variation of Isomer Shift with Weight Percent of Tin Present in the Form of SnO_2 in $SnO_2/SnCl_4.5H_2O$ Mixtures

absence of HCl have shown that the following species may be formed by hydrolysis: $SnCl(H_2O)_5^{3+}$, $SnCl_2(H_2O)_4^{2+}$, $SnCl_3(H_2O)_3^{+}$ and it is therefore probable that a mixture of similar species have been formed within the coal, the tin(IV) chloride having been hydrolysed by the moisture present.

4.3.4.2 Change in ^{119m}Sn Mossbauer Parameters on Exposure of Coal Samples to the Atmosphere

Some of the coal samples whose transmission ^{119m}Sn Mossbauer parameters have been recorded in Section 4.3.4.1 were exposed to the atmosphere and any changes in the isomer shifts and linewidths were monitored. The results obtained are shown in Table 4-10 and Figure 4-9 is a graphical representation of these results.

Coal Type	No. of Days Exposure	Mossbauer Parameters δ (mm s^{-1})	Γ (mm s^{-1})
Cortonwood Silkstone	0	0.12	1.26
	2	0.07	1.37
	58	-0.01	1.61
Cresswell	0	0.21	0.80
	7	0.09	1.17
Gedling	0	0.21	1.46
	5	0.15	1.44
	54	0.05	1.57
Herrin No. 6	0	0.26	1.28
	18	0.18	1.41
	60	0.05	1.58
Hagel	0	0.19	1.57
	4	0.20	1.58
	28	0.14	1.78
	153	0.09	1.72
Morwell	0	0.18	1.41
	3	0.14	1.42
	9	0.14	1.48
	25	0.10	1.58
	157	0.06	1.71
	191	0.08	1.59

Table 4-10 ^{119m}Sn Mossbauer Results After Exposure of Coal Samples to the Atmosphere

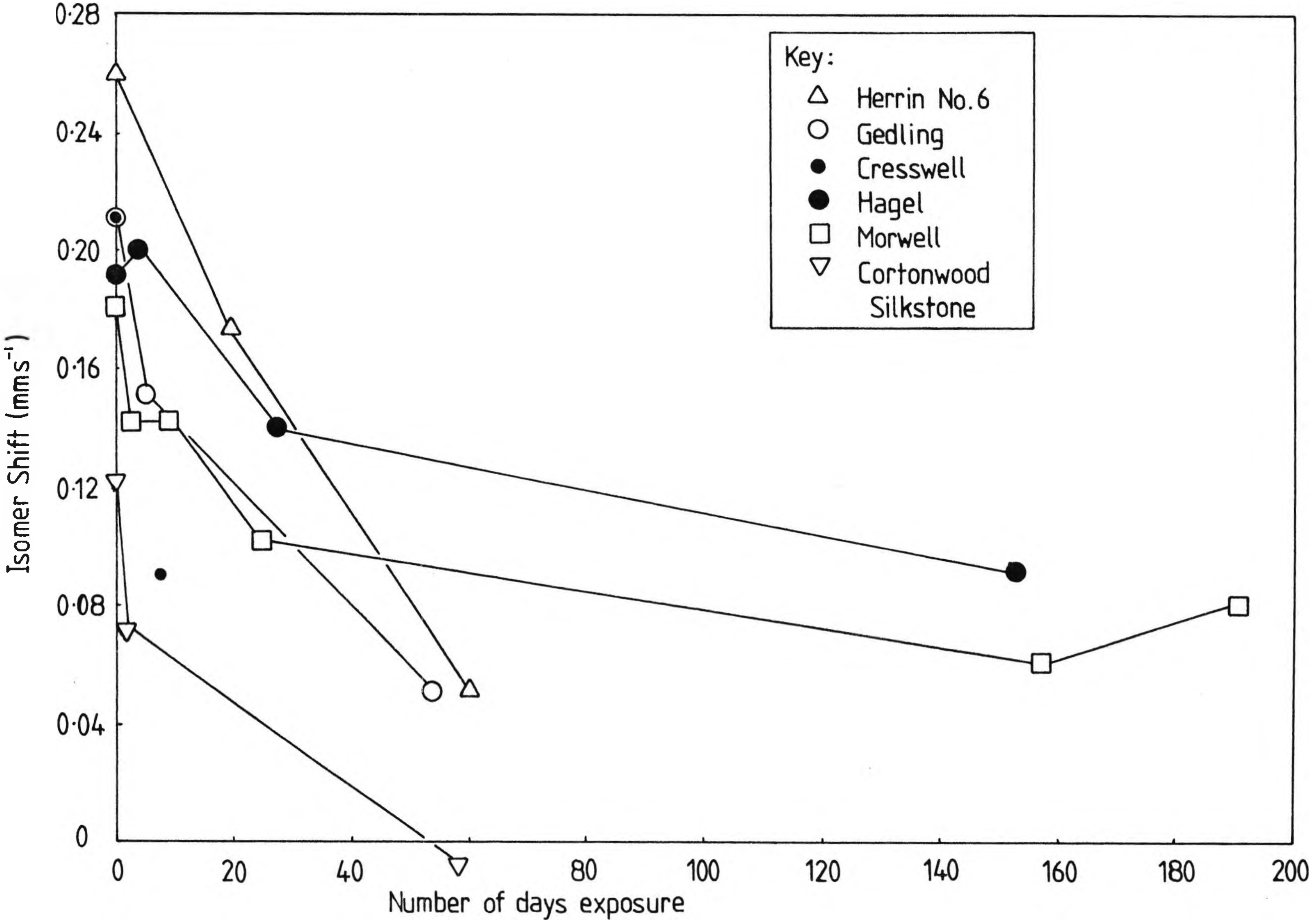


Figure 4-9: Change in Isomer Shift with Exposure to the Atmosphere

In each case, the isomer shift changed, indicating that either some or all of the tin species present immediately after impregnation of the coals were unstable. The isomer shift gradually decreased over a period of time. In only one case-that of Morwell coal-was the sample exposed to the atmosphere until a constant isomer shift was observed, this shift being ca. 0.07mm s^{-1}, although, in all cases, an isomer shift of this order was obtained. This would imply, that, on exposure to the atmosphere, hydrolysis of an unstable tin species within the coal occurred until the tin atom was in a chemical environment similar to that of either SnO_2 or possibly $Sn(OAc)_4$ or $Sn(trop)_4.H_2O$ (Table 4-7). The Mössbauer spectra of the last two compounds have been discussed in Chapter 3. It can therefore be concluded that, after exposure to the atmosphere of the impregnated coal, the tin atoms present were in an environment of oxygen atoms only.

4.3.4.3 Conversion Electron Mossbauer Spectra of Tin-Impregnated Morwell Coal

Conversion Mossbauer Spectroscopy (CEMS) was used to study the surface of the coal samples before exposure to the atmosphere, the principles behind this technique being described in Chapter 1, Section 1.3.1.2. The CEMS parameters of four samples of Morwell coal, which had been impregnated as previously (Section 4.5.1), are shown in Table 4-11.

% Tin Found	Conversion ^{119m}Sn Mossbauer Parameters (mm s^{-1}) δ	Γ
10.2	0.08	0.77
9.7	0.10	0.65
15.2	0.15	0.74
13.2	0.15	0.60

Table 4-11 CEMS Parameters Obtained for Morwell Coal

The isomer shifts and linewidths obtained were significantly lower than the isomer shifts and linewidths observed with the transmission Mössbauer spectroscopy. The lower isomer shift values obtained indicate a greater degree of substitution of chlorine atoms by oxygen atoms in the immediate co-ordination sphere of the tin atoms at the coal surface, as might be expected. This confirms the conclusion that a mixture of tin(IV) species are present within the coal after impregnation (Section 4.3.4.1).

4.4 INTERACTION OF TIN(II) CHLORIDE WITH COALS

Many studies of the effectiveness of tin(II) chloride as a coal liquefaction catalyst have been carried out, as discussed in Chapter 2 (Section 2.2.3.2). Although the interaction of tin(II) chloride with Morwell coal has been extensively studied by Australian workers, [7-10], it was considered of interest to investigate the possible reaction of tin(II) chloride with other coals and study its interaction with Morwell coal in more detail.

A concentration study of the uptake of tin(II) chloride by Morwell coal was carried out, as were Mossbauer studies of the following coals: Morwell, Hagel, Wyodak, Herrin No. 6, Gedling, Cortonwood and Cresswell. The results of these investigations are described in the following subsections.

4.4.1 Concentration Study Using Morwell Coal

The uptake of tin by this coal, both "as received" and after drying, was monitored, the coal samples being impregnated at room temperature from a solution of tin(II) chloride (anhydrous) in acetone following the method outlined in Section 4.6.5. Table 4-12 shows the percentage tin found for both undried and dried coal samples after impregnation for various levels of tin addition. The results are shown graphically in Figure 4-10.

These indicate that drying of the coal has not affected the uptake of tin when added as tin(II) chloride. This contrasts with the results obtained for the tin(IV) chloride (Section 4.3.2) when the tin uptake decreased dramatically on drying the coal. It may therefore be concluded that the tin(II) chloride is not interacting with the moisture present within the coal. However, although a saturation level of tin uptake appears to have been achieved for the dried coal, insufficient experiments were carried out with the undried coal for a definite conclusion to be drawn. The saturation level for the dried coal was found to be 14% Sn.

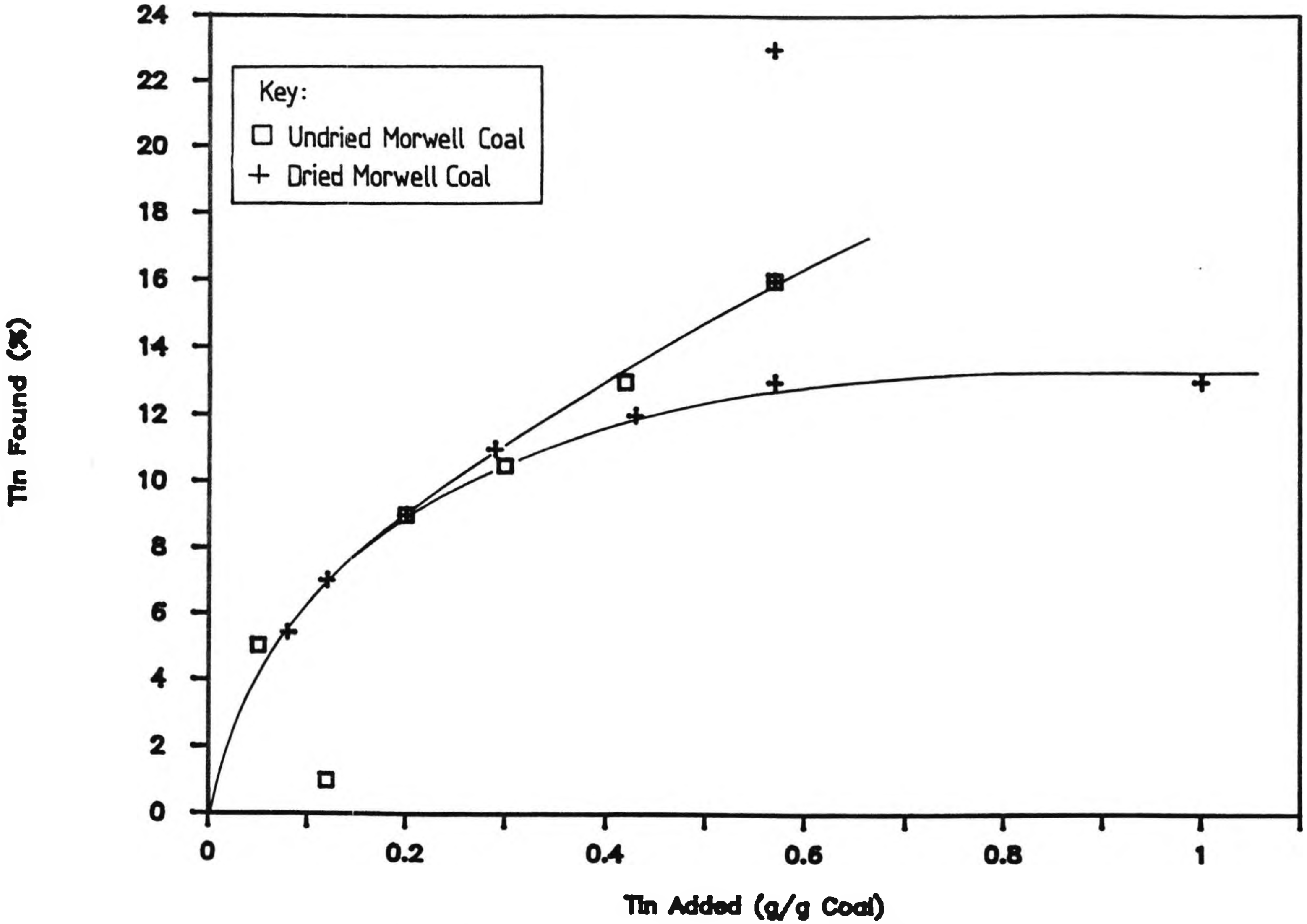


Figure 4-10: Graph of Percentage Tin Uptake by Dried and Undried Morwell Coal Using Tin (II) Chloride

Undried Coal				Dried Coal			
Tin Added (g/g coal)	Tin Found (total) (%)	Tin(II) Found (%)	Chlorine Found (%)	Tin Added (g/g coal)	Tin Found (total) (%)	Tin(II) Found (%)	Chlorine Found (%)
0.05	5.0	<0.1	2.54	0.08	5.5	<0.1	3.0
0.12	<1	<0.1	0.13	0.12	7.0	<0.1	3.67
0.20	9.0	<0.1	4.34	0.20	9.0	<0.1	6.93
0.30	10.5	<0.1	4.52	0.29	11.0	<0.1	6.29
0.42	13.0	<0.1	6.49	0.43	12.0	<0.1	5.87
0.57	16.0	1.6	7.53	0.57	23.0, 16.0, 13.0	<0.1, 0.7, 2.6	5.48, 8.45
				1.00	10.9		

Table 4-12 Results of Concentration Study of Tin(II) Chloride in Dried and Undried Morwell Coal

4.4.2 ^{119m}Sn Mossbauer Studies of Coals Impregnated with Tin(II) Chloride

A series of different coals was impregnated with tin(II) chloride using the procedure described in Section 4.6.5 and the Mossbauer spectra of the resulting samples were run immediately after preparation, to ensure that any tin(II) species present initially would be seen before oxidation. The ^{119m}Sn Mossbauer results obtained for the Morwell coal at various levels of tin addition, and for other coals at a high level of tin addition (1g tin/g coal), both dried and undried, are shown in Table 4-13.

For all of the coal samples, apart from Cortonwood coal, a broad tin(IV) and a tin(II) peak was observed, the value of the isomer shift and the linewidth being similar for all coal types and for both dried and undried coal samples. These results may be compared to those obtained by Cashion and Cook *et al.* [12] (Table 4-13), who suggested that a hydrated tin(IV) oxide species (δ=0.02mm s^{-1}) had been formed *via* ion exchange of tin with metal ions associated with the carboxylate anions found in the coal, followed by hydrolysis of the intermediate tin carboxylate species. A similar isomer shift was obtained by Vaishnava *et al.* [14] on impregnating a different coal (IL6 coal) with an ethanol solution of hydrated tin(II) chloride. However, the values of isomer shift obtained for the coals studied in this work were significicnatly higher than those reported by Cook, Cashion and Vaishnava [12-14]. In fact, the values obtained were very similar to those observed on impregnating the coals with tin(IV) chloride (Section 4.3.4.1). The difference in Mossbauer results observed may result from the impregnation of the Morwell coal by Cook and Cashion [12,13] being carried out using an aqueous solution of the chloride, which may have resulted in the hydrolysis of any intermediate species. In addition, no precautions were taken by the above workers or by Vaishnava [14] to exclude air. It is therefore possible that, in this work, intermediate unstable tin(IV) species have been formed, all experiments being carried out in, and samples being stored under,

Coal Type	Tin Present	Mössbauer Parameters				Ref.
		Tin(IV)		Tin(II)		
		δ	Γ	δ	ΔEq	
Morwell (undried)	5.0%	0.27	1.66	-	-	a
	<1.0%[b]	-	-	-	-	a
	9.0%	0.28	1.21	-	-	a
	13.0%	0.23	1.38	3.39	1.69	a
	16.0%	0.20	1.48	3.30	1.73	a
Morwell (dried)	5.5%	0.24	1.54	-	-	a
	7.0%	0.25	1.58	-	-	a
	9.0%	0.25	1.40	-	-	a
	11.0%	0.23	1.49	3.35	1.72	a
	12.0%	0.24	1.49	3.37	1.76	a
	12.0%	0.24	1.46	3.37	1.74	a
	16.0%	0.24		3.34	1.84	a
	13.0%	0.21	1.42	3.37	1.77	a
Hagel (undried)	17.7%	0.16	1.49	3.26	1.83	a
Hagel (dried)	12.0%	0.21	1.48	3.34	1.70	a
	14.1%	0.19	1.44	3.31	1.79	a
Herrin No. 6 (undried)	8.1%	0.23	1.40	3.25	1.78	a
	12.5%	0.19	1.39	3.23	1.81	a
Herrin No. 6 (dried)	10.4%	0.23	1.43	3.33	1.65	a
Gedling (undried)	8.8%	0.24	1.47	-	-	a
Gedling (dried)	10.4%	0.28	1.36	3.33	1.66	a
Cortonwood (undried)	<0.5%[b]	-	-	-	-	a
Cresswell (undried)	13.1%	0.18	1.42	3.18	1.81	a
Cresswell (dried)	14.9%	0.16	1.58	3.19	1.88	a
Morwell	9.5%	-0.01	-	-	-	c
	2%	0.02	-	-	-	d
IL6	10%	0.01	-	-	-	e
IL6	10%	-	-	3.24	1.62	e

[a] this work.
[b] insufficient tin present for spectrum to be visible.
[c] ref. 13.
[d] ref. 12.
[e] ref. 14.

Table 4-13 <u>^{119m}Sn Mossbauer Results for Tin(II) Chloride Impregnated Coals</u>

an inert atmosphere. The conclusions which may be drawn about the tin(IV) species which have been formed on the basis of the Mossbauer parameters have been discussed in Section 4.3.4.1.

In addition to the broad tin(IV) singlet, a tin(II) doublet was observed in the coal samples having a higher tin content. For all coal samples, whether dried or undried, the values of the isomer shift and quadrupole splitting were similar ($\delta \approx 3.3 mm\ s^{-1}$, $\Delta Eq \approx 1.8 mm\ s^{-1}$). Table 4-13 indicates that a tin(II) doublet with an isomer shift of 3.24mm s^{-1} and quadrupole splitting of 1.62mm s^{-1} was observed by Vaishnava et al. [14] on dry-mixing IL6 (Illinois No. 6) coal with $SnCl_2$, followed by the addition of solvent. They believe that this tin(II) species results from the formation of an addition compound of tin(II) chloride with the coal, although the type of addition compound is not specified. However, Cook, Cashion and their coworkers [12,13] suggest that an unstable tin(II) carboxyl species is formed initially on impregnating Morwell coal with tin(II) chloride.

Some information on the type of species which has been formed may be obtained by comparison of the Mossbauer parameters of the tin(II) impregnated coal with those of model compounds. Some model compounds and their Mossbauer parameters have been listed in Table 4-14.

Model Compound	^{119m}Sn Mossbauer Parameters (mm s^{-1})		Reference
	δ	ΔEq	
$SnCl_2$	4.11 4.17	- -	a b
Acetone solution of $SnCl_2$ stirred under inert atmosphere	} 4.16 } 0.17	- -	a a
$SnCl_2/Me_2CO$	3.53	1.51	b
$SnCl_2.H_2O$	3.87	0.61	b
$SnCl_2.2H_2O$	3.68	1.21	b
$SnCl_2.2THF$	3.39	1.68	b
$SnCl_2.(diox)$	3.76	1.61	b
$Sn(O\ Ph)_2$	2.95	1.76	c
$Sn(OMe)_2$	3.02	1.97	e
$Sn(O.CO.Ph)_2$	3.36	2.10	a
$Sn(O.CO.C_{10}H_7)_2$	3.52	1.62	a
$Sn(O\ Ac)_2$	3.31	1.77	d

[a] this work.
[b] ref. 15.
[c] ref. 16.
[d] ref. 17.
[e] ref. 18.

