Chalcogen-Carbon-Nitrogen Rings, Chains and Coordination Compounds

By

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A Thesis submitted

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I, Colin James Burchell, hereby certify that this thesis, which is approximately 40,000 words in length, has been written by me, that it is the record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

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Abstract

This thesis describes the general area of chalcogen-carbon-nitrogen compounds. The first part of Chapter 1 provides an introduction to chalcogen donor ligands. The second part of Chapter 1 considers the literature reports on polythiocyanogen and related compounds. Chapter 2 details the synthesis and characterisation of a series of homoleptic, heteroleptic and dimeric cyanodithioimidocarbonate complexes prepared by the reaction of dipotassium cyanodithioimidocarbonate with the appropriate transition metal starting materials. Chapter 3 describes the synthesis and characterisation of the cyanodiselenoimidocarbonate complexes. In Chapter 4 we report a convenient one pot synthesis for the preparation of triselenocarbonate complexes. We have prepared mononuclear, binuclear and tetranuclear complexes of this ligand including the first crystallographically characterised example of a triselenocarbonate complex. In Chapter 5 we have prepared a series of 1,2,4-thiadiazole compounds for spectroscopic comparison with $(SCN)_x$. We also report the synthesis of model compounds for $(SCN)_x$ composed of two 1,2,4-dithiazole rings linked by a sulfur bridge. Chapter 6 describes the synthesis and full characterisation of polythiocyanogen $(SCN)_x$ the related small molecules $S_x(CN)_2$ (x = 1, 2, 3) and the selenium analogues. Using the data obtained and comparison with the 1,2,4-thiadiazole model compounds reported in Chapter 5 as well as literature compounds we have determined the structure of polythiocyanogen.

Acknowledgements

Firstly I would like to thank my parents for all their help and support. My sister Karen just for being herself. Also I would like thank Ine for all of her chemical advice but more importantly for cheering me up when reactions didn't work and her constant support. Everyone in the lab deserves a mention. Firstly the postdocs Steve and Petr for their enthusiasm and hours of help. Also Prav and more recently Sahrah. Then everybody else David, Ian, Jo, Matt, Stuart, Richard and Vit. Thanks for making the lab a fun place to work. I would like to acknowledge Caroline (Mass Spec), Melanja (NMR), Marge (Stores) and Sylvia (Microanalysis) for all their technical help. Thanks are also due to Dr Alan Aitken for his helpful discussion and advice. A special mention must go to Prof Alexandra Slawin for all the fantastic crystal structures she has obtained during this project. Finally I would like to thank Prof J. Derek Woollins for providing and interesting topic to study and for all his advice and support over the years. Thanks are due to the School of Chemistry for funding.

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Abbreviations

The following abbreviations are used throughout this thesis

Å	Angstrom unit, 10^{-10} m
^{n}Bu	Butyl, *n*-C_4H_9
cm^{-1}	Wavenumber
°	Degree
°C	Degrees Celsius
cod	cycloocta-1,5-diene
DCTB	T-2-(3-(4-*t*- Butyl-phenyl)- 2-methyl- 2-propenylidene) malononitrile
dmso	Dimethyl sulfoxide
DP	Direct polarisation
dppe	bis(diphenylphosphino)ethane
dppf	bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dto	dithiooxalate
EI	Electron Impact
ES	Electrospray
Et	Ethyl, C_2H_5
FAB	Fast Atom Bombardment
FT	Fourier Transform
HMBC	Heteronuclear Multiple Bond Correlation
HSQC	Heteronuclear Single Quantum Correlation

Hz	Hertz
IR	Infra-red
J	Coupling constant
MALDI	Matrix Assisted Laser Desorption Ionisation
Me	Methyl, CH_3
MS	Mass Spectroscopy
m/z	Mass to charge ratio
NMR	Nuclear Magnetic Resonance
Ph	Phenyl, C_6H_5
^{i}Pr	iso-propyl, *i*-C_3H_7
^{n}Pr	propyl, *n*-C_3H_7
thf	Tetrahydrofuran
TOF	Time of Flight
p-tol	*para*-toluene

Chapter 1: *Introduction*

1.1 *General*

In the first part of this chapter we will examine chalcogen donor ligands. In later chapters we will then discuss three different series of chalcogen donor ligands that we have prepared. In the second part of this chapter we will consider the literature reports on polythiocyanogen and related compounds. In later chapters we will then discuss our investigations into the structure of polythiocyanogen.

1.2 *Chalcogen donor ligands.*

Chalcogen donor ligands are a well investigated area and have many applications ranging from analytical reagents to polarizers in sunglasses.[1] The simplest chalcogen donor ligands are the S, Se and Te atoms (often as the dianion) which can all act as either terminal or bridging ligands.[1,2] The most common bridging modes are shown below (Figure 1.1).[1]

μ_2 bridging S atom μ_3 triply-bridging S atom μ_4 quadruply-bridging S atom

Figure 1.1 The S atom as a bridging ligand.

The disulfur ligand $[S_2]^{2-}$ and chelating polysulfides $[S_n]^{2-}$ are also well established.[1] The selenium and tellurium analogues of these species are also prevalent.[2] The disulfur ligand has been studied considerably because of the

variety of coordination modes displayed by this simple ligand. There are at least eight different coordination modes known (Figure 1.2) and often more than one type of coordination mode occurs in complexes.[3]

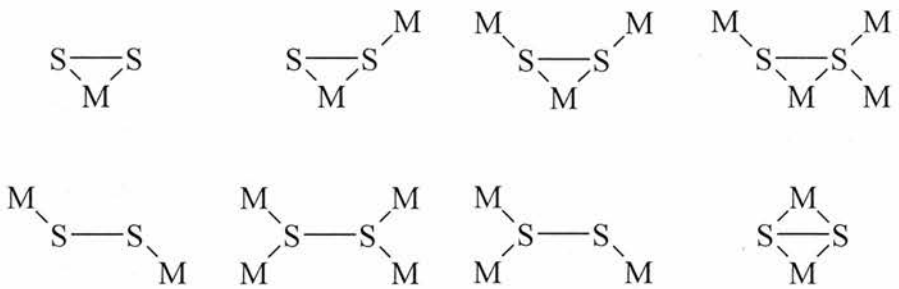
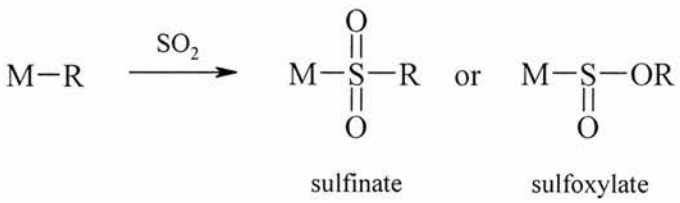


Figure 1.2 Types of metal disulfur complex.

Chelating polysulfides $[S_n]^{2-}$ are commonly prepared by the reaction of hydrido complexes with elemental sulfur[4] or from the reaction of metal halides with solutions of polysulfides.[4] Chelating polyselenides and polytellurides can be prepared in a similar fashion.[4] The most common polychalcogenides are E_4 and E_5 (E = S, Se, Te) which form 5 and 6 membered rings respectively (Figure 1.3).

Figure 1.3 5 and 6 membered rings formed by MS_4 and MS_5 complexes.

Oxides of sulfur are another common type of chalcogen donor ligand. Sulfur dioxide can coordinate to metals in at least nine different ways via sulfur or oxygen.[5] The thiosulfate dianion is also capable of binding to metal centres in various fashions via sulfur or oxygen.[1] Sulfur dioxide can also be inserted into metal carbon bonds to prepare sulfinate or sulfoxylate sulfur donor ligands (Scheme 1.1).[6]



Scheme 1.1 Sulfur dioxide insertion into metal carbon bond.

Oxides of selenium and tellurium chalcogen donor ligands are also known but are much less common.

Coordination of sulfur nitrogen anions is another area which has been of considerable interest in recent times.[7,8] Various sulfur nitrogen fragments have been coordinated to metal centres. $[S_2N_2]^{2-}$, and $[S_4N_4]^{2-}$ are both well established examples (Figure 1.4).[9,10]

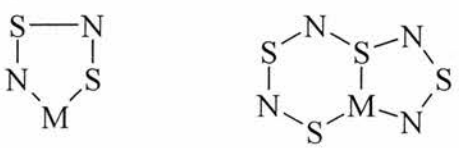


Figure 1.4 $[M(\eta^2\text{-}S_2N_2)]$ and $[M(\eta^3\text{-}S_4N_4)]$ complexes.

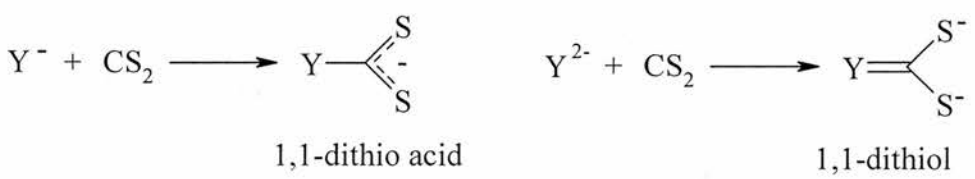
The ambidentate thiocyanate ion can act as either a sulfur or nitrogen donor ligand favouring bonding via sulfur to heavy metals.[11] Various types of bridging modes are also known. The selenocyanate and tellurocyanate ions are also known and have similar behaviour to thiocyanate ion although the tellurocyanate ion is rare.

Monodentate sulfur donor ligands such as thiols thioesters and thioureas are all well established.[1] The selenium analogues are all known and tend to have

similar behaviour to the sulfur compounds.[12] The tellurium analogues are far less common. S,S-bidentate ligands such as dithioethers and a range of 1,1-dithiolato[13-15] and 1,2-dithiolato ligands[16] are also well studied. 1,1-dithiolato ligands have two sulfur donor atoms joined to the same carbon atom and are discussed further below. The majority of the analogous Se,Se-bidentate ligands are known.

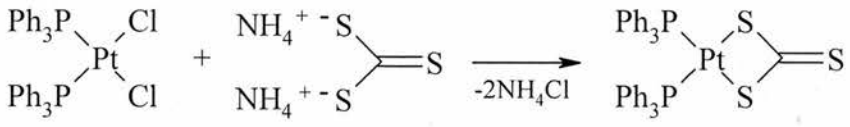
1.3 *1,1-dithiolato complexes.*

S,S-bidentate ligands are well studied and have a variety of industrial applications including vulcanisation of rubber, lubricant additives, fungicides, pesticides and catalysis.[13-17] In this project we are interested in 1,1-dithiolato ligands. 1,1-dithio acids and 1,1-dithiols are commonly formed by the reaction of carbon disulfide with various nucleophiles (Scheme 1.2).[15]



Scheme 1.2 Preparation of 1,1-dithio acids and 1,1-dithiols.

Metal ions and complexes react readily with 1,1-dithio acids and 1,1-dithiols to form four membered chelate rings.[15] A good example is the reaction of $[PtCl_2(PPh_3)_2]$ with ammonium trithiocarbonate, $[NH_4]_2[CS_3]$ (Scheme 1.3).[18]



Scheme 1.3 Preparation of $[Pt(CS)_3(PPh_3)_2]$.

1,1-dithioacids are also capable of acting as unidentate ligands (Figure 1.5).

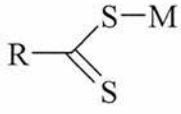
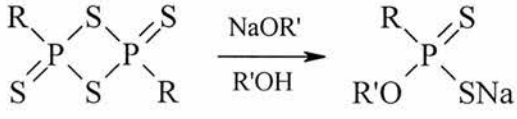


Figure 1.5 1,1-dithioacid acting as a unidentate ligand.

A large number of 1,1-dithiolate complexes are known. The major types of 1,1-dithiolate ligands are summarised in Table 1.1. Phosphinodithioates and phosphorodithioate ligands are derived from reaction of P_4S_{10} with hydrocarbons and alcohols respectively.[19,20] Phosphonodithioate ligands can be prepared by ring opening of Lawesson's Reagent and its derivatives (Scheme 1.4).[21,22]



Scheme 1.4 Preparation of phosphonodithioate ligands.

All the other major types of ligand are prepared by the reaction of carbon disulfide with different nucleophiles (Scheme 1.2).

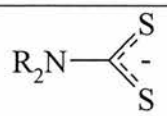
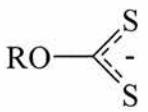
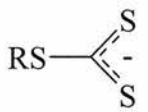
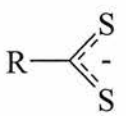
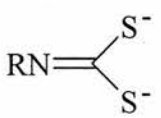
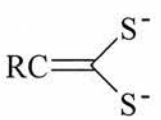
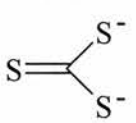
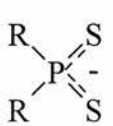
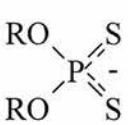
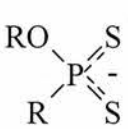
Ligand	Name
	Dithiocarbamate
	*O*-Alkyldithiocarbonate
	Thioxanthate
	Dithiocarboxylate
	Dithiocarbimate
	1,1-Ethenedithiolate
	Trithiocarbonate
	Phosphinodithioate
	Phosphorodithioate
	Phosphonodithioate

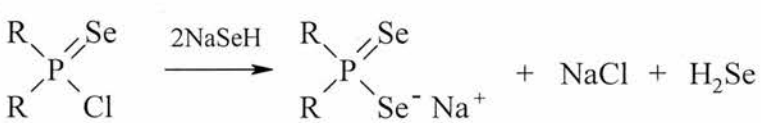
Table 1.1 Major types of 1,1-dithiolate ligands.

The 1,1-ditholate ligands have been studied in great detail. Their synthesis, properties and coordination modes have been discussed in detail by Coucouvanis,[13] Eisenberg[14] and Burns, McCullough and McAuliffe.[15] However there have been surprisingly few studies of the dithiocarbimate ligands.[15]

1.4 *1,1-diselenolato complexes.*

Relative to the significant volume of interest in the sulfur analogues, *Se,Se*-bidentate ligands are rather understudied. There has been significant interest in ZnSe and CdSe semiconductors in photovoltaic devices due to their intermediate energy band gap.[23] Hence *Se,Se*-bidentate compounds such as cadmium and zinc diselenocarbamato complexes have been investigated as single source precursors for deposition of these semiconductor materials.[24]

In this project we are interested in 1,1-diselenolato ligands. The 1,1-diselenolato ligands are far less common than the sulfur analogues and are often unstable. The major types of 1,1-diselenolato ligands are summarised in Table 1.2. Phosphinodiselenoates and phosphorodiselenoate ligands are prepared by reaction of the appropriate chlorophosphine selenide with sodium hydrogen selenide (Scheme 1.5).[19]



Scheme 1.5 Preparation of phosphinodiselenoate ligands.

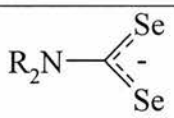
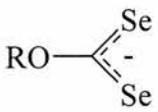
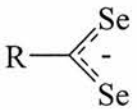
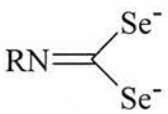
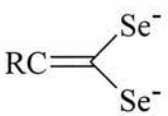
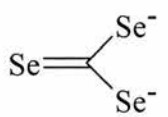
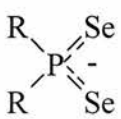
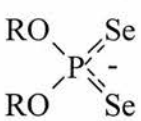
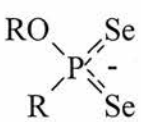
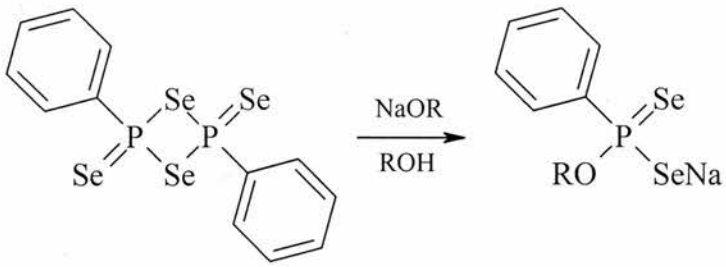
Ligand	Name
	Diselenocarbamate
	*O*-Alkyldiselenocarbonates
	Diselenocarboxylate
	Diselenocarbimate
	1,1-Etheneditselenolate
	Triselenocarbonate
	Phosphinodiselenoate
	Phosphorodiselenoate
	Phosphonodiselenoate

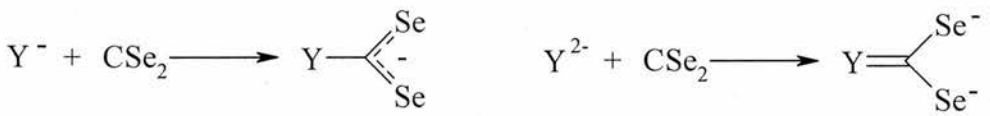
Table 1.2 Major types of 1,1-diselenolate ligands.

Phosphonodiselenoate ligands can be prepared by ring opening of Woollins' Reagent (Scheme 1.6).[25]



Scheme 1.6 Preparation of phosphonodithioate ligands.

The majority of the other types of 1,1-diselenolato ligands can be prepared by the reaction of carbon diselenide with nucleophiles in the same fashion as the sulfur analogues (Scheme 1.7).[26]



1,1-diseleno acid 1,1-diselenol

Scheme 1.7 Preparation of 1,1-diseleno acids and 1,1-diselenols.

One exception is the triselenocarbonate ligand $[CSe_3]^{2-}$ for which a good synthetic route is not known. Three triselenocarbonate complexes have been prepared in low yield by the interaction of carbon diselenide with metal complexes.[27-29] Diselenocarbimates are another area which have received very little attention. This is illustrated by the fact that only one cyanodiselenoimidocarbonate complex is known.[30]

1.5 *Inorganic Polymers.*

The widespread use of polymers in fibres, films and structural materials has established them as being amongst the most versatile of materials. In recent times developments have included electrical conductivity, photoconductivity and electroluminescence. There is already a significant volume of work on polymers with inorganic backbones. Silicone polymers provide a well established example of the versatility of non-organic backbones. Silicone elastomers, oils and resins have applications including the insulation of electrical equipment, suntan lotions, car polish and even space suits.[31] Polyphosphazenes $(NPX_2)_n$ (X = Cl, Br, F) have properties including flame retardancy , water repellence and solvent resistance.[32] Polythiazyl $(SN)_x$, first synthesised by F. B. Burt in 1910 by the solid-state polymerisation of crystalline S_2N_2, was the first metal free material shown to possess super and thermal conductivity.[1] However there have been surprisingly few studies of polymers that incorporate main group atoms or functions mixed with carbon backbones. In this project we are interested in polythiocyanogen $(SCN)_x$ and the recently reported polyselenocyanogen $(SeCN)_x$. Before moving on to these polymers we must first discuss the pseudohalides $S_2(CN)_2$ and $Se_2(CN)_2$ from which these polymers are derived, as well as 1,2,4-thiadiazoles and 1,2,4-dithiazoles.

1.6 *Pseudohalides.*

Ions that have similar chemical and physical properties to the halide ions are known as pseudohalides.[11,33] Examples include azide (N_3^-), cyanide (CN^-), cyanate (NCO^-), thiocyanate (NCS^-), selenocyanate ($NCSe^-$) and tellurocyanate ($NCTe^-$). Some properties common between halides and pseudohalides are the combination with hydrogen to form monobasic acids (HX), the formation of insoluble silver(I), mercury(I) and lead(II) salts (AgX, Hg_2X_2 and PbX_2) and some of the pseudohalides (X^-) can be converted to pseudohalogens (X_2) (Scheme 1.8).

$$2X^- \rightleftharpoons X_2 + 2e^-$$

Scheme 1.8 Conversion of pseudohalides to pseudohalogens.

The pseudohalogens are similar in chemical properties and reactivity to the halogen elements, for example, they are capable of oxidative addition to transition metal substrates (Scheme 1.9) and substitution reactions (Scheme 1.10).

$$[Ni(CO)_2(PPh_3)_2] + (CN)_2 \longrightarrow [Ni(CN)_2(PPh_3)_2] + 2CO$$

Scheme 1.9 Oxidative addition of cyanogen to $[Ni(CO)_2(PPh_3)_2]$.[34]

$$H_2C{=}CH_2 + (CN)_2 \longrightarrow H_2C{=}\underset{H}{C}{-}{\equiv}N + HCN$$

Scheme 1.10 Cyanation of ethene.[35]

Furthermore it is possible to form mixed pseudohalide halides compounds in the same fashion as mixed halides. Molecular pseudohalogens have not been prepared for all known pseudohalides. Some pseudohalogens that have actually been isolated are cyanogen $(CN)_2$, thiocyanogen $S_2(CN)_2$, and selenocyanogen $Se_2(CN)_2$. In this project we are interested in thiocyanate $(SCN)^-$, thiocyanogen $S_2(CN)_2$ and their selenium analogues selenocyanate $(SeCN)^-$ and selenocyanogen $Se_2(CN)_2$.

1.7 *Thiocyanogen.*

The first attempted preparation of thiocyanogen was by Liebig[36] in 1829 but it was not until 1919 that thiocyanogen was first isolated by Soderback.[37] Soderback initially prepared thiocyanogen by allowing iodine to react with a suspension of silver thiocyanate in diethyl ether (Scheme 1.11).

$$2AgSCN + I_2 \rightleftharpoons S_2(CN)_2 + 2AgI$$

Scheme 1.11 First attempted preparation of thiocyanogen.

It was found that reaction with iodine reaches equilibrium and does not go to completion and that reaction with bromine achieves a far better result (Scheme 1.12).

$$2AgSCN + Br_2 \rightleftharpoons S_2(CN)_2 + 2AgBr$$

Scheme 1.12 Standard preparation of thiocyanogen.

It is possible to use other metal thiocyanates such as lead thiocyanate instead of the silver salt for the preparation of thiocyanogen. Other solvents such as carbon disulfide and chloroform have been used successfully. Thiocyanogen can also be formed by oxidation of hydrogen isothiocyanate by manganese dioxide, lead tetraacetate or other oxidising agents and by the electrochemical oxidation of the thiocyanate ion.[38]

The redox potential for thiocyanogen is in between that of bromine and iodine (Scheme 1.13).[38]

$$I^- \rightleftharpoons 1/2I_2 + e^- \quad -0.53V$$

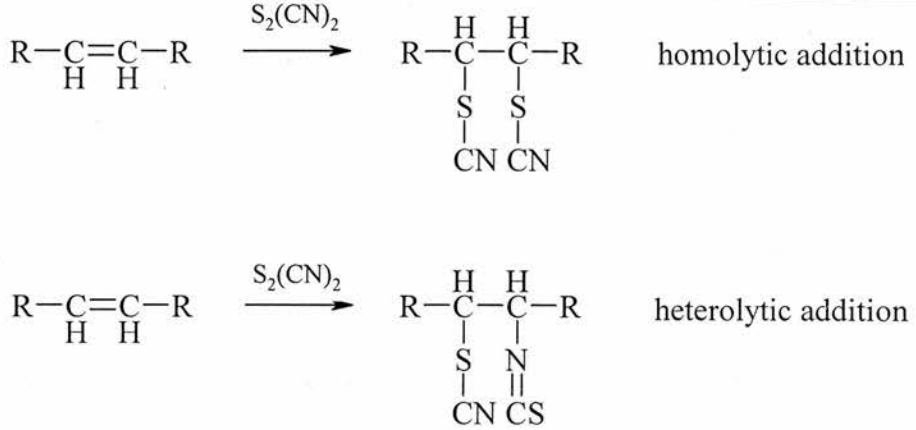
$$SCN^- \rightleftharpoons 1/2S_2(CN)_2 + e^- \quad -0.77V$$

$$Br^- \rightleftharpoons 1/2Br_2 + e^- \quad -1.07V$$

$$Cl^- \rightleftharpoons 1/2Cl_2 + e^- \quad -1.36V$$

Scheme 1.13 Redox potential of thiocyanogen compared to halides.

Hence thiocyanogen has been described as the classic pseudohalogen having halogen like behaviour in between that of bromine and iodine.[39] Solutions of thiocyanogen can liberate iodine from iodides in the same way bromine or chlorine can. In organic chemistry thiocyanogen has been used for generating organic thiocyanates by heterolytic and homolytic addition to alkenes (Scheme 1.14).[40,41]



Scheme 1.14 Example of homolytic and heterolytic addition of thiocyanogen to alkenes.

Infrared,[42-44] Raman[45-47] and ^{13}C NMR[48] data strongly suggests that thiocyanogen has an unbranched structure containing a disulfide bridge as shown below (Figure 1.6).

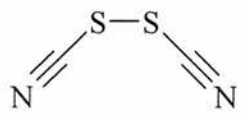


Figure 1.6 Proposed structure of thiocyanogen.

Solid thiocyanogen exists as colourless crystals which melt at -2 to -3 °C and if liquid thiocyanogen is allowed to warm to room temperature it will readily polymerise to form the insoluble brick red solid polythiocyanogen $(SCN)_x$ which we will discuss later. Hence it is difficult to isolate and is usually made and used in solution.

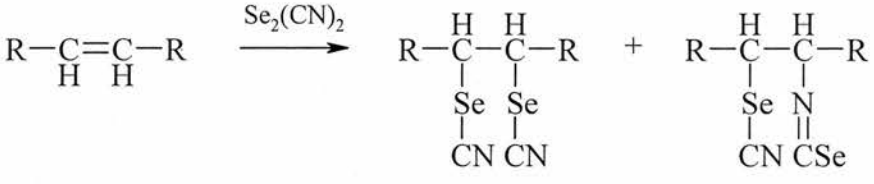
1.8 *Selenocyanogen.*

Selenocyanogen $Se_2(CN)_2$ was first prepared by Birckenbach and Kellermann in 1925 by reaction of silver selenocyanate with iodine in diethyl ether in a similar fashion to the preparation of thiocyanogen (Scheme 1.15).[49]

$$2AgSeCN + I_2 \rightleftharpoons Se_2(CN)_2 + 2AgI$$

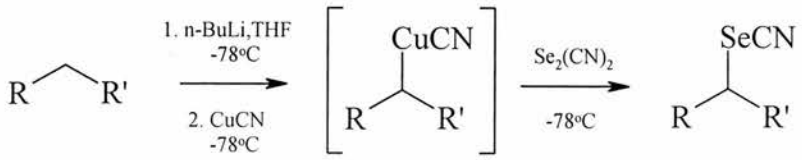
Scheme 1.15 Preparation of selenocyanogen.

Selenocyanogen has also been prepared by the reaction of lead tetraacetate and potassium selenocyanate,[50] anionic oxidation of potassium selenocyanate[51] and by oxidation of potassium selenocyanate by iodine pentafluoride.[52] In organic chemistry just as thiocyanogen is used for forming organic thiocyanates, selenocyanogen is used for the preparation of organic selenocyanates by reaction with unsaturated hydrocarbons (Scheme 1.16).[53]

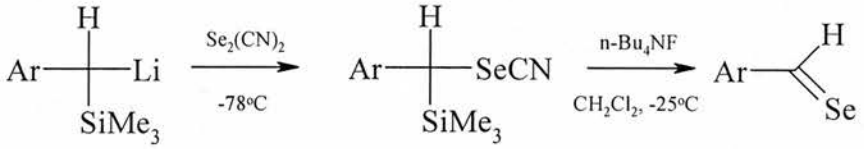


Scheme 1.16 Addition of selenocyanogen to alkenes.

Selenocyanogen has also been used with organic copper reagents to synthesise selenocyanates[54] (Scheme 1.17), for the preparation of selenoaldehydes[55] and selenoketones[56] (Scheme 1.18).



Scheme 1.17 Preparation of organic selenocyanates.



Scheme 1.18 Preparation of selenoaldehydes.

Infrared[48,52,57,58] and ^{13}C NMR[48] data strongly suggests that selenocyanogen has an unbranched structure, analogous to that of thiocyanogen, containing a diselenide bridge (Figure 1.7).

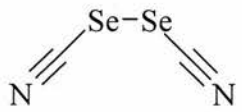
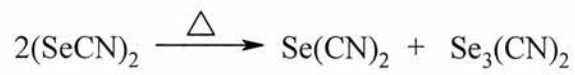


Fig 1.7 Proposed structure of selenocyanogen.

Selenocyanogen can be easily isolated as a yellow solid and can be stored under vacuum at 0 °C for several months. Unlike thiocyanogen which when heated above 0 °C quickly polymerises to give polythiocyanogen, selenocyanogen when exposed to heat in solution disproportionates to give selenium dicyanide and selenium diselenocyanate (Scheme 1.19).[50,51]



Scheme 1.19 Disproportionation of selenocyanogen.

It was reported by Cataldo that when heated to higher temperature selenocyanogen polymerises to give polyselenocyanogen.[48]

1.9 *1,2,4-thiadiazoles.*

There are four possible isomeric forms of thiadiazole (Figure 1.8).

1,2,3- 1,2,4- 1,2,5- 1,3,5-

Figure 1.8 Possible isomeric forms of thiadiazoles.

All of these isomers are known but in this project we will be focusing solely on the 1,2,4-thiadiazoles. The first 1,2,4-thiadiazole ring, perthiocyanic acid (3,5-dithio-1,2,4-thiadiazole), was prepared in 1821 by Wohler.[59] but 1,2,4-thiadiazole was not reported until 1956.[60] The 1,2,4-thiadiazole ring can be formed either from non-heterocyclic compounds or by the transformation of other heterocycles. There are seven common types of cyclisation reactions from non heterocyclic compounds which have been classified A-G (Figure 1.9).[61,62]

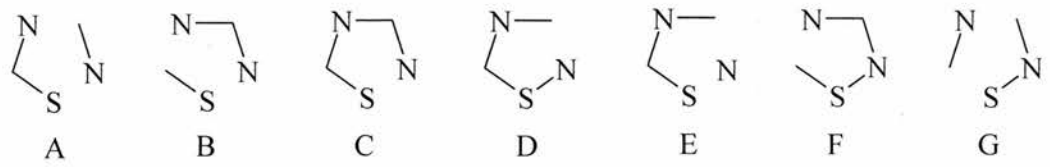
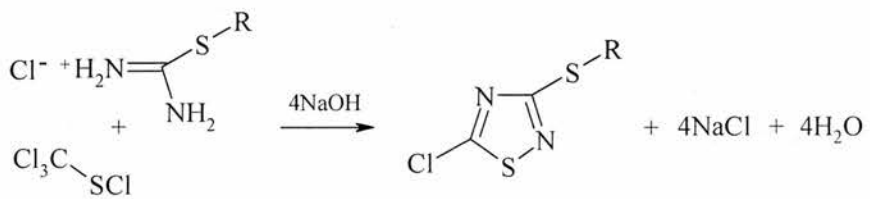


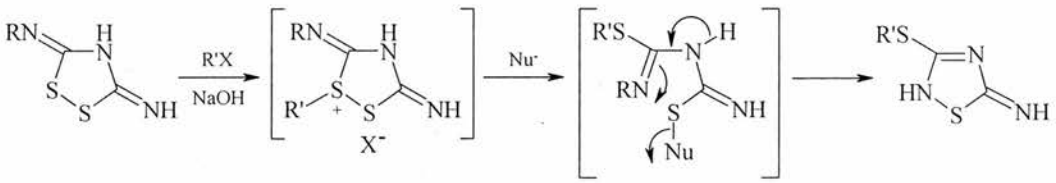
Figure 1.9 Common precursors for cyclisation reactions to form 1,2,4-thiadiazoles.

These synthetic routes have been discussed in detail by Franz and Dinghra, Kurzer and Bambas.[59,61-63] A good example of a cyclisation reaction is the preparation of a 3-alkylsulfanyl-5-chloro-1,2,4-thiadiazole from the appropriate s-alkylthiourea hydrochloride and trichloromethylsulfenyl chloride as reported by Goerdeler (Scheme 1.20).[64] This is a type B synthesis.



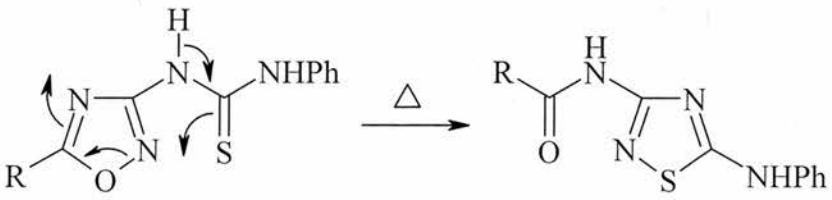
Scheme 1.20 Preparation of 3-alkylsulfanyl-5-chloro-1,2,4-thiadiazoles.

1,2,4-thiadiazoles are also formed by the transformation of other heterocycles. Substituted 1-2,4-dithiazoles are readily converted to 1,2,4-thiadiazoles.[62] An example is the alkylation of amino-1,2,4-dithiazoles under basic conditions to give 5-imino derivatives of 1,2,4-thiadiazole (Scheme 1.21).[62]



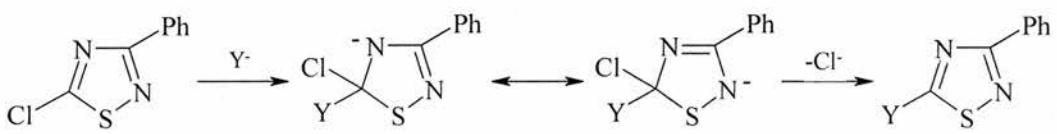
Scheme 1.21 Conversion of amino-1,2,4-dithiazole to 5-imino derivatives of 1,2,4-thiadiazole.

Oxazoles and oxadiazoles can also be rearranged into 1,2,4-thiadiazoles.[62] When 5-alkyl-3-amino-1,2,4-oxadiazoles are heated with phenyl isothiocyanate a thiourea is formed which can undergo rearrangement to give the 1,2,4-thiadiazole (Scheme 1.22).[62,65]



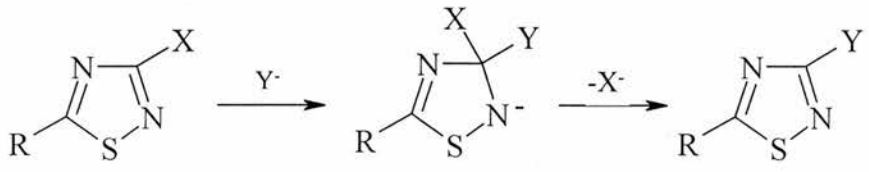
Scheme 1.22 Rearrangement of 5-alkyl-3-ammino-1,2,4-oxadiazoles to 1,2,4-thiadiazoles.

1,2,4-thiadiazole and its derivatives are described as π-excessive sulfur containing heteroaromatic rings.[59,62] The increased number of nitrogens in the ring compared to thiophene and pyrrole ring systems leads to very different properties. In 1,2,4-thiadiazole rings electrophilic substitutions on carbon are very rare.[66] Nucleophilic substitutions at C5 in the 1,2,4-thiadiazole ring are common and occur readily. 5-chloro-3-phenyl-1,2,4-thiadiazole is more reactive towards nucleophiles than many activated six membered heterocycles.[66] Both nitrogen atoms in the ring can stabilise the intermediates (Scheme 1.23) and the inductive effect of the sulfur atom also contributes to the stabilization.[66]



Scheme 1.23 Nucleophilic displacement of chloride at C5 in 5-chloro-3-phenyl-1,2,4-thiadiazole.

However C3 in the 1,2,4-thiadiazole ring is far less reactive towards nucleophilic substitution. In fact 3-chloro-1,2,4-thiadiazoles are very stable. One of the very few successful nucleophilic displacements at C3 in 3-chloro-1,2,4-thiadiazoles is by alkoxide groups.[68] 3-amino and 3-hydroxy-1,2,4-thiadiazoles are more susceptible to nucleophilic substitution[68] but are still unreactive compared to nucleophilic substitution at C5. We attribute this reduced reactivity at C3 to the reduced stability of the tetrahedral intermediate. There is only one possible resonance form for the intermediate as illustrated below (Scheme 1.24) hence only one of the nitrogen atoms can help stabilise the intermediate.



Scheme 1.24 Nucleophilic substitution at C3 in a 1,2,4-thiadiazole.

The electron withdrawing nature of the 1,2,4-thiadiazole ring is further illustrated by diazonium salts obtained from 5-amino-1,2,4-thiadiazoles (Figure 1.10) which undergo coupling reactions very readily.

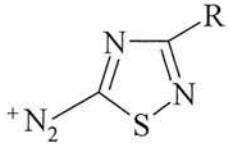
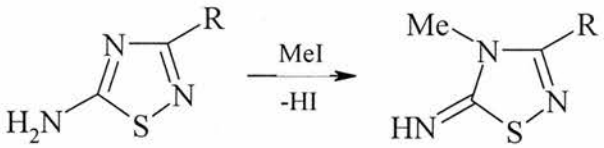


Figure 1.10 Diazonium salt derived from 5-amino-1,2,4-thiadiazole.

A study be Goerdeler has shown that diazonium salts incorporating the 1,2,4-thiadiazole ring are among the most reactive diazonium salts[59,68] and can displace azo groups from weaker coupling reagents.[59,69] It is reported that the electrophilicity of the diazonium cation is enhanced by the electron withdrawing

nature of the 1,2,4-thiadiazole ring.[59,68] Interestingly azo dyes prepared by coupling reactions using diazonium salts derived from 5-amino-1,2,4-thiadiazoles are used commercially particularly for dyeing polymers.[59,61]

1,2,4-thiadiazole rings can also undergo electrophilic attack at nitrogen and nucleophilic attack at sulfur. Alkylation of 5-amino-1,2,4-thiadiazoles results in the formation of N4 derivatives (Scheme 1.25).[62]



Scheme 1.25 Methylation at N4 of 5-amino-1,2,4-thiadiazoles.

It is also possible to form quaternary and diquaternary salts of 1,2,4-thiadiazoles.[62] Nucleophilic attack at the sulfur atom in the 1,2,4-thiadiazole ring generally leads to ring opening. Soft nucleophiles tend to attack at sulfur and hard nucleophiles attack at the C5 carbon atom.[62]

The majority of reactions involving 1,2,4-thiadiazole rings are nucleophilic substitution preferentially at C5. Reactions of 1,2,4-thiadiazole and its derivatives, including, ring cleavage, ring expansion and reactions of substituents are discussed in depth by Kurzer, Franz and Dinghra.[59,61,62] The commercial application of 1,2,4-thiadiazoles as pesticides, fungicides, azo dyes and in polymers is covered in these reviews.[59,61,62]

1.10 *1,2,4-dithiazoles.*

The four possible isomers of dithiazoles (Figure 1.11) are all known and exist as conjugated and non conjugated rings.[70-72]

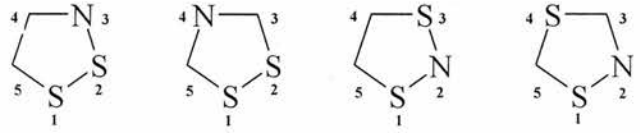
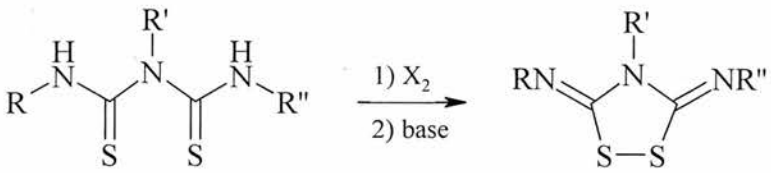


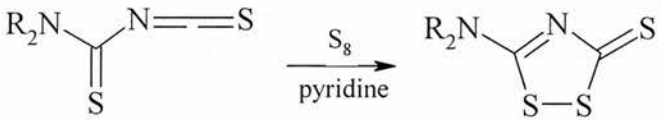
Figure 1.11 Possible isomeric forms of dithiazoles.

In this project we are interested in the 1,2,4-dithiazoles. The first 1,2,4-dithiazole ring, isoperthiocyanic acid (3-amino-5-thione-1,2,4-dithiazole), was isolated from concentrated solutions of isothiocyanic acid, by Wohler in 1821.[71-73] The 1,2,4-dithiazole ring can be formed from non heterocyclic compounds and ring transformation of other heterocycles. The formation of 1,2,4-dithiazole rings from non heterocyclic compounds has been classified by firstly the number of bonds formed and secondly the number of atoms in each fragment.[71,72] These synthetic routes have been discussed in detail by Sammes, Khlemelnitski and Makhova[71,72] so we will discuss each route very briefly. Ring synthesis by the formation of one bond can occur between two heteroatoms. An example is the cyclisation of dithioburets by halides (Scheme 1.26).[72] Alternatively one bond can be formed adjacent to a heteroatom.



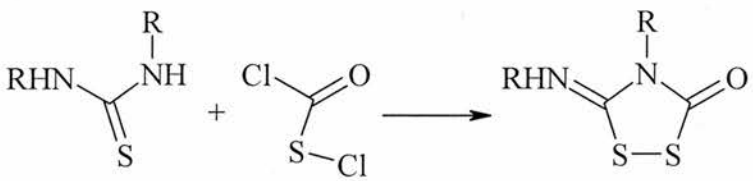
Scheme 1.26 Cyclisation of dithioburets by halides.

Ring synthesis by the formation of two bonds can occur by the addition of sulfur to a four atom fragment. An example is the reaction of aminothiocarbomyl isothiocyanates with sulfur in pyridine (Scheme 1.27).[72]



Scheme 1.27 Reaction of aminothiocarbomyl isothiocyanates with sulfur.

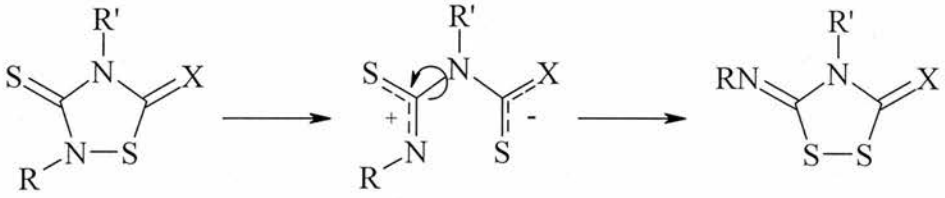
Alternatively two bonds can be formed by the combination of two and three atom fragments such as chlorocarbonylsulfenyl chloride and substituted thioureas (Scheme 1.28).[71,72]



Scheme 1.28 Reaction of chlorocarbonylsulfenyl chloride with substituted thioureas.

Ring synthesis by the formation of either three or four bonds are also possible but are far less common. The 1,2,4-dithiazole ring can be formed by the transformation of other heterocycles. 1,2,4-dithiazoles can be readily prepared

from 1,2,4-thiadiazole rings (Scheme 1.29).[71,72] These reactions are usually conducted under acidic conditions.

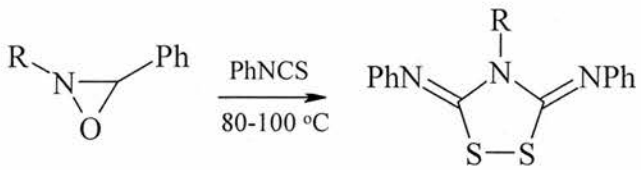


X = O, S, NR

Scheme 1.29 Conversion of 1,2,4-thiadiazoles to 1,2,4-dithiazoles.

This type of rearrangement whereby exo- and endocyclic heteroatoms on a ring are translocated is known as a Dimroth rearrangement.[72]

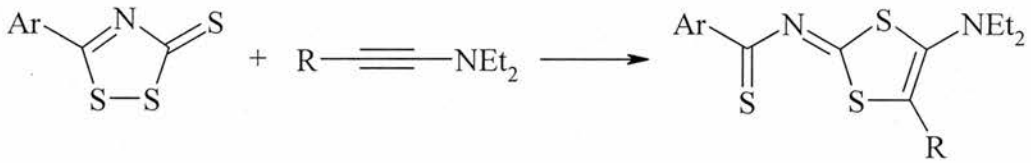
1,2,4-dithiazoles can also be prepared by reaction of oxaziridines with phenylisothiocyanate (Scheme 1.30).[72]



Scheme 1.30 Preparation of 1,2,4-dithiazoles from oxaziridines.

As mentioned earlier 1,2,4-dithiazole rings can be either conjugated or nonconjugated. The reactivity of the conjugated and nonconjugated systems will be discussed separately. In conjugated 1,2,4-dithiazoles nucleophilic attack at ring carbons are very common resulting in either displacement of a good leaving groups or ring opening.[72] This ring opening is often followed by an alternative ring closure to form either 5 or 6 membered rings.[72] 1,2,4-dithiazole cations are particularly reactive in these reactions. Another common reaction of the

conjugated ring systems is 1,3-cycloaddition of compounds with multiple bonds resulting in the formation of a new five membered ring and the cleavage of the S-S bond in the 1,2,4-dithiazole ring.[72] An example is the reaction of ynamines with 5-aryl-1,2,4-dithiazole-3-thiones (Scheme 1.31).[72]



Scheme1.31 reaction of ynamines with 5-aryl-1,2,4-dithiazole-3-thiones.

In nonconjugated 1,2,4-dithiazole rings nucleophilic attack is common at carbon, nitrogen and sulfur.[72] The S-S bond is readily cleaved by reducing agents. 1,3-cycloaddition of compounds with multiple bonds resulting in the formation of a new five membered ring are also common.[72]

Reactions of conjugated and nonconjugated 1,2,4-dithiazole rings and the substituents attached to the ring discussed in depth by Sammes, Khlemelnitski and Makhova.[71,72] The commercial application of 1,2,4-dithiazoles as fungicides, corrosion inhibitors and plant growth inhibitors are discussed in these reviews.[71,72]

1.11 *Polythiocyanogen*

Polythiocyanogen (or parathiocyanogen) is an orange or brick red solid with the empirical formula $(SCN)_x$. Polythiocyanogen was first reported in 1919 by Soderback.[37] He observed that thiocyanogen $(SCN)_2$ was thermally unstable and

spontaneously polymerised to give an orange product $(SCN)_x$. Polythiocyanogen can also be prepared by chemical or electrical oxidation of thiocyanates in melts or solution.[74,75] It can also be prepared in the solid state by passing chlorine gas over alkali metal thiocyanates.[76] All of these routes probably involve forming $(SCN)_2$ at some stage. The published work on polythiocyanogen reports that it is a semiconductor[77], that it is photoactive[78] and has been used in photocatalytic systems.[79,80] Based on these properties several groups have proposed that the mechanism for polymerisation is a radical process involving the radical species $[SCN]^{\cdot}$ and that the polymer has a conjugated double bond structure. A number of speculative structures have thus been proposed in the literature. An early hypothesis was that the structure could be composed of 1,3,5-triazine rings linked by disulfide bridges formed by the trimerization of the nitrile groups in thiocyanogen (Figure 1.12).[81,82]

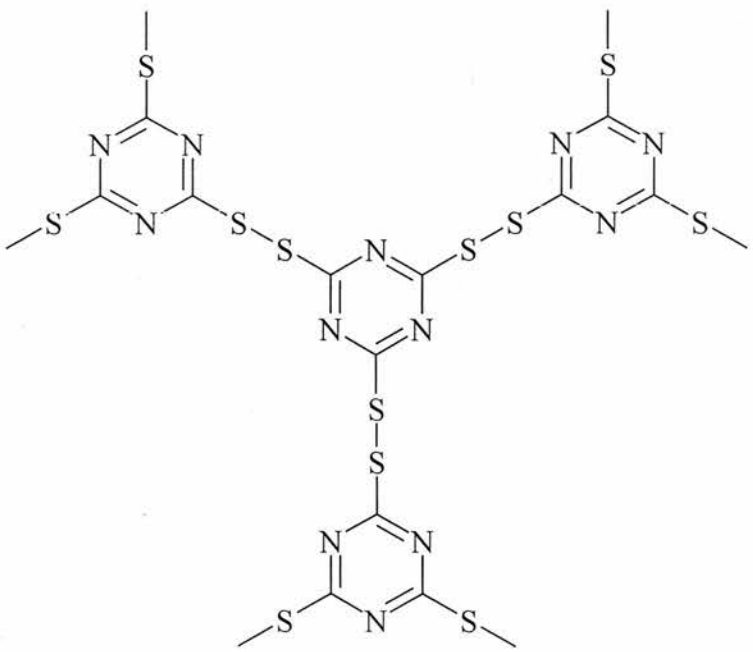


Figure 1.12 Proposed 1,3,5-triazine structure for polythiocyanogen.

An alternative proposal was that polythiocyanogen has a linear structure analogous to that of polythiazyl $(SN)_x$ (Figure 1.13).[76,83]

Figure 1.13 Proposed linear structure for polythiocyanogen.

The most recent structure proposed by Cataldo *et al.* is polyazomethine chains analogous to that of polycyanogen $(CN)_x$ but crosslinked by disulfide bridges (Figure 1.14).[84,85]

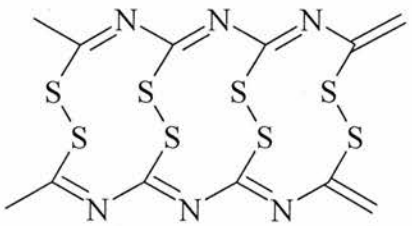


Figure 1.14 Proposed polyazomethine chain structure for polythiocyanogen.

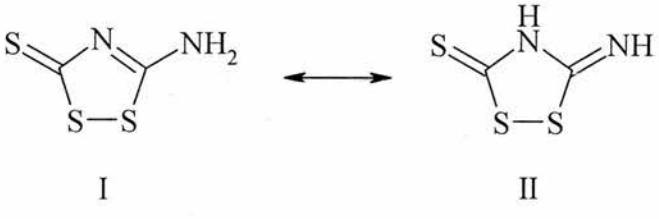
However the spectroscopic data published for polythiocyanogen is limited to IR, UV and ^{13}C NMR spectroscopy.[76,83-85] The IR spectrum is not particularly informative showing only one very broad peak and no useful information can be taken from the reported ^{13}C NMR data because the signal to noise ratio is very poor. Therefore a definitive structure for the polymer has not been obtained because there has been no significant study using the full array of techniques needed.

In previous work by the Woollins' group in collaboration with Knoll Microcheck into the biological activity of SCN containing species preliminary studies were carried out on polythiocyanogen $(SCN)_x$. In these studies, UV/VIS, Raman and

^{14}NMR spectroscopy suggest that the polymer may be based on five membered rings. The literature further supports this theory. It was reported in 1821 by Wohler that concentrated solutions of isothiocyanic acid HNCS deposited isoperthiocyanic acid $(SCN)_2HS_2$ (Scheme 1.32).[71-73]

Scheme 1.32 Synthesis of isoperthiocyanic acid.

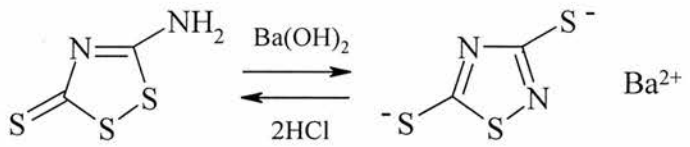
Hordvic confirmed the 3-amino-5-thione-1,2,4-dithiazole structure by X-ray crystallography which clearly showed the presence of two adjacent sulfur atoms in a five membered ring.[86] Of the two possible tautomers Hordvic proposed structure I with the both hydrogen atoms located on the exocyclic nitrogen (Figure 1.15).



I II

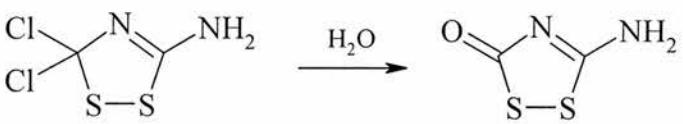
Figure 1.15 Possible tautomers of isoperthiocyanic acid.

This is further supported by IR data published by Emeleus *et al* confirming that a NH_2 group is present.[87] Isoperthiocyanic acid is readily converted into the barium salt of perthiocyanic acid by treatment with barium hydroxide.[59] The isomerisation can be reversed by treatment of the barium salt of perthiocyanic acid with hydrochloric acid (Scheme 1.33).



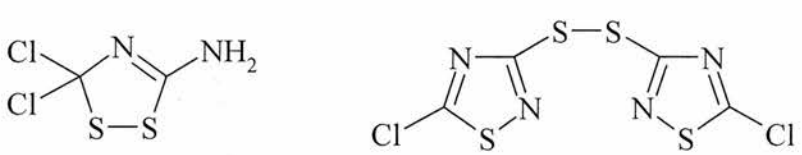
Scheme 1.33 Reaction of isoperthiocyanic acid with barium hydroxide.

Furthermore Soderback reported that reaction of thiocyanogen with HCl in ethereal solution yields two products. A colourless crystalline compound of formula $(SCN)_2.2HCl$ and a yellow solid with molecular formula $(SCN)_4Cl_2$ were obtained.[59,88] The reaction of $(SCN)_2.2HCl$ with water yields $(SCN)_2.H_2O$ (Scheme 1.34).[89]



Scheme 1.34 Reaction of $(SCN)_2.2HCl$ with water.

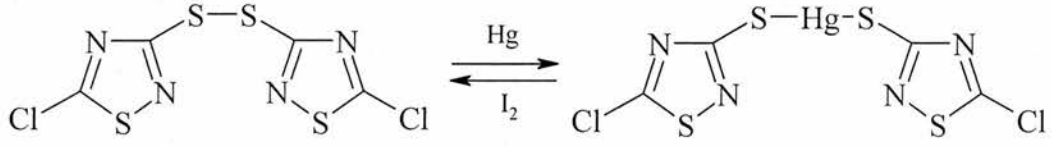
The 1,2,4-dithiazole structure of $(SCN)_2.H_2O$ has been confirmed by X-ray crystallography.[90] Thus structure III has been proposed for $(SCN)_2.2HCl$ (Figure 1.16). The assignment of structure III was further supported by comparison of the IR spectra of $(SCN)_2.H_2O$ and $(SCN)_2.2HCl$.[87]



III IV

Figure 1.16 Proposed structure for $(SCN)_2.2HCl$ and $(SCN)_4Cl_2$.

