A synthetic and crystallographic study of some dithladiazolyl/ium compounds

Simon Ewen Lawrence

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A Synthetic and Crystallographic Study of Some Dithiadiazolyl/ium Compounds.

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A Thesis Submitted in partial fulfilment for the degree of PhD
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To Mum, Dad & Brenda

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Thanks also to the lads and lasses of Labs 19, 70, 72 and 100 - too numerous to mention (and I don't want to leave anyone out). The beers were good, so was the work along the way.

The "dog-handlers", Ray and Gordon, must be thanked for sterling work repairing glassware as quickly as it was generated. The other technical staff are thanked for their endeavours over the years.

Thanks to my family and friends, and finally, thanks to Brenda - for being there when it all mattered.

Memorandum

The work described in this thesis was carried out by the author, in the Department of Chemistry at the University of Durham between October 1991 and September 1994. I declare that this work has not been submitted previously for a degree at this or any other University. This thesis is a report of my own original work, except where acknowledged by reference. The copyright of this thesis rests with the author. No quotation should be published without his written consent, and information derived from it should be acknowledged. Material from this thesis has been or will be included in the following publications.

1. The Preparation and X-Ray Structure of the First Metal-1,3,2,4-Dithiadiazolylium Salt, $[Hg(CNSNS)_2][AsF_6]_2$, a Transfer Agent for the Dithiadiazolylium Ring.

A.J. Banister, I. Lavender, S.E. Lawrence, J.M. Rawson, W. Clegg *J Chem Soc Chem Comm* (1994) 29.

2. Novel Bonding Modes in Metallo-Dithiadiazolyl Complexes: Preparation and Structure of $Pt[SNCPhNS][PPh_3]_2{\cdot}MeCN$ and $Pt_3[SNCPhNS]_2[PPh_3]_4{\cdot}2PhMe$

A.J. Banister, I.B. Gorrell, S.E. Lawrence, C.W. Lehmann, I. May, G. Tate, A.J. Blake, and J.M. Rawson *J Chem Soc Chem Comm* (1994) 1779.

3. A New Type of Dithiadiazolylium Salt: $[p\text{-}Cl.C_6H_4.CNSSN]_6Cl_2$.

A.J. Banister, J.A.K. Howard, S.E. Lawrence *Phosphorus, Sulfur, Silicon and Related Elements* in press.

4. A Study of the Bonding and Packing in Dithiadiazolylium Salts -the Structures of $[\underline{p}Cl.C_6H_4.CNSSN]Cl$, $[(\underline{p}Cl.C_6H_4.CNSSN)_2Cl][S_3N_3]$, and $[\underline{p}Cl.C_6H_4.CNSSN]_6Cl_2$.

A.J. Banister, R.C.B. Copley, J.K. Cockcroft, J.A.K. Howard, S.E. Lawrence *Acta Cryst B* submitted for publication.

5. The Solid State Structures of Two Fluorinated Dithiadiazolyl Radicals: $[NC_5F_4CNSSN]_2$ and $[pNCC_6F_4CNSSN]$ - the First Solid State Paramagnetic Dithiadiazolyl Radical.

C.M. Aherne, A.J. Banister, N. Bricklebank, J.A.K. Howard, I. Lavender, S.E. Lawrence, J.M. Rawson, W. Clegg, C.I. Gregory and B.K. Tanner *J Chem Soc Chem Comm* submitted for publication.

6. Reaction of $[SNS][AsF_6]$ with $Hg(CN)_2$ and PhHgCN: Preparation and Crystal Structure of $[Hg(CNSNS)_2][AsF_6]_2$ and $[PhS_4N_3Ph][AsF_6]$.

A.J. Banister, I. Lavender, S.E. Lawrence, J.M. Rawson, W. Clegg *J Chem Soc Dalton Trans* in preparation.

7. Synthesis and Crystal Structures of Two Dithiadiazolyl Complexes of Pt: $Pt[SNCPhNS][PPh_3]_2 \cdot MeCN$ and $Pt_3[SNCPhNS]_2[PPh_3]_4 \cdot 2PhMe$.

A.J. Banister, I.B. Gorrell, S.E. Lawrence, C.W. Lehmann, I. May, A.J. Blake, and J.M. Rawson *J Chem Soc Dalton Trans* in preparation.

8. Further Studies of Radical Metallo-Dithiadiazolyl complexes: Synthesis and Crystal Structures of Pt[SNCPhNS][dppe] and Pd[SNCPhNS][dppe].

N. Adamson, A.J. Banister, J.A.K. Howard, S.E. Lawrence, I. May, J.M. Rawson, C.I. Gregory and B.K. Tanner *J Chem Soc Dalton Trans* in preparation.

9. A Mixed Bromide/Tribromide Salt of the Dithiadiazolylium Ring.

A.J. Banister, J.A.K. Howard, S.E. Lawrence *Acta Cryst C* in preparation.

Abstract

This work is concerned primarily with the structural aspects of the heterocyclic dithiadiazolyl and dithiadiazolylium rings.

Chapter one reviews both the 7π dithiadiazolyl and the 6π dithiadiazolylium ring systems. The synthetic routes to these ring systems are outlined, as well as the reactions that they are known to participate in.

Chapter two outlines the general methods used to synthesise and analyse the compounds prepared and examined in this thesis.

Chapter three investigates the crystal structures of various salts containing the dithiadiazolylium ring system. All of these salts possess halide anions, and the relationship between the size of the halogen and its position in relation to the heterocyclic ring is examined.

In chapter four the new metallo-dithiadiazolylium species, $Hg[CNSNS]_2[AsF_6]_2$, is examined as a potential transfer reagent for the dithiadiazolylium ring. The previously unknown halogen-substituted compounds, $[X.CNSNS][AsF_6]$ (X = Br, Cl), have been prepared from this metallo-dithiadiazolylium system.

Chapter five outlines the crystal structures of four novel compounds formed by metal-insertion into the S-S bond of the dithiadiazolyl ring.

The sixth chapter indicates possible ideas based on the work outlined in this thesis.

Abbreviations

The following abbreviations have been used in this thesis:

1,2 isomer	refers to the 1,2,3,5-dithiadiazolyl/ium ring system
1,3 isomer	the 1,3,2,4-dithiadiazolyl/ium ring system
C_6H_4	phenylene
CNSNS	the 1,3,2,4-dithiadiazolyl/ium ring system
CNSSN	the 1,2,3,5-dithiadiazolyl/ium ring system
C.S.D.	the Cambridge Structural Database
dbu	diazabicycloundecane
EHMO	extended-Hückel molecular orbital calculation
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
mnt	maleonitriledithiolate
MNDO	modified neglect of orbital overlap
MO	molecular orbital
SOMO	singly occupied molecular orbital

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Chapter 1

Introducing the dithiadiazolyl and dithiadiazolylium rings.

1.1 Introduction.

The chemistry of main group ring and cage systems has been known for many years, since the discovery of S_4N_4 by Gregory [1] and $(NPCl_2)_n$ by Lieber and Wöhler [2] in the 1830^s. However, it was not until the vacuum-line techniques developed by Stock [3] at the turn of the century, that the potential of this branch of science began to be realised. Sulfur-nitrogen chemistry, in particular, was largely neglected until the work of Becke-Göehring [4] in the 1940^s. To some extent this was because there were few methods available for the characterisation of these systems.

The advent of nuclear magnetic resonance as a major analytical tool for the synthetic chemist was less influential in this field than in many others, such as organic chemistry. The reasons for this are three-fold: (i) the active nuclei occur naturally in very low abundance - 0.37% and 0.76% for ^{15}N and ^{33}S respectively [5], (ii) the receptivity of these nuclei is small compared to the other elements (for example, the relative values are 1.04×10^{-3}, 2.26×10^{-3}, 1.00, 1.59×10^{-2}, 0.833 and 6.63×10^{-2} for ^{15}N, ^{33}S, ^{1}H, ^{13}C, ^{19}F and ^{31}P respectively [5]) and (iii) ^{14}N is quadrupolar whilst the active nuclei of S has a spin of 1.5, which both lead to complications in data collection and interpretation.

As a result, the mechanistic knowledge acquired in sulfur-nitrogen chemistry is much less than in its carbon counterpart. Indeed, the nature of trithiazyltrichloride in solution has only recently been determined [6].

For the researcher in the field, the arrival of X-ray crystallography was, and still is, a great boon. At last, the inorganic chemist could attempt to rationalise the structure and bonding present within these compounds [7], based on solid scientific data from the molecular level. In many ways, this was as influential on our understanding of inorganic compounds as n.m.r. was for the organic chemist.

Interest in sulfur-nitrogen chemistry was further stimulated by the discovery of the metallic [8] and superconducting [9] properties of $(SN)_x$ polymer in 1975. The idea was born that materials based on the lighter p-block elements, not metals and their derivatives, may be found to contain unusual magnetic/electrical/optical properties, and quickly generated widespread debate both within the scientific community and the media [10].

The work outlined in this thesis examines the chemistry and bonding of one group of potential organic metals, the five-membered CN_2S_2 dithiadiazolyl/ium rings. The next section will briefly review some aspects of this fascinating heterocyclic ring system. (Note that "dithiadiazolyl" describes the radical species, "dithiadiazolylium" refers to the cationic system and the anion is known as a "dithiadiazolylide").

1.2 The dithiadiazolyl/ium ring: an overview.

1.2.1 Introduction

In 1881 Demarçay reacted S_4N_4 with cold S_2Cl_2 to yield a product of composition $S_6N_4Cl_2$ [11]. Due to its low solubility and lack of chlorine n.q.r. signal [12] this compound remained an enigma until its X-ray structure determination in 1984 [13]. This showed an unusual bonding mode in which two $S_3N_2^{+\cdot}$ species interact through weak S...S contacts; formed by overlap of the appropriate singly occupied p-orbitals of two adjacent S atoms from each ring, see Figure 1.1.

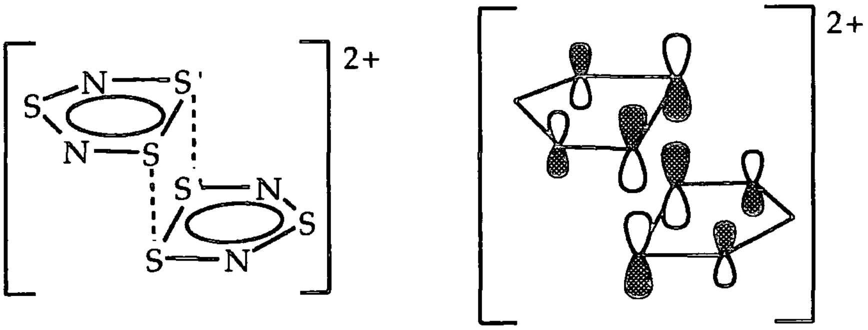
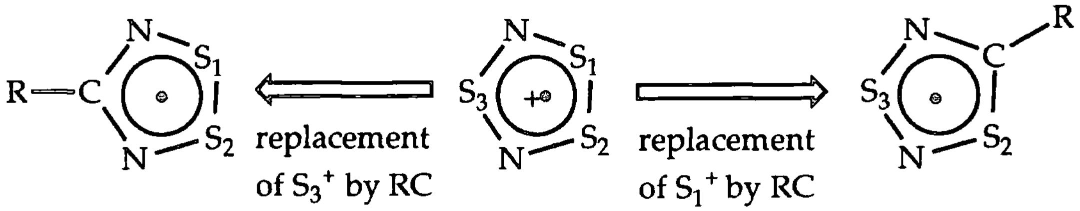


Figure 1.1 The Structure and SOMO present in the $S_6N_4^{2+}$ cation.

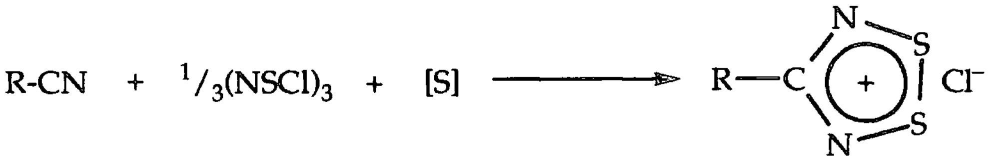
In 1975 Haddon proposed that compounds built-up from perpendicular stacks of neutral radicals rather than those based on charged species may contain unusual electrical or magnetic properties [10]. As shown in Scheme 1.1, replacement of S_1^+ or S_3^+ of $S_3N_2^{+\cdot}$ by the R-C group gives rise to the dithiadiazolyl ring, an attractive building block for such materials since modification of the R functionality can occur. Thus, it is expected that Peierls distortions can be minimised by reducing inter-stack interactions and increasing intra-stack contacts, leading to materials with the desired "metal-like" properties. Presently just two isomers are known.



Scheme 1.1 Showing the relationship between $S_3N_2^{+\circ}$ and the dithiadiazolyl ring. The 1,2,3,5 isomer is on the left, and the 1,3,2,4 isomer on the right.

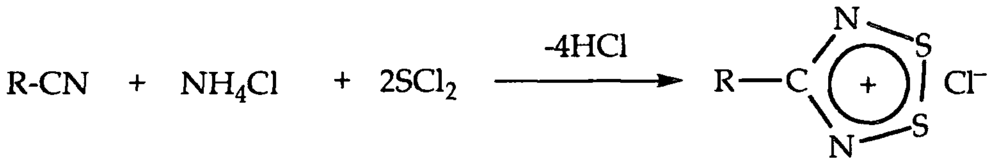
1.2.2 Synthesis

The precursor to the dithiadiazolyl radical species is the cationic 6π dithiadiazolylium system. This was first synthesised [14] as the chloride salt of the 1,2,3,5 isomer by stirring $(NSCl)_3$ with a nitrile for 24 hours at 60°C, see Eqn 1.1. The extra source of sulfur is obtained from the thermal decomposition of excess $(NSCl)_3$.

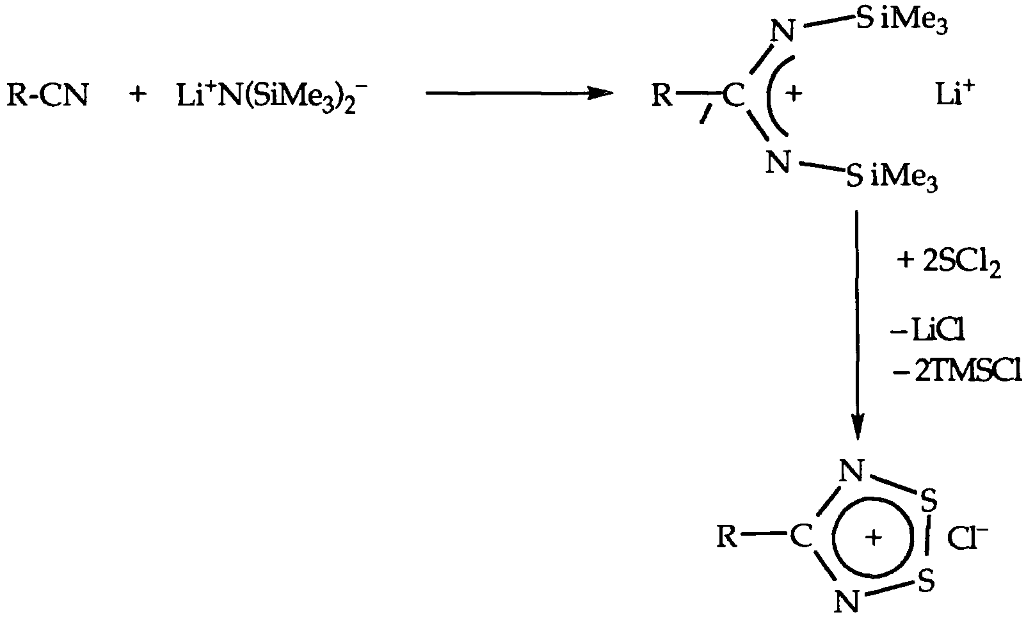


Eqn 1.1

Other routes commonly used have involved (a) the reaction of a nitrile with ammonium chloride and sulfur dichloride [15], Eqn 1.2, and (b) the reaction of a lithiated silylamide with nitrile [16], followed by addition of SCl_2, Eqn 1.3.



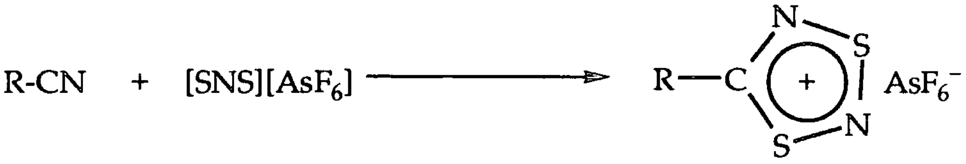
Eqn 1.2



Eqn 1.3

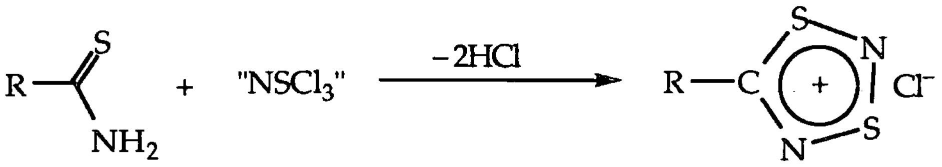
The latter is now used almost universally since it provides the cleanest reactions, typically yields are 70+% after purification by continuous extraction using SO_2. The analogous diselenadiazolylium ring can also be generated [17] using this method; $SeCl_4$/Se or $SeCl_4/Ph_3Sb$ providing an *in situ* supply of "$SeCl_2$".

The 1,3,2,4-isomer is prepared by the reverse 1,3-dipolar cycloaddition between the dithionitronium cation, SNS^+, and a nitrile, Eqn 1.4, with the hexafluoroarsenate(V) salt providing the cleanest reactions [18].



Eqn 1.4

For other salts, e.g. tetrachloroaluminate, side-reactions occur [19] which are thought to involve loss of halide from the anion and corresponding breakdown of the cation. One other route to the cationic 1,3,2,4- system involves the use of "$NSCl_3$" - generated *in situ* by the addition of excess $SOCl_2$ to $(NSCl)_3$ [20]. Subsequent reaction with a thioamide produces the chloride salt in 40-65% yield, Eqn 1.5. This route has not been fully developed since it is less versatile then the cycloaddition reaction mentioned above. To date, the Se analogue has not been prepared.



Eqn 1.5

1.2.3 Theoretical calculations on dithiadiazolylium salts

Molecular orbital calculations on both isomers have been undertaken by several workers at various levels [21-27]. The work endorses the formulation of these systems as 6π aromatic compounds in accordance with the simple electron counting method suggested by Banister [7] for planar S/N heterocycles. The Frontier orbitals of the 1,2 and 1,3 isomers are shown in Figures 1.2 and 1.3 respectively.

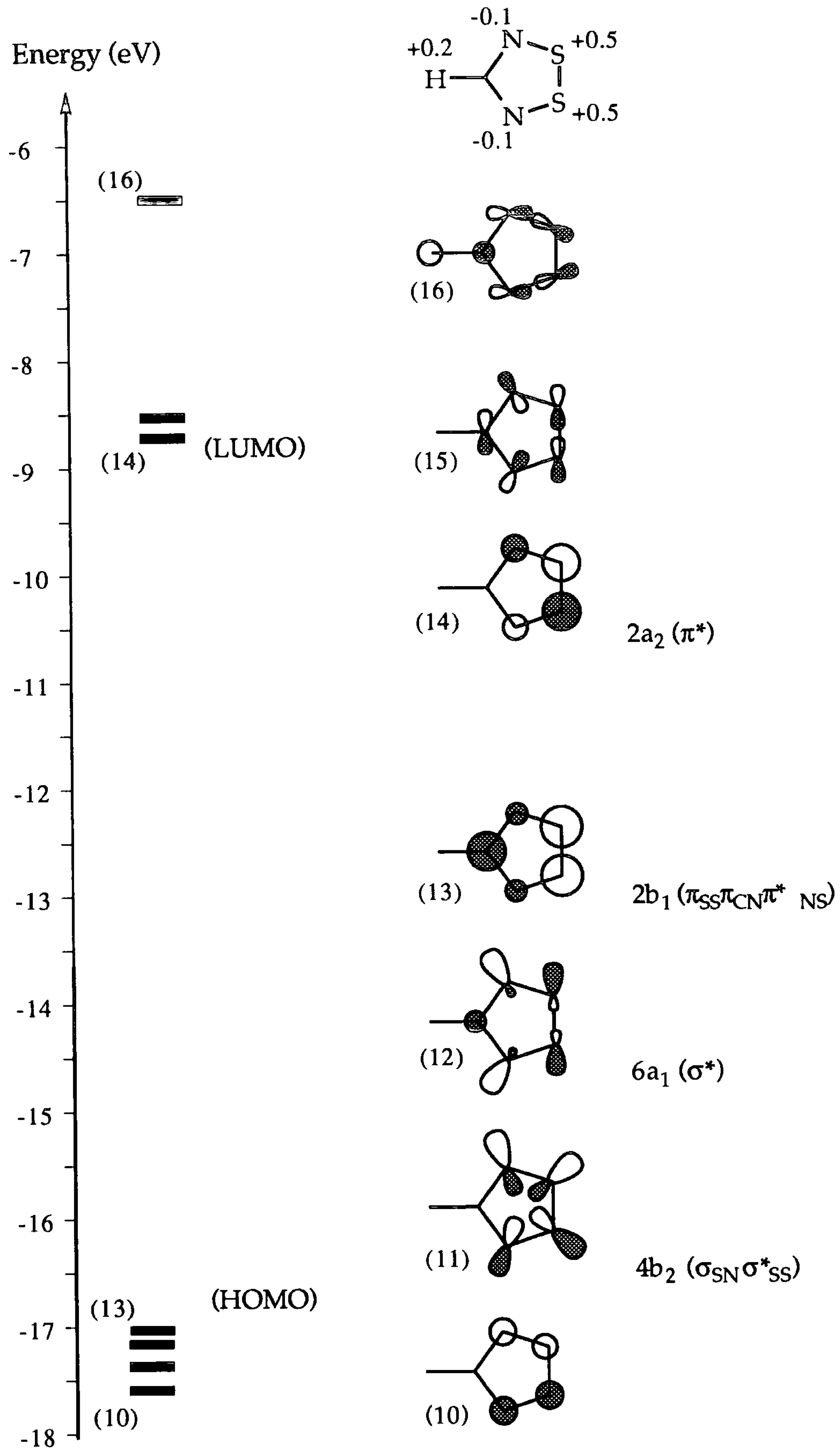


Figure 1.2 MO diagram for the 1,2,3,5 dithiadiazolylium cation.

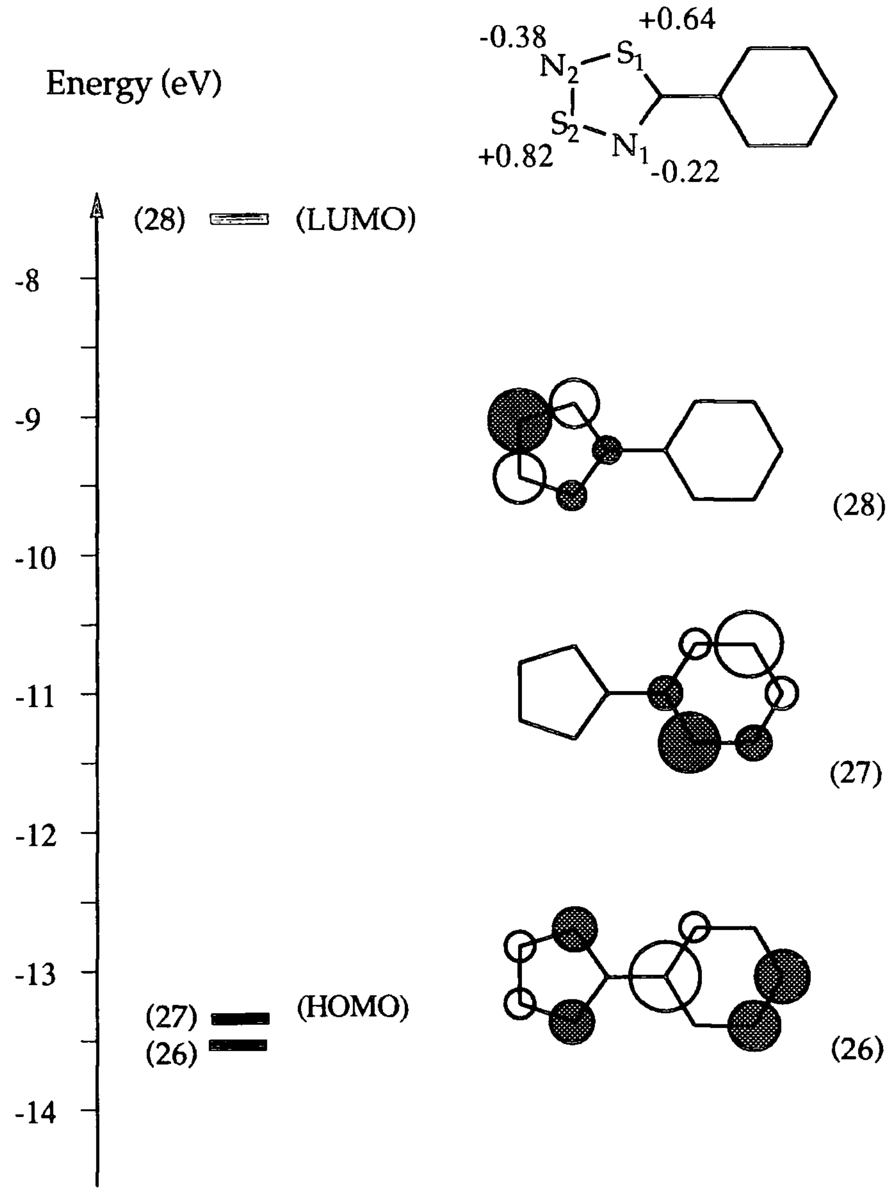


Figure 1.3 MO diagram for the 1,3,2,4 dithiadiazolylium cation.

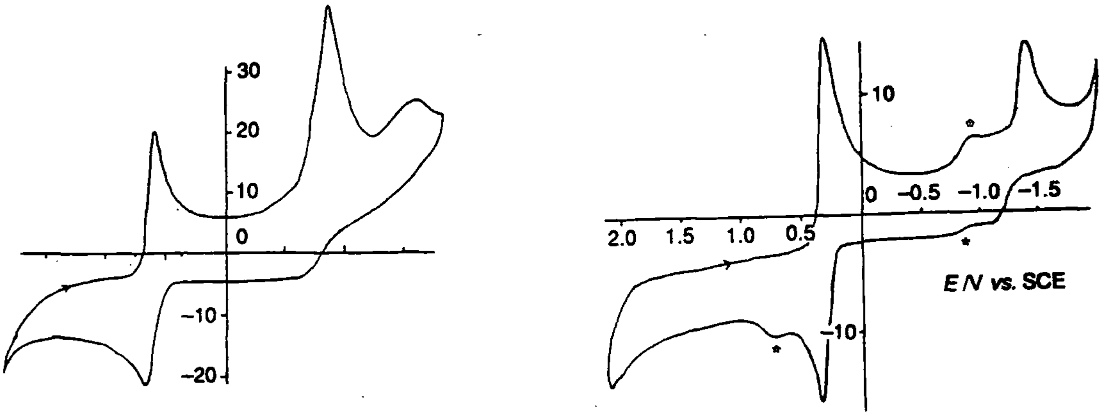
The sulfur atoms of the 1,2 isomer possess the majority of the positive charge, as expected from electronegativity considerations. For the 1,3 isomer the sulfur atom furthest from the carbon is the most positive because it is flanked by two nitrogen atoms, which are the most electronegative atoms in the ring. The position of the positive charge for both isomers is reflected in the cation/anion interactions in the solid state (see section 3.1).

1.2.4 Physical properties of salts

Both isomers are moisture sensitive, although it has been observed that the salts containing planar anions in a layered lattice are less susceptible to hydrolysis [25,27]. This is presumably because the lattice does not accommodate water molecules as easily as non-layered lattices.

The colour of the salt obtained from any reaction is a good indicator of the degree of charge transfer present in these salts [27]. For example, when the substituent group is a phenyl ring the very weakly co-ordinating hexafluoroarsenate salt is a bright yellow colour, the chloride is pale yellow/orange, the bromide is burgundy red, and the iodide is very dark in colour. As a consequence several U.V./visible studies of the 1,2 isomer have been undertaken, [22,24,27-29] and the results correlated with MO studies. Substituents possessing lone pairs, e.g. dialkylamino derivatives, are darkly coloured and absorptions are observed at ca. 530nm [22]. An analysis of the frontier orbitals shows that the allowed transitions are different in this case than when no lone pair is present on the substituent. Thus, the heterocyclic ring is sensitive to electronic effects such as lone pairs and modification of the molecular orbitals occurs. When the substituent does not possess a lone pair which may interact with the ring, the MO diagram is essentially as depicted in Figure 1.3.

Cyclic voltammetry studies have been carried out on a series of substituted-phenylene derivatives for both isomers [30-32]; typical traces are shown in Figure 1.4.



(a) (b)

Figure 1.4 Cyclic voltammograms for the cationic salts: (a) the 1,2,3,5 isomer and (b) the 1,3,2,4 isomer. * indicates re-arrangement of the 1,3,2,4 radical to the 1,2,3,5 species.

The studies show that the 1,2 isomers are easier to reduce than the 1,3 isomers and that there is a good correlation between the half-wave potential, $E_{1/2}$, and the Hammett constant, X, of the substituent on the phenylene ring. The reaction constant, ρ, which is a measure of the sensitivity of the system to electronic influences, is very small for the 1,2 isomer but larger for the 1,3 isomer; as expected from MO calculations. As an approximate guide, the LUMO of the 1,2 isomer has a nodal plane through the carbon atom of the ring (see Figure 1.2) and thus delocalisation of electron density from the substituent on the carbon atom to the heterocyclic ring is not likely to occur. However, for the 1,3 isomer this is not the case and delocalisation of electron density is more able to take place. This is in agreement with the U.V./visible studies since modification of the orbitals occurs when the substituent possesses a lone pair.

These cyclic voltammetric studies have also provided evidence for the formation of the dithiadiazolylide anion in an irreversible process, indicative of combination of the anion with the cation from the bulk solution. This is clearly seen in Figure 1.4.

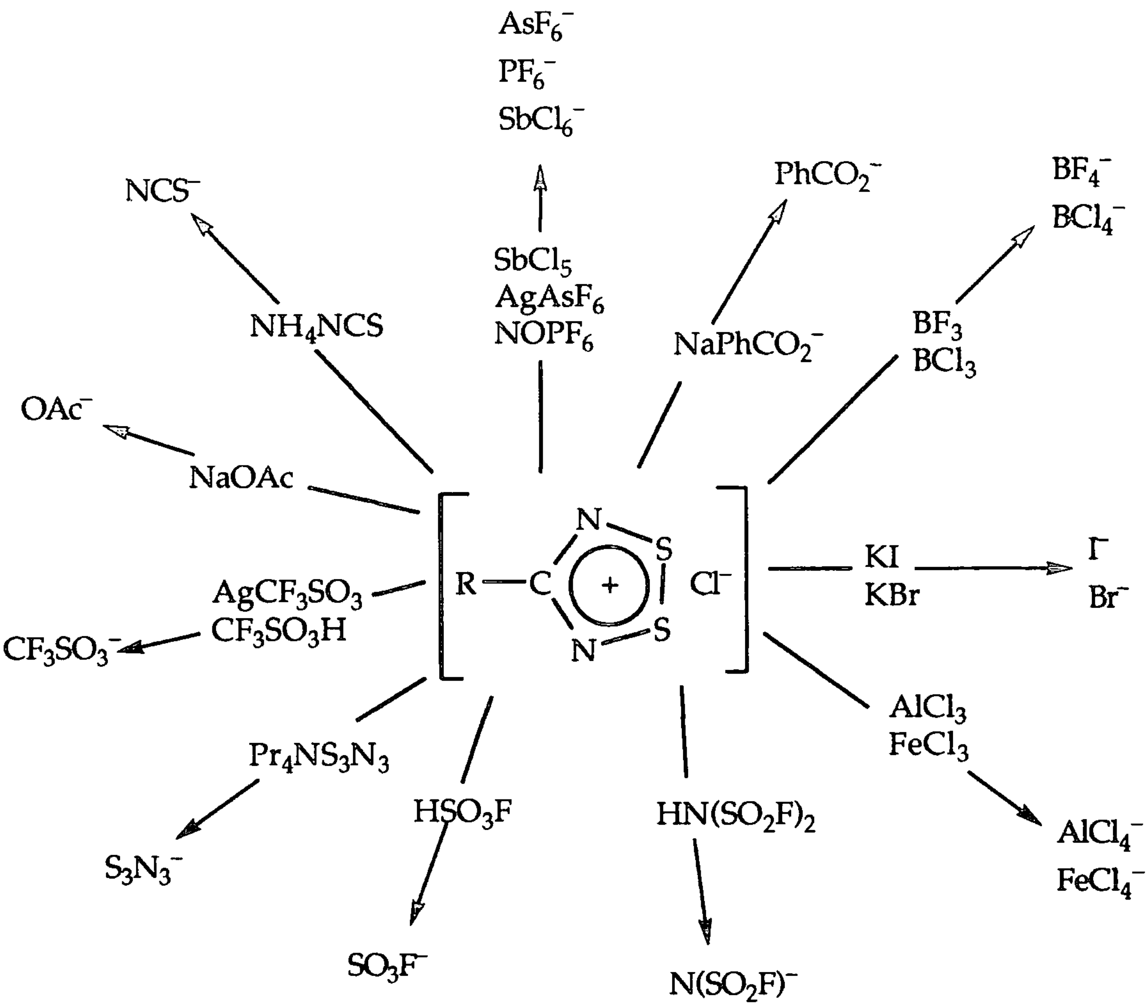
Although there have been few n.m.r. studies on these salts [15,20,33], there is a general shift to lower field for the cations cf. the parent nitrile, as expected for a decrease in the shielding of the nuclei.

1.2.5 Reactions of salts

As can be seen from the preparative routes involved, the 1,2 isomer is usually prepared as the chloride salt and the 1,3 isomer as the hexafluoroarsenate(V) salt. Both isomers can be readily converted to various other salts [15,24,25,28,34-39], although more are known for the 1,2 isomers since they are easier to prepare than the 1,3, isomers (SNS^+ is used by only two or three laboratories in the world since its preparation originally required specialist equipment). Some of the reactions of the 1,2 isomer are shown in Scheme 1.2 (next page).

The strongly co-ordinating salts (e.g. when the anion is I^- or NCS^-) are susceptible to dissociation in organic solvents to give the corresponding radical, with generation of iodine or parathiocyanogen [34-35]. Recent work by Oakley [40] has shown that a compound with the empirical formula of $R\text{-}CNSSN^+I^-$ has been stabilised in organic media. It exists as a tri-iodide salt interacting with three cationic rings.

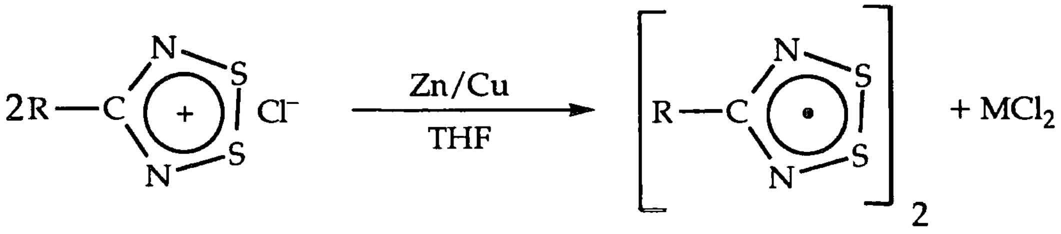
The 1,3 isomer is a good initiator for the cationic ring opening polymerisation of tetrahydrofuran [41]. It was already known that sulfur-nitrogen cations were able to affect this process [42], but the gels produced using the 1,3-dithiadiazolylium cation (as the hexafluoroarsenate(VI) salt) are cleaner, have a high molecular weight and low polydispersity.



Scheme 1.2 Metathesis reactions of dithiadiazolylium chloride. The cation for each product is omitted for clarity.

1.2.6 Preparation of radicals

The 1,2 radical systems are easily made from the corresponding cation using various reducing agents [24,34,36,43-46] in solvents such as SO_2 and t.h.f., Eqn 1.6. Purification is achieved by sublimation [35,46-47] *in vacuo* to give red/green dichroic crystals. Yield is usually only 40%.



Eqn 1.6

The radicals can also be made by metathesis of the chloride to unstable salts, e.g. I^- & NCS^-, but this route is no longer in favour.

The 1,3 radical requires more careful conditions since it has a tendency to re-arrange directly to the 1,2 analogue (see section 1.2.7). Silver or sodium dithionite is used to effect the reduction in the dark [21,48-50]. Insoluble 1,3 radical species are prepared by reduction with Ph_3Sb since washing away the dichloride readily affords separation to a pure product. Both radical systems exist as dimers in the solid state, held by overlap of p-orbitals as already seen in the $S_6N_4^{2+}$ cation (Figure 1.1).

1.2.7 Theory of radicals

The 1,2 radicals have been extensively examined [36,44,51-53] in order to rationalise the observed physical data (section 1.2.8). The reduction of the cation to the radical is accompanied by a partial occupancy of the π^* $2a_2$ orbital (see Figure 1.2, section 1.2.3). The energies of the frontier orbitals are modified slightly compared to the 6π cationic system, with the $2b_1$ and $4b_2$ orbitals becoming closer in energy. It is worth noting that EHMO calculations [51] place the $2b_1$ orbital above the $4b_2$ orbital, in contrast to earlier work [52], and thus the orbitals must be very close in energy.