Table 4-14 ^{119m}Sn Mossbauer Parameters of Tin(II) Model Compounds

Table 4-14 indicates that the tin(II) species present is not simply tin(II) chloride itself, or hydrated tin(II) chloride, the values of the isomer shift obtained in the coal being significantly lower than those of these two species. It is known [15] that tin(II) chloride forms a weak complex with acetone, which was used as a solvent for the coal impregnations. It was therefore important to establish that the isomer shift being observed was not simply due to interaction of the tin(II) chloride with acetone. The Mossbauer parameters of a frozen solution of tin(II) chloride in acetone have been determined by Donaldson and Nicholson [15] (Table 4-14) and the isomer shift obtained is significantly higher than that observed for the impregnated coals. In addition, an experiment has been carried out in which a solution of tin(II) chloride in acetone (degassed) was stirred under an inert atmosphere, thus using similar conditions to those used when impregnating the coal (Section 4.6.5). The solid obtained on removing the solvent was studied by Mossbauer spectroscopy. The tin(II) shift obtained (Table 4-14) is significantly different to that of the coal samples and is in fact similar to that of tin(II) chloride.

Tin(IV) chloride adducts with such ethers as tetrahydrofuran and tetrahydropyran were discussed in Section 3.1.1. Tin(II) chloride adducts with some of these ethers have also been prepared. The values obtained, particularly that of $SnCl_2.2THF$, are similar to those obtained for some of the coal samples. Nicholson and Donaldson [15] believe that the value of the chemical shift obtained in the adducts varies with the strength of the tin-ligand bond, the lower the isomer shift ie. the greater the difference between the isomer shift of the adduct and that of parent compound, the stronger the tin-ligand bond.

However, the values obtained in the coal may also be compared with those of $Sn(OCO.Ph)_2$ and $Sn(OCO.CH_2Ph)_2$ and are found to be similar to that of the $Sn(OCO.Ph)_2$. Such a species would be in agreement with the conclusions of Cashion, Cook et al.

[12,13] who believe that, in Morwell coal, at least, a tin(II) carboxylate species is formed initially. However, Cresswell and Gedling coals do not contain any carboxylate groups and it is therefore not possible that carboxylate species could have been formed in these substrates.

In order to investigate in more detail whether carboxylate species could be formed as a result of reaction of tin(II) chloride with Morwell coal, the interaction of tin(II) chloride with acid–washed and acid–washed decarboxylated Morwell coal was studied.

In acid-washed Morwell coal, the inherent metal ions present in the coal have been replaced by hydrogen ions. In acid-washed decarboxylated coal, these carboxyl groups have been removed. It would therefore be expected that, if the tin(II) chloride were interacting with the carboxyl groups, the tin(II) uptake would be significantly less in the decarboxylated coal sample than in the acid-washed coal. However, the results obtained (Table 4-15) indicate that this is not the case.

Coal Sample	% Tin Found	% Cl Found	Mossbauer Parameters (mm s^{-1})			
			δ	ΔEq	Γ_1	Γ_2
Acid-Washed	10.2	4.29 } 4.70 }	3.74 0.21	1.69 0.0	1.20 1.43	1.28 –
Acid-Washed Decarboxylated	13.2	5.6 } 5.06 }	3.23 0.20	1.81 0.0	0.73 1.40	1.39 –

Table 4-15 Interaction of Tin(II) Chloride with Acid-Washed and Acid-Washed Decarboxylated Morwell Coal

In general, the evidence appears to point to a tin(II) chloride-adduct type of species. This is also more likely in view of the method of impregnation of the coals which was carried out at room temperature. The formation of a tin(II) carboxylate species from tin(II) chloride would require the presence of base, as observed in the commercial synthesis of tin(II) carboxylates [19] (Equation 4-1).

$$SnCl_2 + 2RCOOH + 2NaOH \rightarrow 2NaCl + Sn(OOCR)_2 + 2H_2O \qquad (4-1)$$

4.5 INTERACTION OF TIN(II) OCTOATE WITH COAL

In the small-scale coal liquefaction experiments discussed in Chapter 5, tin(II) octoate {tin(II) bis (2-ethylhexanoate), $[Me(CH_2)_3CHEt.CO.O]_2Sn$}, was used as a catalyst (Section 5.2.1.1) and the Mossbauer spectrum of Morwell coal impregnated with tin(II) octoate and the conclusions drawn are discussed in that Chapter.

4.6 EXPERIMENTAL

4.6.1 Method of Impregnation of the Coals with Anhydrous Tin(IV) Chloride

The Cortonwood Silkstone, Cresswell and Gedling coals were provided by British Coal and they were ground in a mortar and pestle before use. The Morwell coal was provided by Dr. P. Cassidy, Monash University, Victoria, Australia, whereas the Hagel, Wyodak and Schuylkill coals were provided by Dr. A. Grint, B.P. Research Ltd., Sunbury.

For the Cortonwood Silkstone, Gedling and Morwell coals, the coal sample (3.00g) was impregnated by stirring in a solution of tin(IV) chloride in petroleum ether (110cm^3) for 24 hrs, the impregnation being carried out under an atmosphere of dry nitrogen. The coal was then filtered off, washed with petroleum ether (ca. 90cm^3) and dried in vacuo.

For the Hagel, Schuylkill, Wyodak and Cresswell coals, the same procedure was followed and the coal sample (2.00g) was again impregnated by stirring with tin(IV) chloride in petroleum ether (73cm^3).

4.6.2 Drying of Morwell Coal

Figure 4-11 shows the apparatus used for the drying of the coal. The stopper and pyrex tube with tap were weighed and a sample of Morwell coal was then placed inside the tube and the tube, stopper and coal were re-weighed. The glass tube was then placed inside a heating coil and was flushed with nitrogen gas. The heating coil was heated to 105°C and the coal was dried to a constant weight.

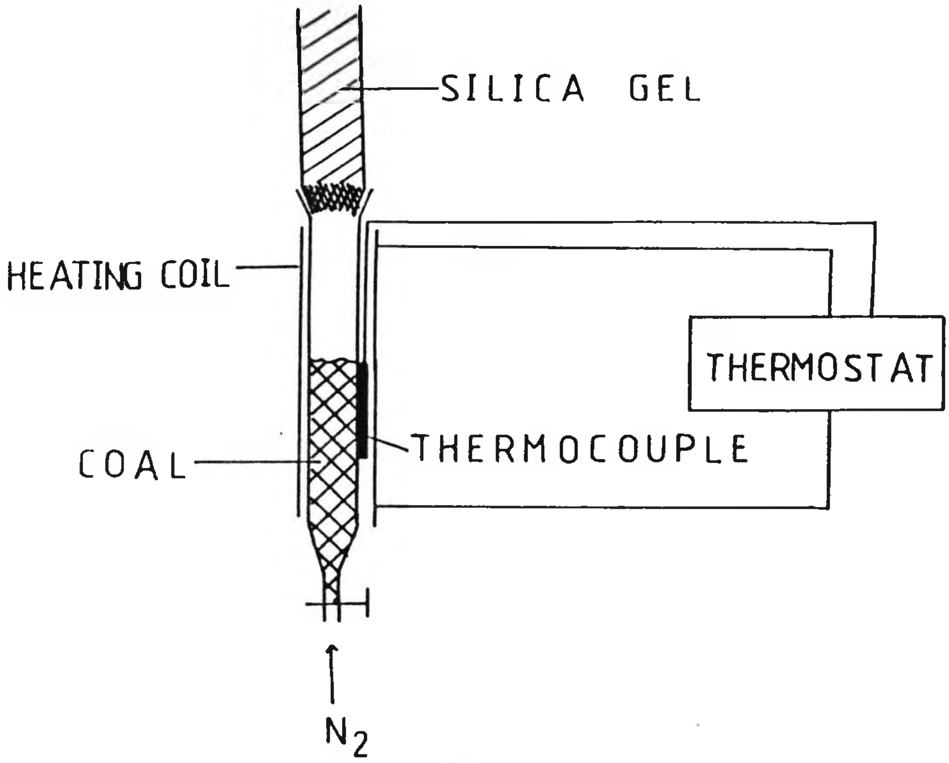


Figure 4-11 Apparatus Used for Drying of Coal

4.6.3 Impregnation of Dried Morwell Coal with Tin(IV) Chloride

The dried coal was impregnated with tin(IV) chloride in the manner described in Section 4.6.1. The masses of coal and tin(IV) chloride and volumes of petroleum ether used are shown in Table 4-16. In addition, a small number of experiments were carried out using toluene as a solvent, rather than petroleum ether, and the quantities used are shown in Table 4-16.

Mass of Coal (g)	Mass of Tin(IV) Chloride (g)	Volume of Petroleum Ether (cm^3)	Volume of Toluene (cm^3)
4.36	0.54	100	-
3.20	0.90	73.3	-
3.16	1.55	73.3	-
3.39	4.12	77.7	-
2.59	4.99	59.0	-
3.69	0.45	-	84.5
3.39	0.94	-	77.7
3.09	5.96	-	70.9

Table 4-16 Table Showing Amounts of Coal, Tin(IV) Chloride and Solvents Used in Dry Coal Experiments

4.6.4 Addition of Water to Morwell Coal

A two-necked flask fitted with stopper and tap was weighed and a sample of air-dried Morwell coal (ie. Morwell coal containing 12.1% moisture on a wet coal basis) was placed in the flask, which was re-weighed. Excess distilled water was added to the coal and the coal-water mixture was placed in vacuo. The flask was periodically flushed with nitrogen gas and re-weighed until the required mass of water was present. The actual percentage water content of a particular coal sample was calculated, assuming that the air-dried coal initially contained 12.1% water, by weight (wet coal basis). In this way, a range of coal samples having different moisture contents were obtained. These coal samples were impregnated with tin(IV) chloride as described previously (Section 4.6.1). For experiments 19-22, the solvent was toluene, whereas, for all other experiments, petroleum ether was used.

Table 4-17 shows the weights of the coal samples and the amount of water present for each experiment. For experiments 1-10, 3.28g of tin per gram of coal were added to the coal sample and, for experiments 11-23, 0.88g of tin per gram of coal were used.

Experiment Number	Mass of Coal (dry) Used (g)	Mass of H_2O Present (g)	Volume of Solvent (cm^3)
1	2.62	1.20	141
2	1.78	1.27	113
3	1.02	0.26	50
4	1.78	0.90	99
5	1.28	0.44	64
6	1.32	1.13	90
7	1.85	1.16	110
8	2.02	1.07	113
9	2.82	2.12	180
10	0.87	0.40	50
11	4.39	1.72	204
12	5.20	1.56	246
13	9.91	1.54	222
14	1.52	1.55	112
15	1.03	0.58	59
16	1.13	0.76	69
17	1.22	0.52	64
18	1.21	0.47	61
19	3.21	1.05	155
20	1.93	0.30	81
21	2.27	0.50	101
22	2.64	0.45	113
23	2.66	0.80	126

Table 4-17 Table Showing the Weights of Components Used When Adding Water to Coal

4.6.5 Method of Impregnation of Coals With Anhydrous Tin(II) Chloride

The undried coal samples (3g) were impregnated by stirring in a solution of tin(II) chloride in acetone (dried and de-gassed, 110cm^3) under an atmosphere of dry nitrogen for 24 hrs. The coal was then filtered off in a glove box, washed with acetone (ca. 90cm^3) and dried in vacuo.

The dried coal samples were impregnated in a similar way and the masses of coal and tin(II) chloride and the volume of acetone used are shown in Table 4-18.

Coal Type	Mass of Coal (g)	Mass of Tin(II) Chloride (g)	Volume of Acetone (cm^3)	Tin Added (g/g coal)
Morwell	2.98	0.37	110	0.08
	3.29	0.62	120	0.12
	2.24	0.70	74	0.20
	2.03	0.95	74	0.29
	1.81	1.25	68	0.43
	2.08	1.90	76	0.57
	1.24	1.14	65	0.57
	2.10	1.98	79	0.59
Hagel	1.48	1.39	55	0.59
	1.67	2.67	61	1.00
	1.74	2.83	65	1.01
Herrin No. 6	2.21	1.98	79	0.56
	2.01	3.24	74	1.01
Gedling	2.79	4.35	99	0.98
	2.16	3.47	80	1.01
Cortonwood	2.05	3.27	120	1.00
Cresswell	1.78	2.80	65	0.98

Table 4-18 Table Showing the Amounts of Coal, Tin(II) Chloride and Acetone Used in Dry Coal Experiments

4.7 CONCLUSIONS

(i) It is probable that, on impregnating the various coals studied with tin(IV) chloride, an interaction between the $SnCl_4$ and the moisture present in the coal occurs.

(ii) ^{119m}Sn Mossbauer spectroscopy (both transmission and conversion) indicates that a mixture of tin(IV) species is formed. In some of these tin species, the tin atoms are believed to have a mixed chloride/oxygen environment. However, at the surface of the sample, it appears that complete hydrolysis to an SnO_2-type species has occurred.

(iii) At least some of the tin species formed were found to be unstable on exposure to the atmosphere.

(iv) Impregnation of the coals with tin(II) chloride does not result in an interaction between this compound and the moisture present in the coals.

(v) Mossbauer spectroscopic studies suggest that the tin(II) chloride appears to be reacting with ether type groups present within the coals and undergoing oxidation.

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CHAPTER FIVE

SMALL-SCALE COAL LIQUEFACTION EXPERIMENTS

5.1 INTRODUCTION

These reactions were carried out to test whether tin could be used as a catalyst for the coal liquefaction process, giving a product which could be upgraded to yield transport fuels. The main requirements of such a catalyst are that it should:

(i) promote cracking to appropriate lower molecular weight compounds;

(ii) promote hydrocracking to upgrade the hydrogen content of the product;

(iii) promote the removal of unwanted heteroatoms;

(iv) withstand the conditions normally adopted in a liquefaction process without being poisoned or deactivated;

(v) be readily regenerated to its original activity;

(vi) be as inexpensive as possible.

5.2 EXPERIMENTS USING TIN(II) OCTOATE

5.2.1 Results and Discussion

In this Section, the potential of tin(II) octoate as a liquefaction catalyst is discussed.

The impregnation experiments described in Chapter 4 involved the use of tin(II) chloride and tin(IV) chloride. As pointed out in Chapter 2, some of the literature supports the claim that the presence of halogen enhances the activity of tin catalysts [1, 2, 3, 4]. However, in this work, it was considered undesirable to liquefy chlorine-containing coals in an autoclave in the absence of a glass liner, because of possible corrosion problems. Tin(II) octoate, $[Me(CH_2)_3 \cdot CH \cdot Et.CO.O]_2Sn$, was chosen because it is commercially available and, since it is soluble in light hydrocarbon solvents, it should be readily dispersed within the coal, this type of solvent being more compatible with the coal than an aqueous solution. This has been noted by other workers [1, 5, 6, 7], who used tin(II) naphthenate and organotins as catalysts.

5.2.1.1 Analysis and Impregnation of the Coals

The analyses of the Morwell (Victorian Brown) and Point of Ayr coals are shown in Table 5-1.

	Element (%)			Proximate Analysis		
	C	H	S	Volatiles	Moisture	Ash
Morwell	60.06	5.10	0.42	46.9	12.4	3.3
Point of Ayr	67.55	4.33	2.70	32.3	3.73	14.0

Table 5-1: **Analyses of Morwell and Point of Ayr Coals**

Three methods of impregnation were investigated in the case of the Morwell coal (Section 5.5.1) on a small scale (5g coal) and these all resulted in a tin content of about 1.6%. Since washing of the sample had no effect on the tin content, this indicates that the tin(II) octoate adheres strongly to the Morwell coal. Tin analysis of two larger samples which were finally submitted for liquefaction (M1 and M2) gave a tin content of 1.5 ± 0.2% Sn. Analysis of several small samples taken from these bulk samples indicated that the tin was homogeneously distributed throughout the coal.

Eight methods of impregnation of the Point of Ayr coal were investigated on a small scale (Section 5.5.1). The levels of tin found are shown in the table below:

Method of Impregnation[a]	1	2	3	4	5	6	7	8
% Tin Found	0.7	0.7	0.8	0.7	0.9	1.3	0.7	0.8

[a] See Section 5.5.1

In most of the impregnation experiments, and in contrast to the data for Morwell Brown coal, not all of the tin added to the Point of Ayr coal was taken up, presumably because of the presence of less absorption sites in the Point of Ayr coal. Even when a higher tin:coal weight ratio of 3.0% (Methods 5 and 8) was used, the level of tin found was not significantly increased above 0.8 - 0.9%. Method 6, however, gave a final tin concentration which indicated that most of the tin(II) octoate had been retained within the coal and this method was therefore used to prepare four larger samples for liquefaction (A1 - A4). Since the presence of moisture may have affected the activity of the tin(II) octoate when used with Morwell coal (which was not pre-dried), the Point of Ayr coal was carefully dried before impregnation, even though it contained less moisture (Table 5-1). Samples A1 and A2 were found to contain 3.4% tin after impregnation and samples A3 and A4 contained 7.0% and 7.4% tin respectively.

The ^{119m}Sn Mossbauer parameters of the tin-impregnated samples M1 and M2 and A1 to A4 are in Table 5-2. These results indicate that the tin(II) species present after impregnation was probably tin(II) octoate, the isomer shift obtained being within the range of values observed for tin(II) carboxylates, including tin(II) octoate. There was no evidence of a strong interaction using the vacant p orbitals of the tin atom, as this would reduce the isomer shift of the tin species. Since there was a reduction in Δ Eq on absorption, the absorption must involve either

(i) use of lone-pair electrons, or

(ii) formation of (coal species)-O-Sn interactions, which weaken the Sn-O bonds.

Although care was taken to keep the coal in an inert atmosphere, some oxidation of tin(II) to tin(IV) was observed in the Mossbauer spectra. This oxidation, which apparently resulted from the interaction of the tin(II) with

Sample	Tin(II)(mm s^{-1})				Tin(IV)(mm s^{-1})			
	δ	ΔE_q	Γ_1	Γ_2	δ	ΔE_q	Γ_1	Γ_2
M1	3.34	1.84	1.32	0.73	0.08	0.0	1.72	-
M2	3.20	1.91	1.31	0.75	0.12	0.70	0.73	0.99
A1	3.25	2.01	0.80	1.64	-0.03	0.0	2.09	-
A2	3.27	1.97	1.23	1.12	0.05	0.0	2.31	-
A3	3.25	1.92	1.27	1.27	-0.03	0.0	2.85	-
A4	3.22	1.96	1.14	1.10	0.11	0.0	2.57	-
$[Me(CH_2)_3CHEt.CO.O]_2Sn$[a]	3.22	2.12	0.93	0.93				
$[Me(CH_2)_3CHEt.CO.O]_2Sn$[b]	3.22	2.02	c	c				
$[HCO.O]_2Sn$[d]	3.15	1.56	c	c				
$[ClCH_2CO.O]_2Sn$[d]	3.20	1.66	c	c				
$[MeCO.O]_2Sn$[d]	3.31	1.77	c	c				
$[C_{17}H_{35}CO.O]_2Sn$[e]	3.57	1.76	0.90	1.26				
SnO_2[f]	0.00	0.65	c	c				
Tin-treated coal containing $SnO_2.xH_2O$[g]					0.02	0.58	c	c
5%$SnO_2.xH_2O$ on cotton[h]					0.07	0.0	1.82	-
5%$SnO_2.xH_2O$ on PVC[i]					-0.01	0.0	1.70	-
10%$SnO_2.xH_2O$ on PVC[i]					-0.02	0.0	2.20	-

[a] Mossbauer parameters of frozen solution
[b] Ref. 8
[c] Line widths not reported
[d] Ref. 9
[e] Ref. 10
[f] Ref. 11
[g] Ref. 12
[h] Ref. 13, x = 1.8
[i] Ref. 14, x = 1.8

Table 5-2: **Mossbauer Parameters of Morwell and Point of Ayr Coals Impregnated with Tin(II) Octoate** oxygen-containing species, has been observed previously [12, 15 - 17] and, in some cases (e.g. $SnCl_2$ in Morwell coal), oxidation was complete [12].

It is possible to compare the ratio of the tin(II) and tin(IV) peak areas for the Morwell and Point of Ayr coals (Table 5-3) although, because of the difference in the Mossbauer fractions between the tin(IV) and tin(II) species, these values do not represent the actual tin(II):tin(IV) ratios. In general, the ratios of the areas under the tin(II) peaks to those under the tin(IV) peaks were greater for the Point of Ayr than for the Morwell coal, indicating that there was less oxidation of the tin(II) species when using the former [as expected because Point of Ayr coal contains less oxygen on a dry weight basis (Chapter 4)].