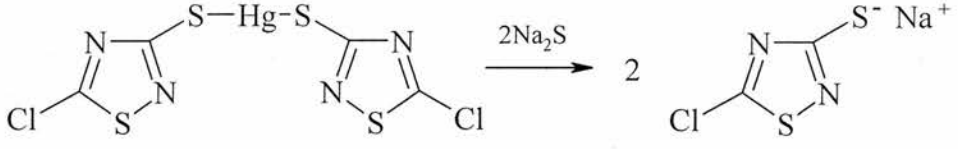
A 1,2,4-thiadiazol-3-yl disulfide structure (IV) has been speculated for the second product $(SCN)_4Cl_2$.[59,88] Some similarities in IR spectra with perthiocyanic acid and its barium salt have been observed[91] but the spectroscopic evidence is not conclusive. Soderback reported that reduction of $(SCN)_4Cl_2$ with mercury gives a compound $Hg[(SCN)_2Cl]_2$ which can be reconverted to $(SCN)_4Cl_2$ by reaction with iodine (Scheme 1.35).[59,88]



IV V

Scheme 1.35 Reduction of $(SCN)_4Cl_2$ with mercury.

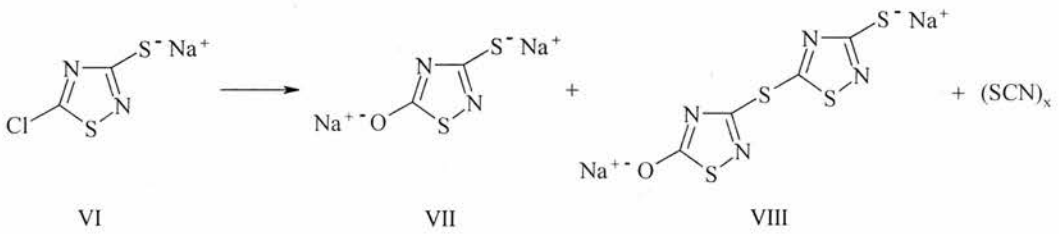
Treatment of the mercury compound (V) with sodium sulfide was reported to give a highly unstable sodium salt speculated to be of 5-chloro-3-thio-1,2,4-thiadiazole (Scheme 1.36).[59,88]



V VI

Scheme 1.36 Reaction of V with sodium sulfide.

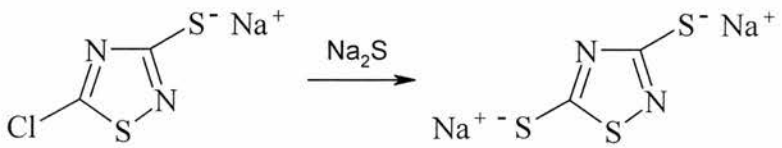
It was reported that reaction of this sodium salt (VI) with sodium hydroxide yielded a mixture of polythiocyanogen, the disodium salt of 5-hydroxy-3-thio-1,2,4-thiadiazole (VII) and a by product with molecular formula $C_4N_4OS_4Na_2$ (Scheme 1.37).[59,88]



VI VII VIII

Scheme 1.37 Reaction of VI with NaOH.

Structure VIII has been proposed for $C_4N_4OS_4Na_2$ since it can also be prepared by the reaction of the sodium salt VI with VII.[59,88] It is also reported that treatment of the sodium salt VI with sodium sulfide results in the formation of the sodium salt of perthiocyanic acid (Scheme 1.38).[59,88]



Scheme 1.38 Reaction of VI with Na_2S.

The literature clearly illustrates the propensity of $(SCN)_2$ and SCN^- to be converted into heterocyclic 5 membered rings. Therefore it is quite possible that polythiocyanogen, which is formed by heating $(SCN)_2$, is composed of these heterocyclic rings. Thus we propose two possible structures for $(SCN)_x$. Firstly a structure based on 1,2,4-thiadiazole rings with sulfur bridges and secondly a series of 1,2,4-dithiazole rings linked by exocyclic nitrogen atoms respectively (Figures 1.17 and 1.18). In both structures the SCN linkage is retained.

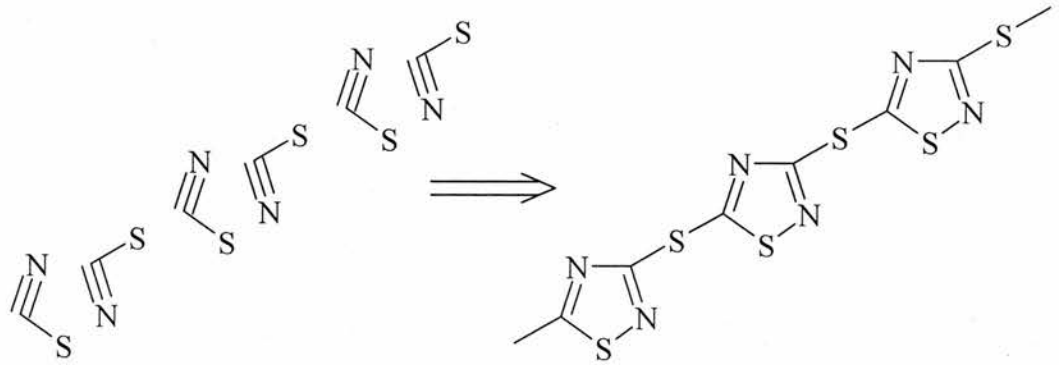


Figure 1.17 Proposed structure of polythiocyanogen based on 1,2,4-thiadiazoles.

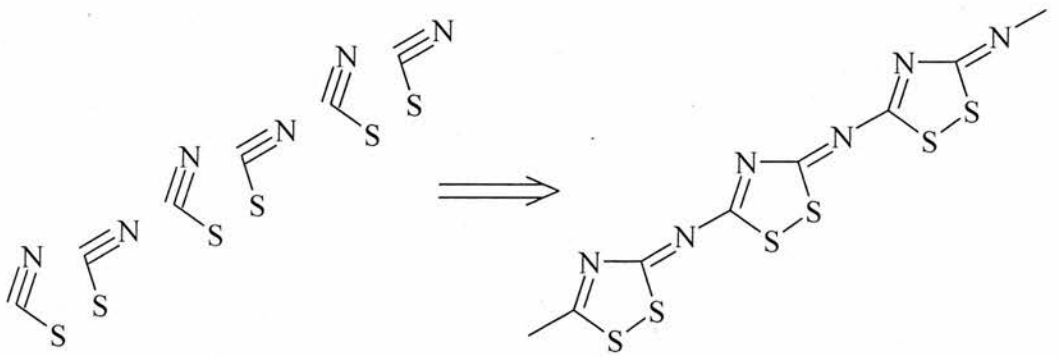


Figure 1.18 Proposed structure of polythiocyanogen based on 1,2,4-dithiazoles.

1.12 *Polyselenocyanogen.*

Very little is known about selenocyanogen polymerisation. The only literature reference to selenocyanogen polymerisation and its products are from Cataldo and co-workers.[48,92] They propose that when selenocyanogen is heated to 180°C in decalin a brown precipitate is formed which they suggest is polyselenocyanogen and a white sublimate selenium dicyanide was also isolated (Scheme 1.39).

$$2xSe_2(CN)_2 \longrightarrow xSe(CN)_2 + [Se_y(CN)_2]_x + xSe$$

(with $0<y<3$)

Scheme 1.39 Proposed polymerisation of selenocyanogen.

They suggest that selenocyanogen also polymerises to polyselenocyanogen when treated with certain organic solvents such as ethanol, acetone and triethylamine. They propose that polyselenocyanogen has the formula $[Se_y(CN)_2]_x$ and assign a structure based on IR data being similar to that of polythiocyanogen. The proposed structure involves polyazomethine chains connected together by selenium bridges (Figure 1.19).

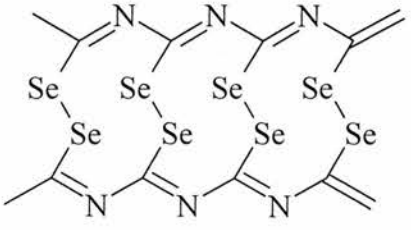


Fig 1.19 Proposed speculative structure of polyselenocyanogen.

1.13 *Aims and Objectives*

The main aim of this project is to determine the structure of polythiocyanogen $(SCN)_x$. The first step will be to prepare and fully characterise the psuedohalides $E_x(CN)_2$ (E = S, Se x = 1, 2, 3). We will then prepare polythiocyanogen from $S_2(CN)_2$ and characterise the polymer by a variety of spectroscopic methods. We also intend to investigate the reactivity of polythiocyanogen to see if this reveals any structural information. A series of model compounds based on 1,2,4-

thiadiazole rings will be prepared for comparison with polythiocyanogen. We will also investigate the recently reported polyselenocyanogen.

At the same time we intend to prepare several bidentate chalcogen donor ligands and use these to form a series of late transition metal complexes. Dipotassium cyanodithioimidocarbonate is an intermediate in the preparation of 1,2,4-thiadiazoles and should be a useful reagent for preparing cyanodithioimidocarbonate complexes. Our next objective is to prepare carbon diselenide so that we can synthesise dipotassium cyanodiselenoimidocarbonate. We will use the dipotassium salt to prepare the analogous cyanodiselenoimidocarbonate complexes. Finally we intend to use carbon diselenide to prepare a series of triselenocarbonate complexes. All complexes will be fully characterised and selected examples will be studied by X-ray crystallography.

Chapter 2: Synthesis of cyanodithioimidocarbonate, $[C_2N_2S_2]^{2-}$, transition metal complexes

2.1 *Introduction*

As part of our study of E,E bidentate (E = S, Se) chalcogen donor ligands we have investigated the cyanodithioimidocarbonate, $[C_2N_2S_2]^{2-}$, dianion. The literature contains surprisingly few examples of cyanodithioimidocarbonate complexes of which only two have been crystallographically characterised $[AsPh_4]_2[Ni(C_2N_2S_2)]$[93] and $[Au_2(C_2N_2S_2)_2]$.[94] The other reported complexes containing the $[C_2N_2S_2]^{2-}$ anion include organotin compounds of the type $[SnR_2(C_2N_2S_2)]$,[95] a vanadium (IV) complex $[V(\eta^5\text{-}C_5H_5)_2(C_2N_2S_2)]$ studied by electron spin resonance,[96] an oxytechnetium (V) complex $[TcO(C_2N_2S_2)_2]$,[97] and a series of salts of the type $[X]_2[M(S_2N_2C_2)_2]$ (X = Ph_4As^+, Ph_4P^+ or $(^nPr)_4N$ M = Ni, Pt, Pd, Zn or Tl).[98,99] The literature also reports a series of bridged dinuclear ruthenium complexes for example $[(\eta^5\text{-}C_5H_5)(PPh_3)Ru(C_2N_2S_2)Ru)(PPh_3)_2[(\eta^5\text{-}C_5H_5)]$ which bridge via the nitrile nitrogen atom of the cyanodithioimidocarbonate ligand as well as being S_2 bound.[100] Here we report examples of mononuclear and binuclear complexes of this ligand with selected examples studied by X-ray crystallography.

2.2 *Results and Discussion*

2.2.1 *Synthesis of dipotassium cyanodithioimidocarbonate.*

The synthesis of dipotassium cyanodithioimidocarbonate **2.1** was first reported by Hantzch and Wolvenkamp in 1904[101] and subsequently by other groups.[102,103] The original synthesis of **2.1** involved the dropwise addition of potassium hydroxide in ethanol to cyanamide and carbon disulfide in the same solvent at 0 °C. In our hands several attempts to repeat the literature procedure proved unsuccessful hence the procedure was modified. Our synthesis was essentially the same (Scheme 2.1) except potassium ethoxide was used in place of potassium hydroxide to prevent water generation during the reaction. As a result the synthesis was much cleaner and a pure product was obtained.

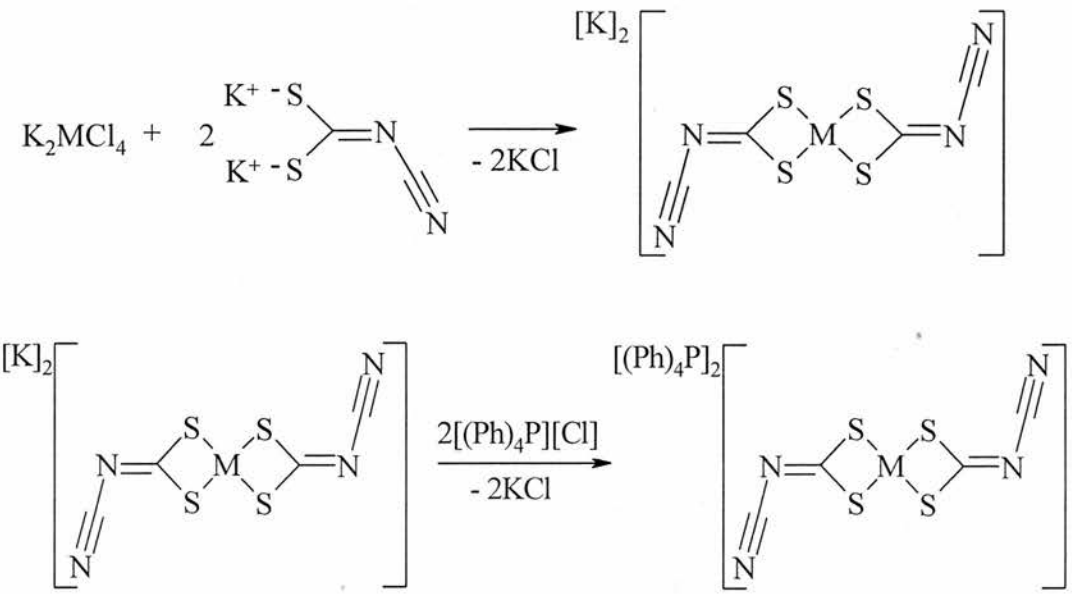
Scheme 2.1 Synthesis of dipotassium cyanodithioimidocarbonate.

After suction filtration the product was isolated as a yellow powder in good yield (65 %). **2.1** was found to be hygroscopic hence it was stored in a sealed container. The salt was found to be soluble in water, methanol and dimethyl sulfoxide. The ^{13}C-{^{1}H} NMR (dmso-d6) exhibits two resonances at δ(C) 228.3 and 122.1 ppm (c.f. 228.2 and 122.7 ppm as reported in the literature[103]) corresponding to (S_2C=N) and (N-C≡N) respectively. In the IR spectrum we

observe a strong ν(C≡N) band at 2146 cm^{-1}, and a strong band at 1315 cm^{-1} assigned as ν(C=N). Satisfactory microanalytical data was obtained.

2.2.2 *Homoleptic cyanodithioimidocarbonate complexes.*

Reaction of $K_2[MCl_4]$ (M = Pt, Pd) with two equivalents of potassium cyanodithioimidocarbonate **2.1** in methanol was followed by the addition of two equivalents of tetraphenylphosphonium chloride. The solvent was removed under reduced pressure and the residual solid dissolved in dichloromethane then filtered through celite (to remove solid KCl). Evaporation of the solvent gave the salts $[PPh_4]_2[M(C_2N_2S_2)_2]$ (M = Pt, Pd) in excellent yields (Scheme 2.2).



Scheme 2.2 Preparation of $[PPh_4]_2[M(C_2N_2S_2)_2]$ (M = Pt **2.2**, Pd **2.3**).

Both the homoleptic complexes $[PPh_4]_2[Pt(C_2N_2S_2)_2]$ **2.2** and $[PPh_4]_2[Pd(C_2N_2S_2)_2]$ **2.3** were found to be exceptionally soluble in

dichloromethane hence it was possible to observe the quaternary carbons of the cyanodithioimidocarbonate ligand in the ^{13}C-{^{1}H} NMR spectra (Table 2.1).

Complex	δ(C) (ppm)		ν(C≡N)	ν(C=N)	ν(M-S)
	(S_2C=N)	(NC≡N)	(cm^{-1})	(cm^{-1})	(cm^{-1})
2.2 $[PPh_4]_2[Pt(C_2N_2S_2)_2]$	218.0	113.9	2171	1436	379 360
2.3 $[PPh_4]_2[Pd(C_2N_2S_2)_2]$	219.2	115.1	2172	1436	377 346

Measured in CD_2Cl_2 at 25 °C

Table 2.1 Selected ^{13}C-{^{1}H} NMR (67.9 MHz) and selected IR data for complexes **2.2** and **2.3**.

In the platinum complex **2.2** the resonance observed at δ(C) 218.0 ppm has been assigned as S_2C=N and the resonance at δ(C) 113.9 ppm as N-C≡N based on comparisons with the dipotassium salt where the S_2C=N resonance was noted at δ(C) 228.3 ppm and the N-C≡N resonance at δ(C) 122.1 ppm. Similarly in the palladium analogue **2.3** the two resonances observed at δ(C) 219.2 and 115.1 ppm correspond to S_2C=N and N-C≡N respectively. In the IR spectra of **2.2** and **2.3** the nitrile (C≡N) band is observed at approximately 2170 cm^{-1}, the imido (C=N) band at approximately 1435 cm^{-1} – considerably increased in frequency compared to the uncoordinated anion indicating the change in delocalisation as a consequence of coordination. The (M-S) bands are in the range 346-379 cm^{-1}. The microanalysis for both species was within the specified limits. Positive ion

ES mass spectroscopy shows the expected tetraphenylphosphonium ion in both cases. Negative ion ES mass spectroscopy shows the $[M(C_2N_2S_2)_2 + PPh_4]^-$ (M = Pt **2.2**, Pd **2.3**) species at *m/z* = 766 and 677 in **2.2** and **2.3** respectively. In **2.3** the $[Pd(C_2N_2S_2)]^{2-}$ ion is also observed at *m/z* = 169. Crystals of both **2.2** and **2.3** were easily obtained by vapour diffusion from chloroform and hexane hence their X-ray crystal structures have been obtained (Table 2.2, Figures 2.1 and 2.2). The X-ray analysis shows that in **2.2** and **2.3** the platinum or palladium core lies at the centre of a distorted square planar coordination sphere with unsymmetrical MS_2C rings (M = Pt **2.2**, Pd **2.3**). For both **2.2** and **2.3** the whole molecule lies in the plane of the coordination sphere. In **2.2** the largest deviation from planarity being S(1) which lies 0.13 [0.06] Å above the plane. The S(1)-Pt(1)-S(2) angle is 75.0(5) ° [74.7(4) ° in the second independent molecule] and the S(1)-Pd(1)-S(2) angle is 75.17(5) ° [75.19(5) ° in the second independent molecule] showing considerable deviation from idealized 90 ° square planar geometry. Within the MS_2C ring the M-S-C angles are in the range 85.1(15) to 92.9(15) ° and the S(1)-C(1)-S(2) angle is 102(2) [109(2)] in **2.2** and 109.8(3) [110.5(3)] ° for **2.3**. The S(1)-S(2) nonbonded distances are 2.82(1) Å and 2.83(1) Å in **2.2** and **2.3** respectively which is ca 80 % of the van der Waals radii of sulfur and implies that there is a significant interaction between the two sulfur atoms. As expected the C=N bond length C(1)-N(1) is longer than the C≡N bond length C(2)-N(2). The N-C≡N group is bent with a C(1)-N(1)-C(2) angle of approximately 120°.

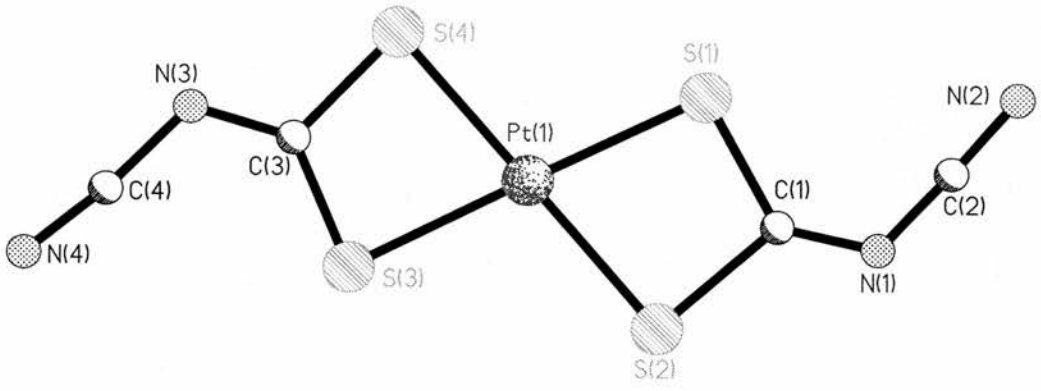


Figure 2.1 X-ray crystal structure of the dianion in **2.2**.

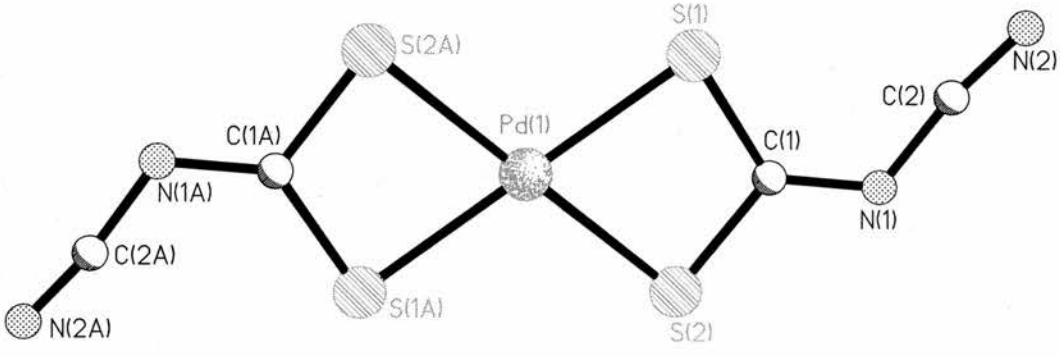


Figure 2.2 X-ray crystal structure of the dianion in **2.3**.

Compound	**2.2**	**2.3**
M(1)-S(1)	2.307(12) [2.317(13)]	2.3293(14) [2.3197(14)]
M(1)-S(2)	2.326(13) [2.338(13)]	2.3111(13) [2.3167(13)]
S(1)-C(1)	1.77(4) [1.86(5)]	1.730(4) [1.715(5)]
S(2)-C(1)	1.86(4) [1.59(4)]	1.729(5) [1.726(5)]
C(1)-N(1)	1.19(5) [1.37(5)]	1.300(5) [1.310(5)]
N(1)-C(2)	1.26(5) [1.46(6)]	1.328(7) [1.325(7)]
C(2)-N(2)	1.15(5) [1.13(6)]	1.138(6) [1.147(7)]
S(1)-M(1)-S(2)	75.0(5) [74.7(4)]	75.17(5) [75.19(5)]
S(1)-M(1)-S(1A)	179.3(6) [180.0(6)]	180.00(7) [180.00(5)]
S(2)-M(1)-S(1A)	104.3(5) [105.3(4)]	104.85(5) [104.83(5)]
S(1)-C(1)-N(1)	131(4) [129(3)]	128.2(4) [128.1(4)
S(2)-C(1)-N(1)	126(4) [121(3)]	121.9(4) [121.4(4)]
M(1)-S(1)-C(1)	92.9(15) [85.1(15)]	87.16(17) [87.21(16)]
M(1)-S(2)-C(1)	90.2(14) [90.6(17)]	87.78(16) [87.11(16)]
C(1)-N(1)-C(2)	120(4) [113(4)]	120.0(4) [117.2(4)]
N(1)-C(2)-N(2)	169(5) [162(6)]	172.3(6) [173.3(6)]

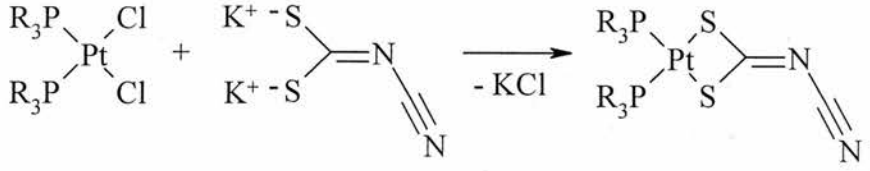
[] indicates the equivalent value for the second independent molecule.

Table 2.2 Selected bond lengths (Å) and angles (°) for **2.2** and **2.3**.

2.2.3 *Platinum(bis-phosphino) cyanodithioimidocarbonate complexes.*

The heteroleptic complexes $[Pt(C_2N_2S_2)(PR_3)_2]$ (PR_3 = PMe_2Ph, PPh_3, ½ dppe, ½ dppm, ½ dppf) were all obtained by the reaction of the appropriate $[PtCl_2(PR_3)_2]$ complex with one equivalent of potassium cyanodithioimidocarbonate in tetrahydrofuran. The solvent was evaporated under reduced pressure and dichloromethane added. The resultant mixture was filtered through a Celite pad

to remove precipitated KCl and the filtrate evaporated to dryness to give the product (Scheme 2.3).



2.4 $PR_3 = PMe_2Ph$
2.5 $PR_3 = PPh_3$
2.6 $PR_3 = ½$ dppe
2.7 $PR_3 = ½$ dppm
2.8 $PR_3 = ½$ dppf

Scheme 2.3 Synthesis of platinum(bis-phosphino) cyanodithioimidocarbonate complexes.

All of the compounds **2.4** to **2.8** gave satisfactory microanalysis and all showed the anticipated M^+ in their mass spectra (Table 2.3).

Complex	C	H	N	*m/z*
2.4 $[Pt(C_2N_2S_2)(PMe_2Ph)_2]$	36.58(36.80)	3.59(3.77)	4.54(4.77)	587
2.5 $[Pt(C_2N_2S_2)(PPh_3)_2]$	54.25(54.61)	3.21(3.62)	3.27(3.35)	836
2.6 $[Pt(C_2N_2S_2)(dppe)]$	47.19(47.39)	3.44(3.41)	3.74(3.95)	710
2.7 $[Pt(C_2N_2S_2)(dppm)]$	46.69(46.62)	2.97(3.19)	3.94(4.03)	696
2.8 $[Pt(C_2N_2S_2)(dppf)]$	49.75(50.18)	3.03(2.81)	3.07(3.25)	867

Table 2.3 Microanalytical data (calculated values in parentheses) and mass spectral data for complexes **2.4-2.8**.

In the IR spectra the ν(C≡N) vibrations were observed in the range 2176 to 2181 cm^{-1} and the ν(C=N) vibrations can be seen in the region of 1476 to 1479 cm^{-1} (Table 2.4). The ν(Pt-S) all lie within the range 350 to 399 cm^{-1} (Table 2.4) which is in accord with the values observed for ν(Pt-S) in trithiocarbonate complexes.[18]

Complex	δ(P) (ppm)	$^{1}J(^{195}Pt-^{31}P)$ (Hz)	ν(C≡N) (cm^{-1})	ν(C=N) (cm^{-1})	ν(Pt-S) (cm^{-1})
2.4 $[Pt(C_2N_2S_2)(PMe_2Ph)_2]$	-19.0	3071[a]	2181	1478	396 374
2.5 $[Pt(C_2N_2S_2)(PPh_3)_2]$	17.0	3179[b]	2177	1479	397
2.6 $[Pt(C_2N_2S_2)(dppe)]$	42.2	3094[a]	2179	1479	396 370
2.7 $[Pt(C_2N_2S_2)(dppm)]$	-53.8	2634[a]	2177	1477	393
2.8 $[Pt(C_2N_2S_2)(dppf)]$	16.0	3312[c]	2176	1478	399 350

[a] Measured in $CDCl_3$ at 25 °C. [b] Measured in CD_2Cl_2 at 25 °C. [c] Measured in D_6-dmso at 90 °C.

Table 2.4 $^{31}P\{^{1}H\}$ NMR (109.4 MHz) and selected IR data for complexes **2.4-2.8**.

The platinum(bis-phosphine) cyanodithioimidocarbonate complexes **2.4** to **2.7** (Table 2.4) all showed sharp singlets with platinum satellites in their $^{31}P\{^{1}H\}$ NMR spectra and have similar δ values to the analogous platinum(bis-

phosphino) trithiocarbonate complexes.[18] The $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling constants lie in the range 2634-3312 Hz. Unlike **2.4** to **2.7** the $^{31}P\{^{1}H\}$ NMR spectra of $[Pt(C_2N_2S_2)(dppf)]$ **2.8** displays fluxional behaviour. It displays two broad singlets at δ(P) 15.7 and 16.1 ppm with platinum satellites ($^{1}J(^{195}Pt\text{-}^{31}P)$ couplings of 3287 and 3331 Hz respectively) at 30 °C. Upon heating, these two peaks coalesce into one broad peak and finally give one distinct peak at δ(P) 16.0 ppm with a $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling of 3312 Hz at 90 °C (Figure 2.3).

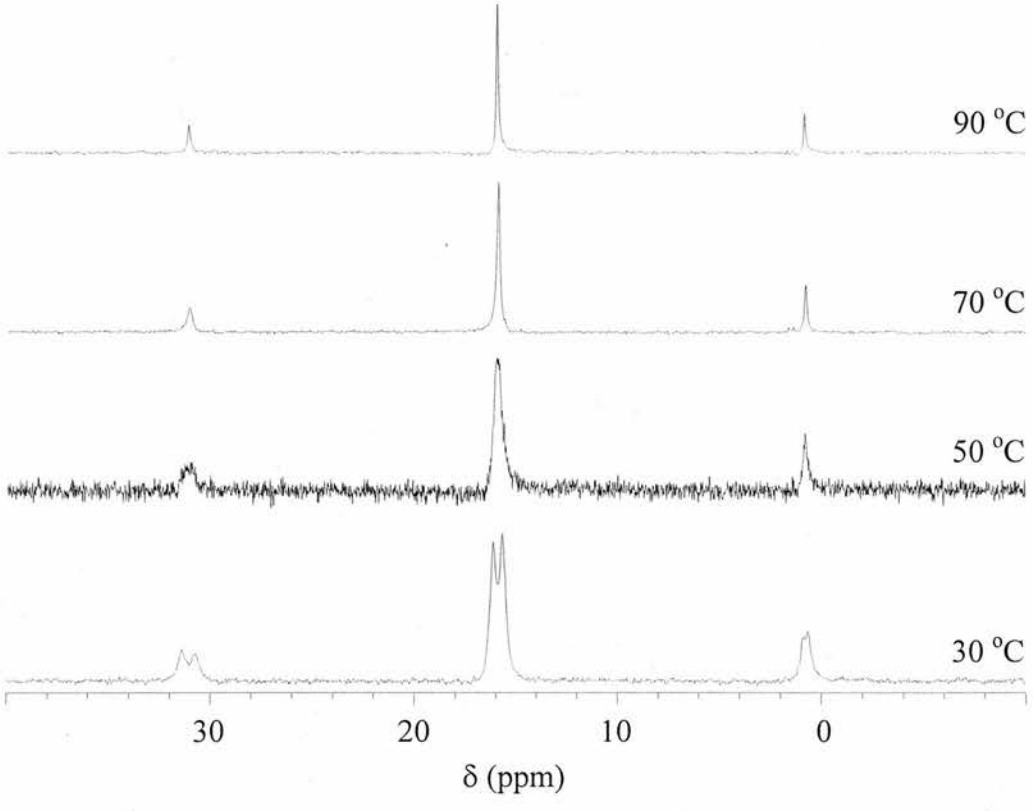


Figure 2.3 Dynamic $^{31}P\{^{1}H\}$ NMR spectra of $[Pt(C_2N_2S_2)(dppf)]$ **2.8**.

We interpret this by postulating that at 30 °C the nitrile group (C≡N) is bent away to one side so that it has a *cis* relationship to one phosphine and *trans* relationship to the other resulting in two magnetically inequivalent phosphorus

environments in the $^{31}P\{^{1}H\}$ NMR spectrum. Upon heating the nitrile group (C≡N) is able to flip between the two conformations (the process is effectively inversion on N1). The activation energy for this inversion calculated by coalescence methods is 68 kJ mol^{-1}. Compounds **2.4**, **2.6** and **2.8** have all been studied by single crystal X-ray diffraction (Table 2.5, Figures 2.4, 2.5 and 2.6). Although the X-ray data for compound **2.6** was of poorer quality than **2.4** and **2.8** it was sufficient for confirmation of connectivity and to establish trends in bond lengths and angles. In all three complexes the platinum lies at the centre of a distorted square planar coordination sphere. The S(1)-Pt(1)-S(2) bite angles in **2.4, 2.6** and **2.8** are 74.62(7) °, 76.2(2) ° and 74.68(6) ° respectively. In the PtS_2C ring for **2.4** the Pt-S-C angles are 87.2(2) ° and 87.4(2) °. The S(1)-C(1)-S(2) angle is 110.7(4) °. Similarly in **2.6** the Pt-S-C angles are 87.4(2) ° and 87.2(2) ° and the S(1)-C(1)-S(2) angle is 107.9(12) °. In compound **2.8** both Pt-S-C angles are identical with a value of 87.7(2) ° and the S(1)-C(1)-S(2) angle is 109.9(3) °. The nonbonded sulfur-sulfur distances all lie in the range 2.8 to 2.9 Å which corresponds to ca 80 % of the van der Waals radii of sulfur, which implies that in all cases there is a significant interaction between the two sulfur atoms. As observed in compound **2.2** the cyanide group is bent, at an angle of approximately 113 ° in **2.6** and 118 ° in both **2.4** and **2.8**. In **2.4** the cyanodithioimidocarbonate ligand lies within the coordination plane with the exception of the nitrile functionality, which is hinged at an angle of 9 ° above the plane. Similarly in **2.8** the nitrile functionality is hinged at an angle of 2 ° above the plane. The cyanodithioimidocarbonate ligand is virtually planar in **2.6**.

Compound	**2.4**	**2.6**	**2.8**
Pt(1)-P(1)	2.2677(18)	2.262(7)	2.2711(17)
Pt(1)-P(2)	2.2670(19)	2.271(5)	2.2833(17)
Pt(1)-S(1)	2.350(2)	2.296(6)	2.3375(16)
Pt(1)-S(2)	2.3566(19)	2.323(6)	2.3519(17)
S(1)-C(1)	1.734(7)	1.77(3)	1.747(6)
S(2)-C(1)	1.733(7)	1.75(2)	1.729(6)
C(1)-N(1)	1.300(8)	1.32(3)	1.302(8)
N(1)-C(2)	1.312(11)	1.37(4)	1.320(9)
C(2)-N(2)	1.176(11)	1.13(3)	1.173(9)
S(1)-Pt(1)-S(2)	74.62(7)	76.6(2)	74.68(6)
P(1)-Pt(1)-P(2)	94.83(7)	86.0(2)	101.04(6)
S(1)-C(1)-N(1)	127.5(6)	128.3(18)	127.3(5)
S(2)-C(1)-N(1)	121.7(6)	122.7(19)	122.9(5)
Pt(1)-S(1)-C(1)	87.4(2)	87.3(7)	87.7(2)
Pt(1)-S(2)-C(1)	87.2(2)	86.9(9)	87.7(2)
P(1)-Pt(1)-S(1)	94.49(7)	97.2(9)	92.68(6)
P(2)-Pt(1)-S(2)	95.96(8)	100.1(2)	91.63(6)
C(1)-N(1)-C(2)	117.6(7)	113(2)	117.6(6)
N(1)-C(2)-N(2)	173.8(8)	172(3)	172.4(8)

Table 2.5 Selected bond lengths (Å) and angles (°) for **2.4**, **2.6** and **2.8**.

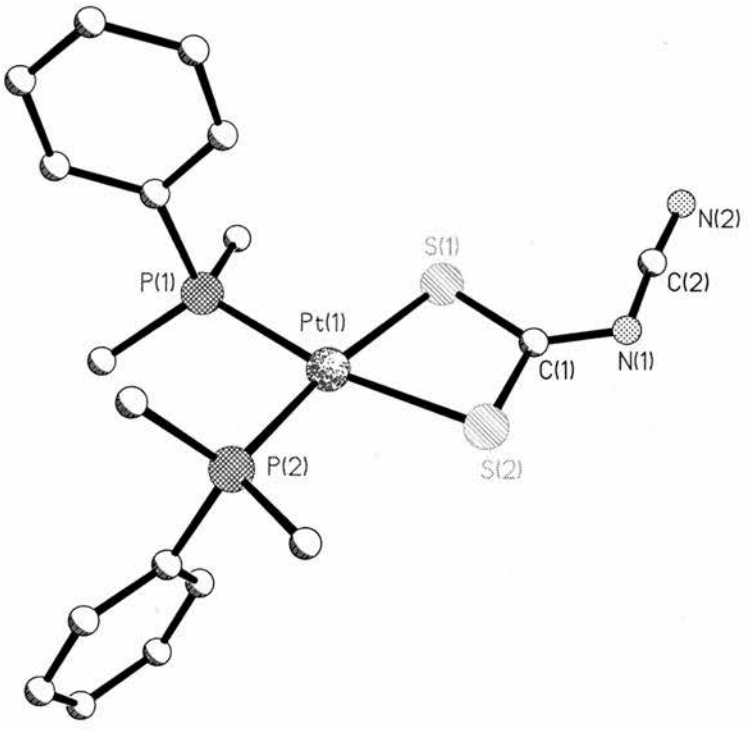


Figure 2.4 X-ray crystal structure of **2.4**.

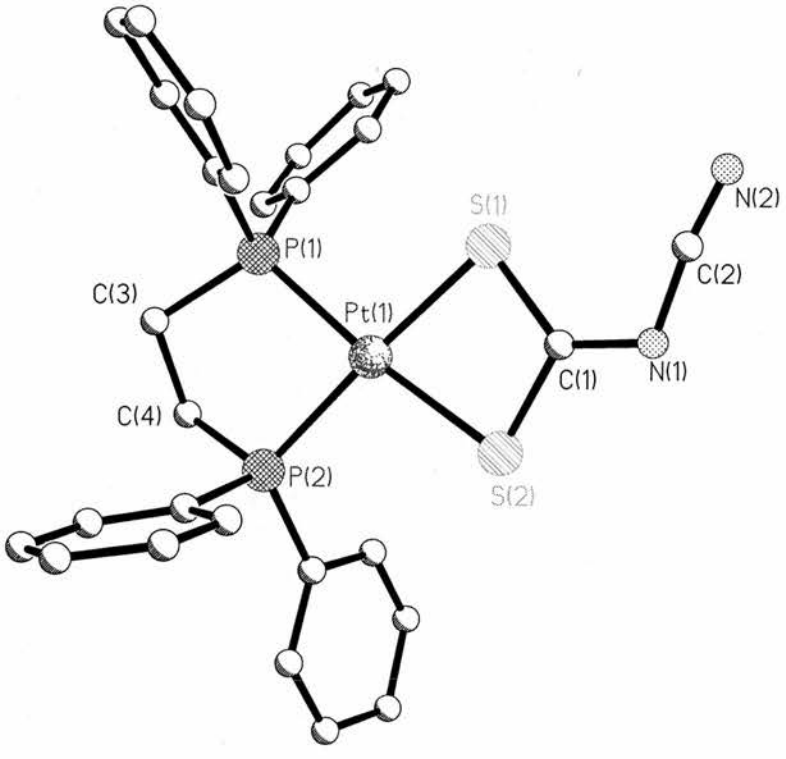


Figure 2.5 X-ray crystal structure of **2.6**.

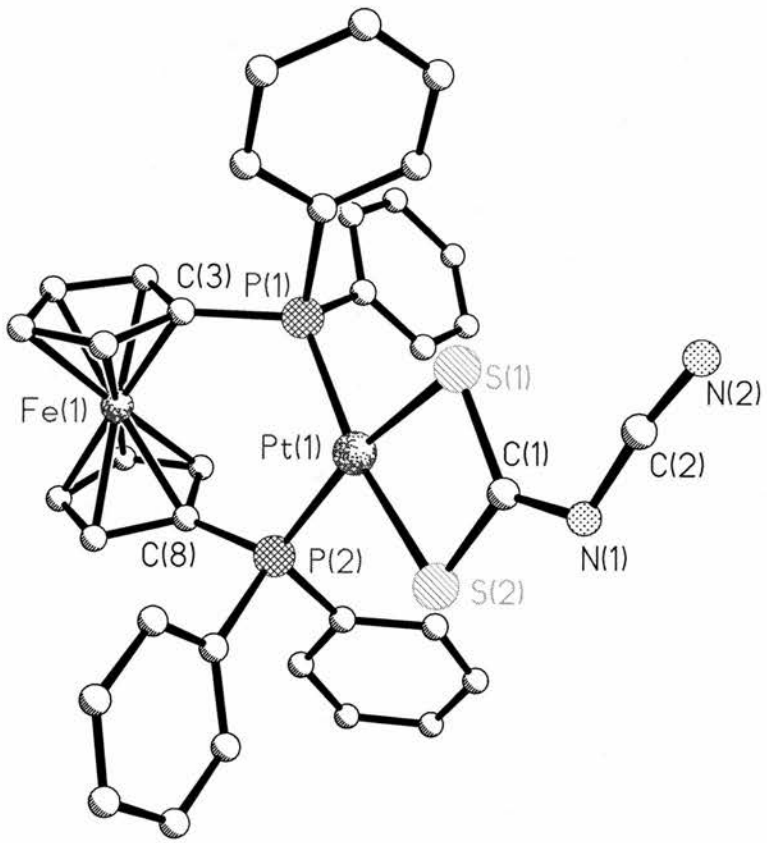
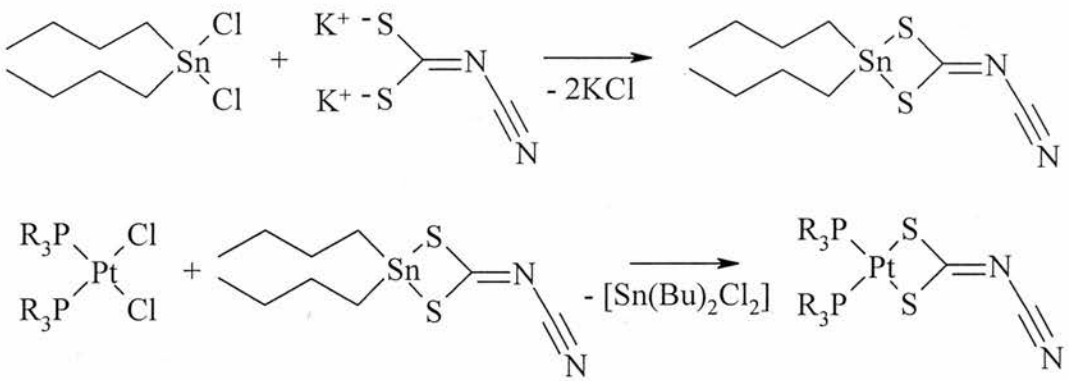


Figure 2.6 X-ray crystal structure of **2.8**.

The literature contains numerous reports where tin reagents have been used as sources of both sulfur-nitrogen fragments or as dithiooxalate transfer reagents. Examples include $[\{(^{n}Bu)_2Sn(S_2N_2)\}_2]$ and $[(Me)_2Sn(dto)]$ (dto = dithiooxalate) used as a metathesis reagents in the preparation of organometallic iridium sulfur nitrogen complexes[104] and platinum and ruthenium complexes[105] containing the dto ligand respectively. Complexes **2.4**, **2.5** and **2.6** have also been prepared using $[Sn(C_2N_2S_2)(^{n}Bu)_2]$**2.9** as a cyanodithioimidocarbonate transfer reagent. $[Sn(C_2N_2S_2)(^{n}Bu)_2]$ **2.9** which has been previously reported in the literature by Seltzer[95] was resynthesised by the slow dropwise addition of a tetrahydrofuran solution of $[SnCl_2(^{n}Bu)_2]$ to dipotassium cyanodithioimidocarbonate in distilled water. **2.9** was isolated in an almost quantitative yield and the microanalysis was

found to be within the specified limits. $[Sn(C_2N_2S_2)(^nBu)_2]$ was found to be sparingly soluble in dichloromethane, methanol and tetrahydrofuran. There has previously been no NMR data recorded for **2.9**. Due to poor solubility we have been unable to obtain any ^{13}C NMR data. The ^1H NMR spectra of $[Sn(C_2N_2S_2)(^nBu)_2]$ showed the expected shifts for the *n*-butyl groups. An intense $\nu(C\equiv N)$ band at 2190 cm^{-1} (c.f. 2180 cm^{-1} reported value in the literature[95]) a strong $\nu(C=N)$ band at 1368 cm^{-1} and a weak $\nu(Sn\text{-}S)$ band at 382 cm^{-1} were noted in the IR spectrum. One equivalent of $[Sn(C_2N_2S_2)(^nBu)_2]$ **2.9** was added to a dichloromethane solution of $[PtCl_2(PR_3)_2]$ (PR_3 = PMe_2Ph, PPh_3, ½dppe). The solution was stirred overnight and the solvent removed under reduced pressure. The remaining solid was redissolved in the minimum dichloromethane and the product precipitated by the addition of diethyl ether. The product was isolated and dried *in vacuo*.



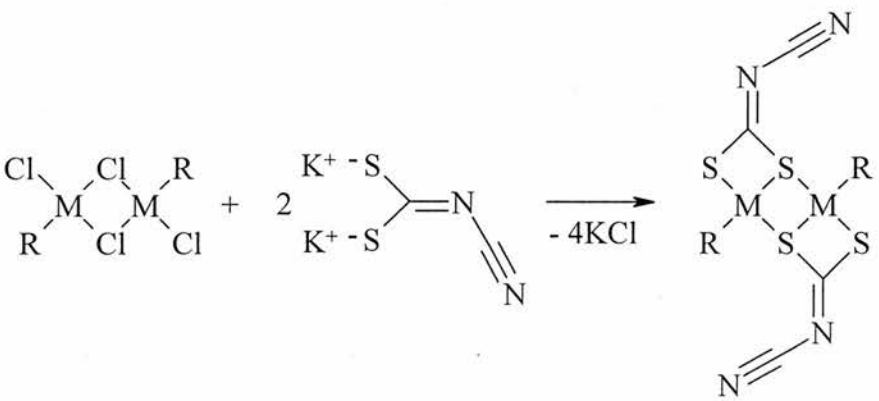
2.4 PR_3 = PMe_2Ph
2.5 PR_3 = PPh_3
2.6 PR_3 = ½dppe

Scheme 2.4 Reaction scheme for alternate preparation of $[Pt(C_2N_2S_2)(PR_3)_2]$ complexes using $[Sn(C_2N_2S_2)(Bu)_2]$ as a metathesis reagent.

The complexes **2.4, 2.5** and **2.6** prepared in this manner (Scheme 2.4) gave identical analytical data to those prepared by the reaction of the platinum(bis-phosphino) dichloride with dipotassium cyanodithioimidocarbonate.

2.2.4 *Bimetallic cyanodithioimidocarbonate complexes.*

The dimeric cyanodithioimidocarbonate complexes $[\{Pt(C_2N_2S_2)(PR_3)\}_2]$ (PR_3 = PMe_2Ph **2.10**), $[M\{(C_2N_2S_2)(\eta^5\text{-}C_5Me_5)\}_2]$ (M = Rh **2.11**, Ir **2.12**) and $[\{Ru(C_2N_2S_2)(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$ **2.13** were synthesised and isolated in a similar fashion to the platinum(bis-phosphine) cyanodithioimidocarbonate complexes **2.4-2.8** by reacting two equivalents of **2.1** with the appropriate transition metal dimer starting material (Scheme 2.5).



2.10 M = Pt, R = PMe_2Ph
2.11 M = Rh, R = $\eta^5\text{-}C_5Me_5$
2.12 M = Ir, R = $\eta^5\text{-}C_5Me_5$
2.13 M = Ru, R = $\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr$

Scheme 2.5 Synthesis of bimetallic cyanodithioimidocarbonate complexes.

2.10-2.13 all gave satisfactory microanalysis and **2.11-2.13** showed the anticipated M^+ in their mass spectra (Table 2.6). The ν(C≡N) vibrations were

noted in the range 2177 to 2188 cm^{-1} and the ν(C=N) vibrations can be seen in the region of 1424 to 1499 cm^{-1}. The bands for ν(M-S) were all observed in the range 326 to 396 cm^{-1}. All compounds showed the expected shifts in their ^{1}H NMR spectra. Compound **2.10** showed a singlet in its $^{31}P\{^{1}H\}$ NMR spectra with $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling constant of 3420 Hz.

Complex	C	H	N	*m/z*
2.10 [{Pt($C_2N_2S_2$)(PMe_2Ph)}$_2$]	26.24 (26.73)	2.22 (2.47)	5.83 (6.23)	-
2.11 [{Rh($C_2N_2S_2$)(η^5-C_5Me_5)}$_2$]	40.21 (38.98)	4.01 (4.08)	7.22 (7.57)	709
2.12 [{Ir($C_2N_2S_2$)(η^5-C_5Me_5)}$_2$]	32.93 (32.49)	3.24 (3.41)	6.16 (6.31)	889
2.13 [{Ru($C_2N_2S_2$)(η^6-p-$MeC_6H_4{}^{I}Pr$)}$_2$]	40.71 (41.01)	3.76 (4.02)	7.69 (7.97)	704

Table 2.6 Microanalytical data (calculated values in parentheses) and mass spectral data for complexes **2.10-2.13**.

Compound **2.11** has also been studied by X-ray crystallography (Figure 2.7). The X-ray crystal structure clearly shows that both cyanodithioimidocarbonate ligands bridge the two rhodium atoms. In each cyanodithioimidocarbonate ligand one of the sulfur atoms S(1) bridges the two metal centres Rh(1) and Rh(1A) while the other sulfur S(2) is solely bound to one of the rhodium atoms Rh(1). Both of the cyanodithioimidocarbonate ligands are planar with the nitrile

functionality bent away at angle of 119.2(5) [118.8(5)] °. The Rh(1)-S(1) bond length is 2.4008(16) [2.3944(16)] Å and the Rh(1)-S(2) distance is 2.3635(16) [2.3654(16)] Å. The Rh(1)-S(1A) distance is 2.4230(15) [2.4284(15)] Å. The central core of the molecule can be described as a distorted cubane type structure. This distortion from idealized 90 ° geometry can be seen in the S(1)-C(1)-S(2) angle of 109.2(3) [108.7(3)] °. The S(1)-Rh(1)-S(2) angle of 73.38(5) [73.46(5)] °, the S(1)-Rh(1)-S(1A) angle of 82.43(5) [81.75(5)] ° and the S(2)-Rh(1)-S(1A) 94.49(5) [94.81(5)] °.

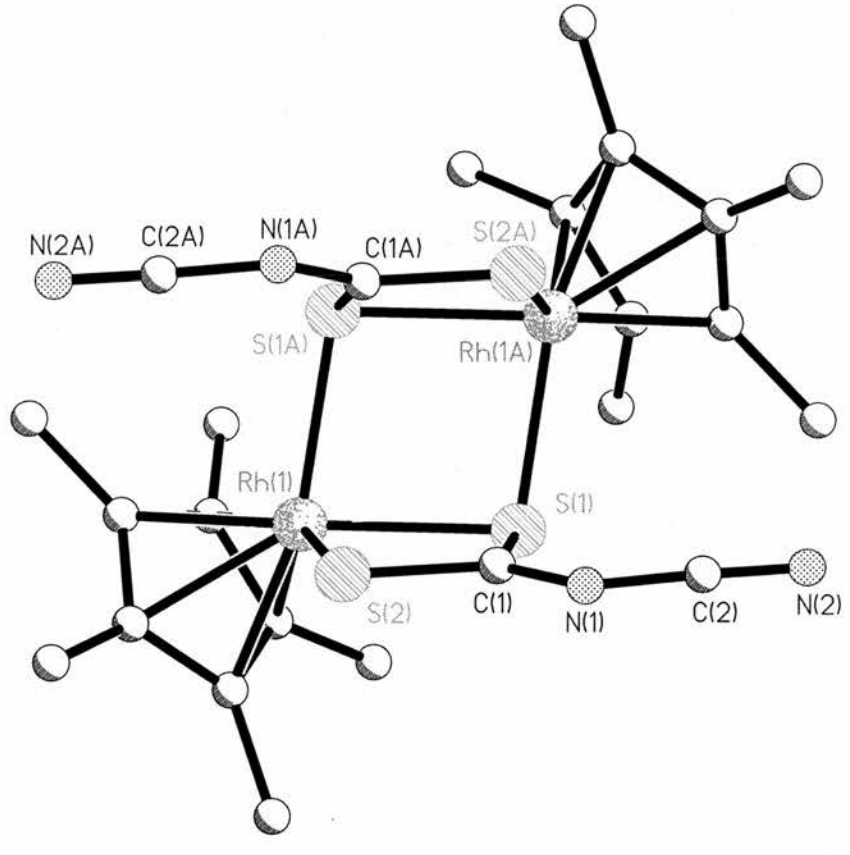


Figure 2.7 X-ray crystal structure of **2.11**.