The radical species are theoretically able to adopt different relative configurations in the solid state depending on the substituent attached to the ring. MNDO calculations [36] on these configurations show that the energy advantage of any one configuration over another is very small and it is the strength and orientation of secondary interactions, as well as the size and shape of the substituent, which is most likely to influence the configuration adopted.

Less work has been carried out for the 1,3 system [21,49-50] but comparisons of the two systems can be made [49-50]. The studies show that the re-arrangement is a thermally-forbidden but photochemically-allowed process [50]. In practice the re-arrangement can occur spontaneously at room temperature, unless the substituent is very bulky and stabilises the ring. The MO calculations have also granted an insight into the re-arrangement process itself, with a co-facial head-to-tail mechanism proposed [49]. This has also been demonstrated to occur in the solid state [54].

For both systems there are good (e.g. S...S distances between rings for the cis-oid and trans-oid structures) and bad (e.g. the ionisation potentials) agreements between experimental data and that predicted by theory. However, the theoretical data does provide new insights into the processes occurring on the experimental level, and can be used in a qualitative fashion by the synthetic chemist.

1.2.8 Physical properties of radicals

The radical species are moisture sensitive in a similar manner to the cationic salts. The 1,3 isomer is also unstable to light and heat in the solvated state, undergoing re-arrangement to the 1,2 isomer.

For the 1,2 isomer in solution there is an equilibrium between the monomer and the dimer pairs (as seen in the solid state and for $S_6N_4^{2+}$) with virtually complete dissociation to the monomeric form at room temperature [23,55]. Thus, the method used most often to characterise the radicals is e.s.r. spectroscopy. The 1,2 isomers show a 1:2:3:2:1 pentet due to splitting by the two equivalent nitrogens, as shown in Figure 1.5. The extra splitting is not usually observed, but can be attributed to ^{33}S coupling.

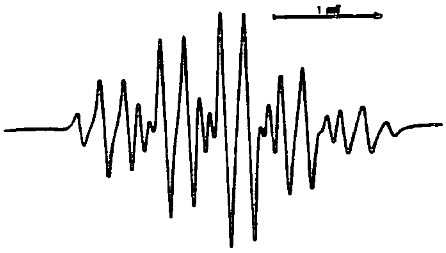


Figure 1.5 E.s.r. spectra for the 1,2,3,5 isomer (from ref 23).

The 1,3 isomers give rise to a 1:1:1 triplet associated with the nitrogen furthest from the carbon . The splitting due to this nitrogen is twenty times larger than that of the closest nitrogen, see Figure 1.6.

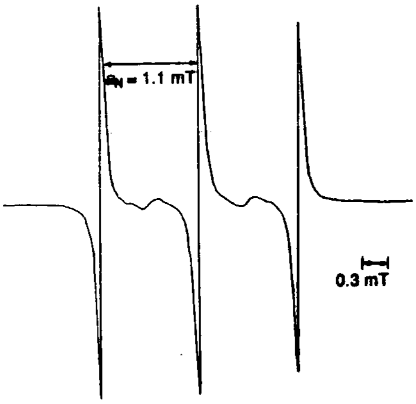


Figure 1.6 E.s.r. spectra for the 1,3,2,4 isomer (from ref 39).

For both systems the coupling due to the S atoms is not usually observed because of the low abundance of the active nuclei. The coupling to the nitrogen for the 1,2 isomer is low (cf. similar N-containing systems [27]) in accordance with MO calculations. Since the SOMO is of a_2 symmetry there will be a low spin concentration on the carbon nuclei and a corresponding delocalisation onto the sulfur atoms, hence the low values for coupling to nitrogen. The observed coupling for the 1,3 species agrees with MO calculations as well. A more detailed examination of the e.s.r data for these radical systems can be found in reference 27.

Photoelectron spectra for the 1,2 isomer show three distinct energy regions [24,44]. The first is associated with ionisation of the electron from the SOMO and occurs ca. 7-9eV. The second and third regions correspond to the ionisation of the heterocyclic electrons and those of the ligand respectively.

Theoretical calculations related to the photoelectron spectra are too high compared to the experimental data (in direct contrast to Koopman's theory [27]) but the relative energies and symmetries obtained are correct.

When the substituent on the heterocyclic ring is a ^tBu group both isomers are liquid at room temperature [50]. Magnetic data for both these compounds show an effective magnetic moment of 1.4 - 1.5BM, independent of temperature. A similar response is seen for the e.s.r. spectra of these compounds, implying the low magnetic susceptibility (cf. 1.73BM for a free electron) is not due to any process involving dimerisation or oligomerisation.

Cyclic voltammetry studies of the radical [30] show that the formation of the dithiadiazolylide anion is a reversible process, in contrast to the studies conducted on the cation (section 1.2.4). This occurs because there is no possibility of ion combination with the bulk solution, see Figure 1.7.

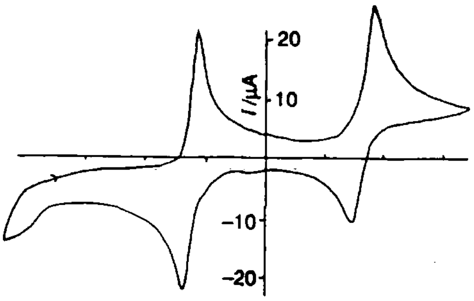
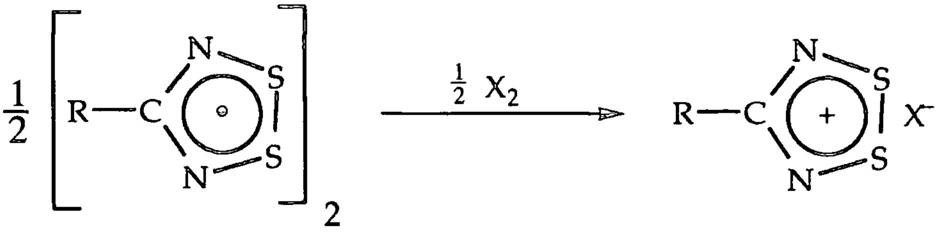


Figure 1.7 Cyclic voltammogram of the 1,2,3,5 radical.

1.2.9 Reactions of radicals

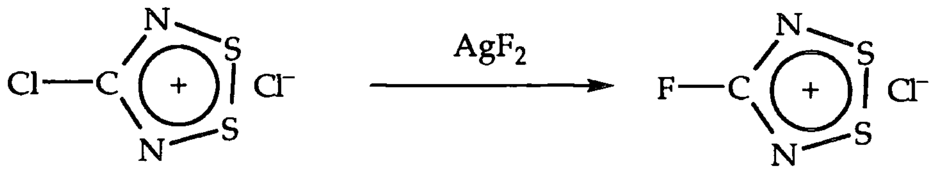
In many ways the chemistry of the dithiadiazolyl ring is more extensive than that of the corresponding cationic salts and is dominated by its radical nature in solution. The reactions are almost exclusively those of the 1,2 isomer since the 1,3 form is inherently unstable in solution [49-50,56], re-arranging after hours or days in solution - depending on the nature of the substituent attached to the ring. In some cases [49] the 1,3 radical is so unstable that polymerisation rather than isomerisation occurs at high concentration.

Oxidation of the 1,2 radical can be achieved using chlorine, sulfuryl chloride, sulfur mono-/dichloride, bromine and iodine, Eqn 1.7, to give salts of the dithiadiazolylium ring [34].

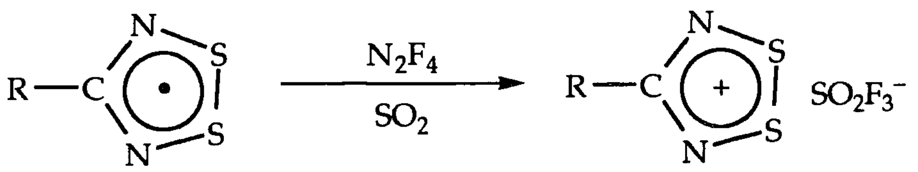


Eqn 1.7

Fluorination, however, is more complicated. Mews [36] has shown that fluorination of the chlorodithiadiazolylium chloride leads to the fluoro-substituted salt rather than the fluoride salt itself, Eqn 1.8. The reaction of the radical with the N_2F_4 fluorinating agent in SO_2 [57] lead to the isolation of the SO_2F_3 anion, Eqn 1.9. A dithiadiazolylium fluoride salt has yet to be isolated and fully characterised.

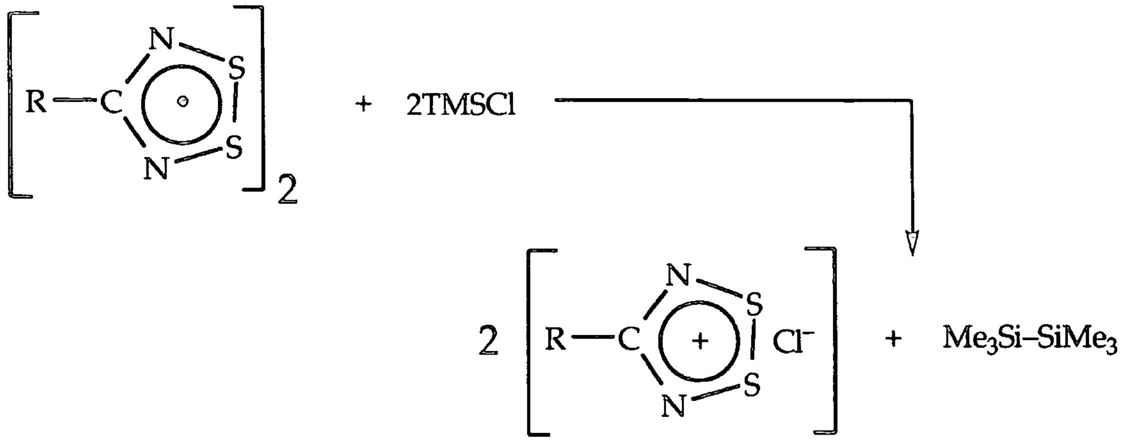


Eqn 1.8



Eqn 1.9

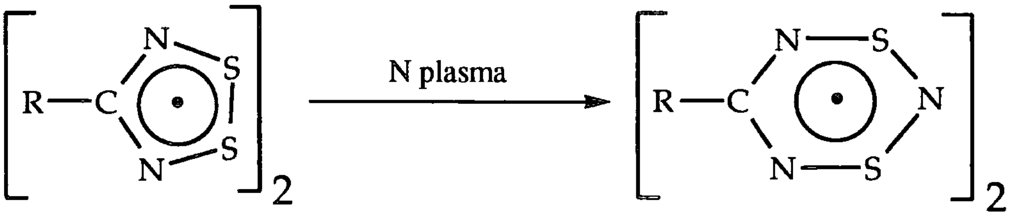
Since oxidation is easily accomplished, the use of the radical species as a reagent for dehalogenating E-X bonds has recently been explored [58]. This has been successful for E=B,P,Si, and activated C, with X=Cl and Br, Eqn 1.10. Since the radical species is more stable in dry organic media than more traditional reducing agents, such as K and Na, it is anticipated that its use may also become as widespread.



Eqn 1.10

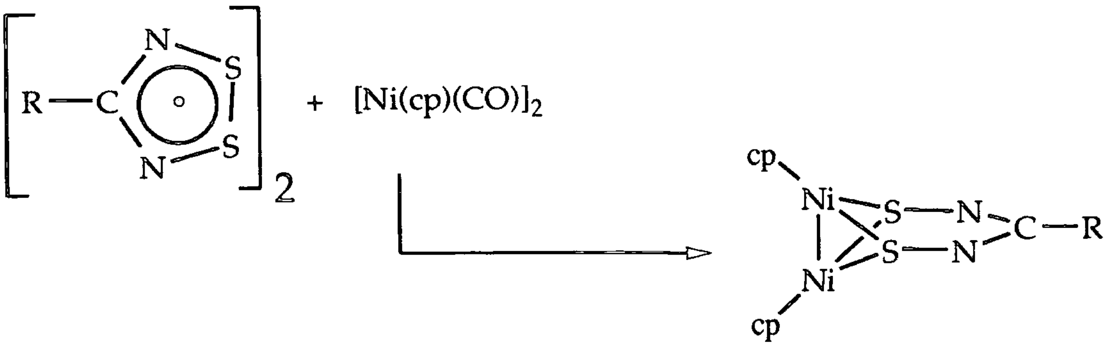
The radical has also featured as a reagent for the trapping of other sulfur-nitrogen radical species [25,59]. Reaction with $[S_5N_5]Cl$ and $[S_4N_3]Cl$ has led to the isolation of the following compounds: $[PhCNSSN][S_3N_2]Cl$, $[PhCNSSN]_2Cl$, $[PhCNSSN][S_3N_3]$, and $[(PhCNSSN)_2Cl][S_3N_3]$, some of which contain radical species.

The passage of a cool d.c. nitrogen plasma over the radical in the solid state induces the incorporation of a nitrogen atom to give the dithiatriazines [45,60] in high yield, Eqn 1.11. The nature of the substituent on the heterocyclic ring has a direct influence on the reaction pathway; only those compounds which pack with channels in the lattice are susceptible to nitrogenation in this manner. This behaviour has been observed for some cationic dithiadiazolylium salts as well.

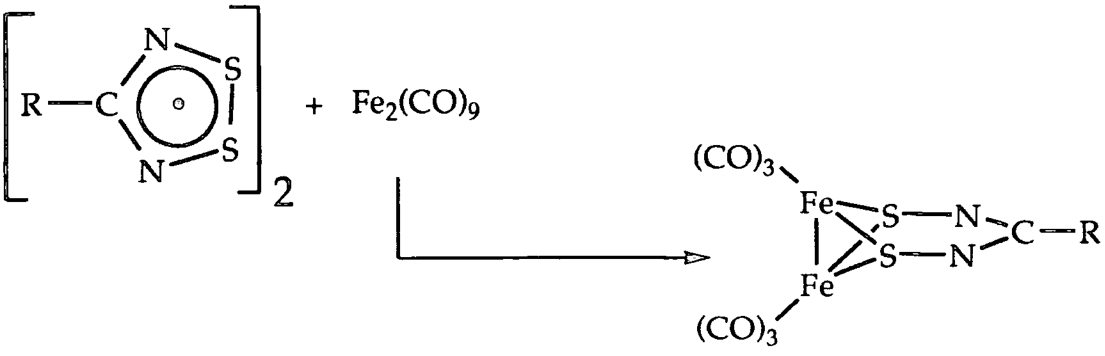


Eqn 1.11

The incorporation of atoms into the dithiadiazolyl ring has also been achieved by reaction of the radical with transition metal complexes [51-52]. The first complexes were isolated from the reactions with iron and nickel carbonyl complexes, see Eqns 1.12 and 1.13. The dithiadiazolyl ligand takes up a bridging position between two metal atoms. Recent work involving platinum and palladium phosphines [61] has shown that the ligand can take up slightly different bonding modes and these will be discussed more fully in Chapter 6.



Eqn 1.12



Eqn 1.13

1.2.10 Multi-dithiadiazolyl/ium systems.

Compounds containing more than one dithiadiazolyl/ium ring have been synthesised [17,30,39,41,46,59,62-70] in attempts to obtain stacked systems with interesting physical properties.

These compounds are usually made using the commonly-used routes developed for the mono-substituted systems. For compounds containing combinations of both the 1,2 and the 1,3 isomers, the 1,2 ring is introduced into the system first, converted to the hexafluoroarsenate(VI) salt, and SNS^+ reacted with the remaining nitrile group(s) to incorporate the 1,3 ring(s). This is because the dithiadiazolylium ring is not affected by the SNS^+ synthon but is degraded by the nucleophiles used in the production of the 1,2 isomer. The SNS^+ reagent is susceptible to attack by the chloride anion, hence metathesis to the hexafluoroarsenate(VI) salt before cyclisation.

All the compounds made to date contain aromatic groups as spacers between the heterocyclic rings, except for those based on $(CN)_2$ and $K^+C(CN)_3^-$. This means that the rings are essentially independent of each other and this has been confirmed by c.v. [17,30] and e.s.r [62-64]. $(CN)_2$ and $K^+C(CN)_3^-$ show different rates of reaction with SNS^+, in contrast to previous work on the rate of reaction of the synthon with nitrile functionalities [65-66]. This is because there is a different mode of attack of the second molecule of SNS^+. When the second molecule reacts there is a 1,3 ring in close proximity to the reacting nitrile and it is possible that the SNS^+ reagent interacts with the nitrogen atom of the CNSNS ring. This would lead to modification of the orbital energies present and an asynchronous cycloaddition mechanism taking place.

The reactions of the multi-substituted compounds are similar to the mono-substituted variety since the rings are non-interacting. Reduction can occur to give various radical/cations and di-radicals, tri-radicals etc. It is the 1,2 ring which is reduced before the 1,3 ring, as expected from consideration of the reduction potentials of the two rings (section 1.2.4) [30].

1.2.11 Concluding remarks.

The interest in this heterocyclic ring system stems from the bonding present in the 7π radical species, which it is anticipated may lead to materials with unusual magnetic or electrical properties, as well as the inherent reactivity due to a free electron in the solution state.

The work in this thesis attempts to improve our understanding of the solid state properties of this fascinating heterocycle, including the factors affecting the packing of both the cation and the radical.

This review has not been completely comprehensive and pertinent material for each chapter will be discussed more fully when appropriate.

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Chapter 2

Experimental methods.

2.1 General experimental techniques

The majority of the compounds outlined in this thesis are hydrolytically unstable and thus rigorous inert-atmosphere techniques have been employed throughout this work. A pressure-regulated Vacuum Atmospheres HE43-2 glove box fitted with an HE493 Dri-Train was used for the handling and storage of all air- and moisture-sensitive solid materials. All glassware was oven-dried at ca. 130°C for a minimum of 30 minutes and usually overnight before use. All manipulations were performed under an atmosphere of nitrogen or *in vacuo*. White spot nitrogen (BOC) was dried by passing through a column of phosphorus pentoxide and thence on to a double-manifold line. A monel vacuum line (designed by Dr Z.V. Hauptman of Durham University Chemistry Department) was used for the manipulation of sulfur dioxide and other volatile chemicals. The line was equipped with stainless steel and monel 'Whitey' taps (IKS4) fitted with Teflon compression ferrules and a Budenberg pressure gauge.

2.2 More specialised apparatus

2.2.1 The "dog"

Sulfur dioxide was used as a solvent for a large proportion of this work and specially designed apparatus has previously been developed for this work [1]. The "dog" is a two-limbed reaction vessel with each limb surmounted by a J. Young tap. The limbs are separated by a glass sinter (usually grade 3 porosity) as shown in Figure 2.1. The vessel can be connected via the $^1/_4$ -inch tubing to the monel vacuum line using Swagelok Teflon compression fittings; alternatively, a suitable glass adaptor with Swagelok fittings can allow connection to a double-manifold line. This apparatus can safely contain a pressure of 3-4 bar.

After reaction the vessel is taken into the glove box and solid material can be recovered from the bulbs by scoring with a glass knife and breaking off the bulb. The apparatus is then cleaned and can be readily reassembled. The apparatus is thoroughly annealed before re-use.

2.2.2 The closed extractor

This is based on the Soxhlet extraction system [2] and was designed by Dr Hauptman [3] (see Figure 2.2). The solvent is heated in the lower bulb and condensed above a glass sinter (usually grade 3 porosity) using a water-cooled jacket. In the majority of cases the system is kept under a static vacuum, allowing low temperature continuous extraction to occur. Sulfur dioxide can be safely used in this apparatus. Material is recovered in a similar manner to the "dog" (see above).

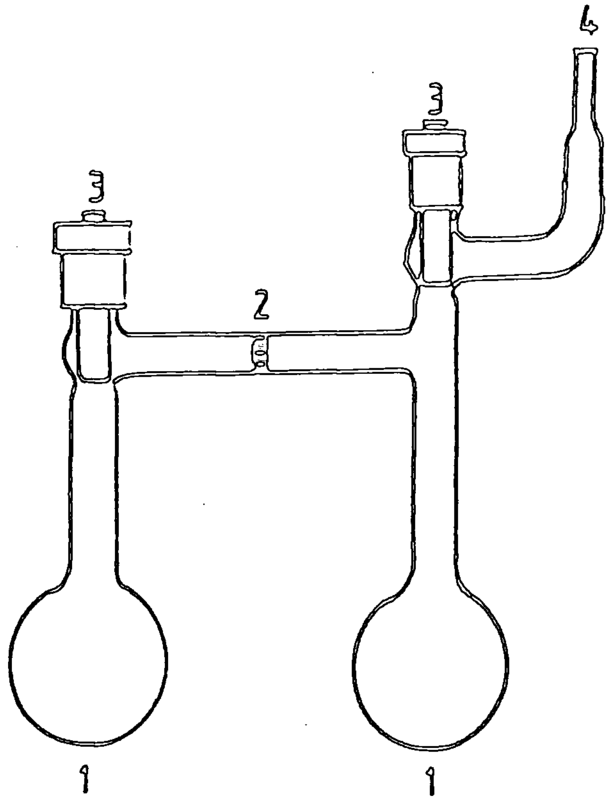

Figure 2.1 The "dog".

1. Reaction bulb.
2. Glass sinter (usually grade 3 porosity).
3. J. Young tap (Teflon).
4. $^1/_4$" ground glass.

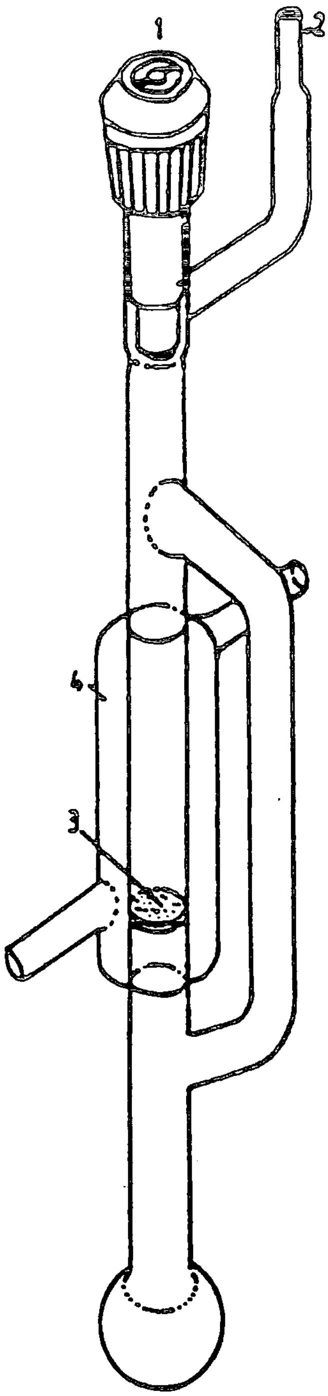

Figure 2.2 The closed extractor.

1. J. Young tap (Teflon).
2. $^{1}/_{4}''$ ground glass.
3. Glass sinter (usually grade 3 porosity).
4. Cooling jacket.

2.3 Temperature control

Temperatures between -78 and -40°C were obtained using dry-ice/acetone baths. A Haake F3 digital bath circulator filled with methylated spirits was used for stable temperatures in the region -40°C to +20°C. For temperatures above 20°C a water-bath, oil-bath or electrical heating tape was employed. Liquid nitrogen was used for the manipulation of volatile materials. A Haake PG10 programmer was utilised for crystal growth via the 'ripple' technique [4].

2.4 Analytical procedures

2.4.1 Differential scanning calorimetry (d.s.c.)

Differential scanning calorimetry was performed on a Mettler FP85 thermal analysis cell linked to a Mettler FP80 control unit, interfaced with an Opus PC III computer. A d.s.c. analysis program written by Dr J.M. Rawson, University of Durham, was used. Samples were hermetically sealed in aluminium pans in the glove box.

2.4.2 Elemental analysis

C, H and N analysis were carried out on a Carlo - Erba 1106 Elemental Analyser. After oxygen combustion, Br and Cl were titrated against silver nitrate, I against sodium dithionite, and S against barium perchlorate. As, Se and Hg were determined by decomposition in acid and the concentration measured using a Perkin-Elmer 5000 atomic absorption spectrophotometer. These were performed by Miss. J. Magee and Mrs. J. Dostal of the Department of Chemistry.

2.4.3 Infrared spectroscopy

Infra-red spectra were recorded as Nujol mulls between KBr or CsI plates on a Perkin-Elmer 457 or 577 grating spectrophotometer, as well as a 1600 or 1720X FT spectrophotometer.

2.4.4 Mass spectroscopy

Mass spectra were measured on a VG analytical 7070E spectrophotometer using either the Electron Impact (EI) or Chemical Ionisation (CI) technique. These were done by Dr. M. Jones and Miss. L.M. Turner of the Chemistry Department.

2.5 Drying of solvents

All solvents were refluxed under a nitrogen atmosphere for a minimum of six hours and collected in clean, dry Pyrex flasks fitted with a J. Young tap. They were then degassed using freeze-thaw cycles and stored under a nitrogen atmosphere.

Acetonitrile (Aldrich HPLC Grade) was refluxed over calcium hydride, distilled and filtered through a column containing pre-dried alumina.

Carbon Tetrachloride was refluxed over phosphorus pentoxide, distilled and collected.

Diethyl Ether (anhydrous) was pre-dried over sodium, refluxed over lithium aluminium hydride, distilled and collected.

Hexane was refluxed over phosphorus pentoxide, distilled and collected.

Methylene Chloride was refluxed over calcium hydride, distilled and collected.

Sulphur Dioxide (BDH Grade) was distilled onto phosphorus pentoxide and left to stand for a minimum of three days. It was further distilled onto calcium hydride at least 24 hours before use, and vacuum transferred into reaction vessels at liquid nitrogen temperatures.

Tetrahydrofuran was fractionally distilled from sodium lumps and stored over sodium wire. This was done by Mr B. Hall of the Department of Chemistry.

Toluene was refluxed over lump sodium and stored over sodium wire.

2.6 Preparation and purification of starting materials

Bromine (BDH Aristar) was dried by repeated distillation *in vacuo* prior to use and stored under vacuum in a tube fitted with a J. Young tap and a $^1/_4$ -inch glass adaptor.

Chlorine was distilled using the monel vacuum line, and stored over P_4O_{10}.

Dithianitronium Hexafluoroarsenate was prepared by the literature method [7] with some modifications [8].

Iodine Cyanide was sublimed *in vacuo.* A sample prepared by Dr Hauptman was available.

Sulfuryl Chloride was distilled under dynamic vacuum immediately prior to use and stored under nitrogen.

$S_3N_2Cl_2$ was prepared by the literature method [9].

Thionyl Chloride was purified by fractional distillation from 10% by weight triphenyl phosphite in apparatus equipped with Teflon sleeves. It was stored in the dark in a Pyrex bulb fitted with a J. Young tap. A sample prepared by Dr. M.I. Hansford was available.

Trithiazyltrichloride was prepared by the literature method [10].

All other reagents were used as received direct from the supplier.

2.7 Crystallographic procedures

2.7.1 Data collection

At the start of this work crystals suitable for data collection were mounted in glass Lindemanns , although they were later mounted direct from the reaction vessel using the "oil drop" technique [11]. A highly viscous perfluoropolyether (Riedel-de Haën) is utilised to coat the crystal, preventing oxygen/moisture attack, solvent loss etc. For the intensity measurements, a Rigaku AFC6S four-circle diffractometer (Molecular Structure Corporation) was used with MoKα X-ray radiation. A highly orientated graphite crystal afforded monochromated X-ray radiation ($\bar{\lambda}$=0.71073Å). Initial unit cell parameters were usually calculated from the setting angles of 20 accurately centred reflections, obtained from the "search" routine. The orientation matrix was transformed to a cell of higher symmetry if necessary. The Laue equivalents were usually checked. Final unit cell parameters were determined from 25 accurately centred high angle reflections. Low temperature experiments were conducted using an Oxford Cryostreams open-flow gas cooling system [12]. Typically, one reflection obtained from the search routine was re-scanned every 10K as the temperature was lowered. The rate of cooling was usually 120K/hour. At the target temperature all the reflections used to calculate the unit cell parameters were re-centred. The corresponding orientation matrix gave the unit cell at the data collection temperature.

The reflection intensity profiles were used to determine the ω-scan width and the aperture of the detector. The background was determined by increasing the scan width 25% on each side of the reflection profile. The collection limits were assessed from the Laue symmetry. In most cases some equivalent reflections were measured.

When a peak was scanned, it was re-scanned if $I/\sigma(I)$ was less than specified limits (typically 0.5 or 1.0) Three standards were collected every 150 reflections. The reason for this was two-fold: (i) any decay the crystal suffered was monitored and could be modelled later, and (ii) the orientation of the crystal was checked at regular intervals for movement. The data were collected in shells increasing in 2θ, in case of sudden crystal decomposition. This also enabled early termination of weakly diffracting crystals.

2.7.2 Computers and programs

Calculations were performed on a digital MicroVAX 3300 computer, or on a Hewlett Packard Apollo 700 Series workstation. The TEXSAN software package [13] was used for data reduction, absorption and decay corrections. Structure solution was performed using SHELXS-86 [14]. Various programs were used for structure refinement (SHELXTL-90, [14] SHELXL-93, [15] CRYSTALS [16]) as well as the SHELXTL-Plus molecular graphics program [14].

2.7.3 Data reduction, structure solution and refinement

The intensity data were corrected for Lorentz-polarisation effects. Appropriate corrections for absorption and decay were made after careful consideration of the psi-scans and standard intensity controls respectively. The structures in this thesis were solved by direct methods [17] or Patterson Fourier Synthesis [17]. Remaining non-hydrogen atoms were found from the difference Fourier maps. Full-matrix least-squares methods were used for structure refinement. Non-hydrogen atoms were initially refined with isotropic displacement parameters. Hydrogen atoms were then added in idealised positions, and the non-hydrogen atoms refined with anisotropic displacement parameters. Exceptions to this procedure are outlined in the text - see Chapters 3 and 5.

A weighting scheme was usually added towards the end of refinement.

The initial work in this thesis involves refinement based on F (where F is the Structure Factor); whereas the latter work (using SHELXL-93) is based on F-squared refinement. This may well lead to confusion and thus some definitions are detailed below.

For refinement based on F:

$$R_{(int)} = \frac{\Sigma \ |Fo^2 - Fo^2(\text{mean})|}{\Sigma \ [Fo^2]} \qquad R = \frac{\Sigma \ |\Delta|}{\Sigma \ |Fo|}$$

$$Rw = \frac{\Sigma \ |\Delta\sqrt{w}\ |}{\Sigma \ |Fo\sqrt{w}\ |} \qquad S\ (\text{Goof}) = \sqrt{\frac{\Sigma\ [w\Delta^2]}{(n-p)}}$$

For refinement based on F^2:

$R_{(int)}$ is the same as in F refinement, and R_1 from SHELXL-93 is the conventional R-value (defined above).

$$wR_2 = \sqrt{\frac{\Sigma\ [w\delta^2]}{\Sigma\ [w(Fo^2)^2]}} \qquad S\ (\text{Goof}) = \sqrt{\frac{\Sigma\ [w\delta^2]}{(n-p)}}$$

where,

Fo is the observed structure factor.
Fc is the calculated structure factor.
$\Delta = |Fo| - |Fc|$.
$\delta = (Fo^2 - Fc^2)$.
n = number of reflections used.
p = number of parameters.
w = weights.

2.8 References

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Chapter 3

Crystallographic studies of some dithiadiazolyl/ium compounds.

3.1 Introduction.

This chapter is concerned with the crystallographic studies of some cationic salts based on the 4-(chlorophenylene)-1,2,3,5-dithiadiazolylium ring system, which is shown in Figure 3.1.

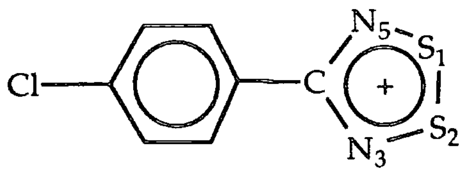


Figure 3.1 The 4-(chlorophenyl)-1,2,3,5-dithiadiazolylium ring is shown as an example of the labelling system for this ring.

The numbering scheme for the tables used within this chapter is shown in Figure 3.2.

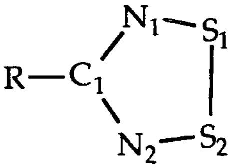


Figure 3.2 The dithiadiazolylium ring with the numbering scheme used in this chapter shown for clarity.

In order to provide as complete an insight as possible, a short review of the crystallographic data presently known for 1,2,3,5-dithiadiazolylium systems will now be discussed.

Salts of the 1,2,3,5-dithiadiazolylium ring can be categorised into four distinct groups, classified by the nature of the associated anion. The four types are listed below:

(i) systems in which the anions essentially do not interact with the ring,

(ii) those systems in which the anions interact with the ring, in the plane of the ring,

(iii) compounds containing anions which interact, but out of the plane of the ring,

(iv) those compounds which possess mixtures of the above types, and also mixtures involving the radical species.

3.1.1 Non-interacting anions.

All of the complexes in the first category contain the anionic octahedral fluorides of As or Sb, i.e. AsF_6^- and SbF_6^-. Six structural studies are known, [1-6] and these are detailed in Table 3.1.

The data from Table 3.1 show that the rings are equivalent within experimental error, as expected for systems of this type. However, there is some evidence that electron transfer does occur from the substituent to the heterocyclic ring since the length of the S-S bonds for R=Cl and R=NMe_2 only just overlap within 3 e.s.d.'s. There is a case for suggesting these are not equivalent, especially since one system is electron-withdrawing and the other electron-releasing. This is in agreement with MO calculations for the 1,2,3,5 isomer since a node exists on the ring carbon atom, section 1.2.3. Slight discrepancies are observed in the cyclic voltammetry studies for these systems, section 1.2.4, although the effect of changing substituents on a phenyl ring is negligible. Thus, the rings should be identical for two reasons, (i) electronic considerations which show that the ring is effectively independent of the nature of the substituent, and (ii) the non-interacting nature of the anion means there are minimal cation/anion attractions perturbing the rings from ideal geometry. As such, the geometry of these systems approximates to the ideal geometry of the totally unperturbed ring.

The secondary contacts in these structures are between S and F, and although they are within the van der Waals radii [7], they are essentially non-bonding in nature, for the reasons stated above. The five-membered heterocyclic ring is planar, in accordance with the electron counting rules of Banister [8].

3.1.2 In-plane anionic interactions.

The complexes of the second category, with the anion in the plane of the cationic ring and interacting with it, are presently only known for the three chloride salts which have been crystallographically characterised [9-11]. The molecular orbitals for this type of interaction are shown in Figure 3.3 (corresponding to the 16th molecular orbital in Figure 1.2, section 1.2.3). The ring data for this type of interaction are summarised in Table 3.2.

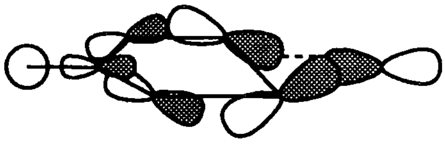


Figure 3.3 The molecular orbitals present when a chloride anion interacts in the plane of the ring.

Table 3.1 Bond lengths and angles for some 1,2,3,5-dithiadiazolylium salts containing "non-interacting" anions.

Compound	Bond Lengths, Å					Bond Angles, °					Ref.
	C_1-N_1	N_1-S_1	S_1-S_2	S_2-N_2	N_2-C_1	$N_1C_1N_2$	$C_1N_2S_2$	$N_2S_2S_1$	$S_2S_1N_1$	$S_1N_1C_1$	
[Cl.CNSSN][AsF_6]	1.325(8)	1.573(5)	1.996(2)	1.573(5)	1.317(8)	120.3(5)	114.2(4)	95.8(2)	95.0(2)	114.6(4)	[1]
[Ph.CNSSN][AsF_6]	1.337(6)	1.573(5)	2.023(2)	1.563(4)	1.354(6)	117.4(4)	116.0(3)	95.3(2)	94.8(2)	116.4(4)	[2]
[Me_2N.CNSSN][SbF_6] †	1.353(10)	1.586(9)	2.022(7)	1.586(9)	1.353(10)	118.5(10)	115.6(9)	95.4(4)	95.4(4)	115.6(9)	[3]
[C_6H_4(CNSSN)$_2$][SbF_6] *	1.334(12)	1.576(9)	2.009(4)	1.577(9)	1.348(13)	119.0(9)	114.6(7)	95.6(4)	95.3(4)	115.3(8)	[4]
[*p*-(CNSNS)C_6H_4(CNSSN)] [AsF_6] †	1.339(10)	1.571(8)	2.019(4)	1.582(7)	1.351(11)	118.7(8)	114.9(6)	95.4(3)	95.4(3)	115.7(6)	[5]
[*p*-Cl.C_6H_4.CNSSN][AsF_6] †	1.341(9)	1.587(8)	2.010(5)	1.587(8)	1.341(9)	119.8(7)	114.5(6)	95.6(3)	95.6(3)	114.5(6)	[6]

† The mean figures and error values are quoted from the paper.

* The two 1,2,3,5-dithiadiazolylium rings are crystallographically equivalent.

Table 3.2 Bond lengths and angles for some 1,2,3,5-dithiadiazolylium salts containing in-plane interacting anions.