Sample	M1	M2	A1	A2	A3	A4
$A_{tin(II)}/A_{tin(IV)}$ [a]	0.51	0.74	1.34	0.99	0.75	2.82

[a] $A_{tin(II)}$ = area under tin(II) peak
$A_{tin(IV)}$ = area under tin(IV) peak

Table 5-3: Ratios of Areas Under Mossbauer Peaks for the Impregnated Coals

5.2.1.2 Yields of Liquid Products

The liquid products obtained on hydrogenating the tin-treated Morwell coal samples M1 and M2, a Morwell coal sample (M3) which contained no catalyst, and the tin-treated Point of Ayr coal samples, A1 to A4, were vacuum distilled into fractions. These products were analysed by gas chromatography and were divided into groups, depending on their boiling points, using the chemical markers designated in Table 5-18 (Section 5.5.5) and numbered 1-4. Table 5-4 shows the yields obtained in each group.

Sample	% Tin	Yield (% daf coal)					
		Group 1 <175° C	Group 2 175 - 220° C	Group 3 220 - 260° C	Group 4 260 - 270° C	Total	
						<260° C	<270° C
M1	1.6	13	1	7	9	21	30
M2	1.6	19	5	12	11	36	47
M3	0	15	6	12	13	33	46
A1	3.4	10.33	8.00	8.63	25.93	26.96	52.89
A2	3.4	7.19	3.59	4.81	20.00	15.59	35.59
A3	7.0	10.42	5.00	6.15	24.27	21.57	45.84
A4	7.4	12.65	5.00	6.58	25.15	24.23	49.38

Table 5-4: **Yields of Products from the Liquefaction of Coals Using Tin(II) Octoate as Catalyst**

The results obtained for the Morwell coal indicated that, under the conditions of the experiment, there was very little improvement in the yields of liquid products obtained in the presence of tin catalyst, sample M1 in particular giving a very low yield.

The yield of liquid products obtained from the Point of Ayr coal was only slightly increased by increasing the amount of tin present. Thus, it may be inferred that there is no particular advantage in increasing the tin concentration from 3.4% to 7.0%. These yields may be expressed in terms of the peak areas obtained from the gas chromatographs and they may then be compared with figures available [18] for the dissolution of Point of Ayr coal in the absence of hydrogen and catalyst, as shown in the table below:

Sample	Yields (% total peak area)[a]	
	<260° C	<270° C
A1	7.28	14.28
A2	4.21	9.61
A3	5.61	11.92
A4	6.30	12.84
Blank sample[b]	2.70	5.60

[a] % total peak area of gas chromatograms

[b] Results obtained for dissolution of Point of Ayr coal in the absence of hydrogen and catalyst

From these results it can be inferred that the presence of both tin and hydrogen increase the yields of liquid products obtained from the coal. In addition, no products were collected in the cold trap in the case of the blank sample, whereas they were when catalyst and hydrogen were used.

Table 5-5 gives details of hydrogen and carbon contents and the H/C ratios of the distillation fractions of the Morwell coal samples.

Fraction	M1			M2			M3		
	C %	H %	H/C Ratio	C %	H %	H/C Ratio	C %	H %	H/C Ratio
Cold Trap	87.86 87.13	10.16 10.04	1.39	88.03 88.03	12.23 12.16	1.67	85.36 84.66	12.79 12.74	1.80
275-300 C	87.73 87.87	10.42 10.53	1.43	87.97 87.75	10.31 10.17	1.40	89.64 88.07	10.45 10.39	1.41
<275 C	No sample			86.28 86.46	10.32 10.19	1.43	No sample		

Table 5-5: **Carbon and Hydrogen Contents and H/C Ratios Obtained for Morwell Coal Samples**

One of the aims when producing liquids from coal is to increase the H/C ratio [19]. For these experiments, the H/C ratio of the liquid products was similar for the catalysed and the uncatalysed reactions, indicating that the presence of tin has not assisted in the addition of hydrogen (Table 5-5).

The fact that this tin compound did not promote the liquefaction of the Morwell coal may seem surprising, in view of the large amount of literature which supports the conclusion that tin compounds are active catalysts for this process (Chapter 2). However, it should be noted that, in the majority of the studies quoted in the literature, the yields were based on solvent solubilities, and would not represent a yield value in a liquefaction process where distillation is used to indicate the product yield. In addition, a higher concentration of catalyst was used for many of the reactions [15, 19, 20, 21].

There is some evidence to suggest that catalytic activity was not observed in this case because the temperature used in the reaction (350°C - 400°C) was too low. Hawk [1] found that tin(II) naphthenate gives higher yields of liquid products at 500°C than at lower temperatures and short residence times. Boucher [2], who studied the upgrading and hydrogenation of nitrogen-containing model compounds, came to the conclusion that tin(II) and tin(IV) phthalocyanines are only active as catalysts in the presence of halogen. This may be true of tin(II) octoate. However, it should be noted that the workers from Monash University, in particular, believe that there is no significant dependence of the liquefaction yield on the initial tin compound [16] and other investigators indicated that some organotin compounds are active, even in the absence of halogen [22, 23].

Another possible cause of the failure of tin to promote the reaction is the presence of moisture within the coal, which has been found [17] to deactivate certain catalysts, including tin, decreasing the yield of oils and asphaltenes, compared with that obtained for dry coal. Hydrolysis of the tin moieties may be the reason for the deactivation in the presence of moisture.

Table 5-6 shows the sulphur contents of the hydrocracked products and the tin and sulphur contents of the insoluble residues obtained from the Point of Ayr coal samples.

Run Number	% Sulphur hydrocracked products	% Sulphur insoluble residues	% Sn insoluble residues
A1	0.118	6.75	16.3
A2	0.122	6.36	16.5
A3	0.132	5.32	25.5
A4	0.121	5.92	21.9

Table 5-6: **Sulphur and Tin Analyses of Hydrocracked Products and Insolubles Residues**

This coal is known to contain 2.70% sulphur (Table 5-1) and, thus, the tin compound has been active in the removal of sulphur, there being only a very small amount of this element present in the hydrocracked product. Tin has been shown previously to be active in the removal of sulphur [22], although Kawa [23] found that it was not as effective at desulphurisation as a molybdenum catalyst.

5.2.1.3 ^{119m}Sn Mossbauer Studies of Liquefaction Residues

The ^{119m}Sn Mossbauer spectra of the washed filter cakes, i.e. the insoluble residues from the liquefaction experiments, were recorded and the parameters obtained are shown in Table 5-7.

The Mossbauer spectrum of the residue from sample M2 is shown in Figure 5-1. Four peaks were distinguishable, two of these being present in the tin(II) region of the spectrum. Comparison of the Mossbauer parameters of the tin(II) species present in all of the coal samples (Table 5-7) with those of tin(II) sulphide and with those obtained by Cook et al. [12] and Vaishnava et al. [21] for their coal liquefaction residues indicate that, after the reaction, the tin was at least partially present in the form of SnS, in agreement with electron microscopy [27]. This indicates that the tin catalyst appears to have an affinity for the sulphur in both coals. The asymmetry of the tin(II) resonances observed in the spectra of M2 and A2 and by Cook [12] suggests that there may be some β-Sn present. The isomer shift of β-Sn in Morwell coal was found by them to be 2.53mms^{-1} (Table 5-7) and its position therefore coincides with that of the low energy peak of tin(II) sulphide. Thus, the presence of β-tin would be expected to increase the height of that peak, as observed. The sulphur

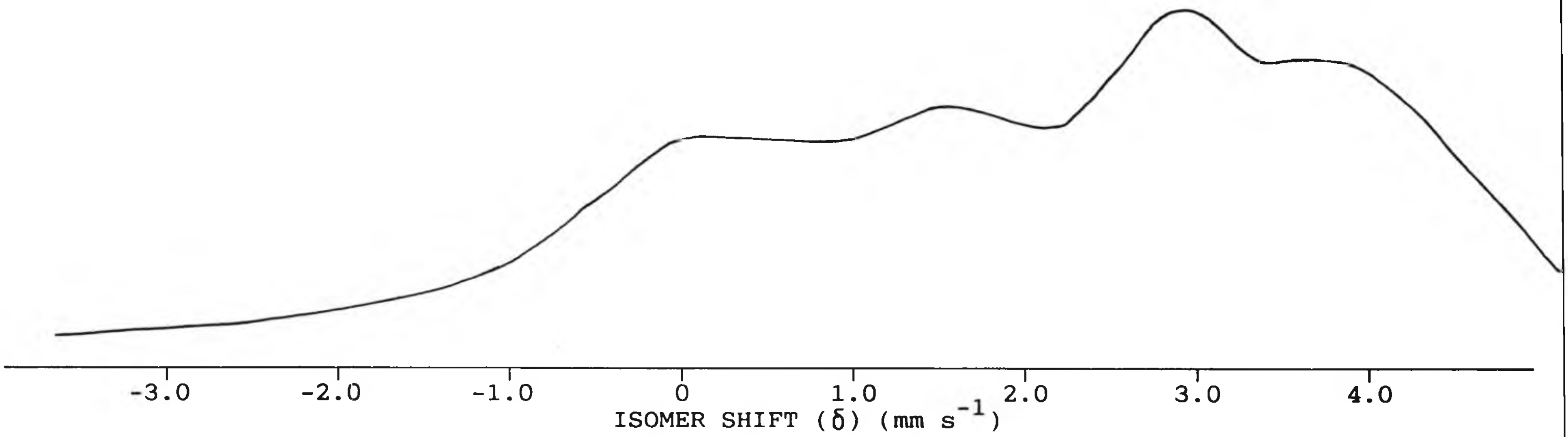


Figure 5-1: <u>Mossbauer Spectrum of Residue from Morwell Coal Sample M2 After Liquefaction</u>

Sample	Mossbauer Parameters							
	Tin(O)		Tin(II)			Tin(IV)		
	δ	ΔE_q	δ	Δ	Γ	δ	ΔE_q	Γ
M1[a]			3.36	0.91				
M2[a]			3.28	1.03		1.53 0.19	0.0 0.0	
A1[a]			3.34	0.92	0.94,1.11			
A2[a]			3.34	0.93	0.99,0.98	0.28	0.0	2.08
A3[a]			3.25	0.87	0.82,1.82	0.37	0.0	2.01
A4[a]			3.30	0.95	0.94,1.58	0.67	0.0	4.17
SnS[a]			3.32	1.05				
SnS in Morwell coal liquefaction residue[b]			3.28	0.96				
SnS in Illinois No.6 coal liquefaction residue[c]			3.30	1.33				
SnO_2[d]						-0.03	0.0	
$SnO_2.xH_2O$ in Morwell coal liquefaction residue[b]						0.03	0.58	
SnO_2 in Illinois No.6 coal liquefaction residue[c]						0.07	0.54	
β-Sn[d]	2.60	0.0						
β-Sn in Morwell coal liquefaction residue[c]	2.53	0.0						
SnS_2[a]						0.73	0.0	
SnS_2[e]						1.05	0.0	
$Sn(SC_6H_{11})_4$[a]						1.31	0.0	
$Sn(SPh)_4$[f]						1.47	0.0	
Unidentified tin(IV) species in Morwell coal liquefaction residue[b]						1.54	0.0	

[a] This Work
[b] Ref. 12
[c] Ref. 21
[d] Ref. 14
[e] Ref. 24
[f] Ref. 25

Table 5-7: Mossbauer Parameters of Coal Liquefaction Residues and Model Compounds contents of the Point of Ayr residues (Table 5-6) were much higher than those of the Morwell coal residues (M1, 0.38%S, M2, 0.25%S and M3, 0.39%S), reflecting the higher sulphur content of the coal itself. Thus, the presence of any β-Sn in the samples A1, A3 and A4 may have been masked by the much greater intensity of the tin(II) sulphide doublet. No asymmetry is observed in the spectrum of sample M1.

Although no tin(IV) species were observed in the M1 spectrum, two peaks were present in this region in the spectrum of sample M2. One of these, a singlet having an isomer shift of 1.53mm s^{-1}, has been observed previously [12]. Its isomer shift was similar to that of tin-sulphur compounds of the type, $Sn(SR)_4$. Tetrakis(cyclohexanethio) stannane, $Sn(SC_6H_{11})_4$, was prepared as a model compound (Chapter 3) and its Mossbauer parameters, and those of $Sn(SPh)_4$ [25], are shown in Table 5-7. These compounds are believed to be tetrahedral monomers and it is possible that the unknown species found in the coal residue contains a tin atom in an environment of four sulphur atoms. SnS_2 is octahedral [26, 27] and this compound was included in Table 5-7 to show that it does not appear to be present.

The other tin(IV) peak (δ = 0.19mm s^{-1}) was probably due to the presence of SnO_2. The abnormally high isomer shift may result from the presence of another tin(IV) species with higher isomer shift.

The spectra of the residues obtained from the Point of Ayr coal, except for sample A1, showed a broad tin(IV) peak, the isomer shift of which varied for each sample. It may therefore be concluded from this information that these residues contained a mixture of tin(IV) species. It is of interest to note that the sample which contained only tin(II) species (sample A1) gave the highest conversion to liquid products. Thus, the conversion of the tin additive to tin(II) sulphide may be an important part of the liquefaction process.

5.3 EXPERIMENTS USING TIN CATALYSTS SUPPORTED ON ALUMINA

Since catalysts consisting of nickel/molybdenum or cobalt/molybdenum on an alumina support are used for the hydrocracking stage of the coal liquefaction process [18], it was of interest to investigate the performance of analogous tin-based materials. A solution of Point of Ayr coal in recycle solvent was used. The first two alumina-supported tin catalysts, in which the tin is believed to be present as SnO_2, were used for duplicate experiments A5 to A8. A higher concentration of tin on alumina was used for sample A9. In experiment A10, the intention was to test alumina-supported SnS_2 as a catalyst, since the SnO_2 catalysts used in the other experiments usually appear in the form of a sulphide in the liquefaction residues. Thus, it was of interest to investigate whether a sulphide form of the tin additive was catalytic. Unfortunately, Mossbauer results have indicated (Table 5-9) that attempts to obtain tin(IV) sulphide on the alumina support were unsuccessful.

5.3.1 Results and Discussion

5.3.1.1 Impregnation of Alumina Support

The results of the Sn, Cl, S and H_2O analyses of the tin-impregnated alumina support before use and the ^{119m}Sn Mossbauer parameters are given in Table 5-8 and 5-9 respectively.

Species	Run Number			
	A5 and A6 (% found)	A7 and A8 (% found)	A9 (% found)	A10 (% found)
Sn	14.5	11.9	18.2	10.3
Cl	0.0	<0.3	not determined	not determined
S	not determined	not determined	not determined	0.16
H_2O	0.4	0.8	0.6	0.6

Table 5-8: **Analysis of Tin-Impregnated Alumina Supports**

The method of preparation of catalyst A10 is given in Section 5.5.3(b) and involved the reaction of tin(IV) chloride on alumina with sodium sulphide. SnS_2 was the expected product but the sulphur analysis of sample A10 indicates that the tin:sulphur mole ratio is 18:1 and not 1:2. Thus, a large amount of the sulphur has been lost. The actual tin species present was deduced from the ^{119m}Sn Mossbauer spectrum of sample A10. The ^{119m}Sn Mossbauer parameters of all samples A5 - A10 are given in Table 5-9.

Number	Mossbauer Parameters (mm s^{-1})[a]		
	δ	Δ Eq	Γ
A5 and A6	-0.26	0.0	2.48
	-0.23	0.0	2.36
A7 and A8	0.06	0.0	2.08
A10	0.05	0.0	2.68

[a] Mossbauer parameters of sample A9 not determined.

Table 5-9: **Mossbauer Parameters of Tin-Impregnated Alumina Support**

Although identical methods of preparation were used for samples A5/A6 and A7/A8, significantly different isomer shift values were obtained. The presence of an SnO_2-type species for A7 and A8, in which the tin atom is co-ordinated to six oxygen atoms, is consistent with the Mossbauer data.
The Mossbauer spectrum of the tin-treated alumina support used for samples A5 and A6 was repeated because of the unusually low isomer shift. Only a species in which the atom is bonded to oxygen atoms is believed to be possible on considering the method of impregnation and the analysis of the support. In general, an increase in co-ordination number of the tin atom is associated with a decrease in the isomer shift, since there is increased polarity, Sn - X , of the tin ligand bonds which are longer for higher co-ordination numbers, thus leading to a decrease in the s electron density [28]. In addition, there will be increased shielding of the s electrons produced by population of the tin d-orbitals. Thus, it is possible that for samples A5 and A6, some of the tin may be present in higher co-ordination number sites. Again, a very broad line was observed, indicating that there may be a mixture of species present.
The Mossbauer parameters of sample A10 confirm that the tin is not present in the form of SnS_2 (Section 5.2.1.1) and indicate that the actual tin species present is SnO_2.

5.3.1.2 **Yields of Liquid Products Obtained**

Table 5-10 shows the yields of the various fractions of liquid products, expressed as a percentage of dry ash free coal, on hydrogenating a solution of Point of Ayr coal in the presence of alumina-supported tin catalysts. The products were again analysed by gas chromatography and were divided into groups using the chemical markers described in Section 5.5.5. Only the yields of the desired products, <u>i.e.</u> those boiling below 270° C, are shown in Table 5-10.

Sample	% Sn[a]	Yield (% d.a.f. coal)							
		Group 1 <175 °C	Group 2 175-220 °C	Group 3 220-260 °C	Group 4 260-270 °C	Total <260 °C	Total <270 °C	Average Values <260 °C	Average Values <270 °C
A5	14.5	9.20	8.28	12.12	28.68	29.60	58.28	44.12	75.28
A6	14.5	22.92	16.36	19.36	33.64	58.64	92.28		
A7	11.9	17.68	17.08	23.68	28.88	58.44	87.32	49.74	77.98
A8	11.9	12.12	10.44	18.48	27.60	41.04	68.64		
A9	18.2	32.80	23.36	26.44	18.56	82.60	101.16		
A10	10.3	20.56	14.16	22.72	19.56	57.44	77.00		

a % Sn on alumina support

Table 5-10: **Yields of Liquid Products Obtained on Using Sn/Al_2O_3 Catalysts**

The yields of liquid products with boiling points below 270° C indicate that the alumina-supported tin catalysts are active in the hydrocracking of Point of Ayr coal. In general, the yields were comparable with, or higher than, those observed in the Co-Mo commercial catalysts (60 - 70%) [30]. Work on bimetallic and single component alumina supported catalysts, using a coal extract from a high volatile weakly coking coal (NCB Class 702), has been carried out by Harrison et al. [30]. A similar procedure to that used for the tin catalysed experiments was employed and some of the results obtained are shown in Table 5-11.

Catalyst	Wt % metal	Yield (wt %) <260° C
Ni Mo	15.1% MoO_3 -3.09%NiO	84
Co Mo	15.4%MoO_3 -4.18%CoO	120
Co Mo	15% Mo - 3% Co	100
Zn Mo	15% Mo - 3% Zn	122
Ni W	15% W - 3% Ni	106
Zn W	15% W - 3% Zn	103
Mo	15%	82
Cu	15%	109
Fe	15%	92
Ni	15%	111
Ca	15%	111

Table 5-11: **Results Obtained by Harrison et al. [30] Using Metal Catalysts**

These yields are generally higher than those obtained using the tin catalyst, although sample A9, which contained a higher concentration of tin, did give results comparable with those of other monometallic-catalysts, such as Fe and Cu (Table 5-11).

Sn/Al_2O_3 catalysts have previously been found to be active in the hydrogenation of coals [31, 32] and, in particular they were more active than iron catalysts [31] and the catalysts tested by Kawa [32], which included a commercial Co/Mo catalyst.

Increasing the tin concentration on the alumina support above ca. 12% led to an increase in the yield of liquid products (Table 5-10 and Figure 5-2). This was largely due to a higher yield of products boiling at temperatures below 260°C rather than those boiling at temperatures between 260°C and 270°C. A similar study has been carried out by Mahoney [22], who increased the amount of tin present on an alumina support. However, in this investigation, there was very little change in coal conversion on increasing the tin concentration. The difference in the results obtained by Mahoney *et al*. [22] and those obtained here may be due to the fact that their catalyst contained molybdenum and its presence was found to enhance the activity of the tin. Thus, the effect of the increase in tin concentration may have been masked by the increased activity due to the presence of molybdenum.

Table 5-12 gives the C and H analyses and the H/C ratio of the hydrocracked products obtained from catalyst A9.