Compound	**2.11**
M(1)-S(1)	2.4008(16) [2.3944(16)]
M(1)-S(2)	2.3635(16) [2.3654(16)]
M(1)-S(1A)	2.4230(15) [2.4284(15)]
S(1)-C(1)	1.796(6) [1.786(5)
S(2)-C(1)	1.695(6) [1.716(6)]
C(1)-N(1)	1.299(7) [1.305(7)]
N(1)-C(2)	1.337(8) [1.327(7)]
C(2)-N(2)	1.149(8) [1.156(7)]
S(1)-M(1)-S(2)	73.38(5) [73.46(5)]
S(1)-M(1)-S(1A)	82.43(5) [81.75(5)]
S(2)-M(1)-S(1A)	94.49(5) [94.81(5)]
S(1)-C(1)-N(1)	125.7(5) [128.1(5)]
S(2)-C(1)-N(1)	125.0(4) [123.2(4)]
M(1)-S(1)-C(1)	86.9(2) [87.53(19)
M(1)-S(2)-C(1)	90.5(2) [90.13(19)]
M(1A)-S(1) –C(1)	107.83(17) [108.99(18)]
C(1)-N(1)-C(2)	119.2(5) [118.8(5)]
N(1)-C(2)-N(2)	174.0(7) [(171.9(7)]

[] indicates the equivalent value for the second independent molecule.

Table 2.7 Selected bond lengths (Å) and angles (°) for **2.1**

2.3 *Conclusions*

In this chapter we have reported a modified synthetic route to potassium cyanodithioimidocarbonate free from water resulting in a much cleaner reaction and greater purity of product. We have used this salt to prepare a range of cyanodithioimidocarbonate complexes showing two different coordination modes. We have prepared two homoleptic group 10 metal complexes (Pd and Pt) which adopt square planar ML_2 conformation. We have also prepared a series of square planar platinum(bis-phosphino) cyanodithioimidocarbonate complexes which have been compared to the trithiocarbonate analogues. We have demonstrated that $[Sn(C_2N_2S_2)(^nBu)_2]$ is an effective cyanodithioimidocarbonate transfer reagent providing an alternative route to the platinum(bis-phosphino) cyanodithioimidocarbonate complexes. Finally we have prepared a series of bimetallic cyanodithioimidocarbonate complexes with group 8 (Ru), 9 (Rh, Ir) and 10 (Pt) metals in which the cyanodithioimidocarbonate ligand is S,S' bidentate S' bridging. All of the isolated compounds have been characterised spectroscopically (^{31}P, ^{1}H, ^{13}C NMR, IR, mass spectroscopy), by elemental analysis and six demonstrative X-ray structures are reported.

2.4 *Experimental*

Unless otherwise stated, all operations were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. All solvents and reagents were purchased from Aldrich, Alfa Aesar, BOC, BDH, Fisons and Strem. We are grateful to Johnson Matthey PLC for the loan of precious metal salts. Diethyl ether and thf (tetrahydrofuran) were purified by reflux over sodium-benzophenone and distillation under nitrogen. Hexane was purified by reflux over sodium and distillation under an atmosphere of nitrogen. Dichloromethane was heated to reflux over powdered calcium hydride and distilled under nitrogen. Chloroform (99 atom % d),CD_2Cl_2 (99.6+ atom D) and d6-dmso (99.5+ atom D) were used as received. $[PPh_4][Cl]$, $K_2[PtCl_4]$, $K_2[PdCl_4]$ and $[SnCl_2(^nBu)_2]$ were all used as received. The metal complexes $[\{PtCl(\mu\text{-}Cl)(PMe_2Ph)\}_2]$[106], $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$[107], $[\{IrCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$[107] and $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$[108], were prepared according to literature procedures. The complexes $[PtCl_2(PMe_2Ph)_2]$, $[PtCl_2(PPh_3)_2]$, $[PtCl_2(dppe)]$ (dppe= bis(diphenylphosphino)ethane), $[PtCl_2(dppm)]$ (dppm= bis(diphenylphosphino)methane) and $[PtCl_2(dppf)]$ (dppf = bis(diphenylphosphino)ferrocene) were prepared by the addition of stoichiometric quantities of the appropriate free phosphine or diphosphine to a dichloromethane solution of$[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene). Infrared spectra were recorded (IR spectra as KBr discs unless otherwise stated) on a Perkin-Elmer System 2000 FT/IR/Raman spectrometer. ^{31}P, ^{13}C and ^1H NMR spectra were recorded using a JEOL DELTA GSX 270 FT NMR spectrometer. Microanalysis was performed by the University of St. Andrews service. Mass

spectra were recorded by both the University of St. Andrews mass spectrometry service and the Swansea mass spectrometry service.

$K_2[C_2N_2S_2]$ 2.1. Carbon disulfide (15.876 g, 0.2085 mol) was added to a stirred solution of cyanamide (8.765 g, 0.2085 mol) in absolute ethanol (20 cm^3). The temperature of the solution was maintained below 0 °C while a solution of potassium ethoxide, (35.131 g, 0.417 mol) in absolute ethanol (160 cm^3), was added over a period of thirty minutes. The resulting mixture was stirred for a further hour. The resulting precipitate was collected by filtration and dried *in vacuo* to give the product as a yellow powder. Yield 26.40 g (65 %). Found (Calc. For $C_2N_2S_2K_2$): C 12.48 (12.36), N 14.60 (14.41)%. ^{13}C-{^1H} NMR (dmso-d6): δ(C) 228.3 (S_2C=N), 122.1 (N-C≡N). IR (KBr): 2331w, 2146s, 1604m, 1315br,s, 1034m, 978s, 683w, 561w, 521w, 399w, 247w cm^{-1}.

$[PPh_4]_2[Pt(C_2N_2S_2)_2]$ 2.2. K_2PtCl_4 (0.200 g, 0.482 mmol) was dissolved in methanol (20 cm^3) and potassium cyanodithioimidocarbonate (0.187 g, 0.964 mmol) was added as a solid in one portion and the mixture was stirred for 2 days. The mixture was filtered to remove a small amount of solid material and washed through with a further portion of methanol (20 cm^3). Tetraphenylphosphonium chloride (0.361 g, 0.964 mmol) was added to the stirred solution and the mixture was stirred for a further hour. The solvent was evaporated *in vacuo* and the remaining solid was extracted with dichloromethane (20 cm^3). The mixture was filtered through a celite pad to remove precipitated KCl and washed through with more dichloromethane (30 cm^3). The filtrate was evaporated to dryness *in vacuo* to give a yellow powder. Crystals suitable for X-Ray diffraction were obtained

by vapour diffusion from chloroform/hexane. Yield 0.426 g (80 %). Found (Calc. for $C_{52}H_{40}N_4S_4P_2Pt$): C 56.82 (56.46), H 4.03 (3.65), N 4.71 (5.06)%. ^{13}C-{^1H} NMR (CD_2Cl_2): δ(C) 218.0 (S_2C=N), 135.7 (d, $^4J(^{31}P\text{-}^{13}C)$ 3 Hz, *p*-phenyl), 134.6 (d, $^2J(^{31}P\text{-}^{13}C)$ 9 Hz, *o*-phenyl), 130.7 (d, $^3J(^{31}P\text{-}^{13}C)$ 13 Hz, *m*-phenyl), 117.7 (d, $^1J(^{31}P\text{-}^{13}C)$ 89 Hz, *i*-phenyl), 113.9 ppm (N-C≡N). ^1H NMR (CD_2Cl_2): δ 7.94-7.60 (m, 40 H, aromatic). ES^+ MS: *m/z* 339 $[PPh_4]^+$. ES^- MS: *m/z* 766 $[Pt(C_2N_2S_2)_2 + PPh_4]^-$. IR (KBr): 3056w, 2171s, 2054s, 1585m, 1482m, 1436s, 1338w, 1312w, 1188w, 1165w, 1109s, 1025w, 996m, 957w, 854vw, 752m, 724s, 690s, 615w, 527w, 379w, 360w, 270w cm^{-1}.

$[PPh_4]_2[Pd(C_2N_2S_2)_2]$ 2.3. This was prepared in the same way as platinum complex **2.2** using K_2PdCl_4 (0.200 g, 0.613 mmol), potassium cyanodithioimidocarbonate (0.238 g, 1.225 mmol) and tetraphenylphosphonium chloride (0.459 g, 1.225 mmol) to give a yellow/brown powder. Crystals suitable for X-Ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.567 g (91 %). Found (Calc. for $C_{52}H_{40}N_4S_4P_2Pd$): C 60.83 (61.38), H 4.05 (3.96), N 5.31 (5.51)%. ^{13}C-{^1H} NMR (CD_2Cl_2): δ(C) 219.2 (S_2C=N), 135.7 (d, $^4J(^{31}P\text{-}^{13}C)$ 3 Hz, *p*-phenyl), 134.6 (d, $^2J(^{31}P\text{-}^{13}C)$ 10 Hz, *o*-phenyl), 130.7 (d, $^3J(^{31}P\text{-}^{13}C)$ 13 Hz, *m*-phenyl), 117.7 (d, $^1J(^{31}P\text{-}^{13}C)$ 89 Hz, *i*-phenyl), 115.1 ppm (N-C≡N). ^1H NMR (CD_2Cl_2): δ 7.93-7.60 (m, 40 H, aromatic). ES^+ MS: *m/z* 339 $[PPh_4]^+$. ES^- MS: *m/z* 677 $[Pd(C_2N_2S_2)_2 + PPh_4]^-$, 169 $[Pd(C_2N_2S_2)_2]^{2-}$. Ir (KBr): 3055w, 2172s, 1620w, 1585m, 1484m, 1436br,s, 1338m, 1317m, 1189w, 1164w, 1108s, 1016m, 997m, 958m, 850w, 757m, 722s, 689s, 616w, 575w, 527s, 458w, 377w, 346m, 254w cm^{-1}.

[Pt($C_2N_2S_2$)(Me_2PPh)$_2$] 2.4. *Method a.* [$PtCl_2(PMe_2Ph)_2$] (0.100 g, 0.184 mmoles) was dissolved in thf (20 cm^3) and potassium cyanodithioimidocarbonate (0.050 g, 0.257 mmoles) was added as a solid in one portion. The resulting colourless solution was stirred for 24 hours. The solvent was evaporated *in vacuo* and the remaining solid was extracted with dichloromethane (20 cm^3). The mixture was filtered through a celite pad to remove precipitated KCl and washed through with additional dichloromethane (30 cm^3). The filtrate was evaporated to dryness *in vacuo* to give a white powder. Crystals suitable for X-Ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.068 g (63 %). Found (Calc. for $C_{18}H_{22}N_2S_2P_2Pt$): C 36.58 (36.80), H 3.59 (3.77), N 4.54 (4.77)%. ^{31}P-{^1H} NMR ($CDCl_3$): δ(P) –19.0 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3071 Hz. ^1H NMR ($CDCl_3$): δ 7.50-7.30 (m, 10 H, aromatic) and 1.60 (d, 12 H, $^3J(^{195}Pt\text{-}^1H)$ 28 Hz, $^2J(^{31}P\text{-}^1H)$ 10 Hz, PMe). FAB$^+$ MS: *m/z* 587 $[MH]^+$, 470 $[M\text{-}S_2N_2C_2]^+$. IR (KBr): 3058vw, 2917w, 2181s, 1983w, 1720vw, 1616vw, 1478brvs, 1436m, 1419m, 1287w, 1107m, 1014w, 944m, 916m, 906m, 841w, 741m, 720m, 692m, 575w, 521w, 482m, 453w, 436w, 396w, 374w, 283w cm^{-1}.

Method b. [$PtCl_2(PMe_2Ph)_2$] (0.070 g, 0.129 mmoles) was dissolved in dcm (20 cm^3) and [$SnS_2N_2C_2(Bu)_2$] **2.9** (0.045 g, 0.129 mmoles) was added as a solid in one portion. The resulting colourless solution was stirred for 24 hours. The solvent was evaporated *in vacuo* and the remaining solid was dissolved in the minimum volume of dichloromethane (5 cm^3) and the product was precipitated with diethyl ether (30 cm^3) to give a white powder. Yield 0.064 g (84 %). The

analytic and spectroscopic data for $[Pt(C_2N_2S_2)(Me_2PPh)_2]$ **2.4** synthesised by *method b* were identical to those found in material produced by *method a*.

$[Pt(C_2N_2S_2)(PPh_3)_2]$ 2.5. *Method a.* This was prepared in the same way as platinum complex **2.4** *method a* using $[PtCl_2(PPh_3)_2]$ (0.100 g, 0.127 mmoles and potassium cyanodithioimidocarbonate (0.040 g, 0.206 mmoles) to give a white powder. Yield 0.088 g (83 %). Found (Calc. for $C_{38}H_{30}N_2S_2P_2Pt$): C 54.25 (54.61), H 3.21 (3.62), N 3.27 (3.35)%. $^{31}P\text{-}\{^1H\}$ NMR (CD_2Cl_2): δ(P) 17.0 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3179 Hz. ^1H NMR (CD_2Cl_2): δ 7.43-7.21 (m, 30 H, aromatic). EI^+ MS: *m/z* 858 $[M+Na]^+$, 836 $[MH]^+$. IR (KBr): 3058w, 2177vs, 1618vw, 1573vw, 1479brvs, 1434m, 1313vw, 1185m, 1160m, 1094s, 1028w, 1011w, 1000w, 956m, 849w, 757m, 739m, 691s, 619w, 573w, 544m, 525m, 518m, 497m, 456vw, 419w, 397m, 301w, 245w cm^{-1}.

Method b. This was prepared in the same way as platinum complex **2.4** *method b* using $[PtCl_2(PPh_3)_2]$ (0.060 g, 0.076 mmoles) and $[SnS_2N_2C_2(Bu)_2]$ **2.9** (0.026 g, 0.076 mmoles) to give a white powder. Yield 0.028 g (44 %). The analytic and spectroscopic data for $[Pt(C_2N_2S_2)(PPh_3)_2]$ **2.5** synthesised by *method b* were identical to those found in material produced by *method a*.

$[Pt(C_2N_2S_2)(dppe)]$ 2.6. *Method a.* This was prepared in the same way as platinum complex **2.4** *method a* using $[PtCl_2(dppe)]$ (0.100 g, 0.151 mmol) and potassium cyanodithioimidocarbonate (0.040 g, 0.206 mmol) to give a white powder. Crystals suitable for X-Ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.046 g (43.9 %). Found (Calc. for

$C_{28}H_{24}N_2S_2P_2Pt$): C 47.19 (47.39), H 3.44 (3.41), N 3.74 (3.95)%. ^{31}P-{^1H} NMR ($CDCl_3$): δ(P) 42.2 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3094 Hz. ^1H NMR ($CDCl_3$): δ 7.72-7.47 (m, 20 H, aromatic), 2.58-2.37 (m, 4H, PCH_2CH_2P). EI^+ MS: *m/z* 732 $[M+Na]^+$, 710 $[MH]^+$. IR (KBr): 3053w, 2953vw, 2179vs, 1618vw, 1586w, 1572vw, 1476brvs, 1435m, 1411m, 1308w, 1276vw, 1187w, 1161w, 1106s, 1026w, 1008m, 998m, 953m, 876m, 824m, 816m, 747m, 718s, 707s, 691s, 656m, 574w, 532s, 488m, 448vw, 396m, 370w, 245vw cm^{-1}.

Method b. This was prepared in the same way as platinum complex **2.4** *method b* using [$PtCl_2$(dppe)] (0.100 g, 0.151 mmoles) and [$SnS_2N_2C_2(Bu)_2$] **2.9** (0.053 g, 0.151 mmoles) to give a white powder. Yield 0.092 g (86 %). The analytic and spectroscopic data for [$Pt(C_2N_2S_2)$(dppe)] **2.6** synthesised by *method b* were identical to those found in material produced by *method a*.

[$Pt(C_2N_2S_2)$(dppm)] 2.7. This was prepared in the same way as platinum complex **2.4** *method a* using [$PtCl_2$(dppm)] (0.100 g, 0.154 mmoles) and potassium cyanodithioimidocarbonate (0.040 g, 0.206 mmoles) to give a white powder. Yield 0.093 g (87 %). Found (Calc. for $C_{27}H_{22}N_2S_2P_2Pt$): C 46.69 (46.62), H 2.97 (3.19), N 3.94 (4.03)%. ^{31}P-{^1H} NMR ($CDCl_3$): δ(P) – 53.8 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 2634 Hz. ^1H NMR ($CDCl_3$): δ 7.74-7.43 (m, 20 H, aromatic), 4.70 (t, 2H, $^2J(^{31}P\text{-}^1H)$ 21.5 Hz, PCH_2P). EI^+ MS: *m/z* 719 $[M+Na]^+$, 696 $[MH]^+$. IR (KBr): 3052vw, 2978vw, 2974vw, 2178vs, 1608vw, 1477brvs, 1436m, 1359w, 1309w, 1188w, 1160vw, 1104m, 1027w, 998w, 950m,

777w, 736m, 714m, 689m, 573w, 551m, 506m, 480m, 444w, 393m, 250m cm^{-1}.

[Pt($C_2N_2S_2$)(dppf)] 2.8. This was prepared in the same way as platinum complex **2.4** *method a* using [$PtCl_2$(dppf)] (0.100 g, 0.122 mmol) and potassium cyanodithioimidocarbonate (0.030 g, 0.154 mmol) to give a yellow powder. Crystals suitable for X-Ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.043 g (41 %). Found (Calc. for $C_{36}H_{24}N_2S_2P_2FePt$): C 49.75 (50.18), H 3.03 (2.81), N 3.07 (3.25)%. ^{31}P-{^1H} NMR (dmso-D_6, 90 °C): δ(P) 16.0 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3312 Hz. ^1H NMR (dmso-D_6, 30 °C): δ 7.66-7.53 (m, 20 H, aromatic), 4.61 (br, m, 4H, α-CH (C_5H_4)), 4.43 (br, m, 4H, β-CH (C_5H_4)). FAB^+ MS: *m/z* 867 $[MH]^+$, 781 $[M\text{-}SN_2C_2]^+$. IR (KBr): 3053vw, 2925vw, 2176vs, 1618vw, 1478brvs, 1435m, 1384w, 1306w, 1263w, 1195vw, 1168w, 1098m, 1057w, 1011w, 1025w, 999w, 957m, 892vw, 852vw, 829w, 745m, 709w, 691m, 640w, 559m, 515m, 484m, 472m, 438w, 399w, 350w, 282w, 249w cm^{-1}.

[Sn($C_2N_2S_2$)(^{n}Bu)$_2$] 2.9. To a stirred solution of dipotassium cyanodithioimidocarbonate (3.127 g, 0.0103 moles) in distilled water (10 cm^3), [$SnCl_2$(^{n}Bu)$_2$] (2.00 g, 0.0103 moles) in thf (10 cm^3), was added dropwise over half an hour. The reaction mixture was stirred for a further 2.5 hours and then poured onto crushed ice. The resulting white solid was filtered and washed with distilled water (20 cm^3) and dried *in vacuo* to give a white powder. Yield 3.56 g (99 %). The product was then recrystallised from methanol. Found (Calc. for $C_{10}H_{18}N_2S_2Sn$): C 34.78 (34.40), H 5.49 (5.20), N 7.81 (8.02)%. ^1H NMR

(CD_3OD): δ 1.81-1.70 (m, 4H, α-CH_2) 1.56-1.44 (m, 8H, βCH_2 and γCH_2) and 1.02-0.97 (t, 6H, δ-CH_3). IR (KBr): 2959m, 2924m, 2857m, 2436w, 2190s, 1636vw, 1462m, 1368brvs, 1177w, 1152m, 1121w, 1079m, 1057m, 1023m, 984s, 877m, 770w, 748w, 681m, 583w, 538w, 525w, 404w, 382w, 278w, 248w cm^{-1}.

[{Pt($C_2N_2S_2$)(PMe_2Ph)}$_2$] 2.10. This was prepared in the same way as platinum complex **2.4** *method a* using [{PtCl(μ-Cl)(PMe_2Ph)}$_2$] (0.100 g, 0.124 mmoles) and potassium cyanodithioimidocarbonate (0.048 g, 0.247 mmoles) to give a yellow powder. Yield 0.083 g (75 %). Found (Calc. for $C_{20}H_{22}N_4S_4P_2Pt_2$): C 26.24 (26.73), H 2.22 (2.47), N 5.83 (6.23)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) -17.9 ppm. $^1J(^{195}Pt$-$^{31}P)$ 3420 Hz. ^1H NMR ($CDCl_3$): δ 7.50-7.30 (m, 10 H, aromatic) and 1.60 (d, 12 H, $^3J(^{195}Pt$-$^1H)$ 28 Hz, $^2J(^{31}P$-$^1H)$ 10 Hz, PMe). IR (KBr): 3052vw, 2980vw, 2916vw, 2223m, 2188s, 1631w, 1508m, 1433vbr, 1286w, 1109w, 949m, 912s, 846w, 744m, 722w, 692m, 569vw, 517vw, 489m, 448w, 384w, 326w, 283w, 244w cm^{-1}.

[{Rh($C_2N_2S_2$)(η^5-C_5Me_5)}$_2$] 2.11. This was prepared in the same way as platinum complex **2.4** *method a* using [{RhCl(μ-Cl)(η^5-C_5Me_5)}$_2$] (0.100 g, 0.162 mmoles) and potassium cyanodithioimidocarbonate (0.063 g, 0.324 mmoles) to give a red powder. Crystals suitable for X-Ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.056 g (49 %). Found (Calc. for $C_{24}H_{30}N_4S_4Rh_2$): C 40.21 (38.98), H 4.01 (4.08), N 7.22 (7.57)%. ^1H NMR ($CDCl_3$): δ 1.83-1.69 (m, 30H, η^5-C_5Me_5). ES^+ MS: *m/z* 747 $[M+K]^+$, 731 $[M+Na]^+$, 709 $[MH]^+$. IR (KBr): 2915w, 2177s, 1980w,

1629vw, 1485brvs, 1379m, 1157w, 1078w, 1021m, 951m, 741w, 690w, 619w, 556w, 515w, 414w, 378w, 352w, 249w cm^{-1}.

[{Ir($C_2N_2S_2$)(η^5-C_5Me_5)}$_2$] 2.12. This was prepared in the same way as platinum complex **2.4** *method a* using [{IrCl(μ-Cl)(η^5-C_5Me_5)}$_2$] (0.100 g, 0.126 mmoles) and potassium cyanodithioimidocarbonate (0.049 g, 0.251 mmoles) to give an orange powder. Yield 0.071 g (64 %). Found (Calc. for $C_{24}H_{30}N_4S_4Ir_2$): C 32.93 (32.49), H 3.24 (3.41), N 6.16 (6.31)%. ^{1}H NMR ($CDCl_3$): δ 1.92-1.63 (m, 30H, η^5-C_5Me_5). ES$^+$ MS: *m/z* 911 $[M+Na]^+$, 889 $[MH]^+$. IR (KBr): 2919w, 2179s, 1499brs, 1383m, 1099w, 1027m, 949m, 853w, 745w, 700w, 553w, 500w, 367w, 349w, 278w, 245w cm^{-1}.

[{Ru($C_2N_2S_2$)(η^6-*p*-$MeC_6H_4{}^iPr$)}$_2$] 2.13. This was prepared in the same way as platinum complex **2.4** *method a* using [{RuCl(μ-Cl)(η^6-*p*-$MeC_6H_4{}^iPr$)}$_2$] (0.100 g, 0.163 mmoles) and potassium cyanodithioimidocarbonate (0.063 g, 0.327 mmoles) to give a dark orange powder. Yield 0.080 g (75 %). Found (Calc. for $C_{24}H_{28}N_4S_4Ru_2$): C 40.71 (41.01), H 3.76 (4.02), N 7.69 (7.97)%. ^{1}H NMR ($CDCl_3$): δ 5.49 and 5.35 (AB system, $^3J(^1H\text{-}^1H)$ 5.5 Hz, 4H, aromatic) 2.61 (m, 1H, $CHMe_2$) 2.06 (s, 3H, CH_3) and 1.15 (d, $(CH_3)_2CH$, 6H). FAB$^+$ MS: *m/z* 704 $[M]^+$. IR (KBr): 3061vw, 2962w, 2225m, 2181s, 1628w, 1473brvs, 1387m, 1278w, 1199w, 1156w, 1089w, 1054w, 1024w, 986m, 935w, 899w, 863w, 802w, 673w, 633vw, 575w, 519w, 454w, 391w, 384w, 248w cm^{-1}.

X-ray Crystallography

Table 2.8 and 2.9 list details of data collections and refinements. For **2.3**, **2.4** and **2.6**, data were collected at room temperature using Mo-Kα radiation with a Rigaku Mercury system and for **2.2** at room temperature using a Bruker SMART system. Data for **2.8** and **2.11** were collected at 125 K using a Bruker SMART system. Several crystals of **2.11** were examined, solvation appears to be causing problems with the crystal quality; the reported data is from the best data set we where able to obtain. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[109]

Compound	**2.2**	**2.3**	**2.4**
Empirical formula	$C_{52}H_{40}N_4P_2PtS_4$	$C_{52}H_{40}N_4P_2PdS_4$	$C_{18}H_{22}N_2P_2PtS_2$
Crystal dimensions/mm	0.1 × 0.02 × 0.02	0.1 × 0.1 × 0.1	0.15 × 0.1 × 0.06
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P $\bar{1}$	P $\bar{1}$	C2/c
a/Å	13.577(5)	10.861(2)	33.846(10)
b/Å	13.978(5)	14.540(3)	11.431(7)
c/Å	19.931(7)	15.163(3)	11.030(7)
α/°	79.837(6)	88.894(11)	90
β/°	83.885(5)	88.705(10)	98.17(3)
γ/°	71.180(6)	83.598(10)	90
U/Å^3	3519(2)	2378.7(8)	4262(4)
Z	3	2	8
M	1106.15	1017.46	587.53
Dc/g cm^{-3}	1.566	1.421	1.831
μ/mm^{-1}	3.278	0.673	6.934
Measured reflections	17365	8060	7744
Independent reflections (R_{int})	9873(0.1456)	5365(0.0239)	3264(0.0352)
Final R1, wR2[I>2σ(I)]	0.1221, 0.2841	0.0338, 0.0715	0.0345, 0.0676

Table 2.8 Details of the X-ray data collections and refinements for compounds **2.2, 2.3** and **2.4**.

Compound	**2.6**	**2.8**	**2.11**
Empirical formula	$C_{28}H_{24}N_2P_2PtS_2$	$C_{36}H_{28}FeN_2P_2PtS_2$	$C_{26}H_{32}Cl_6N_4Rh_2S_4$
Crystal dimensions/mm	0.2 × 0.1 × 0.3	0.25 × 0.06 × 0.06	0.15 × 0.1× 0.01
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	P2/n
a/Å	15.104(3)	9.3113(13)	19.181(4)
b/Å	20.119(4)	9.5996(13)	8.8430(19)
c/Å	18.029(4)	18.070(2)	21.576(5)
α/°	90	99.062(2)	90
β/°	99.01(3)	95.808(2)	102.771(3)
γ/°	90	101.906(2)	90
U/Å^3	5411.0(19)	1545.7(4)	3569.2(13)
Z	8	2	4
M	709.64	865.60	947.32
Dc/g cm^{-3}	1.742	1.860	1.763
μ/mm^{-1}	5.479	5.259	1.633
Measured reflections	19602	7914	16908
Independent reflections	7578(0.0500)	4411(0.0293)	5062(0.1637)
(R_{int})			
Final R1, wR2[I>2σ(I)]	0.1041, 0.2589	0.0316, 0.0655	0.0458, 0.0672

Table 2.9 Details of the X-ray data collections and refinements for compounds **2.6, 2.8** and **2.11**.

Chapter 3: Synthesis of cyanodiselenoimidocarbonate, $[C_2N_2Se_2]^{2-}$ transition metal complexes.

3.1 *Introduction*

As part of our study of E,E bidentate (E = S, Se) chalcogen donor ligands we have reported a series of cyanodithioimidocarbonate complexes $[C_2N_2S_2]^{2-}$ (Chapter 2, p 35). The cyanodiselenoimidocarbonate dianion $[C_2N_2Se_2]^{2-}$ which is the selenium analogue has only been reported twice in the literature both times by Jensen and co-workers.[26,30] They report the synthesis of dipotassium cyanodiselenoimidocarbonate, the Se,Se'-dimethyl and diphenyl derivatives and one nickel complex $[PPh_4]_2[Ni(C_2N_2Se_2)_2]$. The distinct lack of cyanodiselenoimidocarbonate complexes has led us to prepare a series of mononuclear and binuclear complexes for comparison with the sulfur analogues. Selected examples have been chosen for crystallographic study.

3.2 *Results and Discussion*

3.2.1 *Preparation of carbon diselenide*

Carbon diselenide was prepared as a dichloromethane solution by passing dichloromethane vapour over elemental selenium[110,111] (Figure 3.1). Approximately 20 g of elemental selenium were placed in a quartz boat inside tube II as shown below and nitrogen was passed through the system. Flask I is

heated to 200 °C, section IIa of the tube to 375-400 °C, section IIb of the tube to approximately 575 °C and flask III cooled to –78 °C.

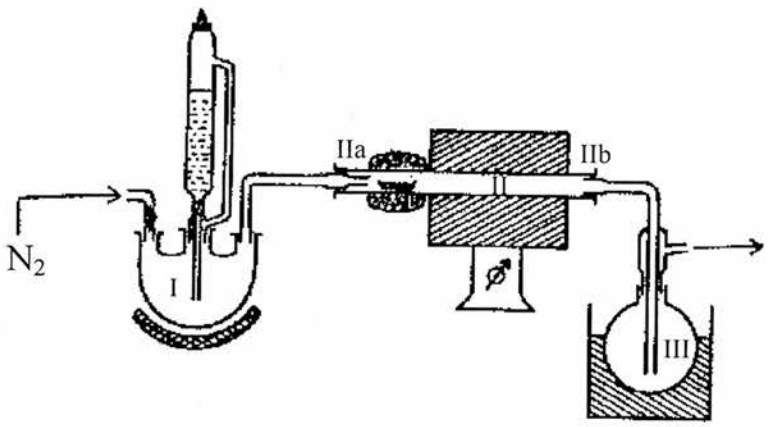


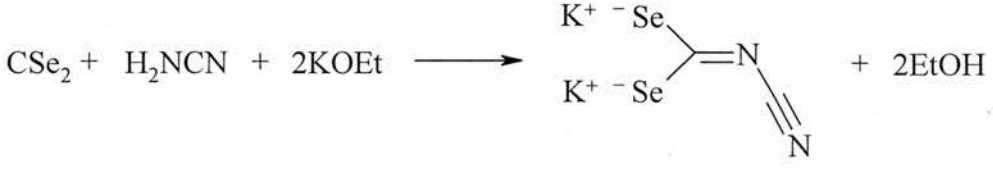
Figure 3.1 Schematic diagram of apparatus used for preparation of CSe_2. Adapted from W. H. Pan, J.P. Fackler Jr. and H.-W. Chen, *Inorg. Chem.*, **1981**, *20*, 856-863.[110]

Dichloromethane was then allowed to drop slowly into flask I where it was vaporised and carried by the stream of nitrogen through the system. As the reaction progressed a white mist with a slight reddish tinge (due to unreacted selenium) was observed in flask III. When the reaction was complete the red mixture in flask III was filtered through neutral alumina to remove residual selenium and any other impurities. This gave the dichloromethane solution of CSe_2 as a green liquid. The concentration of the solution was determined to be approximately 10 % using a plot of the density of the CSe_2/CH_2Cl_2 mixture vs. the weight percent of CSe_2 published by Rosenbaum *et al.*[112] The carbon diselenide solution was stored at 0 °C under nitrogen. After 2 months only minimal decomposition was noted. Carbon diselenide has a very strong unpleasant odour even at very low concentration. Therefore extra care was taken

when handling this compound and any contaminated equipment was treated with concentrated sodium hypochlorite solution.

3.2.2 *Synthesis of dipotassium cyanodiselenoimidocarbonate.*

The synthesis of the $[C_2N_2Se_2]^{2-}$ dianion as the dipotassium salt **3.1** was reported by Jensen and Henriksen in 1970.[26] The dipotassium salt **3.1** is prepared in a similar fashion to the sulfur analogue dipotassium cyanodithioimidocarbonate[101] by the dropwise addition of potassium hydroxide in water to cyanamide and carbon diselenide in dioxane at 0 °C. Our synthesis (Scheme 3.1) was carried out in ethanol and potassium ethoxide was used in place of potassium hydroxide to prevent water generation during the reaction due to the sensitive nature of the dipotassium salt.



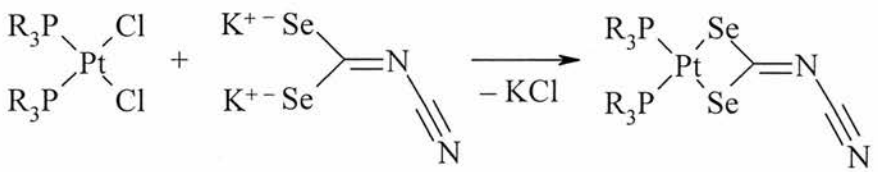
Scheme 3.1 Synthesis of dipotassium cyanodiselenoimidocarbonate.

After suction filtration under a nitrogen atmosphere the product was obtained as an impure off yellow solid. We found **3.1** to be air sensitive and decomposition was noted very readily when it was allowed to stand in air hence it was stored under nitrogen below 0 °C. When stored in this way over several months no further decomposition was noted. In the IR spectrum we observed a strong ν(C≡N) band at 2127 cm^{-1}, and a strong band at 1347 cm^{-1} assigned as ν(C=N).

Purification of **3.1** proved unsuccessful hence we used the dipotassium cyanodiselenoimidocarbonate as obtained for subsequent reaction.

3.2.3 *Platinum(bis-phosphino) cyanodiselenoimidocarbonate complexes.*

The platinum bis-phosphine complexes $[Pt(C_2N_2Se_2)(PR_3)_2]$ (PR_3 = PMe_2Ph, PPh_3, ½ dppe, ½ dppm, ½ dppf) were all obtained by the reaction of the appropriate $[PtCl_2(PR_3)_2]$ complex with excess of potassium cyanodiselenoimidocarbonate in tetrahydrofuran. A large excess of the dipotassium salt was always used as this gave a cleaner reaction. The solvent was removed under reduced pressure and the residual solid dissolved in dichloromethane. The mixture was filtered through a Celite pad to remove precipitated KCl and any residual dipotassium cyanodiselenoimidocarbonate. Evaporation of the solvent gave the complexes **3.2-3.6** as powders in acceptable yields (Scheme 3.2).



3.2 PR_3 = PMe_2Ph
3.3 PR_3 = PPh_3
3.4 PR_3 = ½ dppe
3.5 PR_3 = ½ dppm
3.6 PR_3 = ½ dppf

Scheme 3.2 Synthesis of platinum(bis-phosphino) cyanodiselenoimidocarbonate complexes.

Unlike the dipotassium salt the platinum complexes **3.2-3.6** were all air stable. We found that **3.2-3.6** were soluble in chloroform, dichloromethane, partially soluble in tetrahydrofuran and insoluble in diethyl ether or hexane. The complexes were all stable in solution. All of the compounds showed the anticipated M^+ in their mass spectra and the microanalysis was within the acceptable limits (Table 3.1).

Complex	C	H	N	*m/z*
3.2 $[Pt(C_2N_2Se_2)(PMe_2Ph)_2]$	31.60 (31.73)	3.01 (3.25)	3.83 (4.11)	682
3.3 $[Pt(C_2N_2Se_2)(PPh_3)_2]$	49.41 (49.10)	2.85 (3.25)	2.76 (3.01)	931
3.4 $[Pt(C_2N_2Se_2)(dppe)]$	41.88 (41.86)	2.79 (3.01)	3.29 (3.49)	804
3.5 $[Pt(C_2N_2Se_2)(dppm)].CH_2Cl_2$	38.89 (38.46)	2.68 (2.77)	3.13 (3.20)	791
3.6 $[Pt(C_2N_2Se_2)(dppf)].CH_2Cl_2$	42.83 (42.55)	2.64 (2.69)	2.37 (2.68)	960

Table 3.1 Microanalytical data (calculated values in parentheses) and mass spectral data for complexes **3.2-3.6**.

The characteristic ν(C≡N) vibrations were observed in the range 2174 to 2179 cm^{-1} and the ν(C=N) vibrations can be seen in the region of 1492 to 1495 cm^{-1} (Table 3.2), which are comparable with the corresponding platinum bis-

phosphine cyanodithioimidocarbonate complexes **2.4** to **2.8** synthesised in Chapter 2. In a similar manner to the sulfur analogues the ν(C=N) vibrations are considerably increased in frequency compared to the uncoordinated anion indicating the change in delocalisation as a consequence of coordination. The ν(Pt-Se) bands all lie within the range 246 to 294 cm^{-1} (Table 3.2). The platinum(bis-phosphine) cyanodiselenoimidocarbonate complexes **3.2** to **3.6** all showed sharp singlets with platinum satellites in their $^{31}P\{^{1}H\}$ NMR spectra and have very similar δ values to the sulfur analogues. The chemical shifts for **3.2** to **3.6** can be seen in Table 3.2. The $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling constants lie in the range 2620-3263 Hz (c.f 2634-3312 Hz for $[C_2N_2S_2]^{2-}$ complexes **2.4** to **2.8**) with the variations reflecting the nature of the phosphine group.

Complex	δ(P) (ppm)	$^{1}J(^{195}Pt\text{-}^{31}P)$ (Hz)	ν(C≡N) (cm^{-1})	ν(C=N) (cm^{-1})	ν(Pt-Se) (cm^{-1})
3.2 $[Pt(C_2N_2Se_2)(PMe_2Ph)_2]$	-19.6	3063	2179	1494	294,254
3.3 $[Pt(C_2N_2Se_2)(PPh_3)_2]$	17.3	3190	2177	1497	282,246
3.4 $[Pt(C_2N_2Se_2)(dppe)]$	44.8	3049	2178	1492	280,246
3.5 $[Pt(C_2N_2Se_2)(dppm)]$	-54.2	2620	2175	1492	282,258
3.6 $[Pt(C_2N_2Se_2)(dppf)]$	16.4	3263	2174	1495	279,252

All measured in $CDCl_3$ at 25 °C.

Table 3.2 $^{31}P\{^{1}H\}$ NMR (109.4 MHz) and selected IR data for complexes **3.2-3.6**.

Selenium satellites are also noted for the complexes **3.2** to **3.6** in their $^{31}P\{^{1}H\}$ NMR spectra but we do not have sufficient detail to determine the $^{2}J(^{77}Se\text{-}^{31}P)$ values. Crystals of **3.2** and **3.4** were obtained by vapour diffusion from chloroform and hexane therefore the X-ray crystal structures of both compounds (Table 3.3, Figures 3.2 and 3.3) were obtained. In both examples the X-ray analysis shows that the platinum core lies at the centre of a distorted square planar coordination sphere. The distortion from idealized 90 ° square planar geometry can be illustrated by the P(1)-Pt(1)-P(2) bond angle which is 94.46(9) ° in **3.2** and 86.64(8) ° in **3.4**. The corresponding Se(1)-Pt(1)-Se(2) bite angles in **3.2** and **3.4** are 77.37(4) ° and 77.81(3) ° respectively. As expected, the Pt-Se bond lengths in **3.2** and **3.4** (approximately 2.5 Å) are longer than the corresponding Pt-S bonds in the analogous cyanodithioimidocarbonate complexes (approximately 2.35 Å). In the $PtSe_2C$ ring for **3.2** the Pt-Se-C angles are 86.1(3) ° and 86.9(3) °. The Se(1)-C(1)-Se(2) angle is 109.5(5) °. In compound **3.4** the Pt-Se-C angles are 86.1(2) ° and 85.9(2)°. The Se(1)-C(1)-Se(2) angle is 110.2(4) °. The nonbonded selenium distance is 3.08 Å and 3.09 Å for **3.2** and **3.4** respectively which both correspond to ca 81 % of the van der Waals radii of selenium, implying that in both cases there is a significant interaction between the two selenium atoms. As observed in the sulfur analogues N(1) is trigonal. In **3.2** the cyanodiselenoimidocarbonate ligand lies within the coordination plane with the exception of C(1)-N(1)-C(2)-N(2), which is hinged at an angle of 10.2(5) ° to the plane. In **3.4** the whole complex is almost planar however there is a small hinge angle of 2.0(5) ° for C(1)-N(1)-C(2)-N(2) with respect to the coordination plane.

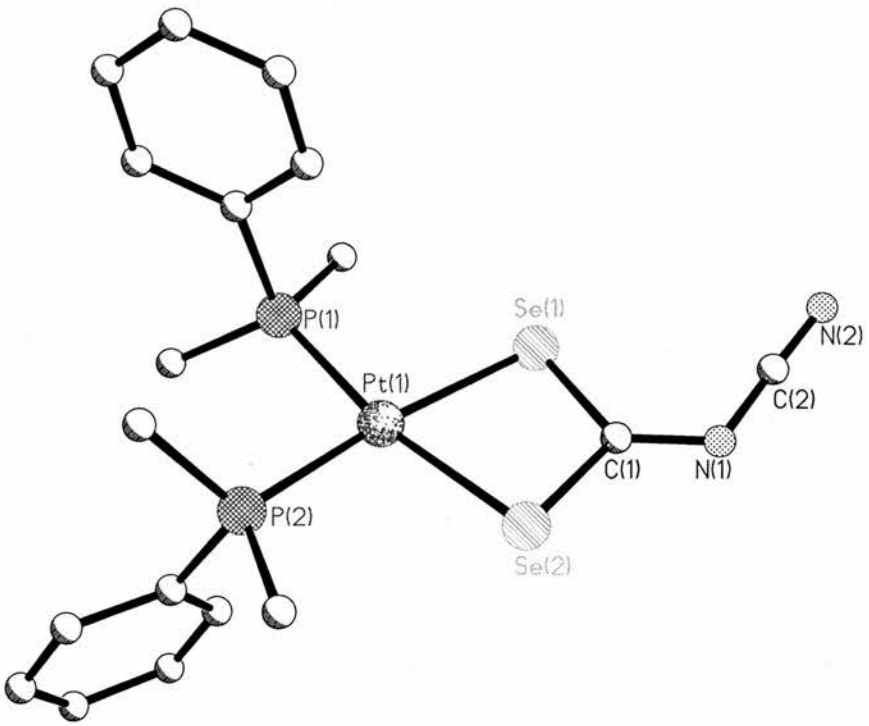


Figure 3.2 X-ray crystal structure of **3.2**.

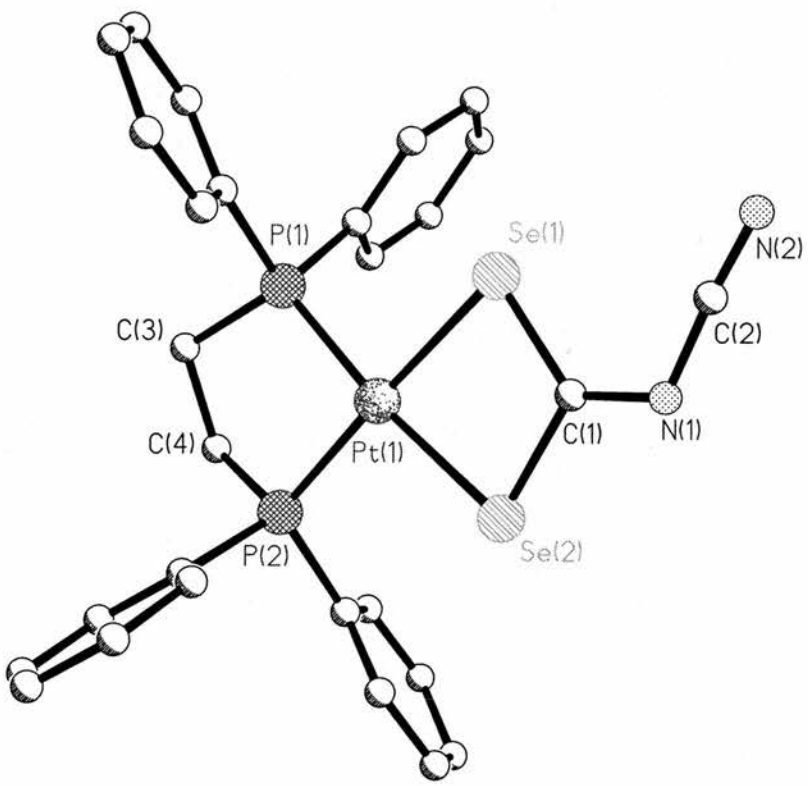


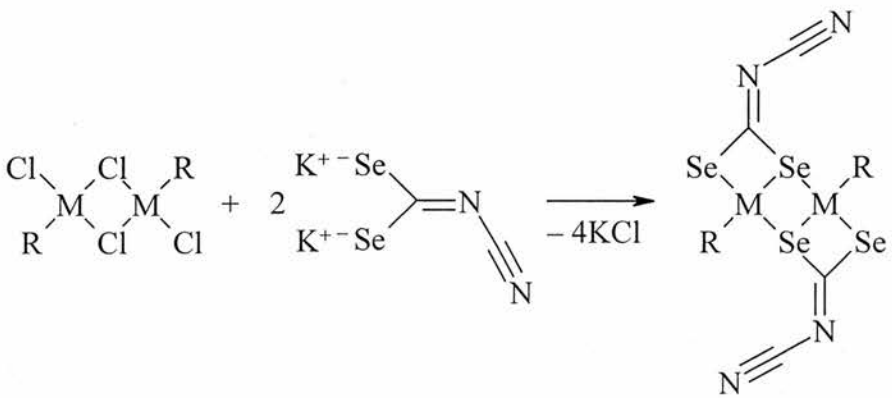
Figure 3.3 X-ray crystal structure of **3.4**.

Compound	**3.2**	**3.4**
Pt(1)-P(1)	2.271(2)	2.245(2)
Pt(1)-P(2)	2.266(3)	2.236(2)
Pt(1)-Se(1)	2.4570(12)	2.4577(9)
Pt(1)-Se(2)	2.4725(11)	2.4617(9)
Se(1)-C(1)	1.916(9)	1.880(8)
Se2)-C(1)	1.856(10)	1.886(7)
C(1)-N(1)	1.305(13)	1.333(9)
N(1)-C(2)	1.329(13)	1.350(10)
C(2)-N(2)	1.184(12)	1.167(10)
Se(1)-Pt(1)-Se(2)	77.37(4)	77.81(3)
P(1)-Pt(1)-P(2)	94.46(9)	86.64(8)
Se(1)-C(1)-N(1)	126.6(7)	127.9(6)
Se(2)-C(1)-N(1)	123.9(7)	121.8(6)
Pt(1)-Se(1)-C(1)	86.1(3)	86.1(2)
Pt(1)-Se(2)-C(1)	86.9(3)	85.9(2)
P(1)-Pt(1)-Se(1)	92.96(7)	95.71(6)
P(2)-Pt(1)-Se(2)	95.11(7)	99.83(6)
C(1)-N(1)-C(2)	119.1(8)	115.0(6)
N(1)-C(2)-N(2)	175.9(12)	175.8(9)

Table 3.3 Selected bond lengths and angles for compounds **3.2** and **3.4**.

3.2.4 *Bimetallic cyanodiselenoimidocarbonate complexes.*

The bimetallic cyanodiselenoimidocarbonate complexes [M{$(C_2N_2Se_2)(\eta^5$-$C_5Me_5)$}$_2$] (M = Rh **3.7**, Ir **3.8**) were prepared and isolated in a similar fashion to the platinum(bis-phosphine) cyanodiselenoimidocarbonate complexes **3.2-3.6** by reacting excess of the dipotassium salt with the appropriate transition metal dimer starting material (Scheme 3.3).



3.7 M = Rh, R = η^5-C_5Me_5
3.8 M = Ir, R = η^5-C_5Me_5

Scheme 3.3 Synthesis of bimetallic cyanodiselenoimidocarbonate complexes.

Complex	C	H	N	*m/z*
3.6 [{Rh$(C_2N_2Se_2)(\eta^5$-$C_5Me_5)$}$_2$]	32.44 (32.17)	3.77 (3.37)	5.76 (6.25)	898
3.7 [{Ir$(C_2N_2Se_2)(\eta^5$-$C_5Me_5)$}$_2$]	27.21 (26.82)	2.39 (2.81)	5.65 (5.21)	1077

Table 3.4 Microanalytical data (calculated values in parentheses) and mass spectral data for complexes **3.7-3.8**.

A large excess of $K_2[C_2N_2Se_2]$ was again used as in **3.2-3.6** because this resulted in a cleaner reaction and an improved yield. Complexes **3.7** and **3.8** both had similar solubility to the platinum complexes. **3.7** and **3.8** both gave satisfactory microanalysis and showed the anticipated M^+ in their mass spectra (Table 3.4). The ν(C≡N) vibrations were observed at approximately 2180 cm^{-1} and the ν(C=N) vibrations can be seen in the region of 1459 to 1492 cm^{-1} which is in accord with the values observed in the sulphur analogues. The bands for ν(M-Se) were all observed in the range 240 to 282 cm^{-1}. The ^1H NMR spectra for **3.7** and **3.8** both exhibited a multiplet corresponding to the pentamethyl cyclopentadienyl protons. Unfortunately it was not possible to grow crystals of either **3.7** or **3.8** therefore no crystallographical data was obtained. We postulate that the most likely structure for these complexes would be analogous to that of $[\{Rh(C_2N_2S_2)(\eta^5\text{-}C_5Me_5)\}_2]$ **2.11** (Figure 2.7, p 51).

3.3 *Conclusions*

In this chapter we have synthesised potassium cyanodiselenoimidocarbonate in a similar fashion to the sulfur analogue. We have used this salt to prepare cyanodiselenoimidocarbonate complexes showing two different coordination modes. We have synthesised a series of square planar platinum(bis-phosphino) cyanodiselenoimidocarbonate complexes in which the ligand is Se,Se' bidentate. The platinum(bis-phosphino) cyanodiselenoimidocarbonate complexes have $^{31}P-\{^{1}H\}$ NMR resonances in the same range as the sulfur analogues with comparable coupling constants. Two bimetallic cyanodiselenoimidocarbonate complexes with group 9 metals (Rh, Ir) were synthesised. We propose the cyanodiselenoimidocarbonate ligand in the bimetallic complexes is Se,Se' bidentate Se' bridging like the analogous sulfur compounds. All of the isolated compounds have been characterised spectroscopically (^{31}P, ^{1}H, ^{13}C NMR, IR, mass spectroscopy), by elemental analysis and two demonstrative X-ray structures are reported.

3.4 *Experimental*

General experimental conditions and instrumentation were as set out on page 55. Carbon diselenide was prepared as a dichloromethane solution by passing dichloromethane over elemental selenium at 600°C in a tube furnace.[110,111] The metal complexes $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$[107] and $[\{IrCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$[107] were prepared according to literature procedures. The complexes $[PtCl_2(PMe_2Ph)_2]$, $[PtCl_2(PPh_3)_2]$, $[PtCl_2(dppe)]$ (dppe= bis(diphenylphosphino)ethane), $[PtCl_2(dppm)]$ (dppm= bis(diphenylphosphino)methane)and $[PtCl_2(dppf)]$ (dppf = bis(diphenylphosphino)ferrocene) were prepared by the addition of stoichiometric quantities of the appropriate free phosphine or diphosphine to a dichloromethane solution of $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene).

$K_2[C_2N_2Se_2]$ 3.1. Carbon diselenide (80 cm^3 10% solution in dichloromethane, 0.063 mmol) was added to a stirred solution of cyanamide (2.642 g, 0.063 mol) in absolute ethanol (20 cm^3). The temperature of the solution was maintained below 0 °C while a solution of potassium ethoxide, (10.558 g, 0.126 mol) in absolute ethanol (50 cm^3), was added over a period of thirty minutes. The resulting mixture was stirred for a further hour. The resulting precipitate was collected by filtration under nitrogen and dried *in vacuo* to give the product as a off yellow solid. Yield 5.474 g (30 %). IR (KBr): 2197w, 2127s, 1619m, 1530m, 1432s, 1347w, 1239w, 1099w, 1020w, 955w, 878w, 602w, 578w, 283w cm^{-1}.

[Pt($C_2N_2Se_2$)(PMe_2Ph)$_2$] 3.2. [$PtCl_2(PMe_2Ph)_2$] (0.050 g, 0.0769 mmoles) was dissolved in tetrahydrofuran (20 cm^3) and potassium cyanodiselenoimidocarbonate (0.167 g, 0.580 mmoles) was added as a solid in one portion. The resulting orange solution was stirred for 48 hours in the absence of light. The solvent was evaporated *in vacuo* and the remaining solid was extracted with dichloromethane (20 cm^3). The mixture was filtered through a celite pad to remove precipitated KCl and washed through with additional dichloromethane (30 cm^3). The filtrate was evaporated to dryness *in vacuo* to give a pale orange powder. The product was recrystallised by vapour diffusion from chloroform/hexane to obtain X-ray quality crystals. Yield 0.027 g (52 %). Found (Calc. for $C_{18}H_{22}N_2Se_2P_2Pt$): C 31.60 (31.73), H 3.01 (3.25), N 3.83 (4.11)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) –19.6 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3063 Hz. ^1H NMR (CD_2Cl_2): δ 7.69-7.48 (m, 10 H, aromatic) and 1.63 (d, 12 H, $^3J(^{195}Pt\text{-}^1H)$ 36 Hz, $^2J(^{31}P\text{-}^1H)$ 10 Hz, PMe). EI$^+$ MS: *m/z* 682 [M]$^+$. IR (KBr): 3050vw, 3000vw, 2179vs, 1655vw, 1494s, 1466m, 1234m, 1417m, 1313w, 1285w, 1106w, 1001w, 945m, 914m, 906m, 872w, 843w, 742m, 719w, 693w, 555w, 484w, 448w, 431w, 369w, 294w, 254w cm^{-1}.