Compound	Bond Lengths, Å					Bond Angles, °					Ref.
	C_1-N_1	N_1-S_1	S_1-S_2	S_2-N_2	N_2-C_1	$N_1C_1N_2$	$C_1N_2S_2$	$N_2S_2S_1$	$S_2S_1N_1$	$S_1N_1C_1$	
[CCl_3.CNSSN][Cl] †	1.308(15)	1.587(10)	2.009(6)	1.579(10)	1.329(13)	122.2(11)	113.4(10)	95.4(4)	95.4(5)	113.5(8)	[9]
[Me.CNSSN][Cl]	1.334(4)	1.596(2)	1.991(1)	1.587(3)	1.329(4)	118.2(2)	115.6(2)	95.5(1)	95.1(1)	115.5(2)	[10]
	1.334(3)	1.593(2)	2.031(1)	1.588(2)	1.338(3)	119.0(2)	115.2(2)	95.4(1)	95.0(1)	115.4(2)	
[Ph.CNSSN][Cl] †	1.345(13)	1.594(10)	1.991(5)	1.590(10)	1.351(13)	118.7(8)	114.6(7)	96.0(3)	95.8(3)	114.8(7)	[11]
	1.358(12)	1.585(10)	1.989(5)	1.595(10)	1.314(12)	119.4(8)	114.4(7)	96.3(3)	95.2(3)	114.7(6)	
	1.356(13)	1.581(10)	1.991(5)	1.595(10)	1.320(13)	118.8(8)	115.4(7)	95.2(3)	96.0(3)	114.5(7)	

† The mean figures and error values are quoted from the paper.

The bonding can be considered to be a 3-centre-2-electron system, in a similar manner to that seen for the bridging methyl groups in Al_2Me_6 [12], and this is responsible for the slight decrease in the length of the S-S bond for the chloride systems cf. those seen for the unperturbed systems in section 3.1.1.

Solvent interactions involving co-ordinating solvents such as acetonitrile have also been observed in cationic salts [5-6], and these occur in an analogous manner to that seen for the chloride systems, see Figure 3.4.

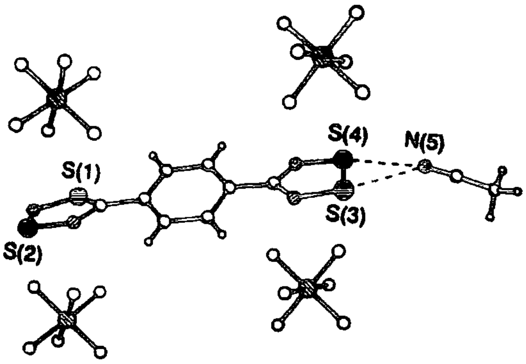


Figure 3.4 Solvent interactions in $[p\text{-}(CNSNS)C_6H_4(CNSSN)][AsF_6]$. The closest anions are also shown.

Similar interactions have also been observed between radicals which contain donor groups on the R substituent, such as $[p\text{-}Cl.C_6H_4.CNSSN]_2$. Several $S^{\delta+}$... $Cl^{\delta-}$ in-plane interactions lead to tetramer units, as shown in Figure 3.5 [13].

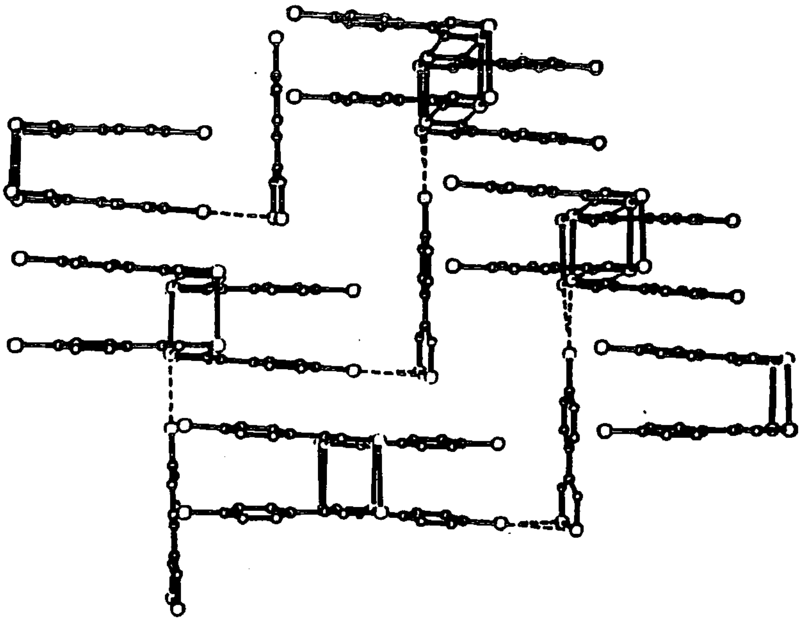


Figure 3.5 View of the tetramer units in $[p\text{-}Cl.C_6H_4.CNSSN]_2$, showing the chlorine interactions with the ring [13b].

3.1.3 Out of plane anionic interactions.

These complexes are characterised by soft anions interacting with the π-system of the dithiadiazolylium cation (the 14th molecular orbital in Figure 1.2, section 1.2.3) in a π-π* donor-acceptor process. Two structures, $[Ph.CNSSN]_2[Pt(mnt)_2]$ [14] and $[Ph.CNSSN][S_3N_3]$ [15] have been determined by single crystal X-ray diffraction and these are shown in Figures 3.6 and 3.7 respectively.

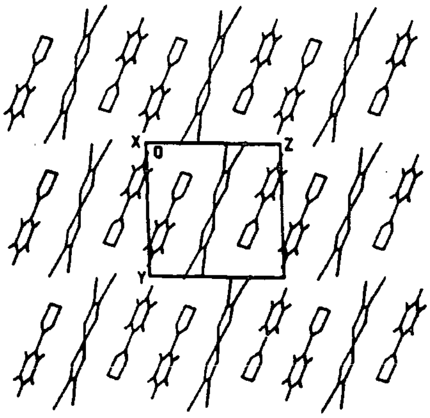


Figure 3.6 The sheets present in $[Ph.CNSSN]_2[Pt(mnt)_2]$.

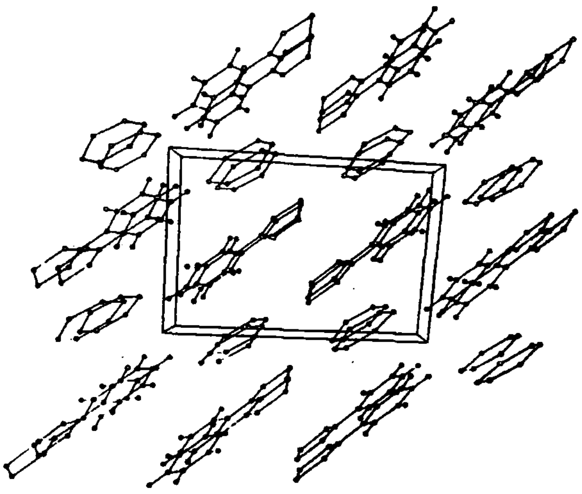


Figure 3.7 View of the layer lattice present in $[Ph.CNSSN][S_3N_3]$.

For both structures, the mean planes of the cations and the anions are approximately co-planar, in order to maximise the π-π* donor-acceptor interactions within the complex. The degree of charge-transfer from the anion to the cation has been calculated as 0.86e⁻ for $[Ph.CNSSN][S_3N_3]$ [15]. It is less for $[Ph.CNSSN]_2[Pt(mnt)_2]$ and this can be seen from a comparison of the crystal data for such systems (Table 3.3).

Table 3.3 S-S bond lengths and cation....anion distances for selected compounds.

Compound	S-S Bond Length	Inter-ion Distance	Ref
[Ph.CNSSN][Cl]	1.991(5) 1.989(5) 1.991(5)	— ¥	[11]
[Ph.CNSSN]$_2$[Pt(mnt)$_2$]	2.050(4)	2.998 ‡	[14]
[Ph.CNSSN][S$_3$N$_3$]	2.064(2)	2.906(3)	[15]
[Ph.CNSSN]$_2$	2.089(5)	3.038 - 3.186 †	[16]

¥ No π-rich anion present in this compound.

‡ No error quoted in paper.

† This is the distance between the two rings of a radical pair.

The data in Table 3.3 show that there is an increase in the length of the S-S bond as electron density is placed in the dithiadiazolylium ring. This is as expected from consideration of the MO Diagram for the cation (see Figure 1.2, section 1.2.3) since the LUMO is anti-bonding w.r.t. the S-S bond length. The inter-ion distance for the [S$_3$N$_3$] salt is less than that of the [Pt(mnt)] salt, indicative of a larger degree of charge-transfer, and this is reflected in the length of the S-S bond in the cation, since charge-transfer increases the electron density in the orbitals which are anti-bonding w.r.t. the S-S bond.

3.1.4 Mixed salts.

Most of the salts in this category are mixtures of salts of the above structural types, although a common feature is the presence of at least one chloride anion. A list of these compounds is given in Table 3.4.

Table 3.4 S-S bond lengths for the compounds in category 4.

Compound	S-S Bond Lengths	Ref.
$[(Ph.CNSSN)_2Cl][S_3N_3]$	2.034(1) 2.047(1)	[15, 17]
$[(Ph.CNSSN)_2Cl][Pt(mnt)_2]$	2.004(5) 2.007(5) 2.006(5) 1.988(5)	[14]
$[Ph.CNSSN]_3[AsF_6]_2Cl$	2.001(2) †	[3]
$[Me.CNSSN]_5[CoCl_4]Cl_3$	1.99(1) 2.02(1) 2.00(1) 2.00(1) 2.02(1)	[10]
$[CF_3.CNSSN]_3Cl$	2.085(2) 2.086(2) 1.989(3)	[18]
$[Ph.CNSSN][S_3N_2]Cl$	2.055(2)	[15, 17]

† Mean S-S bond length quoted.

$[(p\text{-}Cl.C_6H_4.CNSSN)_2Cl][Pt(mnt)_2]$ [14] and $[(Ph.CNSSN)_2Cl][S_3N_3]$ [15,17] both contain two dithiadiazolylium rings held together by S...Cl interactions in a 5-centre-4-electron system, see Figure 3.8. The chloride anion is located in a slightly asymmetric arrangement between the sulfur atoms, presumably because the planar anions are distorting the system. There is an increase in the S-S bond length for $[(Ph.CNSSN)_2Cl][S_3N_3]$ cf. the monochloride salt because of two competing effects. The chloride anion is attempting to maintain a tight bonding arrangement with the sulfur atoms, whereas the influence of the planar anion is to increase the length of the S-S bond.

However, when $[Pt(mnt)_2]$ is present the S-S bonds are similar to that seen for the monochloride systems, since the $[Pt(mnt)_2]$ ion is less able to participate in charge-transfer processes.

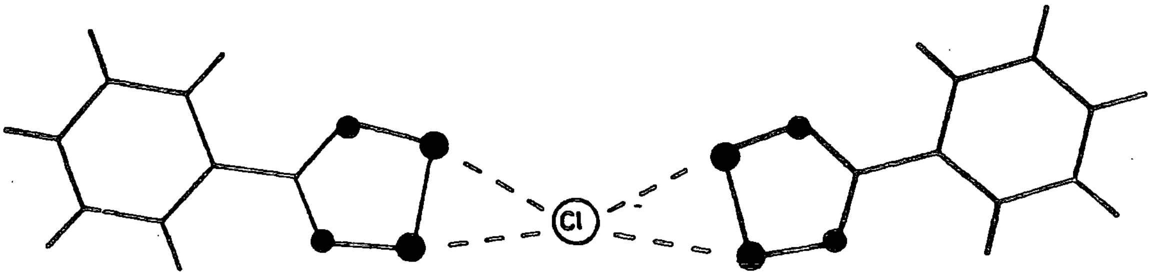


Figure 3.8 Showing the central chloride anion held by the four S atoms in salts containing the $[(Ph.CNSSN)_2Cl]$ cation.

In $[Ph.CNSSN]_3[AsF_6]_2Cl$ [3] and $[Me.CNSSN]_5[CoCl_4]Cl_3$ [10] there are numerous S...Cl contacts, which are further experimental evidence that the S atoms possess the majority of the positive charge in the 1,2,3,5-isomer, as was described in section 1.2.3. The chlorine atoms of the $CoCl_4^-$ anion also participate in this process. The fluorine atoms of the AsF_6^- anion interact very weakly with the cationic rings, as expected due to the non-interacting nature of these octahedral anions, section 3.1.1.

$[CF_3.CNSSN]_3Cl$ [18] is included in this category since an examination of the empirical formula suggests a formal ring charge of plus one-third. However, the crystal structure analysis reveals that the radical species is co-crystallised with the chloride salt, as evidenced by the differing lengths of the S-S bonds (Table 3.4).

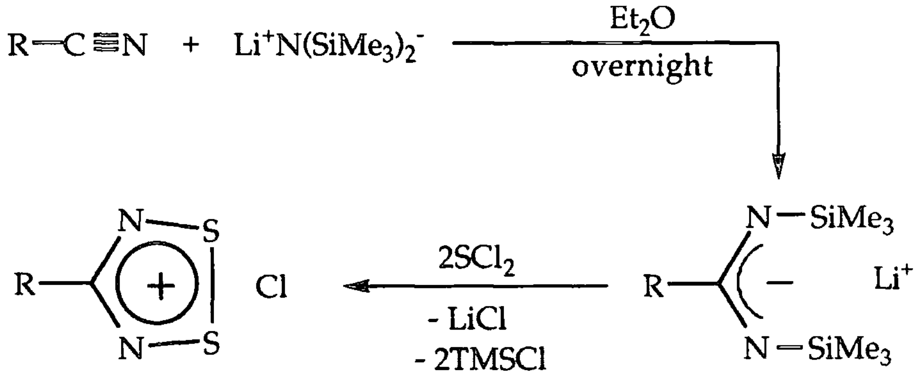
$[Ph.CNSSN][S_3N_2]Cl$ [15,17] is unusual in that it appears to contain a lone dithiadiazolylium radical with $[S_3N_2]Cl$. There is, however, significant π-π^* overlap between the two heterocyclic rings and thus, consideration of the length of the S-S bond suggests that there is a small positive charge associated with the carbon-containing ring.

The above review shows that a wide range of structural motifs is known for the dithiadiazolylium ring system. Classically, spherical anions have been utilised in the crystallisation and characterisation of these compounds and it is only recently that layered anions have been used in an attempt to design compounds with interesting physical properties. Four new crystal structures will now be presented and these are listed below:

(1) $[p\text{-}Cl.C_6H_4.CNSSN]Cl$,
(2) $[(p\text{-}Cl.C_6H_4.CNSSN)_2Cl][S_3N_3]$,
(3) $[p\text{-}Cl.C_6H_4.CNSSN]_6Cl_2$,
(4) $[(p\text{-}Cl.C_6H_4.CNSSN)_2Br][Br_3]$.

3.2 The crystal structure of [p-Cl.C_6H_4.CNSSN]Cl

The title compound was prepared, using the literature method [19], by reacting SCl_2 with the lithium salt of the persilylated amidine, Li[p-Cl.C_6H_4.C($NSiMe_3$)$_2$], Eqn 3.1.



Eqn 3.1

Crystals grew as orange plates by cooling slowly a thionyl chloride solution from boiling point to room temperature. Suitable crystals were selected and placed inside glass Lindemann capillaries. The crystallographic experimental procedure has been described in section 2.7.

Two crystals were used in this experiment; the first crystal deteriorated during the collection of initial unit-cell parameters and the second crystal was used for the rest of the experiment. During the data collection the intensity of the standards fell by 19% over the first 26 hours but stabilised for the remaining 23 hours, in a similar manner to that seen for other dithiadiazolylium salts [11].

Final experimental details for this structural determination are outlined in Table 3.5. Figure 3.9 shows the numbering scheme used for the title compound, although only half the molecule is in the asymmetric unit since there is a mirror plane present in the molecule. Bond lengths and angles for the dithiadiazolylium ring, including the contacts involving the associated chloride anion, are shown in Table 3.6. Atomic co-ordinates, displacement parameters, and a full description of bond lengths and angles are quoted in Appendix C.

Table 3.5 Crystallographic data.

Compound	[*p*-Cl.C_6H_4.CNSSN]Cl	[(*p*-Cl.C_6H_4.CNSSN)$_2$Cl] [S_3N_3]	[*p*-Cl.C_6H_4.CNSSN]$_6$Cl$_2$	[(*p*-Cl.C_6H_4.CNSSN)$_2$Br] [Br_3]
Empirical Formula	$C_7 H_4 Cl_2 N_2 S_2$	$C_{14} H_8 N_7 S_7 Cl_3$	$C_{42} H_{24} N_{12} S_{12} Cl_8$	$C_{14} H_8 N_4 S_4 Cl_2 Br_4$
Colour, habitat	orange plate	gold brick	green plate	red plate
Crystal size, mm	0.35 x 0.20 x 0.08	0.80 x 0.40 x 0.40	0.40 x 0.30 x 0.05	0.9 x 0.5 x 0.05
Crystal System	Monoclinic	Triclinic	Triclinic	Monoclinic
Space Group	$P2_1/m$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions, Å and °	a = 6.225(2) b = 8.212(2) β = 99.41(2) c = 9.671(2)	a =9.435(2) α = 98.22(3) b = 11.087(2) β = 106.85(3) c = 12.150(2) γ = 106.55(3)	a =5.742(3) α = 88.35(3) b = 13.714(4) β = 85.26(4) c = 16.591(6) γ = 84.75(3)	a =7.083(8) b = 9.688(7) β = 92.27(5) c = 33.254(6)
Volume, Å^3	487.7(2)	1130.2(4)	1296.3(10)	2280(3)
Z	2	2	1	4
Formula Weight	251.1	605.0	1365.1	751.0
Density (calc), gcm^{-3}	1.71	1.78	1.75	2.19
Absorption Coefft, mm^{-1}	1.04	1.07	0.97	7.67
F(000)	252	608	1386	1432
Temperature, K	295	110	110	150
No.of Reflections, Range	25, $25 \le 2\theta \le 30$	21, $20 \le 2\theta \le 30$	17, $10 \le 2\theta \le 25$	25, $25 \le 2\theta \le 30$
Scan Type	2θ-ω	2θ-ω	2θ-ω	ω
Scan Speed, °/min	Variable, 0.40 to 4.00	constant, 8.0	constant, 2.0	constant, 16.0
θ Range, °	5.0 - 55.0	5.5 - 55.0	5.0 - 45.0	5.0 - 50.0

Range of h,k,l	0 - 8, 0 - 10, ±12	0 - 14, ±16, ±12	±5, 0 - 13, ±15	0 - 8, 0 - 11, ±39
Standard reflections	$\bar{1}$ 0 $\bar{2}$, 1 0 2, $\bar{1}$ 2 1	$\bar{2}$ 1 2, $\bar{2}$ 2 1, 1 3 1	2 4 $\bar{1}$, 3 3 0, 2 4 0	0 3 $\bar{6}$, 0 2 15, 4 0 $\bar{6}$
Data measured	1311	5434	2552	4378
Independent data, R_{int}	1203, 0.021	5166, 0.016	2077, 0.056	4030, 0.068
Data used [F>nσ(F), n]	684 [4]	3451 [4]	1421 [3]	4019 †
Mean Wavelength, $\bar{\lambda}$, Å	0.71073	0.71073	0.71073	0.71073
Absorption correction	Empirical	Empirical	DIFABS	Empirical
Transmission range	0.837 - 1.000	0.893 - 1.000	0.709 - 1.762	0.403 - 1.000
Parameters	73	312	163	253
Data/parameters	9.4	11.1	8.7	15.9
Final R Indices (obs data)	R(wR) = 0.061, 0.071	R(wR) = 0.036, 0.056	R(wR) = 0.062, 0.068	R(wR) = 0.045, 0.078 †
R Indices (all data)	R(wR) = 0.116, 0.076	R(wR) = 0.072, 0.064	not known *	R(wR) = 0.175, 0.109
Goodness of fit	1.83	1.07	1.19	1.03
Weighting scheme	0.0005 ¥	0.0016 ¥	§	0.0178, 13.817 ≠
Max shift / esd	0.001	0.001	0.031	0.000
Max & min in Fourier synthesis, eÅ^{-3}	±0.50	+0.61, -0.51	+0.54, -0.56	+0.99, -1.02
Program (refinement)	SHELXTL-Plus	SHELXTL-Plus	CRYSTALS	SHELXL-93

† Refinement was based upon F^2. There were 2144 data with F>4σ(F).

* This was not calculated. Since the crystal was of poor quality the interpretation of this number would be suspect.

¥ Weighting scheme based upon $1/[\sigma^2(F_o) + g|F|^2]$. The value g is quoted.

§ Weighting scheme based upon a 5-order Chebyshev series, with parameters 1.2, -0.462, 0.774, -0.576, 0.254.

≠ Weighting scheme based upon $1/[\sigma^2(F_o) + gP^2 + hP]$ where $P = (F_o^2 + 2F_c^2)/3$. The values g and h are quoted.

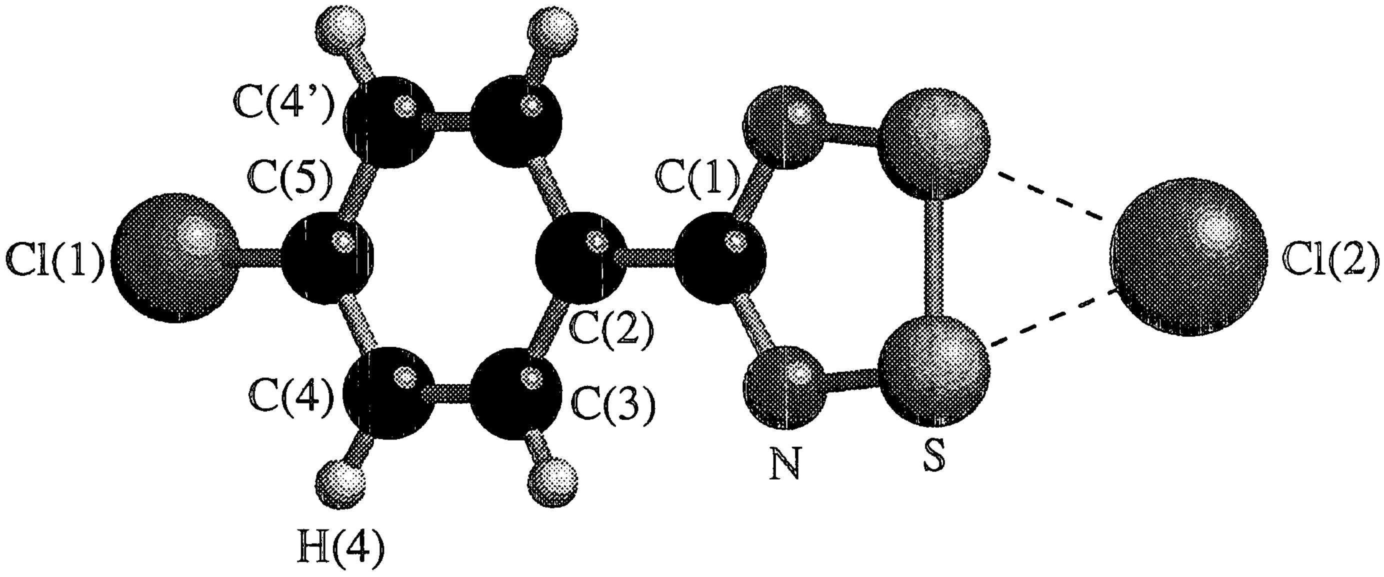


Figure 3.9 Structure of $[p\text{-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}}]\ \text{Cl}$.

Table 3.6 Bond lengths and angles, Å and °, for [*p*-Cl.C_6H_4.CNSSN]Cl, including secondary contacts with the chloride anion.

S-S'	2.007(3)	N-S-S'	95.3(2)
S-N	1.592(4)	S-N-C(1)	115.1(4)
N-C(1)	1.336(6)	N-C(1)-N'	119.1(6)
C(1)-C(2)	1.469(10)	N-C(1)-C(2)	120.4(3)
S...Cl	2.916(2)	S...Cl...S'	40.3(1)
		S'...S...Cl	69.9(0)

Atom S' is related to S by the operation x, 0.5-y, z.

The bond distances and angles for the dithiadiazolylium ring in [*p*-Cl.C_6H_4.CNSSN]Cl are very similar to those seen for other monochloride dithiadiazolylium salts, contrast the data in Table 3.6 with that in Table 3.2. The chloride anion is equidistant from, and coplanar with, both S atoms of the corresponding dithiadiazolylium cation, as expected from the symmetry of the system. Similar 3-centre interactions have been observed previously for numerous 1,2 dithiolium halides [20] as well as the related compound [Ph.CNSSN]Cl, where the S...Cl mean distance is 2.906(2)Å [11].

[*p*-Cl.C_6H_4.CNSSN]Cl has a layer lattice in which each chloride anion is flanked by two further dithiadiazolylium cations, for which the S...Cl distance is 3.255(2)Å. A single layer is shown in Figure 3.10. This is the first example of a layer lattice in dithiadiazolylium chloride salts; other structures contain bulky substituents on the ring or solvent molecules. [Ph.CNSSN]Cl contains a solvent [11] (one toluene molecule per six chloride salts) which prevents a layer lattice forming.

The packing in [*p*-Cl.C_6H_4.CNSSN]Cl is, however, very similar to that seen for 4-phenyl-1,2-dithiolium chloride monohydrate [20], which contains solvent water molecules between the dithiolium rings within each layer, see Figure 3.11. [*p*-Cl.C_6H_4.CNSSN]Cl does not accommodate solvent in a similar manner within the lattice, presumably because of polarity and steric effects; thionyl chloride is less polar than water and too large to fit easily into the lattice without severely disrupting it.

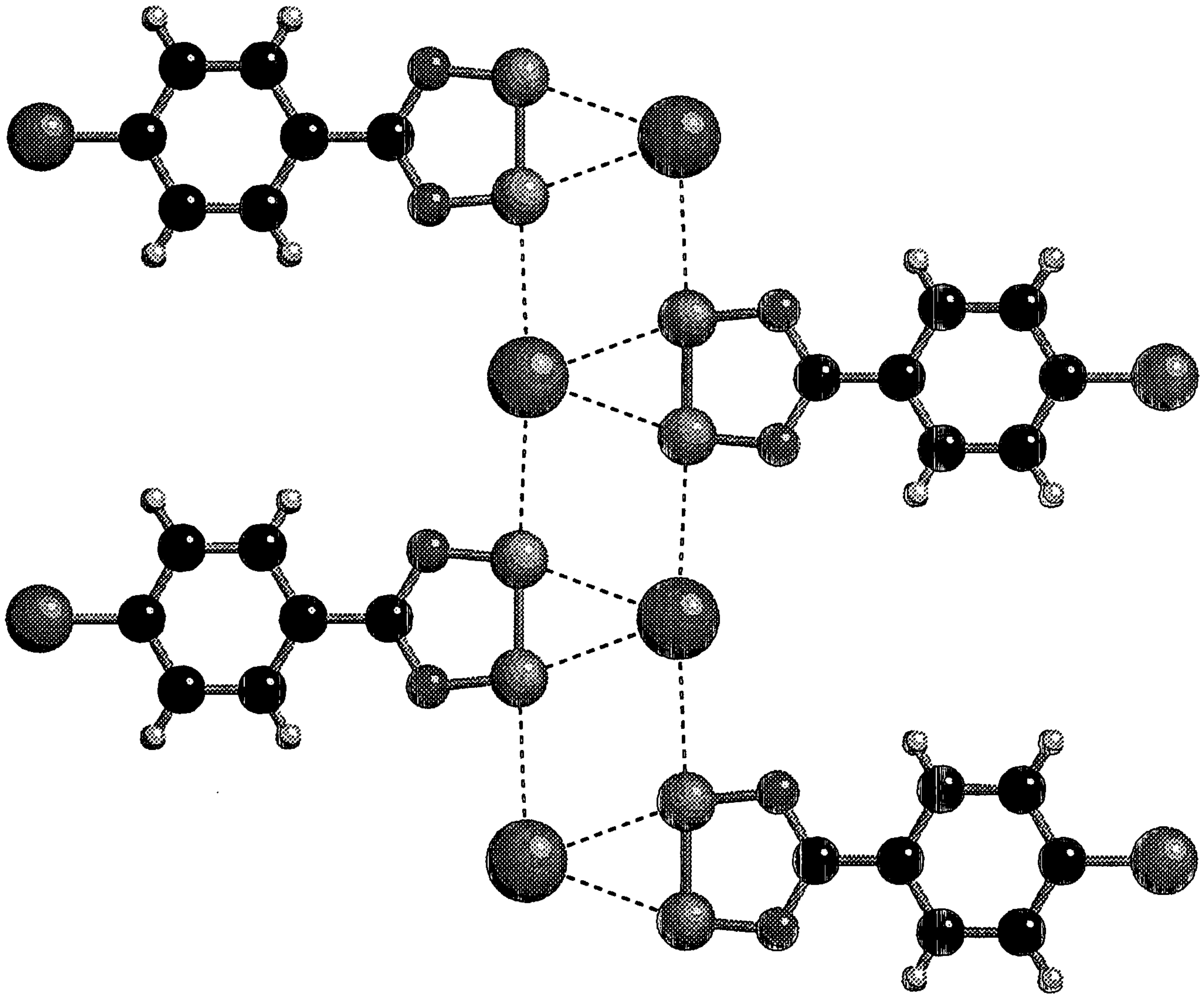


Figure 3.10 Layer packing present in [*p*-Cl.C_6H_4.$\overline{\text{CNSSN}}$] Cl.

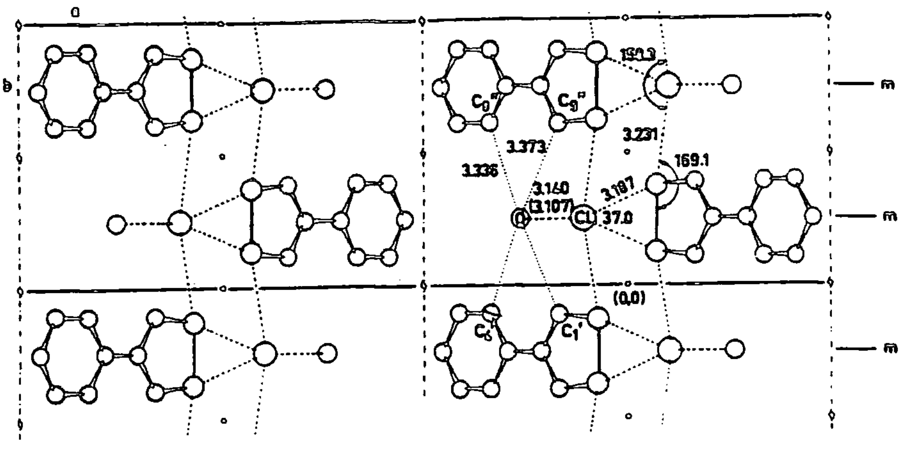


Figure 3.11 Structure of 4-phenyl-1,2-dithiolium chloride monohydrate. The oxygen of the solvent is shown between cations.

From section 3.1.1, it was shown that the effect of substituting chlorine for a hydrogen atom in the 4 position of a phenyl ring is likely to be negligible w.r.t. the length of the S-S bond (d_{SS}) in the dithiadiazolylium ring. This means that we can probably attribute any differences in d_{SS} to packing effects and/or the environment of the chloride anion.

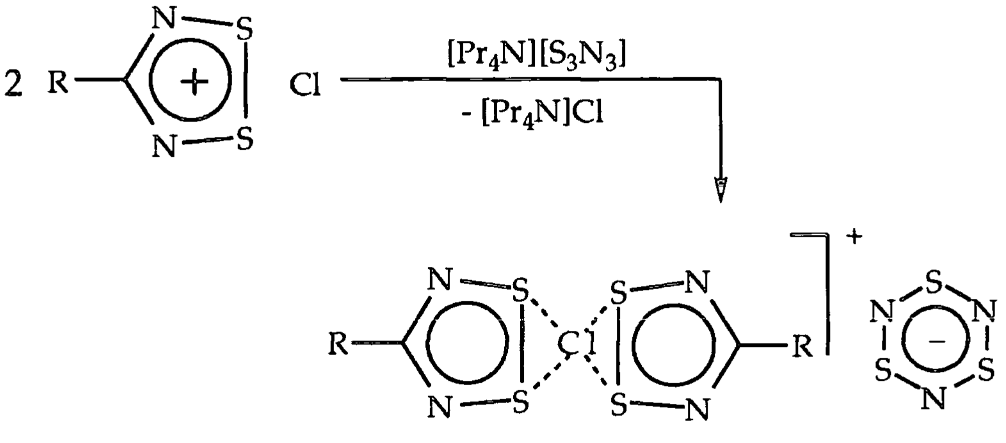
It has been noted previously that d_{SS} in [Ph.CNSSN][AsF_6] is longer than that in solvated [Ph.CNSSN]Cl [15]. However, this is not the case for the *p*-chloro-substituted systems, since d_{SS} for the AsF_6 and the Cl salts are the same within one e.s.d. Thus, the environment of the chloride anion must be influencing the electronic nature of the dithiadiazolylium ring.

In [Ph.CNSSN]Cl, the presence of the solvent prevents the formation of a layer lattice. Hence, the chloride anion is bound quite tightly to the sulfur atoms of the cation and the bonding can be envisaged as a 3-centre-2-electron bond between the sulfur atoms and the chloride anion for each discrete cation/anion pair, section 3.1.2.

Although the bonding in [*p*-Cl.C_6H_4.CNSSN]Cl is similar, there are significant differences, because each sulfur atom is not only influenced by the closest associated chloride anion. In Figure 3.10 interactions between sulfur atoms of one cation and neighbouring anions are also highlighted, and these are well within recognised van der Waals radii [7]. It is these S...Cl interactions which perturb the bonding away from the 3-centre-2-electron bonding model seen in solvated [Ph.CNSSN]Cl.

3.3 The crystal structure of [(p-Cl.C_6H_4.CNSSN)$_2$Cl][S_3N_3]

The title compound was prepared by the slow diffusion from a saturated acetonitrile solution of [Pr_4N][S_3N_3] into a saturated solution of [p-Cl.C_6H_4.CNSSN]Cl, as previously described by Banister *et al* [15]. The partial metathesis reaction occurring is shown in Eqn 3.2. After 9 days, gold blocks of [(p-Cl.C_6H_4.CNSSN)$_2$Cl][S_3N_3] had grown on the surface of [p-Cl.C_6H_4.CNSSN]Cl and an X-ray analysis was undertaken on one of these (placed in a glass Lindemann capillary).



Eqn 3.2

The crystal was a good diffractor of X-rays and data were collected out beyond the usual default settings in the collection software. The hydrogen atoms were refined with isotropic displacement parameters since there was plenty of data available. Experimental details are outlined in Table 3.5. Figure 3.12 shows the numbering scheme for the title compound. Bond lengths and angles for the dithiadiazolylium ring, including the contacts involving the chloride anion, are shown in Tables 3.7 and 3.8 respectively. Atomic co-ordinates, bond lengths and angles and displacement parameters are listed in Appendix C.

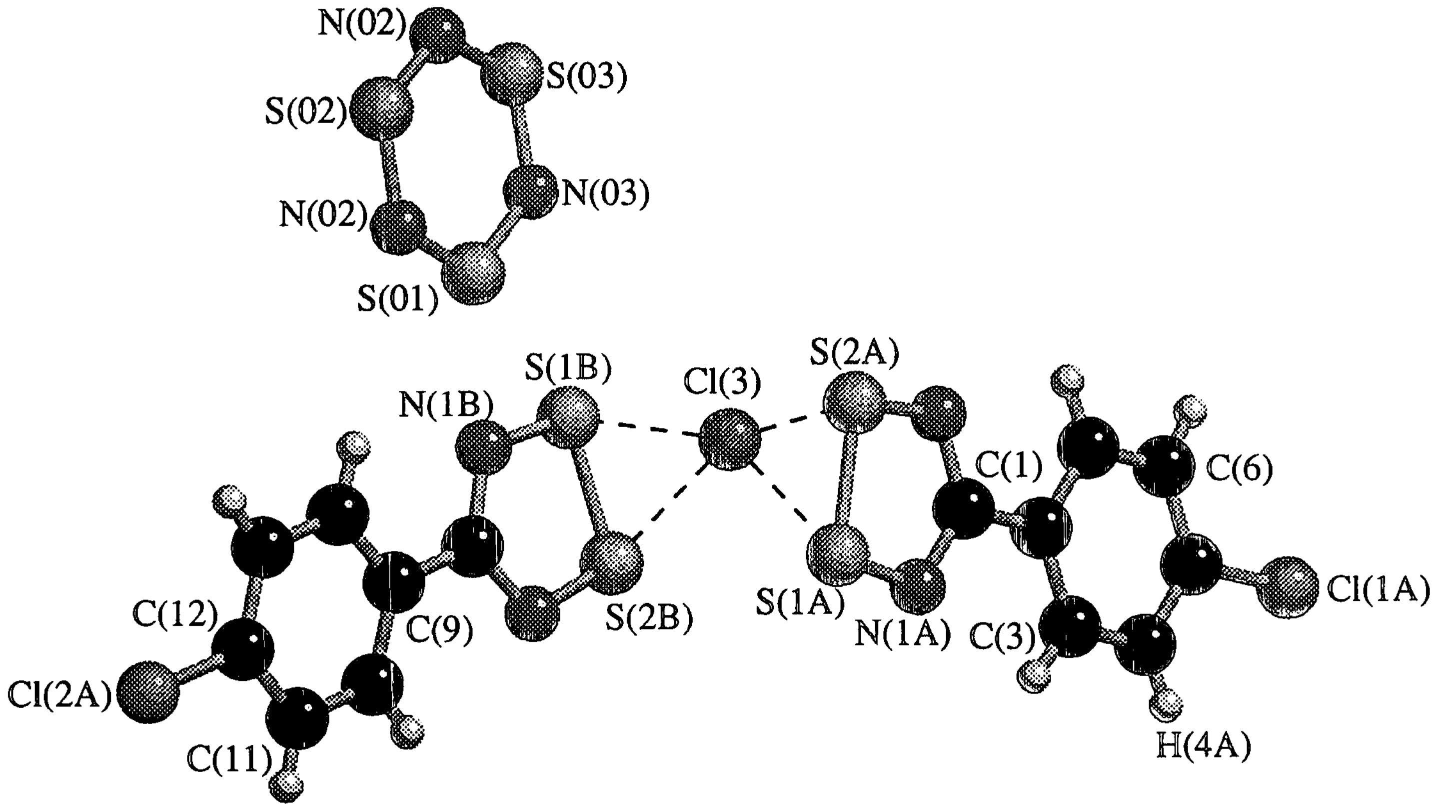


Figure 3.12 Structure of $[(p\text{-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}})_2\text{Cl}][\text{S}_3\text{N}_3]$.