Fraction	% C	% H	H/C Ratio (atom)
Cold Trap	86.31	9.76	1·36
<275°C	89.38	8.17	1·10
275 - 300°C	90.78	7.58	1·00
300 - 475°C	91.64	6.51	0·85

Table 5-12: **Carbon and Hydrogen Contents and H/C Ratios of Fractions Obtained from SnO$_2$/Alumina Catalyst (A9)**

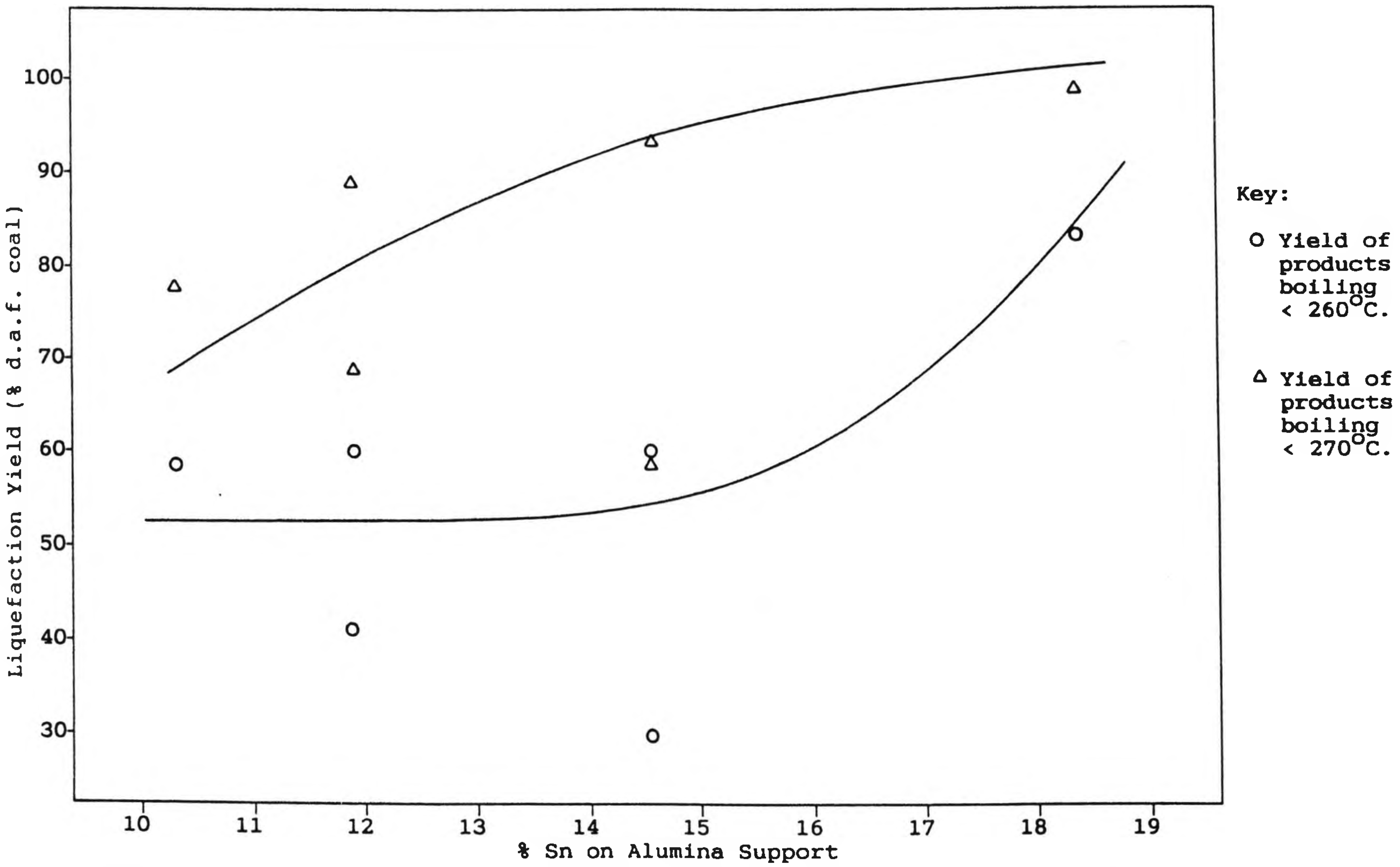


Figure 5-2: <u>Yield of Liquefaction Products (% d.a.f. coal) vs. % Sn on Alumina Support for Point of Ayr Coal</u>

The H/C ratio for Point of Ayr coal itself is 0.77. Assuming that this is not significantly altered by dissolution in the recycle solvent, it appears that there is a slight increase in the H/C ratio on using the SnO_2/alumina catalyst, which, as mentioned previously (Section 5.2.1.2) is one of the aims of coal hydrogenation.

Tin and sulphur analyses of the recovered catalysts were carried out and the results are shown in Table 5-13.

Sample	% Sn in unused catalyst	% Sn in used catalyst	% S in used catalyst	Sn:S atom Ratio used catalyst
A5	14.5	11.0	1.13	9:4
A6	14.5	11.3	1.35	5:2
A7	11.9	a	1.94	-
A8	11.9	11.8	1.64	2:1
A9[b]	18.2	16.0[d]	1.72	13:5
A10[c]	10.3	7.0[d]	1.35	3:2

[a] not determined

[b] %C in used catalyst = 30.40%. %H in used catalyst = 2.17%

[c] %C in used catalyst = 29.70%. %H in used catalyst = 2.15%

[d] Sn analyses after heating used Sn/Al_2O_3 catalysts to 900°C : A9 = 18.7% Sn, A10 = 10.8% Sn

Table 5-13: **Analyses of Alumina Supports After Liquefaction Experiments**

The alumina supports (apart from sample A7) were analysed for tin before and after use. After the liquefaction experiment, the support was black in colour. Samples of recovered catalysts A9 and A10 were heated to 900°C, after which the support was virtually white again. On re-analysing for tin, the results shown in Table 5-13 were obtained. These indicate that there is no loss of tin from the alumina support when the tin is in the form of SnO_2.

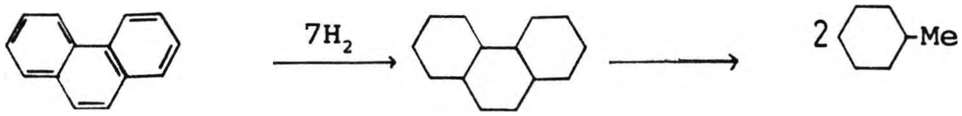
A comparison of the results obtained for sample A9 with those of sample A10 indicates that a higher yield of Group 1 compounds was obtained for the former (Table 5-10). This can be explained by studying the gas chromatography results on these two samples, in which products boiling at temperatures in the range of 270 - 475° C were analysed too, these products being divided into a further 8 groups (Numbers 5 to 11), using the chemical markers named in Tables 5-20 and 5-22 (Section 5.5.5). The yields obtained in the various groups, expressed as a percentage of total peak area of the gas chromatogram for samples A9 and A10, are shown in Table 5-14.

Group Number	Yield (% total peak area)[a]	
	A9	A10
1	8.20	5.14
2	5.84	3.54
3	6.61	5.68
4	4.64	4.89
5	3.79	3.68
6	3.90	4.03
7	11.53	15.18
8	7.70	8.38
9	0.64	1.64
10	10.43	13.37
11	3.34	3.36
12	3.90	5.71

[a] % total peak area of gas chromatograms

Table 5-14: **Yields of Liquid Products Obtained from Point of Ayr Coal Solution in the presence of Sn/Al_2O_3 Catalysts**

The yields shown in Table 5-10 indicate that the higher yield of monoaromatics and cyclohexanes (Group 1 compounds) obtained for sample A9 probably results from a breakdown of the hydrophenanthrenes (Group 7 compounds) and the hydropyrenes (Group 10 compounds), since the yields obtained for these two groups are significantly lower in the A9 than in the A10 case. Previous research [29] has shown that the breakdown of the polynuclear aromatics, such as phenanthrene and pyrene, occurs <u>via</u> hydrogenation to the perhydro derivative, followed by cracking to a single ring derivative (Equation 5-1)



5-1

Phenanthrene Perhydrophenanthrene

The alumina-supported catalysts studied in this work were found to be more active than the impregnated catalysts described in Section 5.2.1.2, the average value of the total liquid yield being approximately double. The following data indicates that the supported catalysts, particularly, increase the yield of products boiling at temperatures below 260° C:

Sample	Average value of yields boiling point <260° C (% daf coal)	Average value of yields, boiling point <270° C (% daf coal)	Average value of total yield boiling point <270° C (% daf coal)
A1 & A2	21.3	23.0	44.3
A3 & A4	22.9	24.6	47.5
A5 & A6	44.2	31.2	75.4
A7 & A8	48.8	29.2	78.0
A9	82.8	18.4	79.2
A10	57.6	21.6	101.2

These results are in agreement with the contention that supporting the active catalyst on alumina increases its effective surface area [2, 33].

The sulphur analyses of the hydrocracked products are shown below:

Sample	A5	A6	A7	A8
% S	0.305	0.305	0.214	0.269

Comparison of these figures with those obtained for the impregnated Point of Ayr coal (Table 5-6) indicates that the impregnated tin compounds are superior for the removal of sulphur. On dissolving the Point of Ayr coal in the recycle solvent, only the inorganic sulphur is lost (ca. 0.7%) and so there is very little difference in the sulphur content of the Point of Ayr coal extract and the coal itself. The superiority of the homogeneous tin(II) octoate catalyst is confirmed by the sulphur analyses of the residues, which are higher for the washed filter cake obtained from the impregnated coals than for the alumina support (Table 5-6 and Table 5-13).

5.3.1.3 ^{119m}Sn Mossbauer Studies of Used Alumina Supports

The Mossbauer parameters of the alumina supports after the liquefaction experiments are shown in Table 5-15. The spectra of samples A5 to A8 are similar, showing a tin(II) doublet and two broad tin(IV) singlets, whereas those of samples A9 and A10 show only a tin(II) doublet and one tin(IV) singlet. As for earlier experiments which used tin-impregnated coals (Section 5.2.1.3), the tin(II) doublet is believed to result from the presence of tin(II) sulphide. For samples A5 to A8 and A10, the high velocity (high energy) peak had a greater intensity than the lower energy peaks. In contrast, the tin(II) doublet in the Mossbauer spectrum of sample A9 was similar in shape to that of the Morwell coal sample M1 (Section 5.2.1.3(a)), the lower energy peak having the greater intensity. As discussed for the Morwell coal, this may indicate the presence of β-Sn, its isomer shift being 2.56mms^{-1}, which coincides in position with the lower energy peak of the SnS doublet. It is not possible to elucidate whether there is any β-Sn present in the used catalysts, A5 - A8 and A10.

Sample Number	Mossbauer Parameters (mms^{-1})			
	Tin(II)		Tin(IV)	
	δ	ΔEq	δ	ΔEq
A5	3.41	1.08	1.99	0.0
			0.07	0.0
A6	3.36	1.00	1.98	0.0
			0.07	0.0
A7	3.39	1.02	1.89	0.0
			0.08	0.0
A8	3.42	1.08	1.95	0.0
			0.09	0.0
A9	3.20	1.13	0.00	0.0
A10	3.20	1.01	0.04	0.0

Table 5-15: ^{119m}Sn Mossbauer Parameters of Used Alumina Supports

From the Sn:S mole ratio, it appears that, if all the sulphur were present in the form of SnS, there would be sufficient of this element in the used catalyst for between 40 - 50% of the tin to be in the form of SnS. This species would, therefore, be clearly visible in the Mossbauer spectrum and confirms the conclusion that the tin(II) doublet is due to SnS.

The identity of the tin(IV) species with isomer shift, $\delta \simeq 1.90$cm^{-1}, in samples A5 - A8, is not known. This isomer shift is significantly higher than that observed both by Cook and in the Mossbauer spectrum of the Morwell coal residue, M1 (δ = 1.54mm s^{-1}, Table 5-7).

The Mossbauer spectra show that there is still some SnO_2 present within the alumina support. For samples A5 and A6, the isomer shift of the tin(IV) species in the spent catalyst (δ = 0.07mms^{-1}) differed from that of the initial catalysts, when a very low value was obtained (Section

5.3.1.1, Table 5-9). This indicates that, for these samples of alumina support, there are no longer any tin atoms present in sites with a high co-ordination number (> 6) within the alumina support.

5.4 EXPERIMENTAL

The coal liquefaction experiments were carried out by Dr. G. Harrison and his co-workers at North Staffordshire Polytechnic.

5.4.1 Impregnation of Coals

(a) Morwell Coal

The coal used in these experiments was Morwell coal, Drum 287 -8, from a 1979 bulk sample. It was supplied by Dr. P. Cassidy of Monash University, Victoria, Australia, and was stored under an inert atmosphere (N_2).

The tin(II) octoate was obtained from the Sigma Chemical Co. Ltd., Poole, and was used without further purification. Three different methods of impregnation of the coal with tin(II) octoate were investigated, one of these methods then being chosen to prepare a larger sample for the liquefaction experiments at North Staffordshire Polytechnic.

Method 1

Tin(II) octoate (0.27g, 7 x 10^{-4} moles) Morwell coal (5.0g), as received (*i.e.* undried) and degassed toluene (35cm^3) were stirred together in an inert atmosphere at room temperature for 24 hours. The coal was then filtered off in a glove box, which had been filled with N_2, washed with 90cm^3 toluene and dried *in vacuo*.

Method 2

The same procedure as for Method 1 was employed, but the coal was not washed after impregnation and filtration.

Method 3

The same procedure as for Method 1 was employed, but the solvent was driven off under a stream of dry nitrogen, following the procedure of Hawk [1].

Method 1 was then used to impregnate the two samples of Morwell coal (M1 and M2) which were submitted for testing. For each impregnation, Morwell coal (30.00g), tin(II) octoate (1.54g) and degassed toluene (90cm^3) were used. Several small samples were taken from each large sample for Sn analysis (Section 5.3.2). The impregnated coals were stored in an atmosphere of dry nitrogen.

(b) Point of Ayr Coal

Eight methods of impregnation of this coal by tin(II) octoate, using both dried and undried substrate, were investigated.

Method 1

Point of Ayr coal, undried (5.00g), tin(II) octoate (0.26g, 6 x 10^{-4} moles; tin:coal weight ratio 0.015:1) and dried, degassed toluene (40cm^3), were stirred together under a nitrogen atmosphere for 24 hours. The coal was then filtered off in a dry box and was washed with toluene (90cm^3).

Method 2

A similar procedure to that used in Method 1 was employed, but the coal was dried before impregnation by heating to 105°C under a nitrogen atmosphere. The dry coal (4.14g) was stirred with a solution of tin(II) octoate (0.21g, 5 x 10^{-4} moles) in dry, degassed toluene (33cm^3; tin:coal weight ratio = 0.015:1).

Method 3

Point of Ayr coal, undried (5.00g) and tin(II) octoate (0.27g, 7 x 10^{-4} moles; tin:coal weight ratio = 0.015:1), were placed in a flask containing toluene (40cm^3) which had been dried over anhydrous sodium sulphate and degassed. The slurry was stirred under nitrogen for 24 hours and the solvent was then evaporated off under a stream of dry nitrogen.

Method 4

A similar procedure to that used in Method 3 was employed, but the solvent was filtered off in an atmosphere of dry nitrogen and the impregnated coal was then dried in vacuo without washing. The dry coal (3.00g) was impregnated with tin(II) octoate (0.15g, 4 x 10^{-4} moles) from a solution of dry, degassed toluene (30cm^3; tin:coal weight ratio = 0.015:1).

Method 5

A similar procedure to that in Method 4 was employed, but a higher tin:coal weight ratio of 0.03:1 was used when impregnating the coal (3.00g) with the tin(II) octoate (0.31g, 8 x 10^{-4} moles) in dry degassed toluene (30cm^3). After slurrying for 24 hours, the coal was filtered off under nitrogen and was washed with dried, degassed toluene (90cm^3).

Method 6

The same procedure as for Method 3 was employed, but the coal was dried by heating to 105°C under a nitrogen atmosphere for 8 hours before impregnation with the tin(II) octoate. The dry coal (2.89g) was stirred with a solution of tin(II) octoate (0.16g, 4 x 10^{-4} moles) in dry degassed toluene (29cm^3; tin:coal weight ratio = 0.015:1).

Method 7

The same procedure as for Method 4 was followed, but the coal was dried before impregnation. The dry coal (2.92g) was stirred with a solution of tin(II) octoate (0.16g, 4 x 10^{-4} moles) in dry, degassed toluene (29cm^3; tin:coal weight ratio = 0.016:1).

Method 8

The same procedure as for Method 5 was followed, but the dry coal (2.58g) was impregnated with tin(II) octoate (0.26g, 6 x 10^{-4} moles) by stirring together in dry, degassed toluene (25cm^3; tin:coal weight ratio = 0.03:1).

Method 6 was chosen for the impregnation of the larger coal samples to be submitted for liquefaction. The concentrations of catalyst used were higher than those investigated in the Morwell coal experiments, in order to test whether the yield of liquid products would benefit from the presence of more catalyst. Two levels of catalyst addition were prepared and the masses of coal and tin compound and the volume of toluene used in the impregnation are shown in Table 5-16. For samples A1 and A2, the ratio of the mass of tin added:coal mass was 0.05:1 and, for samples A3 and A4, it was 0.1:1.

Sample Number	Mass of dried coal (g)	Mass of tin(II) octoate (g)	Volume of toluene (cm^3)
A1	65.68	11.16	100
A2	71.69	12.23	100
A3	75.84	25.88	106
A4	77.53	26.46	108

Table 5-16: **Impregnation Conditions of Samples A1 to A4**

5.4.2 **Analysis of Coals**

(a) **Tin Analysis**

The coal sample was wet-ashed in an HNO_3/H_2SO_4 mixture to remove all organic material and the amount of Sn in the residue determined by Atomic Absorption Spectroscopy in the Analytical Department of the International Tin Research Institute.

(b) **Analysis of Other Elements**

Carbon, hydrogen and sulphur analyses of Morwell and Point of Ayr coals, both before and after impregnation with tin(II) octoate, were carried out at North Staffordshire Polytechnic using a Leco CHN 600 Determinator and a Leco S Determinator. The ash, moisture and volatiles analyses were determined using a Leco Proximate Analysis Determinator, again at North Staffordshire Polytechnic.

5.4.3 Impregnation of Alumina Supports

(a) With SnO_2

The alumina support was supplied by Akzo Chemie (U.K.). It had a pore volume of 0.68cm^3/g. A sample of the support (13.00g) was pre-dried at 300°C for 18 hours to remove absorbed moisture and was placed in a desiccator to cool down. The dried alumina was then weighed and the total pore volume calculated from the known pore density. In order to impregnate the alumina support to a nominal value of 15%, a solution of tin(IV) chloride was prepared, such that the pore volume was just saturated. Tin(IV) chloride (6.06g, 2.68cm^3, 0.02 moles) was added slowly dropwise to ice-cold deionised water (5.72cm^3) with stirring. The clear solution which formed was then added, from a dropping funnel, to the stirred alumina support (12.35g). Stirring was continued for 15 minutes to ensure homogeneity of the sample. The tin-containing support was washed with ammonia solution (10M) until a negative silver nitrate test was obtained, and then with deionised water to remove the ammonia. It was dried at 500°C for 18 hours and the percentages of tin, water and chloride were determined.

The ^{119m}Sn Mossbauer spectrum of the crushed support was run at 80K and the rest of the sample was used in a duplicate set of coal liquefaction experiments (designated A5 and A6). Since the liquefaction results obtained when using these two samples were very promising, the tests were repeated. Thus, a second sample of the alumina support was impregnated in the same way as described above,using pre-dried alumina

(13.78g) and a solution of tin(IV) chloride (6.76g, 2.99cm^3, 0.03 moles) in deionised water (6.38cm^3). Sn,Cl and moisture analyses were again determined, as were the ^{119m}Sn Mossbauer parameters of the sample. The liquefaction experiments which were catalysed by this tin-containing alumina support were designated A7 and A8.

In addition, a support was prepared (used for run A9) which contained a higher concentration of tin (25% SnO_2) by impregnating the pre-dried alumina support (14.29g) with a solution of tin(IV) chloride (8.23g, 3.64cm^3, 0.03 moles) in ice-cold deionised water (9.72cm^3). This sample was designated A9.

(b) With SnS_2

Tin(IV) chloride (4.52g, 9cm^3, 0.02 moles) was added slowly dropwise to ice-cold deionised water (9cm^3). This solution was then added slowly dropwise to the stirred alumina pellets (16.00g). The pellets were then washed with a solution of sodium sulphide (10g in 100cm^3 water) until a negative chloride ion test was obtained. Sn and S analyses were determined, as were the ^{119m}Sn Mossbauer parameters. This sample was designated A10.