[Pt($C_2N_2Se_2$)(PPh_3)$_2$] 3.3. This was prepared in the same way as platinum complex **3.2** using [$PtCl_2(PPh_3)_2$] (0.050 g, 0.0632 mmoles) and potassium cyanodiselenoimidocarbonate (0.208 g, 0.722 mmoles) to give the product as a beige powder. Yield 0.029 g (49 %). Found (Calc. for $C_{38}H_{30}N_2Se_2P_2Pt$): C 49.41 (49.10), H 2.85 (3.25), N 2.76 (3.01)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) 17.3 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3190 Hz. ^1H NMR (CD_2Cl_2): δ 7.52-7.24 (m, 30 H, aromatic). ES$^+$ MS: *m/z* 969 [M+K]$^+$, 953 [M+Na]$^+$, 931 [MH]$^+$. IR (KBr):

3055vw, 2177vs, 1634w, 1572w, 1497s, 1468m, 1435m, 1314w, 1186w, 1160w, 1095m, 1028w, 998w, 869w, 742w, 693m, 544m, 525m, 514m, 497m, 422w, 282w, 246w, 206w cm^{-1}.

[Pt($C_2N_2Se_2$)(dppe)] 3.4. This was prepared in the same way as platinum complex **3.2** using [$PtCl_2$(dppe)] (0.060 g, 0.0903 mmoles) and potassium cyanodiselenoimidocarbonate (0.227 g, 0.788 mmoles) to give the product as an orange powder. The product was recrystallised by vapour diffusion from chloroform/hexane to obtain X-ray quality crystals. Yield 0.049 g (67 %). Found (Calc. for $C_{28}H_{24}N_2Se_2P_2Pt$): C 41.88 (41.86), H 2.79 (3.01), N 3.29 (3.49)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) 44.8 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3049 Hz. ^1H NMR (CD_2Cl_2): δ 7.69-7.48 (m, 20 H, aromatic), 2.59-2.40 (m, 4H, PCH_2CH_2P). EI^+ MS: *m/z* 804 $[M]^+$. IR (KBr): 3051vw, 2178vs, 1586vw, 1572vw, 1492vs, 1461s, 1435s, 1412m, 1308w, 1186w, 1160w, 1105m, 1027w, 998w, 864w, 815w, 747w, 716m, 705m, 690m, 655w, 552w, 531m, 485w, 446w, 400w, 280w, 246m cm^{-1}.

[Pt($C_2N_2Se_2$)(dppm)] 3.5. This was prepared in the same way as platinum complex **3.2** using [$PtCl_2$(dppm)] (0.060 g, 0.0923 mmoles) and potassium cyanodiselenoimidocarbonate (0.211 g, 0.732 mmoles) to give the product as a yellow powder. Yield 0.022 g (30 %). Found (Calc. for $C_{27}H_{22}N_2Se_2P_2Pt.CH_2Cl_2$): C 38.89 (38.46), H 2.68 (2.77), N 3.13 (3.20)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) – 54.2 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 2620 Hz. ^1H NMR (CD_2Cl_2): δ 7.71-7.25 (m, 20 H, aromatic), 4.18-3.89 (m, 2H, PCH_2P). ES^+ MS: *m/z* 791 $[MH]^+$. IR (KBr): 3052w, 2175s, 1586vw, 1492vs, 1458s, 1436s, 1186,

1101m, 998w, 862w, 778w, 736m, 689m, 550w, 535w, 507w, 480w, 282w, 258w, 207w cm^{-1}.

[Pt($C_2N_2Se_2$)(dppf)] 3.6. This was prepared in the same way as platinum complex **3.2** using [$PtCl_2$(dppf)] (0.080 g, 0.0975 mmoles) and potassium cyanodiselenoimidocarbonate (0.085 g, 0.295 mmoles) to give the product as a yellow powder. Yield 0.044 g (45 %). Found (Calc. for $C_{36}H_{24}N_2Se_2P_2FePt.CH_2Cl_2$): C 42.83 (42.55), H 2.64 (2.69), N 2.37 (2.68)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) 16.4 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3263 Hz. ^1H NMR (CD_2Cl_2): δ 7.88-7.36 (m, 20 H, aromatic), 4.44 (br, m, 4H, α-CH (C_5H_4)), 4.36 (br, m, 4H, β-CH (C_5H_4)). EI^+ MS: *m/z* 960 $[M]^+$. IR (KBr): 3052vw, 2174s, 1630w, 1561w, 1495s, 1468m, 1435m, 1385w, 1306w, 1167w, 1098m, 1026w, 998w, 872w, 827w, 745w, 693m, 634w, 557m, 516m, 494m, 470m, 439w, 405w, 349w, 279w, 252w, 225w cm^{-1}.

[{Rh($C_2N_2Se_2$)(η^5-C_5Me_5)}$_2$] 3.7. This was prepared in the same way as platinum complex **3.2** using [{RhCl(μ-Cl)(η^5-C_5Me_5)}$_2$] (0.060 g, 0.0971 mmoles) and potassium cyanodiselenoimidocarbonate (0.359 g, 1.246 mmoles) to give a very dark red powder. Yield 0.037 g (42 %). Found (Calc. for $C_{24}H_{30}N_4Se_4Rh_2$): C 32.44 (32.17), H 3.77 (3.37), N 5.76 (6.25)%. ^1H NMR (CD_2Cl_2): δ 1.89-1.54 (m, 30H, η^5-C_5Me_5). FAB^+ MS: *m/z* 898 $[M]^+$. IR (KBr): 2913w, 2162s, 1638w, 1561w, 1492br,s, 1449m, 1379m, 1334w, 1156w, 1106w, 1022m, 870w, 680w, 618w, 535w, 394w, 279w, 259w cm^{-1}.

[{Ir($C_2N_2Se_2$)(η^5-C_5Me_5)}$_2$] 3.8. This was prepared in the same way as platinum complex **3.2** using [{IrCl(μ-Cl)(η^5-C_5Me_5)}$_2$] (0.040 g, 0.0502 mmoles) and potassium cyanodiselenoimidocarbonate (0.268 g, 0.9308 mmoles) to give the product as an orange powder. Yield 0.021 g (39 %). Found (Calc. for $C_{24}H_{30}N_4Se_4Ir_2$): C 27.21 (26.82), H 2.39 (2.81), N 5.65 (5.21)%. ^{1}H NMR (CD_2Cl_2): δ 1.86-1.57 (m, 30H, η^5-C_5Me_5). ES$^+$ MS: *m/z* 1077 [M]$^+$. IR (KBr): 2919w, 2191s, 1702w, 1655w, 1638w, 1546w, 1459br,s, 1419m, 1382m, 1311w, 1145w, 1117w, 1083w, 1029m, 856w, 804w, 723w, 703w, 539w, 467w, 282w, 256w cm^{-1}.

X-Ray Crystallography

Table 3.5 lists details of data collections and refinements. For, **3.2** and **3.4**, data were collected at 125 K using a Bruker SMART system. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[109]

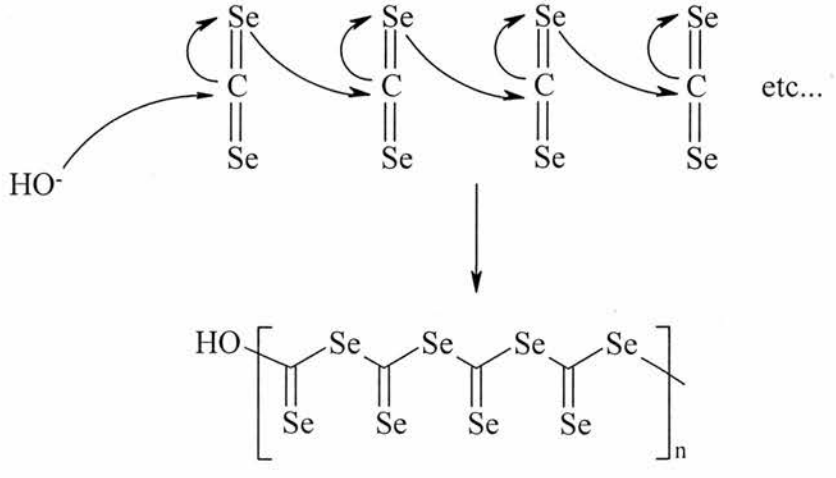
Compound	**3.2**	**3.4**
Empirical formula	$C_{18}H_{22}N_2P_2PtSe_2$	$C_{28}H_{24}N_2P_2PtSe_2$
Crystal dimensions/mm	0.1 x 0.03 x 0.03	0.13 x 0.05 x 0.05
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/n$
a/Å	33.596(8)	12.1941(18)
b/Å	11.542(3)	18.081(3)
c/Å	10.974(3)	12.6978(19)
α/°	90	90
β/°	91.536(5)	105.898(3)
γ/°	90	90
U/Å^3	4253.5(19)	2692.6(7)
Z	8	4
M	681.33	803.44
Dc/g cm^{-3}	2.128	1.982
μ/mm^{-1}	10.175	8.054
Measured reflections	13027	11392
Independent reflections (R_{int})	3804(0.0937)	3816(0.0613)
Final R1, wR2[I>2σ(I)]	0.0426, 0.0687	0.0314, 0.0533

Table 3.5 Details of the X-ray data collections and refinements for compounds **3.2** and **3.4**.

Chapter 4: Synthesis of triselenocarbonate, $[CSe_3]^{2-}$, transition metal complexes

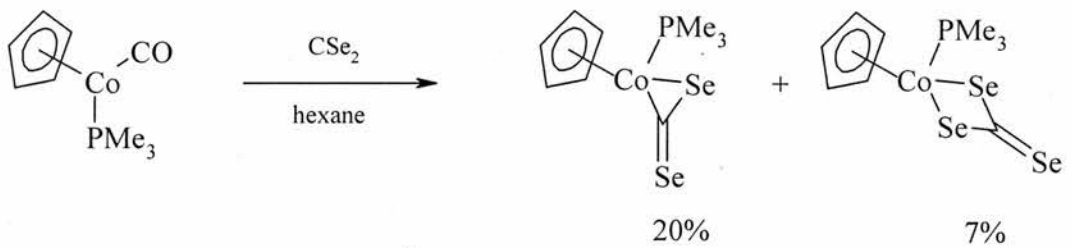
4.1 *Introduction*

The carbonate ion $[CO_3]^{2-}$, is one of the most common and important oxo-anions of carbon. Numerous metal complexes are known with many different binding modes. Carbonate complexes can be prepared from $[CO_3]^{2-}$, oxidation of carbonyl compounds and by other synthetic routes. Trithiocarbonate $[CS_3]^{2-}$ complexes are also well known but far less common than carbonate complexes. Only two different binding modes have been demonstrated so far. It is well established that reaction of carbon disulfide with alkali metal hydroxides in polar solvents leads to the trithiocarbonate dianion,[98] whereas reaction of carbon diselenide under the same conditions yields polymeric material rather than the desired triselenocarbonate dianion $[CSe_3]^{2-}$. Barnard and Woodbridge have proposed a base catalysed ionic addition polymerisation of carbon diselenide (Scheme 4.1).[113]



Scheme 4.1 Base catalysed polymerisation of carbon diselenide.

The absence of a synthetic method for the generation of the triselenocarbonate dianion has meant that at present there are only three literature examples of a complex or metal salt containing this ligand. The organometallic complex [(η-$^5C_5H_5$)Co(CSe_3)(PMe_3)] was formed as a reaction by-product and isolated in only 7% yield (Scheme 4.2).[27]

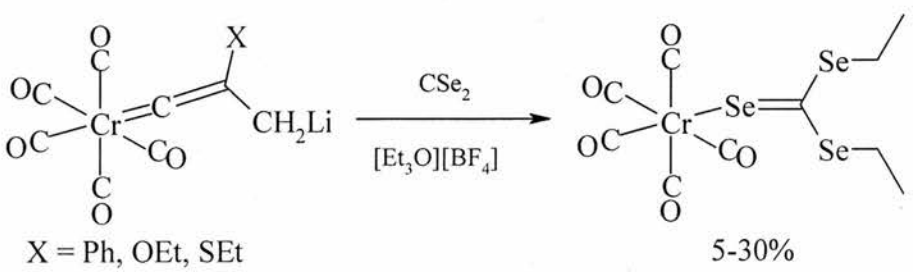


Scheme 4.2 Preparation of [(η-$^5C_5H_5$)Co(CSe_3)(PMe_3)].

Barium triselenocarbonate $Ba(CSe_3)$ was prepared by the action of carbon diselenide on BaSe in 55-60% yield (Scheme 4.3).[28]

Scheme 4.3 Preparation of $Ba(CSe_3)$.

Additionally a single example of a triselenocarbonate complex in which only the selenocarbonyl (Se=C) selenium atom is bound to the metal [$(OC)_5Cr\{Se=C(SeEt)_2\}$] has been reported (Scheme 4.4).[29]

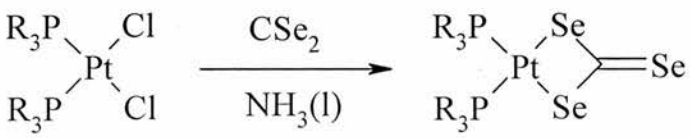


Scheme 4.4 Preparation of [$(OC)_5Cr\{Se=C(SeEt)_2\}$].

Aucott *et al* have reported the preparation of bis-phosphine platinum trithiocarbonate complexes from $[PtCl_2(PR_3)_2]$ and carbon disulfide in liquid ammonia.[18] This prompted us to investigate whether reaction of carbon diselenide in liquid ammonia was a viable route to triselenocarbonate complexes. In this chapter we describe a convenient one pot synthesis for triselenocarbonate complexes. We have prepared examples of mononuclear, binuclear and tetranuclear complexes of this ligand including the first crystallographically characterised example of a triselenocarbonate complex.

4.2 *Results and Discussion*

4.2.1 *Synthesis of platinum(bis-phosphino) triselenocarbonate complexes.*



4.1 $PR_3 = PMe_3$
4.2 $PR_3 = PMe_2Ph$
4.3 $PR_3 = PPh_3$
4.4 $PR_3 = P(p\text{-tol})_3$
4.5 $PR_3 = ½$ dppm
4.6 $PR_3 = ½$ dppf

Scheme 4.5 Synthesis of platinum(bis-phosphino) triselenocarbonate complexes.

The heteroleptic complexes $[Pt(CSe_3)(PR_3)_2]$ ($PR_3 = PMe_3$, PMe_2Ph, PPh_3, $P(p\text{-tol})_3$, ½ dppp, ½ dppf) were all obtained by the reaction of a dichloromethane

solution of carbon diselenide with excess liquid ammonia at –78 °C followed by the addition of the appropriate $[PtCl_2(PR_3)_2]$ species (Scheme 4.5).

All of our attempts to isolate the $[NH_4]_2[CSe_3]$ salt proved unsuccessful possibly because the salt is only stable at –78 °C and prefers to polymerise at higher temperatures. Therefore the $[NH_4]_2[CSe_3]$ salt was always used *in situ* with the appropriate $[PtCl_2(PR_3)_2]$ species to give the desired products. After ammonia was removed the products were readily extracted into dichloromethane. Any residual polymeric material and ammonium chloride were removed by filtration. The resultant solution was reduced in volume followed by slow dropwise addition of diethyl ether to precipitate the product as either a fine powder or crystalline solid in acceptable yields. The platinum(bis-phosphino) triselenocarbonate complexes were found to be reasonably soluble in chloroform, dichloromethane and tetrahydrofuran but insoluble in diethyl ether and hexane. **4.1-4.6** were found to be air stable both in the solid state and in solution. Small red selenium deposits were noted only after exposure to the atmosphere for several months. For all the complexes **4.1-4.6** the microanalyses were within the specified limits and the anticipated M^+ ions were observed in their mass spectra (Table 4.1) with the expected isotopomer distributions. In the IR spectra the ν(C=Se) vibrations are observed at *ca.* 900 cm^{-1} and the ν(Pt-Se) bands are noted in the region 242-285 cm^{-1} (Table 4.2). The $^{31}P\{^1H\}$ NMR spectra of the platinum(bisphosphino) triselenocarbonates **4.1-4.6** all showed sharp singlets with platinum satellites (Table 4.2).

Complex	C	H	*m/z*
4.1 $[Pt(CSe_3)(PMe_3)_2]$	14.14(14.10)	3.08(3.04)	599
4.2 $[Pt(CSe_3)(PMe_2Ph)_2]$	27.96(28.35)	2.87(3.08)	720
4.3 $[Pt(CSe_3)(PPh_3)_2]$	45.56(45.88)	2.65(3.12)	970
4.4 $[Pt(CSe_3)(P(p\text{-}tol)_3)_2]$	48.71(49.06)	3.89(4.02)	1052
4.5 $[Pt(CSe_3)(dppp)]$	39.44(39.27)	2.74(3.06)	856
4.6 $[Pt(CSe_3)(dppf)]$	42.35(42.11)	2.63(2.83)	998

Table 4.1 Microanalytical data (calculated values in parentheses) and mass spectral data for complexes **4.1-4.6**.

Complex	δ(P) ppm	^1J(Pt-P) Hz	ν(C=Se) cm^{-1}	ν(Pt-Se) cm^{-1}
4.1 $[Pt(CSe_3)(PMe_3)_2]$	-29.2	2970	907	285, 255
4.2 $[Pt(CSe_3)(PMe_2Ph)_2]$	-18.6	3017	902	282, 242
4.3 $[Pt(CSe_3)(PPh_3)_2]$	19.1	3146	908	280, 247
4.4 $[Pt(CSe_3)(P(p\text{-}tol)_3)_2]$	17.1	3162	923	256, 242
4.5 $[Pt(CSe_3)(dppp)]$	-2.7	2871	900	282, 247
4.6 $[Pt(CSe_3)(dppf)]$	17.5	3218	915	283, 250

Table 4.2 $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 109.4 MHz) and selected IR data for complexes **4.1-4.6**.

The δ values are shifted by approximately 1 ppm to higher frequency than those of the analogous trithiocarbonate complexes[18] and approximately 9 ppm higher frequency than those of the analogous carbonate complexes.[114] The $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling constants lie in the range 2871-3218 Hz and are of similar magnitude to the corresponding trithiocarbonate species[18] and are generally *ca.* 500 Hz smaller in magnitude than the equivalent carbonate complex.[114] The $^{31}P\{^{1}H\}$ NMR spectra of **4.1-4.6** also exhibit ^{77}Se satellites which can be clearly seen in the spectrum of **4.2** (Figure 4.1).

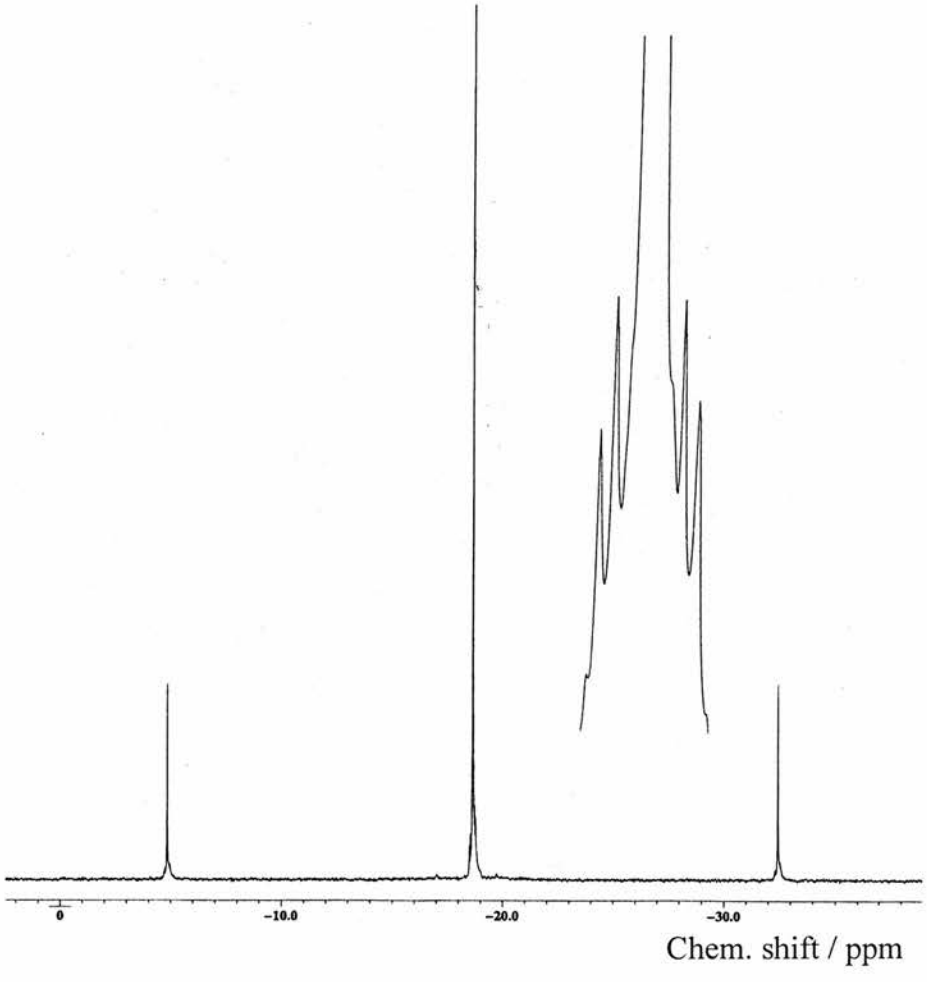


Figure 4.1 $^{31}P\{^{1}H\}$ NMR spectrum of **4.2** with inset enlargement of central peak.

The most comparable compound is $[Pt(Se_2CH_2)(PPh_3)_2]$.[115] The spectra of $[Pt(Se_2CH_2)(PPh_3)_2]$ was analysed in detail as an AA'X system and **4.1-4.6** have the same spin system. We do not have sufficient detail to determine all of the *J* values in **4.1-4.6**, however if we assume a $^3J(^{31}P\text{-}^{31}P)$ of *ca* 20 Hz (c.f. 21.8 Hz in $[Pt(Se_2CH_2)(PPh_3)_2]$[115]) then the *trans* and *cis* $^2J(^{77}Se\text{-}^{31}P)$ from simulations are approximately 35 and 8 Hz respectively (c.f. 31 and 11 Hz in $[Pt(Se_2CH_2)(PPh_3)_2]$[115]).

Crystals of **4.2** suitable for X-ray diffraction were obtained by vapour diffusion from chloroform/hexane. **4.2** is the first crystallographically characterised example of this class of compound. The X-ray analysis of **4.2** (Figure 4.2, Table 4.3) shows that the platinum core lies at the centre of a distorted square planar coordination sphere consisting of two phosphorus and two selenium atoms. The P(1)-Pt(1)-P(2) angle is 95.49(11) ° showing considerable deviation from idealized 90° square planar geometry and is directly comparable to the platinum (bis-phosphino) trithiocarbonate complexes which fall in the range 93.2(1)-98.99(6) °.[18] The corresponding Se(1)-Pt(1)-Se(2) angle is 76.23(4) ° which is slightly enlarged compared to the S(1)-Pt-S(2) angle in $[Pt(CS_3)(PR_3)_2]$ complexes which are typically 73-74 °.[18] The carbonate analogues are significantly more strained with an O(1)-Pt(1)-O(2) angle of approximately 65 °.[114] The differences are a natural consequence of the enlargement of the C-O, C-S to C-Se distances. The Pt-P distances are comparable to those in $[Pt(CS_3)(PMe_2Ph)_2]$ and as expected the Pt-Se distances are longer than the corresponding Pt-S distances. The C-Se bond lengths in the $[CSe_3]^{2-}$ ligand are longer for the coordinated selenium atoms compared to the exocyclic selenium

atom. Within the $PtSe_2C$ ring the Pt-Se-C angles are 87.2(4)-87.9(4) and the Se-C-Se angle is 108.4(6)°. The bond lengths and angles in **4.2** are comparable to those for $[Pt(Se_2CH_2)(PPh_3)_2]$[115] however the Se(1)-C(1)-Se(2) angle is much larger in **4.2** (108.4(6)° compared to 101.1(3)° in $[Pt(Se_2CH_2)(PPh_3)_2]$). The difference in Se(1)-C(1)-Se(2) angle is due to sp^2 nature of **4.2** compared to the sp^3 nature of $[Pt(Se_2CH_2)(PPh_3)_2]$. The Se(1)-Se(2) non bonded distance is 3.04 Å , which is 80 % of the van der Waals radii of selenium and implies that there is a significant interaction between the two selenium atoms. In the P(1)-P(2)-Pt(1)-Se(1)-Se(2) mean plane the maximum deviation from planarity is for Se(2) which lies 0.05 Å above the coordination plane. C(1) and Se(3) lie 0.13 Å and 0.4 Å above the plane respectively. The hinge angle between the P(1), P(2), Pt(1), Se(1), Se(2) mean plane and the Se(1), Se(2), C(1), Se(3) mean plane is 7.9°.

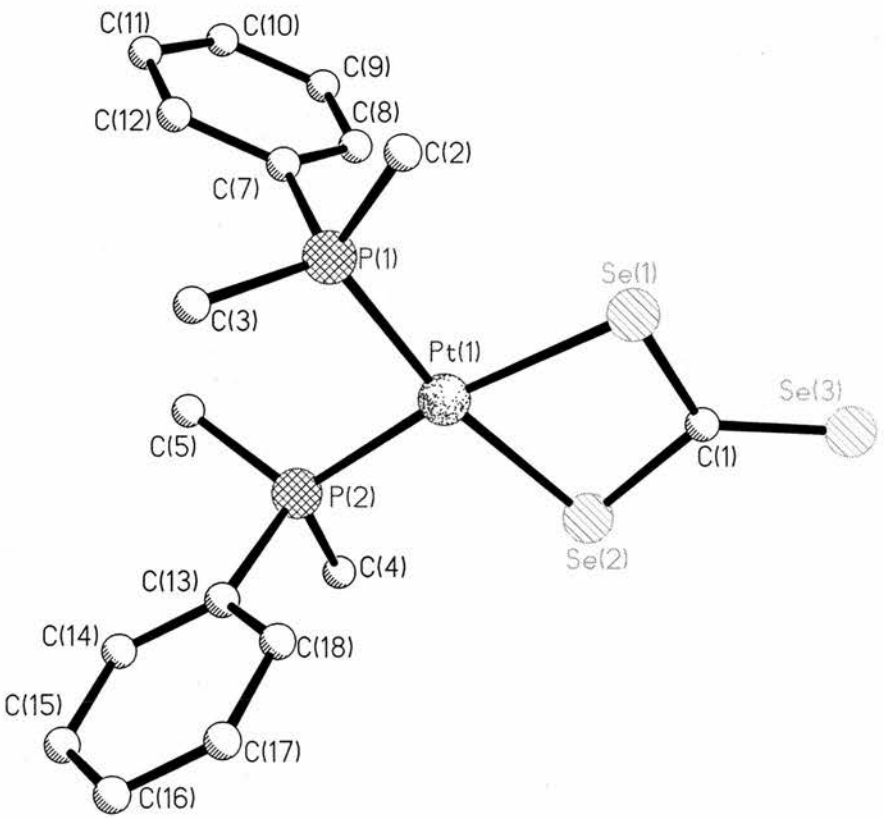


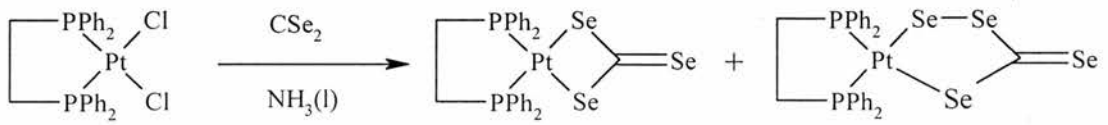
Figure 4.2 X-ray crystal structure of **4.2**.

Compound	**2**
Pt(1)-P(1)	2.264(3)
Pt(1)-P(2)	2.274(3)
Pt(1)-Se(1)	2.4561(12)
Pt(1)-Se(2)	2.4630(13)
Se(1)-C(1)	1.860(13)
Se(2)-C(1)	1.884(13)
C(1)-Se(3)	1.794(13)
Se(1)-Pt(1)-Se(2)	76.23(4)
P(1)-Pt(1)-P(2)	95.49(11)
Se(1)-C(1)-Se(3)	126.5(7)
Se(2)-C(1)-Se(3)	125.0(7)
Pt(1)-Se(1)-C(1)	87.9(4)
Pt(1)-Se(2)-C(1)	87.2(4)
P(2)-Pt(1)-Se(1)	170.15(9)
P(1)-Pt(1)-Se(2)	169.39(8)

Table 4.3 Selected bond lengths and angles for compound **4.2**.

In contrast to the above platinum(bisphosphino) triselenocarbonate complexes **4.1-4.6** the reaction of [$PtCl_2$(dppe)] with carbon diselenide in liquid ammonia results in the formation of a mixture of the expected triselenocarbonate product [Pt(CSe_3)(dppe)] and the perselenocarbonate complex [Pt(CSe_4)(dppe)] (Scheme 4.6). This reaction was repeated several times and in each experiment the same

results were observed. The presence of both species is clearly evident in the $^{31}P\{^{1}H\}$ NMR spectrum.



Scheme 4.6 Synthesis of [Pt(CSe_3)(dppe)]/[Pt(CSe_4)(dppe)] mixture.

A single sharp resonance corresponding to the triselenocarbonate complex is observed at 45.2 ppm with the expected platinum satellites [$^{1}J(^{195}Pt\text{-}^{31}P)$ 3005 Hz]. Selenium satellites are also noted but we do not have sufficient detail to determine the $^{2}J(^{77}Se\text{-}^{31}P)$ values. The perselenocarbonate complex exhibits an AX type system $\delta(P_A)$ 44.4(d) ppm, $^{1}J(^{195}Pt\text{-}^{31}P)$ 2927 Hz and $\delta(P_X)$ 45.5(d) ppm, $^{1}J(^{195}Pt\text{-}^{31}P)$ 2595 Hz with a $^{2}J(^{31}P_A\text{-}^{31}P_X)$ of 9 Hz. In the IR spectrum two different ν(C=Se) vibrations are observed at 898 and 907 cm^{-1} corresponding to the two different species. The ν(Pt-Se) bands are noted in the region 250 to 290 cm^{-1}. Attempts to separate these two species by chromatography proved unsuccessful. Recrystallisation by vapour diffusion from chloroform/hexane did not separate the mixture either however crystals suitable for X-ray diffraction were obtained. A crystallographic study confirmed the existence of both species as they co-crystallise (Figure 4.3). Despite repeated attempts at crystallisation/measurement, the data is of too poor quality to allow discussion of bond lengths or angles however the data is adequate for the confirmation of connectivity.

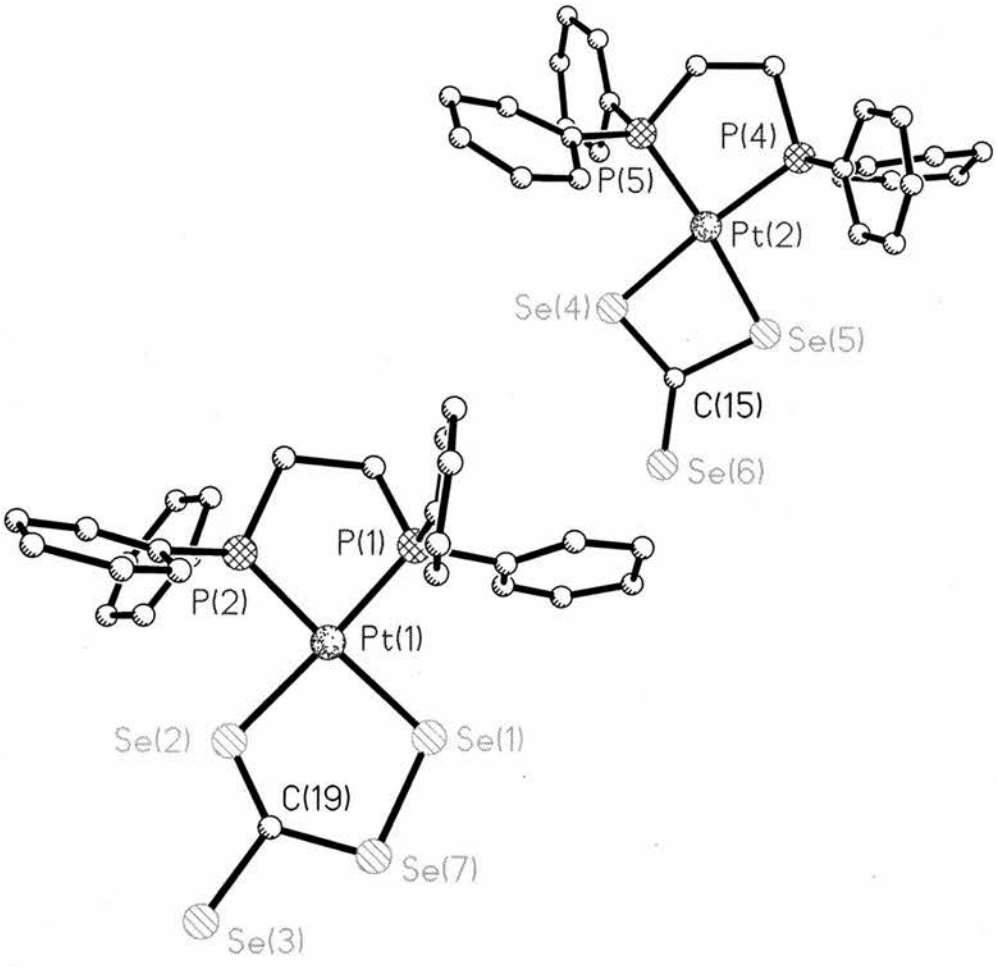
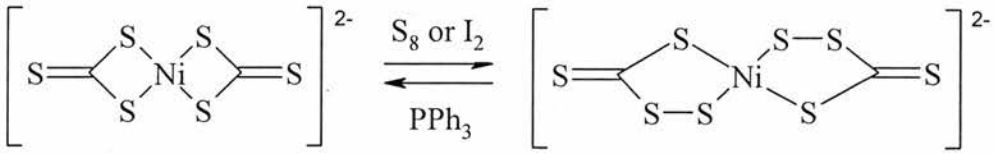


Figure 4.3 X-ray crystal structure of **4.7**.

There are currently only two examples of perselenocarbonate complexes present in the literature. A zinc salt $[PPh_4]_2[Zn(CSe_4)_2]$[116] isolated from a solution of carbon diselenide with sodium metal in the presence of zinc (II) chloride and $[PPh_4]Br$ and a manganese carbonylate species $[(PPh_3)_2N]_2[\{Mn(CSe_4)(CO)_3\}_2]$[117] prepared by the reaction of elemental selenium with $[Mn_2(CO)_{10}]$ and KOH. The perthiocarbonate and percarbonate analogues are far more common in the literature.[118-122] Coucouvanis and Fackler Jr. have reported that a bis(trithiocarbonato) nickel(II) salt is readily oxidised to the bis(perthiocarbonato) nickel(II) salt by reaction with iodine or addition of

elemental sulfur.[120] The perthiocarbonate species was easily converted back to the trithiocarbonate by addition of triphenylphosphine (Scheme 4.7).

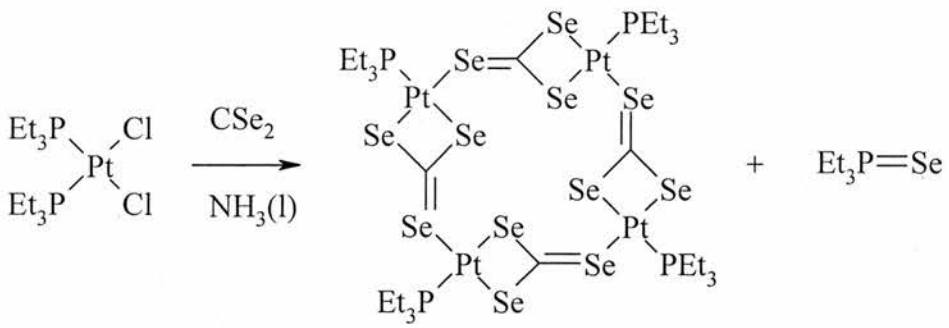


Scheme 4.7 Interconversion of $[PPh_4]_2[CS_3]$ and $[PPh_4]_2[CS_4]$.

Hence we have attempted similar reactions using $[Pt(CSe_3)(dppe)]/[Pt(CSe_4)(dppe)]$ **4.7** to convert the mixture entirely to the perselenocarbonate product. Reaction with excess elemental selenium both at room temperature in dichloromethane and overnight reflux in toluene proved unsuccessful. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture in both cases was identical to that of **4.7**. Attempted reactions with iodine were equally unsuccessful. No reaction occurred when triphenylphosphine or triethylphosphite were added to **4.7** in an attempt to convert the mixture entirely to the triselenocarbonate species. Conversion of $[Pt(CSe_3)(PMe_2Ph)_2]$ **4.2** to the perselenocarbonate complex was also attempted in the same fashion as above but again was unsuccessful. In the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture **4.2** was observed and a small peak corresponding to dimethylphenylphosphine selenide (δ(P) 17.3 ppm, $^1J(^{77}Se\text{-}^{31}P)$ 710 Hz) but no perselenocarbonate species was noted. We have also attempted to prepare the perselenocarbonate dianion by reaction of carbon diselenide with either Na_2Se_2[123] or *n*-$Bu_4N_2Se_2$ prepared from *n*-Bu_4NBH_4 and a stoichiometric quantity of elemental Se. No attempt was made to isolate any perselenocarbonate species made but they were used *in situ* with

$[PtCl_2(PMe_2Ph)_2]$ in an attempt to prepare $[PtCSe_4(PMe_2Ph)_2]$. However in both cases the desired product was not formed. $^{31}P\{^1H\}$ NMR showed the reaction mixture to contain $[PtCl_2(PMe_2Ph)_2]$, $[PtCSe_3(PMe_2Ph)_2]$ and dimethylphenyl phosphine selenide.

We discovered that reaction of $[PtCl_2(PEt_3)_2]$ with carbon diselenide in liquid ammonia generates the novel tetramer $[\{Pt(\mu\text{-}CSe_3)(PEt_3)\}_4]$ (Scheme 4.8).



Scheme 4.8 Synthesis of $[\{Pt(\mu\text{-}CSe_3)(PEt_3)\}_4]$.

In the $^{31}P\text{-}\{^1H\}$ NMR (CD_2Cl_2) of the crude reaction mixture four different phosphorous containing species are observed. These include triethylphosphine selenide (δ(P) 45.2 ppm, $^1J(^{77}Se\text{-}^{31}P)$ 690 Hz), possibly $[Pt(CSe_3)(PEt_3)_2]$ (δ(P) 4.7 ppm, $^1J(^{195}Pt\text{-}^{31}P)$ 3017 Hz) assigned based on comparison with the trithiocarbonate analogue[18] and two unknown platinum species δ(P) 14.2 ppm, $^1J(^{195}Pt\text{-}^{31}P)$ 2160 Hz and δ(P) 5.3 ppm, $^1J(^{195}Pt\text{-}^{31}P)$ 3249 Hz. From this crude reaction mixture **4.8** was obtained in a 15 % yield as insoluble dark red crystals by slow evaporation of the solvent. The crystals of **4.8** were found to be insoluble hence no NMR data has been obtained. In the IR spectrum the

ν(C=Se) stretch can be seen at 875 cm^{-1} and ν(Pt-Se) bands are found at 283 and 257 cm^{-1}. The microanalysis gave satisfactory results.

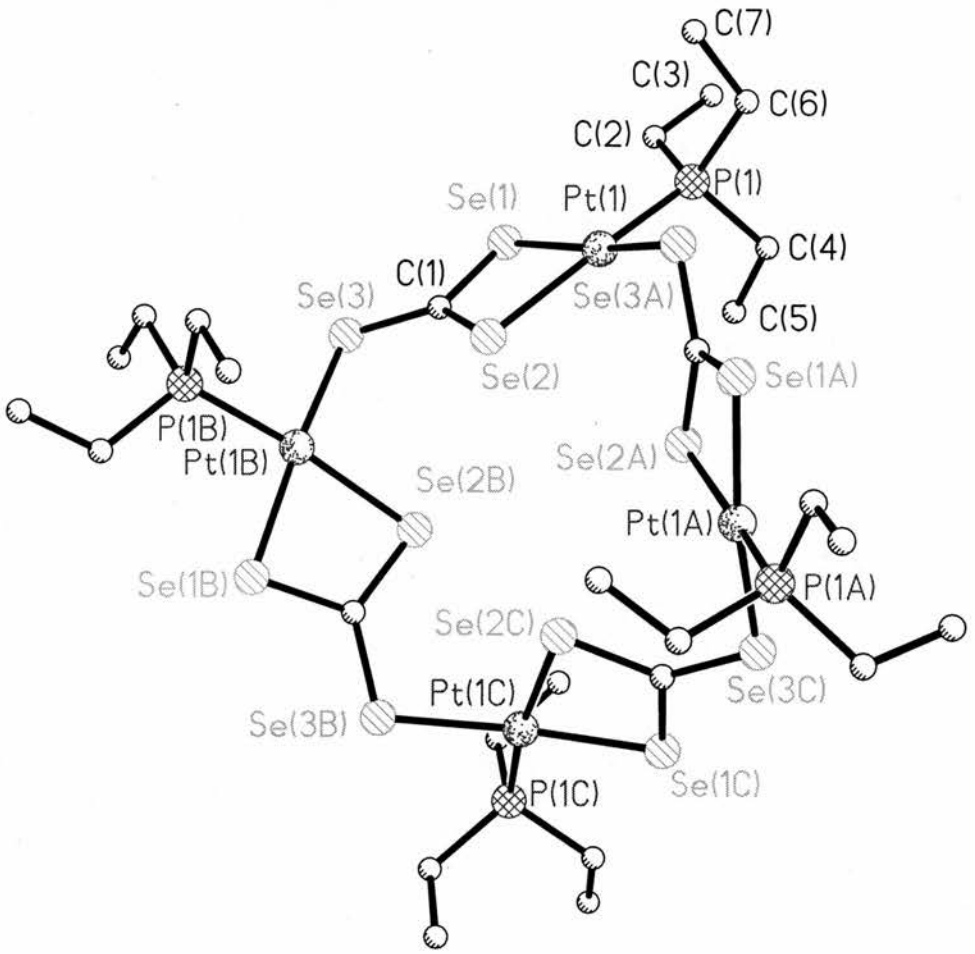


Figure 4.4 X-ray crystal structure of **4.8**.

A single crystal X-ray diffraction study clearly shows the tetrameric structure of **4.8** (Figure 4.4, Table 4.4). The platinum atom lies at the centre of a distorted square planar coordination sphere. The P(1)-Pt(1)-Se(3A) angle is 92.01(6) ° showing considerable deviation from idealized 90 ° square planar geometry. The Se(1)-Pt(1)-Se(2) angle is 76.29(3) ° which is comparable to compound **4.2**.

Compound	**4.8**
Pt(1)-P(1)	2.254(2)
Pt(1)-Se(1)	2.4325(9)
Pt(1)-Se(2)	2.4961(9)
Pt(1)-Se(3)#1	2.4242(9)
Se(1)-C(1)	1.879(8)
Se(2)-C(1)	1.839(9)
C(1)-Se(3)	1.823(8)
Se(1)-Pt(1)-Se(2)	76.29(3)
P(1)-Pt(1)-Se(3)#1	92.01(6)
Se(1)-C(1)-Se(3)	120.7(5)
Se(2)-C(1)-Se(3)	129.4(5)
Pt(1)-Se(1)-C(1)	87.4(3)
Pt(1)-Se(2)-C(1)	86.3(2)
P(1)-Pt(1)-Se(2)	169.54(6)
Se(1)-Pt(1)-Se(3)#1	167.71(4)

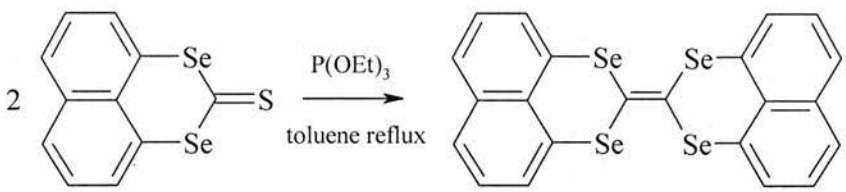
Table 4.4 Selected bond lengths and angles for compounds **4.8**.

The Pt-P distance is 2.254(2) Å which is slightly shorter than in $[Pt(CSe_3)(PMe_2Ph)_2]$ **4.2**. The Se(1)-C(1) and Se(2)-C(1) (1.879(8) and 1.839(9) Å respectively) in the $[CSe_3]^{2-}$ ligand are approximately the same length as is complex **4.2**. The selenocarbonyl Se=C bond Se(3)-C(1) in **4.8** is 1.823(8) Å compared to 1.794(13) Å in **4.2**. The longer Se(3)-C(1) bond in **4.8** is due to Se(3) being three coordinate. The 16 membered macrocycle is disposed about a

crystallographic $\bar{4}$ axis in the centre of the molecule. The four platinum atoms adopt a distorted square planar (or flattened tetrahedral) geometry [Pt(1) – centre – Pt(1C) 154 °, Pt(1) – centre – Pt(1B) 93 °] resulting in a puckered geometry with the Se(2) atoms alternately up/down around the ring.

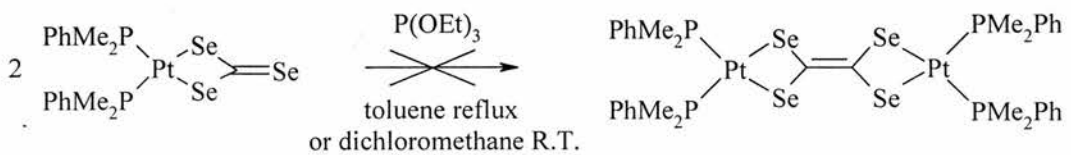
4.2.2 *Further reactions of [Pt(CSe$_3$)(PMe$_2$Ph)$_2$].*

It has been reported in the literature that 2,2'-Binaphtho[1,8-*de*]-1,3-diseleninylidene can be prepared by the reaction of naphtha[1,8-*de*]-1,3-diselenin-2-thione with triethyl phosphite[124] as shown in Scheme 4.9 below.



Scheme 4.9 Synthesis of 2,2'-Binaphtho[1,8-*de*]-1,3-diseleninylidene.

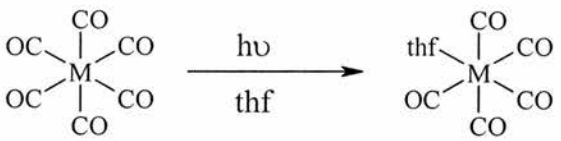
We attempted a similar reaction using [Pt(CSe$_3$)(PMe$_2$Ph)$_2$] **4.2** and triethyl phosphite both in dichloromethane at room temperature and under reflux in toluene (Scheme 4.10).



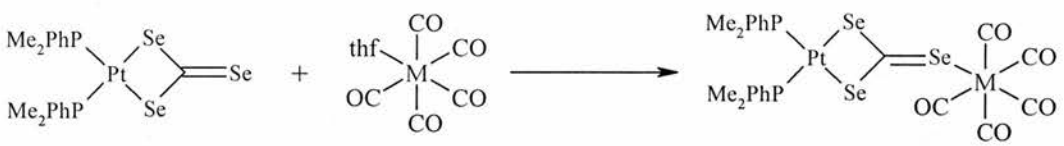
Scheme 4.10 Attempted reaction of [Pt(CSe$_3$)(PMe$_2$Ph)$_2$] with triethyl phosphite.

Unfortunately we did not observe any reaction. In the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture only starting materials were noted.

Further reaction of $[Pt(CSe_3)(PMe_2Ph)_2]$ **4.2** with $[M(CO)_5(thf)]$ (M = Cr, W, Mo) in tetrahydrofuran (Scheme 4.11) yielded bimetallic species of the type $[Pt(PMe_2Ph)_2(CSe_3)M(CO)_5]$ (M = Cr, W, Mo **4.9-4.11**).



4.9 M = Cr
4.10 M = Mo
4.11 M = W



Scheme 4.11 Synthesis of bimetallic triselenocarbonate complexes from $[Pt(CSe_3)(PMe_2Ph)_2]$

Complex	C	H	*m/z*
4.9 $[Pt(PMe_2Ph)_2(CSe_3)Cr(CO)_5]$	28.77(28.96)	2.23(2.43)	912
4.10 $[Pt(PMe_2Ph)_2(CSe_3)Mo(CO)_5]$	27.84(27.63)	2.01(2.32)	956
4.11 $[Pt(PMe_2Ph)_2(CSe_3)W(CO)_5]$	24.98(25.31)	2.12(1.78)	1044

Table 4.5 Microanalytical data (calculated values in parentheses) and mass spectral data for complexes **4.9-4.11**.

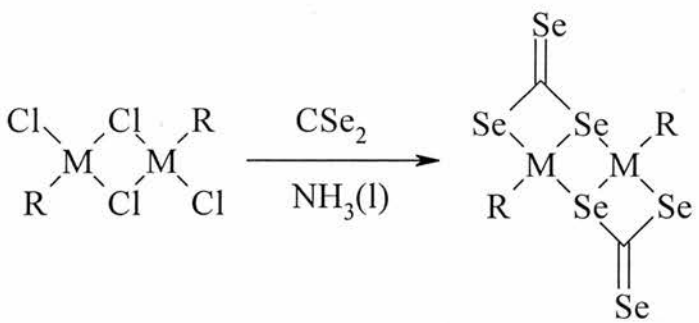
For **4.9-4.11** the microanalyses results were within acceptable limits and all showed the anticipated molecular ion in their mass spectra (Table 4.5). The observation of three carbonyl stretching bands in the infrared spectrum of each of **4.9-4.11** in the region 1885 to 1984 cm^{-1} further confirmed that the desired products had been formed. Only very subtle shifts in the frequency of ν(C=Se) and ν(Pt-Se) bands were observed in the IR spectra (Table 4.6). In the $^{31}P\{^{1}H\}$ NMR spectrum as expected only a very slight change in chemical shift is noted and the $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling constant has increased from 3017 Hz in **4.2** to ca. 3040 Hz in **4.9-4.11** (Table 4.6).

Complex	δ(P) ppm	^{1}J(Pt-P) Hz	ν(C=O) cm^{-1}	ν(C=Se) cm^{-1}	ν(Pt-Se) cm^{-1}
4.9 $[Pt(PMe_2Ph)_2(CSe_3)Cr(CO)_5]$	-19.3	3038	1972 1925 1916	891	282 247
4.10 $[Pt(PMe_2Ph)_2(CSe_3)Mo(CO)_5]$	-18.5	3041	1984 1931 1885	909	279 44
4.11 $[Pt(PMe_2Ph)_2(CSe_3)W(CO)_5]$	-18.3	3045	1975 1919 1889	909	281 244

Table 4.6 $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 109.4 MHz) and selected IR data for complexes **4.9-4.11**.

4.2.3 *Bimetallic triselenocarbonate complexes.*

The bimetallic triselenocarbonate complexes [{M{(CSe_3)(η^5-C_5Me_5)}$_2$] (M = Rh **12**, Ir **13**) and [{M(CSe_3)(η^6-*p*-$MeC_6H_4{}^iPr$)}$_2$] (M = Ru **14**, Os **15)** have been synthesised and isolated in a similar fashion to the platinum(bis-phosphine) triselenocarbonate complexes **4.1-4.6** by reacting carbon diselenide in liquid ammonia with the appropriate transition metal dimer starting material (Scheme 4.12).



4.12 M = Rh, R = η^5-C_5Me_5
4.13 M = Ir, R = η^5-C_5Me_5
4.14 M = Ru, R = η^6-*p*-$MeC_6H_4{}^iPr$
4.15 M = Os, R = η^6-*p*-$MeC_6H_4{}^iPr$

Scheme 4.12 Synthesis of bimetallic triselenocarbonate complexes.

4.12-4.15 all gave satisfactory microanalysis results and displayed the expected M^+ in their mass spectra (Table 4.7). The ν(C=Se) vibrations and the bands for ν(M-Se) were all observed in the anticipated regions. Proton NMR clearly identified the respective alkyl groups present. Unfortunately no crystallographic data was obtained for **4.12-4.14** so the exact connectivity of these species is not certain. A feasible structure previously noted in [{Rh($C_2N_2S_2$)(η^5-C_5Me_5)}$_2$]

2.11 (Figure 2.7, p 52) and other E,E bidentate ligands[116,117] is proposed above (Scheme 4.12).

Complex	C	H	*m/z*
4.12 [{Rh(CSe_3)(η^5-C_5Me_5)}$_2$	26.68(27.13)	2.84(3.10)	979
4.13 [{Ir(CSe_3)(η^5-C_5Me_5)}$_2$]	23.14(22.92)	2.17(2.62)	1154
4.14 [{Ru(CSe_3)(η^6-p-$MeC_6H_4{}^iPr$)}$_2$]	27.59(27.29)	3.07(2.91)	969
4.15 [{Os(CSe_3)(η^6-p-$MeC_6H_4{}^iPr$)}$_2$]	23.46(23.04)	2.44(2.46)	1148

Table 4.7 Microanalytical data (calculated values in parentheses) and mass spectral data for complexes **4.12-4.15**.