Table 3.7 [(*p*-Cl.C_6H_4.CNSSN)$_2$Cl][S_3N_3], bond lengths and secondary contacts, Å.

Dithiadiazolylium Ring A			
S(1A)-S(2A)	2.047(1)	N(1A)-C(1)	1.355(5)
N(1A)-S(1A)	1.603(2)	N(2A)-C(1)	1.339(3)
S(2A)-N(2A)	1.610(3)	C(1)-C(2)	1.471(4)
S(1A)...Cl3	2.967(1)	S(2A)...Cl3	2.941(1)
Dithiadiazolylium Ring B			
S(1B)-S(2B)	2.049(1)	N(1B)-C(8)	1.334(4)
N(1B)-S(1B)	1.610(3)	N(2B)-C(8)	1.356(3)
S(2B)-N(2B)	1.613(3)	C(8)-C(9)	1.473(5)
S(1B)...Cl3	3.039(1)	S(2B)...Cl3	2.882(1)
Trisulfur Trinitride Anion			
S(01)-N(02)	1.586(3)	S(03)-N(03)	1.599(3)
S(02)-N(02)	1.608(3)	N(01)-S(03)	1.578(4)
S(02)-N(03)	1.601(4)	S(01)-N(01)	1.612(4)

Table 3.8 Bond angles, °, for [(*p*-Cl.C_6H_4.CNSSN)$_2$Cl][S_3N_3].

Dithiadiazolylium Ring A			
N(1A)-S(1A)-S(2A)	95.3(1)	N(1A)-C(1)-N(2A)	120.0(3)
S(1A)-S(2A)-N(2A)	94.9(1)	N(1A)-C(1)-C(2)	119.9(2)
S(1A)-N(1A)-C(1)	114.7(2)	N(2A)-C(1)-C(2)	120.1(3)
S(2A)-N(2A)-C(1)	115.1(3)		
Dithiadiazolylium Ring B			
N(1B)-S(1B)-S(2B)	94.6(1)	N(1B)-C(8)-N(2B)	120.3(3)
S(1B)-S(2B)-N(2B)	95.5(1)	N(1B)-C(8)-C(9)	120.1(2)
S(1B)-N(1B)-C(8)	115.5(2)	N(2B)-C(8)-C(9)	119.6(3)
S(2B)-N(2B)-C(8)	114.0(2)		
Trisulfur Trinitride Anion			
N(01)-S(01)-N(02)	115.0(2)	S(01)-N(01)-S(03)	124.4(2)
N(02)-S(02)-N(03)	114.6(2)	S(01)-N(02)-S(02)	125.1(3)
N(01)-S(03)-N(03)	116.1(2)	S(02)-N(03)-S(03)	124.2(2)

The four sulfur atoms of the two cationic dithiadiazolylium rings of the [(*p*-Cl.C_6H_4.CNSSN)$_2$Cl] unit are approximately coplanar (mean deviation from planarity is 0.05Å) and are linked to the central chloride anion by S...Cl interactions (see Figure 3.12). The chloride ion is 0.24Å above the plane containing the sulfur atoms. The slight distortion of the chloride anion from a symmetrical environment between the cationic rings is probably due to an interaction with the sulfur atom of a neighbouring dithiadiazolylium ring, see Figure 3.13.

Each [S3N3] anion is sandwiched between two dithiadiazolylium rings with S...Cl and S...N contacts (Figure 3.13) in the range 2.882(2) to 3.467(1)Å, as shown in Table 3.9. The anion is very similar to that seen for $[Bu_4N][S_3N_3]$ [21]. The [S3N3] ring is at an angle of 0.9° to the plane of the four sulfur atoms. A packing diagram is shown in Figure 3.14. This shows the ABAB packing present in this material.

Table 3.9 Secondary contacts, Å, for $[(p\text{-}Cl.C_6H_4.CNSSN)_2Cl][S_3N_3]$.

Chloride...Dithiadiazolylium Contacts			
Cl(3)...S(1a)	2.967(1)	Cl(3)...S(2b)	2.882(2)
Cl(3)...S(2a)	2.941(1)	Cl(3)...S'(1b)	3.226(2)
Cl(3)...S(1b)	3.039(1)	Cl'(b)...S(1a)	3.467(1)
Contacts involving the Trisulfur Trinitride anion			
Cl(1a)..S(03)	3.308(2)	S'(2b)...S(02)	2.916(2)
S(1a)...S(03)	2.940(2)	S'(1b)...N(02)	3.173(2)
S(2a)...S(01)	3.116(2)	S'(2b)...N(03)	3.230(2)
S'(1b)...S(01)	3.173(2)		

Atom S' is related to S by the operation -x, -y+1, -z+1.

The S-S bond lengths for the cationic rings are identical, in contrast to that seen in the analogous $[(Ph.CNSSN)_2Cl][S_3N_3]$ [15,17], see Table 3.4. The difference in the lengths of the S-S bond for the latter compound was not fully explained (in fact a mean figure was quoted and used in the subsequent discussion). The S-S bond is longer than in the monochloride case, for the reasons mentioned in section 3.1. The effect of the [S3N3] ring is to lengthen the S-S bond and this dominates the shortening influence of the chloride anion.

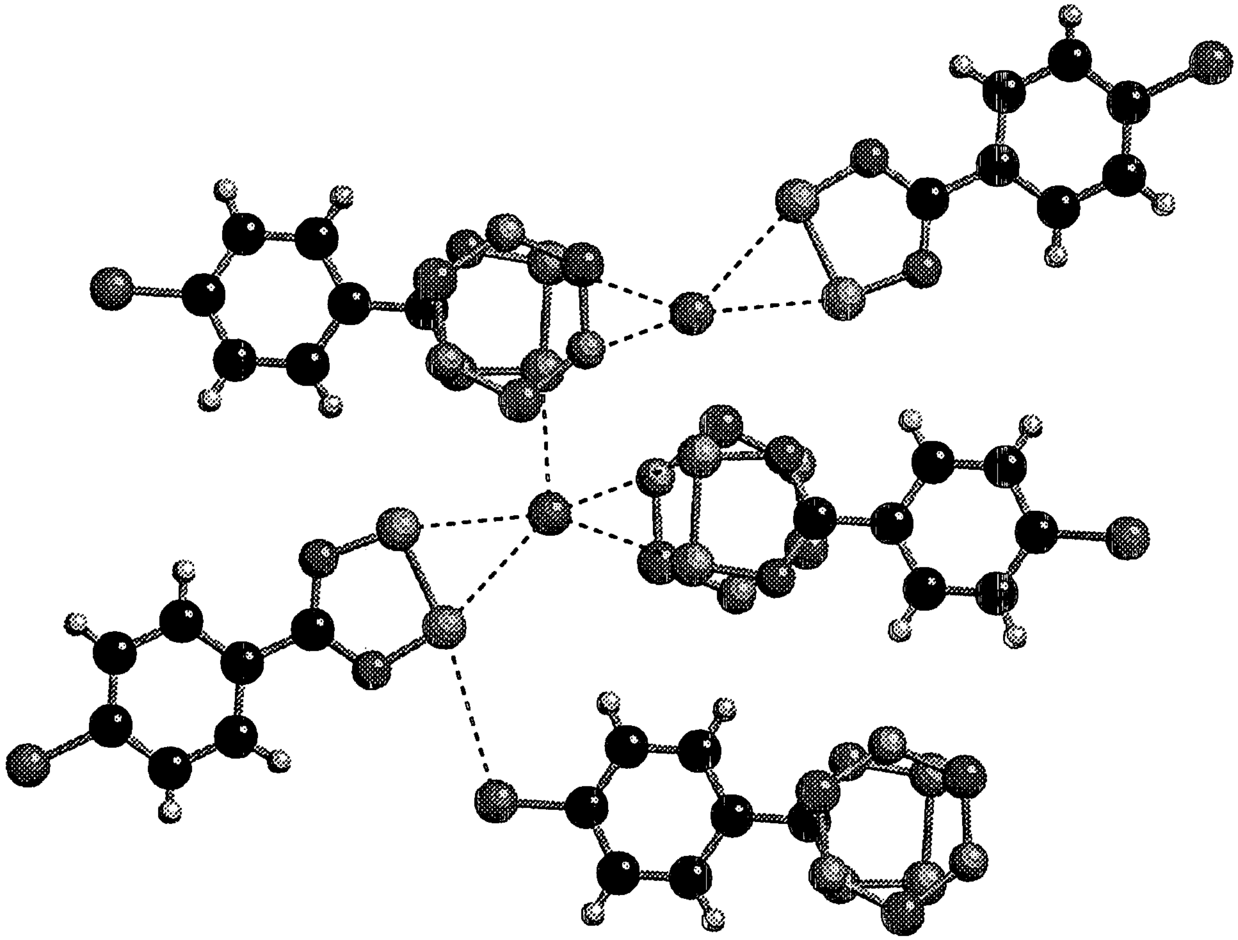


Figure 3.13 Showing how the secondary contacts in $[(p\text{-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}})_2\text{Cl}][\text{S}_3\text{N}_3]$ build up the lattice.

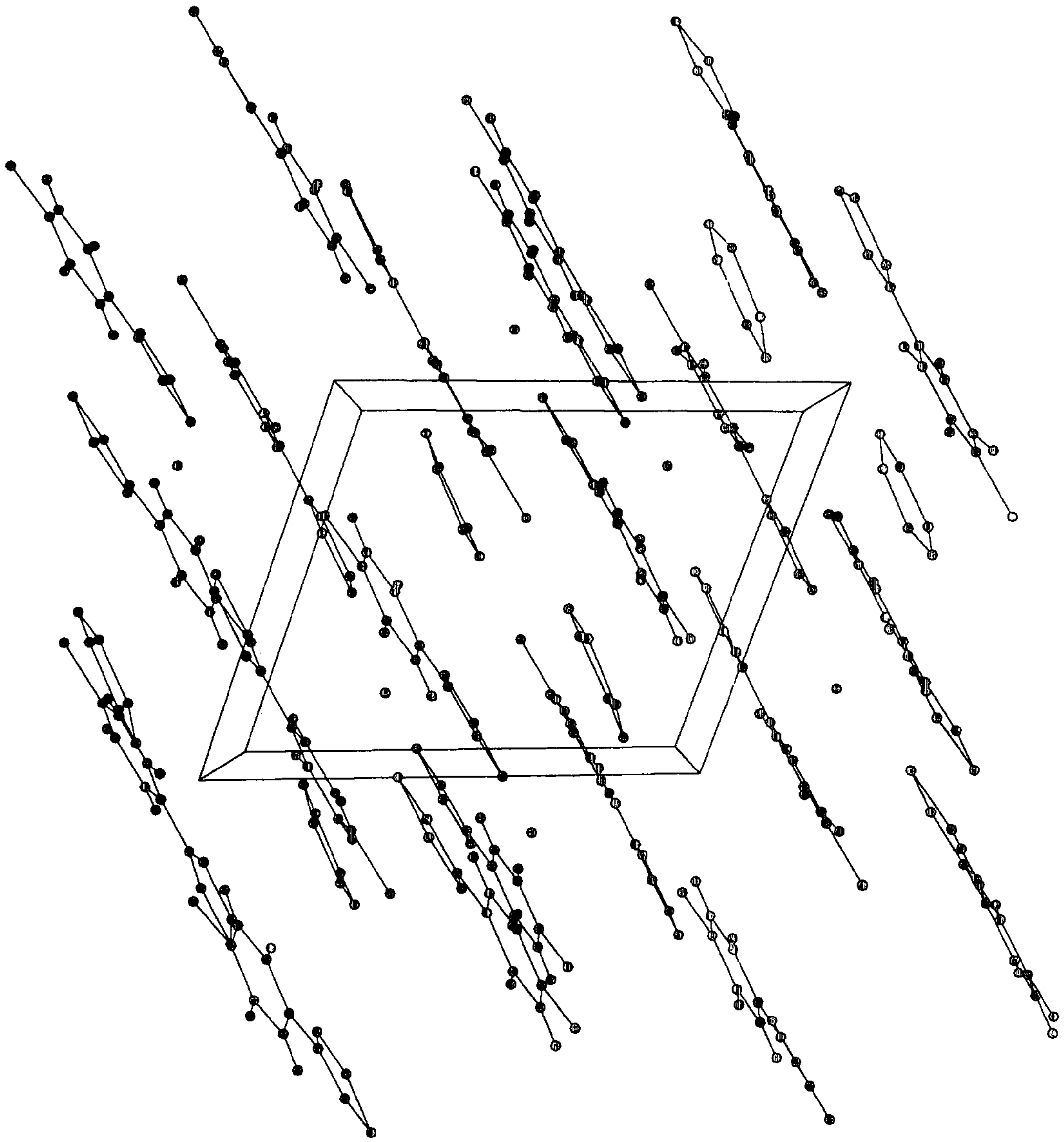
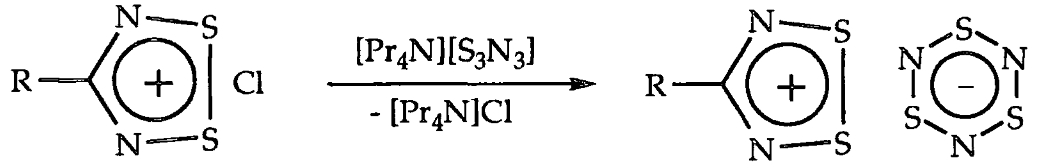


Figure 3.14 The layer packing in $[(p\text{-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}})_2\text{Cl}][\text{S}_3\text{N}_3]$

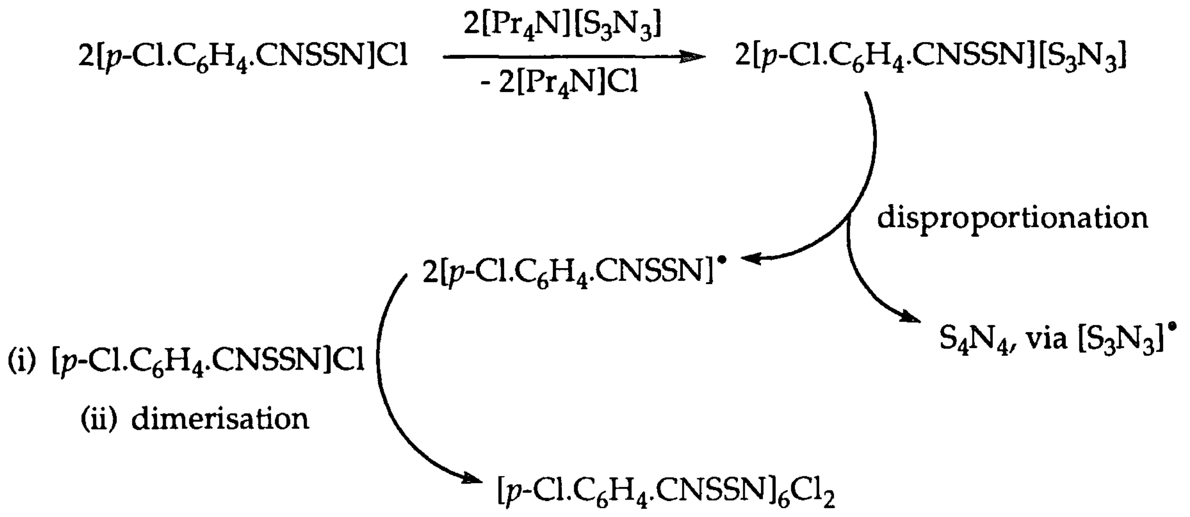
3.4 The crystal structure of [p-Cl.C_6H_4.CNSSN]$_6Cl_2$

The title compound was surprisingly prepared in the same crystal growth experiment that yielded the expected golden blocks of [(p-Cl.C_6H_4.CNSSN)$_2$Cl][S_3N_3]. After 9 days, some green plates were also present on the surface of both [p-Cl.C_6H_4.CNSSN]Cl and [(p-Cl.C_6H_4.CNSSN)$_2$Cl][S_3N_3]. By analogy with the reactions which had occurred for the phenyl-dithiadiazolylium system [15], these were thought to be crystals of [p-Cl.C_6H_4.CNSSN][S_3N_3] and they were mounted in glass Lindemann capillaries. The supposed reaction is outlined in Eqn 3.3. Obviously, [(p-Cl.C_6H_4.CNSSN)$_2$Cl][S_3N_3] is an intermediate in the reaction pathway depicted below.



Eqn 3.3

However, the crystal chosen for the X-ray determination was actually [p-Cl.C_6H_4.CNSSN]$_6Cl_2$. It is very likely that this was a very minor side-product which grew during the crystal growth experiment. The most realistic reaction pathway which rationalises the formation of this product involves the formation of a dithiadiazolyl radical pair and various S/N containing species; most probably S_4N_4, see scheme 3.1.



Scheme 3.1 Possible mechanism for the formation of [(p-Cl.C_6H_4.CNSSN]$_6Cl_2$.

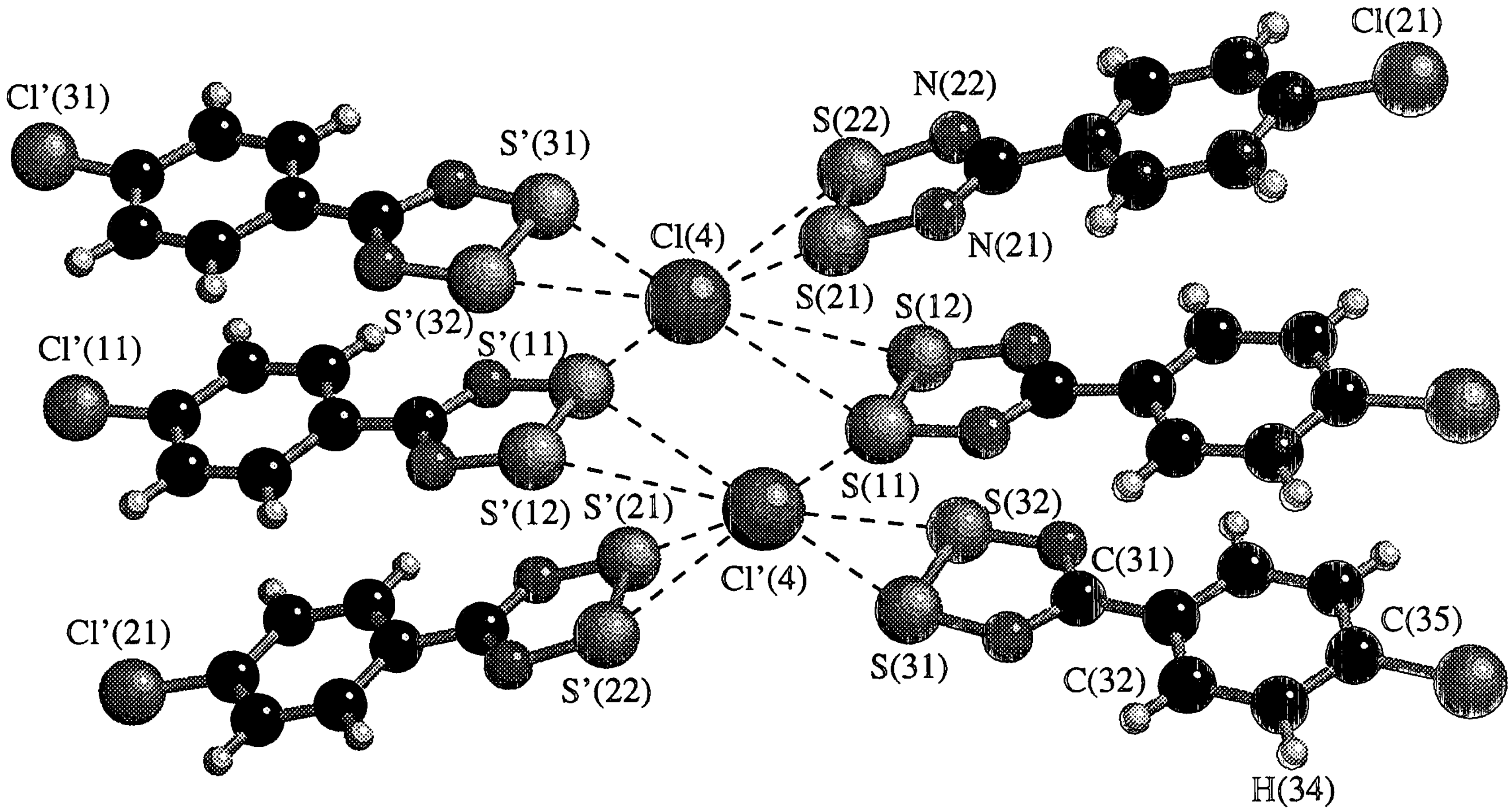
This reaction occurs due to internal redox of the intermediate [(*p*-Cl.C_6H_4.CNSSN$)_2$Cl][S_3N_3] in a similar manner to that seen for iodide salts [22]. [Ph.CNSSN][S_3N_3] was produced in low yield [15,17] and it is likely other products from oxidation and reduction reactions were present in solution.

Despite the weakly diffracting nature of the selected crystal, intensity data were collected and the experiment was terminated at an upper 2θ limit of 40°.

Careful consideration of the results obtained from structure solution suggested that the applied absorption correction was invalid. Therefore, structure solution with uncorrected data was undertaken. Analysis of the results obtained from this structure solution showed the formation of a novel compound, which was not the intended product.

Since the crystal was a poor diffractor of X-rays, there was a shortage of observed data and the criterion for an observed reflection was reduced to $F_o>3\sigma F_o$. Although this did not improve matters greatly, it did allow the refinement of the data. The phenyl rings were treated as rigid groups, the heavy atoms (chlorine and sulfur) were refined with anisotropic displacement parameters, and the other non-hydrogen atoms with isotropic displacement parameters. The hydrogen atoms were refined "riding" on the bonded carbon atoms, with fixed isotropic displacement parameters (120% of U[iso] for the ligated carbon atom). Further details of the refinement for this crystal can be found in Table 3.5.

Figure 3.15 shows the numbering scheme used for the title compound, an inversion centre is present in this compound and so there is only one structural unit in the unit-cell. Bond lengths and angles for the dithiadiazolylium ring are shown in Tables 3.10 and 3.11 respectively. Secondary contacts involving the chloride anion are detailed in Table 3.12. Atomic co-ordinates, displacement parameters, and a full description of bond lengths and angles are quoted in Appendix C.



<u>Figure 3.15</u> Structure of $[p\text{-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}}]_6\,\text{Cl}_2$.

Table 3.10 Bond lengths, Å, for [p-Cl.C_6H_4.CNSSN]$_6$$Cl_2$.

First Dithiadiazolylium Ring			
S(11) - S(12)	2.079(4)	C(11) - C(12)	1.44(1)
S(11) - N(11)	1.615(8)	N(11) - C(11)	1.33(1)
S(12) - N(12)	1.628(8)	N(12) - C(11)	1.34(1)
Second Dithiadiazolylium Ring			
S(21) - S(22)	2.064(4)	N(21) - C(21)	1.33(1)
S(21) - N(21)	1.594(8)	N(22) - C(21)	1.36(1)
S(22) - N(22)	1.616(8)	C(21) - C(22)	1.46(1)
Third Dithiadiazolylium Ring			
S(31) - S(32)	2.066(4)	N(31) - C(31)	1.36(1)
S(31) - N(31)	1.616(8)	N(32) - C(31)	1.33(1)
S(32) - N(32)	1.612(8)	C(31) - C(32)	1.45(1)

Table 3.11 Bond angles, °, for [p-Cl.C_6H_4.CNSSN]$_6$$Cl_2$.

First Dithiadiazoylium Ring			
N(11) - S(11) - S(12)	94.2(3)	N(12) - C(11) - N(11)	118.3(8)
N(12) - S(12) - S(11)	93.4(3)	C(12) - C(11) - N(11)	121.1(9)
C(11) - N(11) - S(11)	117.1(7)	C(12) - C(11) - N(12)	120.6(8)
C(11) - N(12) - S(12)	116.8(6)		
Second Dithiadiazoylium Ring			
N(21) - S(21) - S(22)	94.0(3)	C(22) - C(21) - N(21)	121.4(9)
N(22) - S(22) - S(21)	94.9(3)	N(22) - C(21) - N(21)	118.6(8)
C(21) - N(21) - S(21)	117.6(7)	C(22) - C(21) - N(22)	120.0(8)
C(21) - N(22) - S(22)	114.9(7)		
Third Dithiadiazoylium Ring			
N(31) - S(31) - S(32)	94.6(3)	N(32) - C(31) - N(31)	118.7(8)
N(32) - S(32) - S(31)	94.3(3)	C(32) - C(31) - N(31)	118.7(9)
C(31) - N(31) - S(31)	115.7(8)	C(32) - C(31) - N(32)	122.5(8)
C(31) - N(32) - S(32)	116.8(6)		

Table 3.12 S...Cl secondary perpendicular contacts, Å.

S...Cl interactions within molecular unit			
Cl(4)...S′(21)	2.839(4)	Cl(4)...S′(11)	3.376(4)
Cl(4)...S(31)	2.882(4)	Cl(4)...S(12)	3.420(4)
Cl(4)...S(32)	3.009(3)	Cl(4)...S(11)	3.462(4)
Cl(4)...S(22′)	3.033(4)	Cl(4)...S′(12)	3.728(4)
S...Cl interactions between molecular units			
Cl(4)...S″(12)	3.486(4)		

Atom S′ is related to S by the operation -x, -y, -z.
Atom S″ is related to S by the operation x-1, y, z.

$[p\text{-Cl.C}_6\text{H}_4\text{.CNSSN}]_6\text{Cl}_2$ exists in a new structural arrangement unprecedented in dithiadiazolylium chemistry. There are two stacks of three $[p\text{-Cl.C}_6\text{H}_4\text{.CNSSN}]$ units linked together by S...Cl interactions between the sulfur atoms of the cationic rings and the chloride anions, as shown in Figure 3.15. Each stack is held together through S...S interactions (2.994(3) to 3.130(3)Å, see Table 3.13) which are perpendicular to the plane of the dithiadiazolylium rings. These perpendicular interactions are similar to those found in the spin-paired radical systems, as shown for $[p\text{-Cl.C}_6\text{H}_4\text{.CNSSN}]_2$ in Figure 3.5, section 3.1.2. A triple-decker arrangement of dithiadiazolylium rings has recently been discovered by Oakley and co-workers in the compound $[\text{Ph.CNSSN}]_3\text{I}_3$ [23]. This contains three cationic rings held together by the tri-iodide anion.

Table 3.13 S...S secondary perpendicular contacts, Å.

S(11)...S(21)	3.019(3)	S(11)...S(31)	3.111(3)
S(12)...S(22)	3.130(3)	S(12)...S(32)	2.995(3)

In $[p\text{-Cl.C}_6\text{H}_4\text{.CNSSN}]_6\text{Cl}_2$ each chloride is surrounded by eight sulfur atoms, which are in two co-ordination "shells" about the anion. The shell containing the closest S...Cl contacts has four approximately coplanar sulfur atoms (maximum deviation from the mean plane containing these sulfur atoms is 0.009Å) in the range 2.839(4) to 3.033(4)Å from the chloride anion. These are the peripheral sulfur atoms labelled as S(22), S(21), S′(31) and S′(32) in Figure 3.15. The other shell contains four sulfur atoms which are slightly further away from the anion, 3.376(4) to 3.728(4)Å, labelled as S(11), S(12), S′(11) and S′(12). It is these atoms of the second shell which distort the chloride anion away from the plane of the first shell, as shown in Figure 3.16. There is slight perturbation of the chloride anion from a symmetrical orientation between the sulfur atoms, which is due to a contact between the chloride anion and a neighbouring stack, see Figure 3.17.

It is obviously the $S...Cl_{anion}$ interactions which dominate the packing of this material; their influence in the construction of one layer of the lattice is shown in Figure 3.17. $S...Cl_{substituent}$ interactions have been known to affect similar systems in which no cation/anion interactions have been present [13b], such as the radical system $[p\text{-}Cl.C_6H_4.CNSSN]_2$, in which the very weak S..Cl interactions are a major factor in the formation of the observed tetramer array, Figure 3.5, section 3.1.2. However, it is not surprising that the $S...Cl_{substituent}$ interactions in $[p\text{-}Cl.C_6H_4.CNSSN]_6Cl_2$ are far weaker than the $S...Cl_{anion}$ interactions purely because the electrostatic interactions between anions and cations are larger that those arising from small dipole moments generated within uncharged molecules.

A packing diagram of $[p\text{-}Cl.C_6H_4.CNSSN]_6Cl_2$ viewed down the x-axis is shown in Figure 3.18. It is not immediately obvious how this packing is obtained from the initial pictures of the unit-cell. The easiest way to understand how this lattice is built-up is by examining Figure 3.17. There is a line of chloride anions across the Figure, which is depicted in Figure 3.18 as the line out of the plane of the page towards the reader.

The empirical formula for $[p\text{-}Cl.C_6H_4.CNSSN]_6Cl_2$ suggests that there is a charge of plus one-third for each heterocyclic ring. From section 3.1.4, the only other known compound in dithiadiazolylium chemistry with a similar anion : ring ratio is the alkyl-substituted $[CF_3CNSSN]_3Cl$ [18]. This consisted of the radical co-crystallised with the monochloride salt.

This is obviously not the case for $[p\text{-}Cl.C_6H_4.CNSSN]_6Cl_2$. The length of the S-S bonds is quite unusual in this compound because they are identical within the accuracy of the experiment, Table 3.10. Therefore, it is likely that the three rings possess a similar charge, of approximately plus one-third. On the other hand, there are two different sets of S...Cl contacts; one with the middle heterocyclic rings [for which the S-S bond is 2.079(4)Å] and the other with the outer rings [2.064(4) and 2.066(4)Å]. This may well indicate that there is more positive charge concentrated on the out-lying rings, with the canonical form containing two rings of plus one-half and one neutral species sandwiched between them. The perpendicular S...S interactions, see Table 3.13, do not resolve the issue. The true electronic environment of the dithiadiazolylium rings is probably a mixture of these two extreme canonical forms.

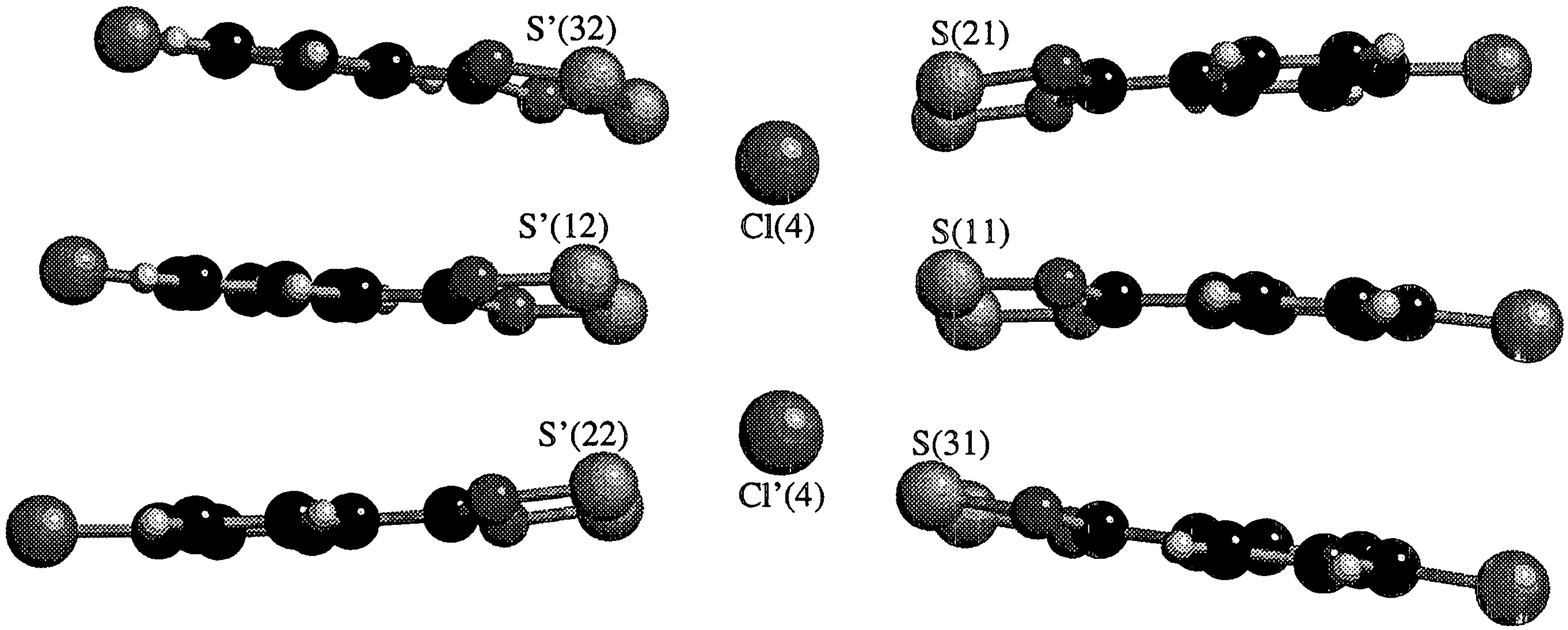


Figure 3.16 Side-on view of $[p\text{-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}}]_6\ \text{Cl}_2$, showing the chlorine atoms out of the plane of the cationic rings.