5.4.4 Analysis of Alumina Support

(a) Tin Analysis

The sample was treated with NH_4I, thus volatilising the tin as SnI_4. This was then dissolved in dilute HCl and the tin determined by Atomic Absorption Spectroscopy [34].

(b) Analysis of Other Elements

Sulphur contents were determined by the Microanalytical Department, University College, London, and chlorine contents by the Analytical Department of the International Tin Research Institute.

5.4.5 Liquefaction Methodology

(a) Morwell Coal

The liquefaction of the coal under hydrogen pressure was carried out in a 0.51 stainless steel autoclave manufactured by Baskerville and Lindsay plc., and the experimental conditions for each run are shown in Table 5-17. All experiments were carried out in the presence of a process recycle solvent (solvent:coal ratio = 2:1), which was supplied by the National Coal Board, CRE. The reactor was charged with hydrogen to <u>ca.</u> 100 bar pressure at ambient temperature and was then heated to the reaction temperature. After hydrogenation, the autoclave was depressurised to atmospheric pressure. The liquid product was distilled (<u>ca.</u> 0.6mm Hg) into a cold trap, the products boiling at temperatures below 275° C at atmospheric pressure and those boiling at temperatures between 275 and 300° C at atmospheric pressure being collected. These fractions were analysed by gas chromatography using the same temperature profile (80 -250°C at 5°C min^{-1} ramp rate). A 25m, 0.32mm capillary column coated with Silicon OV 101 was used with "on column" injection of 0.5 μl of a 1 wt% solution of the fraction in cyclohexane.

Run Number	Weight (g)		Starting H_2 Pressure (bar)	Working H_2 Pressure (bar)	Temperature (°C)
	Coal	Solvent			
M1[a]	21	41	120	215	350
M2[a]	20	40	100	190	400
M3[b]	16	33	100	190	400

[a] Tin-containing samples
[b] Morwell coal alone

Table 5-17: **Reaction Conditions for Autoclave Experiments**

Using chemical markers, the yields of products were subdivided as shown in Table 5-18.

Group	Temperature Range (°C)	Product Type
1	<175	Single ring compounds
2	175 - 220	Unsubstituted hydro-naphthalenes and naphthalene
3	220 - 260	Methylnaphthalenes and methylhydro-naphthalenes
4	260 - 280	Dimethylnaphthalenes and dimethylhydro-naphthalenes

Table 5-18: **Details of Gas Chromatographic Markers**

The percentage dissolution of the coal was determined from an ash analysis of the residual filter cakes and the ash content of the coal. The concentration of coal within the extracts was then calculated as follows:

weight of dissolved coal, W = weight of coal, daf x percentage of coal dissolution

$$\text{Percentage of coal in the extract} = \frac{W}{W + \text{weight of solvent}} \times 100$$

Thus, the final percentage yield is:

$$\text{Percentage yield} = \frac{\text{percentage material boiling} <170^{o}\text{C}^{a}}{\text{percentage coal in extract}} \times 100$$

[a] Determined from gas chromatography results.

The proportion of the product boiling at temperatures below 260°C was also calculated.

(b) **Point of Ayr Coal**

These experiments used a recycle solvent and the tin-impregnated Point of Ayr coal was subjected to a combined dissolution and hydrogenation process. The same procedure as for the Morwell coal was followed and the experimental conditions are shown in Table 5-19.

Run Number[a]	Weight of solvent (g)	Weight of coal (g)	Weight of coal(daf)(g)[a]
A1	100.30	49.97	39.62
A2	101.10	49.99	39.64
A3	101.50	49.97	37.82
A4	100.60	50.01	37.66

[a] All experiments were carried out at 400°C, 200 bar working hydrogen pressure and 4 hours contact time.

[b] Corrected for tin content.

Table 5-19: Experimental Conditions for Point of Ayr Experiments

After liquefaction, the liquid products were vacuum distilled, as described in Section 5.5.5(a), and the fractions analysed by gas chromatography, using the apparatus described previously.

The products boiling at temperatures below 270° C were classified according to their boiling points in accordance with the four groups described in Table 5-18 (Section 5.4.5(a)). In addition, products boiling above this temperature were divided into the groups shown in Table 5-20.

Group	Species
5	Fluorene
6	Perhydrophenanthrenes
7	Hydrophenanthrenes
8	Phenanthrene and compounds with higher boiling points (<340° C)

Table 5-20: **Details of Chemical Markers Used in Gas Chromatography**

The yields of desired products were expressed as total material boiling at temperatures below 260° C (Groups 1 - 4) and below 270° C (Groups 1 - 5) as a percentage of daf coal.

(c) Alumina-Supported Catalysts

These experiments used a Point of Ayr coal extract, dissolved in a solvent recycled after the hydrocracking stage of a coal hydrogenation. The solvent has a boiling range of 275 - 475° C and contains 3 and 4 ring hydroaromatic species. The hydrocracking experiments were carried out in a 0.5l stainless steel autoclave containing a spinning/falling basket in which the extrudate catalyst (ca. 4g) was placed. The basket was retained above the charge until the reaction temperature was reached, when it was lowered into the coal liquid (ca. 110g), rotating on the stirrer shaft which is driven magnetically and has a maximum speed of 1000 rpm. The autoclave was heated by a quick release unit. The experimental conditions are detailed in Table 5-21.

Run Number[a]	Weight of coal extract (g)	Weight of catalyst (g)
A5	111.00	4.0
A6	110.80	4.0
A7	not known	not known
A8	not known	not known
A9	102.1	5.0
A10	105.7	5.0

[a] All experiments were carried out at 400° C, 200 bar working hydrogen pressure and 4 hours contact time.

Table 5-21: **Experimental Conditions for Hydrogenations Using Alumina-Supported Catalysts**

After hydrocracking, the same procedure as for the impregnated coals was followed, the products being distilled under reduced pressure and analysed by gas chromatography. For runs A5 to A10, the same groups as previously (Table 5-18 and Table 5-20) were used and, for runs A9 and A10, the distillation range was extended to 475° C to provide information on the recycle solvent fraction. Thus, chromatographic analysis of the products was extended to include the groups shown in Table 5-22.

Group	Species
9	Anthracene
10	Hydropyrenes
11	Pyrene
12	Pyrene plus

Table 5-22: **Additional Chemical Markers Used for Runs A9 and A10**

5.5 CONCLUSIONS

(i) Impregnation of Morwell coal with tin(II) octoate did not improve the yield of liquid products obtained.

(ii) In addition, the yield of liquid products from Point of Ayr coal was not improved by increasing the percentage tin(II) octoate present from 3.4% to 7.0%. However, the presence of both tin and hydrogen did increase the yield.

(iii) The presence of tin did not appear to assist in the addition of hydrogen to Morwell coal.

(iv) Tin(II) octoate was found to be active in the removal of sulphur from Point of Ayr coal.

(v) After liquefaction of both tin-impregnated Morwell and Point of Ayr coal, the tin was at least partially present in the form of tin(II) sulphide, . There was also evidence to suggest the presence of β-Sn in some of the residues obtained from Morwell and Point of Ayr coal.

(vi) Alumina-supported tin catalysts were found to be active in the hydrocracking of Point of Ayr coal, the yields being comparable with those obtained for a Co-Mo commercial catalyst. However, the impregnated tin compounds were superior for the removal of sulphur.

(vii) Increasing the tin concentration on the alumina support from ca. 12% to 18% led to an increase in the yield of liquid products obtained.

(viii) After hydrogenation using the supported tin catalyst, the tin was again believed to be partially present in the form of tin(II) sulphide.

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CHAPTER SIX

PHARMACEUTICAL USES OF INORGANIC TIN COMPOUNDS

6.1 CHEMOPREVENTION OF NEONATAL JAUNDICE

Hyperbilirubinaemia is a chronic haemolytic disorder (breakdown of haeme in the bloodstream) which causes jaundice in newborn infants. It results from the presence of excessive levels of the bile pigment, bilirubin, in the plasma which the newly formed liver is unable to detoxify. Thus, there is a build-up of this bile pigment in the bloodstream during the first week or so of neonatal life. The agent responsible for the degradation of haeme to bilirubin is haeme-oxygenase. It has been shown that trans-dichlorotin(IV) protoporphyrin IX (Figure 6-1) is able to inhibit the activity of haeme-oxygenase in the liver, spleen, kidney and skin of rats [1]. In this study, it was found that there was significant lowering of the serum bilirubin levels when the tin(IV) protoporphyrin IX complex was administered and near-normal levels were reached after only three days of treatment [1]. It was therefore concluded that this compound may be suitable for treatment of severe haemolytic disorders. These tests have subsequently been extended to monkeys [2, 3], in which the bilirubin levels were again found to decline to near-normal adult levels within 30 hours of administration of the tin compound, and to normal levels in human adults [4], in which this complex was rapidly cleared from the plasma.

The present study was undertaken in an attempt to synthesise the trans-dichlorotin(IV) protoporphyrin IX complex for a spectroscopic and structural examination. It was, in particular, hoped to carry out an X-ray crystal structure

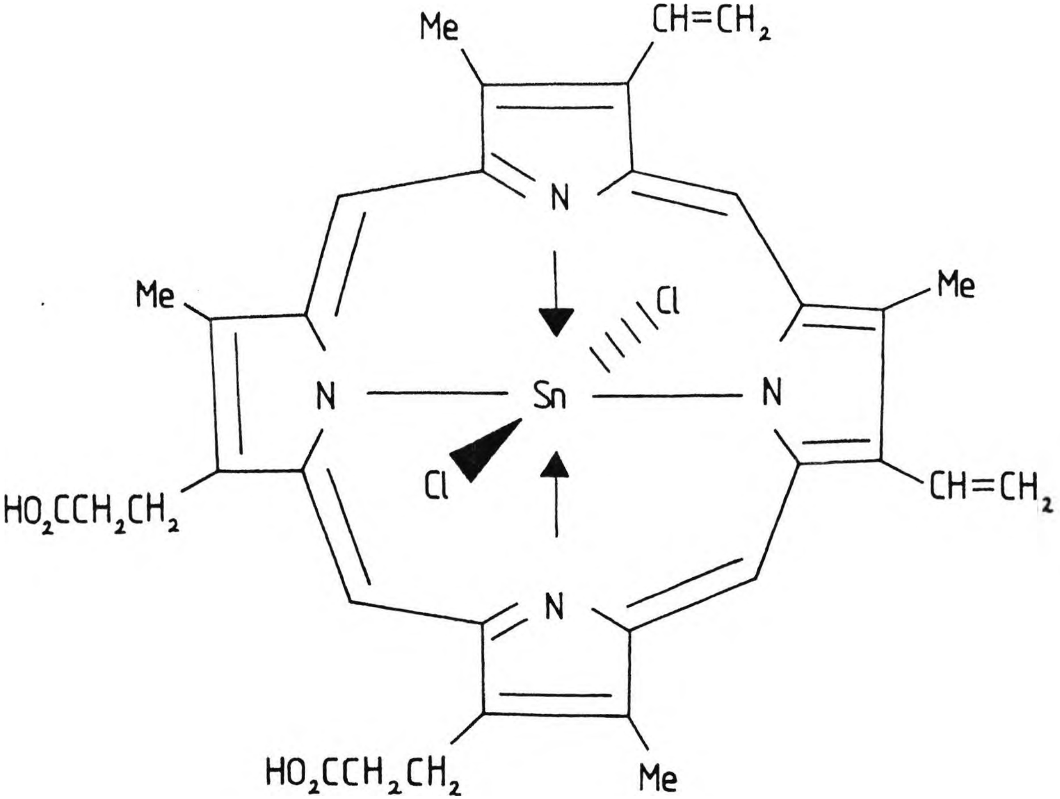

Figure 6-1: **Structure of trans-dichlorotin (IV) protoporphyrin IX**

determination of this compound, in order to elucidate its mode of chemotherapeutic action. The synthesis of a pure sample however, proved to be difficult, and this was therefore obtained commercially for infrared and Mossbauer investigations.

6.1.1 Spectroscopic Studies of Dichlorotin(IV) Protoporphyrin IX

(a) Infrared Studies

Dichlorotin(IV) protoporphyrin IX was prepared following the method of O'Rourke and Curran [5], from tin(II) chloride and the free base porphyrin, the reaction being carried out in pyridine. The infrared spectrum of the crude (unsublimed) $SnCl_2$(protoporphyrin IX) contained the bands shown in Table 6-1. Microanalytical data indicated that the product was impure and, on attempting to purify it by means of sublimation, a white solid formed on the cold finger of the apparatus. The infrared spectrum of the residue which did not sublime differed from that of the initial product in that some bands were no longer present (Table 6-1). The microanalytical and infrared data of the sublimate (Table 6-1) indicated that this was probably the inorganic tin(IV) oxychloride complex, $SnOCl_2.1.5py$ (py = pyridine), which has previously been synthesised by Dehnicke [6]. Many of the bands observed by Dehnicke were present in the infrared spectrum of the sublimate, although the intensities varied in some cases. The formation of this pyridine adduct may be rationalised by assuming that some of the tin(II) chloride

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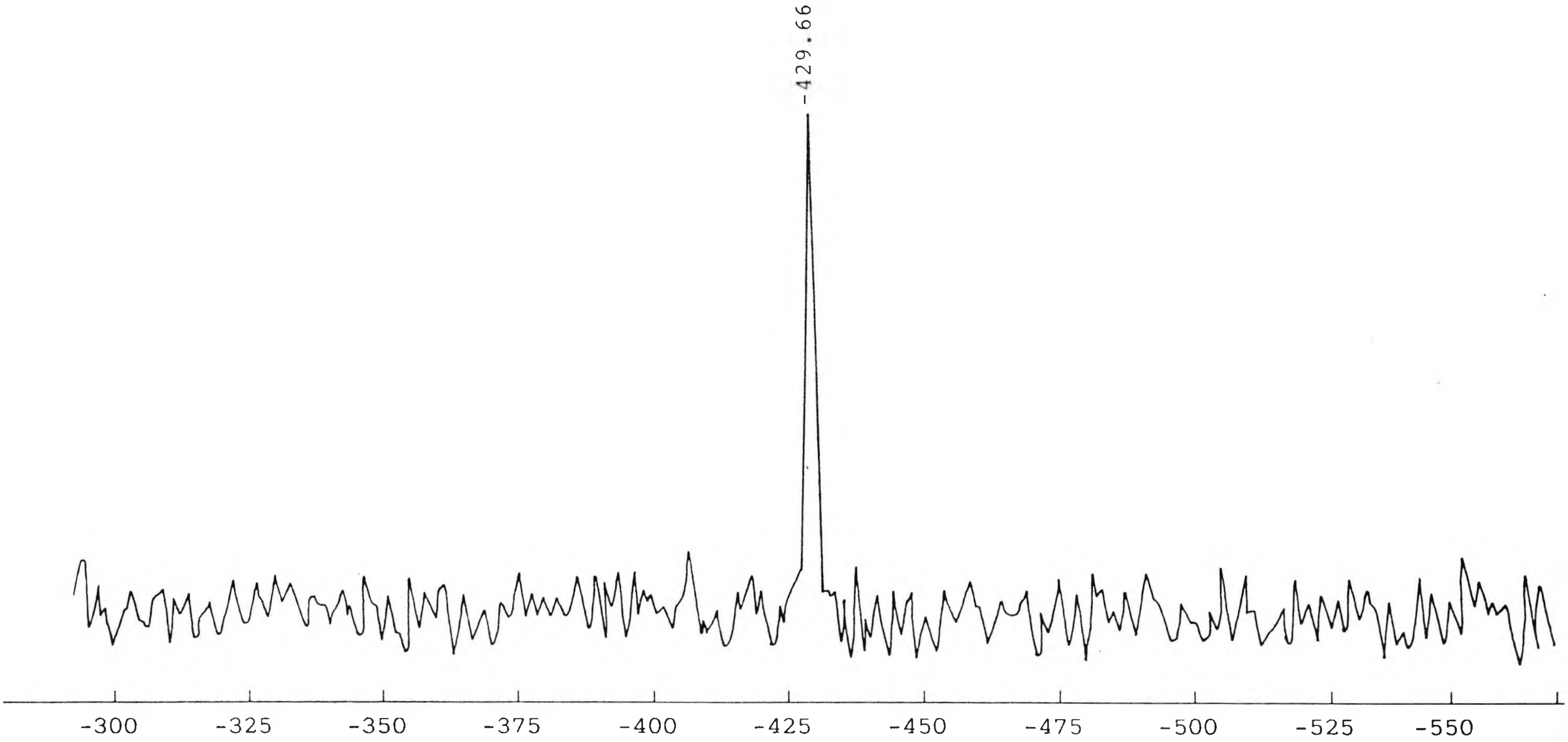


Figure 3-4: Solid State ^{119}Sn NMR Spectrum of $Sn(OSiPh_3)_4$

3.2 TIN(II) COMPOUNDS

It has been suggested that the uptake of tin from tin(II) chloride in aqueous solution can be correlated with the carboxylic acid content of a wide range of low-rank, sub-bituminous and bituminous coals [84]. It is therefore possible that a tin(II) carboxylate species may be formed on impregnating at least some of the coals studied in this thesis, with tin(II) chloride (Chapter 4). Thus, the tin(II) carboxylates, tin(II) benzoate, $Sn(O.CO.Ph)_2$, and tin(II) β-naphthoate, $Sn(O.CO.C_{10}H_7)_2$, were synthesised as possible model compounds, in order that their ^{119m}Sn Mossbauer isomer shifts could be compared with those of the tin-impregnated coals (Chapter 4). The ^{119m}Sn Mossbauer parameters of the tin-containing coals are compared with other tin(II) species in Chapter 4, but these model compounds have not been prepared, the comparisons being made using literature values.

The tin(II) benzoate and β-naphthoate were synthesised from tin(II) chloride, via tin(II) methoxide (Equations 3-12 and 3-13 [85]).

$$SnCl_2 + 2MeOH + 2R_2R^1N \xrightarrow{r.t.} Sn(OMe)_2 + 2R_2R^1NH^+Cl \qquad (3\text{-}12)$$

R = Et, R^1 = Et or H

$$Sn(OMe)_2 + 2ArCOOH \xrightarrow[toluene]{Reflux} Sn(O.CO.Ar)_2 + 2MeOH \qquad (3\text{-}13)$$

Ar = Ph or $C_{10}H_7$

Experiment Number	wt. % H_2O Present (wet coal basis)	wt. % Tin Found After Impregnation	wt. % Chlorine Found After Impregnation
1	31.4	26.0	n.d. [a]
2	41.6	31.0	n.d.
3	20.3	14.0	n.d.
4	33.7	25.0 [b]	n.d.
5	25.6	20.0	n.d.
6	46.1	27.0	n.d.
7	38.5	25.0	n.d.
8	34.6	28.0	n.d.
9	42.9	29.0	n.d.
10	31.5	26.0	n.d.
11	28.2	18.2	24.9
12	23.1	17.3	19.9
13	15.0	11.2	12.7
14	50.5	30.5 [c]	n.d.
15	36.0	24.0	24.5
16	40.2	28.0	30.8
17	29.9	13.0	n.d.
18	28.0	9.0	14.4
19	24.6	19.4	20.1
20	13.5	12.4	15.2
21	18.1	25.8	26.8
22	14.6	12.4	13.3
23	23.1	21.1	21.9

[a] n.d. = not determined.
[b] average of two values: 21.0 and 29.0.
[c] average of two values: 31.0 and 30.0.

Table 4-6 Uptake of Tin by Morwell Coal Samples Having Different Moisture Contents

This implies that the tin is interacting with the water present in the coal.