4.3 *Conclusions*

In this chapter we report a convenient one pot synthetic route to complexes of the elusive $[CSe_3]^{2-}$ anion. The complexes were all obtained by the reaction of a dichloromethane solution of carbon diselenide with excess liquid ammonia at –78 °C followed by the addition of the appropriate transition metal starting material. Reaction of different $[PtCl_2(PR_3)_2]$ species yielded a series of square planar platinum(bis-phosphino) triselenocarbonate complexes which we have compared to the carbonate and trithiocarbonate analogues. Interestingly reaction of $[PtCl_2(dppe)]$ with carbon diselenide in liquid ammonia yielded a mixture of the expected triselenocarbonate product $[Pt(CSe_3)(dppe)]$ and the perselenocarbonate complex $[Pt(CSe_4)(dppe)]$. We discovered that reaction of $[PtCl_2(PEt_3)_2]$ with carbon diselenide in liquid ammonia generates the novel tetramer $[\{Pt(\mu\text{-}CSe_3)(PEt_3)\}_4]$. Further reaction of $[Pt(CSe_3)(PMe_2Ph)_2]$ with $[M(CO)_5(thf)]$ (M = Cr, W, Mo) yielded bimetallic species of the type $[Pt(PMe_2Ph)_2(CSe_3)M(CO)_5]$ with the group 6 metal bonded to the exocyclic selenium of the triselenocarbonate ligand. Finally we have prepared a series of bimetallic cyanodithioimidocarbonate complexes with group 8 (Ru, Os) and 9 (Rh, Ir) metals in which the triselenocarbonate ligand is Se,Se' bidentate Se' bridging. All of the isolated compounds have been characterised spectroscopically (^{31}P, ^{1}H, ^{13}C NMR, IR, mass spectroscopy), by elemental analysis and three demonstrative X-ray structures are reported.

4.4 *Experimental*

General experimental conditions and instrumentation were as set out on page 55. Carbon diselenide was prepared as a dichloromethane solution by passing dichloromethane over elemental selenium at 600°C.[110,111] Ammonia (BOC) was used as received. The metal complexes $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$,[107] $[\{IrCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$,[107] $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$[108] and $[\{OsCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$,[108] prepared according to literature procedures. The complexes $[PtCl_2(PMe_3)_2]$, $[PtCl_2(PMe_2Ph)_2]$, $[PtCl_2(PEt_3)_2]$, $[PtCl_2(PPh_3)_2]$, $[PtCl_2(P(p\text{-}tol)_3)_2]$, [Pt([$PtCl_2$(dppe)] (dppe= bis(diphenylphosphino)ethane), [$PtCl_2$(dppp)] (dppp= bis(diphenylphosphino)propane)and [$PtCl_2$(dppf)] (dppf = bis(diphenylphosphino)ferrocene) were prepared by the addition of stoichiometric quantities of the appropriate free phosphine or diphosphine to a dichloromethane solution of [$PtCl_2$(cod)] (cod = cycloocta-1,5-diene). $[Cr(CO)_6]$, $[Mo(CO)_6]$ and $[W(CO)_6]$ (all Aldrich) were used as received.

$[Pt(CSe_3)(PMe_3)_2]$ 4.1. Liquid ammonia (approximately 20 cm^3) was distilled into a Schlenk tube that had previously been cooled to –78 °C. $[PtCl_2(PMe_3)_2]$ (0.100 g, 0.239 mmol) was added as a solid in one portion followed by carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol). The resulting mixture was stirred for 2 hours at –78 °C and then slowly warmed to room temperature with continual stirring until the excess ammonia had evaporated. The remaining solvent was removed under reduced pressure and the red residue was extracted three times with dichloromethane (3 x 20 cm^3). The mixture was filtered through a celite pad and the resulting red solution was reduced in volume

to approximately 10 cm^3, and diethyl ether (50cm^3) was added slowly to precipitate the product as a bright red crystalline solid. Yield 0.044 g (31 %). Found (Calc. for $C_7H_{18}P_2Se_3Pt$): C 14.14 (14.10), H 3.08 (3.04)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) –29.2(s) ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 2970 Hz. ^1H NMR (CD_2Cl_2): δ 1.61 (d, 18H, PMe_3, $^3J(^{195}Pt\text{-}^1H)$ 35 Hz, $^2J(^{31}P\text{-}^1H)$ 10 Hz). ES^+ MS: *m/z* 623 $[M+Na]^+$, 599 $[M]^+$. IR (KBr): 2966vw, 2904vw, 1655vw, 1638vw, 1561vw, 1509vw, 1459vw, 1414vw, 1414w, 1285w, 966m, 947m, 907s, 859w, 740w, 724w, 685w, 392w, 363w, 285w, 255w cm^{-1}.

[Pt(CSe$_3$)(PMe$_2$Ph)$_2$] 4.2. This was prepared in the same fashion as platinum complex **4.1** using [$PtCl_2(PMe_2Ph)_2$] (0.150g, 0.225 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol) to give the product as a brick red powder. Yield 0.092 g (48 %). Found (Calc. for $C_{17}H_{22}P_2Se_3Pt$): C 27.96 (28.35), H 2.87 (3.08)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) -18.6(s) ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3017 Hz. ^1H NMR (CD_2Cl_2): δ 7.52-7.35 (m, 10 H, aromatic) and 1.57 (d, 12 H, $^3J(^{195}Pt\text{-}^1H)$ 35 Hz, $^2J(^{31}P\text{-}^1H)$ 10 Hz, PMe). ES^+ MS: *m/z* 743 $[M+Na]^+$, 720 $[M]^+$. IR (KBr): 1655vw, 1560vw, 1435m, 1416w, 1283w, 1105m, 943m, 902s, 839w, 738m, 729m, 717w, 689m, 480w, 444w, 429w, 396w, 375w, 352w, 282w, 242w cm^{-1}.

[Pt(CSe$_3$)(PPh$_3$)$_2$] 4.3. This was prepared in the same fashion as platinum complex **4.1** using [$PtCl_2(PPh_3)_2$] (0.100g, 0.126 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol) to give the product as a brick red powder. Yield 0.038 g (31 %). Found (Calc. for $C_{37}H_{30}P_2Se_3Pt$): C 45.56 (45.88), H 2.65 (3.12)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) 19.1(s) ppm. $^1J(^{195}Pt\text{-}$

^{31}P) 3146 Hz. ^{1}H NMR (CD_2Cl_2): δ 7.78-7.14 (m, 30 H, PPh_3). ES$^+$ MS: *m/z* 970 $[M]^+$. IR (KBr): 3051vw, 1719vw, 1686vw, 1655vw, 1571vw, 1509vw, 1480m, 1435m, 1311w, 1184w, 1159w, 1095m, 1027w, 998w, 908m, 743m, 692m, 536m, 524m, 498w, 457vw, 438vw, 428vw, 280w, 247w cm^{-1}.

[Pt(CSe_3)($P(p\text{-}tol)_3$)$_2$] 4.4. This was prepared in the same fashion as platinum complex **4.1** using [$PtCl_2(P(p\text{-}tol)_3)_2$] (0.110 g, 0.126 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol) to give the product as a brown powder. Yield 0.037 g (28 %). Found (Calc. for $C_{43}H_{42}P_2Se_3Pt$): C 48.71 (49.06), H 3.89 (4.02)%. ^{31}P-{^{1}H} NMR (CD_2Cl_2): δ(P) 17.1(s) ppm. $^{1}J(^{195}Pt\text{-}^{31}P)$ 3162 Hz. ^{1}H NMR (CD_2Cl_2): δ 7.59-7.01 (m, 24 H, aromatic) and 2.38(s, 18H, CH_3). EI$^+$ MS: *m/z* 1052 $[M]^+$. IR (KBr): 2918w, 1598w, 1498vw, 1443, 1398vw, 1309w, 1188w, 1101m, 1020w, 923m, 807m, 708w, 647m, 632m, 623m, 544m 523w, 511m, 444w, 409w, 390w, 365w, 345w, 318w, 256w, 242w cm^{-1}.

[Pt(CSe_3)(dppp)] 4.5. This was prepared in the same fashion as platinum complex **4.1** using [$PtCl_2$(dppp)] (0.100 g, 0.0.179 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol) to give the product as a dark orange powder. Yield 0.046 g (35 %). Found (Calc. for $C_{28}H_{26}P_2Se_3Pt$): C 39.44 (39.27), H 2.74 (3.06)%. ^{31}P-{^{1}H} NMR (CD_2Cl_2): δ(P) –2.7(s) ppm. $^{1}J(^{195}Pt\text{-}^{31}P)$ 2871 Hz. ^{1}H NMR (CD_2Cl_2): δ 7.61-7.35 (m, 20 H, aromatic) and 2.81-2.54(m, 6H, CH_2). EI$^+$ MS: *m/z* 856 $[M]^+$. IR (KBr): 2924vw, 1655w, 1638w, 1561w, 1509w, 1482w, 1459w, 1435m, 1187w, 1159w, 1102m, 999w,

970w, 900m, 813w, 744w, 692m, 666w, 514m, 432w, 398w, 371w, 282w, 247w cm^{-1}.

[Pt(CSe$_3$)(dppf)] 4.6. This was prepared in the same fashion as platinum complex **4.1** using [PtCl$_2$(dppf)] (0.100 g, 0.122 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol) to give the product as a light brown powder. Yield 0.083 g (68 %). Found (Calc. for $C_{35}H_{28}P_2Se_3PtFe$): C 42.35 (42.11), H 2.63 (2.83)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) 17.5(s) ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3218 Hz. ^1H NMR (CD_2Cl_2): δ 7.74-7.39 (m, 20 H, aromatic) 4.42 (br, m, 4H, α-CH (C_5H_4)), 4.37 (br, m, 4H, β-CH (C_5H_4)). EI^+ MS: *m/z* 998 $[M]^+$. IR (KBr): 2921vw, 1655vw, 1542vw, 1480w, 1435m, 1307w, 1168w, 1098m, 1027w, 999w, 915m, 826w, 744w, 694m, 637w, 554m, 516m, 493m, 469m, 441w, 390w, 350w, 303w, 283w, 250w cm^{-1}.

[Pt(CSe$_3$)(dppe)]/[Pt(CSe$_4$)(dppe)] 4.7. This was prepared in the same fashion as platinum complex **4.1** using [PtCl$_2$(dppe)] (0.300 g, 0.451 mmol) and carbon diselenide (6 cm^3 10% solution in dichloromethane, 0.265 mmol) to give an inseparable mixture of the two species as a brick red powder. Yield 0.252 g (66 %). Found (Calc. for $C_{27}H_{24}P_2Se_3Pt$/ $C_{27}H_{24}P_2Se_4Pt$): C 38.47 (38.50/35.20), H 2.64 (2.87/2.62)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) 45.2 (s) ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3005 Hz. $\delta(P_A)$ 44.4(d) ppm, $^1J(^{195}Pt\text{-}^{31}P)$ 2927 Hz and $\delta(P_X)$ 45.5(d) ppm, $^1J(^{195}Pt\text{-}^{31}P)$ 2595 Hz $^2J(^{31}P_A\text{-}^{31}P_X)$ 9 Hz. ^1H NMR (CD_2Cl_2): δ 7.81-7.32 (m, 20 H, aromatic) and 2.59-2.41(m, 4H, PCH_2CH_2P). IR (KBr): 2917vw, 1549w, 1482w, 1435m, 1409w, 1307w, 1185w, 1159w, 1103m, 1026w, 998w, 907m,

898m, 875w, 819m, 746w, 715m, 690m, 654w, 530m, 482w, 395, 369w, 290w, 283w, 254w, 250w, 218w cm^{-1}.

[{Pt(μ-CSe_3)(PEt_3)}$_4$] 4.8. This was prepared in the same fashion as platinum complex **4.1** using [$PtCl_2(PEt_3)_2$] (0.100 g, 0.199 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol). The remaining solvent was removed under reduced pressure and the red residue was extracted three times with dichloromethane (3 x 20 cm^3) and the mixture was filtered through a celite pad. The product was obtained as a dark red crystalline solid by crystallisation from the resulting dichloromethane solution. Yield 0.018 g (15 %). Found (Calc. for $C_{28}H_{60}P_4Se_{12}Pt_4$): C 15.39 (14.96), H 2.52 (2.69)%. IR (KBr): 2957vw, 1719vw, 1655vw, 1561vw, 1509vw, 1450w, 1413w, 1377w, 1251w, 1037m, 1005w, 875s, 767m, 732m, 636w, 430w, 380w, 332w, 303w, 283w, 257w cm^{-1}.

[Pt(PMe_2Ph)$_2$(CSe_3)$Cr(CO)_5$] 4.9. [$Cr(CO)_6$] (0.021 g, 0.0971 mmol) was dissolved in tetrahydrofuran (30 cm^3) and the solution was irradiated with a 125 Watt U. V. lamp for 20 minutes. Complex **4.2** (0.070 g, 0.0971 mmol) was added as a solid in one portion. The resulting mixture was stirred for 24 hours followed by evaporation of the solvent under reduced pressure. The dark red residue was dissolved in the minimum volume of dichloromethane (3 cm^3) and diethyl ether (50cm^3) was added slowly to precipitate the product as a brick red powder. Yield 0.068 g (76 %). Found (Calc. for $C_{22}H_{22}O_5P_2Se_3PtCr$): C 28.77 (28.96), H 2.23 (2.43)%. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) –19.3(s) ppm. $^1J(^{195}Pt$-$^{31}P)$ 3038 Hz. ^1H NMR (CD_2Cl_2): δ 7.48-7.36 (m, 10 H, aromatic) and 1.59 (d,

12 H, $^{3}J(^{195}Pt\text{-}^{1}H)$ 36 Hz, $^{2}J(^{31}P\text{-}^{1}H)$ 12 Hz, PMe). EI^{+} MS: *m/z* 912 $[M]^{+}$, 772 $[M\text{-}(CO)_5]^{+}$, 720 $[M\text{-}Cr(CO)_5]^{+}$. IR (KBr): 2051w, 1972w, 1925br,s, 1916s, 1686vw, 1638vw, 1561vw, 1459vw, 1437w, 1420w, 1299w, 1108w, 943w, 891m, 838w, 742w, 716w, 692w, 666, 651, 487w, 451w, 303w, 282w, 247w cm^{-1}.

$[Pt(PMe_2Ph)_2(CSe_3)Mo(CO)_5]$ 4.10. This was prepared in the same fashion as platinum complex **4.9** using $[Mo(CO)_6]$ (0.022 g, 0.0833 mmol) and complex **4.2** (0.060 g, 0.0833 mmol) to give the product as a brown powder. Yield 0.020 g (25 %). Found (Calc. for $C_{22}H_{22}O_5P_2Se_3PtMo$): C 27.84 (27.63), H 2.01 (2.32)%. $^{31}P\text{-}\{^{1}H\}$ NMR (CD_2Cl_2): δ(P) –18.5(s) ppm. $^{1}J(^{195}Pt\text{-}^{31}P)$ 3041 Hz. ^{1}H NMR (CD_2Cl_2): δ 7.47-7.36 (m, 10 H, aromatic) and 1.58 (d, 12 H, $^{3}J(^{195}Pt\text{-}^{1}H)$ 36 Hz, $^{2}J(^{31}P\text{-}^{1}H)$ 11 Hz, PMe). EI^{+} MS: *m/z* 956 $[M]^{+}$, 720 $[M\text{-}Mo(CO)_5]^{+}$. IR (KBr): 2142w, 2070w, 1984w, 1931br,s, 1885m, 1638vw, 1509vw, 1489vw, 1435w, 1420w, 1299w, 1284w, 1106w, 946w, 909m, 872w, 844w, 788w, 742w, 718w, 692w, 599w, 488w, 442w, 359w, 279w, 244w cm^{-1}.

$[Pt(PMe_2Ph)_2(CSe_3)W(CO)_5]$ 4.11. This was prepared in the same fashion as platinum complex **4.9** using $[W(CO)_6]$ (0.034 g, 0.0972 mmol) and **4.2** (0.070 g, 0.0972 mmol) to give the product as a brown powder. Yield 0.043 g (42 %). Found (Calc. for $C_{22}H_{22}O_5P_2Se_3PtW$): C 28.77 (28.96), H 2.23 (2.43)%. $^{31}P\text{-}\{^{1}H\}$ NMR (CD_2Cl_2): δ(P) –18.3(s) ppm. $^{1}J(^{195}Pt\text{-}^{31}P)$ 3045 Hz. ^{1}H NMR (CD_2Cl_2): δ 7.54-7.30 (m, 10 H, aromatic) and 1.57 (d, 12 H, $^{3}J(^{195}Pt\text{-}^{1}H)$ 36 Hz, $^{2}J(^{31}P\text{-}^{1}H)$ 12 Hz, PMe). EI^{+} MS: *m/z* 1044 $[M]^{+}$, 720 $[M\text{-}W(CO)_5]^{+}$. IR (KBr): 2140vw, 2060w, 1975w, 1919br,s, 1889s, 1655vw, 1638vw, 1509vw, 1490vw,

1436w, 1420w, 1299w, 1285w, 1106w, 946w, 909m, 876w, 844w, 742w, 717w, 692w, 595w, 488w, 444w, 371w, 281w, 244w cm^{-1}.

[{Rh(CSe$_3$)(η^5-C$_5$Me$_5$)}$_2$] 4.12. This was prepared in the same fashion as platinum complex **4.1** using [{RhCl(μ-Cl)(η^5-C$_5$Me$_5$)}$_2$] (0.080g, 0.129 mmol) and carbon diselenide (4 cm^3 10% solution in dichloromethane, 0.530 mmol) to give the product as a brick red powder. Yield 0.106 g (84 %). Found (Calc. for $C_{22}H_{30}Se_6Rh$): C 26.68 (27.13), H 2.84 (3.10)%. ^{1}H NMR (CD_2Cl_2): δ 1.85-1.73 (m, 30H, η^5-C$_5$Me$_5$). EI$^+$ MS: *m/z* 979 [M]$^+$, 900 [M-Se]$^+$. IR (KBr): 2906w, 2104w, 1719w, 1686vw, 1655vw, 1638vw, 1561vw, 1542vw, 1509vw, 1449m, 1377m, 1154w, 1075w, 1021w, 851s, 784w, 616w, 535w, 390w, 313w, 281w cm^{-1}.

[{Ir(CSe$_3$)(η^5-C$_5$Me$_5$)}$_2$] 4.13. This was prepared in the same fashion as platinum complex **4.1** using [{IrCl(μ-Cl)(η^5-C$_5$Me$_5$)}$_2$] (0.080g, 0.104 mmol) and carbon diselenide (4 cm^3 10% solution in dichloromethane, 0.530 mmol) to give the product as a brown powder. Yield 0.065 g (54 %). Found (Calc. for $C_{22}H_{30}Se_6Ir$): C 23.14 (22.92), H 2.17 (2.62)%. ^{1}H NMR (CD_2Cl_2): δ 1.94-1.64 (m, 30H, η^5-C$_5$Me$_5$). EI$^+$ MS: *m/z* 1153 [M]$^+$, 577 [1/2M]$^+$. IR (KBr): 2907w, 2108w, 2022w, 1655w, 1638vw, 1561vw, 1509vw, 1449m, 1378m, 1155w, 1076w, 1027m, 857s, 788m, 611w, 536w, 384w, 376w, 279w, 246w cm^{-1}.

[{Ru(CSe$_3$)(η^6-*p*-MeC$_6$H$_4$^{I}Pr)}$_2$] 4.14. This was prepared in the same fashion as platinum complex **4.1** using [{RuCl(μ-Cl)(η^6-*p*-MeC$_6$H$_4$^{I}Pr)}$_2$] (0.140g, 0.229 mmol) and carbon diselenide (6 cm^3 10% solution in dichloromethane, 0.795

mmol) to give the product as a brown powder. Yield 0.096 g (43 %). Found (Calc. for $C_{22}H_{28}Se_6Ru_2$): C 27.59 (27.29), H 3.07 (2.91)%. ^{1}H NMR (CD_2Cl_2): δ 5.61 and 5.47 (AB system, $^3J(^1H\text{-}^1H)$ 6 Hz, 4H, aromatic) 2.84 (sept, 1H, $CHMe_2$) 2.28 (s, 3H, CH_3) and 1.19 (d, $(CH_3)_2CH$, 6H). EI^+ MS: *m/z* 969 $[M]^+$. IR (KBr): 2960w, 2105wm, 2058m, 1619m, 1500w, 1459w, 1388w, 1278m, 1112w, 1089w, 1055w, 1031w, 849s, 803m, 660w, 453w, 396w, 369w, 354w, 274w, 247w cm^{-1}.

[{Os(CSe$_3$)(η^6-*p*-MeC$_6$H$_4$^{i}Pr)}$_2$] 4.15. This was prepared in the same fashion as platinum complex **4.1** using [{OsCl(μ-Cl)(η^6-*p*-MeC$_6$H$_4$^{i}Pr)}$_2$] (0.080 g, 0.101 mmol) and carbon diselenide (4 cm^3 10% solution in dichloromethane, 0.530 mmol) to give the product as a dark brown powder. Yield 0.034 g (29 %). Found (Calc. for $C_{22}H_{28}Se_6Os_2$): C 23.46 (23.04), H 2.44 (2.46)%. ^{1}H NMR (CD_2Cl_2): δ 6.01 and 5.86 (AB system, $^3J(^1H\text{-}^1H)$ 6 Hz, 4H, aromatic) 2.83 (sept, 1H, $CHMe_2$) 2.40 (s, 3H, CH_3) and 1.30 (d, $(CH_3)_2CH$, 6H). EI^+ MS: *m/z* 1148 $[M]^+$. IR (KBr): 2957w, 2055w, 1619w, 1459w, 1384w, 1310m, 1196vw, 1135w, 1085w, 1053w, 1027w, 997w, 851m, 801w, 660w, 522w, 445w, 373w, 350w, 277w, 245w cm^{-1}.

X-Ray Crystallography

Table 4.8 lists details of data collections and refinements for **4.2** and **4.8**. Data were collected at 125 K using a Bruker SMART diffractometer with graphite monochromated Mo radiation. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were

idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[109]

Compound	**4.2**	**4.8**
Empirical formula	$C_{17}H_{22}P_2PtSe_3$	$C_{28}H_{60}P_4Pt_4Se_{12}$
Crystal dimensions/mm	0.1 × 0.1 × 0.03	0.1 × 0.1 × 0.1
Crystal system	Triclinic	Tetragonal
Space group	P $\bar{1}$	P $\bar{4}2_1c$
a/Å	8.9878(14)	12.5946(11)
b/Å	11.0937(18)	12.5946(11)
c/Å	11.6242(19)	16.047(2)
α/°	86.035(3)	90
β/°	76.775(3)	90
γ/°	69.554(3)	90
U/Å^3	1057.1(3)	2545.5(4)
Z	2	2
M	720.26	2248.52
Dc/g cm^{-3}	2.263	2.934
μ/mm^{-1}	11.949	19.683
Measured reflections	6302	14330
Independent reflections (R_{int})	3753(0.0543)	2283(0.0914)
Final R1, wR2[I>2σ(I)]	0.0517, 0.1090	0.0277, 0.0610

Table 4.8 Details of the X-ray data collections and refinements for compounds **4.2** and **4.8**.

Chapter 5: 1,2,4-thiadiazole model compounds.

5.1 *Introduction*

As we discussed in chapter 1 (p 32) a possible structure for polythiocyanogen may be 1,2,4-thiadiazole rings linked by sulfide bridges to form a chain.

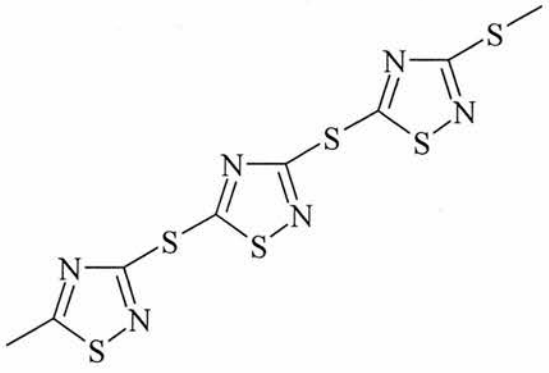


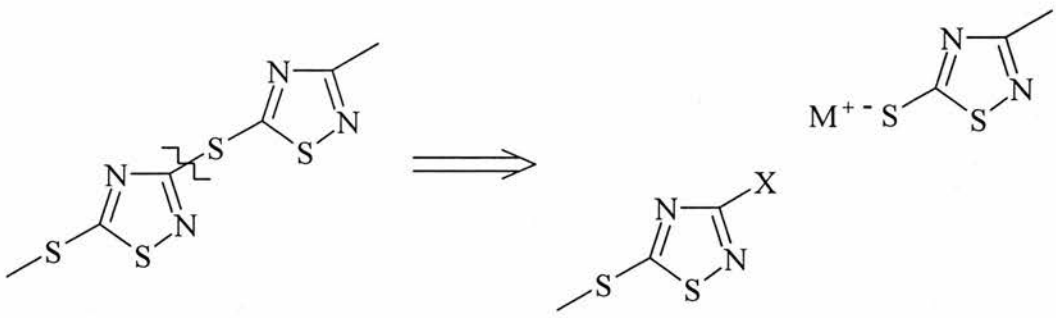
Figure 5.1 Possible 1,2,4- thiadiazole structure of polythiocyanogen.

Therefore in this section we have synthesised a series of 1,2,4-thiadiazoles for spectroscopic comparison with $(SCN)_x$ **6.7**. Many of these 1,2,4-thiadiazoles have been synthesised before but because they were made a long time ago the data is very limited[59,61-63] and only one compound has published ^{13}C NMR data.[125] We also report the synthesis of model compounds composed of two 1,2,4-dithiazole rings linked by a sulfur bridge. Selected examples have been studied by X-ray crystallography.

5.2 *Results and Discussion*

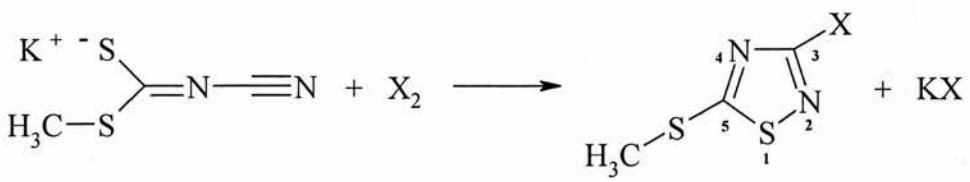
5.2.1 *Synthesis of 1,2,4-thiadiazoles.*

Using a retrosynthetic approach (Scheme 5.1) we have attempted to prepare 1,2,4-thiadiazole monomer units that we can then link together by nucleophilic substitution at C3 to form dimers and higher oligomers.



Scheme 5.1. Retrosynthetic approach to prepare 1,2,4-thiadiazole model compounds.

Thus we synthesised the 3-halo-1,2,4-thiadiazoles **5.1** and **5.2** (Scheme 5.2).



5.1 X = Cl
5.2 X = Br

Scheme 5.2 Synthesis of 3-halo-1,2,4-thiadiazoles **5.1** and **5.2**

Compounds **5.1** and **5.2** were prepared by the reaction of potassium methyl cyanodithioimidocarbonate with the appropriate halogen in a similar fashion to the literature preparation.[126] Only melting point and IR spectra were reported in the literature. Both **5.1** and **5.2** gave satisfactory microanalysis and showed the anticipated M^+ in their mass spectra. In the IR and Raman spectra the C-H stretching bands are observed at approximately 2950 cm^{-1}. The absence of a nitrile band in the region 2000-2200 cm^{-1} confirmed no starting material remained in our samples. Wittenbrook *et al.* have reported that 3-halo-1,2,4-thiadiazole sulfides have 2 strong bands in the ranges 1381-1441 and 1175-1232 cm^{-1} assigned as ring vibrations.[126] They noted that different substituents attached to the exocyclic sulfur at C5 do not affect the ring stretches but different halogen atoms at C3 produce a detectable shift in both bands. For **5.1** they report values of 1425 and 1228 cm^{-1}. In **5.2** they report the ring stretches at 1404 and 1202 cm^{-1}. The change in ring vibrations between **5.1** and **5.2** is attributed to chlorine being replaced by bromine. We observe the ring stretching bands at 1425 and 1229 cm^{-1} in **5.1** and 1415 and 1208 cm^{-1} in **5.2**. A C-S stretching band is noted at 678 and 665 cm^{-1} in **5.1** and **5.2** respectively. In the ^{13}C-$\{^1H\}$ NMR spectra of **5.1** the signals of the ring carbons were observed at 191.9 ppm and 156.1 ppm which were indisputably assigned as C5 and C3 respectively by H-C HMBC and H-C HSQC experiments. In compound **5.2** C5 was noted at 191.6 ppm and C3 had shifted to 144.3 ppm due to bromine replacing chlorine. The structure was confirmed by a single crystal X-ray diffraction study (Figure 5.2). All the crystal structures of 1,2,4-thiadiazoles obtained are discussed together on page 143.

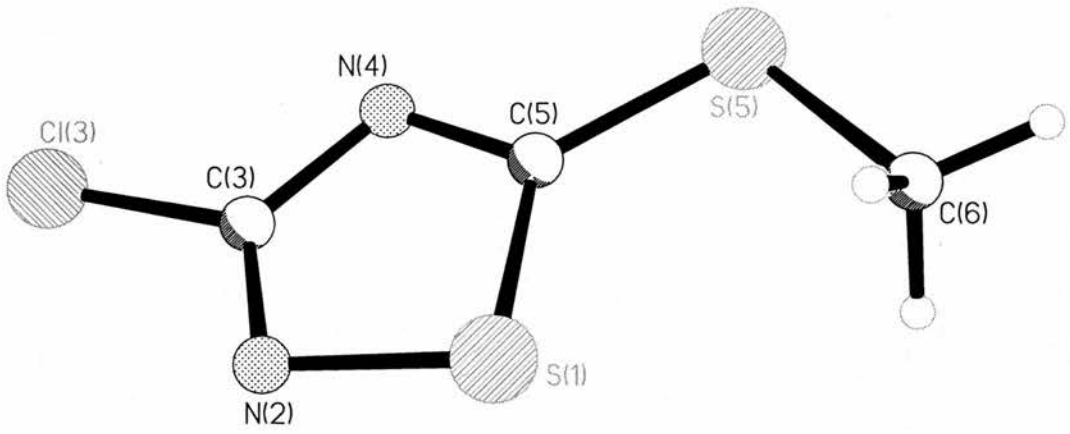
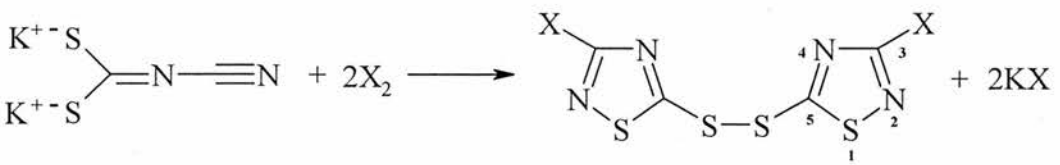


Figure 5.2 X-ray crystal structure of **5.1**.

The next stage was to prepare a metal salt of a 1,2,4-thiadiazole-5-thiol. First we prepared bis(3-halo-1,2,4-thiadiazol-5-yl) disulfides **5.3** and **5.4** by the reaction of potassium cyanodithioimidocarbonate **2.1** and the appropriate halogen (Scheme 5.3).



5.3 X = Cl
5.4 X = Br

Scheme 5.3 Synthesis of bis(3-halo-1,2,4-thiadiazol-5-yl) disulfides **5.3** and **5.4.**

Both species were prepared in excellent yields. **5.3** and **5.4** have previously been reported in the literature but only melting point and IR spectroscopy was recorded.[102] Compounds **5.3** and **5.4** showed the anticipated M^+ ions in their mass spectra with the expected isotopomer distributions and the microanalyses were within the specified limits. In the IR spectra the S-S stretch is observed at 481 and 448 cm^{-1} respectively in **5.3** and **5.4**. The ring vibrations are noted at

1435 and 1216 cm^{-1} in **5.3** and at 1415 and 1208 cm^{-1} in **5.4**. These are comparable to the literature values for ring vibrations in these compounds which are 1435 and 1215 cm^{-1} in **5.3** and 1427 and 1192 cm^{-1} in **5.4**.[102] In the ^{13}C-{^{1}H} NMR spectra of **5.3** C5 and C3 were observed at 188.5 ppm and 158.0 ppm respectively. Similarly in **5.4** C5 and C3 were noted at 188.5 ppm and 145.9 ppm. ^{14}N NMR spectra of **5.4** revealed 2 broad singlets centred at 310.6 and 278.4 ppm assigned as N2 and N4 respectively. Crystals of both **5.3** and **5.4** were easily obtained hence their X-ray crystal structures have been determined (Figures 5.3 and 5.4). It is interesting to note that both structures adopt a gauche conformation as is the case for $Se_2(CN)_2$ **6.4**.

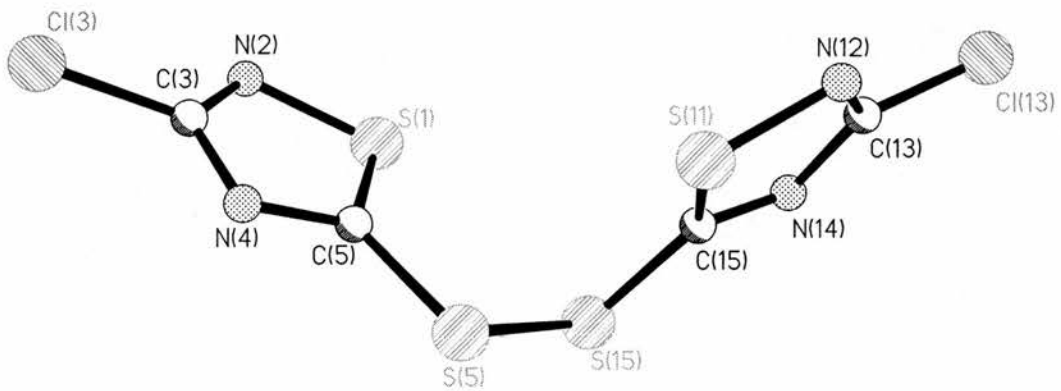


Figure 5.3 X-ray crystal structure of **5.3**.

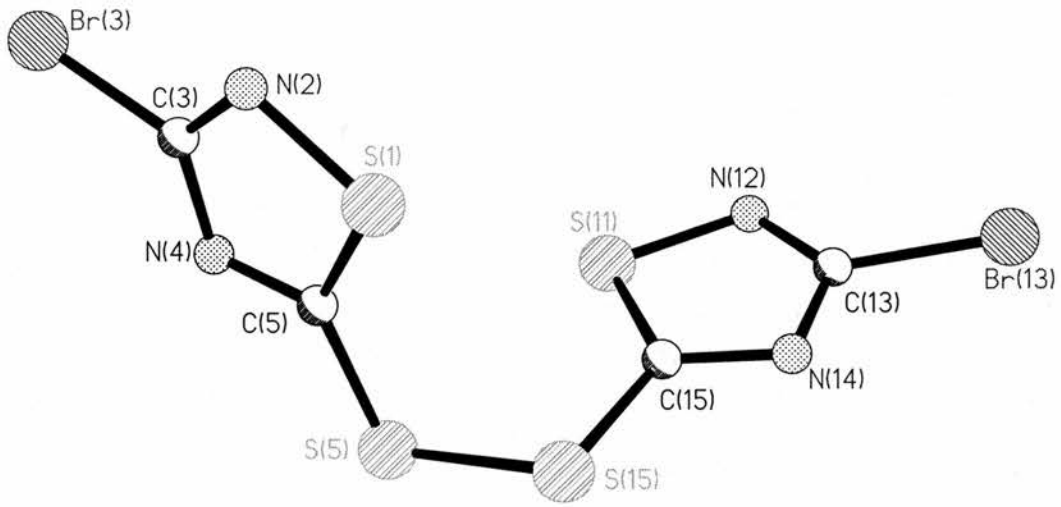
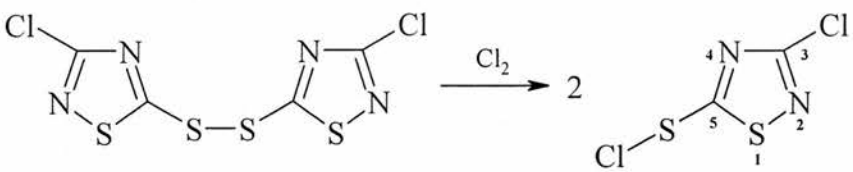


Figure 5.4 X-ray crystal structure of **5.4**.

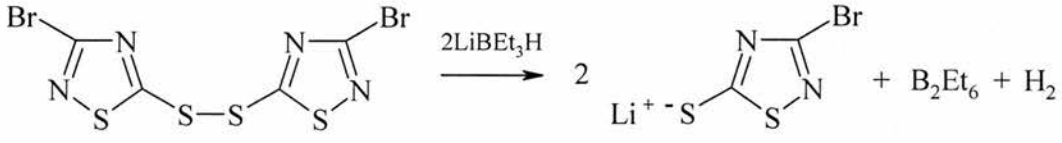
5.3 was readily converted into the sulfenyl chloride **5.5** by chlorinating with excess Cl_2 (Scheme 5.4) in the same fashion as reported by Thaler and McDivett[102]



Scheme 5.4 Synthesis of **5.5**.

Compound **5.5** is air sensitive therefore it was stored under nitrogen and no mass spectroscopy microanalytical or IR data was collected. In the ^{13}C-{^{1}H} NMR C5 and C3 were noted at 180.2 and 155.9 ppm respectively.

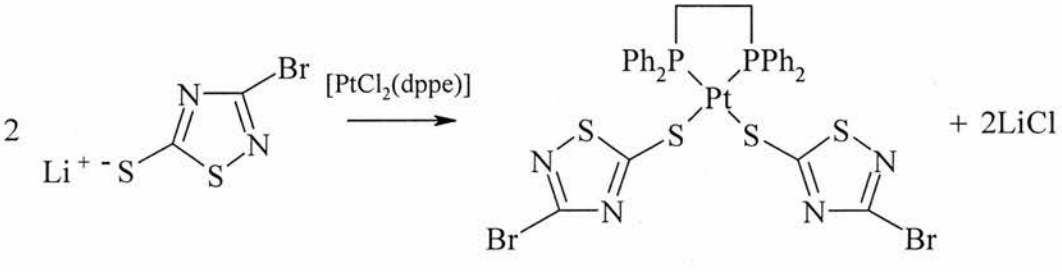
Reaction of the disulfide **5.4** in tetrahydrofuran at -40 °C with $LiBEt_3H$ yielded, after removal of solvent and B_2Et_6 *in vacuo*, the lithium salt **5.6** (Scheme 5.5) in good yield.



Scheme 5.5 The synthesis of the lithium salt of 3-bromo-1,2,4-thiadiazole-5-thiol.

The lithium salt **5.6** was found to be an air stable yellow solid. Microanalysis supported the purity of this sample and the anion was observed by ES^- mass spectroscopy. In the IR spectrum the ring vibrations were observed at 1434 and 1225 cm^{-1}. The lithium salt **5.6** was not soluble enough to record ^{13}C NMR data.

Therefore we confirmed that we had successfully synthesised the lithium salt by trapping the anion as a platinum complex. The lithium salt **5.6** was prepared *in situ* and $[PtCl_2(dppe)]$ was added to give $[Pt(C_2N_2S_2Br)_2(dppe)]$ **5.7** in an acceptable yield as a pale yellow powder (Scheme 5.6).



Scheme 5.6 Synthesis of platinum complex **5.7**

Microanalysis and mass spectroscopy gave the expected results. The ring stretches were observed at 1411 and 1200 cm^{-1} in the IR spectrum. In the $^{31}P-\{^{1}H\}$ NMR spectra of **5.7** we noted a sharp singlet at 47.6 ppm with platinum satellites [$^{1}J(^{195}Pt-^{31}P)$ 3012 Hz]. The coupling constant was comparable to those of other platinum diphosphine complexes with sulfur donor ligands.[18] Crystals suitable for X-ray analysis were obtained by vapour diffusion from chloroform/hexane. The crystal structure is shown below in figure 5.5.

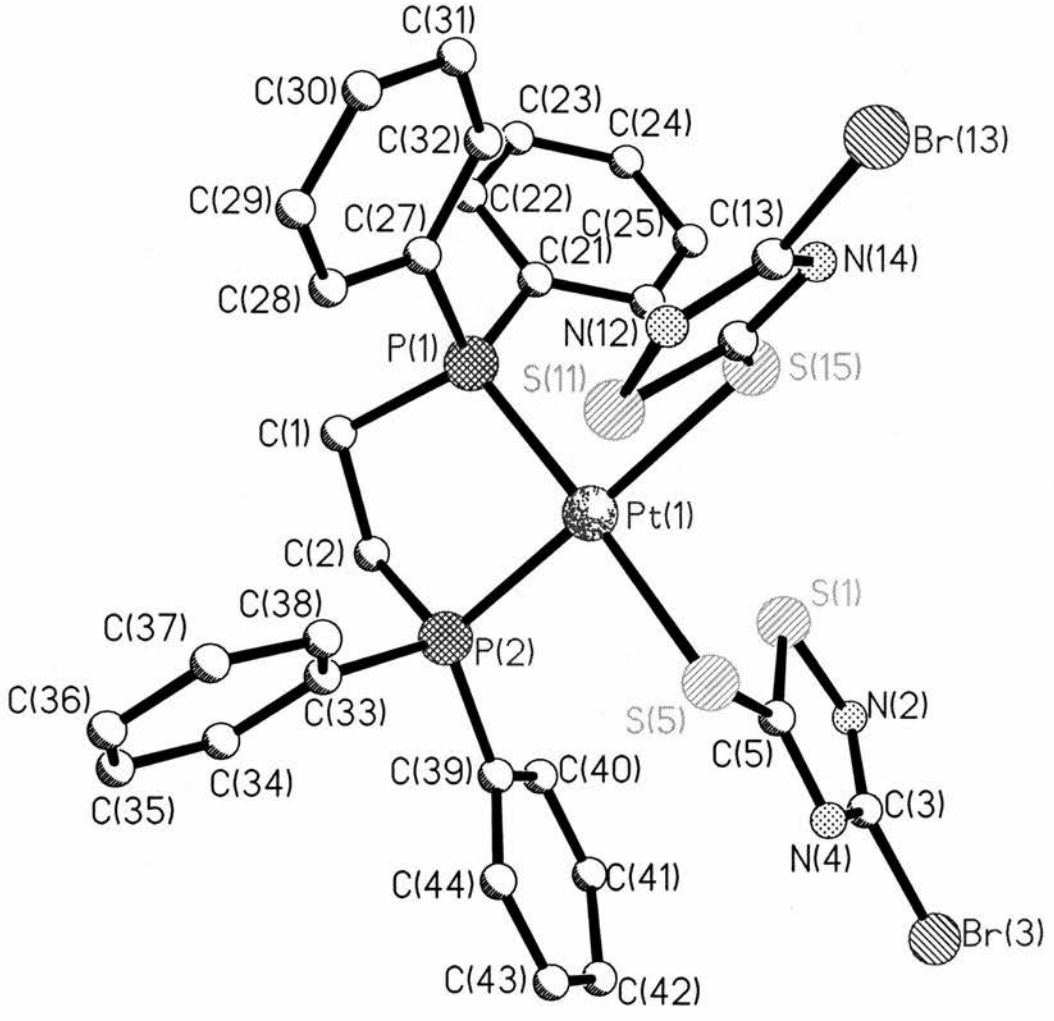
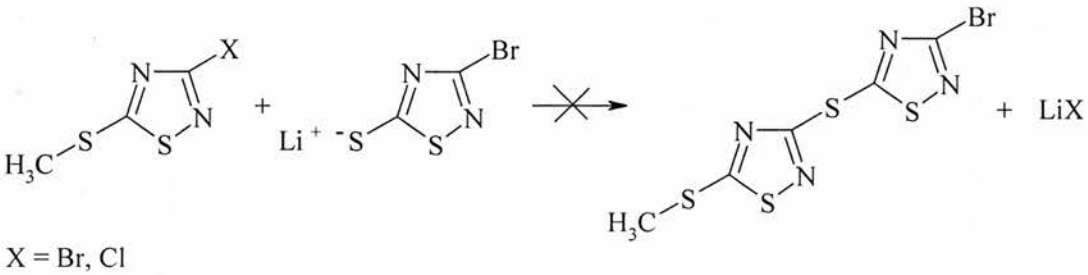


Figure 5.5 X-ray crystal structure of **5.7**.

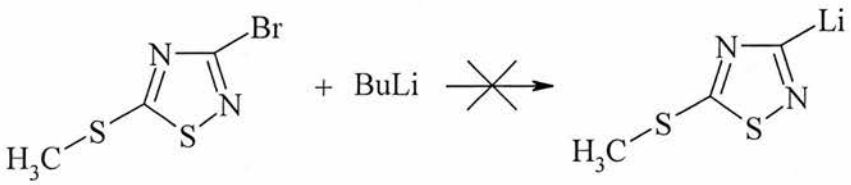
Having successfully synthesised two 3-halo-1,2,4-thiadiazoles (**5.1** and **5.2**) and the lithium salt of 3-bromo-1,2,4-thiadiazole-5-thiol **5.6** the next step was to combine the two species to prepare a dimer by nucleophilic substitution at C3 as shown below in scheme 5.7.



X = Br, Cl

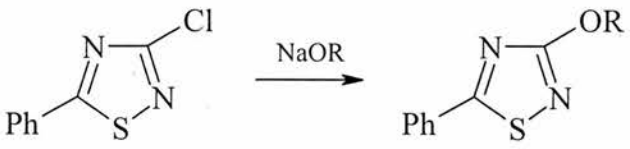
Scheme 5.7 Attempted preparation of dimer by nucleophilic substitution at C3.

Unfortunately we have been unable to react our lithium salt **5.6** with either the chloride **5.1** or bromide **5.2** even under reflux conditions. No reaction occurred at all and both starting materials were observed in the ^{13}C NMR of the reaction mixture. We have also attempted reaction of the bromide **5.2** with BuLi (Scheme 5.8) but no reaction occurred.



Scheme 5.8 Attempted reaction of **5.2** with BuLi.

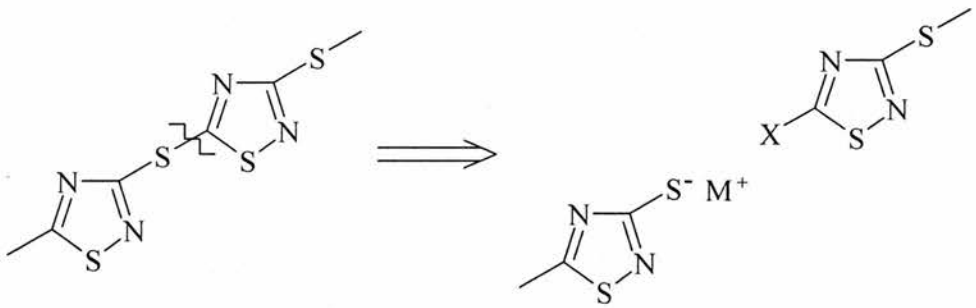
The low reactivity of C3 of 1,2,4-thiadiazoles has been discussed in chapter 1 (p 20). One of the very few successful nucleophilic displacements is reported by Kurzer *et al.* (Scheme 5.9).[67]



R = Me, Ph

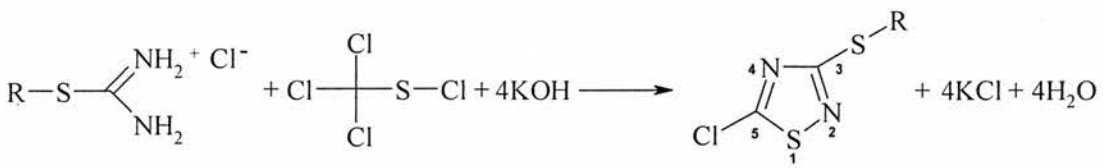
Scheme 5.9 Nucleophilic substitution at C3 of a 1,2,4-thiadiazole.

Due to the low reactivity at C3 in 1,2,4-thiadiazole rings we changed our approach and attempted to prepare monomer units that could be linked by nucleophilic substitution at the more reactive C5.



Scheme 5.10 Alternative strategy to prepare 1,2,4-thiadiazole model compounds.

The 3-alkylsulfanyl-5-chloro-1,2,4-thiadiazoles **5.8** and **5.9** were prepared by the reaction of the appropriate S-alkylisothiourea hydrochloride with trichloromethylsulfenyl chloride and four equivalents of potassium hydroxide in a mixture of dichloromethane and water (Scheme 5.11).



5.8 R = Me
5.9 R = ^{t}Bu

Scheme 5.11 Synthesis of 3-alkylsulfanyl-5-chloro-1,2,4-thiadiazoles **5.8** and **5.9**.

After dichloromethane extraction of the organic phase followed by removal of the solvent **5.8** or **5.9** was isolated by distillation *in vacuo* using a Kugelrohr apparatus at 50 °C or 70 °C respectively. This was a small modification to the literature preparation of **5.8** and **5.9** in water followed by steam distillation.[64] Only melting point and IR spectroscopy were mentioned in this report. More recently the ^{13}C NMR of **5.8** was reported by Morel *et al.*[125] **5.8** is a pale yellow oil which upon cooling slightly became a pale yellow crystalline solid. **5.9** is a yellow oil. Microanalysis and mass spectroscopy gave the expected results for both species. In both species the C-H stretching bands were noted in the region 2865-3002 cm^{-1}. We observed the ring vibrations at 1452 and 1216 cm^{-1} in **5.8** and 1447 and 1222 cm^{-1} in **5.9**. Goerdeler *et al* have reported the ring stretching bands for 3-alkylsulfanyl-1,2,4-thiadiazoles in the ranges 1435-1445 cm^{-1} and 1220-1255 cm^{-1}.[64] In the ^{13}C-{^{1}H} NMR spectra of **5.8** the shifts for the ring carbons were observed at 173.1 ppm and 171.8 ppm which were assigned as C5 and C3 respectively (cf. Morel *et al.* C5 173.2 ppm and C3 172 ppm) Our assignment was confirmed by H-C HMBC and H-C HSQC experiments. For compound **5.9** C5 and C3 were noted at 171.8 ppm and 171.2 ppm respectively. A single crystal X-ray diffraction study confirmed the structure of **5.8** (Figure 5.6).

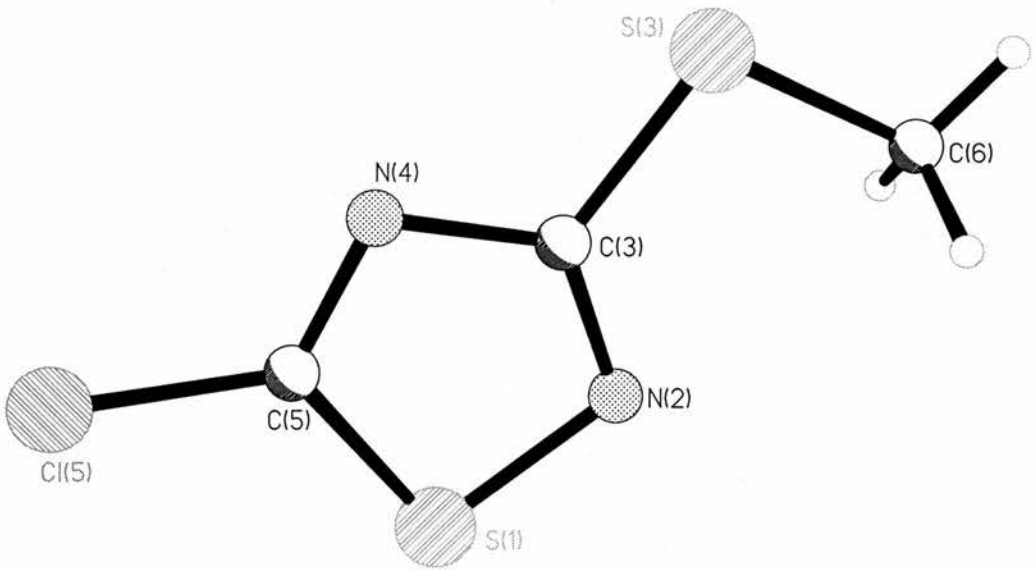
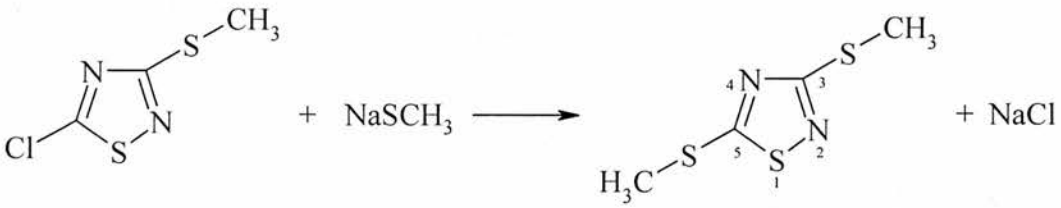


Figure 5.6 X-ray crystal structure of **5.8**.

Reaction of **5.9** with sodium thiomethoxide in methanol (Scheme 5.12) gave 3,5-bis-methylsulfanyl-1,2,4-thiadiazole **5.10** in excellent yield.

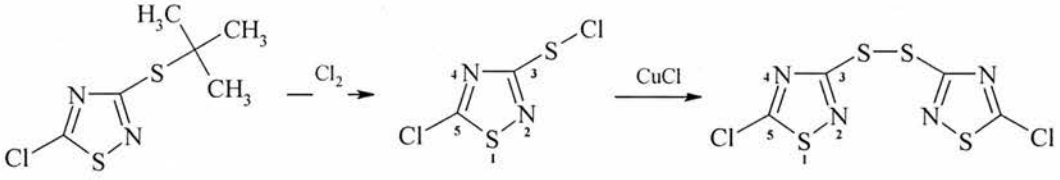


Scheme 5.12 Synthesis of 3,5-bis-methylsulfanyl-1,2,4-thiadiazole **5.10**.