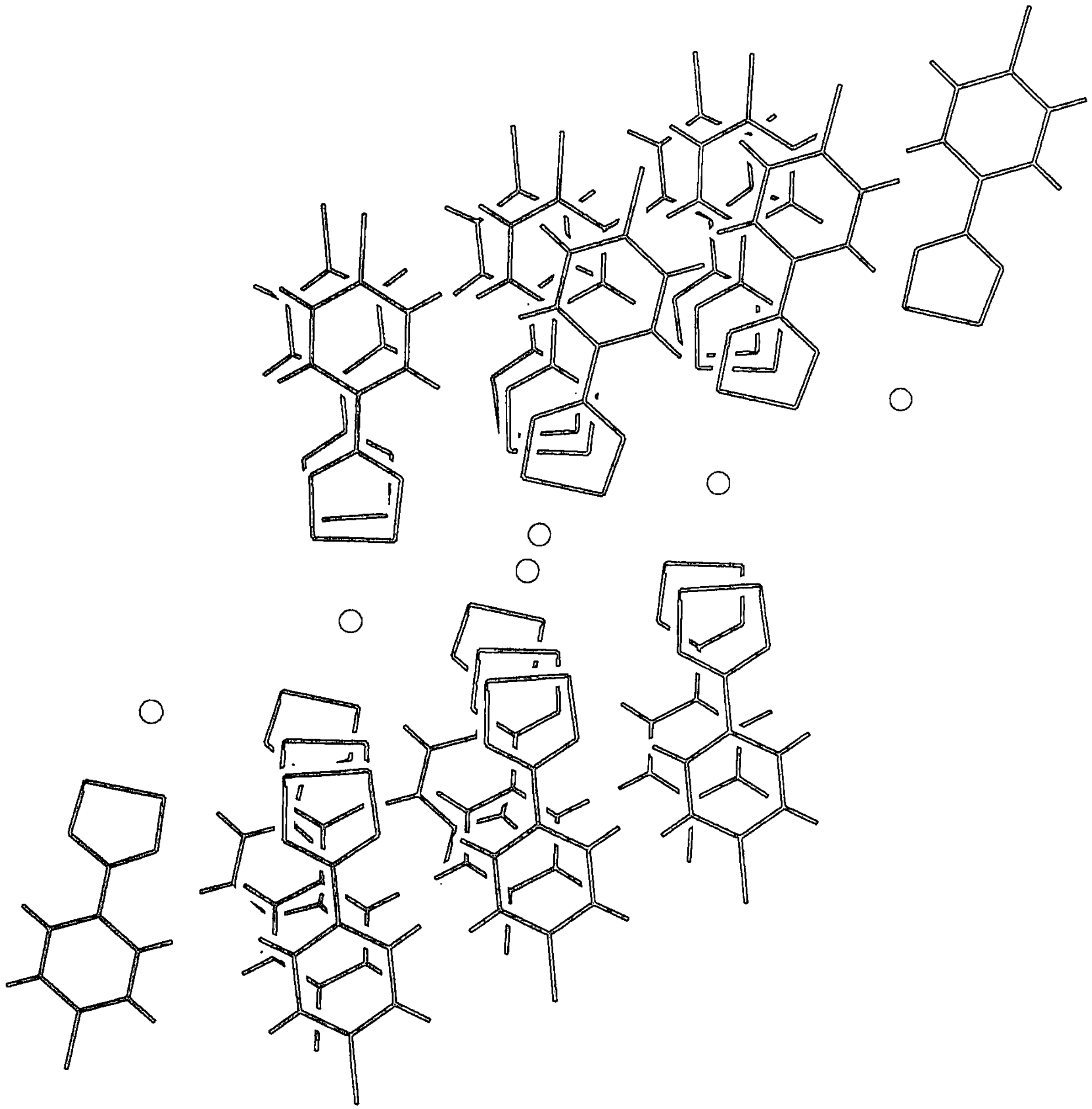


Figure 3.17 The layer packing in $[(p\text{-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}}]_6\ \text{Cl}_2$

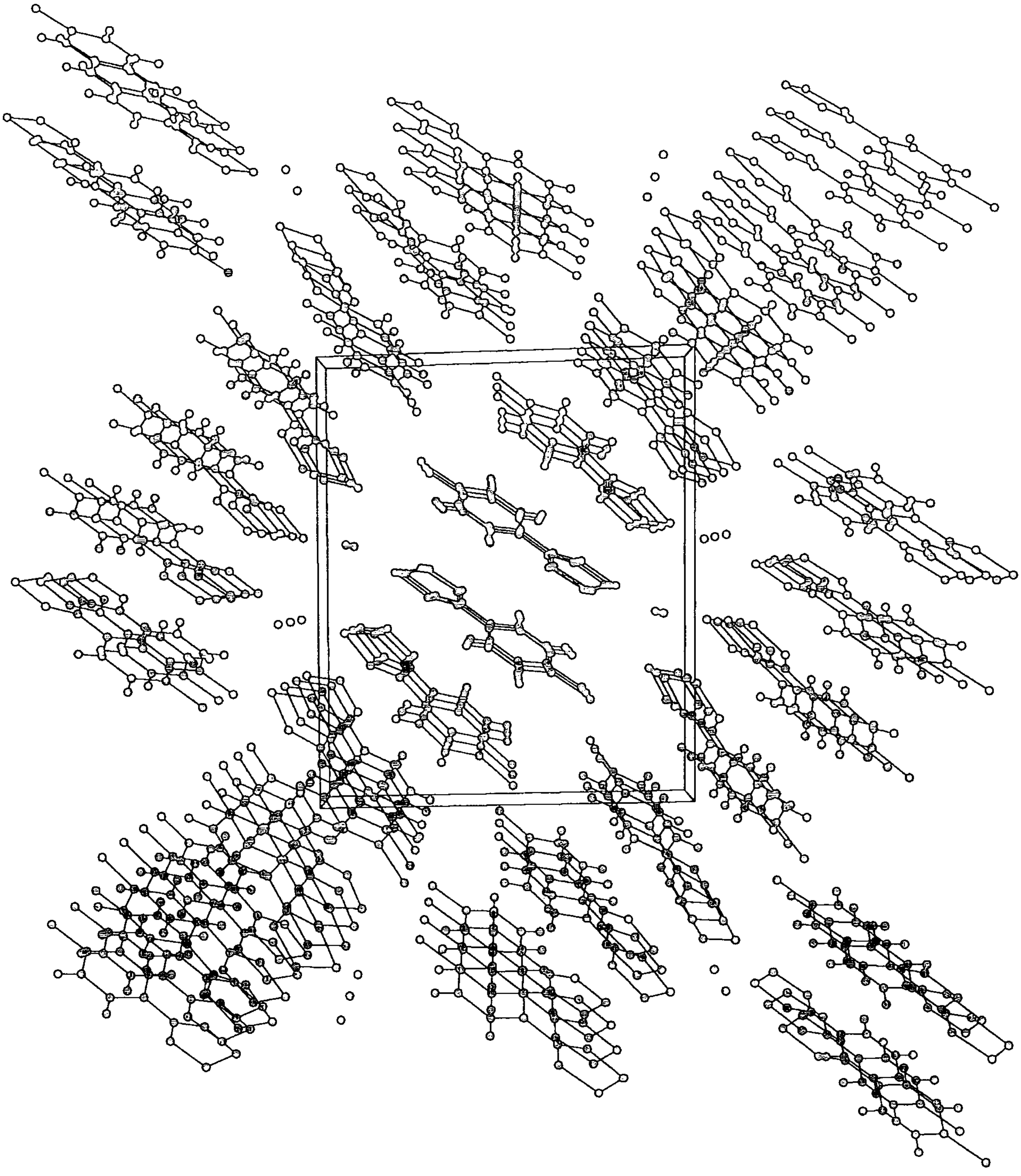
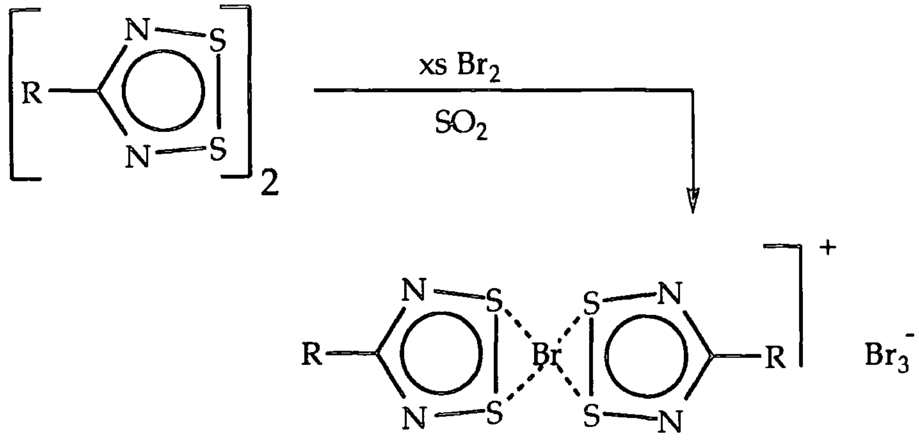


Figure 3.18 The layer packing in $[(p\text{-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}}]_6\ \text{Cl}_2$

3.5 The crystal structure of $[(p\text{-Cl.C}_6\text{H}_4\text{.CNSSN})_2\text{Br}][\text{Br}_3]$

This was prepared by the oxidation of the radical species using excess bromine in sulfur dioxide. Crystals suitable for X-ray analysis were grown over a period of three weeks from a saturated solution in acetonitrile. Suitable crystals were mounted using the oil-drop technique mentioned in section 2.7.



Eqn 3.4

The consistently low C,H,N analysis obtained for $[\text{p-Cl.C}_6\text{H}_4\text{.CNSSN}]\text{Br}$, although in the correct C:H:N ratio, indicated that there may be polybromide anions present in the compound, and thus an X-ray analysis was undertaken.

Experimental details are outlined in Table 3.5. Figure 3.19 shows the numbering scheme for the title compound. Bond lengths and angles for the dithiadiazolylium ring, including the contact with the bromide, are shown in Tables 3.14 and 3.15 respectively. Atomic co-ordinates, bond lengths and angles and displacement parameters are listed in Appendix C.

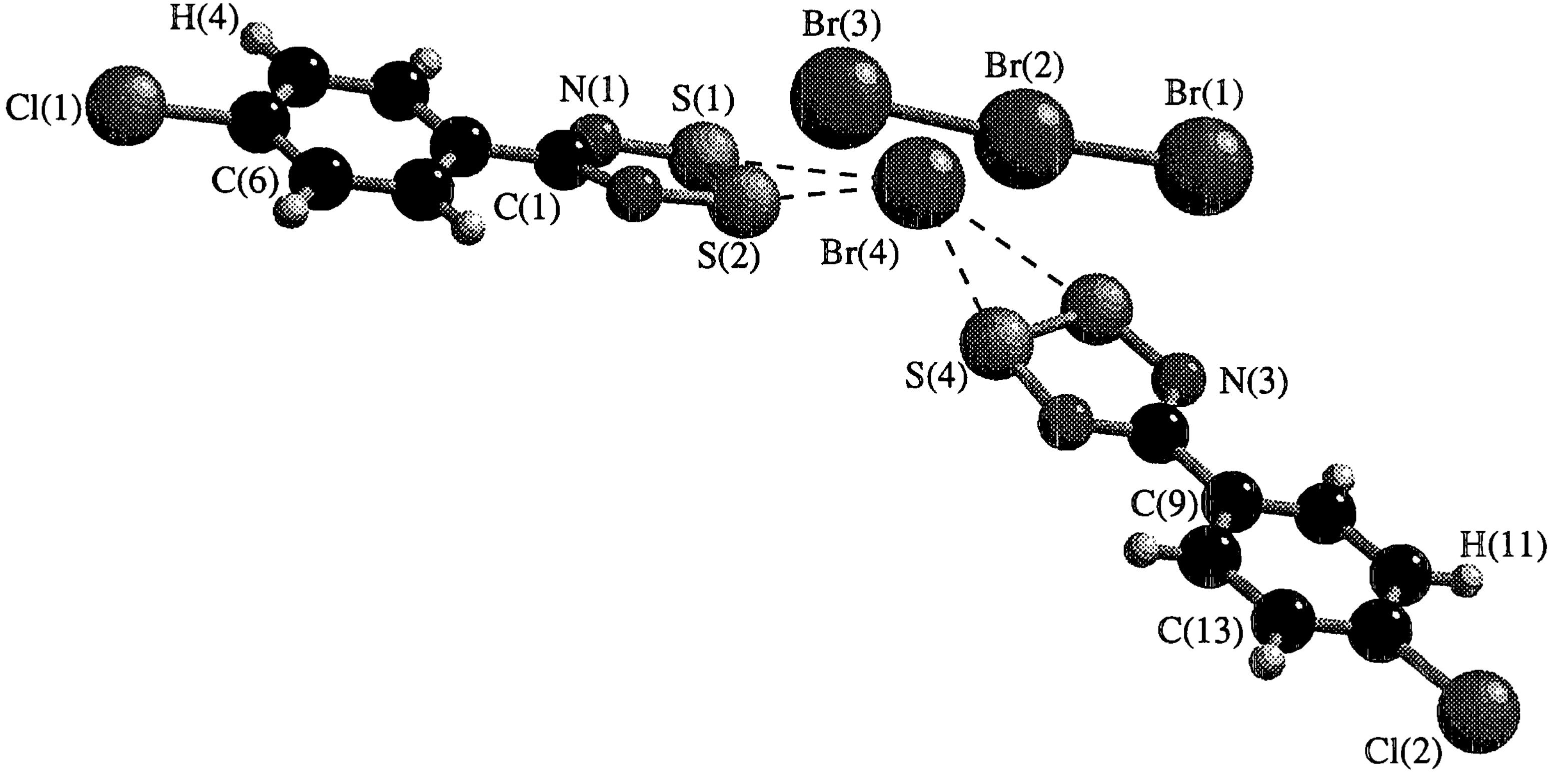


Figure 3.19 Structure of $[(p\text{-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}})_2\text{Br}][\text{Br}_3]$.

Table 3.14 Bond lengths, Å, for [*p*-Cl.C_6H_4.CNSSN)$_2$Br][Br_3].

First Dithiadiazolylium Cation			
N(1) - C(1)	1.361(11)	S(2) - N(2)	1.594(9)
N(1) - S(1)	1.573(8)	N(2) - C(1)	1.362(12)
S(1) - S(2)	2.030(4)	C(1) - C(2)	1.455(12)
Second Dithiadiazolylium Cation			
N(3) - S(3)	1.576(8)	C(8) - C(9)	1.455(12)
S(3) - S(4)	2.028(3)	N(4) - C(8)	1.362(11)
S(4) - N(4)	1.582(7)	N(3) - C(8)	1.330(11)
Tribromide Anion			
Br(2) - Br(1)	2.543(2)	Br(2) - Br(3)	2.547(2)

Table 3.15 Angles, °, for [*p*-Cl.C_6H_4.CNSSN)$_2$Br][Br_3].

First Dithiadiazolylium Ring			
N(1) - S(1) - S(2)	95.2(3)	N(1) - C(1) - N(2)	117.2(9)
N(2) - S(2) - S(1)	95.4(3)	N(1) - C(1) - C(2)	122.2(9)
C(1) - N(1) - S(1)	116.8(7)	N(2) - C(1) - C(2)	120.6(9)
C(1) - N(2) - S(2)	115.4(7)		
Second Dithiadiazolylium Ring			
N(3) - S(3) - S(4)	95.6(3)	N(3) - C(8) - N(4)	117.5(8)
N(4) - S(4) - S(3)	94.3(3)	N(3) - C(8) - C(9)	122.7(8)
C(8) - N(3) - S(3)	116.3(6)	N(4) - C(8) - C(9)	119.8(8)
C(8) - N(4) - S(4)	116.3(6)		
Tribromide Anion			
Br(1) - Br(2) - Br(3)	176.37(6)		

This is the first example of a bromide containing 1,2,3,5-dithiadiazolylium salt, the only other example being the 1,3,2,4-isomer, [BrS.CNSNS][Br_3]. That was prepared during the reaction of S_4N_4 with Br_2 in CS_2 [24]. Tribromide salts of multi-1,2,3,5-dithiadiazolylium systems have previously been described [25]. These, however, were unstable in solution, losing bromine, and no crystals suitable for X-ray analysis were obtained. The [(*p*-Cl.C_6H_4.CNSSN)$_2$Br] unit, analogous to the [(*p*-Cl.C_6H_4.CNSSN)$_2$Cl] unit in section 3.3, is observed for the first time. In general, the geometry of the dithiadiazolylium rings is similar to those discussed earlier in this chapter, section 3.1. There is ABAB packing of the [(*p*-Cl.C_6H_4.CNSSN)$_2$Br] units and tribromide anions, and this can be seen clearly in Figure 3.20.

The tribromide anion is not linear since there are secondary contacts with the [(*p*-Cl.C_6H_4.CNSSN)$_2$Br] unit which distort the anion from its idealised geometry. These secondary interactions are listed in Table 3.16.

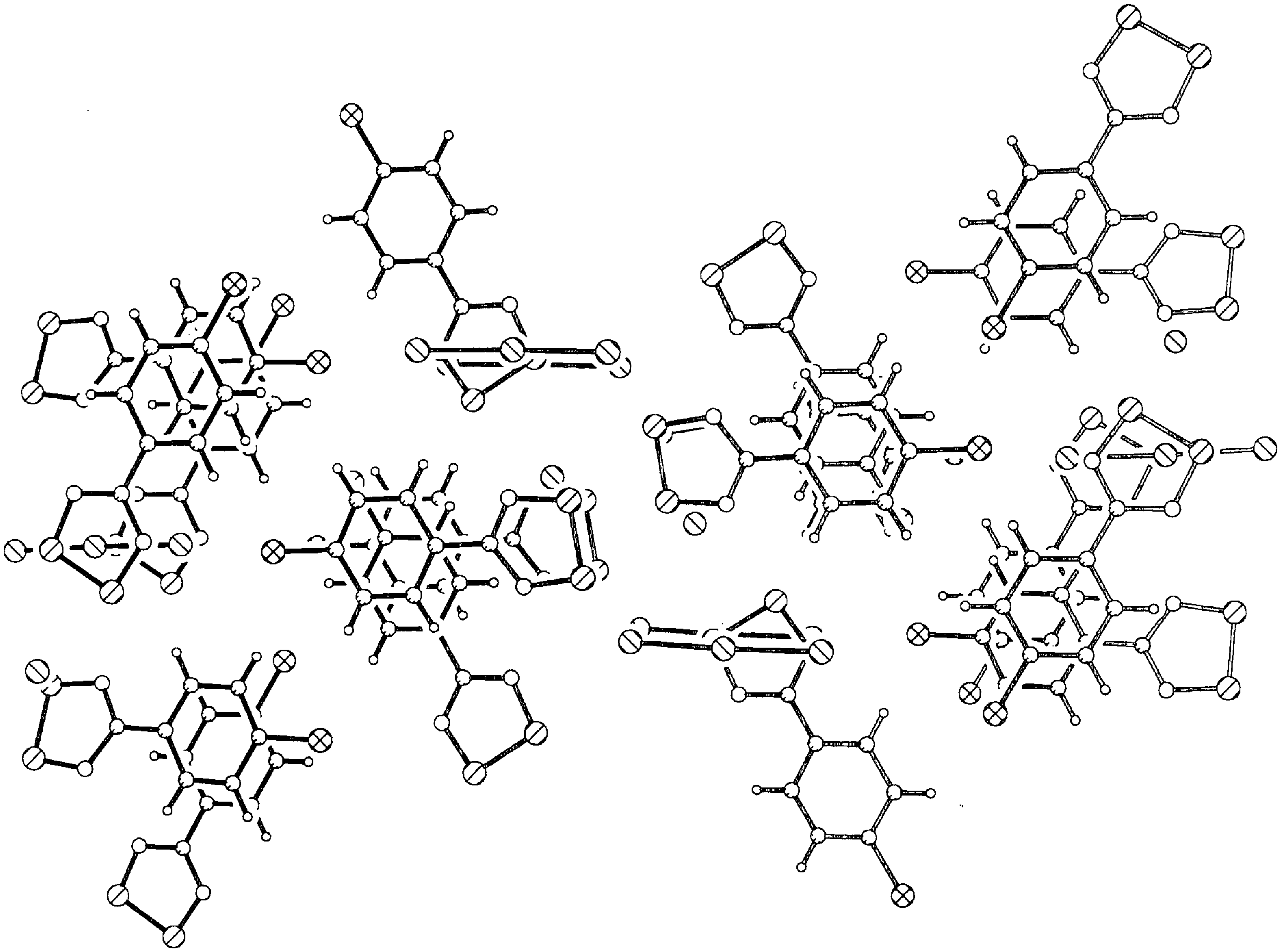


Figure 3.20 The unitcell of $[(p\text{-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}})_2\text{Br}]\ \text{Br}_3$, showing the AB packing present in the crystalline state.

Table 3.16 Secondary contacts, Å, for [p-Cl.C_6H_4.CNSSN$)_2$Br][Br_3].

Bromide contacts (not closest S)			
S(1)...Br(4)	3.059(3)	S(2)...Br(4)	3.127(3)
S(3)...Br(4)	3.103(3)	S(4)...Br(4)	3.160(3)
Br(4)...S′(1)	3.327(3)		
Tribromide contacts			
Br(2)..S″(3)	3.556(3)	Br(2)..S″(4)	3.631(3)
Br(3)..S″(4)	3.461(3)	Br(3)..S‴(4)	3.535(3)
Br(3)..S⁗(2)	3.511(3)		

Atom S′ is related to S by the operation x-1, y, z.
Atom S″ is related to S by the operation x+1, y, z.
Atom S‴ is related to S by the operation 1-x, 1-y, -z.
Atom S⁗ is related to S by the operation 1-x, 2-y, -z.

The S-S bond lengths in [(p-Cl.C_6H_4.CNSSN$)_2$Br][Br_3] are shorter than those observed in [(p-Cl.C_6H_4.CNSSN$)_2$Cl][S_3N_3], even though there is a larger bromide anion present. This is because the S_3N_3 anion exerts a large influence on the cationic rings, tending to increase the S-S bond length. The tribromide anion has less influence on the cationic heterocycles in this way. The effect of the halogen is to encourage a shortening in the length of the S-S bond. Bromine is larger than chlorine, and thus the propensity of the anion to tighten the S-S bond is less noticeable for this compound than in [(Ph.CNSSN$)_2$Cl][Pt(mnt$)_2$], for steric reasons.

3.6 Concluding remarks

The structures presented have added to the rich diversity of structural forms which have been observed for the cationic dithiadiazolylium heterocycle.

[*p*-Cl.C_6H_4.CNSSN]Cl is the first unsolvated structure of an aryl-dithiadiazolylium chloride, with an extended layered network formed by S...Cl interactions. [(*p*-Cl.C_6H_4.CNSSN$)_2$Cl][S_3N_3] further shows the ability of the dithiadiazolylium ring to maximise secondary bonding with (i) spherical anions in the plane of the ring, and (ii) planar π-rich anions above and below the plane of the ring.

This is also illustrated in [(*p*-Cl.C_6H_4.CNSSN$)_2$Br][Br_3], the first determination of a compound containing the [(R.CNSSN$)_2$Br] unit. The tribromide anion is positioned to maximise cation/bromine interactions as well.

The most unusual compound in this study is [*p*-Cl.C_6H_4.CNSSN$]_6$[Cl$]_2$ - the first dithiadiazolyl/ium system truly containing [R.CNSSN] rings with a charge intermediate between the 6π cation and the 7π radical systems. The S...Cl contacts show that perturbation of the "in-plane" interactions can occur to a small extent. It is this, coupled with the S...S inter-ring interactions that are induced by the close contact of the heterocyclic rings, which suggest that one-dimensional stacks of the type shown below, Figure 3.21, may be possible.

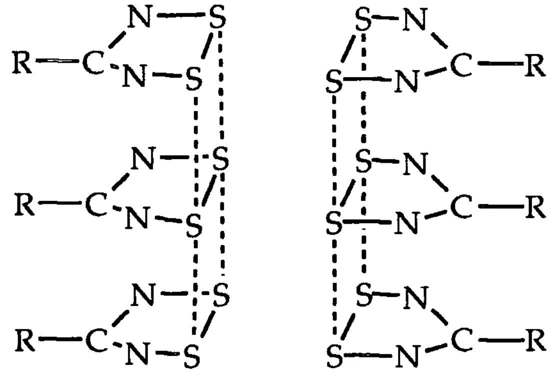


Figure 3.21 The elusive one-dimensional packing in which metal or halogen atoms may help form the stacks.

This study has also shown that our ideas about the electronic environment of the dithiadiazolyl/ium ring and its relationship to the length of the S-S bond are correct. The S-S bond lengths of all four compounds can be explained readily by consideration of factors such as (i) the size of the anion, (ii) full/partial charge on the dithiadiazolylium ring,

(iii) the orientation of the secondary contacts above/in the plane of the ring, (iv) the majority of the positive charge of the dithiadiazolylium ring is located on the S atoms, and (v) the electronic influence of the substituent group.

3.7 References.

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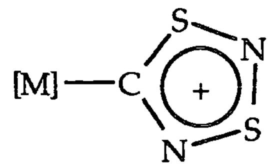
Chapter 4

$[Hg(CNSNS)_2][AsF_6]_2$, a potential ring-transfer reagent.

4.1 Introduction.

The extensive use of the [SNS][AsF_6] synthon in cycloaddition reactions with multiply-bonded systems is well-documented. Reactions are known for C≡C [1], C≡N [1], C≡P [2], N≡S [3], C=C [4], C=N [5], N=N [5], N=P [5], and P=P [6] multiple bonds. Despite the use of [SNS][AsF_6] in cycloaddition reactions involving multiply bonded species, its widespread applicability is hampered by its extreme sensitivity since it is highly susceptible to nucleophilic attack, e.g. by moisture.

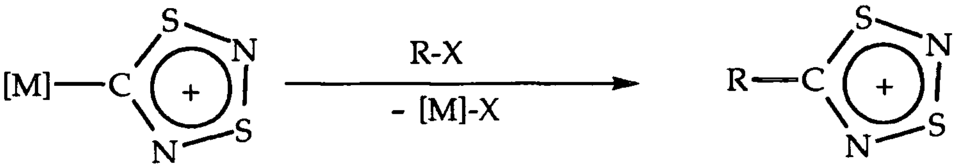
Hence, any system which can transfer a dithiadiazolylium ring to an organic substrate <u>without</u> the need to use the highly-sensitive [SNS][AsF_6] reagent is of great potential in this field. One such system involves a dithiadiazolylium ring bound to a metal through the carbon atom of the ring, as shown in Figure 4.1.



[M] = any metal species not possessing halogen atoms or other reactive functionalities.

Figure 4.1 A hypothetical metallo-dithiadiazolylium system.

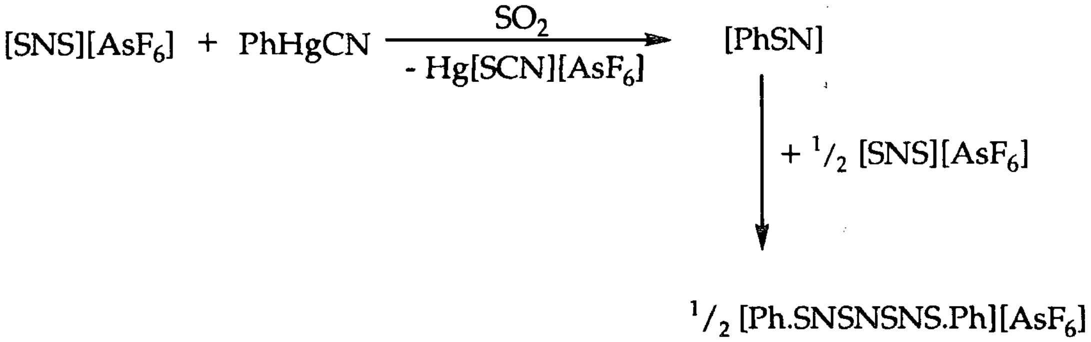
The potential of such a metallo-dithiadiazolylium system is enormous since reaction with organic halides and similar compounds is likely to yield compounds which have previously been inaccessible by present methods. Eqn 4.1 outlines a hypothetical transfer reaction between a metallo-dithiadiazolylium derivative and an alkyl halide.



Eq 4.1

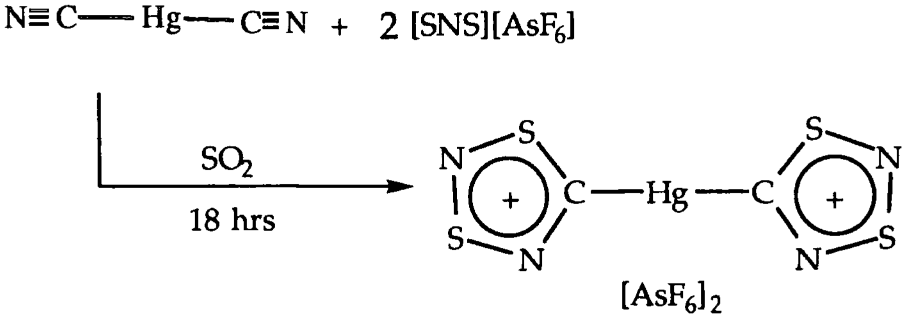
Few studies have been undertaken on the reactions of [SNS][AsF_6] with metal/metalloid cyanides. Dr. A.W. Luke [7] reacted the $M(CN)_4^{2-}$ systems (M = Pt/Pd) with [SNS][AsF_6], obtaining very sensitive polymeric material which is thought to contain material of composition $M(CN)_2(CN_2S_2)_2$. It is postulated that oligomerisation occurs through a cross-linking process involving the dithiadiazolyl units.

Dr. I. Lavender [8] investigated the reactions involving PhHgCN, Ph_3SnCN and $Na(Ph_3BCN)$ with $[SNS][AsF_6]$. For the first reaction, the main product identified was the $[Ph_2S_4N_3]$ cation, previously described by Kuyper *et al* [9]. Although not the required product, this does show some unusual reactivity; the proposed reaction pathway is shown in Scheme 4.1. The [SNS] synthon is converted to a phenylating agent in this process. The products from the other reactions were not so well-defined.



Scheme 4.1 Formation of $[Ph_2S_4N_3][AsF_6]$ from PhHgCN and $[SNS][AsF_6]$.

Simultaneously, Dr. J.M. Rawson [10] was investigating the reactivity of $Hg(CN)_2$ with the $[SNS][AsF_6]$ synthon. This cyanide was chosen because it is molecular in the solid state [11a], unlike most other neutral metal cyanides. $[Hg(CNSNS)_2][AsF_6]_2$, a new metallo-dithiadiazolylium species, was synthesised as shown in Eqn 4.2.



Eqn 4.2

The compound can be prepared easily, potentially in large quantities because yields are in excess of 85%. It is easy to handle using standard vacuum-line techniques and appears to be indefinitely stable when stored under an inert-atmosphere; decomposing slowly in the open-air. It is very soluble in acetonitrile, slightly soluble in sulfur dioxide, and insoluble in methylene chloride and hexane. Reduction in acetonitrile results in ring breakdown, forming $Hg(NCS)_2$ and S_4N_4, Eqn 4.3 [12].

$$[Hg(CNSNS)_2][AsF_6]_2 \xrightarrow[MeCN]{Ag} Hg(CNS)_2 + S_4N_4 + \text{other products}$$

Eqn 4.3

The X-ray structural determination of $[Hg(CNSNS)_2][AsF_6]_2$ shows interactions between the mercury atom and the fluorine atoms of neighbouring anions leading to a polymeric chain of cations and anions extending along the crystallographic a axis. This can be seen in Figure 4.3. The Hg...F interactions are 2.814(9) and 2.916(11)Å, and lead to an octahedral coordination about the metal centre (the Hg is located on an inversion centre). Thus, the digonal mercury atom has an effective coordination of six. This is not surprising since it is only "light" fluorine atoms which are interacting with the mercury; a tetrahedral coordination is preferred when the interacting atoms are heavier than sulfur [13].

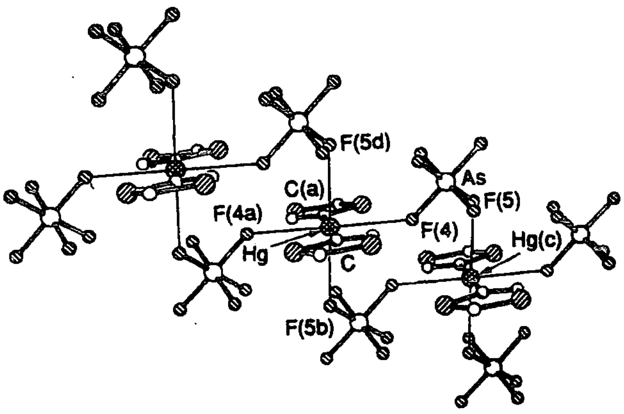


Figure 4.3 Polymeric chains in $[Hg(CNSNS)_2][AsF_6]_2$, caused by cation...anion interactions.

A view of the numbering scheme used for the cation is shown in Figure 4.4, and geometric details for this cation and similar systems are outlined in Table 4.1.

Table 4.1 Bond lengths and angles for various charged and neutral 1,3,2,4-dithiadiazolyl/ium compounds.

Compound	Bond Lengths, Å					Bond Angles, °					Ref.
	C-N_1	N_1-S_1	S_1-N_2	N_2-S_2	S_2-C	S_2CN_1	CN_1S_1	$N_1S_1N_2$	$S_1N_2S_2$	N_2S_2C	
$[Hg(CNSNS)_2][AsF_6]_2$ ¥	1.29(2)	1.622(11)	1.590(10)	1.617(12)	1.734(11)	113.6(9)	114.1(9)	102.8(6)	111.5(6)	98.0(5)	[10,12]
$[CNSNS]_2[AsF_6]_2$ † ¥	1.285(10)	1.622(7)	1.604(7)	1.597(8)	1.715(7)	116.9(6)	111.9(5)	102.1(4)	112.9(4)	96.2(4)	[14]
	1.311(10)	1.608(7)	1.595(8)	1.589(8)	1.721(8)	116.0(6)	112.0(5)	102.3(4)	113.8(4)	96.0(4)	
$[C(CNSNS)_3][AsF_6]_2$	1.329(7)	1.599(4)	1.557(5)	1.602(5)	1.745(5)	113.9(3)	112.7(3)	103.1(2)	114.5(3)	95.7(2)	[15]
	1.316(6)	1.594(4)	1.571(5)	1.626(4)	1.756(6)	114.5(4)	113.2(4)	103.4(2)	113.7(3)	95.1(2)	
	1.328(6)	1.592(5)	1.578(5)	1.629(5)	1.755(5)	113.4(4)	113.6(4)	104.0(2)	112.5(3)	96.5(2)	
$[Ph.CNSNS][AsF_6]$	1.332(9)	1.576(7)	1.563(8)	1.566(4)	1.735(8)	111.8(5)	114.4(5)	103.3(4)	112.9(4)	97.5(4)	[16]
$[Me.CNSNS][AsF_6]$	1.32(3)	1.57(2)	1.59(2)	1.63(2)	1.77(2)	110.6(1.5)	115.7(1.6)	104.6(9)	110.4(1.0)	98.4(9)	[17]
$[C_6H_4(CNSNS)_2][AsF_6]_2$ ¥	1.276(4)	1.646(4)	1.695(4)	1.632(4)	1.775(4)	120.2(3)	113.7(3)	102.2(2)	110.8(2)	97.0(2)	[18]
$[(NC)_2C(CNSNS)]$ †	1.356(4)	1.589(3)	1.576(3)	1.624(3)	1.765(3)	113.4(2)	112.1(2)	105.3(1)	112.5(2)	96.5(1)	[15]
	1.347(4)	1.586(3)	1.575(3)	1.637(3)	1.767(3)	113.3(2)	112.9(2)	105.2(1)	112.3(2)	96.4(1)	
O=CNSNS	1.374(7)	1.584(4)	1.572(5)	1.630(4)	1.813(5)	110.0(4)	113.9(4)	106.4(2)	111.7(3)	97.9(2)	[19]

¥ Molecule sits across an inversion centre.

† Two crystallographically independent molecules in the asymmetric unit.

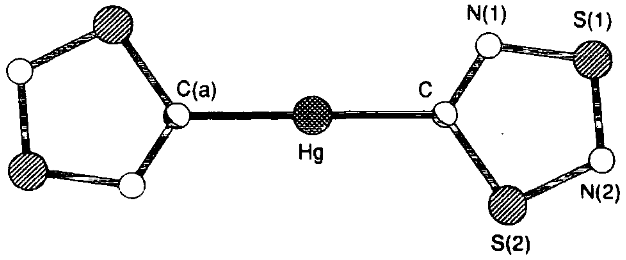


Figure 4.4 The numbering scheme used in $[Hg(CNSNS)_2][AsF_6]_2$.

The LUMO for the 1,3,2,4-dithiadiazolylium cation possess anti-bonding character along all the bonds in the ring except the C-N bond, see Figure 4.5. The C-S bond is the longest in the heterocyclic ring, and hence is the bond where changes in the electronic nature of the ring are most apparent.

The data from Table 4.1 indicate that the length of the C-S bond is less for the cationic systems cf. the neutral rings, as expected from consideration of the LUMO. The sulfur atom is the softest atom in the ring, and the positive charge reduces the anti-bonding nature of the S-N bonds. It is therefore likely that the positive charge in $[Hg(CNSNS)_2][AsF_6]_2$ is concentrated in the heterocyclic rings.

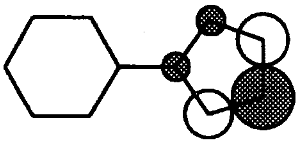
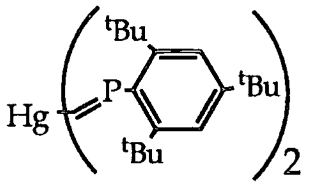
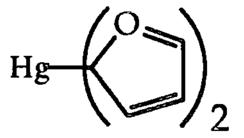
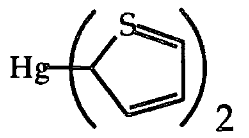
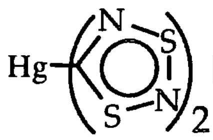
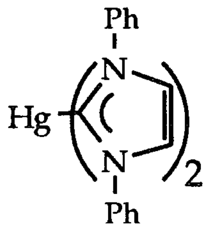
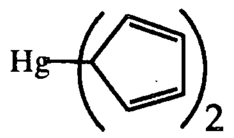
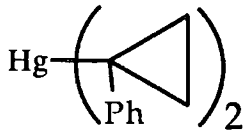


Figure 4.5 The LUMO of $[Ph.CNSNS][AsF_6]$ (the orientation of the ring is the same as for Figure 4.4).

However, the length of the Hg-C bond is also of interest since this may provide further insights into the electronic nature of the dithiadiazolylium rings and the central mercury atom. A comparison of the Hg-C bond lengths for various organomercury compounds is given in Table 4.2.

The bond length for a given pair of atoms is influenced by the degree of hybridisation of the atoms [31], and this is mirrored in the Hg-C bond lengths from Table 4.2. The shorter bonds are observed for sp hybridised carbon atoms, and the longer bonds seen for sp^3 hybridised carbon atoms. A graphical representation of the data in Table 4.2 is shown in Figure 4.6.

Table 4.2 Hg-C bond lengths for selected organomercury compounds.

Compound	Hg-C (Å)	Hg-C-X (°) ‡	C hybrid$^{\underline{n}}$	ref
Hg(CN)$_2$	2.019(3)	177.0(3)	sp	[20]
Ph-Hg-CN	2.051(15) 2.094(16)	176(1) 121(1) 119(1)	sp sp^2	[21]
Hg(Ph)$_2$	2.085(7) †	122.4(5) 120.0(7)	sp^2	[22]
	2.042(11) † 2.079(11)	127.4(6) ¶ 124.1(6)	sp^2	[23]
	2.059(5) †	117.1(4) 134.9(5)	sp^2	[24]
	2.061(18) †	123.1(11) 126.9(14)	sp^2	[25]
 $[AsF_6]_2$	2.074(12) †	124.0(6) 122.1(8)	sp^2	[10,12]
 $[ClO_4]_2$	2.06(1) †	124, 128 (values from C.S.D.)	sp^2	[26]
[Me_2NCH_2FcHg]$_2$ [Ph_3BCN]$_2$ ¥	2.06(1) 2.07(1)	123(1) 128(1)	sp^2	[27]
	2.12(1) 2.15(1)	106, 104, 120 (values from C.S.D.)	sp^3	[28]
	2.124(8) 2.104(8)	115, 119, 119 (values from C.S.D.)	sp^3	[29]
Hg(CF$_3$)$_2$	2.118(16) †	111.7(7)*	sp^3	[30]

‡ X = C/N/O/F/P/S.

† Mercury atom located on an inversion centre.

¶ Only angle to P is quoted, two molecules in the asymmetric unit.

¥ Fc refers to the ferrocene (CpFeCp) unit.

* Molecule lies along a three-fold axis.