Coal Type	Tin Present	Mössbauer Parameters				Ref.
		Tin(IV)		Tin(II)		
		δ	Γ	δ	ΔEq	
Morwell (undried)	5.0%	0.27	1.66	-	-	a
	<1.0%[b]	-	-	-	-	a
	9.0%	0.28	1.21	-	-	a
	13.0%	0.23	1.38	3.39	1.69	a
	16.0%	0.20	1.48	3.30	1.73	a
Morwell (dried)	5.5%	0.24	1.54	-	-	a
	7.0%	0.25	1.58	-	-	a
	9.0%	0.25	1.40	-	-	a
	11.0%	0.23	1.49	3.35	1.72	a
	12.0%	0.24	1.49	3.37	1.76	a
	12.0%	0.24	1.46	3.37	1.74	a
	16.0%	0.24		3.34	1.84	a
	13.0%	0.21	1.42	3.37	1.77	a
Hagel (undried)	17.7%	0.16	1.49	3.26	1.83	a
Hagel (dried)	12.0%	0.21	1.48	3.34	1.70	a
	14.1%	0.19	1.44	3.31	1.79	a
Herrin No. 6 (undried)	8.1%	0.23	1.40	3.25	1.78	a
	12.5%	0.19	1.39	3.23	1.81	a
Herrin No. 6 (dried)	10.4%	0.23	1.43	3.33	1.65	a
Gedling (undried)	8.8%	0.24	1.47	-	-	a
Gedling (dried)	10.4%	0.28	1.36	3.33	1.66	a
Cortonwood (undried)	<0.5%[b]	-	-	-	-	a
Cresswell (undried)	13.1%	0.18	1.42	3.18	1.81	a
Cresswell (dried)	14.9%	0.16	1.58	3.19	1.88	a
Morwell	9.5%	-0.01	-	-	-	c
	2%	0.02	-	-	-	d
IL6	10%	0.01	-	-	-	e
IL6	10%	-	-	3.24	1.62	e

[a] this work.
[b] insufficient tin present for spectrum to be visible.
[c] ref. 13.
[d] ref. 12.
[e] ref. 14.

Table 4-13 ^{119m}Sn Mossbauer Results for Tin(II) Chloride Impregnated Coals compatability with the organic vehicle used to slurry coal in many liquefaction reactions. Sharma [44] studied the effectiveness of several organometallics as catalysts for the liquefaction of both a sub-bituminous (Navajo) coal and a bituminous (York Canyon) coal. Some of the results obtained are shown in Table 2-4. The organotin compounds only showed a high catalytic activity for the sub-bituminous coal.

Catalyst	% Conversion	
	Navajo	York Canyon
None	61	44
$Mo(CO)_6$	79	73
Ph_4Sn	73	58
Ph_3SnH	67	--
$Pd(acac)_2$	84	72
$Ir(CO)_3Cl$	83	77

Table 2-4 Results of Hydrogenation of Navajo Mine and York Canyon Coals [44]

Suzuki et al. [45] used an Australian Brown coal for their studies and found that the conversion and yield of oils increased in the presence of the organotins, these compounds decomposing to metallic tin during the course of the reaction. Increasing the amount of catalyst increased the coal conversion, but had no effect on the oil yield, indicating that these compounds do not catalyse the degradation of the heavier oil fractions. However, increasing the hydrogen pressure did have an effect on the oil yield. Addition of a large excess of sulphur to the tin catalyst decreased its catalytic ability, whereas addition of $Fe(CO)_5$ increased it slightly and addition of sulphur to this binary catalyst led to a further improvement. These authors, like Mizumoto et al. [39], concluded that the tin acted as a catalyst by stabilising the coal radicals.

5.3.1.2 Yields of Liquid Products Obtained

Table 5-10 shows the yields of the various fractions of liquid products, expressed as a percentage of dry ash free coal, on hydrogenating a solution of Point of Ayr coal in the presence of alumina-supported tin catalysts. The products were again analysed by gas chromatography and were divided into groups using the chemical markers described in Section 5.5.5. Only the yields of the desired products, i.e. those boiling below 270°C, are shown in Table 5-10.

Sample	% Sn[a]	Yield (% d.a.f. coal)							
		Group 1 <175°C	Group 2 175-220°C	Group 3 220-260°C	Group 4 260-270°C	Total <260°C	Total <270°C	Average Values <260°C	Average Values <270°C
A5	14.5	9.20	8.28	12.12	28.68	29.60	58.28	44.12	75.28
A6	14.5	22.92	16.36	19.36	33.64	58.64	92.28		
A7	11.9	17.68	17.08	23.68	28.88	58.44	87.32	49.74	77.98
A8	11.9	12.12	10.44	18.48	27.60	41.04	68.64		
A9	18.2	32.80	23.36	26.44	18.56	82.60	101.16		
A10	10.3	20.56	14.16	22.72	19.56	57.44	77.00		

[a] % Sn on alumina support

Table 5-10: Yields of Liquid Products Obtained on Using Sn/Al_2O_3 Catalysts

The yields of liquid products with boiling points below 270°C indicate that the alumina-supported tin catalysts are active in the hydrocracking of Point of Ayr coal. In general, the yields were comparable with, or higher than, those observed in the Co-Mo commercial catalysts (60 - 70%) [30]. Work on bimetallic and single component alumina supported catalysts, using a coal extract from a high volatile weakly coking coal (NCB Class 702), has been

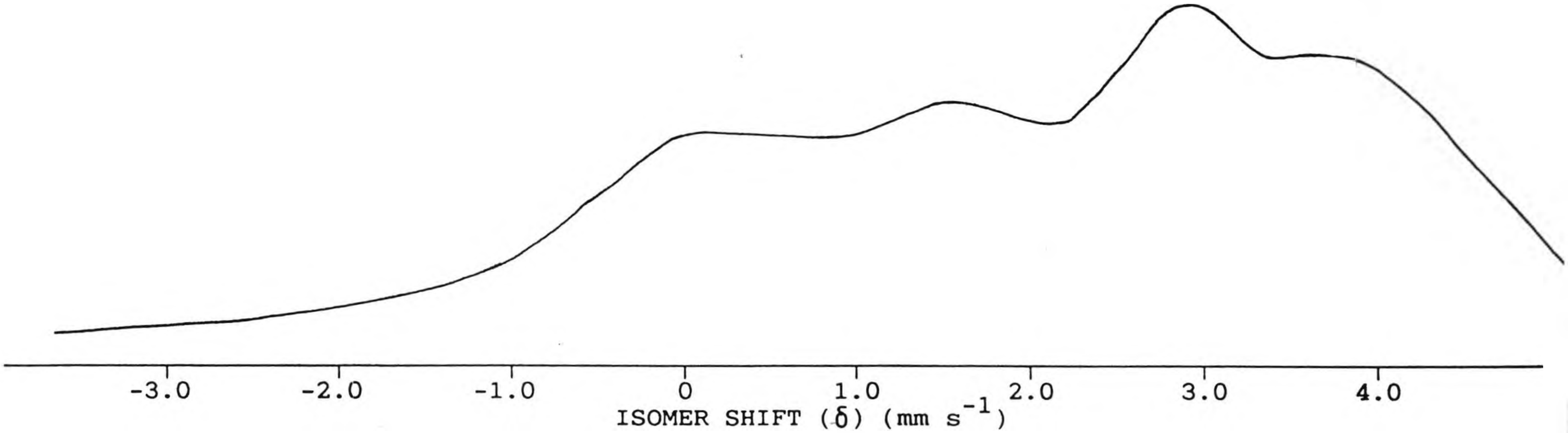


Figure 5-1: Mossbauer Spectrum of Residue from Morwell Coal Sample M2 After Liquefaction

Microanalytical Data[a]				
		Synthesised Product[b]		
	Commercial Product	Before Sublimation	After Sublimation (Residue)	Sublimate
C	52.88	46.92	53.37	26.30
	(54.43)	(54.43)	(54.43)	(27.91)
H	4.34	3.90	4.22	2.74
	(4.30)	(4.30)	(4.30)	(1.87)
N	7.11	7.47	7.07	5.99
	(6.90)	(6.90)	(6.90)	(6.51)

I R Bands (cm^{-1})		
Before Sublimation	After Sublimation (Residue)	Sublimate
		3260
		3240
		3190
		3130
		3100
		3070
	1750m	
	1715s	
	1650w	
		1630
	1620w	
1605m	1595s	1602
1570w		
1540w		
1510w	1515w	
1490sh		1490
1440sh		
1415w	1420w	
1350sh		1370
1340sh	1340w	
1300m	1310m	1320

I R Bands (cm^{-1}) (cont.)		
Before Sublimation	After Sublimation (Residue)	Sublimate
1260w	1260w	1260
1240vw	1235w	
1215sh		
1210m		1210
1180w	1190w	1195
1160m	1160m	1165
1145m	1145m	
1130m	1130m	
1100m	1110m	
1080m	1080m	
1060m	1050w	1060
		1050
1040m		1035
1015m		1015
990w	990w	
975w	980vw	980
945m	945m	
910m	910m	
860m	860m	860
840sh	840sh	
810w	810w	
755sh	750s	755
720s	725s	
680s		
645m	635w	645
620w	625w	
		610
	595vw	
570w		
	520w	520br
510w	505vw	
500w		
	455vw	
430m		

[a] calculated values in parenthesis

[b] product synthesised for this study

Table 6-1: **Microanalytical Data and Infrared Bands of Sublimate and $SnCl_2$(Protoporphyrin IX) Both Before and After Sublimation** was oxidised during the course of the reaction, forming $SnOCl_2$, which subsequently reacted with excess pyridine. These conclusions were supported by the fact that Dehnicke [6] formed the $SnOCl_2$.1.5py adduct by the addition of excess pyridine to an ethyl acetate solution of $SnOCl_2$.

The microanalytical data of the unsublimed product would appear to indicate that this was trans-dichlorotin(IV) protoporphyrin IX, its purity having been significantly improved by the sublimation procedure.

The microanalytical data of a commercial sample of trans-dichlorotin(IV) protoporphyrin IX (Table 6-1) indicated that this too was slightly impure.

The N-H stretching band present at 3320cm^{-1} in the infrared spectrum of the porphyrin itself was absent from the spectrum of the product, both before and after sublimation. Boucher et al. [7] have studied several metal derivatives of protoporphyrin IX dimethyl ester and found that the C=C and C=N stretching modes of the porphyrin macrocycle gave rise to as many as 5 absorption bands in the region 1700 - 1500cm^{-1}. Four bands were observed in this region in the spectrum of $SnCl_2$(protoporphyrin IX), but one of these, the band at 1620cm^{-1}, was believed to be due to the C=C stretch of the vinyl substituents [7]. In addition, bands were observed at 1715cm^{-1} and 1750cm^{-1}. The stronger of these at 1715cm^{-1} is probably due to the carbonyl stretching frequency of the $-CH_2CH_2.CO.OH$ groups. The band at 945cm^{-1} is assigned to an in-plane porphyrin deformation mode.

Ogoshi *et al*. [8] have found the position of this band to be sensitive to the nature of the metal in studies of metallocomplexes of octaethylporphyrins.

The far infrared spectrum of this complex was studied, but most of the bands observed were also present in the spectrum of protoporphyrin IX itself [7], with the exception of two new bands at 246cm^{-1} and 223cm^{-1}.

Sutton *et al*. [9] and Kroenke *et al*. [10] assigned the strong band at 335cm^{-1} to the Sn-Cl stretching vibration in similar porphyrins. However, a medium intensity band is also present at this frequency in the spectrum of the free protoporphyrin IX [7] and, thus, it is difficult to make an assignment in this case.

(b) ^{119m}Sn Mossbauer Studies

The Mossbauer spectrum of the unsublimed product was highly asymmetric, again implying the presence of impurities. After sublimation, a quadrupole split doublet with an isomer shift, δ of 0.29mms^{-1} and a quadrupole splitting, Δ Eq of 0.95mms^{-1} was obtained. Some asymmetry was again observed, but this had been reduced compared to that present before sublimation. In fact the spectra of several dichlorotin(IV) tetraphenylporphyrin complexes which were run by Debye *et al*. [11] were found to be asymmetric, the high energy wing having a smaller area than the low energy wing. Mossbauer parameters for similar complexes, as recorded in the literature, are shown in Table 6-2. The isomer shift of $SnCl_2$(protoporphyrin IX) was similar to that observed by May *et al*. [12] for $SnCl_2$(deuteroporphyrin-IX-DiMe) and to the values obtained by Curran *et al*. [5] for various complexes.

Only weak correlations of isomer shift with the basicity of the porphyrins have so far been obtained. May et al. [12] found that the two most electron withdrawing porphyrins which they studied had the most

Complex	Mossbauer Parameters δ(mms^{-1})	 ΔEq(mms^{-1})
$SnCl_2$ Protoporphyrin (IX)	0.29	0.95
$SnCl_2$ Protoporphyrin (IX)[a]	0.27	0.96
$SnCl_2$ TmeOxPP[b]	0.24	0.0
$SnCl_2$ TTolP[c]	0.23	0.0
$SnCl_2$ T(p-Cl)PP[d]	0.23	0.0
$SnCl_2$ TPP[e]	0.23	0.0
$SnCl_2$ TPP[f]	0.146	0.588
$SnCl_2$ T(p-i-Pr)PP[f]	0.160	0.512
$SnCl_2$ T(p-O Me)PP[f]	0.147	0.555
$SnCl_2$ T(p-Cl)PP[f]	0.154	0.642
$SnCl_2$ (OEP)[g]	0.34	0.47
$SnCl_2$ (DP-IX-DiMe)[h]	0.34	0.58
$SnCl_2$ T(p-CN)PP	0.10	1.74
$SnCl_2$ (Trimethylanilinium-porphyrin)[i]	0.13	0.53

[a] Sample purchased from Porphyrin Products
[b] H_2 TMeOxPP = tetra(p-methoxyphenyl)porphyrin, Ref. 5.
[c] H_2 TTolP = tetra(p-tolyl)porphyrin, Ref. 5.
[d] H_2 TClPP = tetra(p-chlorophenyl)prophyrin, Ref. 5.
[e] H_2 TPP = tetraphenylporphyrin, Ref. 5.
[f] Ref. 11.
[g] H_2OEP = octaethylporphyrin, Ref. 12.
[h] H_2DP-IX-DiMe = Deuteroporphyrin-IX-Dimethyl, Ref. 12.
[i] H_2TMAP = trimethylaniliniumporphyrin, Ref. 12.

Table 6-2: Mossbauer Parameters of Dichlorotin(IV) Porphyrins negative isomer shift but, in general, no quantitative relationship between isomer shift and the first reduction potential of the porphyrin, a measure of its basicity, was observed. Thus, from the results obtained here for the protoporphyrin IX complex, the only conclusion which can be drawn is that protoporphyrin IX is not as basic as (p-CN) tetraphenylporphyrin or trimethylanilinium porphyrin. The presence of the vinyl groups in the protoporphyrin IX do not appear to have significantly affected the isomer shift or, by implication, the total s electron density of the protoporphyrin IX complex, its isomer shift being within experimental error (± 0.05mm s^{-1}) of that of deuteroporphyrin-IX-dimethyl ester (1,3,5,8-tetramethyl-porphine-6,7-dimethylpropionate) (Table 6-2). Although Debye et al. [11] believe that the occurrence of a quadrupole splitting is surprising, it is in accordance with the conclusions of other workers for trans complexes [13]. The Mossbauer parameters of the dichlorotin(IV) protoporphyrin IX complex obtained from Porphyrin Products were very similar to those of the complex synthesised for this work (Table 6-2).

6.2 ANTITUMOUR AGENTS

Recent investigations have shown [18, 19] that certain organotin compounds, e.g. $(Et_2SnO)_n$ and $ClMe_2SnOSnMe_2Cl$, are marginally active against P388 lymphocytic leukaemia. In addition, octahedral complexes of the type $R_2SnX_2L_2$ (R = alkyl or aryl group, X = F, Cl, Br, I or NCS and L = N or O-donor ligand) have been shown to be active against the same tumour [18, 20, 21]. It is usual for L to be a bidentate ligand, which frequently gives rise to a cis configuration of the halogen atoms, and this has been found for Pt(II) complexes to be an essential requirement for activity [22]. To date, four inorganic tin(IV) compounds have shown antitumour activity and these are summarised in Table 6-3. In addition, a number of dichlorotin(IV) phthalocyanine and dichlorotin(IV) purpurin derivatives have been examined as photodynamic therapy (PDT) agents. Photodynamic therapy involves the use of a chemical photosensitiser for the treatment of solid malignancies in tumours, these photosensitisers accumulating in the tumours. Certain atoms and molecules may be excited to a reactive state by absorption of UV or visible light. However, many biologically active molecules do not absorb electromagnetic radiation of these wavelengths. It therefore becomes necessary to use a sensitiser molecule which will absorb the UV or visible light and transfer this energy to the molecule of interest.

Dichlorotin(IV) and chloroaluminium(III) phthalocyanines have been found to produce total cell death following red light illumination, but no toxicity after exposure to room light [14]. In recent studies by Morgan et al. dichlorotin(IV) etiopurpurin, Cl_2SnET2, has been found to give 100% cures of tumours at a drug dose of 1.0mg/kg body weight, whereas, at the lower dose of 0.5mg/kg body weight, 20% of the treated animals (rats) were tumour free [15, 16]. The tin(IV) purpurin gave superior results to zinc(II) etiopurpurin, which was also studied [15]. In addition, the same workers found [17] that, for FANFT (FANFT=N-[4-(5-nitro-2-furyl)-2-thiogolyl] formamide) induced bladder tumours in rats, the tin purpurin, Cl_2SnET2, caused complete necrosis of the tumour, i.e. death of the tumour, and that it was much more active than the corresponding metal-free purpurin.

A knowledge of the structural factors which influence antitumour properties of inorganic tin(IV) complexes is of considerable importance as their toxicity is expected to be significantly lower than their organotin counterparts. Since $SnCl_2(bzac)_2$ (Hbzac = $Ph.CO.CH_2.CO.Me$) has been shown to be active against the Sarcoma 180 tumour, by Keller et al. [23], it was decided to synthesise this compound and the analogous $SnCl_2(bzbz)_2$ (Hbzbz = $Ph\ CO.CH_2\ CO.Ph$) for in vivo testing against P388 leukaemia. In addition, both compounds were sent for testing in vitro against B16 murine melanoma following the work of Cima et al. on tin(IV) diethylthiocarbamates [24].

Compound	Tumour	Dose (mg/kg)	T/C[a] (%)	Reference
$SnCl_4.bipy^b$	P388 Leukaemia	400	130	17
$SnCl_4.phen^c$	P388 Leukaemia	100	123	17
$SnCl_2(bzac)_2$	Sarcoma 180	52	230	19
$SnBr_2(bzac)_2$	Sarcoma 180	84	141	19
$SnCl_2(DDTC)^d{}_2$	B16 Murine Melanoma	10^{-4}-10^{-5}M[e]	Significant inhibition of cell growth	20

[a] T/C is the ratio of the survival time (in days) of treated (T) and untreated (C) mice. A compound is considered to be active at T/C values > 120%

[b] bipy = $2,2^1$-bipyridyl

[c] phen = 1,10-phenanthroline

[d] DDTC = diethyldithiocarbamate

[e] *in vitro* study

Table 6-3: **Antitumour Activity of Inorganic Tin Compounds from the Literature**

The crystal structure of $SnCl_2(bzbz)_2$ was determined and particular attention was paid to the Cl-M-Cl angle which, in metallocene dichlorides (η^5-C_5H_5)$_2$ MCl_2(M=Ti, Zr, Hf, V or Mo), is believed to influence the antitumour properties [25, 26]. An X-ray crystal structure determination of $SnCl_2(bzac)_2$ was precluded by a lack of suitable crystals. The results of a spectroscopic and structural investigation of $SnCl_2(bzac)_2$ and $SnCl_2(bzbz)_2$ is included in the following Sections.

Table 6-4 shows the melting points and microanalytical data obtained for the two complexes.

Compound	M.p.(°C)	Analysis: Found (Calc.)			
		C	H	Cl	Sn
$SnCl_2(bzac)_2$	223-4[a]	46.45	3.54	14.01	22.6
	224-5[b]	46.48	3.57	14.01	n.d.[d]
	(221-3)[c]	(46.92)	(3.54)	(13.85)	(23.18)
$SnCl_2(bzbz)_2$	263-4[a]	56.65	3.60	11.28	18.3
	265-7[b]	56.60	3.66	10.52	n.d.[d]
	(263-4)[e]	(56.65)	(3.49)	(11.15)	(18.66)

[a] Sample sent for antitumour testing
[b] Sample sent for X-ray crystal structure determination
[c] Ref. 27
[d] n.d. = not determined
[e] Ref. 28

Table 6-4: **Microanalytical and Melting Point Data for Bis(diketonato-O,O) dichlorotin(IV) Complexes**

6.2.1 Spectroscopic Studies of Bis(diketonato-O,O) dichlorotin(IV) Complexes

(a) Infrared Studies

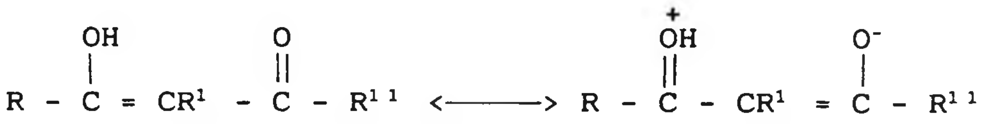
Selected infrared bands for both $SnCl_2(bzac)_2$ and $SnCl_2(bzbz)_2$ are shown in Table 6-5.