C5 and C3 were observed at 189.1 ppm and 171.5 ppm respectively in the ^{13}C-$\{^1H\}$ NMR spectra of **5.10**. Two different methyl groups were noted at δ(C) 16.8 ppm and 15.1 ppm assigned as C5SMe and C3SMe respectively. In the IR and Raman spectra the C-H stretches are observed at approximately 2950 cm^{-1} and the ring stretching bands noted at 1424 and 1218 cm^{-1}. The expected $[MH]^+$

with the correct isotope distribution pattern was observed in the ES^+ mass spectra. The microanalysis was within the specified limits.

The disulfide **5.11** was prepared from **5.9** as shown below in scheme 5.13.

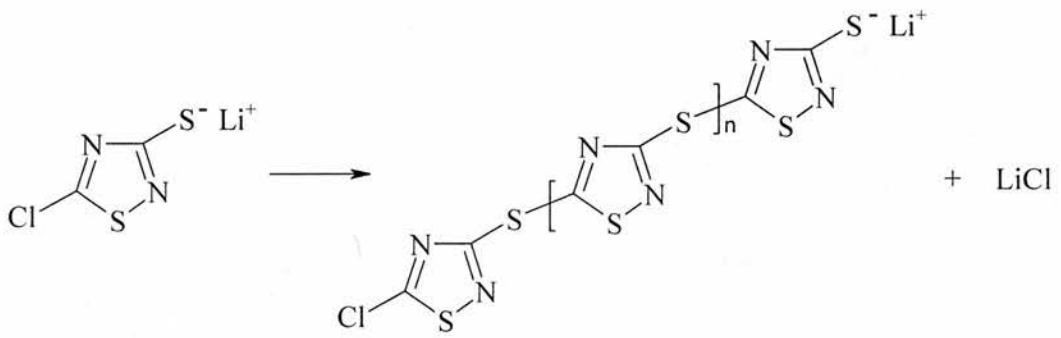


Scheme 5.13 Synthesis of disulfide **5.11**

Compound **5.9** was dissolved in dichloromethane and excess chlorine gas was passed through the solution at 0 °C. This reaction gave a mixture of products including the desired sulfenyl chloride. The ^{13}C-{^1H}NMR of the mixture showed C5 and C3 of the sulfenyl chloride at 175.2 ppm and 166.9 ppm respectively. Due to the air sensitive nature of the sulfenyl chloride no attempt was made to isolate this species. Instead the reaction mixture was used as obtained for the next stage. A stoichiometric amount of copper(I) chloride was added to the mixture to reduce the sulfenyl chloride to the disulfide **5.11**. The reaction was observed to be complete when the green copper(I) chloride had been converted to brown copper(II) chloride. The product was isolated from the resultant mixture by column chromatography on silica eluting with a 50:50 mixture of dichloromethane/hexane. **5.11** gave satisfactory microanalysis and showed the $[MNa]^+$ species in its mass spectrum. In the IR spectra the bands assigned as ring stretch were noted at 1443 and 1202 cm^{-1}. The S-S stretch is

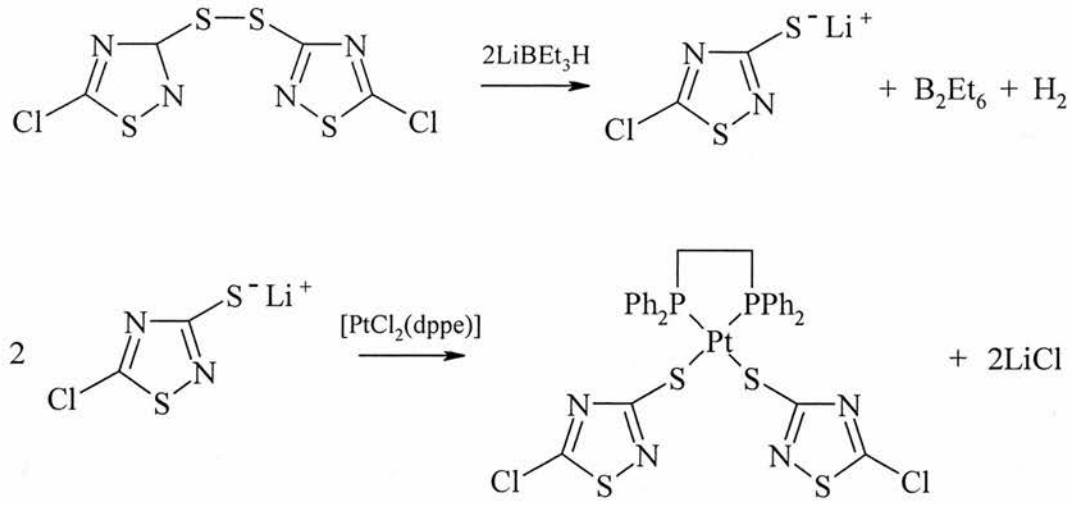
assigned as the peak at 471 cm^{-1}. The ring carbons C5 and C3 were noted at 174.9 ppm and 167.5 ppm in the ^{13}C -{^{1}H} NMR.

$LiBEt_3H$ was added to the disulfide **5.11** in tetrahydrofuran at -40 °C. The solution turned yellow. After stirring for an hour the yellow solution was allowed to slowly warm to room temperature. As the solution warmed a pale yellow solid precipitated. This solid was isolated by filtration. The solid was insoluble in all common solvents and water. Solid state ^{13}C NMR did not yield any useful data. We speculate that at -40 °C the lithium salt is formed but at higher temperatures it reacts with itself to an oligomeric/polymeric material (Scheme 5.14).



Scheme 5.14 Proposed polymerisation of the lithium salt of 5-chloro-1,2,4-thiadiazole-3-thiol.

To confirm that the lithium salt was formed at low temperature we trapped the anion as a platinum complex. $LiBEt_3H$ was added to the disulfide **5.11** in tetrahydrofuran at -40 °C. The solution was maintained at -40 °C and $[PtCl_2(dppe)]$ was added. This resulted in the formation of $[Pt(C_2N_2S_2Cl_2)_2(dppe)]$ **5.12** (Scheme 5.15).



Scheme 5.15 Synthesis of $[Pt(C_2N_2S_2Cl_2)_2(dppe)]$ **5.12**.

The microanalysis for **5.12** was acceptable. In the mass spectra the $[MNa]^+$ was noted at *m/z* 919. The ring stretches were observed at 1436 and 1183 cm^{-1} in the IR spectrum. In the $^{31}P\text{-}\{^1H\}$ NMR spectra of **5.12** we observed a sharp singlet at 46.3 ppm with platinum satellites [$^1J(^{195}Pt\text{-}^{31}P)$ 3045 Hz]. These values were comparable to complex. **5.7** [47.6 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3012 Hz]. Crystals suitable for X-ray crystallography were obtained by vapour diffusion from chloroform and hexane. The X-ray structure confirmed the connectivity of the compound (Figure 5.7).

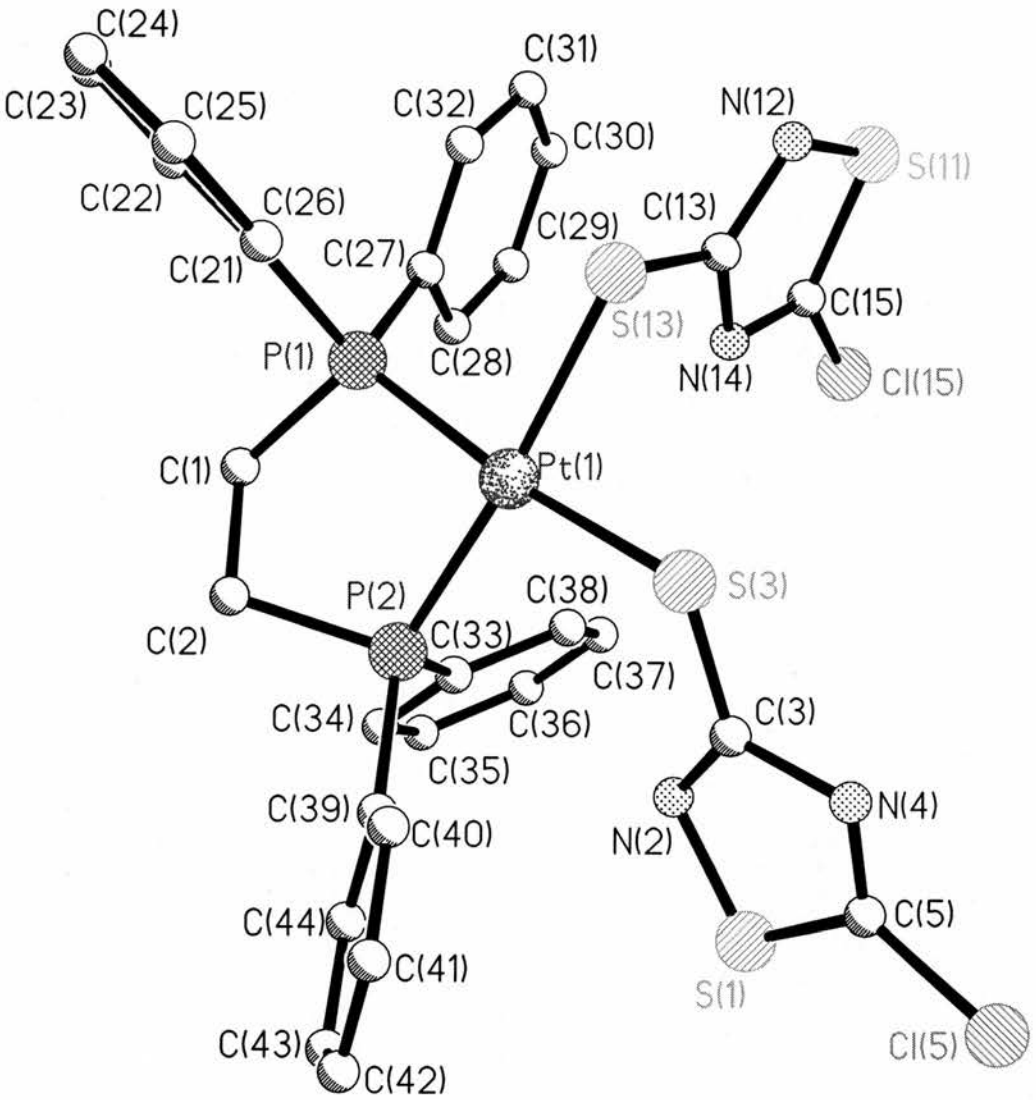
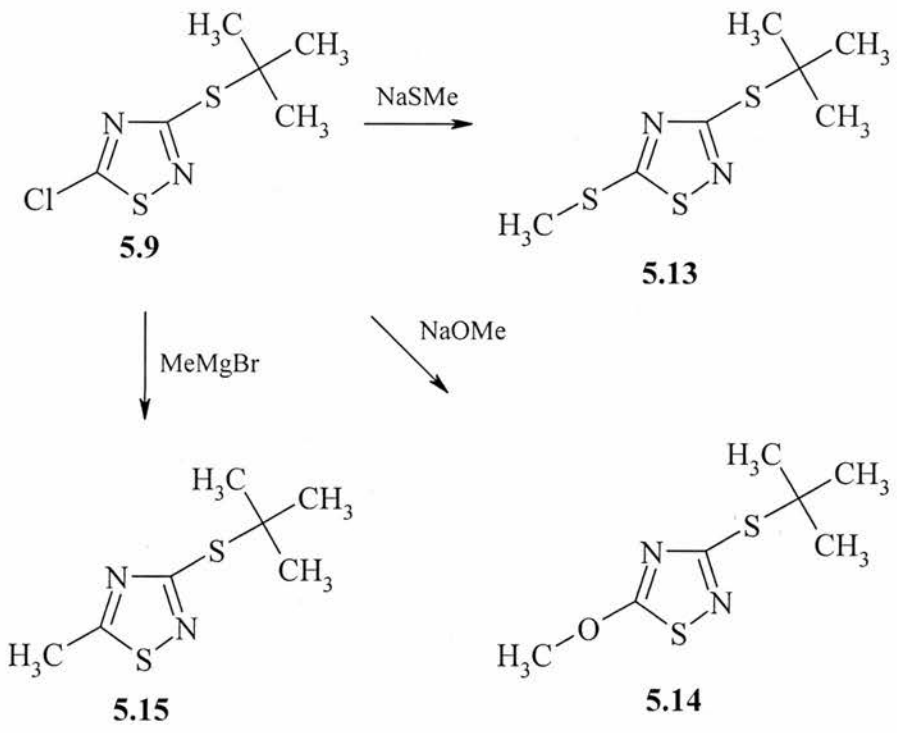


Figure 5.7 X-ray crystal structure of **5.12**.

Due to the reactivity of the 1,2,4-thiadiazole ring at C5 we replaced chlorine with SMe, OMe, and Me in **5.13**, **5.14** and **5.15** respectively (Scheme 5.16) so that we could prepare a stable lithium salt.



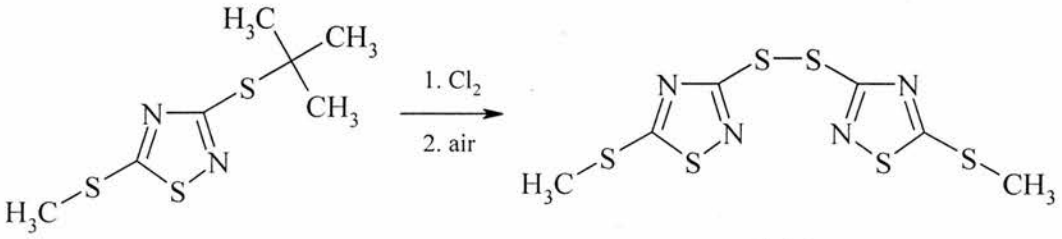
5.9 **5.13** **5.15** **5.14**

Scheme 5.16 Synthesis of **5.13**, **5.14** and **5.15**.

5.13 and **5.14** prepared by heating **5.9** in methanol with a stoichiometric amount sodium methoxide and sodium thiomethoxide respectively. **5.15** was prepared by reaction of **5.9** with methylmagnesium bromide with a catalytic amount of ferric acetylacetonate. All three species exhibited the expected ions in their mass spectra and the microanalysis showed the purity of the compounds. In the IR and Raman spectra of all three compounds the C-H stretching bands were noted in the range 2864-2996 cm^{-1}. The ring vibrations were observed at approximately 1435 and 1230 cm^{-1}. In the ^{13}C NMR spectra of **5.13**, **5.14** and **5.15** C5 was noted at approximately 188 ppm and C3 was observed in the range 166.7-170.5 ppm.

5.13 was dissolved in dichloromethane and chlorinated at 0 °C. Further reaction with copper(I) chloride did not successfully convert the sulfenyl chloride to the

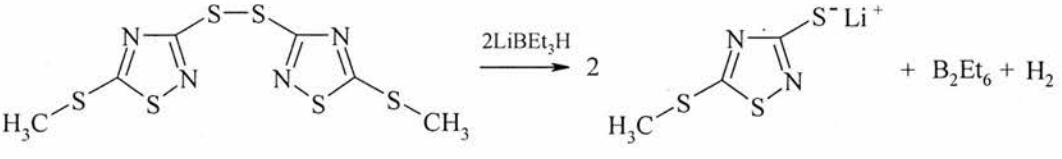
disulfide. However, we found that if the reaction mixture was exposed to the atmosphere after chlorination then it was possible to obtain the disulfide **5.16**. The disulfide **5.16** was then isolated by column chromatography on silica eluting with a 50:50 mixture of dichloromethane/hexane to give the product as an off white solid. The yield of **5.16** was very low probably due to low conversion of the sulfenyl chloride to the disulfide.



5.13 **5.16**

Scheme 5.17 Synthesis of disulfide **5.16**.

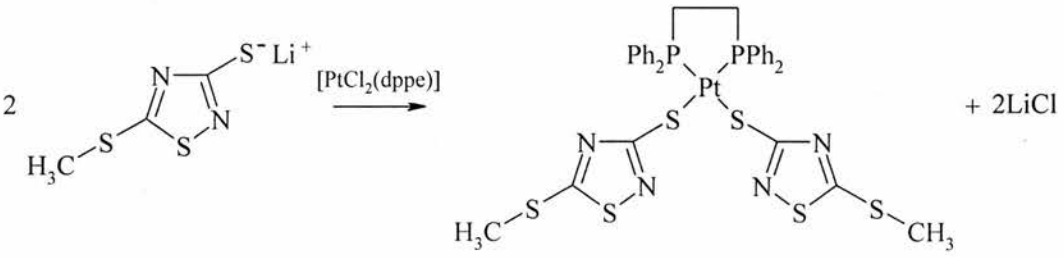
The $[MNa]^+$ ion was observed *m/z* 349 in the ES^+ mass spectrum. Microanalysis gave the expected results. The IR spectrum showed the C-H stretching bands in the appropriate range and the ring stretches at 1415 and 1211 cm^{-1}. The S-S stretch was observed at 461 cm^{-1}. In the ^{13}C-{^1H} NMR spectrum peaks were noted at 191.0, 167.7 and 16.8 ppm corresponding to C5, C3 and SCH_3 respectively. Analogous reactions were attempted using **5.14** or **5.15** but we did not manage to prepare disulfides from these compounds. The lithium salt **5.17** was synthesised from **5.16** in an analogous fashion to **5.6** (Scheme 5.18).



Scheme 5.18 Synthesis of lithium salt **5.17**.

Compound **5.17** was found to be pure by microanalysis and ES^- mass spectroscopy showed the $[M]^-$ anion. The ring stretches were observed at 1399 and 1179 cm^{-1}. Unfortunately the lithium salt **5.17** was too insoluble to record ^{13}C NMR data.

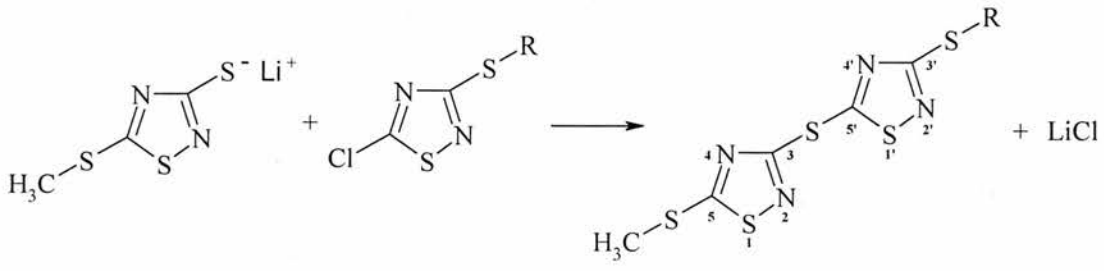
Therefore platinum complex **5.18** was prepared in the same way as **5.12** to confirm the lithium salt had been formed (Scheme 5.19).



Scheme 5.19 Synthesis of platinum complex **5.18**.

5.18 showed a sharp singlet at 46.2 ppm with a $^1J(^{195}Pt\text{-}^{31}P)$ coupling constant of 3047 Hz in its $^{31}P\text{-}\{^1H\}$ NMR spectra. As expected the values noted were almost identical to those for **5.12** [46.3 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3045 Hz]. The ring stretches were observed at 1412 and 1175 cm^{-1} in the IR spectrum. Microanalysis and mass spectroscopy gave the expected results.

We had now successfully synthesised our monomer units the 3-alkylsulfanyl-5-chloro-1,2,4-thiadiazoles (**5.8** and **5.9**) and the lithium salt of 5-methylsulfanyl-1,2,4-thiadiazole-3-thiol **5.17**. The next step was to combine the two species by nucleophilic substitution at C5 to form a model compound as shown below (Scheme 5.20).



5.19 R = Me
5.20 R = ^{t}Bu

Scheme 5.20 Synthesis of **5.19** and **5.20**.

The lithium salt **5.17** was prepared *in situ* in tetrahydrofuran and a stoichiometric amount of the appropriate 3-alkylsulfanyl-5-chloro-1,2,4-thiadiazole was added and the resulting solution stirred overnight. After the solvent was removed *in vacuo* the residue was extracted with dichloromethane and filtered to remove LiCl. The solvent was then removed *in vacuo* to give the product. In this fashion both **5.19** and **5.20** were prepared as cream powders in good yield. In both compounds the microanalysis confirmed the purity of the compounds and mass spectroscopy showed the $[MNa]^+$ species. In the IR and Raman spectra the C-H stretching bands are observed at approximately 2950 cm^{-1}. The ring vibrations are observed at approximately 1430 and 1230 cm^{-1}. The methyl protons were observed in the ^1H NMR spectrum at 2.80 ($C5SCH_3$) and 2.65 ppm ($C3'SCH_3$). In the ^{13}C-{^1H} NMR spectra of **5.19** the methyl carbons were observed at 17.0 ($C5S\underline{C}H_3$) and 14.7 ppm ($C3'S\underline{C}H_3$). The signals of the ring carbons were observed at 191.9, 180.8, 170.5 and 163.4 ppm. The peaks at 191.9 and 170.5 were indisputably assigned as C5 and C3' respectively by H-C HMBC and H-C HSQC experiments. We have assigned the peaks at 180.8 and 163.4 as C5' and C3 based on comparison with the shifts recorded in the other 1,2,4-

thiadiazole compounds. In compound **5.20** the expected signals were observed in the correct ratio in the ^{1}H NMR. In the ^{13}C-{^{1}H} NMR spectra the peaks were noted at 191.8, 179.4, 169.4 and 163.6 ppm assigned as C5, C5', C3' and C3 respectively. H-C HMBC and H-C HSQC experiments confirmed the assignment of C5. X-ray quality crystals were obtained for both **5.19** and **5.20**. The X-ray structures confirmed that we had successfully linked our monomeric units together (Figures 5.8 and 5.9).

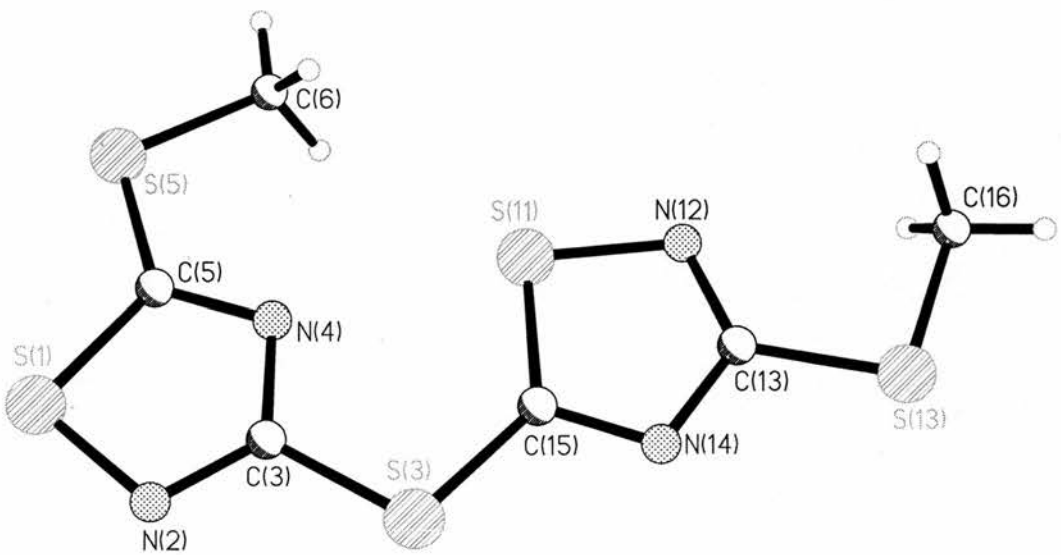


Figure 5.8 X-ray crystal structure of **5.19**.

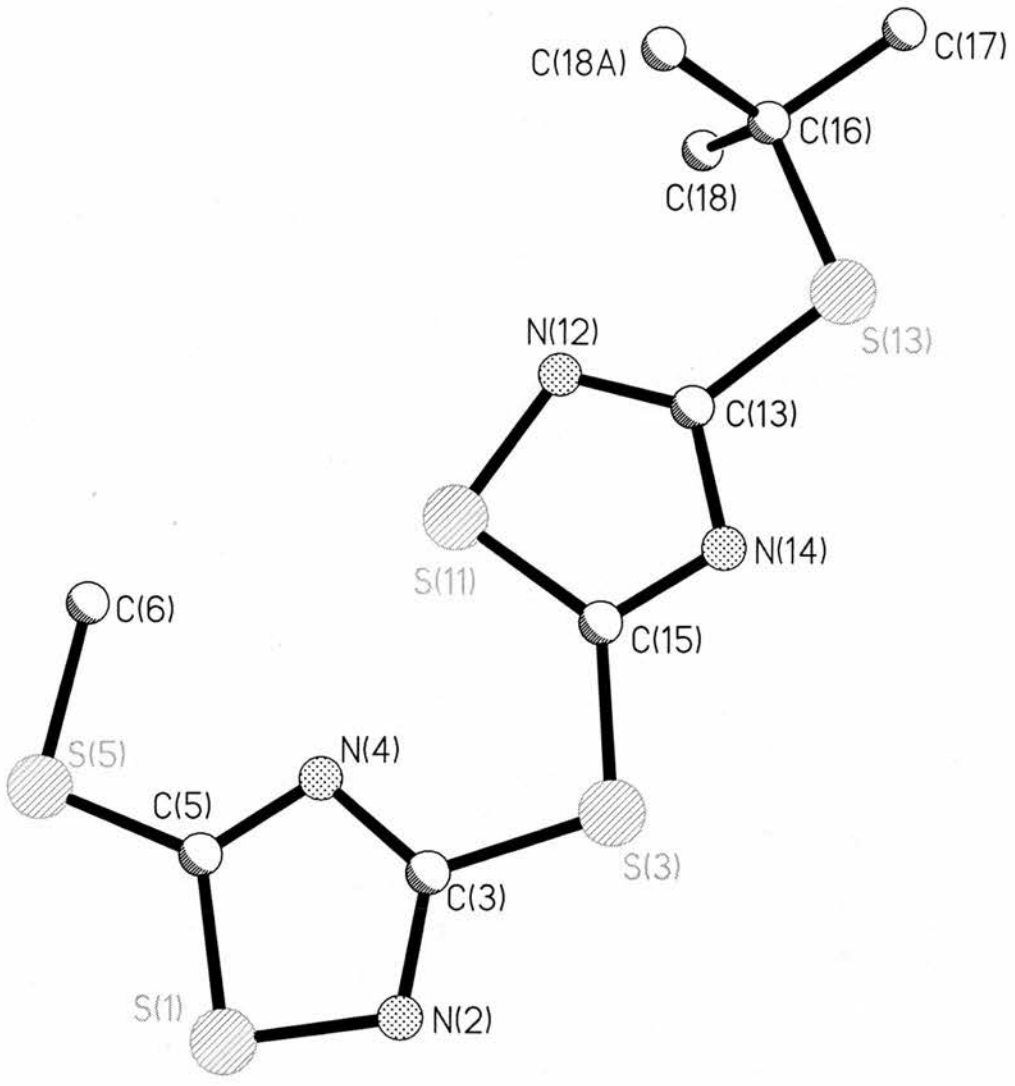
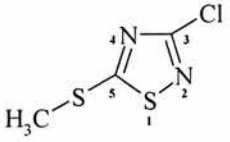
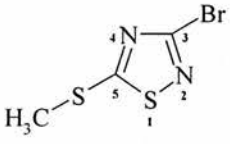
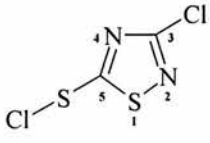
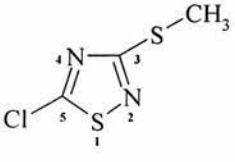
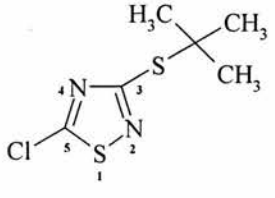
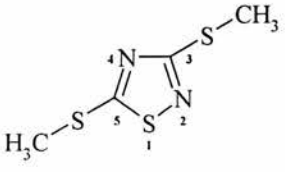


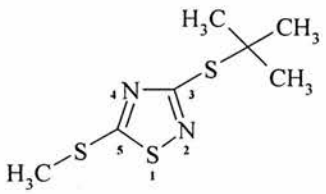
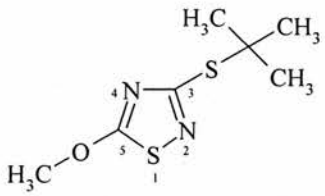
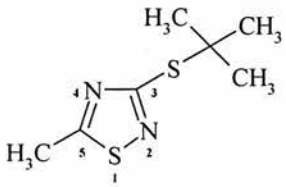
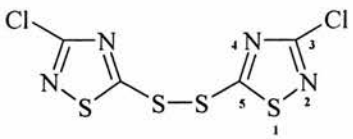
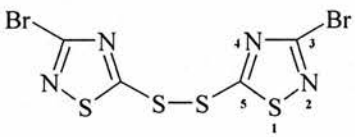
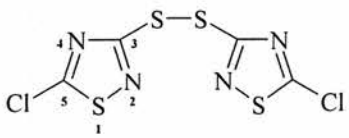
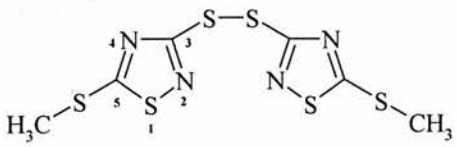
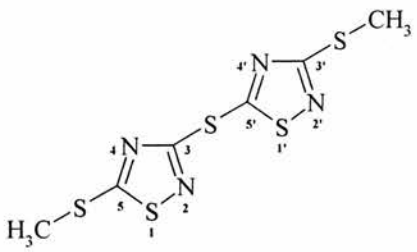
Figure 5.9 X-ray crystal structure of **5.20**.

5.2.3 *Discussion of data in relation to (SCN)x*

All of the 1,2,4-thiadiazole compounds **5.1-5.20** were found to be pure by microanalysis and the expected ions were observed in the mass spectra. X-ray crystallography has been used to establish the connectivity in selected examples. In the IR and Raman spectra the ring vibration are observed at approximately 1400 and 1200 cm^{-1}. The exact values were dependant on the nature of the

groups attached to the ring. These vibrations are in a similar range to the large central peak observed in polythiocyanogen. The ^{13}C NMR shifts for the ring carbons C5 and C3 are shown below in Table 5.1.

	Compound	δ(C) (ppm)	
		C5 [C5']	C3 [C3']
5.1		191.6	156.1
5.2		191.6	144.3
5.5		180.2	155.9
5.8		173.1	171.8
5.9		171.8	171.2
5.10		189.1	171.5

5.13		187.6	170.5
5.14		190.8	166.7
5.15		185.6	170.1
5.3		188.5	158.0
5.4		188.5	145.9
5.11		174.9	167.5
5.16		190.0	167.7
5.19		191.9 [180.5]	163.4 [170.5]

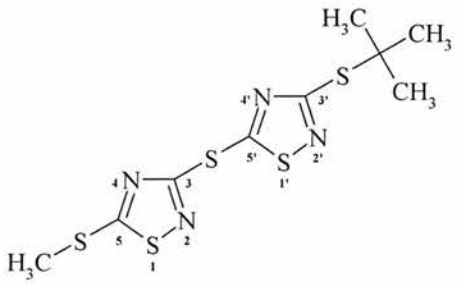
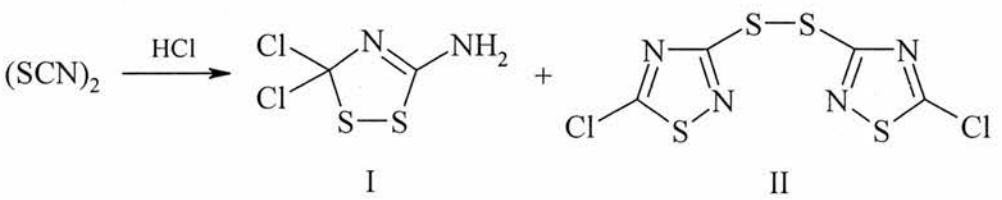
5.20		191.8 [179.4]	163.6 [169.4]

Table 5.1 ^{13}C-{^{1}H} NMR shifts for ring carbons in 1,2,4-thiadiazoles.

We note that C5 is observed in the range 180-192 ppm when bonded to alkyl, alkoxy and thioalkoxy groups. This value shifts upfield shift to approximately 172 ppm when C5 is bonded to chlorine. The peak corresponding to C3 is observed at approximately 171 ppm when bonded to thioalkoxy groups. When C3 is bonded to chlorine there is an upfield shift to approximately 156 ppm. If chlorine is replaced by bromine there is a further upfield shift to approximately 145 ppm. Thus C5 is always observed downfield of C3. In the ^{13}C-{^{1}H} NMR of polythiocyanogen, which we will discuss further in chapter 6, the main peaks are observed at 187 and 184 ppm. In the 1,2,4-thiadiazole model compounds the most downfield shift observed for C3 is 172 ppm. If $(SCN)_x$ had a 1,2,4-thiadiazole structure the C3 environment in the polymer would be comparable to that of C3 in **5.19** and **5.20** which are noted at approximately 163.5 ppm. In the 1,2,4-thiadiazole model compounds the most downfield shift observed for C3 is 172 ppm. This is strong evidence against a 1,2,4-thiadiazole structure for polythiocyanogen. Also ^{15}N NMR does not support a 1,2,4 thiadiazole structure for $(SCN)_x$. In the polymer peaks are observed in the range 170-237 ppm. In compound **5.4** the ^{14}N NMR spectrum shows two peaks at 310.6 and 278.4 ppm

assigned as N2 and N4 respectively. These nitrogen environments are clearly different to those in polythiocyanogen. Thus we conclude that polythiocyanogen does not have a 1,2,4-thiadiazole structure. This is further supported by the reaction of the lithium salt of bis(5-chloro-1,2,4-thiadiazol-3-yl) disulfide with itself. If the polymer was made of 1,2,4-thiadiazole rings this would form polythiocyanogen. Instead it gave a yellow solid which may be an oligomeric material as shown in scheme 5.21. In fact both ^{13}C and ^{15}N NMR data fit better with a 1,2,4-dithiazole structure which we will discuss in chapter 6.

As discussed in chapter 1 (p 29) Soderback reported that reaction of thiocyanogen $(SCN)_2$ with HCl yields two products $(SCN)_2.2HCl$ and $(SCN)_4Cl_2$ (Scheme 5.21).



I II

Scheme 5.21 Reaction of thiocyanogen with HCl

The structure of $(SCN)_2.2HCl$ is supported by IR data and the crystal structure of the derivative $(SCN)_2.H_2O$ has been determined by Hordvik.[86] We have resynthesised $(SCN)_2.2HCl$ and our data is in agreement with the 1,2,4-dithiazole ring structure except we propose that $(SCN)_2.2HCl$ is a salt (Figure 5.10).

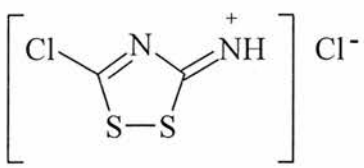


Figure 5.10 Proposed salt structure for $(SCN)_2.2HCl$.

This proposal is supported by EI positive mass spectroscopy which displays the $[S_2N_2C_2H_2Cl]^+$ ion at *m/z* 152 and not the $[S_2N_2C_2H_2Cl_2]^+$ ion at *m/z* 188. Soderback has proposed a bis(5-chloro-1,2,4-thiadiazol-3-yl) disulfide (II) for $(SCN)_4Cl_2$. In this chapter we have synthesised bis(5-chloro-1,2,4-thiadiazol-3-yl) disulfide **5.11**. Therefore we repeated the reaction of Soderback and isolated $(SCN)_4Cl_2$ to determine whether it is the same compound as **5.11**. $(SCN)_4Cl_2$ is an insoluble yellow powder. EI positive mass spectroscopy confirmed the molecular formula. The IR spectrum of $(SCN)_4Cl_2$ was comparable to $(SCN)_x$ consisting of a broad central peak comprised of several overlapping peaks. Strong peaks at 1630, 1500, 1406 and 1302 cm^{-1} can be picked out from this central peak. An intense peak is observed at 3038 cm^{-1} and a further peak at 642 cm^{-1} is noted. Raman spectroscopy did not yield any useful data. Due to the insolubility of $(SCN)_4Cl_2$ ^{13}C NMR was recorded in the solid state. The spectra showed two intense peaks at 175.2 and 168.5 ppm. The peak at 168.5 is split by residual coupling between carbon and chlorine. Lower intesity peaks are noted at 176.4, 143.0 and 125.3 ppm. Comparison with bis(5-chloro-1,2,4-thiadiazol-3-yl) disulfide **5.11** and bis(3-chloro-1,2,4-thiadiazol-5-yl) disulfide **5.3** shows some important differences. The most obvious difference is that **5.3** and **5.11** are soluble in organic solvents whereas $(SCN)_4Cl_2$ is not. In the IR spectra $(SCN)_4Cl_2$ displays strong peaks at 3038, 1630 and 1500 cm^{-1} but **5.3** and **5.11** do not. Both **5.3** and **5.11** display strong bands at approximately 1000 cm^{-1} but $(SCN)_4Cl_2$ does not. In the ^{13}C NMR spectra **5.3** displays peaks at 188.5 and 158.0 ppm corresponding to C5 and C3. **5.11** displays two peaks at 174.9 and 167.5 ppm corresponding to C5 and C3 respectively. Interestingly the ^{13}C NMR

shifts of **5.11** are very similar to the intense bands observed in $(SCN)_4Cl_2$. However in **5.11** the peak at 174.9 ppm corresponds to C5 which is next to chlorine whereas in $(SCN)_4Cl_2$ the peak at 168.5 ppm corresponds to carbon next to chlorine. Having assessed all the data we conclude that this compound does not have a 1,2,4-thiadiazole disulfide structure. We speculate that $(SCN)_4Cl_2$ is more likely to have a 1,2,4-dithiazole structure like isoperthiocyanic acid, $(SCN)_2.2HCl$ and other related compounds. A structure which would fit both ^{13}C NMR and mass spectroscopy is shown below but this is purely speculative (Figure 5.11).

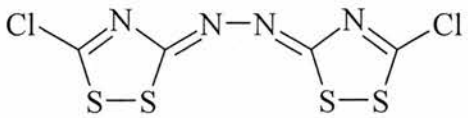


Figure 5.11 A speculative structure for $(SCN)_4Cl_2$.

An alternative speculative structure that is a logical progression from $(SCN)_2.2HCl$ is shown below (Figure 5.12).

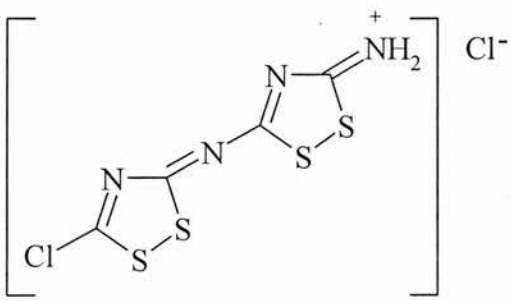


Figure 5.12 Alternative speculative structure for $(SCN)_4Cl_2$.

The RNH_2^+ group would explain the vibrations at 3038 and 1630 cm^{-1} in the IR spectrum but does not fit well with the mass spectrum and ^{13}C NMR data.

5.2.3 *X-ray Studies.*

We have carried out single crystal X-ray diffraction studies on 8 different 1,2,4-thiadiazole compounds to establish connectivity and for structural comparison. Selected bond lengths and angles for these compounds are shown below in Tables 5.2 and 5.3. In all the compounds bond lengths and angles within the 1,2,4-thiadiazole ring are very similar. The groups attached at C3 and C5 appear to have very little effect on bond lengths within the ring. The S(1)-N(1) bonds are in the range 1.650(3)-1.692(7) Å and the S(1)-C(5) bonds in the range 1.702(5)-1.737(5) Å indicating that these bonds are both single bonds. N(2)-C(3) and N(4)-C(5) have mostly double bond character and lie in the range 1.271(10)-1.349(10) Å. There is some delocalisation to C(3)-N(4) which is in the range 1.338(7)-1.425(11) Å and thus this bond has some double bond character. The angles in the ring are all lie in the range 103.7(5)-125.1(7) ^{o} with the exception of N(2)-S(1)-C(5) which are in the range 91.2(4)-93.0(4) ^{o} because it is constrained by the ring. The disulfide bridge S-S distance is approximately 2.05 Å in the 1,2,4-thiadiazole disulfides **5.3** and **5.4**. In complexes **5.7** and **5.12** the platinum core lies at the centre of a distorted square planar coordination sphere. The deviation from ideal geometry is illustrated by the S(3)-Pt(1)-S(13) angle [91.60(5) ^{o}] in **5.7** and the S(5)-Pt(1)-S(15) angle [83.61(8) ^{o}] in **5.12**.

Compound	**5.1**	**5.3**	**5.4**	**5.7**
S(1)-N(2)	1.661(2)	1.661(7)	1.659(4)	1.666(5)
S(11)-N(12)	-	1.662(7)	1.658(4)	1.692(7)
S(1)-C(5)	1.730(3)	1.716(5)	1.719(5)	1.737(5)
S(11)-C(15)	-	1.723(8)	1.702(5)	1.724(8)
N(2)-C(3)	1.310(4)	1.310(10)	1.313(6)	1.307(7)
N(12)-C(13)	-	1.307(10)	1.320(6)	1.271(10)
C(3)-N(4)	1.350(4)	1.355(9)	1.358(6)	1.338(7)
C(13)-N(14)	-	1.352(10)	1.378(6)	1.356(9)
N(4)-C(5)	1.319(3)	1.317(10)	1.321(6)	1.321(7)
N(14)-C(15)	-	1.314(10)	1.312(6)	1.302(9)
N(2)-S(1)-C(5)	92.29(12)	91.4(4)	91.7(2)	92.9(3)
N(12)-S(11)-C(15)	-	91.4(4)	92.1(2)	93.0(4)
C(3)-N(2)-S(1)	106.22(18)	106.7(5)	107.1(3)	105.6(4)
C(13)-N(12)-S(11)	-	107.2(5)	107.2(3)	103.7(5)
N(2)-C(3)-N(4)	122.3(4)	122.3(4)	121.5(4)	122.5(5)
N(12)-C(13)-N(14)	-	121.6(7)	120.2(4)	125.1(7)
C(5)-N(4)-C(3)	107.2(2)	105.7(6)	106.5(4)	108.6(5)
C(15)-N(14)-C(13)	-	106.9(6)	106.5(4)	107.1(6)
N(4)-C(5)-S(1)	111.9(2)	113.9(6)	113.2(4)	110.3(4)
N(14)-C(15)-S(11)	-	113.0(6)	113.9(4)	111.2(6)

Table 5.2 Selected bond lengths (Å) and angles (°) for **5.1**, **5.3**, **5.4** and **5.7**.

Compound	**5.8**	**5.12**	**5.19**	**5.20**
S(1)-N(2)	1.6629(13)	1.657(8)	1.667(3)	1.650(3)
S(11)-N(12)	-	1.653(8)	1.666(3)	1.657(2)
S(1)-C(5)	1.7074(14)	1.712(11)	1.735(3)	1.723(3)
S(11)-C(15)	-	1.719(9)	1.721(3)	1.719(3)
N(2)-C(3)	1.3160(18)	1.312(12)	1.312(4)	1.314(4)
N(12)-C(13)	-	1.349(10)	1.305(4)	1.309(4)
C(3)-N(4)	1.383(2)	1.425(11)	1.367(4)	1.356(4)
C(13)-N(14)	-	1.382(10)	1.384(4)	1.383(4)
N(4)-C(5)	1.2999(18)	1.275(12)	1.319(4)	1.320(4)
N(14)-C(15)	-	1.284(10)	1.316(4)	1.312(4)
N(2)-S(1)-C(5)	91.80(7)	91.2(4)	92.55(15)	92.41(15)
N(12)-S(11)-C(15)	-	91.8(4)	91.97(15)	91.66(13)
C(3)-N(2)-S(1)	107.10(10)	109.6(7)	106.7(2)	107.2(2)
C(13)-N(12)-S(11)	-	107.6(6)	107.8(2)	108.8(2)
N(2)-C(3)-N(4)	120.36(13)	116.4(8)	121.2(3)	120.7(3)
N(12)-C(13)-N(14)	-	118.4(7)	120.0(3)	118.8(3)
C(5)-N(4)-C(3)	106.53(12)	108.2(8)	108.1(3)	107.8(3)
C(15)-N(14)-C(13)	-	108.1(7)	107.5(3)	108.0(2)
N(4)-C(5)-S(1)	114.22(12)	114.3(7)	111.5(3)	111.8(2)
N(14)-C(15)-S(11)	-	114.1(6)	115.5(2)	112.7(7)

Table 5.3 Selected bond lengths (Å) and angles (°) for **5.8**, **5.12**, **5.19** and **5.20**.

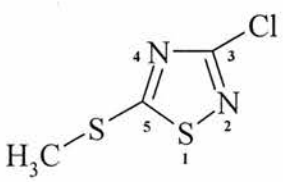
5.3 *Conclusions*

In this chapter we report the synthesis and characterisation of a series of 1,2,4-thiadiazole compounds. We have successfully linked two 1,2,4-thiadiazole rings together by nucleophilic substitution at C5. Selected examples have been studied by X-ray crystallography. Comparison of ^{13}C and ^{14}N NMR data with polythiocyanogen $(SCN)_x$ does not support a 1,2,4-thiadiazole structure for the polymer. The NMR data favours a 1,2,4-dithiazole structure for polythiocyanogen which we will discuss further in chapter 6. Furthermore we have shown the compound with molecular formula $(SCN)_4Cl_2$ generated by reaction of $(SCN)_2$ with HCl is not bis(5-chloro-1,2,4-thiadiazol-3-yl) disulfide. We speculate that it may have a 1,2,4-dithiazole structure like isoperthiocyanic acid.

5.4 *Experimental*

General experimental conditions and instrumentation were as set out on page 55. Dipotassium cyanodithioimidocarbonate **2.1** was prepared as in chapter 2. potassium methyl cyanodithioimidocarbonate was prepared by reaction of **2.1** with methyl iodide.[126] S-methylisothiourea hydrochloride and S-*tert*-butylisothiourea hydrochloride were prepared by the reaction of thiourea, HCl and methanol or tertiary butanol respectively.[128] $[PtCl_2(dppe)]$ (dppe= bis(diphenylphosphino)ethane was prepared by the addition of a stoichiometric quantity of the diphosphine to a dichloromethane solution of $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene). Chlorine (BOC) was dried by passing the gas over phosphorus pentoxide. Ammonium hydroxide, bromine, copper (I) chloride, ferric acetylacetonate, lithium triethylborohydride 1M in tetrahydrofuran, *N*-methylpyrrolidone, methyl magnesium bromide, sodium hydroxide, sodium methoxide, sodium thiomethoxide, sulfuryl chloride, trichloromethylsulfenyl chloride (all Aldrich) were used as received.

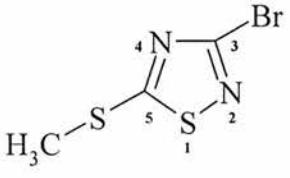
5.1



A slurry of potassium methyl cyanodithioimidocarbonate (1.257 g, 7.381 mmol) in dichloromethane (30 cm^3) was stirred at 0 °C while sulfuryl chloride (1.267 g, 9.387 mmol) was added dropwise. The resultant mixture was stirred for a further 24 hours at room temperature. The mixture was filtered to remove precipitated

KCl then the solvent was then removed in vacuo to give the product as a pale yellow crystalline solid. Yield 1.048g (85 %). Found (Calc. for $C_3H_3N_2S_2Cl$): C 21.74 (21.62), H 1.42 (1.81) N 16.99 (16.81) %. ^{13}C-{^1H} NMR (CD_2Cl_2): δ(C) 191.9 (s, C5), 156.1 (s, C3), 16.5 (s, CH_3). ^1H NMR (CD_2Cl_2): δ 2.70 (s, 3H, C5CH_3). ES^+ MS: *m/z* 167 $[MH]^+$. IR (KBr): 2990w, 2959vw, 2922w, 2854w, 1433s, 1425s, 1363w, 1345m, 1330w, 1229s, 1174w, 1073s, 1050m, 977m, 969m, 919m, 897w, 804m, 711w, 678m, 550w, 535w, 482w, 376w cm^{-1}. Raman (glass capillary): 3006w, 2995m, 2921s, 1365w, 1347vs, 1327w, 1233w, 918w, 806w, 715w, 680vs, 421vs, 380w, 258w cm^{-1}.

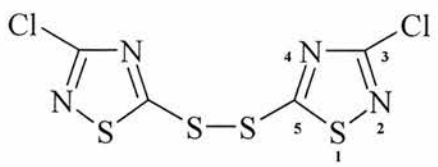
5.2



This was prepared in the same fashion as compound **5.2** using potassium methyl cyanodithioimidocarbonate (4.330 g, 0.025 mol) and bromine (4.063 g, 0.025 mol) to give the product as a pale yellow crystalline solid. Yield 5.043 g (95 %). Found (Calc. for $C_3H_3BrN_2S_2$): C 17.07 (17.36), H 1.01 (1.43) N 13.45 (13.27) %. ^{13}C-{^1H} NMR ($CDCl_3$): δ(C) 191.6 (s, C5), 144.3 (s, C3), 16.6 (s, CH_3). ^1H NMR ($CDCl_3$): δ 2.73 (s, 3H, C5CH_3). ES^+ MS: *m/z* 213 $[MH]^+$. IR (KBr): 2989w, 2918w, 1561w, 1491w, 1415s, 1354m, 1332m, 1324m, 1208br,s, 1192s, 1096w, 1071s, 1048m, 974m, 968m, 894s, 786m, 712w, 667m, 547w, 456m, 378w, 305w, 250w cm^{-1}. Raman (glass capillary): 3004w,

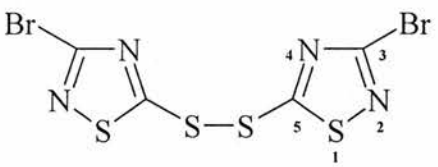
2993w, 2920s, 1423vw, 1354m, 1347m, 1322s, 1210w, 891m, 714m, 673s, 381m, 307s, 228w cm^{-1}.

5.3



A slurry of dipotassium cyanodithioimidocarbonate **2.1** (7.535 g, 0.039 mol) in dichloromethane (40 cm^3) was stirred at –40 °C while chlorine (5.498 g, 0.078 mol) in dichloromethane (50 cm^3) was slowly added. The reaction mixture was stirred for 1 hour at 0 °C then suction filtered. The dichloromethane was then removed *in vacuo* to give the product as a yellow crystalline solid. Yield 4.748g (81 %). Found (Calc. for $C_4N_4Cl_2S_4$): C 15.99 (15.84), N 18.45 (18.48) %. ^{13}C-$\{^1H\}$ NMR ($CDCl_3$): δ(C) 188.5 (s, C5), 158.0 (s, C3). EI^+ MS: *m/z* 302 $[M]^+$. IR (KBr): 2757w, 2423w, 1606w, 1435s, 1362m, 1342s, 1216br,s, 1096w, 1061s, 951w, 806s, 677m, 555w, 542w, 481m, 418w, 410w, 373m, 357w cm^{-1}. Raman (glass capillary): 1436w, 1365m, 1342vs, 1223w, 915m, 809m, 681m, 560w, 538w, 471w, 419m, 376w, 360w cm^{-1}.

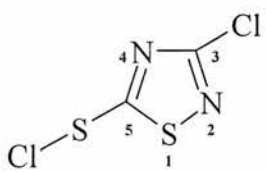
5.4



A slurry of dipotassium cyanodithioimidocarbonate **2.1** (2.00 g, 0.010 mol) in dichloromethane (20 cm^3) was stirred at –40 °C while bromine (3.289 g, 0.021 mol) in dichloromethane (10 cm^3) was added dropwise. The mixture was stirred

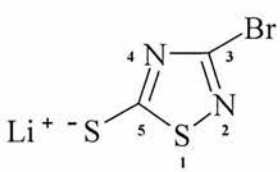
for a further 2 hours at 10 °C. The solvent and excess bromine was removed *in vacuo*. The product was dissolved in dichloromethane (40 cm^3) and the solution was filtered. The solvent was removed *in vacuo* and the product recrystallised from dichloromethane/ether to give a cream crystalline solid. Yield 1.530 g (76 %). Found (Calc. for $C_4N_4S_4Br_2$): C 12.56 (12.25), N 14.18 (14.29) %. ^{13}C-{^1H} NMR ($CDCl_3$): δ(C) 188.5 (s, C5), 145.9 (s, C3). ^{14}N NMR ($CDCl_3$): δ = 310.6 (s, N2), 278.4 ppm (s, N4). IR (KBr): 1586w, 1561w, 1424s, 1348m, 1325m, 1193br,s, 1082w, 1059m, 942w, 891s, 796m, 784m, 679w, 665m, 547m, 535m, 338m, 438m cm^{-1}. Raman (glass capillary): 1426w, 1350s, 1326m, 1194w, 1065w, 895m, 798m, 782w, 674s, 534m, 440w, 403w, 359w, 301s cm^{-1}.