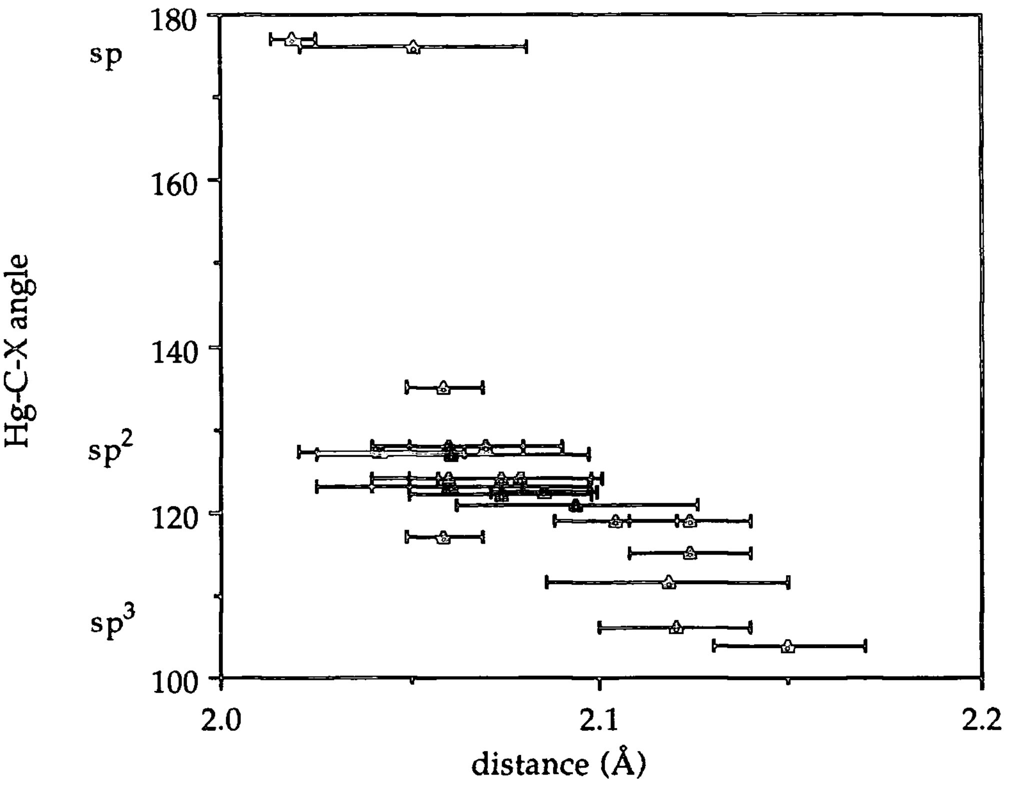


Figure 4.6 Scatter-plot of the organomercury compounds in Table 4.2. (The error bars indicate double the esd for each bond length).

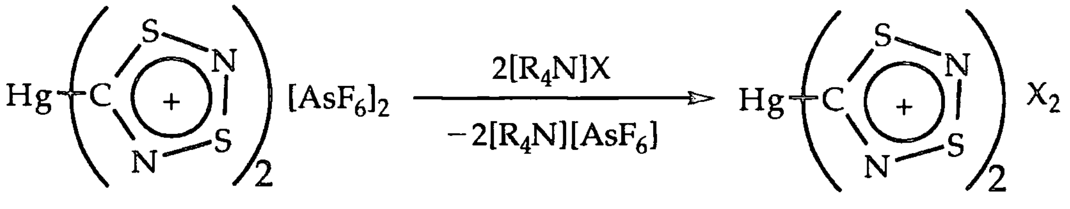
The effect of positive charge on the mercury or carbon atoms does not seem to greatly perturb the length of the Hg-C bond away from those seen for the uncharged species. Thus, the Hg-C bond is probably longer in $[Hg(CNSNS)_2][AsF_6]_2$ than in $Hg(CN)_2$ because of the hybridisation of the carbon atom.

Therefore, the positive charge in $[Hg(CNSNS)_2][AsF_6]_2$ seems to reside mainly on the dithiadiazolylium rings rather than localised solely on the mercury atom. The destruction of the heterocycles on reduction, however, and the Hg...F contacts in the solid state, suggest that a small degree of delocalisation of this charge over the entire σ-framework does occur.

In view of the solid state structure and initial chemistry of the first metallo-dithiadiazolylium salt, $[Hg(CNSNS)_2][AsF_6]_2$, the reactions with various X-X, C-X, N-X and S-X bonds (X = Cl/Br/I) have been examined, and are reported herein.

4.2 Reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with tetraalkylammonium halides.

The crystal structure of $[Hg(CNSNS)_2][AsF_6]_2$ has Hg...F interactions which are less than the sum of the van der Waals radii of the two atoms. Thus, derivatives of the $[Hg(CNSNS)_2]$ dication which contain simpler anions, e.g. X= Cl^-, Br^-, I^-, may well possess some interesting Hg...X contacts in the solid state. Therefore, metathesis reactions with tetraalkylammonium halides, $[R_4N]X$, were carried out (Eqn 4.4).



Eqn 4.4

Addition of acetonitrile to a mixture of $[Hg(CNSNS)_2][AsF_6]_2$ and the appropriate tetraalkylammonium halide gave the required products as orange, dark-orange and burgundy solids for the Cl^-, Br^-, I^- salts respectively. These solids were relatively air-stable, although decompostion was observed after four hours in the atmosphere.

The i.r. spectra show no sign of Hg...X contacts, although the CHN analysis was good. Therefore a crystal growth experiment was attempted. Extraction of $[Hg(CNSNS)_2]Cl_2$ with SO_2 in a sealed extractor for 4 days gave a small quantity of yellow-brown crystalline material which was suitable for single crystal X-ray diffraction. The solvent was removed, and perfluoropolyether placed in the extractor. This was allowed to run down and cover the crystals, whereupon the extractor was broken open and a crystal mounted on the diffractometer. Initial cell parameters were obtained, which matched no crystal forms on the C.S.D. Intensity data were duly collected.

The structure was solved by Patterson structure solution methods [32], and an investigation of the solution obtained showed that the structure of the crystal placed on the diffractometer was not the anticipated compound, $[Hg(CNSNS)_2]Cl_2$. Instead, the crystal was $[S_4N_3][HgCl_3]$, which has been determined previously [33]. It was subsequently shown that the i.r. spectrum for the crystalline material obtained from the crystal growth matched the literature values [34] for $[S_4N_3][HgCl_3]$, and was different to the i.r. spectrum obtained for $[Hg(CNSNS)_2]Cl_2$ before the crystal-growth experiment. Therefore, decomposition of the required chloride salt had occurred.

The decomposition of $[Hg(CNSNS)_2]Cl_2$ to $[S_4N_3][HgCl_3]$ appears to be very complex. Several alkyl organomercury salts are known to be both thermodynamically and photochemically unstable, and are often kept in the cool and in the dark [35]. The decomposition of $[Hg(CNSNS)_2]Cl_2$ suggests that it too is photochemically unstable.

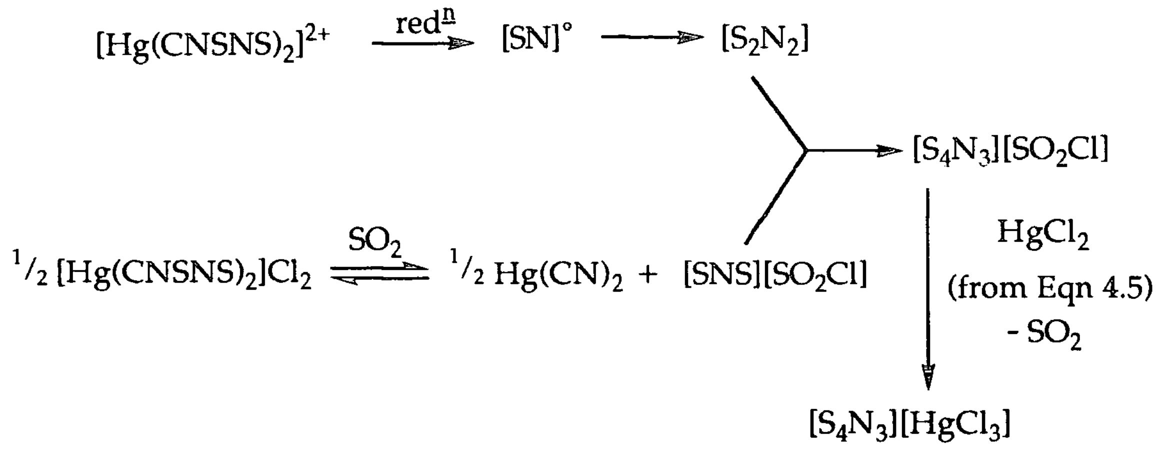
Numerous $[S_4N_3]$ salts are known [36]; some of which have been formed from unusual reactions. In S/N chemistry the $[S_4N_3]$ cation is similar to the neutral S_4N_4 molecule, in that it can act as a "thermodynamic sink" to which unstable S/N species are prone to re-arrange/decompose [37].

The crystal structure of $[Hg(CNSNS)_2][AsF_6]_2$ shows significant Hg...F interactions which may help to stabilise the $[Hg(CNSNS)_2]$ dication in the solid state. For the halide salts, it is likely that there are increased covalent interactions between the dication and the halide anions. There will therefore be a lower contribution to the stabilisation energy of these systems from the lattice energy. Consequently, $[Hg(CNSNS)_2]Cl_2$ may be more liable to fall apart than $[Hg(CNSNS)_2][AsF_6]_2$. One possible decomposition involves the formation of $HgCl_2$, plus products based on the dithiadiazolyl/ium ring, see Eqn 4.5.

$$[Hg(CNSNS)_2]Cl_2 \longrightarrow HgCl_2 + 2\text{"CNSNS" units.}$$

<u>Eqn 4.5</u>

Reduction of $[Hg(CNSNS)_2][AsF_6]_2$ is known to lead to decomposition of the intermediate radical species [12], with the eventual production of S_4N_4, probably via S_2N_2. The breakdown of $[Hg(CNSNS)_2]Cl_2$ may also occur to give $Hg(CN)_2$ and $[SNS][SO_2Cl]$, i.e. the reverse of the initial cycloaddition reaction used in the preparation of $[Hg(CNSNS)_2][AsF_6]_2$, but with a chloride anion stabilised by the solvent. Subsequent combination of S_2N_2 and $[SNS][SO_2Cl]$ could result in the formation of the observed $[S_4N_3]$ cation. The anion could be formed from combination of $HgCl_2$ (Eqn 4.5) and the $[SO_2Cl]$ anion. This is all summarised in Scheme 4.2.



Scheme 4.2 Possible formation of $[S_4N_3][HgCl_3]$ from the decomposition of $[Hg(CNSNS)_2]Cl_2$.

The exact mechanism is obviously still unclear, especially since only a small quantity of crystalline material was produced. However, the evident stability of the $[AsF_6]$ salt cf. the halide systems meant that further experiments on the reactivity of this metallo-dithiadiazolylium dication, $[Hg(CNSNS)_2]$, were conducted exclusively using the $[AsF_6]$ salt.

4.3 Reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with halogens.

The reaction of halogens with $[Hg(CNSNS)_2][AsF_6]_2$ has its precedent in both organomercury chemistry and inorganic Hg/N chemistry. The reactions of mercury bis(trifluoromethylamine) with iodine [38] (Eqn 4.6), mercury bis(sulfurdifluoroimide) with chlorine [39] (Eqn 4.7) and a general organomercurial with chlorine [35] are summarised below (Eqn 4.8).

$$Hg[N(CF_3)_2]_2 + 2I_2 \longrightarrow 2(CF_3)_2NI + HgI_2$$

Eqn 4.6

$$Hg(NSF_2)_2 + 2Cl_2 \longrightarrow 2\,ClNSF_2 + HgCl_2$$

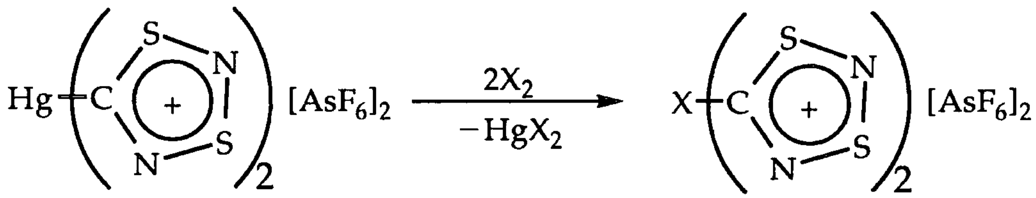
Eqn 4.7

$$R_2Hg + 2Cl_2 \longrightarrow 2\,R\text{-}Cl + HgCl_2$$

Eqn 4.8

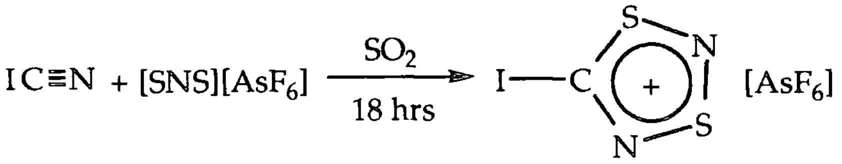
In view of the above reactions, initial investigations into the transfer properties of $[Hg(CNSNS)_2][AsF_6]_2$ were carried out by reaction with Cl_2, Br_2 and I_2. The $[AsF_6]$ salt was chosen for all the attempted transfer reactions in view of its photochemical stability and the non-participating nature of the $[AsF_6]$ anion.

Addition of the appropriate halogen to $[Hg(CNSNS)_2][AsF_6]_2$ under SO_2 and stirring (for up to 4 days in the case of the I_2 reaction) gave the expected products in good yield, Eqn 4.9.



Eqn 4.9

The iodo derivative, $[I.CNSNS][AsF_6]$, has previously been described [3,40], prepared by the reaction of $[SNS][AsF_6]$ with ICN (Eqn 4.10). The chloro- and bromo- derivatives are new. This is because the halocyanides, BrCN and ClCN, are more volatile and more susceptible to polymerisation than ICN and consequently their reactions with $[SNS][AsF_6]$ have not been investigated [41].



Eqn 4.10

A comparison of the i.r. spectra for all three compounds is given in Table 4.3. Assignments for the 1,3,2,4,-dithiadiazolylium ring system are based on previous work [14,40]], and those due to the [AsF_6] anion have also been described [42]. Absorptions due to aryl-halogen stretches, to which these compounds can be approximated, are usually found in the region 1000 - 1250 cm^{-1} [43]. Although complete assignment of every absorption band is not possible, the characteristic bands due to the heterocyclic ring can be readily assigned.

Table 4.3 I.R. data for [X.CNSNS][AsF_6], X = Cl, Br and I.

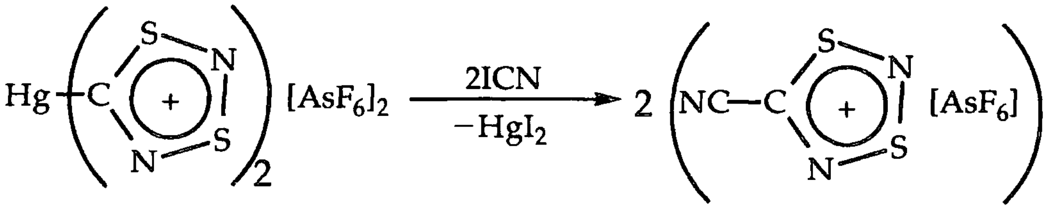
I [3,40]	Cl	Br	I	assignment
1328m	1303w	1352m	1332m	
1295sh	1290sh	1291sh		
1255sh				
	1157m	1170w br	1152m vbr	
		1050sh	1075w	
1020w	1036ms br	1036w	1030w	
992w		997m		*
975ms	953w sh	923w	977m	*
	935m	912m		* $\nu_{asym}(SN)$
885m	883m		893w	*
875m		882sh	877w	* and
845m	837w	860m	846w	*
		802w	831w	* $\nu_{sym}(SN)$
783ms	798m	791m	784w	*
		779w	768w	*
	721vs br		720vs	
690vs		695vs br	695vs br	$\nu_3(AsF_6)^-$
649sh	651sh	654sh	660sh	$\nu_1(AsF_6)^-$
580m	579ms	585m	584m	$\nu(CS)$
550w		566sh	563w	$\nu_2(AsF_6)^-$
			450m	
438ms	441ms	440m	434w	
390s				$\nu_4(AsF_6)^-$
		370s		$\nu_5(AsF_6)^-$

The reaction of [Hg(CNSNS)$_2$][AsF_6]$_2$ with halogens provides a clean, high yielding route to compounds of the general type, [X.CNSNS][AsF_6], (X= Cl, Br, I).

4.4 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with C-I bonds.

4.4.1 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with ICN.

$[Hg(CNSNS)_2][AsF_6]_2$ has proven successful for transfer of the 1,3,2,4-dithiadiazolylium ring during the reactions with halogens, the expected products being easily synthesised. Therefore, the reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with a compound containing a pseudo-halide was thought to be worth further investigation. ICN was chosen because it is easier to handle than the chloro- or bromo- derivatives, and the XNCS compounds have only been observed as transient species in Ar matrices [44]. A pure sample of ICN was also available in the laboratory glove-box. The proposed reaction is outlined below, Eqn 4.11.



Eqn 4.11

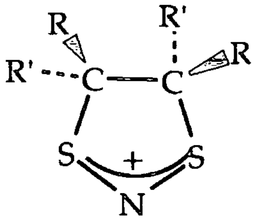
However, addition of SO_2 to a mixture of both reactants and stirring for 2 weeks did not give rise to the required ring-containing compound, $[NC\text{-}CNSNS][AsF_6]$. Instead $[(CNSNS)_2][AsF_6]_2$ was synthesised (CHN and i.r. spectrum agreed with the literature values [14]), along with the expected HgI_2 (a characteristic red colour) and $(CN)_2$. The volatiles from the reaction were passed over aqueous KOH solution (giving KCN from the $(CN)_2$) and some extra chloros base bath was required due to some initial decolourisation from this KCN.

It is extremely unlikely that any $[NC.CNSNS][AsF_6]$ formed would breakdown to give $[(CNSNS)_2][AsF_6]_2$ and paracyanogen, since this process would involve the destruction of C-C bonds. Therefore, it is possible that the metal reagent, $[Hg(CNSNS)_2][AsF_6]_2$, is involved in an equilibrium process in the solvated state, which means it is not behaving solely as $[Hg(CNSNS)_2][AsF_6]_2$. A possible description of such a process is depicted in Eqn 4.12; it is similar to the equilibrium proposed in Scheme 4.2.

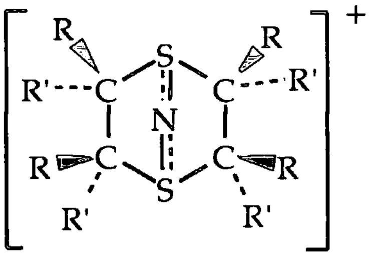
$$[Hg(CNSNS)_2][AsF_6]_2 \rightleftharpoons Hg(CN)_2 + 2[SNS][AsF_6]$$

Eqn 4.12

A similar effect has been seen in the reactions of [SNS][AsF_6] with C=C double bonds [4] in which the initial reaction proceeds smoothly to give a 1,3,2-dithiolium species, (I). The carbon atoms are fully saturated, so the positive charge is still associated with the SNS fragment. Thus, a second equivalent of alkene leads to the formation of the heterocyclic norbornane cation, (II).



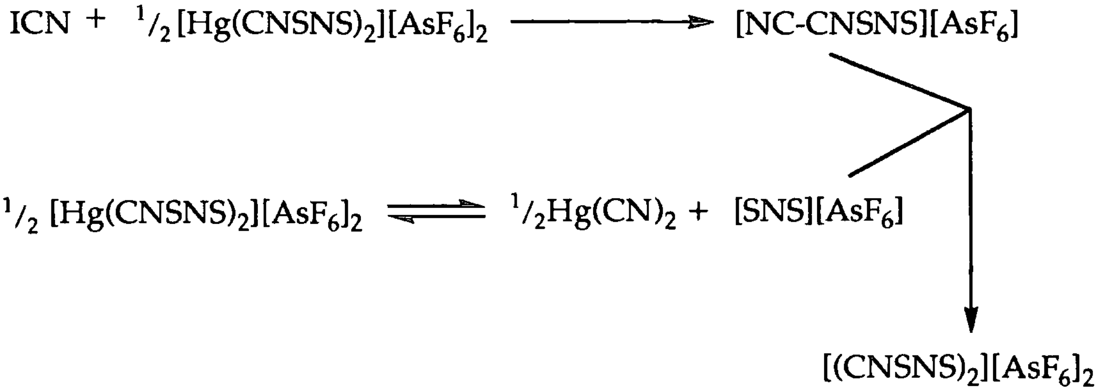
(I)



(II)

It is the second reaction which is reversible, although it does require heating with a molar equivalent of [SNS][AsF_6] at 70°C. Despite this, there is some precedent for an equilibrium process involving the SNS fragment. It is possible that the equilibrium process described in Eqn 4.12 has some influence in all of the reactions that follow in this chapter.

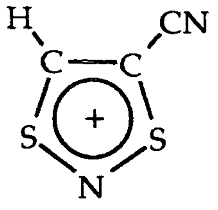
Scheme 4.3 shows a possible reaction mechanism for the formation of the observed product, [$(CNSNS)_2$][AsF_6]$_2$, which involves the reaction of [Hg$(CNSNS)_2$][AsF_6]$_2$ with one equivalent of ICN to give the expected nitrile-containing product, followed by reaction of this [NC.CNSNS][AsF_6] species with [SNS][AsF_6] at the nitrile functionality.



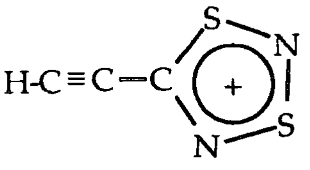
Scheme 4.3 Proposed mechanism for the formation of [$(CNSNS)_2$][AsF_6]$_2$ from ICN and [Hg$(CNSNS)_2$][AsF_6]$_2$.

4.4.2 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with IC≡CI.

The reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with IC≡CI was tried in an attempt to produce the unknown salt, $[SNSNC\text{-}C{\equiv}C\text{-}CNSNS][AsF_6]_2$. This compound cannot be made by reaction of $[SNS][AsF_6]$ with a suitable nitrile containing starting material since the [SNS] synthon attacks the alkyne bond in preference to the nitrile functionality [3]. This has been investigated and explained in terms of the size of the ionisation potential of the triple bond; the reaction is slower for dieneophiles with larger ionisation potentials. Therefore, it has been demonstrated that the reaction of HC≡C-CN with $[SNS][AsF_6]$ leads to the 1,3,2-dithiolium compound (III), and not the 1,3,2,4-dithiadiazolylium compound (IV). The reaction of a second equivalent of [SNS][AsF6] (to react with the nitrile group) requires heating at 50°C for ten weeks [3,14].

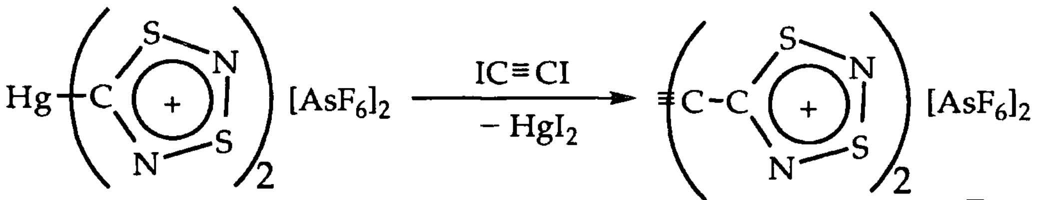


(III)



(IV)

The intended reaction sequence between $[Hg(CNSNS)_2][AsF_6]_2$ and IC≡CI is shown in Eqn 4.13, with substitution taking place at the electrophilic carbon centres.

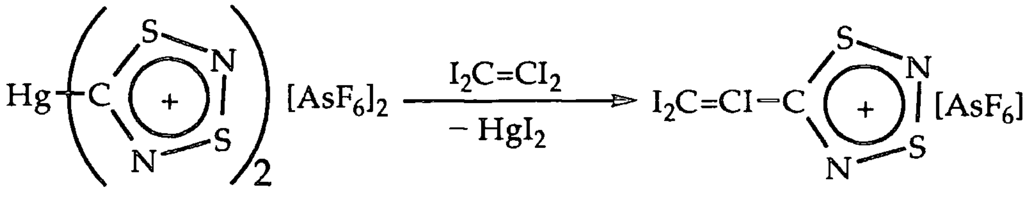


Eqn 4.13

Addition of solvent and stirring gave HgI_2 as the only identifiable product. The other product could not be identified because it was an intractable oil. It is not possible to say whether HgI_2 was produced before or after possible break-down and polymerisation of the alkyne.

4.4.3 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with $I_2C{=}CI_2$.

The reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with $I_2C{=}CI_2$ was attempted in order to obtain a 1,3,2,4-dithiadiazolylium ring substituted adjacent to a double bond in the manner shown in Eqn 4.14.



Eqn 4.14

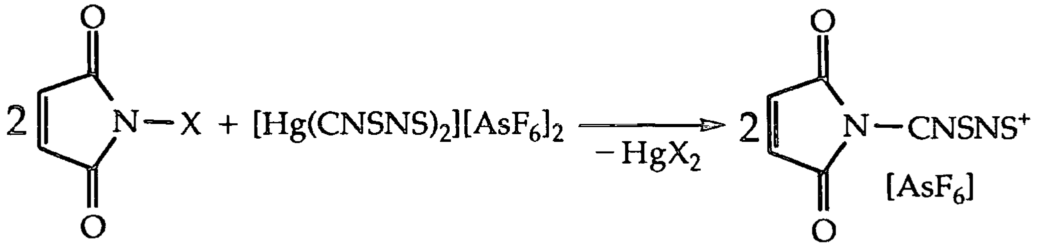
Addition of the solvent (MeCN) to the reactants and stirring for 4 days gradually yielded a red precipitate of HgI_2. Work-up produced only an intractable oily-brown material similar in appearance to that observed for the analogous reaction with IC≡CI. The reaction was kept in the dark since tetraiodoethylene is known to be photosensitive [45], but breakdown of the alkene must be occurring.

4.5 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with other M-X bonds (M=N/S).

The reactivity of N-X (X=Cl/I) bonds with $[Hg(CNSNS)_2][AsF_6]_2$ was investigated because of the lack of successfully characterised compounds from the reactions of $[Hg(CNSNS)_2][AsF_6]_2$ with C-I bonds. These results will be presented here, along with one reaction with a compound containing an S-Cl bond.

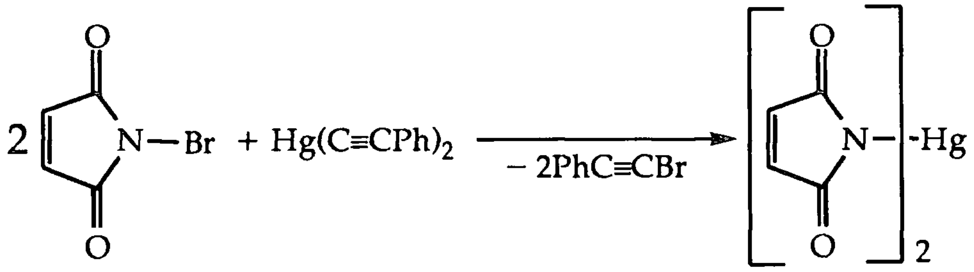
4.5.1 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with N-halosuccinimide.

The first possible reaction pathway envisaged for the reaction of N-halosuccinimide with $[Hg(CNSNS)_2][AsF_6]_2$ is detailed below, Eqn 4.15. As before, it was anticipated that a mercuric halide would be formed.



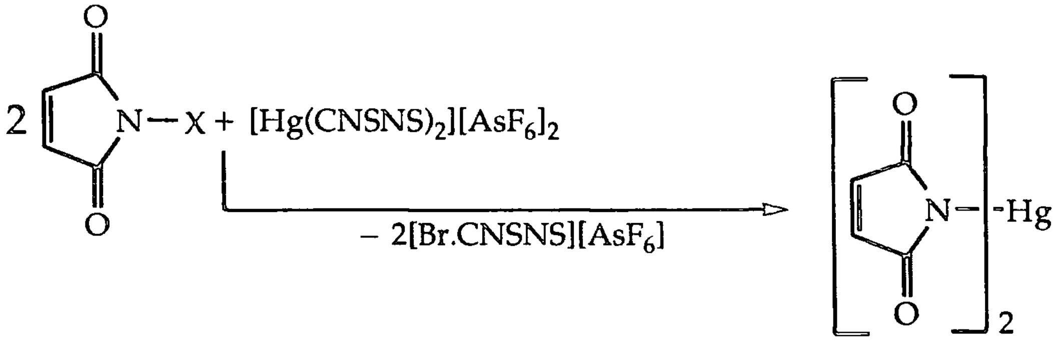
Eqn 4.15

However, the reaction of N-bromosuccinimide with mercury bis(phenylacetylide) produces mercury bis(succinimide) and bromophenylacetylene [46] (Eqn 4.16).



Eqn 4.16

Therefore, it is possible that the reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with N-halosuccinimide would proceed in a different manner to that described in Eqn 4.14. This would give rise to the formation of mercury bis(succinimide) and $[Br.CNSNS][AsF_6]$, Eqn 4.17.

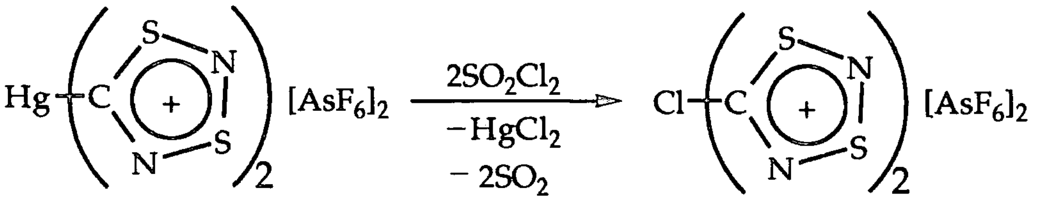


Eqn 4.17

In view of the two possible reactions, it was very disappointing to find that the reaction in MeCN also gave an intractable brown oil. The equilibrium described in Eqn 4.11 may well be contributing to the observed reaction. A fuller explanation is given in section 4.7.

4.5.2 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with sulfuryl chloride.

The reaction was initially conceived as a route to $[Cl.CNSNS][AsF_6]$ without the use of chlorine gas. Sulfuryl chloride is well-known as a chlorinating agent [47a], and the expected reaction is shown in Eqn 4.18.



Eqn 4.18

A beige powder was obtained from the reaction mixture after washing with methylene chloride. The carbon analysis matched the expected product, $[Cl.CNSNS][AsF_6]$, but the nitrogen analysis was poor. A comparison of the i.r. spectrum of this compound with that of a pure sample of $[Cl.CNSNS][AsF_6]$ indicated significant differences.

Substitution at the sulfur atom is unlikely since no S=O stretches are observed in the i.r. spectrum, and the exact nature of the compound obtained remains an enigma.

4.6 Miscellaneous reactions of [SNS][AsF_6] with metallo-nitrile systems.

The toxicity of mercury has meant that the search for other metallo-dithiadiazolylium systems has received attention, as well as an investigation into the reactivity of [$Hg(CNSNS)_2$][AsF_6]$_2$. These will now be reported.

4.6.1 Attempted reaction of [SNS][AsF_6] with $Zn(CN)_2$.

The reaction of $Hg(CN)_2$ with [SNS][AsF_6] proceeds smoothly to give the first metallo-dithiadiazolylium species, [$Hg(CNSNS)_2$][AsF_6]$_2$. However, since mercury is quite toxic, the preparation of other systems based upon less poisonous metals is interesting. A sample of $Zn(CN)_2$ was available in the laboratory and thus, the reaction of [SNS][AsF_6] with $Zn(CN)_2$ was attempted, see Eqn 4.19.

$$Zn(CN)_2 + 2[SNS][AsF_6] \longrightarrow [Zn(CNSNS)_2(AsF_6)_2]_n$$

Eqn 4.19

The reactants were stirred for 2 months in SO_2, but no reaction had taken place when the experiment was worked up. This is probably due to the polymeric nature of $Zn(CN)_2$, which exists in the anti-cuprite array, [11b] Figure 4.5.

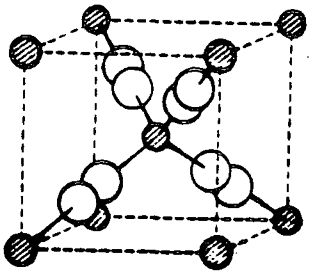


Figure 4.5 The anti-cuprite structure of $Zn(CN)_2$.

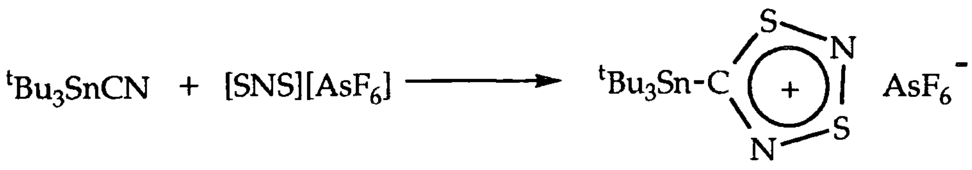
The success of the reaction between $Hg(CN)_2$ and [SNS][AsF_6] must be due in part to the slight solubility of $Hg(CN)_2$ in sulfur dioxide, which is monomeric in the solid state [11a] and therefore more easily dissolved than the polymeric $Zn(CN)_2$.

4.6.2 Attempted reaction of $[SNS][AsF_6]_2$ with Ph_3SnCN.

This reaction was tried in an attempt to characterise fully the products since previous reactions had resulted in hydrolysis. The reaction proceeds in a similar manner to that seen for the reaction between PhHgCN and $[SNS][AsF_6]$, with the formation of a highly insoluble yellow solid and a dark blue solution from which $[Ph_2S_4N_3][AsF_6]$ was recovered. The evidence in the experimental supports the formation of the yellow solid as $[Ph_2SnNCS][AsF_6]$, and the reaction has occurred in an analogous manner to that mentioned in Scheme 4.1 [8].

4.6.3 Attempted reaction of $[SNS][AsF_6]_2$ with $^tBu_3SnCN$.

During the reaction between Ph_3SnCN and $[SNS][AsF_6]$ a colour change is observed, involving an intermediate red solution. Since Sn-C bonds are stronger for *tertiary*-butyl groups bound to the metal than phenyl groups, and are thus more likely to remain bound to the metal [47b], the reaction of $^tBu_3SnCN$ with $[SNS][AsF_6]$ was attempted. It was thought that the intermediate species may be more stable, and isolable, with the presence of *tertiary*-butyl groups on the tin. The proposed reaction is outlined in Eqn 4.20.



Eqn 4.20

Stirring in sulfur dioxide gave an immediate red-coloured solution which remained red after stirring for 24 hours. Solvent removal gave a sticky red oil which was unsuitable for CHN analysis. However, an i.r. spectrum of this oil was obtained, which showed some hydrolysis has occurred. Comparison with an i.r. spectrum of the starting material showed a broad peak at 2108cm-1 which may be attributable to NCS stretches. This could be due to hydrolysis of a metallo-dithiadiazolylium species rather than the formation of a S/N chain compound.

Since the purity of the solvent was questionable (a new procedure had just been adopted in the laboratory when this reaction was carried out) the reaction should be repeated. The stabilisation of a red material, rather than a deep blue compound, suggests that the intermediate species, $[^tBuCNSNS][AsF_6]$, may be formed.

4.7 Concluding remarks.

Metathesis of $[Hg(CNSNS)_2][AsF_6]_2$ to the corresponding halide salts, $[Hg(CNSNS)_2]X_2$ ($X = Cl^-, Br^-, I^-$), proceed smoothly in fair yield. The $[AsF_6]_2$ salt are possibly lattice stabilised - note the Hg...F contacts in the solid state. It is likely the halide salts are less well stabilised and thus, more susceptible to decomposition, (especially since the mercury dihalides are very stable systems).

The transfer properties of $[Hg(CNSNS)_2][AsF_6]_2$ have been clearly demonstrated for reactions involving the halogens, yielding the previously unknown chloro- and bromo- analogues of $[I.CNSNS][AsF_6]$.

It is possible that $[Hg(CNSNS)_2][AsF_6]_2$ is unstable in the solvated state, particularly as oils were produced in the majority of reactions involving $[Hg(CNSNS)_2][AsF_6]_2$ in solution. It seems likely that the equilibrium process outlined in Eqn 4.12, section 4.4.1 is occurring.

$$[Hg(CNSNS)_2][AsF_6]_2 \rightleftharpoons Hg(CN)_2 + 2[SNS][AsF_6]$$

Eqn 4.12

The preparation of $[Hg(CNSNS)_2][AsF_6]_2$ in sulfur dioxide, in which it has a low solubility, suggests that the equilibrium is mainly on the left-hand side of the equation. However, in solution there is probably an appreciable shift to the right of the equilibrium process. This will be due to a reduced contribution from lattice energy stabilisation.

One other factor to consider is the strength of the Hg-C bond. Despite the low values quoted for the strength of the Hg-C bond in dialkyl and diaryl organomercury compounds, these are usually average values. The data in Table 4.4 (from reference 35) show that this can be misleading, with a substantial difference in bond enthalpy terms for the breakage of the first and second Hg-C bonds. This may well explain the slow reaction times observed in many of these experiments.

Table 4.4 Bond enthalpy terms for selected organomercury compounds (kJ/mol).

Compound	D_1	D_2	$D_1 + D_2$
Me_2Hg	213.8 ± 8	28.9 ± 13	
Et_2Hg	177.8 ± 8	24.7 ± 16	
Pr_2Hg			205 ± 16
$^iPr_2Hg$	113.0 ± 21	62.8 ± 29	
Ph_2Hg			271.1 ± 16
$(CH_2{=}CH_2)Hg$	202.1 ± 14	79.9 ± 25	

(D_1 is the term associated with breaking the first Hg-C bond, D_2 the second).