$SnCl_2(bzac)_2$	$SnCl_2(bzbz)_2$	Assignment
1595	1595	$\nu_{as}(C \overset{\cdots}{-} C)$
1585	1585	
1560		
1545	1535}	$\nu_s(C \overset{\cdots}{-} O)$
1510	1510}	
1340	1345	$\nu_{as}(C \overset{\cdots}{-} O)$
620	630	
570	570	
555	560	
	540	
	530	
	465	
450	455	$\nu(Sn - O)$
435	4	
336	347	$\nu_{as}(Sn - Cl)$
314	334	$\nu_s(Sn - Cl)$

Table 6-5: **Infrared Assignments of $SnCl_2(bzac)_2$ and $SnCl_2(bzbz)_2$**

The differences between the spectra of benzoylacetone and dibenzoylmethane and their respective dichlorotin(IV) derivatives are consistent with complex formation. A splitting of many bands on complexation was observed, indicating a lowering of symmetry.

In general, the spectra of $SnCl_2(bzac)_2$ and $SnCl_2(bzbz)_2$ were similar to those reported by Nelson and Martin [29] for the same complexes and to those of $Pd(acac)_2$ [30] and $SnCl_2(acac)_2$ [27], for which assignments have been made. Many β-diketones are known to exist in the mono-keto enol form and they do not show the normal carbonyl stretching band. The spectra of benzoylacetone and dibenzoylmethane contained resonances at $1595cm^{-1}$ and $1593cm^{-1}$ respectively. Rasmussen et al. [31] believe that this low carbonyl stretching frequency is due to a reduction in the double bond character because of the existence of the following resonance forms:



$$\mathrm{R - \overset{OH}{\overset{|}{C}} = CR^{1} - \overset{O}{\overset{||}{C}} - R^{11}} \longleftrightarrow \mathrm{R - \overset{\overset{+}{OH}}{\overset{||}{C}} - CR^{1} = \overset{O^{-}}{\overset{|}{C}} - R^{11}}$$

On complexation with tin, the C - O stretching frequency is further reduced, to $1545cm^{-1}$ for $SnCl_2(bzac)_2$. This band was assigned to $\nu(C \overset{\cdots}{-} O)$, following the conclusions of Nelson et al. [29]. However, the band at $1510cm^{-1}$ was in fact the strongest band. In the case of $SnCl_2(bzbz)_2$, this band has been split into a doublet with wave numbers

1535cm^{-1} and 1510cm^{-1}. Splitting of the carbonyl resonance has been observed previously for the complex $SnCl_2(acac)_2$ by Jones et al. [27], who believe that this is caused by coupling through the metal atom of the $\nu_s(C \overset{\cdots}{-} O)$ vibrations of the two chelate rings. The carbonyl bands of other similar complexes, such as $SnCl_2(acac)_2$ [27, 29] and $SnCl_2(tacac)_2$ (Htacac = monothioacetylacetone) [32], have wave numbers which are slightly higher than those of $SnCl_2(bzac)_2$ and $SnCl_2(bzbz)_2$. From these low $\nu(C \overset{\cdots}{-} O)$ values, it appears that strong complexes have been formed. Table 6-6 shows the wave numbers of the Sn-Cl and Sn-O stretches observed in the literature.

Complex	ν(cm^{-1}) Sn-O	Sn-Cl	References
$SnCl_2(acac)_2$	461	334	23
		332	24
		345,338	29
$SnCl_2(tacac)_2$	492	310,295	28
$SnCl_2(bzac)_2$	450	325	25
$SnCl_2(bzbz)_2$	455	320	25

Table 6-6: Literature Values of ν(cm^{-1}) for Sn-O and Sn-Cl Stretches

For $SnCl_2(bzac)_2$, some difficulty was experienced in assigning a band to the Sn-O stretch. A shoulder to a band was observed at 450cm^{-1}, which was not present in the spectrum of benzoylacetone itself, and it is possible that this peak is due to the Sn-O stretching vibration. The spectra of dibenzoylmethane and its tin complex were very different in the Sn-O stretching region, the dibenzoylmethane showing two bands at 485 and 440cm^{-1}, whilst the $SnCl_2(bzbz)_2$ showed two peaks at 465 and 455cm^{-1}. The band at 455cm^{-1} was the stronger band and has been assigned to ν(Sn-O). These are comparable to those of $SnCl_2(acac)_2$.

Two bands were observed at 336cm^{-1} and 314cm^{-1} in the far infrared region of the $SnCl_2(bzac)_2$ spectrum and at 347cm^{-1} and 334cm^{-1} for $SnCl_2(bzbz)_2$, and they are νas(Sn-Cl) and νs(Sn-Cl). The fact that two resonances are observed indicates the non-linearity of the Cl-Sn-Cl group implying that the chlorine atoms are cis to each other, a result confirmed by the X-ray studies. Trans complexes have not been formed despite the fact that the diketone ligands used were bulky. The preference of tin for forming cis complexes, even with large ligands, has also been observed for the analagous β-diketonate-alkoxide derivatives synthesised by Chandler et al. [33].

Nelson and Martin [29] observed only one band in their spectra of $SnCl_2(bzac)_2$ and $SnCl_2(bzbz)_2$ in this region. The difference between the spectra reported by them and those herein may be due to higher resolution of the spectra in this case. The bands observed for the $SnCl_2(bzbz)_2$ complex are very similar to those observed by Douek et al. [34] for $SnCl_2(acac)_2$ and have higher wavenumbers than those recorded for $SnCl_2(tacac)_2$ [32]. This implies Sn-Cl bond strengths for $SnCl_2(bzbz)_2$ which are comparable to those in $SnCl_2(acac)_2$ but greater than those in $SnCl_2(tacac)_2$ and indicates that, as for $SnCl_2(acac)_2$ [28], the Sn-Cl bonds possess some double bond character due to $(p \longrightarrow d)\Pi$ bonding from the Cl atom to the Sn atom.

(b) ^{119m}Sn Mossbauer Studies

The Mossbauer parameters of both $SnCl_2(bzac)_2$ and $SnCl_2(bzbz)_2$ are shown in Table 6-7, along with values for $SnCl_2(acac)_2$.

Compound	δ (mms^{-1})	Δ Eq (mms^{-1})
$SnCl_2(acac)_2$[a]	0.21	0
$SnCl_2(acac)_2$[b]	0.25	0
$SnCl_2(acac)_2$[c]	0.28	0.50
$SnCl_2(bzac)_2$	0.23	0.39
$SnCl_2(bzac)_2$[b]	0.18	0
$SnCl_2(bzbz)_2$	0.21	0
$SnCl_2(bzbz)_2$[c]	0.21	0.45

[a] Chapter 3 of this thesis.
[b] Ref. 35.
[c] Ref. 36.

Table 6-7: **^{119m}Sn Mossbauer Parameters of Bis(diketonato-O,O) dihalotin(IV) Complexes**

The isomer shifts are similar for all three compounds, indicating an approximately equal degree of s-electron density at the ^{119m}Sn nucleus. No trend in δ was observed for the β-diketones $RCO.CH_2CO.R^1$, in the series $R = R^1 = Me_3$, $R = Me_3$, $R^1 = Ph$, and $R = R^1 = Ph$, and thus the nature of the R (or R^1) group does not appear to be exerting an effect.

This is in contrast to the results obtained by Greenwood *et al*. [35], who found that, for compounds of the type $SnCl_2L_2$ [L = ox, (oxH = 8-hydroxyquinoline), acac or bzac], there was a considerable variation in isomer shift.

The absence of, or very small value obtained for, the quadrupole splitting indicates that these compounds have a structure in which the two Cl atoms are *cis* to each other [37]. $SnCl_2(acac)_2$ has been shown by X-ray crystal structure determination to be *cis* and, since the quadrupole splitting observed for that compound is zero, it is expected that other similar compounds whose quadrupole splitting is zero or near to zero would also have a *cis* structure.

6.2.2 X-ray Crystal Structure Determination of Bis(dibenzoylmethanato-O,O) dichlorotin(IV)

6.2.2.1 Crystal Data

$C_{30}H_{22}Cl_2O_4Sn$, M= 636.1, Orthorhombic, a = 18.7677, b = 17.6109, c = 16.5634A, $U = 5474.5A^3$, F(O O O) = 2544, space group P_{bca}, z = 8, $D_c = 1.54 gcm^{-3}$, MoK radiation, λ = 0.71069A, $(MoK_\alpha) = 10.6 cm^{-1}$.

6.2.2.2 Structure Determination and Refinement

The position of the tin atom was located from the three-dimensional Patterson Function while the remaining atoms were located from successive difference electron-density maps. All atoms except those of hydrogen were assigned anisotropic thermal parameters. Hydrogen atoms were included in the F_c calculation with an idealised geometry (C-H, 1.08A) and were given common isotropic temperature factors which refined to final values of U = 0.1061(199) for H12 and H30 and 0.0724(74)A for all other hydrogen atoms. Complex neutral atom scattering factors [38] were employed and in the final cycles of refinement the weighting scheme $w = 0.3554/[\sigma^2(Fo) + 0.0041(Fo)^2]$ was adopted. Full matrix refinement gave a final R value of 0.030 and R^1 of 0.036. Final positional parameters are given in Table 6-8, bond distances and angles in Table 6-9. Additional material, available from the Cambridge Crystallographic Data Centre, comprises thermal parameters, H atom co-ordinates and mean plane equations.

Atom	x	y	z
Sn	50665(2)	76826(2)	80183(2)
Cl1	4062(1)	7770(1)	7192(1)
Cl2	5737(1)	8575(1)	7293(1)
O1	5548(2)	6779(2)	7445(2)
O2	4518(2)	6876(2)	8685(3)
C11	5645(3)	6110(3)	7772(3)
C12	5232(3)	5799(3)	8386(3)
C13	4667(3)	6170(3)	8784(3)
C14	4217(3)	5767(3)	9362(3)
C15	4156(3)	4979(4)	9353(4)
C16	3695(4)	4617(4)	9873(5)
C17	3308(4)	5031(5)	10435(5)
C18	3370(4)	5811(5)	10453(5)
C19	3830(4)	6170(4)	9928(4)
C1	6277(3)	5691(3)	7486(3)

Atom	x	y	z
C2	6318(3)	4900(4)	7508(3)
C3	6937(4)	4533(4)	7266(4)
C4	7515(4)	4953(5)	7024(4)
C5	7493(4)	5727(5)	6999(5)
C6	6870(4)	6106(4)	7234(4)
O3	5915(2)	7527(3)	8793(3)
O4	4685(2)	8448(2)	8856(2)
C30	5495(3)	8187(3)	9926(4)
C31	5976(3)	7734(3)	9538(3)
C32	6650(3)	7488(3)	9914(3)
C33	7210(3)	7244(4)	9436(4)
C34	7830(3)	7003(4)	9771(4)
C35	7909(4)	7987(4)	10585(5)
C36	7365(3)	7211(4)	11078(4)
C37	6731(3)	7469(4)	10728(4)
C41	4898(3)	8541(3)	9593(3)
C42	4479(3)	9080(3)	10076(3)
C43	4028(3)	9594(3)	9679(3)
C44	3623(3)	10104(4)	10114(4)
C45	3663(3)	10109(4)	10941(4)
C46	4096(4)	9621(4)	11332(4)
C47	4506(3)	9097(4)	10913(4)

Table 6-8: Final Fractional Co-ordinates (Sn x 10^5; other atoms x 10^4) with Estimated Standard Deviations in Parentheses.

Distances (Å)

Sn-Cl1	2.335(2)	C6-C1	1.395(9)
Sn-Cl2	2.344(2)	C14-C15	1.393(9)
Sn-O1	2.062(4)	C15-C16	1.378(10)
Sn-O2	2.074(4)	C16-C17	1.387(11)
Sn-O3	2.063(4)	C17-C18	1.379(13)
Sn-O4	2.063(4)	C18-C19	1.379(11)
O1-C11	1.309(7)	C19-C14	1.382(9)
O2-C13	1.284(7)	C32-C33	1.383(8)
O3-C31	1.292(7)	C33-C34	1.357(9)
O4-C41	1.295(7)	C34-C35	1.356(11)
C11-C12	1.391(8)	C35-C36	1.366(10)
C11-C1	1.476(8)	C36-C37	1.398(9)
C12-C13	1.409(8)	C37-C32	1.358(8)
C13-C14	1.461(8)	C41-C42	1.470(7)
C31-C30	1.366(8)	C42-C43	1.402(8)
C31-C32	1.475(7)	C43-C44	1.380(8)
C30-C41	1.395(7)	C44-C45	1.371(10)
C1-C2	1.396(9)	C45-C46	1.350(10)
C2-C3	1.387(10)	C46-C47	1.387(10)
C3-C4	1.373(11)	C47-C42	1.387(8)
C4-C5	1.364(12)	C41-H30	1.865
C5-C6	1.402(10)	C30-H30	1.08

Angles (°)	
C11-Sn-C12	95.1(1)
C11-Sn-01	97.7(1)
C11-Sn-02	87.5(1)
C11-Sn-03	175.2(1)
C11-Sn-04	94.1(1)
C12-Sn-01	92.7(1)
C12-Sn-02	177.3(1)
C12-Sn-03	89.6(1)
C12-Sn-04	95.4(1)
01-Sn-02	86.2(2)
01-Sn-03	81.1(2)
01-Sn-04	165.1(1)
02-Sn-03	87.8(2)
02-Sn-04	85.2(2)
03-Sn-04	86.4(2)
Sn-01-C11	124.4(3)
Sn-02-C13	128.5(4)
Sn-03-C31	128.7(3)
Sn-04-C41	127.6(3)
01-C11-C1	115.4(5)
01-C11-C12	125.5(5)
C11-C1-C2	122.4(5)
C1-C2-C3	120.3(6)
C2-C3-C4	119.6(7)
C3-C4-C5	121.6(7)
C4-C5-C6	119.5(7)
C5-C6-C1	120.0(7)
C6-C1-C2	119.1(6)
C6-C1-C11	118.4(5)
C1-C11-C12	119.0(5)
C11-C12-C13	125.2(5)
C12-C13-C14	121.0(5)
C13-C14-C15	121.7(5)
C14-C15-C16	120.4(b)
C15-C16-C17	120.4(7)
C16-C17-C18	119.5(7)
C17-C18-C19	119.8(7)
C18-C19-C14	121.4(7)
C19-C14-C15	118.4(6)
C19-C14-C13	119.9(5)
C14-C13-02	115.3(5)
C12-C13-02	123.7(5)
03-C31-C32	113.3(5)
03-C31-C30	123.7(5)
C31-C32-C33	120.1(5)
C32-C33-C34	121.0(6)
C33-C34-C35	120.5(6)
C34-C35-C6	120.4(6)
C35-C36-C37	118.8(6)
C36-C37-C32	121.0(6)
C37-C32-C33	118.3(5)
C37-C32-C31	121.5(5)
C32-C31-C30	122.8(5)
C31-C30-C41	127.3(5)
C30-C41-C42	120.2(5)
C41-C42-C43	118.9(5)
C42-C43-C44	120.5(5)
C43-C44-C45	119.7(6)
C44-C45-C46	120.6(6)
C45-C46-C47	121.2(6)
C46-C47-C42	119.6(6)
C47-C42-C43	118.5(5)
C47-C42-C41	122.5(5)
C42-C41-04	115.5(4)
C30-C41-04	124.3(5)

Table 6-9: **Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses**

6.2.2.3 Discussion

The structure of $SnCl_2(bzbz)_2$ (Figure 6-2) consists of discrete monomeric units. As for $SnCl_2(acac)_2$ [39], $SnCl_2(etac)_2$ (Hetac = ethylacetoacetate, Me CO.CH_2CO. Et) [40], $SnCl_2(btbm)_2$ (Hbtbm = benzoyl(thiobenzoylmethane), $SnCl_2(tacac)_2$ [32] and other bis-chelate tin(IV) compounds [40 - 46], the chloro groups occupy cis positions,

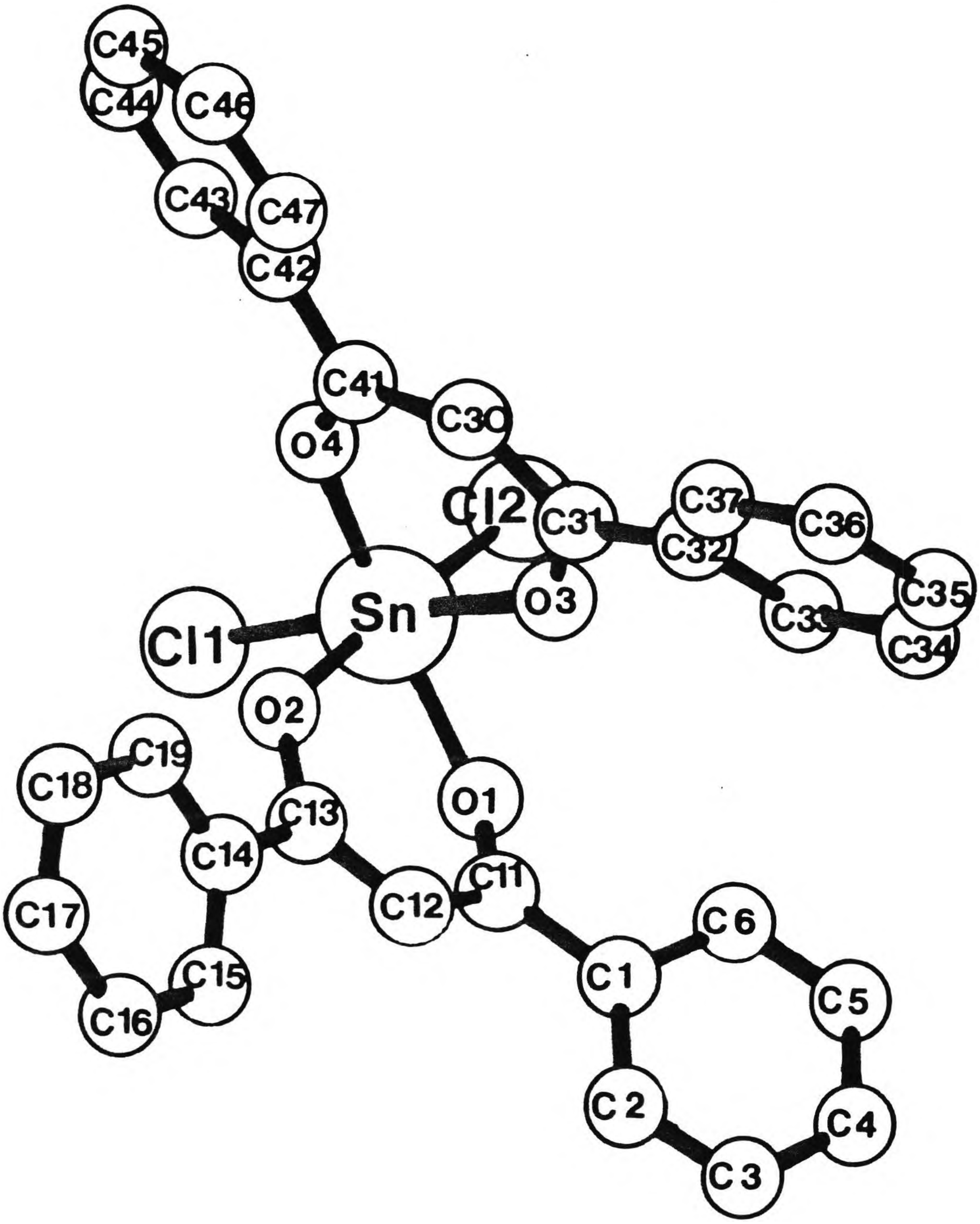


Figure 6-2: Molecular Structure of $SnCl_2(bzbz)_2$

confirming the far infrared results. The fact that cis complexes have formed, even when using bulky ligands, has been observed for the analogous β-diketonate-alkoxide derivatives $Sn(OR)_2(acac)_2$, where R = Pr^i or Bu^t, synthesised by Chandler *et al.* [33]. The tin atom in $SnCl_2(bzbz)_2$ is octahedrally co-ordinated, the other four positions being occupied by the oxygen atoms of the bidentate β-diketonate ligands. The geometry is distorted from an ideal octahedron, the angles subtended at the tin atom varying from 87.5(1)° (Cl(1)-Sn-O(2)) to 97.7(1)° (Cl(1)- Sn-O(1)). The geometry of the phenyl groups is unexceptional.