5.5



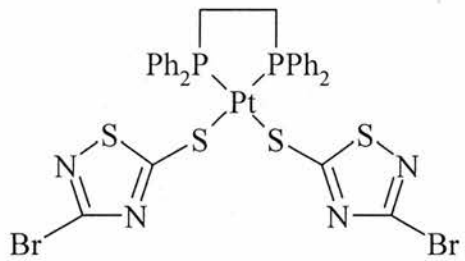
Bis(3-chloro-1,2,4-thiadiazol-5-yl) disulfide **5.3** (1.000 g, 3.298 mmol) was dissolved in dichloromethane and cooled to 0 °C. Chorine gas (excess) was bubbled through the solution. The solution was then stirred for a further hour at room temperature then the solvent was removed in vacuo to give the product as a yellow solid. Yield 1.041g (84%). ^{13}C-{^1H} NMR ($CDCl_3$): δ(C) 180.2 (s, C5), 155.9 (s, C3).

5.6



Bis(3-bromo-1,2,4-thiadiazol-5-yl) disulfide **5.4** (0.200 g, 0.510 mmol) was dissolved in tetrahydrofuran (20 cm^3). The solution was cooled to -40 °C and a 1.0 M tetrahydrofuran solution of $LiBEt_3H$ (0.108 g, 1.020 mmol) was added dropwise. The clear solution was observed to change to pale yellow on addition of $LiBEt_3H$. The reaction mixture was then allowed to warm to room temperature and stirred for a further hour. The solvent was evaporated *in vacuo* to yield the product as a yellow powder. Yield 0.171 g (83 %). Found (Calc. for $C_2N_2S_2BrLi$) ES^- MS: *m/z* 197 $[M]^-$. IR (KBr): 2215s, 1639s, 629s, 1434s, 1426m, 1323m, 1225s, 1096w, 1078w, 1064w, 1052w, 938m, 908m, 790w, 780w, 722w, 675w, 594w, 571w, 462w, 307w cm^{-1}.

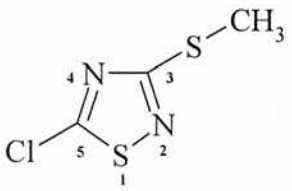
5.7



Bis (3-bromo-1,2,4-thiadiazol-5-yl) disulfide **5.4** (0.089 g, 0.226 mmol) was dissolved in tetrahydrofuran (10 cm^3). The solution was cooled to -40 °C and a 1.0 M tetrahydrofuran solution of $LiBEt_3H$ (0.048 g, 0.452 mmol) was added dropwise. The clear solution was observed to change to pale yellow on addition of $LiBEt_3H$. The reaction mixture was then stirred for a further hour at –40 °C then $[PtCl_2(dppe)]$ (0.150 g, 0.226 mmol) was added as a solid in one portion with a further portion of tetrahydrofuran (10 cm^3). The solution was allowed to warm to room temperature and stirred for 24 hours. The solvent was then removed under reduced pressure and the residue dissolved in dichloromethane

(30 cm^3). The resultant mixture was filtered through a celite pad (to removed precipitated LiCl) and the solvent removed in vacuo to give the product as a pale yellow powder. Crystals suitable for X-Ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.119 g (53 %). Found (Calc. for $C_{30}H_{24}Br_2P_2PtN_4S_4.C_4H_4O$): C 38.14 (38.61), H 2.75 (3.05), N 5.43 (5.30) %. ^{31}P-{^1H} NMR (CD_2Cl_2): δ(P) 47.6 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3012 Hz. ^1H NMR (CD_2Cl_2): δ 7.91-7.33 (m, 20 H, aromatic), 2.58-2.30 (m, 4H, PCH_2CH_2P). ES^+ MS: *m/z* 1009 $[M+Na]^+$. IR (KBr): 3055w, 2990vw, 2958w, 2925w, 1484w, 1437m, 1411s, 1333w, 1308s, 1200s, 1160w, 1150w, 1106m, 1040m, 1028w, 998w, 882s, 819w, 744w, 718m, 706m, 689s, 536s, 484m, 357w cm^{-1}.

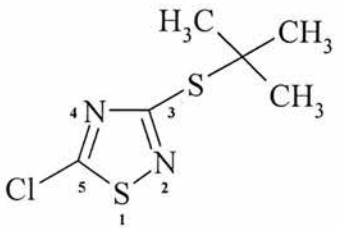
5.8



S-methylisothiourea hydrochloride (20.000 g, 0.158 mol) was suspended in dichloromethane (200 cm^3). A small volume of water (4 cm^3) was added and the mixture cooled to -10 °C. Trichloromethylsulfenyl chloride (29.364 g, 0.158 mol) in diethyl ether (50 cm^3) and sodium hydroxide (25.273 g, 0.632 mol) in water (50 cm^3) were added dropwise over one hour while the mixture was kept at -10 °C. The mixture was then stirred for a further two hours at room temperature followed by the addition of ammonium hydroxide (5 cm^3). The organic layer was then extracted with dichloromethane (2 x 150 cm^3). The solvent was then removed *in vacuo*. The product was then isolated by distillation *in vacuo* at 50

°C using Kugelrohr apparatus. The product was found to be a pale yellow oil which upon cooling became a pale yellow crystalline solid. Crystals suitable for X-Ray diffraction were obtained. Yield 15.830 g (60 %). Found (Calc. for $C_3H_3ClN_2S_2$): C 21.80 (21.62), H 1.84 (1.81), N 16.51 (16.81) %. ^{13}C-{^1H} NMR (CD_2Cl_2): δ(C) 173.1 (s, C5), 171.8 (s, C3), 14.8 (s, CH_3). ^1H NMR (CD_2Cl_2): δ 2.58 (s, 3H, SCH_3). ES^+ MS: *m/z* 167 $[MH]^+$. IR (KBr): 3002w, 2928m, 2783w, 2511vw, 1606w, 1452s, 1347m, 1334w, 1316m, 1216s, 1065s, 977m, 907s, 807w, 722w, 538w, 508w, 489m, 442w, 344w cm^{-1}.

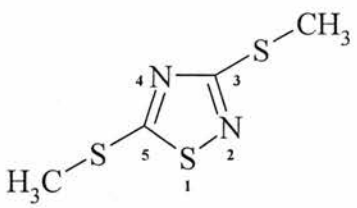
5.9



This was prepared in the same fashion as compound **5.8** using S-*tert*-butylisothiourea hydrochloride (20.000 g, 0.119 mol), trichloromethylsulfenyl chloride (22.039 g, 0.119 mol) and sodium hydroxide (18.968 g, 0.474 mol). The product was then isolated by distillation *in vacuo* at 70 °C using Kugelrohr apparatus. This gave the product as a yellow oil. Yield 18.743 g (76 %). Found (Calc. for $C_6H_9ClN_2S_2$): C 34.07 (34.52), H 4.59 (4.35), N 13.01 (13.42) %. ^{13}C-{^1H} NMR (CD_2Cl_2): δ(C) 171.8 (s, C5), 171.2 (s, C3), 48.1 (s, $\underline{C}(CH_3)_3$), 30.3 (s, $C(\underline{C}H_3)_3$). ^1H NMR (CD_2Cl_2): δ 1.56 (s, 9H, $C(CH_3)_3$). ES^+ MS: *m/z* 152.9 $[MH\text{-}^tBu]^+$. IR (KBr): 2992s, 2964s, 2925s, 2865s, 2777m, 2745w, 2717w, 2507w, 1602m, 1476s, 1448s, 1393s, 1365s, 1344s, 1321s, 1222s, 1197s, 1156s, 1063s, 1037m, 1027m, 957w, 934m, 908s, 807m, 740w, 713w, 688s, 589m, 538m, 524m, 484s, 436w, 409w, 374w, 306w cm^{-1}.

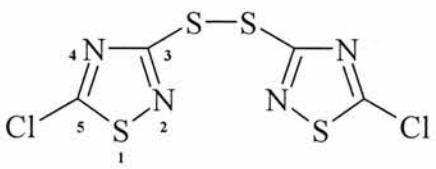
Raman (glass capillary): 2970 s, 2927vs, 1452w, 1347s, 1200w, 1162w, 936vw, 911vw, 809w, 687s, 591m, 411m, 309s cm^{-1}.

5.10



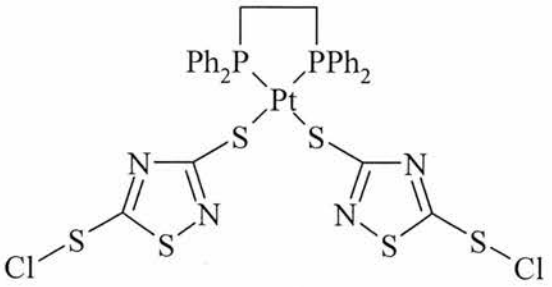
3-methylsulfanyl-5-chloro-1,2,4-thiadiazole **5.8** (1.000 g. 6.001 mmol) was dissolved in methanol (40 cm^3). Sodium thiomethoxide (0.421 g, 6.001 mmol) was added as a solid in one portion. The resultant solution was heated to 40 °C for 24 hours. The solvent was removed *in vacuo* and dichloromethane (50 cm^3) added. The resultant mixture was filtered through a celite pad to remove precipitated NaCl. The solvent was then removed *in vacuo* to give the product as a yellow oil. Yield 0.883 g (83 %). Found (Calc. for $C_4H_6N_2S_3$): C 26.93 (26.95), H 3.36 (3.39), N 15.64 (15.71) %. ^{13}C-{^1H} NMR (CD_2Cl_2): δ(C) 189.1 (s C5), 171.5 (s, C3), 16.8 (s, C5S<u>C</u>H_3), 15.1 (s, C3S<u>C</u>H_3). ^1H NMR (CD_2Cl_2): δ 2.59 (s, 3H, C3SCH_3), 2.53 (s, 3H, C5CH_3). ES^+ MS: *m/z* 178 $[MH]^+$. IR (KBr): 3000w, 2927m, 2845vw, 2413vw, 2282vw, 1591w, 1526m, 1424s, 1371w, 1348m, 1314m, 1218s, 1091w, 1067s, 1050s, 968s, 932w, 908s, 802m, 736w, 714w, 684m, 588vw, 546w, 508vw, 489w, 470w, 443w, 383w, 331vw cm^{-1}. Raman (glass capillary): 3001w, 2929vs, 1426w, 1372m, 1350s, 1316m, 1219w, 910w, 803w, 721m, 683m, 672m, 448m, 409vw, 384w, 335w, 302w, 261w cm^{-1}.

5.11



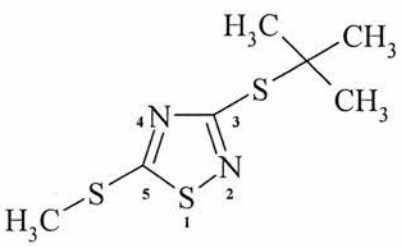
3-*tert*-butylsulfanyl-5-chloro-1,2,4-thiadiazole **5.9** (1.000g, 4.791 mmol) was dissolved in dichloromethane (30 cm^3) and cooled to 0 °C. Chlorine gas (excess) was bubbled slowly through the solution for 20 minutes. The dichloromethane and excess chlorine were removed under reduced pressure. The residue was then dissolved in tetrahydrofuran (30 cm^3) and copper (I) chloride (0.474 g, 4.791 mmol) was added. The resultant solution was stirred in the dark for two hours. Reaction was observed to be complete when the green copper (I) chloride was converted to brown copper (II) chloride. The solvent was removed *in vacuo* and the residue dissolved in dichloromethane (30 cm^3). The mixture was filtered through celite and the solvent removed *in vacuo*. The product was isolated by column chromatography on silica eluting with a 50:50 mixture of dichloromethane/hexane. The product was obtained as a cream powder. Yield 0.256 g (35 %). Found (Calc. for $C_4Cl_2N_4S_4$): C 15.68 (15.84), N 18.27 (17.82) %. ^{13}C-{^1H} NMR (CD_2Cl_2): δ(C) 174.9 (s, C5), 167.5 (s, C3). ES^+ MS: *m/z* 325 $[MNa]^+$, 303 $[MH]^+$. IR (KBr): 2764w, 1442s, 1436s, 1379w, 1360w, 1339m, 1213s, 1203s, 1082s, 1072s, 1007br,s, 905s, 801w, 685m, 674m, 539m, 486m, 471m, 380m, 348m, 302w, 282w, 271w cm^{-1}. Raman (glass capillary): 1359m, 1341m, 1211w, 907w, 805w, 693vs, 547m, 473w, 443m, 318vs, 271vw, 241s cm^{-1}.

5.12



This was prepared in the same fashion as compound **5.7** using **5.11** (0.046 g, 0.151 mmol), a 1.0 M tetrahydrofuran solution of $LiBEt_3H$ (0.032 g, 0.302 mmol) and $[PtCl_2(dppe)]$ (0.100 g, 0.151 mmol) to give the product as a pale yellow powder. Crystals suitable for X-Ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.098 g (73 %). Found (Calc. for $C_{30}H_{24}Cl_2P_2PtN_4S_4$): C 38.93 (39.18), H 2.36 (2.63), N 5.70 (6.09) %. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ(P) 46.3 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3045 Hz. ^1H NMR ($CDCl_3$): δ 7.83-7.27 (m, 20 H, aromatic), 2.61-2.21 (m, 4H, PCH_2CH_2P). EI^+ MS: *m/z* 919 $[M+Na]^+$. IR (KBr): 3050w, 2920w, 2851w, 2179w, 1478m, 1445s, 1436s, 1308wm 1183m, 1164m, 1105m, 1051m, 1027w, 999w, 897w, 882w, 817w, 749w, 705m, 690m, 534m, 487w, 282w cm^{-1}.

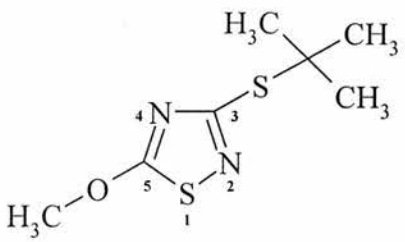
5.13



This was prepared in the same fashion as compound **5.10** using 3-*tert*-butylsulfanyl-5-chloro-1,2,4-thiadiazole **5.9** (2.000 g, 9.582 mmol) and sodium thiomethoxide (0.672 g, 9.588 mmol) to give the product as a yellow oil. Yield 1.475 g (70 %) Found (Calc. for $C_7H_{12}N_2S_3$): C 38.56 (38.15), H 5.48 (5.49), N

12.89 (12.71) %. ^{13}C-{^{1}H} NMR ($CDCl_3$): δ(C) 187.6 (s C5), 170.5 (s, C3), 47.9 (s, $\underline{C}(CH_3)_3$), 30.5 (s, $C(\underline{C}H_3)_3$), 16.6 (s, C5S$\underline{C}H_3$). ^{1}H NMR ($CDCl_3$): δ 2.62 (s, 3H, C5SCH_3), 1.50 (s, 9H, $C(CH_3)_3$). ES^+ MS: *m/z* 243 $[MNa]^+$. IR (KBr): 2992m, 2963s, 2923s, 2864m, 2715vw, 1587w, 1526m, 1475m, 1456m, 1427br,s, 1391m, 1364s, 1347m, 1313m, 1230s, 1199br,s, 1157s, 1063s, 1050s, 969m, 934m, 910s, 800m, 738m, 706w, 686m, 590w, 547w, 521w, 485w, 466w, 411w, 376w cm^{-1}. Raman (glass capillary): 2996w, 2967m, 2922vs, 1454w, 1374w, 1349s, 1316w, 1201w, 1160vw, 912w, 808w, 711w, 685m, 675m, 593m, 489w, 414w, 353w, 312m, 226w cm^{-1}.

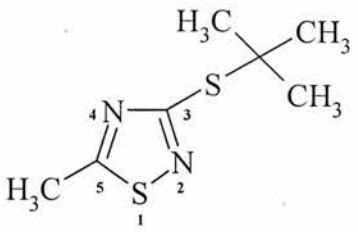
5.14



This was prepared in the same fashion as compound **5.10** using 3-*tert*-butylsulfanyl-5-chloro-1,2,4-thiadiazole **5.9** (0.500 g, 2.395 mmol) and sodium methoxide (0.129 g, 4.054 mmol). The solution was heated under reflux for 24 hours. This gave the product as yellow oil. Yield 0.412 g (84 %). Found (Calc. for $C_7H_{12}N_2OS_2$): C 40.88 (41.15), H 5.80 (5.92), N 14.10 (13.71) %. ^{13}C-{^{1}H} NMR (CD_2Cl_2): δ(C) 190.3 (s C5), 166.7 (s, C3), 60.4 (s, OCH_3), 47.6 (s, $\underline{C}(CH_3)_3$), 30.1 (s, $C(\underline{C}H_3)_3$). ^{1}H NMR (CD_2Cl_2): δ 4.10 (s, 3H, OCH_3), 1.55 (s, 9H, $C(CH_3)_3$). ES^+ MS: *m/z* 227 $[MNa]^+$. IR (KBr): 2994m, 2963s, 2923s, 2866m, 2757w, 1528s, 1476m, 1434br,s, 1401s, 1389s, 1364s, 1230br,s, 1181s, 1158s, 1065w, 1031m, 975m, 935m, 792, 779m, 738w, 689m, 591m, 492w, 407m, 377m cm^{-1}. Raman (glass capillary): 2964s, 2925vs,

1528w, 1456m, 1436m, 1403w, 1224w, 1157w, 935w, 810m, 782m, 690w, 591s, 494w, 427w, 409m, 376w, 307w cm^{-1}.

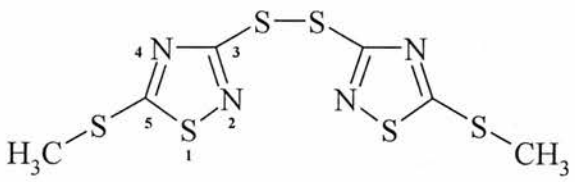
5.15



3-*tert*-butylsulfanyl-5-chloro-1,2,4-thiadiazole **5.9** (1.00 g, 4.791 mmol) was dissolved in tetrahydrofuran (35 cm^3) with *N*-methylpyrrolidone (3.5 cm^3) and a catalytic amount of [Fe(acac)$_3$] (0.077g, 0.240 mmol). A solution of methyl magnesium bromide (3.0M in diethyl ether, 1.76 cm^3, 5.270 mmol) was added dropwise to the resultant red solution. This caused the colour to change to brown. After 10 minutes when the colour had changed to dark purple the reaction mixture was diluted with diethyl ether (40 cm^3) and quenched by the addition of hydrochloric acid (1.0M, 2 cm^3). After extraction of the organic phase the product was isolated by column chromatography on silica eluting with a 50:50 mixture of dichloromethane/hexane. This gave the product as a pale yellow oil. Yield 0.632 g (70 %). Found (Calc. for $C_7H_{12}N_2S_2$): C 44.42 (44.65), H 6.11 (6.42), N 14.31 (14.88) %. ^{13}C-{^1H} NMR (CD_2Cl_2): δ(C) 185.6 (s C5), 170.1 (s, C3), 47.5 (s, $\underline{C}(CH_3)_3$), 30.3 (s, $C(\underline{C}H_3)_3$), 16.6 (s, $C5\underline{C}H_3$). ^1H NMR (CD_2Cl_2): δ 2.68 (s, 3H, $C5CH_3$), 1.54 (s, 9H, $C(CH_3)_3$). ES^+ MS: *m/z* 211 $[MNa]^+$. IR (KBr): 2993m, 2962s, 2923s, 2865s, 2715w, 1611w, 1488s, 1448s, 1393m, 1377s, 1364s, 1343m, 1234s, 1207s, 1159s, 1065m, 1035w, 1025w, 993w, 935m, 909w, 852w, 810m, 695m, 675w, 587m, 533w, 493w, 424w, 378w cm^{-1}. Raman (glass capillary): 2967m, 2928s,

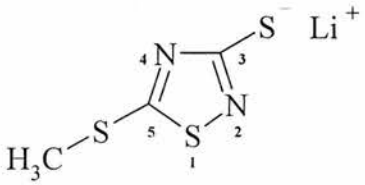
1454w, 1395w, 1380m, 1346w, 1216w, 1163w, 933w, 813m, 677m, 596m, 496w, 425w, 378vww, 338w, 307vw, 279vw cm^{-1}.

5.16



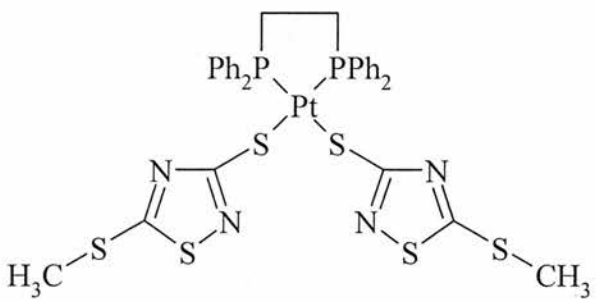
3-*tert*-butylsulfanyl-5-methylsulfanyl-1,2,4-thiadiazole **5.13** (1.000 g, 4.538 mmol) was dissolved in dichloromethane (30 cm^3) and cooled to 0 °C. Chlorine gas (excess) was bubbled slowly through the solution for 20 minutes. The dichloromethane and excess chlorine were removed under reduced pressure to yield a yellow oil. The product was isolated by column chromatography on silica eluting with a 50:50 mixture of dichloromethane/hexane. The product was obtained as a off white solid. Yield 0.191g (13 %). Found (Calc. for $C_6H_6N_4S_6$): C 21.74 (22.07), H 1.81 (1.85), N 16.89 (17.16) %. ^{13}C-{^1H} NMR (CD_2Cl_2): δ(C) 190.0 (s C5), 167.7 (s, C3), 16.8 (s, C5$\underline{C}H_3$). ^1H NMR (CD_2Cl_2): δ 2.67 (s, 3H, C5CH_3). ES^+ MS: *m/z* 349 $[MNa]^+$. IR (KBr): 3000vw, 2926w, 2913w, 2853w, 1595w, 1518w, 1433m, 1415s, 1357w, 1337m, 1317w, 1211s, 1151w, 1089w, 1067m, 1020s, 974m, 966w, 910m, 801m, 715w, 682w, 671w, 543w, 461w, 385w, 278w, 258w cm^{-1}.

5.17



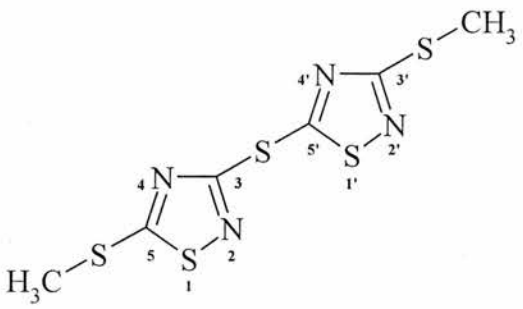
This was prepared in the same fashion as compound **5.6** using **5.16** (0.100 g, 0.306 mmol) and a 1.0 M tetrahydrofuran solution of $LiBEt_3H$ (0.065 g, 0.613 mmol) to give the product as a yellow powder. Yield 0.064 g (63 %). Found (Calc. for $C_3H_3N_2S_3Li$): C 20.91(21.55), N 16.32 (16.76) %. ES^- MS: *m/z* 163 $[M]^-$, 131 $[M\text{-}S]^-$. IR (KBr): 3038w, 2970w, 2928w, 2902s, 2182w, 1509w, 1399s, 1316w, 1306m, 1179s, 1167s, 1097w, 1078m, 980w, 957w, 923w, 805w, 728w, 697m, 668w, 495w, 438w, 381w, 323w cm^{-1}.

5.18



This was prepared in the same fashion as **5.7** using **5.16** (0.049g, 0.151 mmol), a 1.0 M tetrahydrofuran solution of $LiBEt_3H$ (0.032 g, 0.302 mmol) and $[PtCl_2(dppe)]$ (0.100 g, 0.151 mmol) to give the product as a pale yellow powder. Yield 0.107 g (78 %). Found (Calc. for $C_{32}H_{30}P_2PtN_4S_6$): C 41.42 (41.78), H 2.89 (3.29), N 6.23 (6.09) %. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ(P) 46.2 ppm. $^1J(^{195}Pt\text{-}^{31}P)$ 3047 Hz. ^1H NMR ($CDCl_3$): δ 7.81-7.23 (m, 20 H, aromatic), 2.70-2.16 (m, 4H, PCH_2CH_2P). EI^+ MS: *m/z* 942 $[M+Na]^+$. IR (KBr): 3050w, 2961w, 2920w, 2866w, 1483w, 1435m, 1412s, 1309m, 1262m, 1175s, 1103s, 1042m, 1027m, 997m, 966w, 898w, 879w, 817m, 802m, 748m, 714m, 704m, 690s, 660w, 532s, 485m, 397w cm^{-1}.

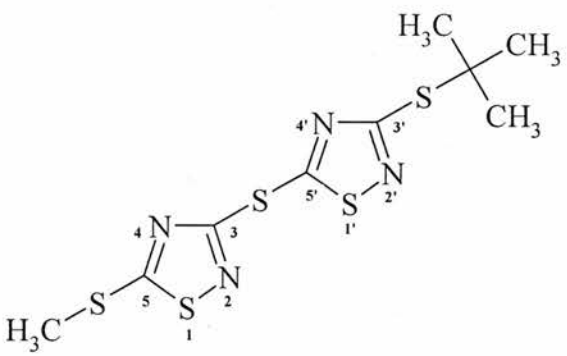
5.19.



5.16 (0.100 g, 0.306 mmol) was dissolved in tetrahydrofuran (20 cm^3). The solution was cooled to -40 °C and a 1.0 M tetrahydrofuran solution of $LiBEt_3H$ (0.065 g, 0.613 mmol) was added dropwise. The clear solution was observed to change to pale yellow on addition of $LiBEt_3H$. The reaction mixture was then stirred for a further hour. 3-methylsulfanyl-5-chloro-1,2,4-thiadiazole **5.8** (0.102 g, 0.613 mmol) was then added as a solid in one portion. The resulting solution was stirred for 24 hours. The solvent was evaporated *in vacuo* and the remaining solid was extracted with dichloromethane (20 cm^3). The mixture was filtered through a celite pad to remove precipitated LiCl and washed through with additional dichloromethane (30 cm^3). The filtrate was evaporated to dryness *in vacuo* to give a cream powder. Crystals suitable for X-Ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.120 g (67 %). Found (Calc. for $C_6H_6N_4S_5$): C 24.72 (24.47), H 1.64 (2.05), N 18.63 (19.03)%. ^{13}C-{^1H} NMR (CD_2Cl_2): δ(C) 191.9 (s, C5), 180.8 (s, C5'), 170.5 (s, C3'), 163.4 (s, C3), 17.0 (s, C5S$\underline{C}H_3$), 14.7 ppm (s, C3'S$\underline{C}H_3$).. ^1H NMR (CD_2Cl_2): δ 2.80 (s, 3H, C5SCH_3), 2.65 ppm (s, 3H, C3'SCH_3). ES^+ MS: *m/z* 317 $[MNa]^+$. IR (KBr): 2996w, 2966w, 2924w, 1443m, 1416s, 1367w, 1343w, 1331m, 1308m, 1249s, 1217s, 1094w, 1066m, 1058m, 977w, 966w, 916w, 906w, 801m, 681m, 482w, 420w, 387w, 285w cm^{-1}. Raman (glass capillary):

3004w, 2928s, 1421w, 1370w, 1346s, 1334m, 1310w, 1252m, 1227w, 919w, 808m, 724m, 694s, 524m 422w, 313w, 268w cm^{-1}.

5.20.



This was prepared in the same way as compound **5.19** using **5.16** (0.050 g, 0.153 mmol), $LiBEt_3H$ (0.065 g, 0.306 mmol) and 3-*tert*-butylsulfanyl-5-chloro-1,2,4-thiadiazole **5.9** (0.032 g, 0.306 mmol) to give a cream powder. Crystals suitable for X-Ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.053 g (51 %). Found (Calc. for $C_9H_{12}N_4S_5$): C 31.88 (32.11), H 3.15 (3.59), N 16.42 (16.65)%. ^{13}C-{^1H} NMR (CD_2Cl_2): δ(C) 191.8 (s, C5), 179.4 (s, C5'), 169.4 (s, C3'), 163.6 (s, C3), 47.9 (s, $\underline{C}(CH_3)_3$), 30.3 (s, $C(\underline{C}H_3)_3$), 17.0 ppm (s, $C5S\underline{C}H_3$). ^1H NMR (CD_2Cl_2): δ 2.80 (s, 3H, $C5SCH_3$), 1.59 ppm (s, 9H, $C(CH_3)_3$). ES^+ MS: *m/z* 359 $[MNa]^+$. IR (KBr):2959w, 2920w, 2858w, 1475w, 1459w, 1436s, 1427s, 1362m, 1342w, 1244m, 1221m, 1208m, 1159m, 1074m, 1061, 971w, 917w, 797w, 675w, 501w, 475w, 402w, 278w cm^{-1}. Raman (glass capillary): 2999w, 2965m, 2915s, 1458w, 1435w, 1362w, 1339s, 1323w, 1222w, 1212vw, 1166vw, 932vw, 919w, 812w, 801w, 714w, 676s, 598m, 490w, 478m, 443w, 383w, 368w, 319m cm^{-1}.

X-Ray Crystallography

Tables 5.4, 5.5 and 5.6 list details of data collections and refinements. Intensities were corrected for Lorentz-polarisation and for absorption. All data were collected at 93 K using a Rigaku Mercury system. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[109]

Compound	**5.1**	**5.3**	**5.4**
Empirical formula	$C_3H_3ClN_2S_2$	$C_4Cl_2N_4S_4$	$C_4Br_2N_4S_4$
Crystal dimensions/mm	0.2 × 0.05 × 0.05	0.2 × 0.1 × 0.05	0.1 × 0.1 × 0.01
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$	$P2_1/c$
a/Å	3.9264(3)	11.3849(13)	5.8977(11)
b/Å	9.6948(9)	8.1655(10)	7.1476(13)
c/Å	8.2410(6)	11.7320(14)	25.310(5)
α/°	90	90	90
β/°	101.8476(10)	111.840(9)	95.044(3)
γ/°	90	90	90
U/Å^3	307.02(4)	1012.4(2)	1062.8(3)
Z	2	4	4
M	166.64	303.22	392.14
Dc/g cm^{-3}	1.803	1.989	2.451
μ/mm^{-1}	1.184	1.426	8.375
Measured reflections	1632	4752	4388
Independent reflections (R_{int})	937(0.0236)	1694(0.1449)	1513(0.0304)
Final R1, wR2[I>2σ(I)]	0.0228, 0.0491	0.0936, 0.2082	0.0293, 0.0686

Table 5.4 Details of the X-ray data collections and refinements for compounds **5.1, 5.3** and **5.4**.

Compound	**5.7**	**5.8**	**5.12**
Empirical formula	$C_{30}H_{24}Br_2N_4P_2PtS_4$	$C_3H_3ClN_2S_2$	$C_{30}H_{24}Cl_2N_4P_2PtS_4$
Crystal dimensions/mm	0.2 × 0.05 × 0.03	0.2 × 0.2 × 0.05	0.1 × 0.03 × 0.01
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	C2/c
a/Å	20.878(4)	7.615(2)	29.675(2)
b/Å	11.8171(17)	9.474(4)	8.5789(7)
c/Å	13.827(2)	8.961(4)	25.351(2)
α/°	90	90	90
β/°	99.919(5)	106.938(10)	94.429(4)
γ/°	90	90	90
U/Å^3	3360.5(9)	618.4(4)	6434.5(9)
Z	4	4	8
M	985.62	166.64	896.70
Dc/g cm^{-3}	1.948	1.790	1.851
μ/mm^{-1}	6.926	1.176	4.916
Measured reflections	20176	3097	20800
Independent reflections (R_{int})	5983(0.0364)	1017(0.0277)	5626(0.0445)
Final R1, wR2[I>2σ(I)]	0.0385, 0.1003	0.0240, 0.0557	0.0451, 0.0867

Table 5.5 Details of the X-ray data collections and refinements for compounds **5.7, 5.8** and **5.12**.

Compound	**5.19**	**5.20**
Empirical formula	$C_6H_6N_4S_5$	$C_9H_{12}N_4S_5$
Crystal dimensions/mm	0.1 × 0.03 × 0.01	0.18 × 0.1 × 0.01
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/m$
a/Å	3.9232(11)	9.5487(8)
b/Å	8.451(3)	6.9794(5)
c/Å	33.094(11)	10.8821(18)
α/°	90	90
β/°	90	91.592(3)
γ/°	90	90
U/Å^3	1097.2(6)	724.95(14)
Z	4	2
M	294.45	336.53
Dc/g cm^{-3}	1.782	1.542
μ/mm^{-1}	1.025	7.272
Measured reflections	6257	9453
Independent reflections (R_{int})	1807(0.0354)	1311(0.0510)
Final R1, wR2[I>2σ(I)]	0.0322, 0.0643	0.0364, 0.0984

Table 5.6 Details of the X-ray data collections and refinements for compounds **5.19** and **5.20**.

Chapter 6: Polythiocyanogen and Related Compounds

6.1 *Introduction*

There has been minimal research into the structure and chemistry of polythiocyanogen. There have been a number of speculative structures drawn and a few reports stating that polythiocyanogen is a semiconductor and has some photoactivity, all of which have been discussed in Chapter 1. In order to obtain some insight into the structure and possible chemistry we have synthesised the polythiocyanogen polymer, thiocyanogen and some related compounds as well as the selenium analogues. All compounds have been fully characterised principally by NMR, IR and Raman spectroscopy.

6.2 *Results and Discussion*

6.2.1 *$E_2(CN)_2$ (E = S, Se) and related compounds.*

Although the syntheses of thiocyanogen and selenocyanogen have been reported in the literature several times[37-39,42-48] the spectral data is incomplete and there has been no single crystal X-ray diffraction study on either molecule which necessitates the resynthesis and further characterisation of these compounds for comparison with $(SCN)_x$ and $(SeCN)_x$ respectively.

Thiocyanogen $S_2(CN)_2$ **6.1** was synthesised by the reaction of silver thiocyanate with bromine in sulfur dioxide below –20 °C (Scheme 6.1).

$$2Ag(SCN) + Br_2 \longrightarrow 2AgBr + S_2(CN)_2$$

Scheme 6.1 Synthesis of thiocyanogen **6.1**.

We have also carried out the reaction in chloroform, dichloromethane and diethyl ether but sulfur dioxide was found to be the solvent that gave the cleanest reaction and was readily removed at low temperature. The mixture was filtered to remove precipitated silver bromide and the solvent removed *in vacuo*. The product was isolated in good yield as a colourless crystalline solid that was stable only when maintained at temperatures below –20 °C. In solution thiocyanogen is slightly more stable and can be stored without significant change spectroscopically at temperatures below 0 °C. On allowing thiocyanogen to warm slowly the colourless crystals melt to give a yellow liquid before spontaneously polymerising to give polythiocyanogen as an amorphous brick red solid. Thiocyanogen is readily soluble in chlorinated solvents such as chloroform and dichloromethane and nonhalogenated solvents such as tetrahydrofuran and diethyl ether. Due to thermal instability no microanalytical or mass spectral data have been obtained. Thiocyanogen exhibits a single $^{13}C-\{^1H\}$ NMR ($CDCl_3$, -20 °C) resonance at $\delta(C) = 108.3$ ppm which is comparable to the value recorded by Cataldo[48] (107.4 ppm in $CDCl_3$). **6.1** shows a single peak at $\delta(N) = 286.6$ in the ^{14}N NMR ($CDCl_3$) spectrum.

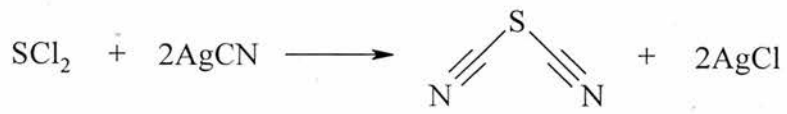
Compound	δ(C) (ppm)	δ(N) (ppm)
KSCN[a]	133.8	211.4
6.1 $S_2(CN)_2$[b]	108.3	286.6
6.2 $S(CN)_2$[c]	100.1	293.4
6.3 $S(SCN)_2$	-	-

[a] recorded in D_2O at 25 °C, [b] recorded in $CDCl_3$ at –20 °C, [c] recorded in CD_2Cl_2 at –20 °C. **6.3** did not have sufficient solubility to record NMR data.

Table 6.1 ^{13}C-{^1H} NMR (67.9 MHz) and ^{14}N NMR (21.7 MHz) data for KSCN, **6.1**, **6.2** and **6.3**.

The IR spectrum shows a strong ν(C≡N) band at 2160 cm^{-1}, a ν(C-S) band at 669 cm^{-1}, a ν(S-S) band at 492 cm^{-1} and two δ(S-C≡N) bands at 404 and 372 cm^{-1}. The Raman spectrum shows bands at 2160, 668, 494 and 399 cm^{-1} corresponding to ν(C≡N), ν(C-S), ν(S-S) and δ(S-C≡N) respectively. These observations are in accord with the literature IR and Raman data.[42-47] The single resonances in both the ^{13}C-{^1H} and ^{14}N NMR spectra show that there is only one carbon and one nitrogen environment in the molecule. These observations and the ν(S-S) band present in the IR and Raman spectra concur with the proposed disulfide bridged structure of thiocyanogen.

Sulfur dicyanide **6.2** and sulfur dithiocyanate **6.3** were prepared for comparison. **6.2** and **6.3** were prepared by the reaction of sulfur dichloride in dichloromethane at 0 °C with silver cyanide (Scheme 6.2) and silver thiocyanate respectively.



Scheme 6.2 Synthesis of sulfur dicyanide **6.2**.

After filtration to remove precipitated AgCl the solvent was removed *in vacuo* to give a colourless crystalline solid in both cases. **6.2** and **6.3** were both found to be stable when kept below 0 °C. Due to thermal instability no microanalytical or mass spectral data have been obtained.

assignment	**6.1** $S_2(CN)_2$		**6.2** $S(CN)_2$		**6.3** $S(SCN)_2$	
	IR (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})
ν(C≡N)	2161	2160	2184	2196	2153	2156
ν(C-S)	669	668	697 670	693 675	668	672
ν(S-S)	492	494	-	-	489 454	492 458
δ(S-C≡N)	404 372	399	379	389	400	-

Table 6.2 Selected IR and Raman data for compounds **6.1-6.3.**

$S(CN)_2$ **6.2** displays a single $^{13}C-\{^1H\}$ NMR (CD_2Cl_2, -20 °C) resonance at δ(C) = 100.1 ppm and a single resonance at δ(N) = 293.4 in the ^{14}N NMR (CD_2Cl_2, -20 °C) spectrum. No NMR data was obtained for $S(SCN)_2$ **6.3** due to insufficient solubility. IR and Raman data for both species (Table 5.2) was in agreement with published data.[48]

The reaction of silver selenocyanate with iodine in liquid sulfur dioxide at –20 °C, after filtering to remove precipitated silver iodide, results in the formation of $Se_2(CN)_2$ **6.4** (Scheme 5.3) as a yellow crystalline solid in good yield (74%).

$$2Ag(SeCN) + I_2 \longrightarrow 2AgI + Se_2(CN)_2$$

Scheme 6.3 Synthesis of selenocyanogen **6.4**.

Selenocyanogen **6.4** exhibits a single $^{13}C-\{^1H\}$ NMR ($CDCl_3$, -20 °C) resonance at δ(C) = 96.0 ppm, a single ^{14}N NMR ($CDCl_3$, -20 °C) resonance at δ(N) = 298.5 ppm and a single ^{77}Se NMR ($CDCl_3$, -20 °C) resonance at δ(Se) = 0.45 ppm in agreement with the proposed diselenide bridged structure. Cataldo has previously reported the $Se_2(CN)_2$ $^{13}C-\{^1H\}$ NMR ($CDCl_3$) resonance at δ(C) = 89.92 ppm.[48] However the sample was reported to be prepared at 13 °C before the solvent was distilled off under reduced pressure in a water bath. Selenocyanogen is thermally unstable and under these conditions it is very likely decomposition occurred to selenium dicyanide and selenium diselenocyanate as discussed below. The shift recorded by Cataldo is much closer to selenium dicyanide **6.5** ($^{13}C-\{^1H\}$ NMR ($CDCl_3$): δ(C) = 91.5 ppm) rather than selenocyanogen **6.4**.

compound	δ(C) (ppm)	δ(N) (ppm)	δ(Se) (ppm)
KSeCN[a]	120.7	243.9	-342.3
6.4 $Se_2(CN)_2$[b]	96.0	298.5	0.45
6.5 $Se(CN)_2$[c]	91.5	299.8	0.29
6.6 $Se(SeCN)_2$	-	-	-

[a] recorded in D_2O at 25 °C, [b] recorded in $CDCl_3$ at –20 °C, [c] recorded in CD_2Cl_2 at –20 °C. **6.6** did not have sufficient solubility to record NMR data.

Table 6.3 ^{13}C-{^1H} NMR (67.9 MHz), ^{14}N NMR (21.7 MHz) and ^{77}Se NMR (67.9 MHz) data for KSeCN, **6.4**, **6.5** and **6.6**.

The Raman spectrum of **6.4** shows a strong ν(C≡N) band at 2158 cm^{-1}, a medium ν(C-Se) band at 522 cm^{-1} and a weak δ(Se-C≡N) band at 380 cm^{-1} which agree with the previously published vibrational spectroscopic data.[52] No IR data was obtained because thermal instability prohibited the preparation of samples. Thermal instability also prevented us from recording mass spectra or microanalytical data. A single crystal X-ray diffraction study of **6.4** confirmed the diselenide bridged structure (Figure 6.1, Table 6.4). The Se-Se bond was found to be 2.356(1) Å which is similar to the diselenium dihalides $(SeX)_2$ (X = Br, Cl)[129] which have Se-Se bonds of 2.241(1) and 2.232(1) Å respectively. The C≡N bonds were typical for nitrile groups at 1.145(6) and 1.157(6) Å. In common with the structures of the related parent halides E_2X_2 [E= S, Se X = Cl, Br][129] the cyano groups are arranged in an approximately gauche relationship [C-Se-Se-C torsion angle 86.7°, c.f. 83.9- 87.4 in E_2X_2] reflecting the importance of

the lone pairs in conformational control. As a consequence of this gauche arrangement E_2X_2 molecules [including hydrogen peroxide] are chiral. To date all previous structures have contained both enantiomers but in the case of **6.4** the crystal selected only contained one enantiomer and crystallises in the space group $P2_12_12_1$. We have no evidence that the compound is synthesised as one optical isomer. The packing diagram (Figure 6.2) clearly illustrates the importance of intermolecular interactions [Se(1)...N(1') 2.876, Se(1)...N(2'') 2.936, Se(2)...N(1') 3.199, Se(2)...N(2'') 3.157].

Compound	**6.4**
Se(1)-C(1)	1.867(5)
Se(2)-C(2)	1.855(5)
Se(1)-Se(2)	2.3558(7)
N(1)-C(1)	1.145(6)
N(2)-C(2)	1.157(6)
C(1)-Se(1)-Se(2)	95.33(12)
N(2)-C(2)-Se(2)	178.3(4)
Se(2)-Se(1)-C(1)-N(1)	167(6)
C(1)-Se(1)-Se(2)-C(2)	-86.7(2)

Table 6.4 Selected bond lengths (Å) and angles (°) for **6.4**.

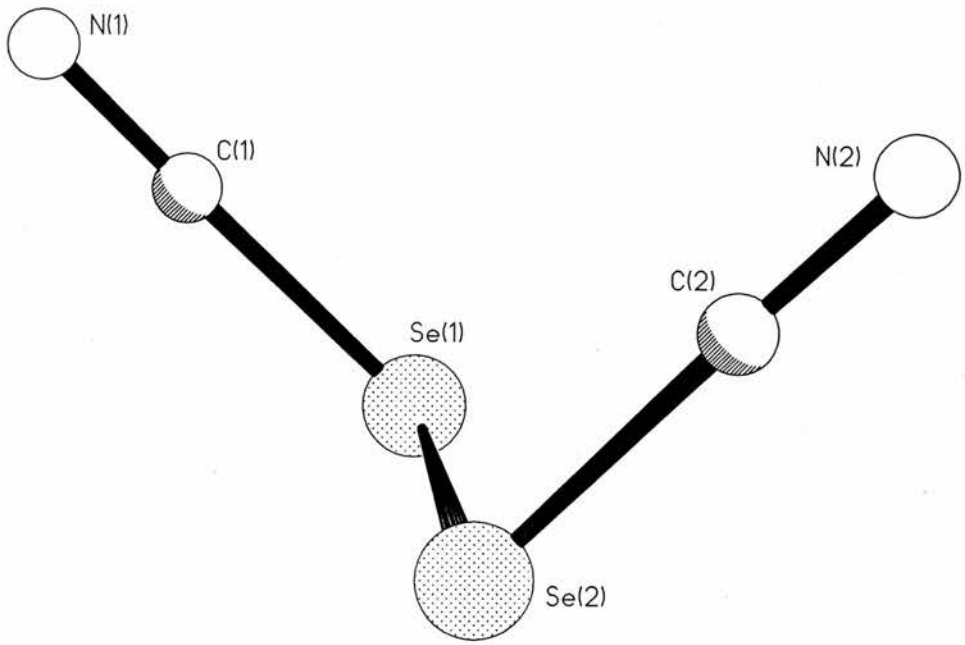


Figure 6.1 X-ray crystal structure of $Se_2(CN)_2$ **6.4**.

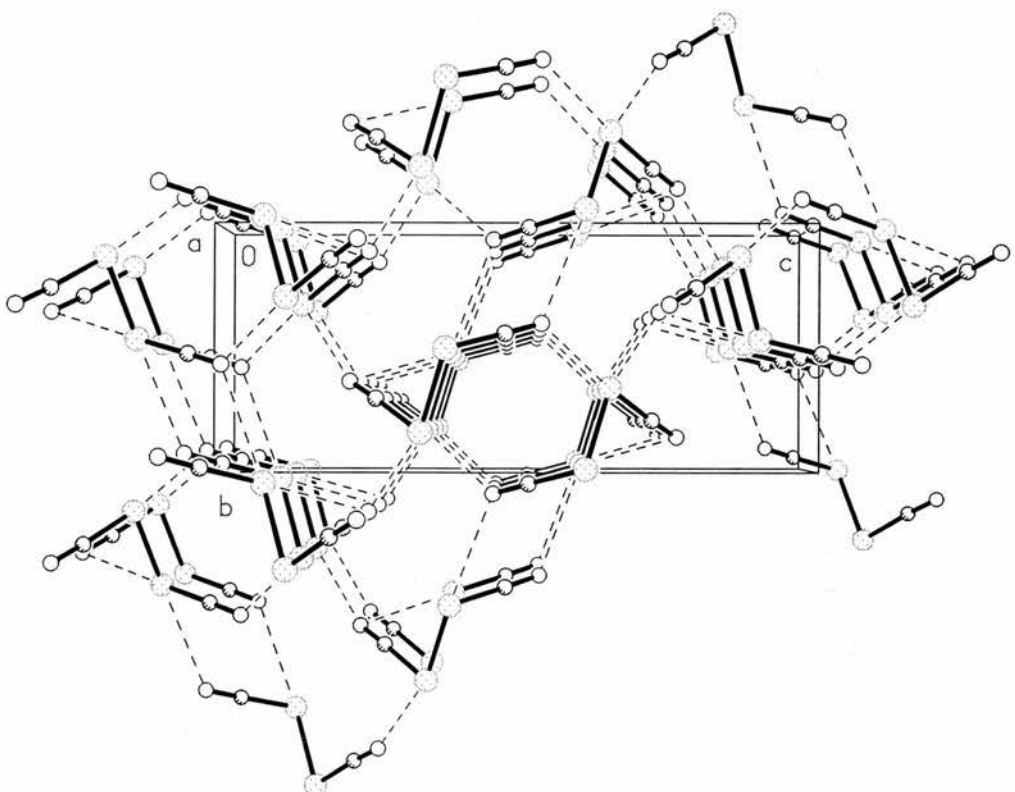
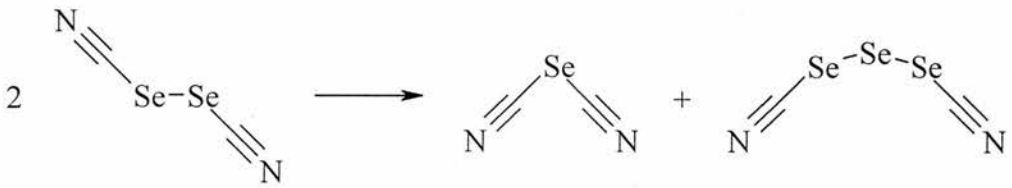


Figure 6.2 Packing in the solid state structure of **6.4**.

Selenocyanogen does not readily polymerise like the sulfur analogue thiocyanogen. Instead when we allowed selenocyanogen to warm slowly it disproportionated to give a mixture of selenium dicyanide and selenium diselenocyanate (Scheme 6.4).



Scheme 6.4. Disproportionation of $Se_2(CN)_2$

No visible change was noted because selenium dicyanide is colourless and selenium diselenocyanate is also a yellow crystalline solid however the disproportionation was followed spectroscopically. When selenocyanogen began to disproportionate a new peak was noted in the ^{13}C-{^1H} NMR ($CDCl_3$) spectra at 90.6 ppm corresponding to selenium dicyanide. No peak was observed for selenium diselenocyanate because of its poor solubility. Disproportionation was also observed in the Raman spectrum by the emergence of two new cyanide stretches at 2188 and 2144 cm^{-1} corresponding to selenium dicyanide and selenium diselenocyanate respectively.

Both selenium dicyanide $Se(CN)_2$ **6.5** and selenium diselenocyanate $Se(SeCN)_2$ **6.6** have been previously reported in the literature[48,50-52] and studied by single crystal X-ray diffraction.[130,131] However it was necessary to resynthesise both to obtain accurate spectral data for comparison with selenocyanogen. Selenium dicyanide **6.5** was prepared by the reaction of two equivalents of silver cyanide

with selenium dichloride (prepared *in situ* by reacting selenium powder with sulfuryl chloride) in tetrahydrofuran. Removal of the solvent under reduced pressure followed by extraction of the residue with dichloromethane furnished, after filtration through Celite (to remove solid AgCl) and evaporation of the filtrate to dryness, the product as a white powdery solid in a 66 % yield. Although no decomposition of selenium dicyanide was noted the sample was stored under a nitrogen atmosphere at 0°C as a precaution. Microanalysis was within acceptable limits and positive ion EI mass spectroscopy showed the expected M^+ and other fragments. Selenium dicyanide exhibits a single ^{13}C-{^1H} NMR (CD_2Cl_2, -20 °C) resonance at δ(C) = 91.5 ppm a single ^{14}N (CD_2Cl_2) resonance at δ(N) = 299.8 ppm and a single ^{77}Se (CD_2Cl_2) resonance at δ(Se) = 0.29 ppm. The IR and Raman spectra displayed the anticipated bands (Table 6.5) for the (C≡N), (C-Se) and (Se-C≡N) functionalities.

assignment	**6.4** $Se_2(CN)_2$		**6.5** $Se(CN)_2$		**6.6** $Se(SeCN)_2$	
	IR (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})
ν(C≡N)	-	2157vs	2179vs	2188vs	2141vs	2144vs
ν(C-Se)	-	523m	509vs	512s	511m	509w
δ(Se-C≡N)	-	380w	338m	343w	362w	360w

Table 6.5 Selected IR and Raman data for compounds **6.4-6.6.**

Selenium diselenocyanate **6.6** was prepared in an analogous fashion to selenium dicyanide **6.5** by reacting two equivalents of silver selenocyanate with selenium

dichloride in tetrahydrofuran. After a similar work up to that used above the product was isolated as a bright yellow crystalline solid in a 71 % yield. When left to stand at room temperature it was noted that some decomposition occurred producing a red solid which is probably selenium. As a result selenium diselenocyanate was stored under a nitrogen atmosphere at 0 °C and no further decomposition was observed. Microanalysis and positive ion EI mass spectroscopy showed the expected results. Selenium diselenocyanate was found to have poor solubility in organic solvents and therefore no NMR data was recorded. The IR spectrum shows a strong ν(C≡N) band at 2141 cm^{-1}, a medium ν(C-Se) band at 511 cm^{-1} and a weak δ(Se-C≡N) band at 362 cm^{-1}. In addition the Raman spectrum also showed the anticipated bands (Table 6.5).

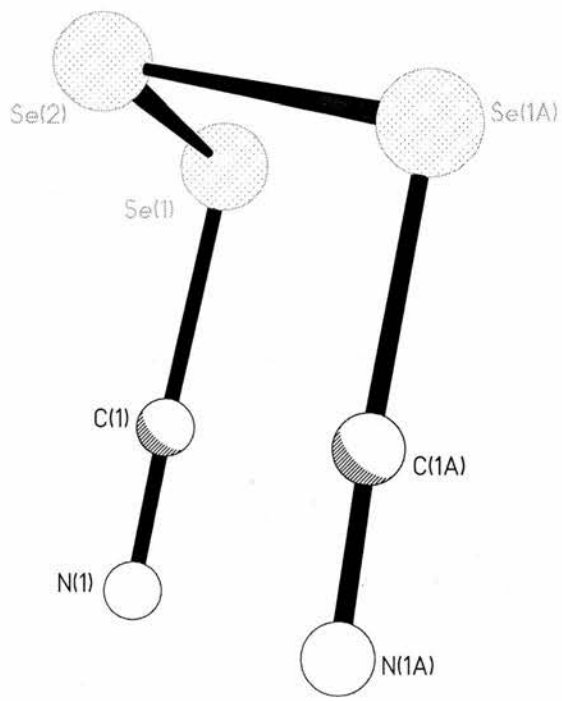


Figure 6.3 X-ray crystal structure of $Se(SeCN)_2$ **6.6**.