Some reactions look promising, especially with the formation of mercury dihalide salts. Further work in these reactions should yield more concrete results. The reaction of $[SNS][AsF_6]$ with ^tBuSnCN also merits further attention - a crystal structure determination may well yield information about the reaction pathway and the nature of the intermediate in the reactions between $[SNS][AsF_6]$ and organometalcyanides.

4.8 Experimental

4.8.1 Preparation of [Hg(CNSNS)$_2$][AsF$_6$]$_2$

Hg(CN)$_2$ (0.493g, 1.95mmol) and [SNS][AsF$_6$] (1.057g, 3.96mmol) were placed together with a magnetic follower in one limb of a two-limbed reaction vessel and SO$_2$ (8ml) was condensed onto the reactants. Initially, there was a white solid under a dark-brown solution. This lightened after stirring (24 hours) to yield a pale yellow solution over a white solid. The solvent was removed and a single wash with CH$_2$Cl$_2$ gave the required product as a white powder (1.448g, 94%).

Found	C	3.27	N	7.13
Calculated	C	3.05	N	7.12

I.R. (ν_{max}/cm^{-1}) 1335m, 1019w, 984m, 874, 766s, 703vs br, 583s, 560s, 449s, 398vs.

4.8.2 Preparation of [Hg(CNSNS)$_2$]Cl$_2$

[Hg(CNSNS)$_2$][AsF$_6$]$_2$ (200mg, 0.25mmol) and [NBu$_4$]Cl (141mg, 0.51mmol) were placed in one limb of a two-limbed reaction vessel with a magnetic follower and MeCN (7ml) syringed in. After stirring (18 hrs) an orange solid was visible under a pale orange solution. Filtration and solvent removal gave an orange yellow solid (156mg, 64%).

Found	C	5.33	N	11.97
Calculated	C	5.01	N	11.68

I.R. (ν_{max}/cm^{-1}) 1308m, 1186m, 1082w, 1034w, 1007w, 965w br, 931w, 892w, 799m, 580w, 548w, 463w.

4.8.3 Preparation of [Hg(CNSNS)$_2$]Br$_2$

[Hg(CNSNS)$_2$][AsF$_6$]$_2$ (200mg, 0.25mmol) and [NBu$_4$]Br (164mg, 0.51mmol) were placed in one limb of a two-limbed reaction vessel with a magnetic follower and MeCN (7ml) syringed in. After stirring (18 hrs) a dark orange solid was visible under a pale orange solution. Filtration and solvent removal gave an orange solid (169mg, 58%).

Found	C	4.46	N	10.02
Calculated	C	4.22	N	9.85

I.R. (ν_{max}/cm^{-1}) 1315m, 1182m, 1157w, 1078w, 1032w, 999w, 962w br, 930w, 887w, 798m, 579w, 546w, 462w.

4.8.4 Preparation of $[Hg(CNSNS)_2]I_2$

$[Hg(CNSNS)_2][AsF_6]_2$ (200mg, 0.25mmol) and $[NEt_4]I$ (128mg, 0.5mmol) were placed in one limb of a two-limbed reaction vessel with a magnetic follower and MeCN (6ml) syringed in. An immediate colour change was observed, producing a brown solid under a colourless solution. After stirring for 2 minutes a red solution was present over an orange-brown solution. After a further three minutes, a cherry-red solution was over a burgundy-brown solid. After stirring for a further 4 hours there was an orange solution over a small quantity of brown solid. The mixture was cooled slightly and a white solid precipitated out of solution. The solution was decanted off the solids and the solvent removed *in vacuo* to give a burgundy solid (157mg, 46%).

Found	C	3.85	N	8.82
Calculated	C	3.62	N	8.46

I.R. (ν_{max}/cm^{-1}) 1310m, 1185m, 1143w, 1078w, 1032w, 1015sh, 1004w, 962w br, 930w br, 890w, 796m, 582w, 550w, 466w.

4.8.5 Preparation of $[Cl.CNSNS][AsF_6]$

$[Hg(CNSNS)_2][AsF_6]_2$ (160mg, 0.2mmol) was placed in one limb of a two-limbed reaction vessel with a magnetic follower and SO_2 (8ml) was condensed onto the solid reactant. Cl_2 (excess) was condensed into the vessel, which was allowed to warm to room temperature. Initially, a bright magenta-coloured solution was present over a white solid. After stirring (30 hours) a pale yellow solid was visible under a colourless solution. This was filtered, washed twice with back-condensed SO_2 and the solvent removed *in vacuo*. The filtrate was washed twice with hexane (solvent removal *in vacuo* after each wash) to give a white crystalline solid (139mg, 85%).

m. pt 149 - 151°C.

Found	C	3.39	N	8.27
Calculated	C	3.66	N	8.53

I.R. (ν_{max}/cm^{-1}) 1303w, 1290sh, 1157m, 1036ms br, 953w sh, 935m, 883m, 837w, 798m, 721vs br, 651sh, 579ms, 441ms.

4.8.6 Preparation of [Br.CNSNS][AsF_6]

[Hg(CNSNS)$_2$][AsF_6]$_2$ (150mg, 0.19mmol) was placed in one limb of a two-limbed reaction vessel with a magnetic follower and SO_2 (8ml) was condensed onto the solid reactant. Br_2 (excess) was condensed into the vessel, which was allowed to warm to room temperature. After stirring (2 days) a pale yellow solid was visible under a colourless solution. This was filtered, washed twice with back-condensed SO_2 and the solvent removed *in vacuo*. The filtrate was washed twice with hexane (solvent removal *in vacuo* after each wash) to give a yellow solid (113mg, 81%). Decomposes at 234 - 238°C.

Found	C	3.08	N	7.22	Br	21.00
Calculated	C	3.22	N	7.51	Br	21.42

I.R. (ν_{max}/cm^{-1}) 1352m, 1291sh, 1170w br, 1050sh, 1036w, 997m, 923w, 912m, 882sh, 860m, 802w, 791m, 779w, 695vs br, 654sh, 585m, 566sh, 440m, 370s.

4.8.7 Preparation of [I.CNSNS][AsF_6]

[Hg(CNSNS)$_2$][AsF_6]$_2$ (197mg, 0.25mmol) and I_2 (126mg, 0.5mmol) were placed in the front limb of a two-limbed reaction vessel and SO_2 (8ml) was condensed onto the solid reactants. After stirring (4 days) a vermilion solid was visible under a pale pink solution. This was filtered, washed twice with back-condensed SO_2 and the solvent removed *in vacuo*. The filtrate was washed twice with hexane (solvent removal *in vacuo* after each wash) to give a bright yellow, mimosa, solid (165mg, 78%).

Found	C	3.22	N	6.40
Calculated	C	2.86	N	6.67

I.R. (ν_{max}/cm^{-1}) 1332m, 1152m vbr, 1075w, 1030w, 977m, 893w, 877w, 846w, 831w, 784w, 768w, 720vs, 695vs br, 660sh, 584m, 563w, 450m,434w.

4.8.8 Attempted reaction of [Hg(CNSNS)$_2$][AsF_6]$_2$ with IC≡N

[Hg(CNSNS)$_2$][AsF_6]$_2$ (200mg, 0.25mmol) and ICN (78mg, 0.51mmol) were put in one limb of a two-limbed reaction vessel with a magnetic follower and SO_2 (8ml) was condensed onto the reactants. After stirring (2 weeks) a pink solid was visible under a colourless solution. Filtration and solvent removal gave a yellow solid which analysed as [(CNSNS)$_2$][AsF_6]$_2$ [14] (30mg).

Found	C	3.89	N	9.31
Calculated	C	4.10	N	9.56

I.R. (ν_{max}/cm^{-1})1389m, 976s, 861m, 831m, 751s, 698vs, 660w, 589m, 576m, 552m, 446s, 390m.

4.8.9 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$with IC≡CI

$[Hg(CNSNS)_2][AsF_6]_2$ (200mg, 0.25mmol) and IC≡CI (70mg, 0.25mmol) were placed in one limb of a two-limbed reaction vessel with a magnetic follower and MeCN (8ml) syringed in to give a colourless solution. After stirring (10 days) a red crystalline solid (HgI_2 by mercury analysis) was visible under a muddy-brown solution. The solution was filtered off the solid and the solvent removed in vacuo to give an-oily brown material. This was washed unsuccessfully with hexane and methylene chloride to yield only an oil. No CHN analysis was possible on this intractable oil. The red solid was identified as HgI_2. A similar result is seen when the solvent used was sulfur dioxide.

Found	Hg	44.57
Calculated	Hg	44.14

4.8.10 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with $I_2C=CI_2$

$[Hg(CNSNS)_2][AsF_6]_2$ (200mg, 0.25mmol) and $I_2C=CI_2$ (86mg, 0.16mmol) were placed in one limb of a two-limbed reaction vessel with a magnetic follower and MeCN (7ml) syringed in, yielding a pale yellow solution. To prevent decomposition of the alkene, aluminium foil was wrapped around the reaction bulb. After stirring (2 days) a red solid, identified as HgI_2 by its colour, was observed under a brown solution (in a similar manner to that already observed for the analogous alkyne reaction). Filtration and solvent removal gave an intractable oily-brown material which was also unsuitable for analysis.

4.8.11 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with SO_2Cl_2

$[Hg(CNSNS)_2][AsF_6]_2$ (200mg, 0.25mmol) was placed together with a magnetic follower in one limb of a two-limbed reaction vessel and SO_2Cl_2 (8ml) syringed in.. After stirring (6 days) no observable reaction had occurred and the mixture was heated to a gentle reflux. This led to the formation of an oily-brown material which was cleaned in methlyene chloride to yield a brown solid. The calculation is for the expected product, $[Cl.CNSNS][AsF_6]$.

Found	C	3.46	N	7.51
Calculated	C	3.66	N	8.53

I.R. (ν_{max}/cm^{-1}) 1324m, 1190m, 1080w, 1044w, 1007w br, 980w br, 930w, 898w, 766s, 703vs br, 580w, 548w, 463w, 390s. (No S=O bonds present in the i.r.)

4.8.12 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with N-chlorosuccinimide

$[Hg(CNSNS)_2][AsF_6]_2$ (200mg, 0.25mmol) and N-chlorosuccinimide (68mg, 0.5mmol) were placed, together with a magnetic follower, in one limb of a two-limbed reaction vessel and MeCN (8ml) syringed in. After stirring (4 days) no observable reaction had occurred and the solvent was removed *in vacuo*. This gave a sticky brown oil which was insoluble in hexane, methylene chloride and sulfur dioxide. No analysis was obtainable on this material.

4.8.13 Attempted reaction of $[Hg(CNSNS)_2][AsF_6]_2$ with N-iodosuccinimide

$[Hg(CNSNS)_2][AsF_6]_2$ (200mg, 0.25mmol) and N-iodosuccinimide (113mg, 0.5mmol) were placed, together with a magnetic follower, in one limb of a two-limbed reaction vessel and MeCN (7ml) syringed in. After stirring (4 days) no observable reaction had occurred and the solvent was removed *in vacuo*. This gave a sticky brown oil which was insoluble in hexane, methylene chloride and sulfur dioxide. No analysis was obtainable on this material.

4.8.14 Attempted reaction of $Zn(CN)_2$ with $[SNS][AsF_6]$

$Zn(CN)_2$ (117mg, 1mmol) and $[SNS][AsF_6]$ (267mg, 1mmol) were placed together with a magnetic follower in one limb of a two-limbed reaction vessel and SO_2 (8ml) was condensed on. Initially, there was a white solid under a brown solution. No colour change was observed even after stirring for 2 months! Filtration and solvent removal gave a white solid and a pale brown solid, both of which were identified as starting materials by their i.r. spectra.

4.8.15 Reaction of Ph_3SnCN with $[SNS][AsF_6]$

Ph_3SnCN (376mg, 1mmol) and $[SNS][AsF_6]$ (267mg, 1mmol) were placed together with a magnetic follower in one limb of a two-limbed reaction vessel. SO_2 (7ml) was condensed onto the reactants and the system allowed to warm to room temperature. The solids dissolved to give a deep red/brown coloured solution. After stirring (24 hours) there was a deep blue/purple solution over a green solid. Filtration and washing with back-condensed SO_2 gave a yellow solid and a deep-blue solution. Solvent removal *in vacuo* yielded a blue solid which was identified as $[PhSNSNSNSPh][AsF_6]$ by its i.r. spectra.

I.R. (ν_{max}/cm^{-1}) 1735w, 1670w, 1652w, 1600w, 1308w, 1283w, 1185m, 1069m, 978s, 822m, 710vs br, 560sh, 507m, 402m.

The yellow solid was very insoluble in SO_2 and was identified as $[Ph_2SnNCS][AsF_6]$.

Found	C	29.71	H	1.73	N	2.36	Sn	20.97	As	14.02
Calculated	C	30.03	H	1.94	N	2.69	Sn	22.83	As	14.41

I.R. (ν_{max}/cm^{-1}) 2025m br, 1654w br, 1578w, 1302w, 1212w, 1143w, 1120w, 1077w, 1022w, 998w, 929w, 731m, 700m, 590w, 537w, 468sh.

4.8.16 Attempted reaction of $^tBu_3SnCN$ with $[SNS][AsF_6]$

$^tBu_3SnCN$ (316mg, 1mmol) and $[SNS][AsF_6]$ (267mg, 1mmol) were placed together with a magnetic follower in one limb of a two-limbed reaction vessel. and SO_2 (7ml) condensed in. There was an immediate colour change to yield a red solution, which remained red after stirring for 24 hours. Slow solvent removal gave a sticky red oil which was unsuitable for CHN analysis.

I.R. (ν_{max}/cm^{-1}) 3781w, 3317sh, 2953vs br, 2673w, 2588w, 2360m, 2108vs br, 1750w, 1629sh, 1462s, 1378s, 1341s, 1251s, 1158s, 1078s br, 961s, 919s, 878s, 849s, 773s, 704vs br, 542s br.

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Chapter 5

Pt and Pd complexes derived from the dithiadiazolyl ring.

5.1 Introduction

Transition metal compounds incorporating sulfur/nitrogen ligands have been known since the turn of the century [1,2]. There has been both synthetic and theoretical interest in such systems. From the synthetic viewpoint, such systems may provide novel reagents for ring synthesis, and help to stabilise unknown sulfur/nitrogen species. The theoretician wishes to improve our understanding of the bonding involved in such complexes. There is also interest in practical applications, such as non-linear optical properties. The main types of sulfur/nitrogen ligands presently known will now be reviewed briefly under the following broad categories:

1) NS bonded ligands.
2) The N_2S^{2-} ligand and related systems.
3) NSO^- bound species.
4) The S_2N_2 ligand and MS_2N_2 compounds.
5) MS_2N_3 and MS_3N_2 rings.

5.1.1 NS bonded ligands

Thionitrosyl complexes were first prepared by refluxing certain metal nitrido compounds with sulfur [3]. This route is not generally applicable, and thus other routes utilising the versatile reagent, $(NSCl)_3$, have been developed [4-6]. This can involve *in situ* generation of the [NS] cation from $(NSCl)_3$, see Eqns 5.1 to 5.3. In all cases, the ligand is bound to the metal via the nitrogen atom.

$$\mathrm{Na[Cr(CO)_3Cp]} + {}^1/_3\mathrm{(NSCl)_3} \xrightarrow[\text{- CO}]{\text{- NaCl}} \mathrm{Cr(CO)_2Cp(NS)}$$

Eqn 5.1

$$\mathrm{RuCl_2(PPh_3)_2} + {}^1/_3\mathrm{(NSCl)_3} \longrightarrow \mathrm{RuCl_3(NS)(PPh_3)_2}$$

Eqn 5.2

$$\mathrm{Re(CO)_5Br} + \mathrm{[NS][SbF_6]} \xrightarrow[\text{- Br}]{} \mathrm{[Re(CO)_5NS][SbF_6]}$$

Eqn 5.3

5.1.2 The N_2S^{2-} ligand and related systems

Silyl-NSN-Silyl is a useful reagent in the synthesis of sulfur/nitrogen containing systems, and has therefore been used in complex formation with metals. Reaction with metal halides can involve simple co-ordination to the metal centre [7], or condensation reactions with the elimination of Silyl-Cl. The mono-substituted compound, p-$NO_2C_6H_4$-NSN-Silyl, has also been used and representative examples of this chemistry are shown in Eqns 5.4 and 5.5.

$$SnCl_4 + \text{Silyl-NSN-Silyl} \longrightarrow (\text{Silyl-NSN-Silyl-}N,N)SnCl_4$$

Eqn 5.4

$$PtCl_2(dppe) + 2(\text{R-NSN-Silyl}) \longrightarrow Pt(\text{NSN-R})_2(dppe)$$

Eqn 5.5

5.1.3 NSO^- bound species

The use of Silyl-NSO has received attention by analogy with the Silyl-NSN-Silyl reagent mentioned in the previous section [8]. However, cleaner reactions have been obtained using the mercury transfer agent, Hg(NSO)2 [9], or the highly reactive salt, K[NSO] [10], see Eqns 5.6 and 5.7.

$$Hg(NSO)_2 + Pt(C_2H_4)(PPh_3)_2 \longrightarrow \text{trans } Pt(NSO)_2(PPh_3)_2 + Hg + C_2H_4$$

Eqn 5.6

$$2K[NSO] + TiCp_2Cl_2 \longrightarrow TiCp_2(NSO)_2 + 2KCl$$

Eqn 5.7

For all known complexes, the length of the N-S bond is shorter than in the organic derivatives, R-NSO, and the NSO angle is also correspondingly larger. This has been attributed to little or no π overlap between the nitrogen atom and the transition metal [11], in contrast to the organic derivatives where some delocalisation from the nitrogen to the carbon does occur.

5.1.4 The S_2N_2 ligand and MS_2N_2 compounds

Transition metal complexes containing the neutral S_2N_2 ring have been made from both S_2N_2 and S_4N_4. Reactions involving S_2N_2 tend to be simple adduct formation [12], see Eqn 5.8.

$$S_2N_2 \quad + \quad 2SbCl_5 \longrightarrow S_2N_2.2SbCl_5$$

Eqn 5.8

When S_4N_4 is the starting reagent the reactions are often more complicated. For example, reaction of $[PPh_4][Pd_2Cl_6]$ with S_4N_4 led to the isolation of three products, $[PPh_4]_2[Pd_2(S_2N_2)Cl_6]$, $[PPh_4]_2[Pd_2(S_3N_2)Cl_4]$ and $[PPh_4][Pd_2(S_2N_2H)Cl_2]$ [13]. The first of these is almost entirely planar, with the S_2N_2 ligand bridging the two palladium centres via Pd-N bonds. This is the preferred bridging mode of the S_2N_2 ligand.

Systems containing the MS_2N_2 ring have been obtained from various reactions involving the S_4N_4 cage and transition metal complexes. General routes have been developed using $Na[S_3N_3]$ or $S_4N_4H_4$ [14-15], see Eqns 5.9 and 5.10. $Na[S_3N_3]$ is no longer in favour since it is explosive.

$$PtCl_2(PPh_3)_2 \; + \; 2Na[S_3N_3] \longrightarrow Pt(S_2N_2)(PPh_3)_2 \; + \; 2NaCl \; + \; S_4N_4$$

Eqn 5.9

$$2PtCl_2(PPh_3)_2 \; + \; S_4N_4H_4\text{-dbu} \longrightarrow 2Pt(S_2N_2)(PPh_3)_2 \; + \; dbuHCl \; + \; 3HCl$$

Eqn 5.10

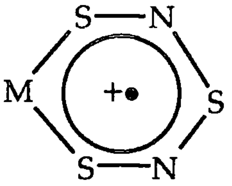
The organotin system, $Me_2SnS_2N_2$, has also been used for the transfer of the S_2N_2 ligand to other transition metals [8].

5.1.5 MS_2N_3 and MS_3N_2 rings

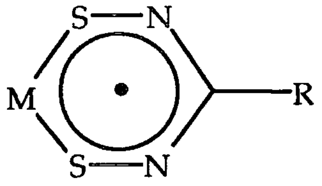
Both the MS_2N_3 and MS_3N_2 rings can be obtained from the reactions of S_4N_4 with transition metal complexes, although the MS_2N_3 ring is usually formed in reactions with the early transition metals in high oxidation states [8].

The use of S_4N_4 in this, and the previously discussed reactions, is haphazard, with many reactions yielding two or more products. Presumably, this is because the S_4N_4 cage can fragment in several different ways.

In section 1.2, the relationship between the $[S_3N_2]$ radical cation and the dithiadiazolyl radical was highlighted. There is a similar relationship between the MS_3N_2, (I), cation, and the MS_2N_2C, (II), radical. The latter is derived from the dithiadiazolyl ring, after metal insertion into the S-S bond has occurred.



(I)



(II)

Difficulties have been associated with the transition metal chemistry of the dithiadiazolyl ring. To date, only two transition metal complexes containing the dithiadiazolyl ligand have been reported, $[Fe_2(CO)_6(\mu\text{-SNCPhNS-}S,S)]$ [16] and $[Ni_2(Cp)_6(\mu\text{-SNCPhNS-}S,S)]$ [17]. They exist as dimetallic systems which are bridged by the SNCPhNS ligand, see Figure 5.1.

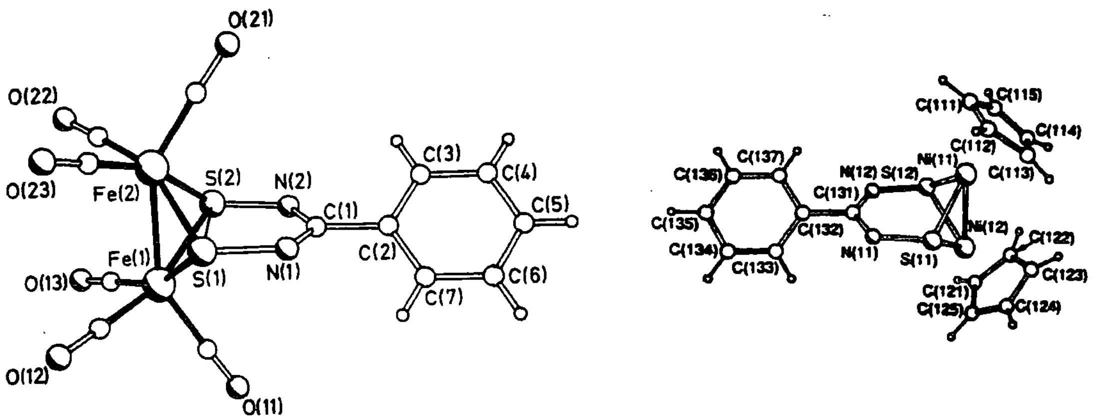


Figure 5.1 $[Fe_2(CO)_6(SNCPhNS\text{-}S,S)]$ and $[Ni_2(Cp)_6(SNCPhNS\text{-}S,S)]$, showing the bridging mode of the SNCPhNS ligand.

They were obtained from the reaction of a metal carbonyl with 4-phenyl-1,2,3,5-dithiadiazolyl, and most reactions gave mixtures of products. The reactions between platinum or palladium phosphines and the dithiadiazolyl ring have been systematically studied, and this chapter describes the crystal structures of four of these platinum or palladium complexes.

5.2 The structures of three monometallic dithiadiazolyl complexes

This section is concerned with the structures of three metal-dithiadiazolyl complexes of the general formula M(SNCPhNS-*S*,*S*)L_x, where M = Pt/Pd and the ligand L_x is either dppe or $(PPh_3)_2$.

The compounds were synthesised by Mr. I. May (Durham University) according to the routes outlined below, Eqns 5.11 and 5.12.

$$Pt(PPh_3)_4 + {}^1/_2\,[Ph.CNSSN]_2 \xrightarrow{-2(PPh_3)} [Pt(SNCPhNS)(PPh_3)_2]$$

Eqn 5.11

$$M(dppe)_2 + {}^1/_2\,[Ph.CNSSN]_2 \xrightarrow{-\,(dppe)} [M(SNCPhNS)(dppe)]$$

(M = Pt/Pd)

Eqn 5.12

$[Pt(SNCPhNS\text{-}S,S)(PPh_3)_2]$ was crystallised as an acetonitrile solvate by the slow diffusion of a saturated solution of $[Ph.CNSSN]_2$ into a saturated solution of $Pt(PPh_3)_4$. [M(SNCPhNS-*S*,*S*)(dppe)] (M = Pt/Pd) were crystallised in a similar manner to $[Pt(SNCPhNS\text{-}S,S)(PPh_3)_2]$; *viz* slow diffusion into a saturated solution of $M(dppe)_2$.

Full experimental details for all three X-ray structural determinations are outlined in Table 5.1. Dr A.J. Blake (Edinburgh University) collected the intensity data for $[Pt(SNCPhNS\text{-}S,S)(PPh_3)_2]$ using a Stoë Stadi-4 four-circle diffractometer fitted with an Oxford Cryosystems low temperature device. The experimental data for the other two complexes were collected in the manner already outlined in section 2.7. Refinements of all the structures in this chapter were carried out using SHELXL-93 [19].

There were experimental difficulties because of icing during the data collection for [Pt(SNCPhNS-*S*,*S*)(dppe)]. Thus, the structure was corrected for absorption using DIFABS [20] since the data obtained from the psi-scan method [21] was considered unreliable. Therefore it must be stressed that the geometric and other data for this compound are not as good as for the related structural determinations. However, the platinum and palladium complexes containing the dppe ligand are essentially isostructural. The labelling schemes for the three compounds are shown in Figures 5.2 to 5.4 and the geometric data presented in Table 5.2. Full bond lengths and angles are presented in Appendix D.

Table 5.1 Crystallographic data for the monomeric complexes in section 5.2.

Compound	[Pt(SNCPhNS-S,S)(PPh$_3$)$_2$].MeCN	[Pt(SNCPhNS-S,S)(dppe)]	[Pd(SNCPhNS-S,S)(dppe)]
Empirical Formula	$C_{45} H_{38} N_3 P_2 S_2$ Pt	$C_{33} H_{29} N_2 P_2 S_2$ Pt	$C_{33} H_{29} N_2 P_2 S_2$ Pd
Colour, habitat	dark green-blue lath	green hexagonal column	green block
Crystal size, mm	0.5 x 0.25 x 0.1	0.35 x 0.18 x 0.15	0.35 x 0.18 x 0.08
Crystal System	Triclinic	Orthorhombic	Orthorhombic
Space Group	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions, Å and °	a = 13.240(6) α = 63.57(1) b = 13.366(6) β = 76.38(2) c = 14.090(8) γ = 60.71(2)	a = 11.618(11) α = 90 b = 12.265(13) β = 90 c = 20.994(6) γ = 90	a = 11.653(4) α = 90 b = 12.258(8) β = 90 c = 20.826(11) γ = 90
Volume, Å^3	1946.9(7)	2992(4)	1974.8(9)
Z	2	4	4
Mean Wavelength, $\bar{\lambda}$, Å (MoKα)	0.71073	0.71073	0.71073
Formula Weight	941.93	774.73	686.04
Density (calc), g/mm^{-1}	1.607	1.720	1.532
Absorption Coefft, mm^{-1}	3.830	4.963	0.898
F(000)	938	1524	1396
Temperature, K	150	150	150
No. of reflections, Range	46, $30 \leq 2\theta \leq 32$	20, $10 \leq 2\theta \leq 25$	24, $20 \leq 2\theta \leq 22$
Scan Type	ω - 2θ	ω - 2θ	ω - 2θ

2θ Range, °	5.0 - 45.0	5.0 - 50.0	5.0 - 50.0
Range of h,k,l	-13 14, -12 14, 0 15	-11 13, -7 14, -20 24	-1 13, -1 14, -1 24
Standard reflections	$\bar{9}\ \bar{2}\ 2$, 0 8 0, 1 10 $\bar{2}$	$\bar{1}$ 2 $\bar{2}$, $\bar{1}$ 4 $\bar{1}$, $\bar{1}$ 4 0	$\bar{4}$ 0 0, 0 4 0, 4 0 0
Data measured	5273	5155	3764
Independent data, R_{int}	5086, 0.0328	3344, 0.062	3566, 0.0471
Data used	5080	3339	3565
Absorption correction	psi - scans, DIFABS	DIFABS	psi - scans, DIFABS
Transmission range	0.838 - 1.088	0.675 - 1.829	0.907 - 1.069
Parameters	478	186	361
Data/parameters	10.6	18.0	9.9
Final R Indices (obs data)	0.0353 0.0946	0.0633, 0.1683	0.0444, 0.1142
R Indices (all data)	0.0456 0.1029	0.1168, 0.2071	0.0865, 0.1055
Goodness of fit	1.075	1.034	1.502
Weighting scheme †	0.0611, 9.4422	0.1293, 22.8794	0.0151, 2.8374
Flack Parameter [18]	N/A	0.01(3)	-0.09(7)
Max shift / esd	0.001	0.000	0.001
Max & min in Fourier synthesis, $e\text{Å}^{-3}$	1.409, -1.740	2.588, -3.214	0.644, -0.682

† Weighting scheme based upon $1/[\sigma^2(F_o) + gP^2 + hP]$ where $P = (F_o^2 + 2F_c^2)/3$. The values g and h are quoted.

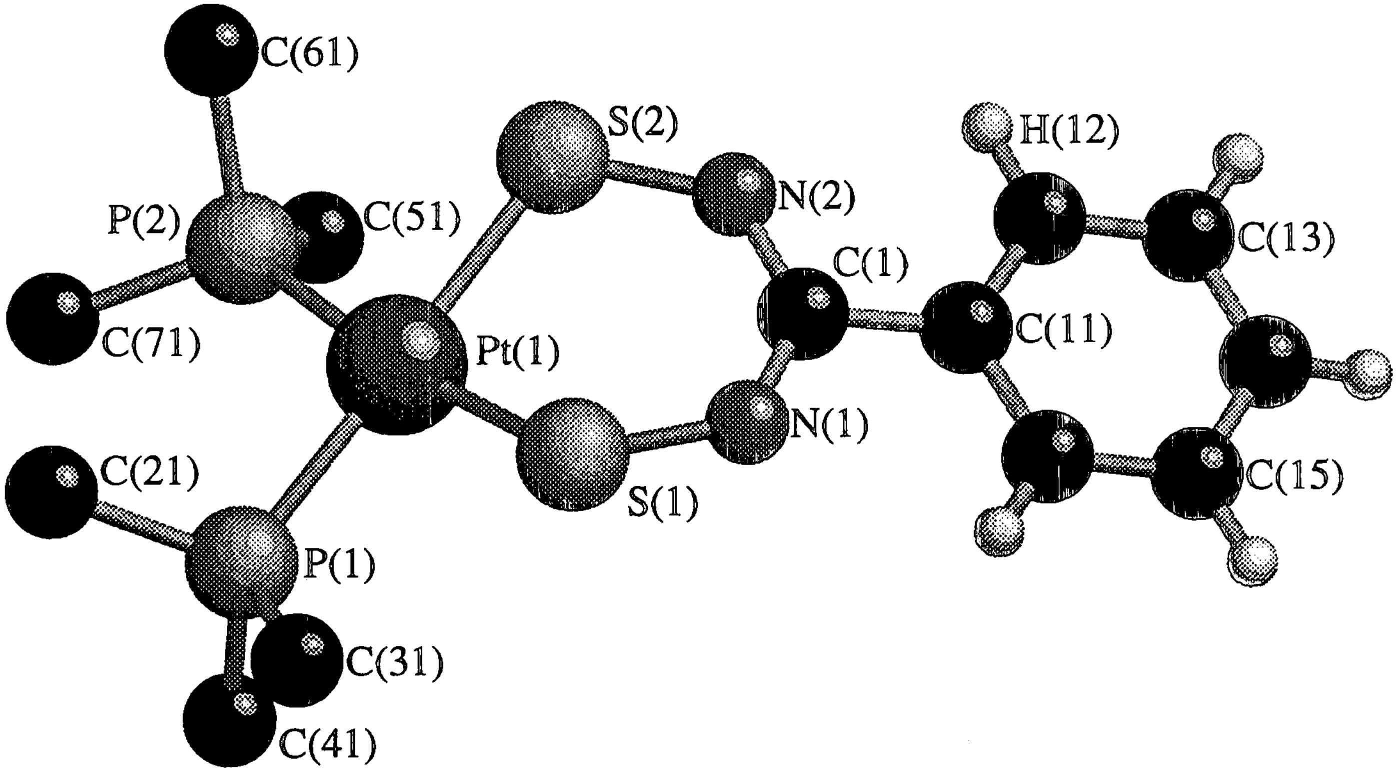


Figure 5.2 Structure of [Pt(SNCPhNS-*S*,*S*)$(PPh_3)_2$]·MeCN.
Only the main backbone of the structure is shown for clarity.

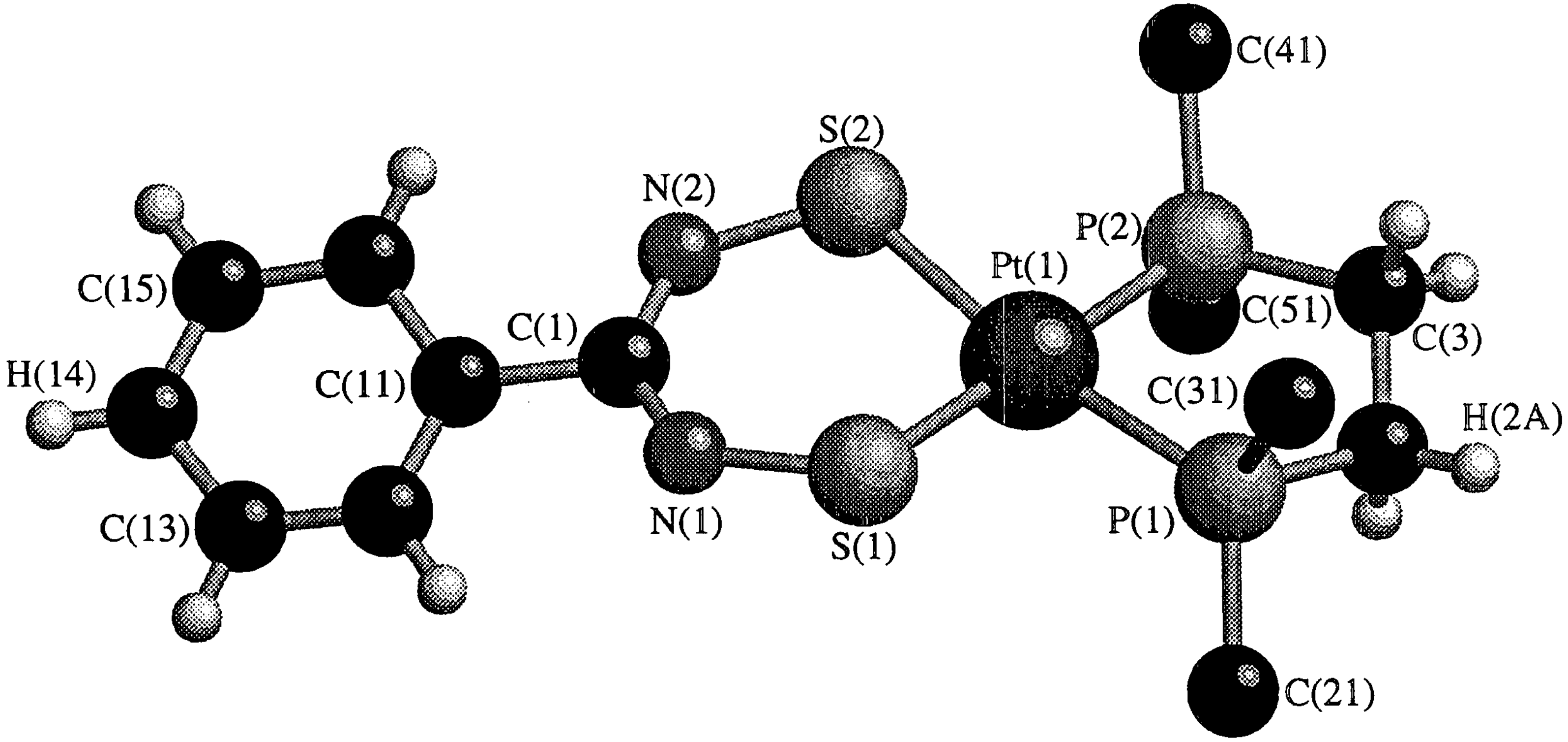
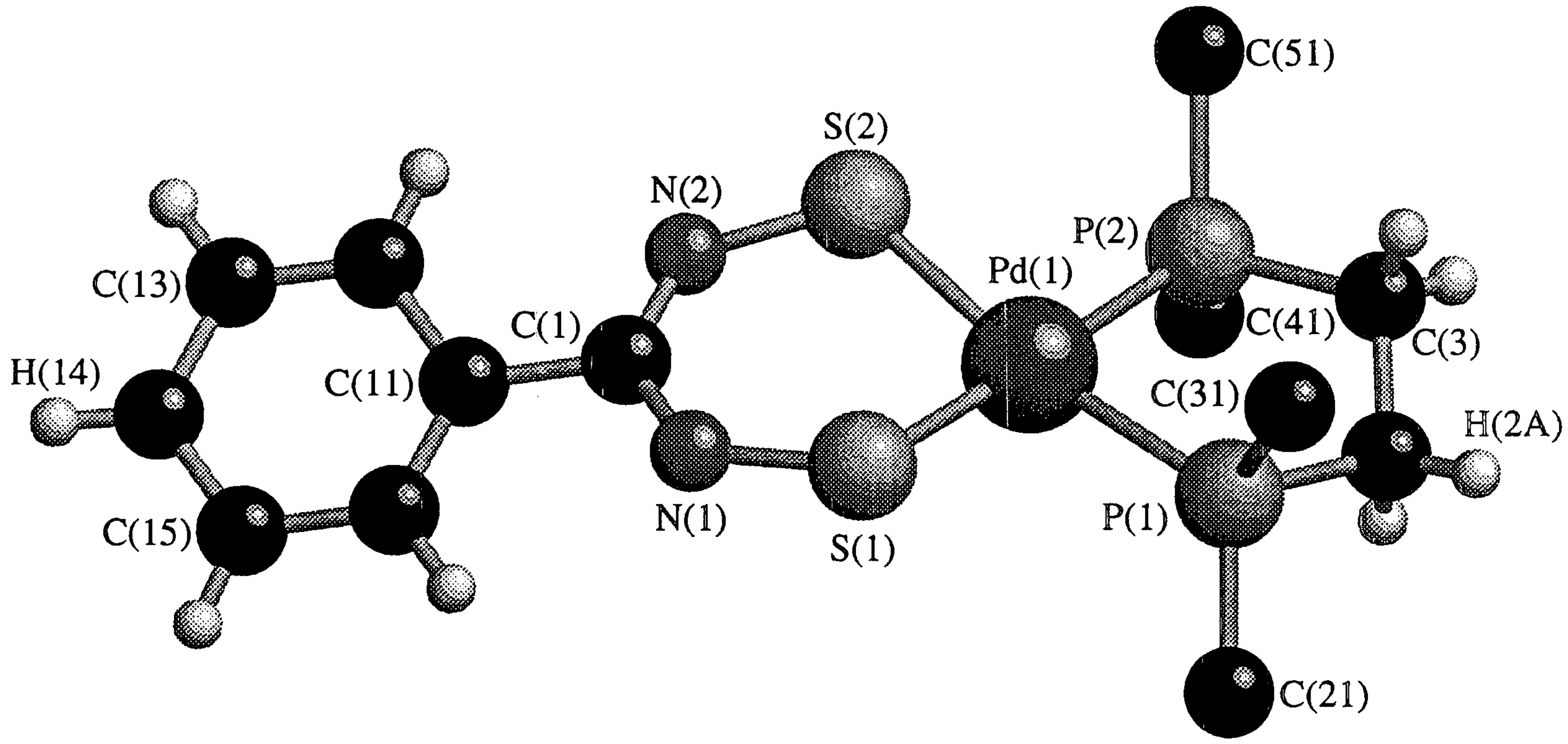


Figure 5.3 Structure of [Pt(SNCPhNS-*S*,*S*)(dppe)].
Only the main backbone of the dppe ligand is shown for clarity.