Sn-O bond lengths usually fall within the range 2.11 - 2.45A in octahedral tin(IV) complexes [47], but the Sn-O bond lengths in $SnCl_2(bzbz)_2$ are all shorter than this; in addition, they are shorter than those found in the following compounds: $SnCl_2(btbm)_2$ [7], $SnCl_2(tacac)_2$ [32] and $[Sn(acac)(OPr^i)_3]_2$ (Table 6-10). They are similar to the Sn-O bond distances in $SnCl_2(acac)_2$ [39], $SnCl_2(ONPhCOPh)_2$ [42] and $SnCl_2(etac)_2$ [40] (Table 6-10). It can therefore be concluded that the bulky dibenzoylmethane ligand is more strongly chelated to the tin atom than either benzoyl, (thiobenzoyl)methane or monothioacetylacetone and is not exhibiting the anisobidentate behaviour observed for the dimethyltin complexes with the latter two diketonates [32]. In addition, it appears that the strength of the interaction in $SnCl_2(bzbz)_2$ is similar to that observed for $SnCl_2(acac)_2$, $SnCl_2(ONPhCOPh)_2$ and $SnCl_2(etac)_2$. This is in agreement with the observation that similar Mossbauer isomer shift and ν(Sn-O) values were obtained for $SnCl_2(bzbz)_2$ and $SnCl_2(acac)_2$. However, from the assignment made, $SnCl_2(tacac)_2$ has a much higher Sn-O stretching vibration than $SnCl_2(bzbz)_2$ which would not be expected on comparing the Sn-O bond lengths.

Gable et al. [48] found that, in $Br_2Sn(SCS.OEt)_2$ and $I_2Sn(SCS.OEt)_2$, mutually trans Sn-S distances were shorter than the Sn-S bond lengths trans to the halides, and a similar effect was observed in $SnCl_2(etac)_2$ [40] for the Sn-O distances. However, this feature was not observed for $SnCl_2(bzbz)_2$, since only the Sn-O(2) bond distance (2.074(4)Å was appreciably greater than the other three (2.062(4)Å 2.063(4)Å and 2.063(4)Å). $SnCl_2(bzbz)_2$ therefore differs from $SnCl_2(acac)_2$ [39], $[Sn(OPr^i)_3(acac)]_2$ [33], $SnCl_2(btbm)_2$ and $SnCl_2(tacac)_2$ [32], for which similar bond lengths are obtained for like bonds. However, considerable irregularities in the Sn-O bond distances were observed for tin(IV) tetraacetate, $Sn(OAc)_4$ [49], in order to relieve overcrowding. It may be that the slight lengthening of one of the Sn-O bonds in $SnCl_2(bzbz)_2$ is also due to steric effects.

All angles subtended by the C and O atoms of the chelate ring are larger than the ideal 120° and range from 123.7(5)° [C(12)-C(13)-C(2), C(3)-C(31)-C(30)] to 128.5(4)° [Sn-O(2)-C(13)]. This indicates an opening of the angles after chelation, which has been observed in other complexes [32, 39, 40].

Complex	Sn-O	Reference
$SnCl_2(bzbz)_2$	2.074(4), 2.062(4), 2.063(4)	a
$SnCl_2(acac)_2$	2.051(2), 2.064(2)	39
$SnCl_2(ONPh.COPh)_2$	2.05(2), 2.04(2)	42
$SnCl_2(etac)_2$	2.101(15), 2.066(15)	40
$SnCl_2(btbm)_2$	2.117(9), 2.120(7)	32
$SnCl_2(tacac)_2$	2.149(3)	32
$[Sn(O^iPr)_3\ (acac)]_2$	2.112(7), 2.106(5)	33
$[NHEt_3][Sn(acac)Cl_4]$	2.094(4)	50

[a] This work

Table 6-10: Sn-O Bond Distances (Å) Involving Ketone Ligands

Both Sn-Cl distances are shorter than those of $SnCl_2(tacac)_2$ [32] and are comparable to those observed in $SnCl_2(acac)_2$ [39], in agreement with the far infrared data, where ν_s and ν_{as}(Sn-Cl) for $SnCl_2(bzbz)_2$ are similar to those of $SnCl_2(acac)_2$ [39] and higher than those of $SnCl_2(tacac)_2$. According to Sreelatha _et al_ [32], these short Sn-Cl bond distances confirm that a strong complex has been formed.

The angle subtended by the two chloro groups is 95.1(1)° and is greater than the ideal 90°, probably because of the steric requirements of the chloro groups and the small bite of the diketonate ligands. Only $SnCl_2(SC_5H_4N\text{-}2)_2$ has a Cl-Sn-Cl angle which is lower than that of $SnCl_2(bzbz)_2$. It has been suggested [25, 26] that, for metallocene dichlorides of the type $(\eta^5\text{-}C_5H_5)_2MCl_2$, where M = Ti, Zr, Hf, V or Mo, the Cl-M-Cl angle must lie within the range

82.0 - 94.5° and, hence, the non-bonding Cl....Cl distance (bite) must be less than 3.6A and may be important for their antitumour activity, since this is the upper limit for DNA-metal crosslinks. This criterion has been applied to some of the complexes, including $SnCl_2(bzbz)_2$ mentioned in Table 6-11 [41].

Complex 2 and complexes 5 - 8 have been tested as antitumour agents and are inactive. None of these compounds had a Cl-Sn-Cl bond angle within the range mentioned above. The Cl-Sn-Cl bond angle of $SnCl_2(bzbz)_2$ is just outside this range too, and, on this basis, would not be expected to show any antitumour activity. Section 6.2.3 gives the results obtained when this compound was tested against P388 leukaemia and B16 murine melanoma.

No.	Complex	Chelate Ring Size	Cl-Sn-Cl Bond Angle (°)	References
1	$SnCl_2(bzbz)_2$[a]	6-membered	95.1(1)	a
2	$SnCl_2(acac)_2$	6-membered	96.86(5)	39
3	$SnCl_2(btbm)_2$	6-membered	95.3(1)	32
4	$SnCl_2(tacac)_2$	6-membered	98.5(1)	32
5	$SnCl_2\{SCH_2CH(NH)_2COOMe\}_2$	5-membered	99.4(1)	41
6	$SnCl_2(ONPhCOPh)_2$	5-membered	99.0(2)	42
7	$SnCl_2(OCMe{:}CHCOOEt)_2$	6-membered	98.1(1)	40
8	$SnCl_2(SC_5H_4N\text{-}2)_2$	4-membered	94.8(1)	43

[a] This work

Table 6-11: Cl-Sn-Cl Bond Angle of Complexes of the type $SnCl_2L_2$ (L = chelating ligand)

6.2.3 Evaluation of Antitumour Properties of Bis(diketonato-O,O) dihalotin(IV) Complexes

6.2.3.1 Against P388 Leukaemia

These *in vivo* antitumour tests were carried out by Dr. G. Atassi of the Institut Jules-Bordet, Brussels, and the results obtained are detailed in Table 6-12.

Compound	Doses (mg/kg)	Med.S.T.[a] (days)	T/C (%)
$SnCl_2(bzac)_2$	240	10.2	108
	120	10.0	106
	60	10.0	106
$SnCl_2(bzbz)_2$	240	10.0	106
	120	10.5	111
	60	10.0	106
Controls		9.4	

[a] Med.S.T. = Median Survival Time

Table 6-12: Results of Antitumour Testing Against P388 Leukaemia

The results show that neither of the tin complexes were active against this tumour despite the high doses used.

6.2.3.2 Against B16 Murine Melanoma

These *in vitro* experiments were carried out by Professor L. Cima, Department of Pharmacology, University of Padua. The results obtained are shown in Figure 6-3.

A statistically significant inhibition of cell growth was observed after 24 hours and 48 hours exposure to 10^{-4}M $SnCl_2(bzac)_2$ or $SnCl_2(bzbz)_2$, the percentage cell growth being reduced to *ca*. 70% in the case of $SnCl_2(bzac)_2$ and to

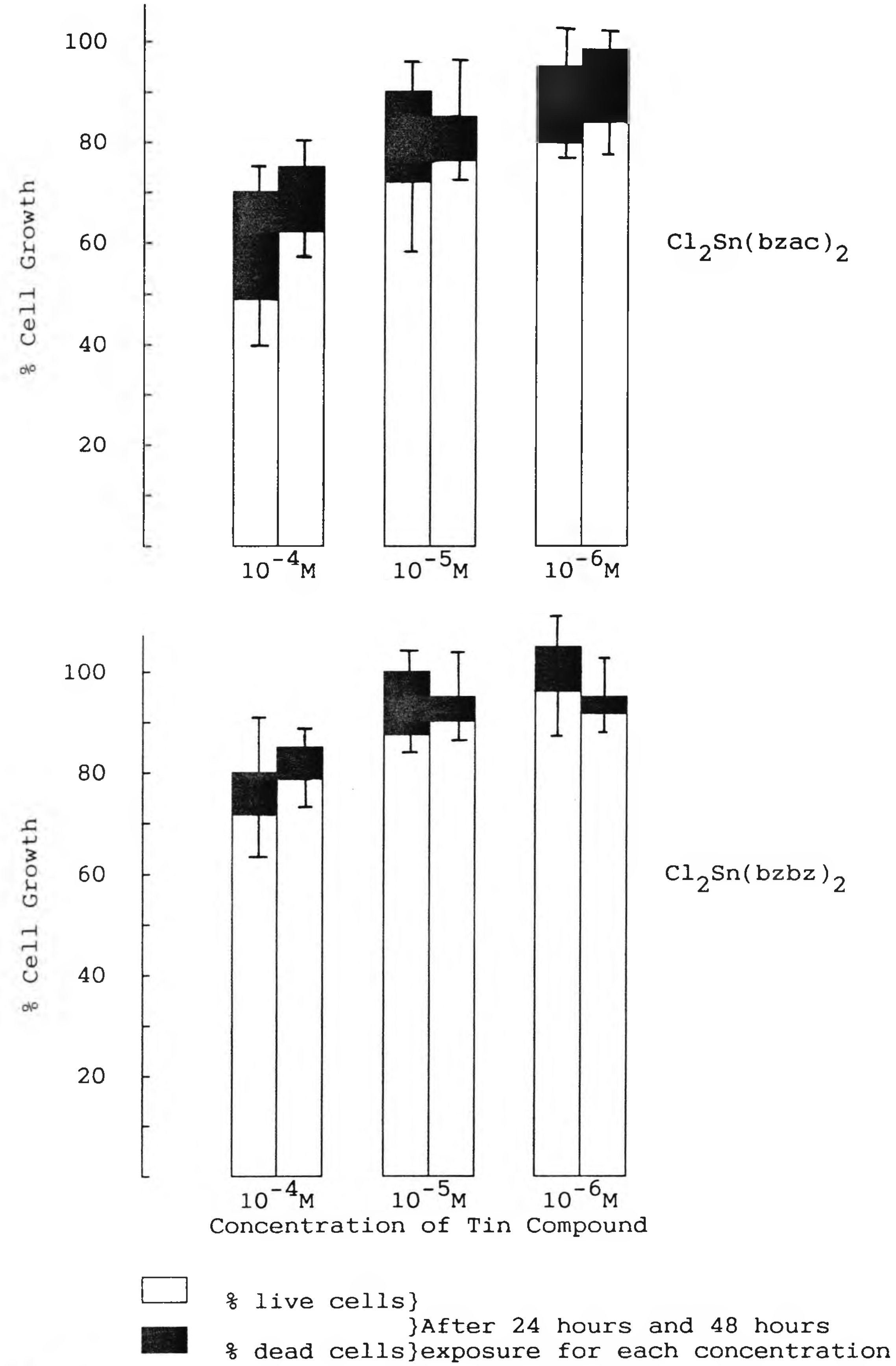


Figure 6-3: <u>Antitumour Activity of Cl$_2$Sn(bzac)$_2$ and Cl$_2$Sn(bzbz)$_2$ Against B16 Murine Melanoma</u>

ca. 80% in the case of $SnCl_2(bzbz)_2$. However, lower concentrations did not cause a significant reduction of cell proliferation.

6.2.3.3 Correlation of the Antitumour Activity of $SnCl_2(bzbz)_2$ with its Structure

As stated in Section 6.2.2.3, the Cl-Sn-Cl angle of tin compounds containing *cis* chlorine atoms may be important in determining their effectiveness as antitumour agents. The Cl-Sn-Cl bond angle of $SnCl_2(bzbz)_2$ [95.1° (1)] is just outside the required range (82.1 - 94.5°) [25, 26] and thus it would not be expected to be active. This is in agreement with the results obtained on testing against P388 leukaemia, but is not in accord with activity observed against B16 murine melanoma. Activity for tin complexes with Cl-Sn-Cl bond angles > 94.5° has been observed for some organotin adducts of the type, $R_2SnX_2.L$ (R = alkyl or aryl group; X = F, Cl, Br, I, NCS; L = *N-* or *O-* donor ligands) [49], and it has been concluded that the formation of metal-base crosslinks with DNA takes place *via* a different route for the organotin compounds. A similar conclusion may be drawn in this case. An alternative suggestion results from the observation that, for $R_2SnX_2.L_2$ (where L = *N*-donor ligand), the more stable complexes, i.e. those with shorter Sn-N bond lengths, had lower activities [22]. This implies that predissociation of the bidentate ligand may be a crucial step in the formation of a tin-DNA complex. However, from the values of the Sn-O bond lengths of $SnCl_2(bzbz)_2$, it appears that this may not be the case for this complex, which contains a strongly chelating ligand and yet is still active against B16 murine melanoma.

6.3 EXPERIMENTAL

6.3.1 Synthesis of trans-Dichlorotin(IV) Protoporphyrin IX

This compound was prepared following the method of O'Rourke and Curran [5] and involved the reaction of the free base porphyrin with anhydrous tin(II) chloride (Equation 6-1).

$$SnCl_2 + C_{34}H_{34}N_4O_4 \xrightarrow{[O]} Cl_2Sn(C_{34}H_{32}N_4O_4) + H_2O \qquad (6\text{-}1)$$

Protoporphyrin IX (a black/purple solid, 0.5g) was dissolved in pyridine (*ca* 160cm^3) and an equal weight of $SnCl_2$ in concentrated pyridine solution was added. The resulting purple solution was refluxed for 2 hours and after cooling was poured into diethyl ether (*ca* 400cm^3). The solution was then washed three times with hydrochloric acid (5M, 280cm^3 portions) and with distilled water. A red-coloured solid precipitated during these washings and this was filtered off and dried *in vacuo*; mp > 340° C.

The microanalysis (Table 6-1) indicated that the product was impure and, since it was very insoluble in most organic solvents, purification was attempted by sublimation. At 130° C, a white solid was observed on the cold finger and infrared and microanalytical data were obtained for both the sublimate and the unsublimed product (Table 6-1).

An attempt to recrystallise a commercial sample of dichlorotin IV protoporphyrin IX (from Prophyrin Products Inc., Logan, Utah), the microanalysis of which showed it to be slightly impure (Table 6-1) from nitromethane or ethyl acetate was unsuccessful, both solvents giving powdered solids.

6.3.2 **Synthesis of Bis(diketonate)dichlorotin(IV) Complexes for Antitumour Studies**

Care was taken to exclude moisture. The ligands were commercially available and were not purified before use. Microanalyses were carried out.

6.3.2.1 **Bis(benzoylacetonato-O,O)dichlorotin(IV)**

This complex was prepared by the method of Dilthey [51]. A chloroform solution of tin(IV) chloride (9.04g, 4cm^3, 0.034 moles) was added slowly dropwise to an excess of benzoylacetone (14.09g, 0.087 moles) in chloroform (90cm^3). As the tin(IV) chloride was added, the colour of the solution changed from yellow to orange. The solution was then refluxed under an inert atmosphere for 2 hours. No further colour change was observed. On cooling, a cream coloured precipitate formed. This was filtered off and dried in vacuo. The product was recrystallised from toluene and then from dichloromethane forming off-white crystals. Infrared and Mossbauer spectra were determined. A portion of this sample was sent to Sheffield Polytechnic for X-ray Crystal structure determination, but the product was not sufficiently crystalline.

A second preparation of this compound was carried out and was recrystallised from dichloromethane. Samples were then sent to Dr. G. Atassi of the Institut Jules-Bordet, Brussels for in vivo antitumour testing against P388 lymphocytic leukaemia and Dr. L. Cima, of the University of Padua for in vivo antitumour testing against B16 murine melanoma.

6.3.2.2 Bis(dibenzoylmethanato-O,O)dichlorotin(IV)

This complex was prepared by a similar route to that of the above compound using tin(IV) chloride (6.78g, 3cm^3, 0.026 moles) and dibenzoylmethane (11.67g, 0.052 moles). The yellow solid which precipitated on cooling was recrystallised from ethyl acetate/toluene (Sample I). The product was characterised by infrared and ^{119m}Sn Mossbauer spectra.

A sample of this product was recrystallised again from dichloromethane and the yellow crystalline solid which formed was sent to Sheffield Polytechnic for X-ray crystal structure determination.

The rest of Sample I was recrystallised again from chloroform and portions were sent to Dr. Atassi and Dr. Cima for antitumour testing.

6.3.3 Crystal Structure Determination of Bis(dibenzoylmethanato-O,O) - dichlorotin(IV)

This was carried out by Dr. N.A. Bell at Sheffield Polytechnic.

6.3.3.1 Crystallographic Information

$SnCl_2(bzbz)_2$ was recrystallised from dichloromethane as yellow needles. A crystal of approximate dimensions 0.04x0.20x0.60 mm was mounted with its c-axis coincident with the ω-axis of a Stoe-Stadi 2 two circle diffractometer. Data were collected using the background-ω scan-background technique and with graphite monochromated

MoK radiation. 3224 unique reflections were measured of which 2116 had $I/\sigma(I) \geqslant 4.0$ and were used for subsequent analysis. Data were corrected for Lorentz and polarisation effects, but not for absorption.

6.3.4 Antitumour Testing

6.3.4.1 In Vivo Antitumour Testing Against P388 Leukaemia

In vivo testing of $SnCl_2(bzac)_2$ and $SnCl_2(bzbz)_2$ was carried out by Dr. G. Atassi of the Institut Jules Bordet, Brussels. The tumour cells were intraperitoneally (ip) inoculated and the drug was administered ip.*ie*. the tumour cells and the drug are in direct contact. The P388 leukaemic cells were inoculated on day 0 and treatment was administered from day 1 to day 5. The dose of tin compound used ranged from 60 to 240mg/kg. The activities of the tin compounds were evaluated by computing the T/C value *ie* the median survival time of the treated group of animals (T) divided by that of the control group(C) expressed as a percentage. A compound is termed active if T/C > 120%.

6.3.4.2 In Vitro Antitumour Testing Against B16 Murine Melanoma

These experiments were carried out by Professor L. Cima and Dr. M. Carrara, Department of Pharmacology, University of Padua. They were performed using F10 metastatic cells of B16 murine melanoma (Fidler's Source). The cells were seeded at 3×10^4 cells/ml in Dulbecco's modification of Eagle's medium supplemented with 10% foetal calf serum, 1% 200mM glutamine, 1% Hepes buffer, 100 U/ml penicillin, 500 g/ml kanamycin. Each experiment was set up in triplicate in petri dishes. The cultures were exposed to the two compounds, incubated in an atmosphere containing 5% CO_2 at 37°C, recovered from culture dishes by 0.25% trypsin, neutralised by foetal calf serum, centrifuged at 1000 rpm for 10 minutes and counted in a haemocytometer.

The compounds were dissolved in a Cremopher EL alcoholic solution 1:0.42 which was diluted 1:100 in saline and finally 1:10 in the culture medium [52].

The cell growths were tested at 10^{-4}, 10^{-5} and 10^{-6}M after 24 and 48 hours exposure.

6.4 CONCLUSIONS

(i) The X-ray crystal structure of $SnCl_2(bzbz)_2$ has been determined and the tin atom found to be octahedrally co-ordinated, with the chloro groups occupying <u>cis</u> positions.

(ii) The angle subtended by the two chloro groups was greater than the ideal 90°.

(iii) Both complexes $SnCl(bzac)_2$ and $SnCl_2(bzbz)_2$ were found to cause significant inhibition of B16 Murine Melanoma cell growth at a concentration of 10^{-4} M. This would not be expected for $SnCl_2(bzbz)_2$ which had a Cl-Sn-Cl angle outside the range believed to be suitable for antitumour activity. However neither compound was active against P388 Leukaemia.

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