The crystal structure of selenium diselenocyanate was obtained by chance as a disproportionation product from selenocyanogen (Figure 6.3). Although the crystal structure of selenium diselenocyanate has been previously reported[130] we thought that it was worthwhile including in this report as it has been recorded with modern technology at low temperature. The orthorhombic space group was found to be the same but there were some differences in bond lengths and angles, which are included in the table below (Table 6.6).

	A	B
Se(1)-C(1)	1.83	1.859(4)
Se(1)-Se(2)	2.33	2.3388(5)
C(1)-N(1)	1.05	1.146(5)
Se(2)-Se(1)#1	1.83	2.3388(5)
C(1)-Se(1)-Se(2)	95	96.61(10)
N(1)-C(1)-Se(1)	164	177.6(3)
Se(1)#1-Se(2)-Se(1)	101	102.71(3)

Table 6.6 Comparison of bond lengths (Å) and angles (°) of selenium diselenocyanate A and B (A = data in *Acta. Chem. Scand.*, 1954, **8**, 1787;[130] B = This Work)

6.2.2 *Polythiocyanogen* $(SCN)_x$.

We have synthesised polythiocyanogen by two different methods. Firstly by allowing thiocyanogen **6.1** prepared as above to slowly warm to room temperature resulting in spontaneous polymerisation to give **6.7**. The second method involved passing excess chlorine gas through powdered potassium thiocyanate, followed by heating. We found that chlorinating for approximately 30 seconds and heating for 1 minute then repeating the procedure a further 5 times optimized the yield of $(SCN)_x$. Using this method we also prepared ^{13}C and ^{15}N labelled samples of $(SCN)_x$ using ^{13}C labelled and ^{15}N labelled potassium thiocyanate respectively. Polythiocyanogen obtained by both methods gave identical analytical and spectral data. Polythiocyanogen **6.7** is an air stable, brick red, amorphous solid. Polythiocyanogen is insoluble in all organic solvents with the exception of dimethyl formamide and dimethyl sulfoxide in which it is very sparingly soluble. Polythiocyanogen is also insoluble in water. Microanalysis of $(SCN)_x$ confirmed the composition of the polymer. MALDI-TOF mass spectra using DCTB as the matrix were recorded several times with the addition of various metal salts (NaI, LiCl, $Cu(NO_2)_2$, $Ag(NO_2)$). The spectra with addition of LiCl did not yield any useful information, however the spectra with addition of NaI, $Cu(NO_2)_2$ and $Ag(NO_2)$ showed identical sets of peaks. As an example the spectrum with $Cu(NO_2)_2$ added (Figure 6.4) showed the series at *m/z* 1149 $[S_{20}C_{20}N_{19}]^+$, 1030 $[S_{18}C_{18}N_{17}]^+$, 914 $[S_{16}C_{16}N_{15}]^+$, 798 $[S_{14}C_{14}N_{13}]^+$, 682 $[S_{12}C_{12}N_{11}]^+$, 566 $[S_{10}C_{10}N_9]^+$, 450 $[S_8C_8N_7]^+$, 334 $[S_6C_6N_5]^+$, 218 $[S_4C_4N_3]^+$, 102 $[S_2C_2N]^+$. The isotope pattern for each peak in the series matches the predicted pattern exactly.

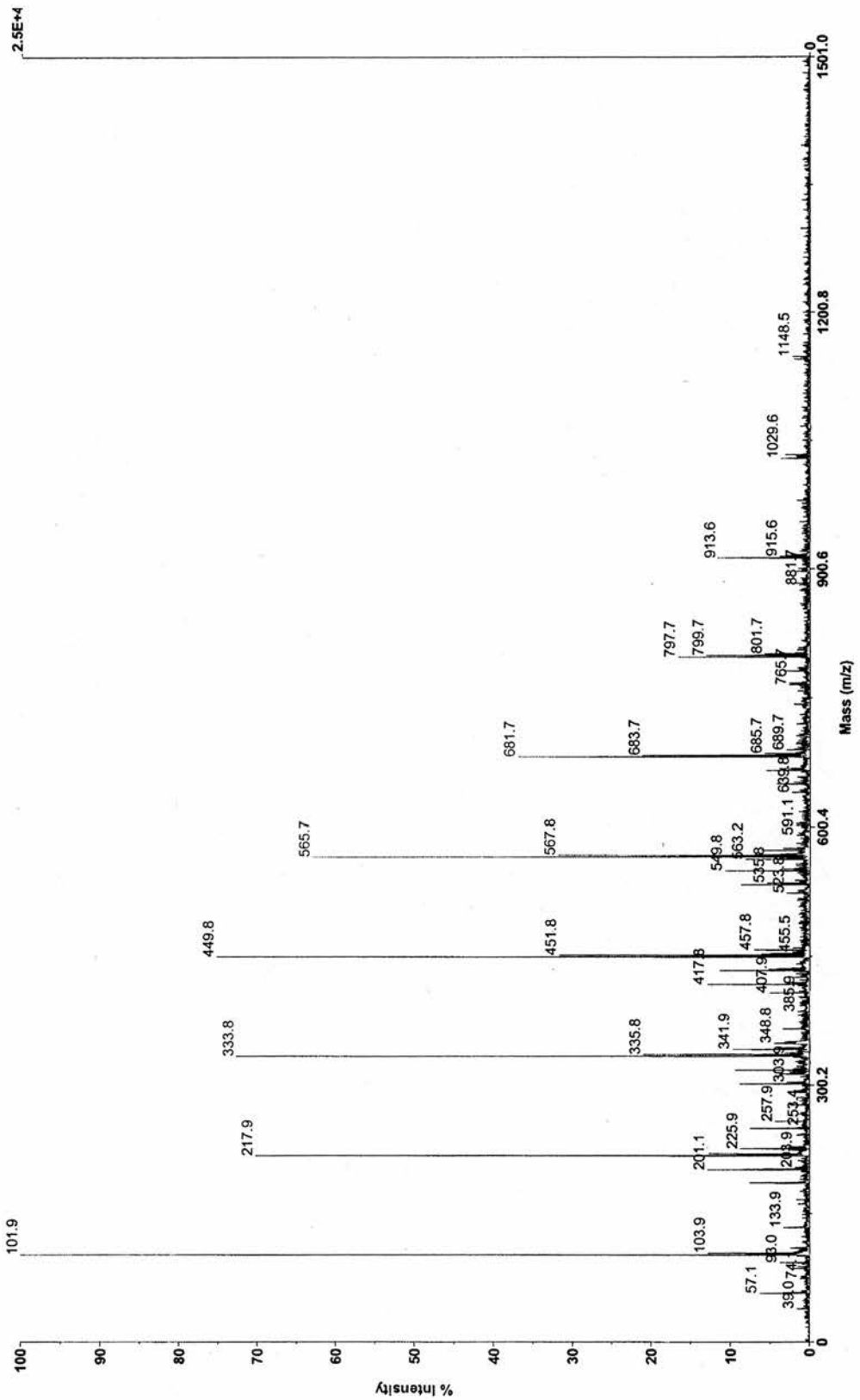


Figure 6.4 MALDI TOF mass spectrum of polythiocyanogen **6.7**.

The largest peak observed in the NaI and $Ag(NO_2)$ series was noted at 1030 m/z, corresponding to $[\{(SCN)_2\}_8S_2C_2N]^+$. The repeat unit of 116 *m/z* corresponds to $(SCN)_2$ which suggests that this may be the monomeric unit. The $(SCN)_2$ repeat unit fits very well with our proposed structures of linked heterocyclic 5 membered rings (Figures 1.17 and 1.18, p 32). The absence of any series with a 58 *m/z* (SCN) repeat unit is strong evidence against the $(SCN)_x$ polymer being composed of linear chains of linked SCN units as proposed in the literature.[76,83]

The IR spectrum of $(SCN)_x$ shows a very broad peak with a maximum at 1134 cm^{-1} (Figure 6.5) consisting of several overlapping peaks and is comparable with IR spectra reported in the literature.[76,83-85] The Raman spectrum (Figure 6.6) was more informative but there is still considerable broadness caused by overlapping peaks. In the Raman spectra there are no peaks in the range 1600-3500 cm^{-1}. The absence of any bands in the region 2000-2200 cm^{-1} strongly suggests that there are no nitrile groups present in $(SCN)_x$. In the range 800-1600 cm^{-1} there is a small peak at 1508, a very broad, intense peak at 1207 with an obvious shoulder, a strong peak at 1155 and a low intensity peak at 994 cm^{-1}. In the range 200-800 cm^{-1} there are several overlapping peaks at approximately 650, several overlapping peaks in the range 400-480 and two further peaks at 289 and 229 cm^{-1}. We propose that the peak at 650 cm^{-1} is due to ν(C-S) vibrations and we speculate that the peaks in the range 400-480 may correspond to ν(S-S) vibrations. The IR and Raman spectral data for $(SCN)_x$ is very different to the linear small molecules $S_n(CN)_2$ (n = 1, 2, 3) which show virtually no peaks in the range 800-1600 cm^{-1}. Interestingly the 1,2,4-thiadiazole compounds **5.1–5.20** which we have discussed in chapter 5 and 1,2,4-dithiazole compounds[71,72,87,91]

show strong ring vibrations in the same region as the large central peak in the IR spectrum of $(SCN)_x$.

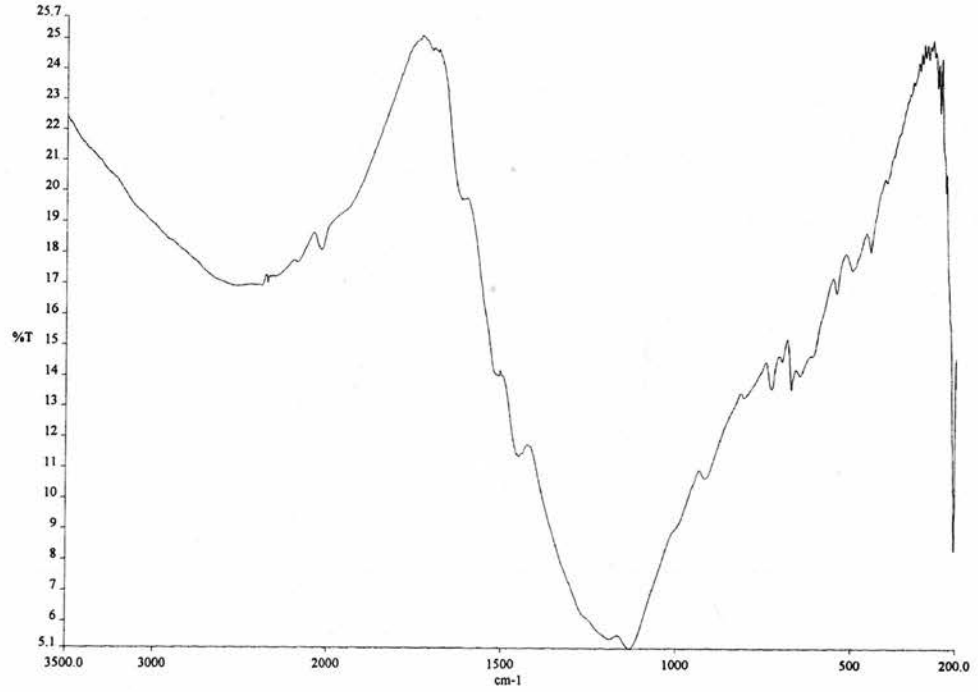


Figure 6.5 IR spectrum for $(SCN)_x$ **6.7**.

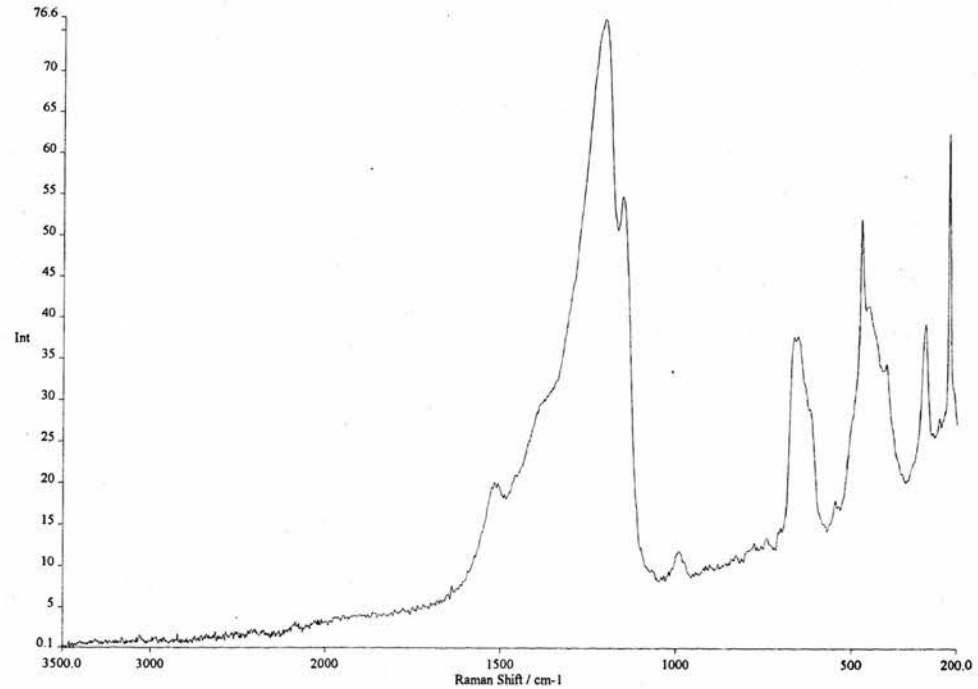


Figure 6.6 Raman spectrum for $(SCN)_x$ **6.7**.

We attempted to record the ^{13}C NMR data for $(SCN)_x$ in dimethyl formamide as twice reported in the literature by Cataldo.[83,84] We found only a trace amount of the polymer dissolved resulting in a faint yellow colour of the solution and no signal was observed (except for dimethyl formamide) even with a 99 % ^{13}C labelled sample of $(SCN)_x$ after 29000 scans. Hence we recorded the ^{13}C and ^{15}N NMR spectra in the solid state. In the ^{13}C-{^{1}H} DP-MAS NMR polythiocyanogen exhibits a resonance at δ 186.8 ppm. The signal is broad and slightly asymmetric with low intensity spinning side bands. We have also recorded the ^{13}C DP-MAS NMR spectra of a 99 % ^{13}C labelled sample of $(SCN)_x$ (Figure 6.7). As expected the signal to noise ratio was substantially improved in the ^{13}C labelled sample.

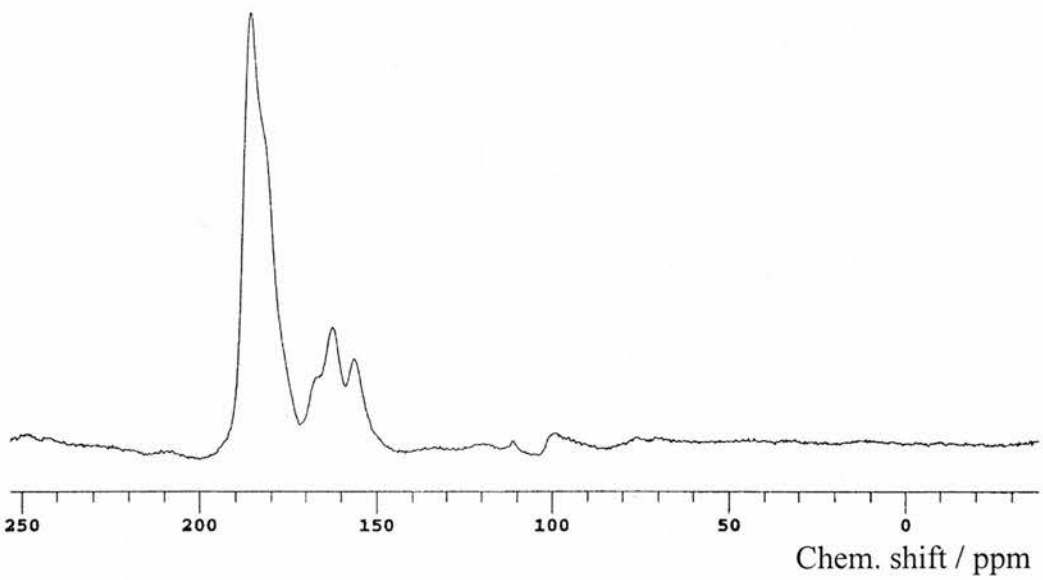


Figure 6.7 ^{13}C DP-MAS NMR spectrum of ^{13}C labelled $(SCN)_x$.

In the spectrum there is a broad peak centred at δ 186.6 ppm with a visible shoulder. Deconvolution yielded two singlets at δ 187.1 ppm (integral intensity 0.88) and δ 183.8 ppm (integral intensity 1). Additionally there is a multiplet at

δ 152-172 ppm with significantly lower intensity. Deconvolution of the multiplet yielded 3 singlets at δ 156.6 ppm (integral intensity 0.24), δ 163.2 ppm (integral intensity 0.35) and 168.1 ppm (integral intensity 0.16). Thus, the ^{13}C NMR spectrum of $(SCN)_x$ is dominated by two carbon shifts at δ 183.8 ppm and 187.1 ppm of approximately equal intensity. We attribute these two peaks to the polymer chain and the lower intensity peaks may be due to terminal groups or impurities. The carbon environments in the polymer **6.7** are clearly different to that of KSCN (δ 133.8 ppm), $S_2(CN)_2$ **6.1** (δ 108.3 ppm) and $S(CN)_2$ **6.2** (δ 100.1 ppm). The ^{13}C shifts recorded for polythiocyanogen are in the same range as 1,2,4 thiadiazoles which we have report in chapter 5 and 1,2,4-dithiazoles.[71,72] The close proximity of the two peaks at 183.8 and 187.1 ppm indicates that the two carbon environments in the polymer are very similar. In the proposed 1,2,4-thiadiazole structure C5 is bonded to one nitrogen and two sulfurs whereas C3 is bonded to two nitrogens and one sulfur. The difference between C5 and C3 is noted in the ^{13}C NMR spectra of 1,2,4-thiadiazole compounds we have prepared in chapter 5. Typically C5 bonded to one nitrogen and two sulfurs is observed in the range 180-192 ppm whereas C3 bonded to two nitrogens and one sulfur is noted in the range 163-172 ppm. The ^{13}C NMR data for polythiocyanogen may support a structure comprised of 1,2,4-dithiazole rings linked by exocyclic nitrogen atoms where both carbons are in very similar environments bonded to two nitrogen atoms and one sulfur atom. Butler and Glidewell have reported ^{13}C NMR data for isoperthiocyanic acid (3-amino-5-thione-1,2,4-dithiazole).[132] Two peaks are observed at 208 and 183 ppm. We resynthesised isoperthiocyanic acid by the method of Cotton and McCleverty[99] and obtained almost identical ^{13}C NMR data. The peaks at 208 and 183 ppm correspond to C5 and C3

respectively. C3 is bonded to two nitrogen atoms and one sulfur atom and is comparable to the carbon environments in our proposed 1,2,4-dithiazole structure. The value for C3 is 183 ppm is very similar to the main peaks observed in $(SCN)_x$ (183.9 and 187.1 ppm).

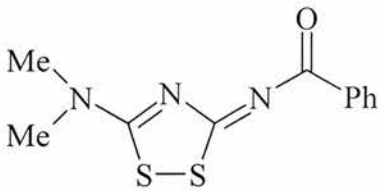
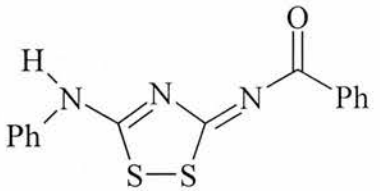
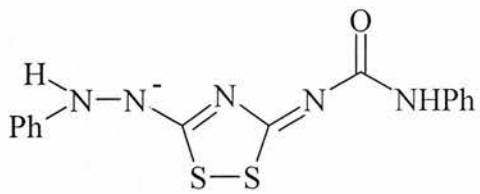
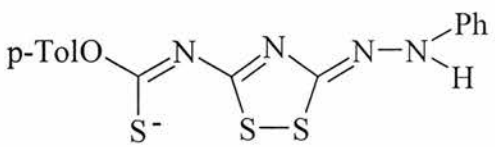
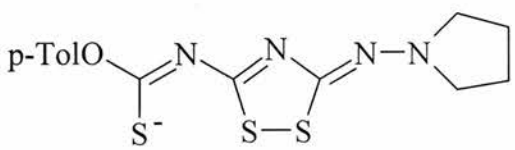
Compound	δ(C) (ppm)	
	C5	C3
6.7 $(SCN)_x$	187.1	183.8
	184.5	180.1
	185.6	178.9
	180.7	174.9
	193.3	180.8
	192.6	183.0

Table 6.7 ^{13}C NMR data for 1,2,4-dithiazoles reported by Graubaum *et al.*[133,134]

Furthermore Graubaum *et al.* have prepared several 1,2,4-dithiazole compounds[133,134] in which both carbons in the ring are in environments comparable to the carbon environments in our proposed 1,2,4-dithiazole structure for $(SCN)_x$. The ^{13}C NMR shifts reported are very similar to those which we have recorded for polythiocyanogen and are shown above in Table 6.7.

The ^{15}N NMR spectrum of **6.7** was recorded using a ^{15}N labelled sample (Figure 6.8). The spectrum is broad and the signal to noise ratio is not ideal. Two peaks of equal intensity are noted at 236.9 and 197.2 ppm. A lower intensity peak is observed at 170.2 ppm.

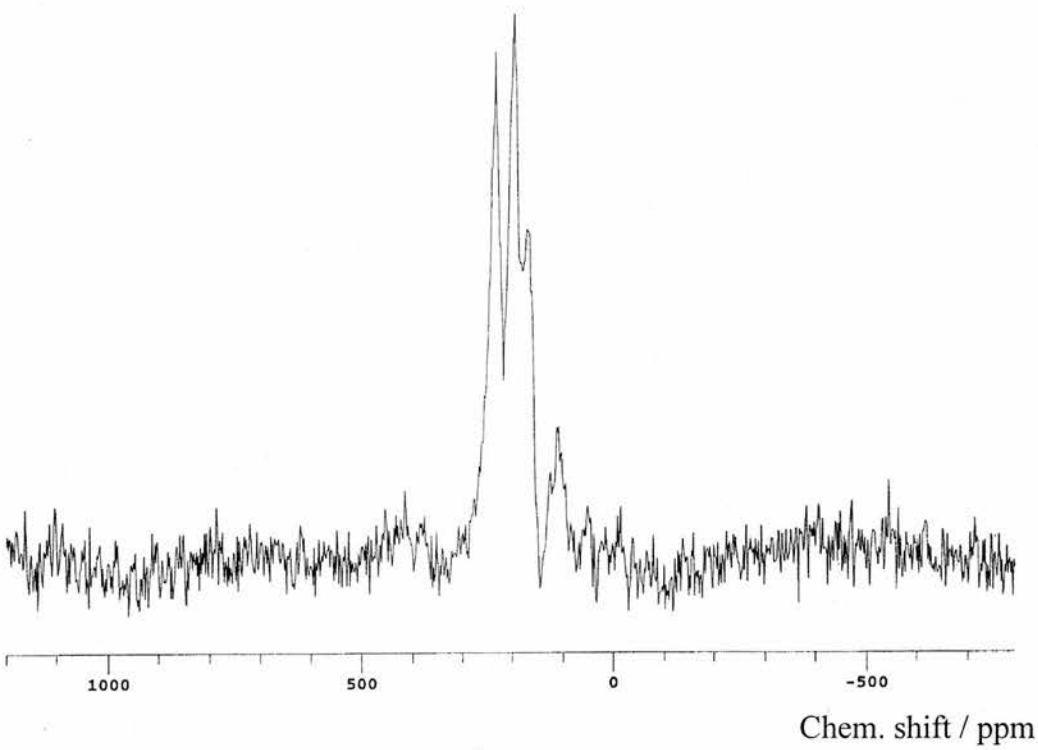


Figure 6.8 Solid state ^{15}N NMR spectrum of $(SCN)_x$ **6.7**.

These ^{15}N NMR resonances are different from the ^{14}N NMR shifts recorded for the small molecules $S_n(CN)_2$ (n = 1, 2) which are observed at approximately 290

ppm indicating the difference between the nitrogen environments in the polymer and the linear small molecules. The literature reports that thiazoles have ^{15}N NMR shifts at approx 300 ppm.[135] The ^{14}N NMR spectra for bis(3-bromo-1,2,4-thiadiazol-5-yl) disulfide **5.4** which we have reported in chapter 5 displays two shifts at 310.6 and 278.4 ppm assigned as N2 and N4 respectively. Thus the nitrogen NMR data does not favour a 1,2,4-thiadiazole structure for $(SCN)_x$. Butler and Glidewell recorded the ^{15}N NMR spectrum of isoperthiocyanic acid (3-amino-5-thione-1,2,4-dithiazole).[132] They reported two peaks in the ^{15}N NMR spectra at 263 and 107 ppm. We have recorded the ^{14}N NMR spectrum of isoperthiocyanic acid. In the spectrum we observed two broad peaks at 221 and 106 ppm. The peak at 221 ppm is assigned as N4 and the peak at 106 corresponds to the exocyclic NH_2. Interestingly ^{15}N NMR shifts for imino groups are observed in the range 170-200 ppm.[134] If polythiocyanogen has a structure comprised of 1,2,4-dithiazole rings linked by exocyclic nitrogen atoms we would expect a shift for N4 in a 1,2,4-dithiazole ring and also a shift for an exocyclic imino group . This theory explains the observed peaks in the ^{15}N NMR spectra very well.

An X-ray powder diffraction study was attempted but due to the amorphous nature of polythiocyanogen no useful data was obtained.

We studied the reactivity of polythiocyanogen as part of our investigation into the structure of the polymer. In the literature it has been reported that polythiocyanogen undergoes reaction with NaCN, Na_2S and NaOH.[84] We used this as a starting point for our study. We refluxed a slight excess of $(SCN)_x$ **6.7**

with KOH in methanol overnight. The resultant red solution was filtered to remove any residual $(SCN)_x$ and the water removed under reduced pressure yielding a yellow solid. The ^{13}C-$\{^1H\}$ NMR (D_2O) of the product showed two distinct peaks at 182.4 ppm and 133.7 ppm. Several lower intensity peaks were observed in the range 155-184 ppm with two further peaks at 120.6 ppm and 124.2 ppm. The peak at 182.4 is comparable with thiourea (183.9 ppm in CD_3OD). We assign the peak at 133.7 as SCN^- (c.f. KSCN 133.8 ppm). The peak at 165.4 ppm could possibly be CN^- (c.f. KCN 166.5 ppm). Attempts at separating the mixture of products were unsuccessful. Reflux with NaHS and Na_2S yielded similar results with obvious thiocyanate peak at approximately 133 ppm and further peaks in the range 162-189 ppm. In the mass spectra of the reaction mixture S_8 and smaller sulfur fragments are noted. In a similar fashion $(SCN)_x$ was refluxed with NaOMe in methanol. The ^{13}C-$\{^1H\}$ NMR (CD_3OD) spectrum of the product showed peaks at approximately 132 ppm and 169 ppm assigned as thiocyanate and carbonate ions respectively. $(SCN)_x$ refluxed with NaO^iPr and Bu_4NOH in methanol yielded the same results. In these three reactions $(SCN)_x$ is simply being broken down to SCN^-. Reaction with excess H_2SO_4 or HNO_3 completely destroyed the polymer and no useful data was obtained. Polythiocyanogen was found to react with chlorine when refluxed overnight in dichloroethane but unreactive towards bromine and iodine. Unfortunately no useful data was obtained. No reaction occurred with butyl lithium. Reaction with $LiBEt_3H$ yielded a sticky orange material. The ^{13}C-$\{^1H\}$ NMR (CD_3OD) spectrum of the product showed thiourea, thiocyanate and carbonate ions and an unknown peak at 198.0 ppm. We have been unsuccessful in isolating any of the products from this mixture. Unfortunately in all of the

reactions attempted we have been unable to isolate any fragments of $(SCN)_x$ which would allow us to determine the structure of the polymer. Interestingly the decomposition products we have been able to assign are comparable with those formed by the decomposition of isoperthiocyanic acid (3-amino-5-thione-1,2,4-dithiazole).[132] The hydrolysis products reported for isoperthiocyanic acid are CO_2, H_2S, sulfur and ammonium thiocyanate. It is speculated that the primary hydrolysis products are thiourea, carbonyl sulfide and sulfur. Thus the observed products are formed by hydrolysis of carbonyl sulfide to CO_2 and H_2S and thermal isomerisation of thiourea to ammonium thiocyanate. Heating isoperthiocyanic acid with concentrated sulfuric acid yielded sulfur, ammonium sulfate, thiourea, CO_2 and SO_2 and HCN.

The data we have collected and the propensity of HNCS and $(SCN)_2$ to form 1,2,4-dithiazole rings as discussed in chapter 1 leads us to propose that polythiocyanogen has a structure comprised of 1,2,4-dithiazole rings linked by nitrogen bridges (Figure 6.9).

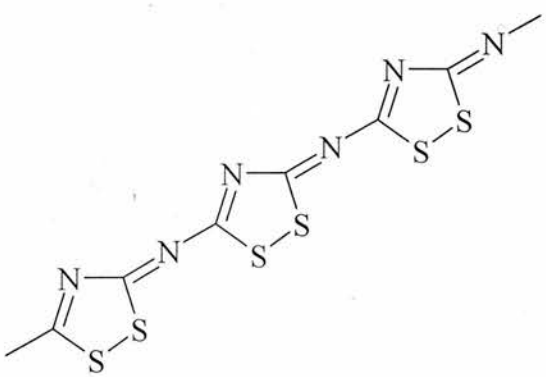
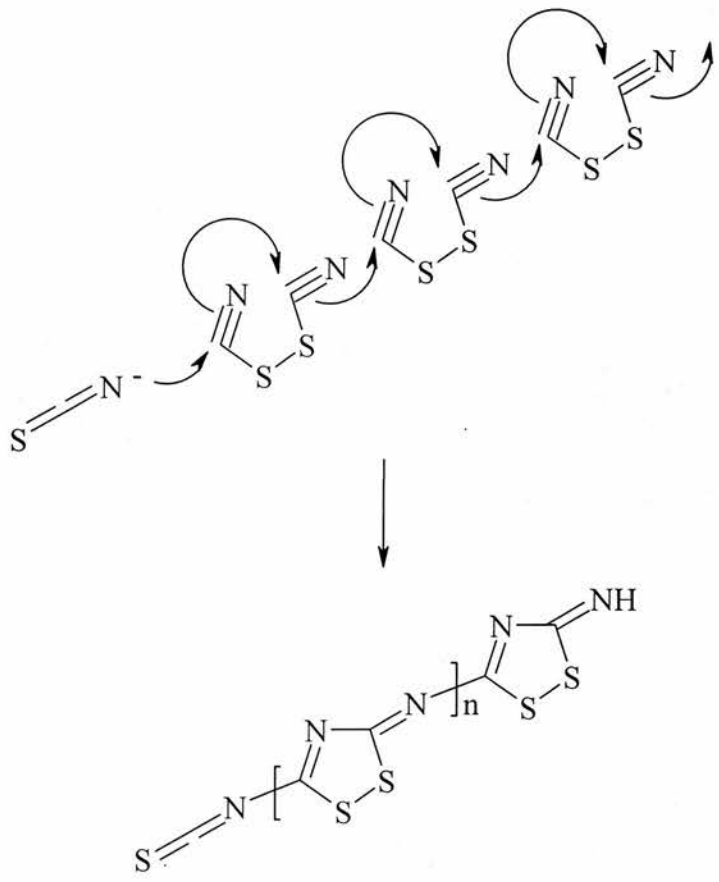


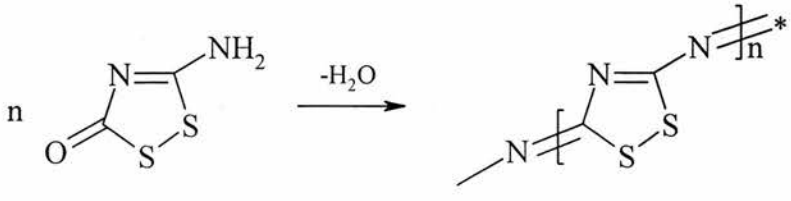
Figure 6.9 Our proposed structure for $(SCN)_x$ 1,2,4-dithiazole rings linked by nitrogen bridges.

The composition of $(SCN)_x$ has been confirmed by microanalysis. MALDI-TOF mass spectroscopy showed a series of peaks with a $(SCN)_2$ repeat unit (116 *m/z*) which implies this may be the monomer unit of the polymer. The $(SCN)_2$ repeat unit fits very well with our proposed structures of linked heterocyclic 5 membered rings. The IR spectrum shows a very broad peak with maximum at 1134 cm^{-1} consisting of several overlapping peaks. Ring vibrations for 1,2,4-thiadiazole and 1,2,4-dithiazole compounds are observed in the same region. The reactivity of the $(SCN)_x$ towards chlorine and $LiBEt_3H$ and the peaks in the Raman spectra in the range 400-480 cm^{-1} support the presence of sulfur sulfur bonds within the polymer. This supports our 1,2,4-dithiazole structure. The ^{13}C NMR spectrum is dominated by two singlets of equal intensity at approximately 187 and 184 ppm with low intensity peaks in the range 152-172 ppm. The ^{13}C NMR shifts in polythiocyanogen are in the same range as both 1,2,4-thiadiazoles and 1,2,4-dithiazoles. The close proximity of the two main peaks in the ^{13}C NMR spectrum favours the 1,2,4-dithiazole structure in which both carbons are in very similar environments. The 1,2,4-dithiazole structure of $(SCN)_x$ is further supported by comparison with 1,2,4-dithiazole compounds with similar carbon environments to our proposed structure. The ^{15}N NMR spectrum displays two peaks of similar intensity at 236.9 and 197.2 ppm with a lower intensity peak at 170.2 ppm. These environments are clearly different to those observed in bis(3-bromo-1,2,4-thiadiazol-5-yl) disulfide **5.4**. Comparison with isoperthiocyanic acid revealed that ^{15}N NMR data for the polymer is compatible with a 1,2,4-dithiazole structure. We propose a straightforward mechanism for the polymerisation of $S_2(CN)_2$ initiated by an isothiocyanate ion (Scheme 6.5).



Scheme 6.5 Proposed mechanism for polymerisation of $S_2(CN)_2$.

Further experiments that could confirm our proposed structure are synthesis of 1,2,4-dithiazole model compounds and linking them to form dimers and higher oligomers to compare with $(SCN)_x$. We will also attempt to synthesise polythiocyanogen by a Schiff's base condensation as shown below in Scheme 6.6.



Scheme 6.6 Proposed Schiff's base condensation.

6.2.3 *Polyselenocyanogen* $(SeCN)_x$.

It has been reported by Cataldo[48,92] that selenocyanogen $Se_2(CN)_2$ when treated with certain organic solvents (acetone, dimethyl formamide, methanol and triethylamine) spontaneously polymerises to give polyselenocyanogen $(SeCN)_x$. In the same work it was reported that polyselenocyanogen could alternatively be prepared from selenocyanogen by heating in high boiling solvents such as xylenes and decalin. We therefore attempted to repeat the above reactions to prepare a sample of polyselenocyanogen for further study. We added selenocyanogen to acetone and a red solid precipitated as reported. The solid was isolated by suction filtration and dried in vacuo. Analysis of the insoluble red solid showed it was red selenium rather that $(SeCN)_x$. Microanalysis showed 2.25 % C and 0.42 % N compared to the expected 11.44 % C and 13.35 % N for $(SeCN)_x$. Positive ion electron impact mass spectroscopy displayed the $[M]^+$ at m/z = 632 corresponding to Se_8. Se_7 m/z = 553, Se_6 m/z = 474, Se_5 m/z = 395, Se_4 m/z = 316, Se_3 m/z = 238, Se_2 m/z = 158 and Se m/z = 79 were all observed with the expected isotopomer distributions. Raman spectroscopy showed only one vibration at 253 cm^{-1} corresponding to ν(Se-Se). Similar results were obtained from reaction with methanol and by heating in high boiling solvents. Bowmaker *et al* have prepared thin films of polythiocyanogen by oxidation of potassium thiocyanate in methanol.[136] When they carried out oxidation of potassium selenocyanate the results were far less conclusive. They obtained a patchy orange red film which exhibited bands due to grey selenium in the Raman spectrum. Within a day the film had decomposed to give grey selenium. On the

basis of our evidence we have no reason to believe that $(SeCN)_x$ exists and the results of Bowmaker *et al* further support this theory.

6.3 *Conclusions*

We have successfully synthesised and fully characterised $S_x(CN)_2$ and $Se_x(CN)_2$ (x = 1,2,3). Unfortunately no NMR data was obtained for $E(ECN)_2$ (E = S,Se) due to poor solubility. A single crystal X-ray diffraction study of $Se_2(CN)_2$ showed the molecule crystallised as a single enatiomer and confirmed the diselenide bridged structure which had been proposed since it was first synthesised. We have successfully prepared polythiocyanogen by two different methods and for the first time fully characterised the polymer by microanalysis, ^{13}C and ^{15}N NMR, IR, Raman and mass spectroscopy. Based on the spectral data recorded and further literature evidence we propose that polythiocyanogen has a structure comprised of 1,2,4-dithiazole linked by nitrogen bridges. Our attempts to synthesise $(SeCN)_x$ in the same fashion as reported in the literature gave a red solid as reported. Full characterisation of this solid confirmed that it was red selenium rather than a $(SeCN)_x$ polymer. On the basis of our results and the observations of Bowmaker *et al* we propose that $(SeCN)_x$ does not exist.

6.4 *Experimental*

General experimental conditions and instrumentation were as set out on page 55. Sulfur dioxide (BOC) was used as received. Chlorine (BOC) was dried by passing the gas over phosphorus pentoxide. Bromine, iodine, potassium thiocyanate, potassium selenocyanate, selenium, silver cyanide and sulfuryl chloride (all Aldrich) were used as received. Sulfur dichloride was purified by distillation over a small amount of phosphorus trichloride. Silver thiocyanate and silver selenocyanate was prepared by mixing equimolar quantities of potassium thiocyanate or potassium selenocyanate respectively with silver nitrate (all Aldrich) in water.

$S_2(CN)_2$ 6.1. Silver thiocyanate (3.319 g, 0.02mol) was suspended in sulfur dioxide (20 cm^3) with vigorous stirring and bromine (1.598 g, 0.01 mol) was added dropwise. The mixture was stirred for 2 hours below –20 °C. The loss of the red/brown colour afforded by bromine indicated that the reaction was complete. The mixture was filtered to remove precipitated silver bromide leaving the colourless thiocyanogen solution. The sulfur dioxide was removed *in vacuo* below –20 °C to give **6.1** as a colourless crystalline solid. Yield 0.801 g (69 %). ^{13}C-{^1H} NMR ($CDCl_3$, -20 °C): δ(C) = 108.3 ppm (S-C≡N, singlet); ^{14}N NMR ($CDCl_3$, -20°C): δ = 286.6 ppm (C≡N, singlet). IR (CH_2Cl_2): 2161vs, 1612w, 1098w, 669s, 492m, 404w, 372w cm^{-1}. Raman (CH_2Cl_2 glass capillary): 2160vs, 668w, 494s, 399m, 176m cm^{-1}.

$S(CN)_2$ 6.2. Dichloromethane (40 cm^3) was added to sulphur dichloride (0.697 g, 6.769 mmol) and the resultant solution cooled to 0 °C. Silver cyanide (1.813 g, 13.538 mmol) was then added and the mixture was stirred for approximately 1 hour. The reaction was observed to be complete when the red/brown colour of sulphur dichloride had dissipated. The mixture was filtered to remove silver chloride followed by removal of solvent under reduced pressure below 0 °C to isolate the product as a white solid. Yield 0.384 g (67 %). ^{13}C-{^1H} NMR (CD_2Cl_2, -20 °C): δ(C) = 100.1 ppm (S-C≡N, singlet); ^{14}N NMR (CD_2Cl_2, -20°C): δ = 294 ppm (C≡N, singlet). IR (KBr): 2184vs, 697m, 670m, 376m, 278w, 252w cm^{-1}. Raman (glass capillary): 2196vs, 693w, 675w, 509w, 389w cm^{-1}.

$S(SCN)_2$ 6.3. This was prepared in the same fashion as **6.2** using sulfur dichloride (0.908 g, 8.818 mmol) and silver thiocyanate (2.927 g, 17.636 mmol). The mixture was filtered to remove silver chloride followed by removal of solvent under reduced pressure below 0 °C to isolate the product as a white solid. Yield 0.771 g (59 %). IR (KBr): 2153vs, 668m, 489m, 454m, 400m, 280w, 253w, 230w cm^{-1}. Raman (glass capillary): 2156vs, 672w, 492m, 458w, 433m, 214m, 202m cm^{-1}.

$Se_2(CN)_2$ 6.4. This was prepared in the same fashion as **6.1** using silver selenocyanate (2.028 g, 9.526 mmol) and iodine (1.209 g, 4.763 mmol). The mixture was stirred for 2 hours below –20 °C. The mixture was filtered to remove precipitated silver iodide leaving the yellow selenocyanogen solution. The sulfur dioxide was removed *in vacuo* below –20 °C to give **6.4** as a yellow

crystalline solid. Yield 0.742 g (74 %). ^{13}C-{^{1}H} NMR ($CDCl_3$, -20 °C): δ(C) = 96.0 ppm (Se-C≡N, singlet); ^{14}N NMR ($CDCl_3$, -20 °C): δ = 298.5 ppm (C≡N, singlet); ^{77}Se NMR ($CDCl_3$, -20 °C): δ = 0.45 ppm (Se-C≡N, singlet). Raman (glass capillary): 2157vs, 523m, 380w, 268s cm^{-1}.

$Se(CN)_2$ 6.5. Sulfuryl chloride (0.417 g, 3.090 mmol) was added to selenium powder (0.244 g, 3.090 mmol) and the mixture was stirred for 10 minutes. Then tetrahydrofuran (5 cm^3) was added and the solution was stirred for an hour to give a clear brown solution of selenium dichloride. Silver cyanide (0.827 g, 6.180 mmol) was added with tetrahydrofuran (20 cm^3) and the solution stirred for an hour. The solvent was then removed *in vacuo* and dichloromethane (30 cm^3) was added. The solution was filtered through a celite pad, washed with dichloromethane (20 cm^3) and the solvent removed *in vacuo* to yield the product as a white solid. Yield 0.268 g (66 %). Found (Calc. for $Se(CN)_2$): C 18.91 (18.33), N 21.26 (21.39)%. ^{13}C-{^{1}H} NMR (CD_2Cl_2, -20 °C): δ(C) = 91.5 ppm (Se-C≡N, singlet); ^{14}N NMR (CD_2Cl_2, -20 °C): δ = 299.8 ppm (C≡N, singlet); ^{77}Se NMR (CD_2Cl_2, -20 °C): δ = 0.29 ppm (Se-C≡N, singlet). EI^+ MS: *m/z* 132 $[M]^+$, 106 $[M\text{-}CN]^+$. IR (KBr): 2926vw, 2179vs, 1261w, 1096w, 1024w, 802w, 509vs, 338m, 305m, 279w, 270w, 250w, 244w cm^{-1}. Raman (glass capillary): 2188vs, 512s, 454w, 343w, 309w, 178w cm^{-1}.

$Se(SeCN)_2$ 6.6. This was prepared in the same fashion as **6.5** using sulfuryl chloride (0.295 g, 2.186 mmol), selenium powder (0.173 g, 2.186 mmol) and silver selenocyanate (0.930 g, 4.371 mmol). The solvent was then removed *in vacuo* and dichloromethane (30 cm^3) was added. The solution was filtered

through a celite pad, washed with dichloromethane (20 cm^3) and the solvent removed *in vacuo* to yield the product as a yellow crystalline solid. Yield 0.446 g (71 %). Found (Calc. for $Se(SeCN)_2$): C 8.41 (8.31), N 9.58 (9.70)%. EI^+ MS: *m/z* 292 $[M]^+$, 212 $[M\text{-}Se]^+$, 132 $[M\text{-}2Se]^+$. IR (KBr): 2929vw, 2141vs, 511m, 362w, 280w, 262w, 247w cm^{-1}. Raman (glass capillary): 2144vs, 1491w, 509w, 383w, 360w, 270s cm^{-1}.

$(SCN)_x$ 6.7. *Method a.* $S_2(CN)_2$ **6.1** was prepared exactly as above. The thiocyanogen formed was allowed to warm to room temperature resulting in spontaneous polymerisation to give polythiocyanogen as a brick red solid. Yield 0.672 g (58 %). Found (Calc. for $(SCN)_x$): C 20.44 (20.68), N 23.89 (24.12)%. ^{13}C DP-MAS NMR (75.4 MHz): δ(C) = 186.8 ppm (broad slightly asymmetric signal with low intensity spinning side bands) MALDI-TOF MS: *m/z* 1149 $[S_{20}C_{20}N_{19}]^+$, 1030 $[S_{18}C_{18}N_{17}]^+$, 914 $[S_{16}C_{16}N_{15}]^+$, 798 $[S_{14}C_{14}N_{13}]^+$, 682 $[S_{12}C_{12}N_{11}]^+$, 566 $[S_{10}C_{10}N_9]^+$, 450 $[S_8C_8N_7]^+$, 334 $[S_6C_6N_5]^+$, 218 $[S_4C_4N_3]^+$, 102 $[S_2C_2N]^+$. Selected IR data (KBr): 1206vbr,s cm^{-1}. Raman (glass capillary): 1508m, 1207vbr,s, 1155sh,s, 994w, 652vbr,m, 473s, 453sh,br,m, 400sh,br,m, 289m, 229m cm^{-1}.

Method b. Potassium thiocyanate (0.500g, 5.145 mmol) was ground to a very fine powder and added to a flask. Chlorine gas (excess) was then passed through the powder for 30 seconds. The mixture was then heated using a heat gun for approximately 1 minute. Reaction was observed to have occurred by the mixture turning a brick red colour. Once cool the mixture was ground to a fine powder and the process of chlorination followed by heating then grinding was repeated 5

times to ensure complete reaction. The resulting mixture was washed with water (30 cm^3) and filtered to remove KCl and any residual KNCS. The red powder collected was washed with methanol (20 cm^3) followed by diethyl ether (20 cm^3) then dried *in vacuo*. Yield 0.202g (68 %). The analytic and spectroscopic data for $(SCN)_x$ **6.7** synthesised by *method b* were identical to those found in material produced by *method a*. ^{13}C and ^{15}N labelled samples of $(SCN)_x$ were prepared by this method using ^{13}C and ^{15}N labelled KNCS respectively.

X-Ray Crystallography

Table 6.8 lists details of data collections and refinements. Intensities were corrected for Lorentz-polarisation and for absorption. For, **6.4** and **6.6**, data were collected at 125 K using a Bruker SMART system. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[109]

compound	**6.4**	**6.6**
Empirical formula	$C_2N_2Se_2$	$C_2N_2Se_3$
Crystal dimensions/mm	0.18 × 0.05 × 0.05	0.10 × 0.10 × 0.02
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	Pnma
a/Å	5.04488(11)	10.054(2)
b/Å	6.4597(14)	13.332(3)
c/Å	15.589(3)	4.4540(10)
α/°	90	90
β/°	90	90
γ/°	90	90
U/Å^3	508.01(19)	597.0(2)
Z	4	4
M	209.955	288.915
Dc/g cm^{-3}	2.745	3.215
μ/mm^{-1}	14.395	18.354
Measured reflections	2426	2043
Independent reflections (R_{int})	708(0.0568)	392(0.0960)
Final R1, wR2[I>2σ(I)]	0.191, 0.0377	0.0218, 0.0494

Table 6.8 Details of the X-ray data collections and refinements for compounds **6.4** and **6.6**.

Chapter 7: *Conclusions*

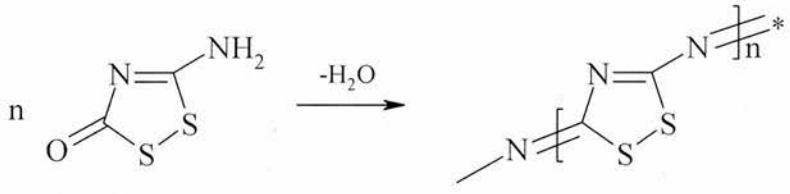
We have successfully prepared late transition metal complexes containing three different E,E-bidentate chalcogen donor ligands. Potassium cyanodithioimidocarbonate was used to prepare a range of cyanodithioimidocarbonate complexes showing two different coordination modes. We have prepared two homoleptic group 10 metal complexes (Pd and Pt) which adopt square planar ML_2 conformation. We have also prepared a series of square planar platinum(bis-phosphino) cyanodithioimidocarbonate complexes. In addition a series of bimetallic cyanodithioimidocarbonate complexes with group 8 (Ru), 9 (Rh, Ir) and 10 (Pt) metals have been prepared in which the cyanodithioimidocarbonate ligand is S,S' bidentate S' bridging. Cyanodiselenoimidocarbonate complexes were prepared in a similar fashion to the sulfur analogues. A series of square planar platinum(bis-phosphino) cyanodithioimidocarbonate complexes and two bimetallic group 9 (Rh, Ir) complexes were synthesised. These were observed to be similar to the sulfur analogues both spectroscopically and crystallography. We have also prepared a similar series of triselenocarbonate complexes. Interestingly reaction of $[PtCl_2(dppe)]$ with carbon diselenide in liquid ammonia yielded a mixture of the expected triselenocarbonate product $[Pt(CSe_3)(dppe)]$ and the perselenocarbonate complex $[Pt(CSe_4)(dppe)]$. We discovered that reaction of $[PtCl_2(PEt_3)_2]$ with carbon diselenide in liquid ammonia generates the novel tetramer $[\{Pt(\mu\text{-}CSe_3)(PEt_3)\}_4]$. Further reaction of $[Pt(CSe_3)(PMe_2Ph)_2]$ with $[M(CO)_5(thf)]$ (M = Cr, W, Mo) yielded bimetallic species of the type $[Pt(PMe_2Ph)_2(CSe_3)M(CO)_5]$ with the group 6 metal bonded to the exocyclic selenium of the

triselenocarbonate ligand. Further work in this area could include the rational synthesis of a series of perselenocarbonate complexes.

The pseudohalides $S_x(CN)_2$ and $Se_x(CN)_2$ (x = 1,2,3) were all successfully synthesised and fully characterised. Unfortunately no NMR data was obtained for $E(ECN)_2$ (E = S,Se) due to poor solubility. A single crystal X-ray diffraction study of $Se_2(CN)_2$ showed the crystal chosen contained a single enatiomer and confirmed the diselenide bridged structure which had been proposed since it was first synthesised.

We have successfully prepared polythiocyanogen by two different methods and for the first time fully characterised the polymer by microanalysis, ^{13}C and ^{15}N NMR, IR, Raman and mass spectroscopy. A series of 1,2,4-thiadiazole compounds were prepared for comparison with the polymer. We have successfully linked two 1,2,4-thiadiazole rings together by nucleophilic substitution at C5. Comparison of ^{13}C and ^{14}N NMR data with polythiocyanogen $(SCN)_x$ does not support a 1,2,4-thiadiazole structure for the polymer. In fact the spectroscopic data obtained for polythiocyanogen fits well with a 1,2,4-dithiazole structure. The ^{13}C and ^{15}N NMR spectra of the polymer shows that the observed peaks are in very similar environments to those noted in known 1,2,4-dithiazole compounds. The reactivity of the $(SCN)_x$ towards chlorine and $LiBEt_3H$ and the peaks in the Raman spectra in the range 400-480 cm^{-1} support the presence of sulfur sulfur bonds within the polymer. The MALDI-TOF mass spectroscopy of $(SCN)_x$ showed a series of peaks with a $(SCN)_2$ repeat unit (116 *m/z*) which implies this may be the monomer unit of the polymer. The $(SCN)_2$ repeat unit

fits very well with a structures of linked heterocyclic 5 membered rings. Based on the data obtained and the propensity of HNCS and $(SCN)_2$ to form 1,2,4-dithiazole rings (as discussed in chapter 1) we propose that polythiocyanogen has a structure comprised of 1,2,4-dithiazole linked by nitrogen bridges. To further confirm our structure for polythiocyanogen there are several experiments we would like to carry out. Firstly we would like to prepare a series of 1,2,4-dithiazole compounds to compare with the polymer. Then we will attempt to link 1,2,4-dithiazole rings together to make model compounds. Another objective would be to investigate whether it is possible to prepare polythiocyanogen from a 1,2,4-dithiazole ring. A possible method would be a Schiff's base condensation reaction as shown below.



Scheme 7.1 Proposed Schiff's base condensation.

Our attempts to synthesise $(SeCN)_x$ in the same fashion as reported in the literature gave a red solid as reported. Characterisation of this solid by microanalysis, mass spectroscopy and Raman spectroscopy confirmed that it was red selenium rather than a $(SeCN)_x$ polymer. On the basis of our results and the observations of Bowmaker *et al* we propose that $(SeCN)_x$ does not exist.

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Appendix – Publications

Synthesis and characterisation of triselenocarbonate complexes, Colin J. Burchell, Stephen M. Aucott, Alexandra M. Z. Slawin and J. Derek Woollins, *Dalton Trans.*, 2005, 735.

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