<u>Figure 5.4</u> Structure of [Pd(SNCPhNS-*S*,*S*)(dppe)].
Only the phosphorus-bound carbon atoms of the dppe ligand are shown for clarity.

Table 5.2 Selected geometric data for the three monometallic compounds described in section 5.2.

Compound	[(SNCPhNS-*S*,*S*) Pt(PPh$_3$)$_2$]·MeCN	[(SNCPhNS-*S*,*S*) Pt(dppe)]	[(SNCPhNS-*S*,*S*) Pd(dppe)]
M - S, Å	2.294(2) 2.309(2)	2.285(6) 2.293(6)	2.285(3) 2.294(3)
M - P, Å	2.322(2) 2.311(2)	2.300(7) 2.308(6)	2.312(3) 2.339(3)
S - N, Å	1.628(7) 1.648(7)	1.64(2) 1.66(2)	1.629(9) 1.630(9)
C - N, Å	1.36(1) 1.33(1)	1.31(3) 1.34(3)	1.33(1) 1.36(1)
S(1)...S(2), Å	3.161(3)	3.281(9)	3.227(4)
S(1) - M - S(2), °	86.78(8)	91.2(2)	89.6(1)
P(1) - M - P(2), °	100.01(7)	85.9(2)	85.1(1)
S(1) - M - P(1), °	87.82(7)	93.9(2)	95.0(1)
S(2) - M - P(2), °	85.43(7)	88.7(2)	89.8(1)
M - S - N, °	115.2(2) 115.1(2)	116.5(8) 116.7(8)	117.6(3) 117.4(3)
S - N - C, °	128.4(5) 128.0(6)	130(2) 128(1)	129.0(8) 129.7(7)
angle δ, °	20.6(2)	10.6(4)	11.0(2)

angle δ is the angle between the two planes defined by the atoms M(1),S(1),S(2),N(1),N(2),C(1) and M(1),S(1),S(2),P(1),P(2).

The metal-sulfur bond lengths for all three compounds are essentially identical, which is not surprising since platinum and palladium have similar metallic radii; an effect of the lanthanide contraction [22]. The M-S bond lengths are of a similar magnitude to a large number of M-S bond lengths for compounds stored on the C.S.D. [23], as shown in the following histogram , Figure 5.5.

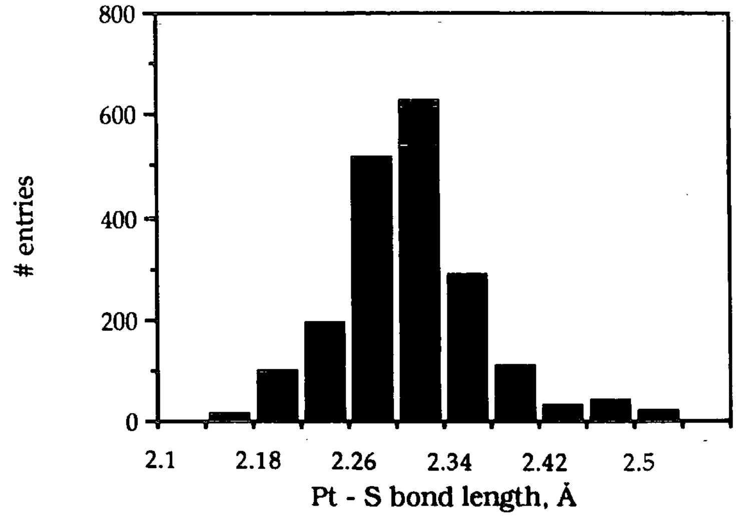


Figure 5.5 Pt-S bond lengths for compounds stored on the C.S.D.

The N-S [24] and C-N [25] bond lengths are similar, and intermediate between the lengths associated with single and double bonds. Therefore, there is some degree of delocalisation over the SNCNS framework. Various valence-bond canonical forms are depicted in Figure 5.6, showing delocalisation of the free electron around the 6-membered metallo-heterocycle. This is in agreement with preliminary e.s.r. studies [26], which indicate that the free electron is located over the entire skeletal framework. Coupling with the phosphorus atoms has also been observed, and thus the metal can be viewed as a 16/17 electron complex. This delocalisation of the free electron is in agreement with theoretical calculations on the previous dimetallic dithiadiazolyl complexes [16-17].

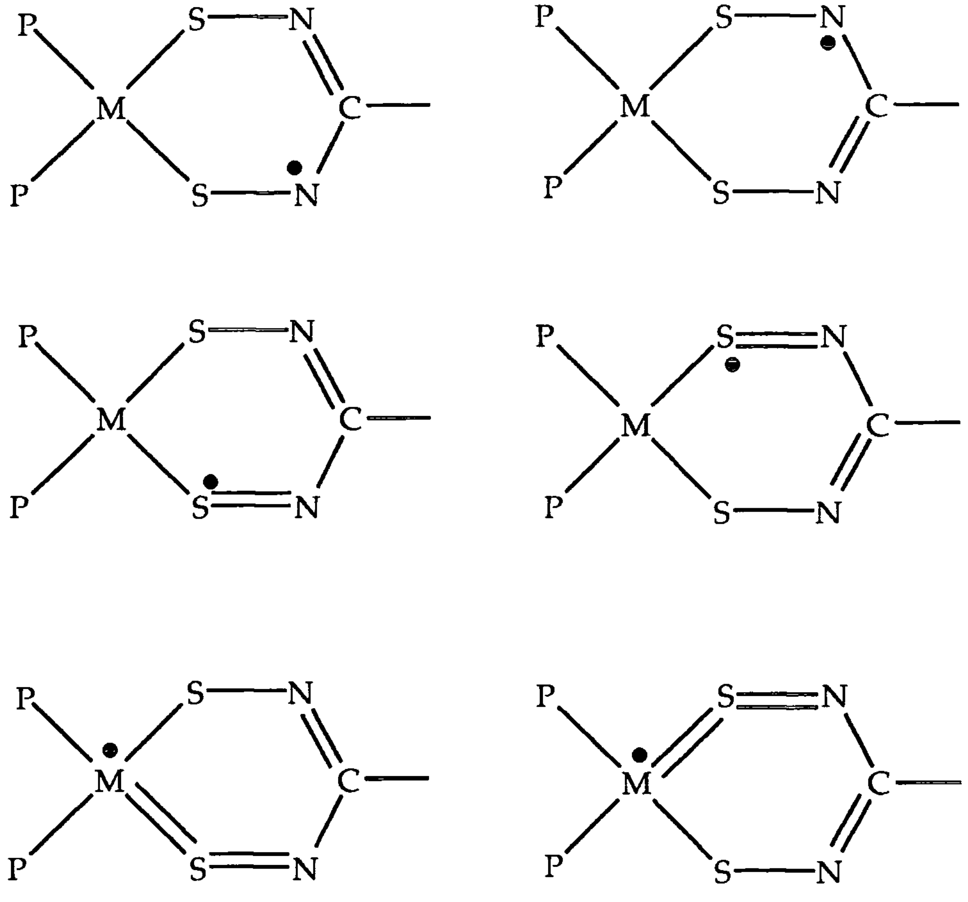


Figure 5.6 Selected canonical forms for the monometallic systems described in section 6.2.

The chair conformation is the most stable conformation found for six-membered rings containing singly-bonded atoms, whereas a planar ring is preferred for a fully delocalised π-system. For these metallic radical systems, there is some delocalisation around the SNCNS framework. Therefore, the chair form will not be adopted. However, it is possible to compare the conformation of the MSNCNS ring with the chair conformation. The metallo-cycle is similar to a chair conformer, but with the carbon in the plane of the N_2S_2 atoms, because of the delocalisation within the ring. This is shown in Figure 5.7.

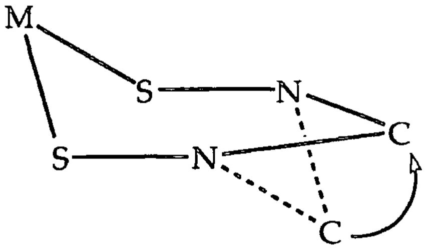


Figure 5.7 The relationship between the chair conformation and the metallo-heterocycles described in section 5.2. The carbon atom is "pulled-up", into the plane of the N_2S_2 atoms.

The PMP angle is larger for the complex containing the two (PPh_3) groups cf. the dppe-containing complexes, because of the increased steric bulk of the (PPh_3) groups. The dppe ligand is constrained by the ethylene bridge between the two phosphorus atoms, forming a 5-membered ring.

The larger size of the (PPh_3) groups means that there is extra strain placed on the sulfur atoms which the system will want to remove. One way this might be achieved is by an increase in the length of the M-S bond, so that the phosphine groups are further away from the sulfur atoms. The M-S bond lengths indicate that this is not the case. Another way to relieve the strain is to push the sulfur atoms together, reducing the length of the transannular S...S contact. This will decrease the SMS angle, and increase the MSN angle. However, the MSN angle will become strained if it exceeds 120°, and therefore the metal atom is pushed out of the plane of the CN_2S_2 atoms. The SNC angle is unaffected by the change in phosphine at the metal centre.

These effects are strikingly seen in the large angle, δ, between the CN_2S_2 and PtS_2P_2 planes, and the short transannular S...S contact for $[Pt(SNCPhNS\text{-}S,S)(PPh_3)_2]\cdot MeCN$. In the metal complexes containing the dppe ligand, there is less steric pressure on the sulfur atoms of the SNCPhNS ligand. Thus, the metal atom is closer to the plane defined by the SNCPhNS ligand, i.e. the angle δ is smaller, and the ring does not contract along the transannular S...S vector. The transannular distance between these sulfur atoms is similar to those found for the numerous platinum/sulfur complexes presently located in the C.S.D. [23].

5.3 The structure of a trimetallic dithiadiazolyl complex

Some of the monometallic complexes just described are not indefinitely stable in solution. They re-arrange to give stable trimetallic systems, although the mechanism for this process is unknown at the present time (see Eqn 5.13). These trimetallic systems have been shown to be diamagnetic. Crystals suitable for X-ray diffraction were obtained as the toluene solvate by the slow diffusion of a saturated solution of $[Ph.CNSSN]_2$ into a saturated solution of $Pt(PPh_3)_4$. Dr A.J. Blake (Edinburgh University) collected the experimental data for $[Pt_3(SNCPhNS\text{-}S,S)_2(PPh_3)_4]$, as described in section 5.2.

$$\begin{aligned} 3[Pt(SNCPhNS)(PPh_3)_2] &\longrightarrow [Pt_3(SNCPhNS)_2(PPh_3)_4] \\ &\quad + {}^{1}/_{2}\,[Ph.CNSSN]_2 + 2(PPh_3) \end{aligned}$$

Eqn 5.13

The details of the solution and refinement for this trimetallic species are given in Table 5.3. The labelling scheme is shown in Figure 5.8 and the geometric data are presented in Table 5.4. The central platinum atom is located on an inversion centre. Full bond lengths and angles are presented in Appendix D. The solvent was disordered and could not be modelled satisfactorily. A partial occupancy model of 0.5 was tried since there is an inversion centre present, but this had a negligible effect on geometric and other parameters. Therefore the model with full occupancy of the toluene solvent is presented here. The solvent does not interact with the complex.

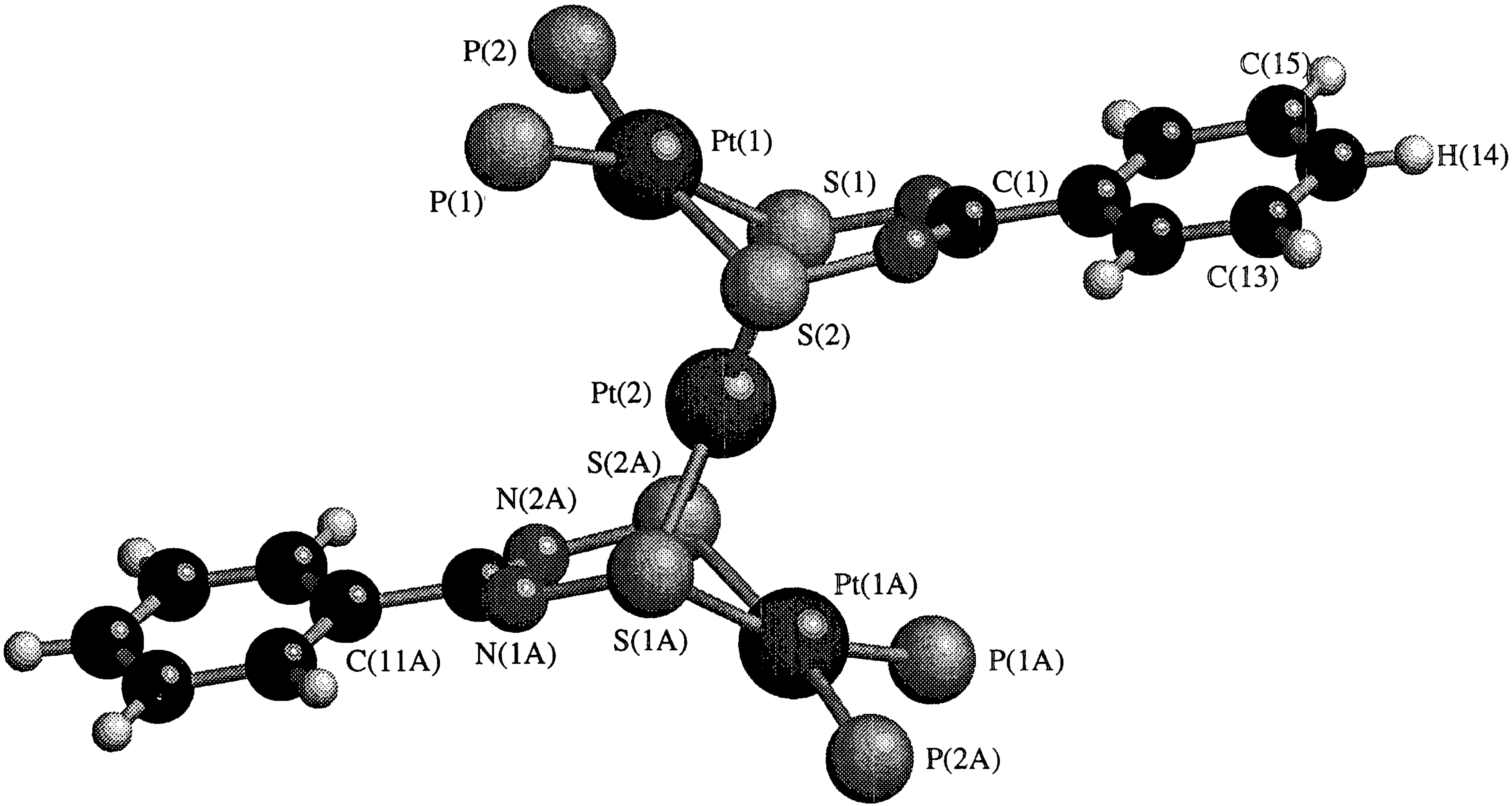
Table 5.4 Selected bond lengths, Å, angles, °, and contacts, Å, for $[Pt_3(\mu\text{-}SNCPhNS\text{-}S,S)_2(PPh_3)_4]\cdot 2PhMe$.

Pt(1) - P(1)	2.300(5)	P(1) - Pt(1) - P(2)	103.3(2)
Pt(1) - P(2)	2.301(4)	P(1) - Pt(1) - S(1)	90.5(2)
Pt(1)...Pt(2)	2.865(1)	P(2) - Pt(1) - S(2)	87.8(2)
Pt(1) - S(1)	2.367(4)	S(1) - Pt(1) - S(2)	78.8(2)
Pt(1) - S(2)	2.387(4)	S(1) - Pt(2) - S(2)	80.4(2)
Pt(2) - S(1)	2.332(5)	Pt(1) - S(1) - N(1)	113.2(5)
Pt(2) - S(2)	2.344(4)	Pt(1) - S(2) - N(2)	111.1(5)
S(1) - N(1)	1.66(1)	Pt(2) - S(1) - N(1)	109.3(5)
S(2) - N(2)	1.64(1)	Pt(2) - S(2) - N(2)	107.4(6)
S(1)...S(2)	3.019(6)	S(1) - N(1) - C(1)	122.5(13)
Pt(1)...Pt(2)	2.865(1)	S(2) - N(2) - C(1)	126.1(13)

Table 5.3 Crystallographic data for $[Pt_3(\mu\text{-}SNCPhNS\text{-}S,S)_2(PPh_3)_4]\cdot 2PhMe$.

Empirical Formula	$C_{100}H_{86}N_4P_4S_4Pt_3$	Crystal size, mm	0.78 x 0.15 x 0.08
Colour	habitat, orange column	Space Group	$P2_1/c$
Crystal System	Monoclinic	Volume, $Å^3$	4313(3)
Unit cell dimensions, Å and °	a = 12.704(16) α = 90 b = 24.988(11) β = 101.94(3) c = 12.888(6) γ = 90	Mean Wavelength, $\bar{\lambda}$, Å	0.71073
Z	2 (Pt on inversion site)	Density (calc), g/mm^{-1}	1.679
Formula Weight	2181.12	F(000)	2144
Absorption Coefft, mm^{-1} ($\bar{\lambda}$)	5.075	Reflections for Unit Cell	26, 28 - 30
Temperature, K	150	θ Range, °	5.0 - 45.0
Scan Type	$\omega - 2\theta$	Standard reflections	-8 0 2, 0 14 0, -1 1 9
Range of h,k,l	±13, 0 26, 0 14	Independent data	5528
Data measured	5943	Absorption correction	psi - scans, DIFABS
Data used, R_{int}	5504, 0.0437	Parameters	485
Transmission range	1.179, 0.754	Final R Indices (obs data)	0.0477 0.1271
Data/parameters	11.3	Goodness of fit	1.080
R Indices (all data)	0.1064, 0.1405	Max shift / esd	0.056
Weighting scheme ≠	0.0151, 108.1618	Max & min in Fourier synthesis, $eÅ^{-3}$	1.413, -1.007

≠ Weighting scheme based upon $1/[\sigma^2(F_o) + gP^2 + hP]$ where $P = (F_o^2 + 2F_c^2)/3$. The values g and h are quoted.



<u>Figure 5.8</u> Structure of $[Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh_3)_4]\cdot 2MePh$. The phosphine phenyl groups are omitted for clarity.

The structure of $[Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh_3)_4]\cdot 2PhMe$ shows a linear arrangement of three platinum atoms, bridged by two SNCPhNS ligands. The central PtS_4 core is planar, with the central platinum atom located on an inversion centre. The core is distorted from a square planar environment, with a small SMS angle of 80.4(2)°. The terminal PtP_2S_2 core has distorted square planar geometry, with a large MPM angle of 103.3(2)° and a smaller SMS angle of 78.8(2)°. The steric bulk of the phosphine groups is responsible for this.

The SNCPhNS ligand is in a bridging mode, similar to that seen in the previous dithiadiazolyl complexes, $[Fe_2(CO)_6(\text{SNCPhNS-}S,S)]$ [16] and $[Ni_2(Cp)_6(\text{SNCPhNS-}S,S)]$ [17]. For these two complexes the S...S contact is approx 2.9Å. Thus, for all three metallic species containing a bridging SNCPhNS ligand there is a reduction in the length of the transannular S...S contact cf. the monometallic systems.

Overall, the structure is very similar to the analogous Pd structure [27], which contained severely disordered solvent (methylene chloride) and was also a poor diffractor of X-rays.

The electron counting for each platinum centre in the trimetallic complex, $[Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh_3)_4]$, is shown in Figure 5.9.

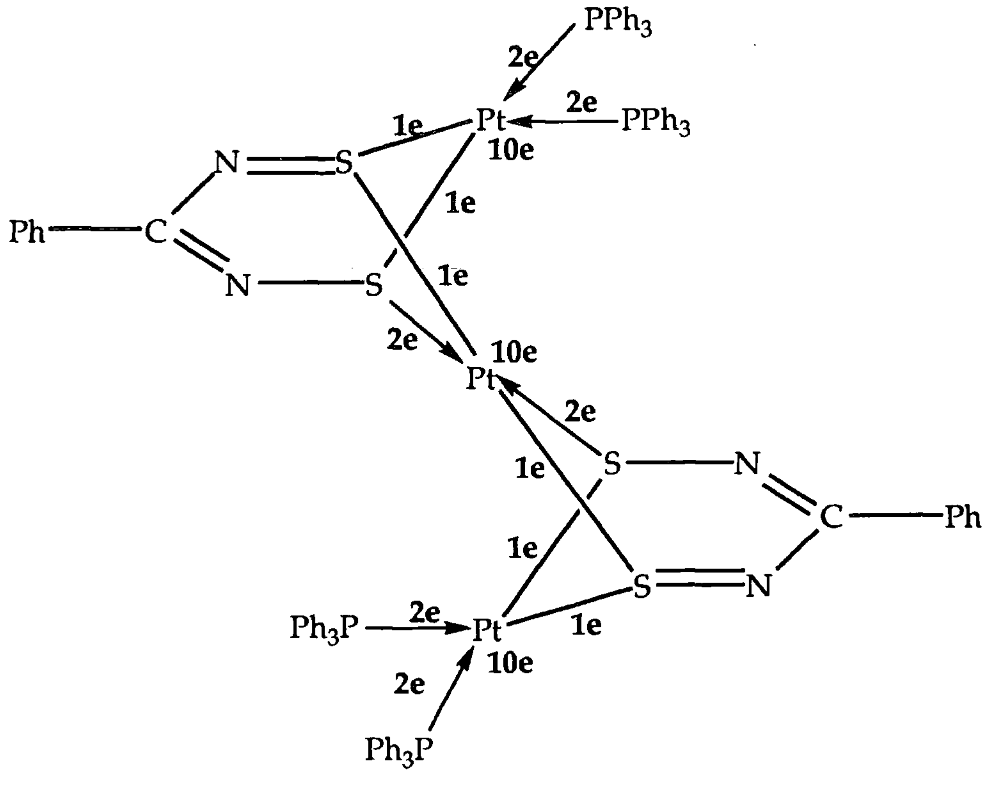


Figure 5.9 Electron counting for the $[Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh_3)_4]$ complex.

A consideration of the canonical form in Figure 5.9 suggests that the sulfur atoms in each ring have different oxidation states. One sulfur is formally +2, with lone pair donation to the central platinum. The other sulfur is formally +4, in a similar manner to the sulfilimines, $R_2S=NR$. Obviously, the sulfur atoms can vary between the two oxidation states, which is why a delocalised system is observed.

This picture does not allow for any formal bonding between the two different platinum centres, even though they are only 2.865(1)Å apart. Similar close contacts between platinum centres of 2.88Å have been observed in several tetracyanoplatinate complexes [28], and these have been attributed to overlap of $5dz^2$ orbitals of the platinum atoms. It is possible that there is overlap of the $5dz^2$ orbital in $[Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh_3)_4]$, as depicted in Figure 5.10. The geometry around the terminal platinum atoms is not too distorted from the expected square-planar geometry suggested by the electron counting method used in Figure 5.9. This implies that the $5dz^2$ orbital overlap between the platinum centres does not have a significant role in the formation of this complex. It is likely that it is the size of the bite angle of the bridging SNCPhNS ligand which is the crucial factor affecting the geometry seen in this complex.

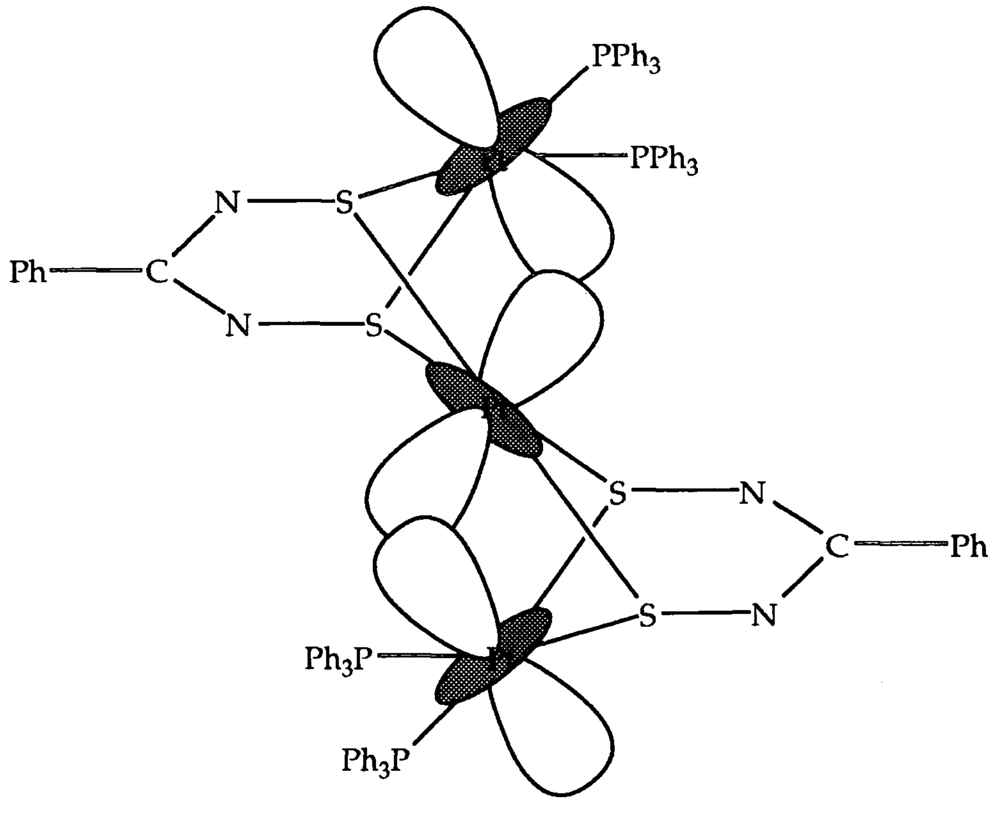


Figure 5.10 Overlap of the $5dz^2$ orbitals in $[Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh_3)_4]$.

Although numerous dimetallic species with bridging sulfur atoms are known [29-33], few tri- and tetrametallic systems have been reported. One tetrametallic system containing two bridging thiolato ligands between each metal centre has been crystallographically examined [34]. The structure of the $[(C_6F_5)_2Pd(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$ anion is shown in Figure 5.11.

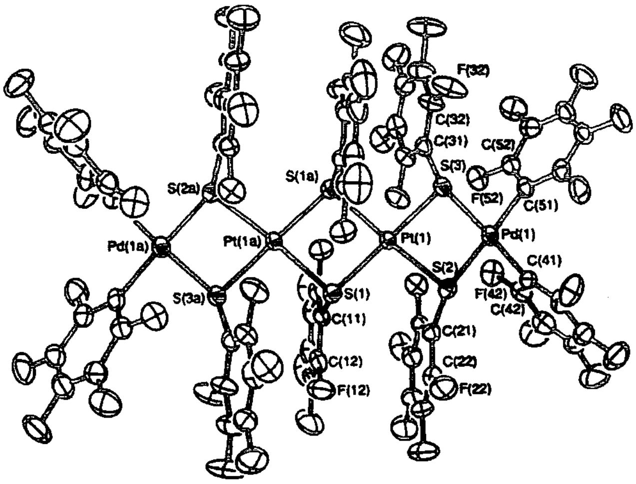


Figure 5.11 The $[(C_6F_5)_2Pd(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}C_6F_5)_2Pt(\mu\text{-}C_6F_5)_2Pd(C_6F_5)_2]$ anion.

The SMS angles are 79.6°, 82.6° and 83.7° (all others are defined since there is an inversion centre in the molecule). These angles are very similar to those observed in the Pt_3 system above. The transannular S...S contacts are 3.059 and 3.109Å. There is remarkable similarity in the metal/sulfur backbone between $[Pt_3(\mu\text{-}SNCPhNS\text{-}S,S)_2(PPh_3)_4]$ and this anionic system.

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Chapter 6

Suggestions for future work

6.1 Suggestions for future work

This thesis has examined the behaviour of systems derived from or containing the dithiadiazolyl/ium ring. In Chapter three, the emphasis was on the interaction of the 1,2 isomer with halide and polyhalide anions.

Chapter four examined the first metallo-dithiadiazolylium derivative, $[Hg(CNSNS)_2][AsF_6]_2$, and its potential as a transfer reagent. In this case, the feature of interest was the strength of the carbon-metal bond, and the bonding of the 1,3,2,4-dithiadiazolylium ring through the carbon atom.

Metal insertion into the S-S bond of the dithiadiazolyl ring was of interest in Chapter 5, and the bonding modes adopted by the SNCPhNS ligand at different metal centres.

Each chapter has examined different bonding modes of the dithiadiazolyl/ium ring, and there is certainly more work that can be undertaken in this field.

6.2 Ideas based on chapter three

The magnetic properties of $[p\text{-}Cl.C_6H_4.CNSSN]_6Cl_2$ are of interest because of the highly unusual arrangement of equivalent rings. The basic question that still needs to be answered is concerned with the location of the "extra electrons" within the lattice.

Empirically, there are three heterocyclic rings for every halide anion in this structure, which exists as discreet moieties with no capacity for electron hopping between stacks. A ring:halide ratio of 2:1 rather than 3:1 may lead to one-dimensional stacking, as depicted in Figure 6.1. Each chloride anion is interacting with eight sulfur atoms, in a similar manner to that observed for $[p\text{-}Cl.C_6H_4.CNSSN]_6Cl_2$.

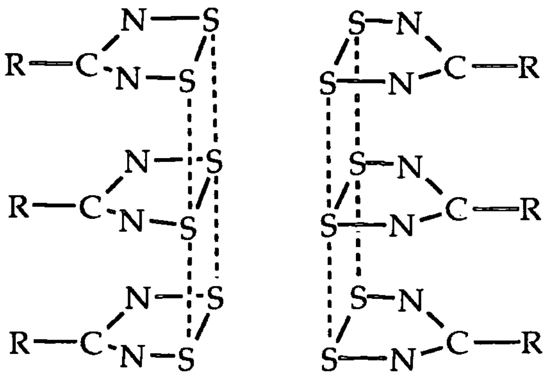


Figure 6.1 Possible stacking in compounds with one chlorine atom per two heterocyclic rings.

Alternatively, the selenium analogues of the compounds described above can be prepared. This may lead to enhanced orbital overlap between rings, and different electrical and/or magnetic responses may be observed.

6.3 Ideas based on chapter four

The main conclusion from the investigation into the transfer properties of $[Hg(CNSNS)_2][AsF_6]_2$ is probably chose the solvent carefully. The reactions which worked cleanly were carried out in sulfur dioxide. It is therefore logical to suggest that future work is undertaken primarily in this solvent. The reactions with systems such as RS-SR, RSe-SeR, $AlCl_3$ seem a good starting point, although those systems which have appreciable solubility in sulfur dioxide must be preferred.

6.4 Ideas based on chapter five

The transition metal complexes which have been described are the first monometallic systems containing a six-membered CN_2S_2M ring which is radical in nature. The formation of complexes which possess planar auxiliary ligands may lead to stacking. The investigation of the physical properties of the [M(SNCPhNS-S,S)(dppe)] complexes may provide surprises, especially since several physical phenomena, e.g. piezoelectricity, non-linear optical effects, require non-centrosymmetric packing in the solid state.

The trimetallic system appears to be formed by reaction of the monometallic species with a "naked" metal atom. Therefore, reactions with Ag^I or Au^I complexes, as well as the more obvious Ni or Pd phosphine complexes may be fruitful. Further oligomerisation, by careful removal of the remaining phosphine functionalities, is another area of interest.

Appendix A

Preparation of [ClSNSeCl][AsF_6]

A.1 Introduction

The chemistry of simple S/N compounds is well-developed with several cationic, neutral and anionic species well-known [1,2], including $[SN]^+$, $[S_2N]^+$, $[S_3N_2]^+$, $[S_4N_3]^+$, $[S_5N_5]^+$, S_4N_4, $(NSCl)_3$, $[S_3N_3]^-$ and $[S_4N_5]^-$.

The corresponding Se/N chemistry is less advanced [3], although those species which are known include $[Se_3N_2]^+$, $[Se_3N_2]^{2+}$, Se_4N_4, $[Se_3N]^-$, and $[Se_2N_2]^{2-}$. Similarly, systems containing mixed S/Se/N species are relatively unknown; a well-characterised example is $[Se_{3-n}S_nN_2]^+$ (n=1,2) [4].

The [SNS] cation has been shown to be a very versatile cycloaddition reagent in the preparation of numerous ring-containing compounds [5]. It can be safely prepared by reduction of the $[N(SCl)_2]$ cation using $SnCl_2$ [6-7], (see Eqn A.1).

$$[N(SCl)_2][AsF_6] + SnCl_2 \xrightarrow[-\ SnCl_4]{SO_2} [SNS][AsF_6]$$

<u>Eqn A.1</u>

The analogous Se compound, $[N(SeCl)_2]^+$, has also recently been prepared [8-9] by reaction of $[SeCl_3]^+$ salts with $N(SiMe_3)_3$, Eqn A.2.

$$2[SeCl_3][SbCl_6] + N(SiMe_3)_3 \xrightarrow[-\ SbCl_5]{-\ Cl_2} [N(SeCl)_2][SbCl_6] + 3TMSCl$$

<u>Eqn A.2</u>

To date the mixed S/Se cation, $[ClSNSeCl]^+$, has not been synthesised.

A.2 Preparation of dichloroselenathianitronium hexafluoroarsenate (V)

This was undertaken in an analogous manner [7] to the preparation of $[N(SCl)_2][AsF_6]$; Se/$SeCl_4$ providing an *in situ* supply of "$SeCl_2$", Eqn A.3.

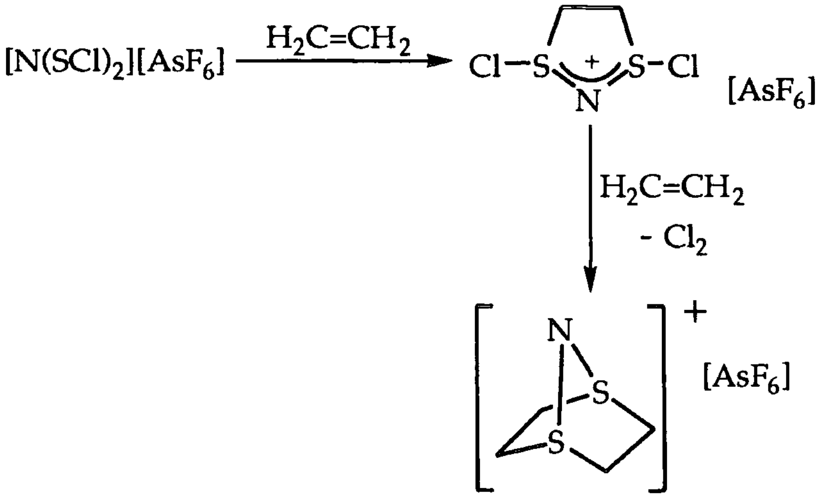
$$\begin{tikzcd}
(NSCl)_3 + AgAsF_6 \arrow[r, "SO_2", "- AgCl"'] & \text{"[NS][AsF}_6\text{]"} \arrow[d, "\text{"SeCl}_2\text{"}"] \\
 & [ClSNSeCl][AsF_6]
\end{tikzcd}$$

Eqn A.3

The required product was obtained in good yield with good analytical data (C,N,S,As). Only a broad hump was obtained from the ^{77}Se n.m.r., which may be due to the quadrupolar broadening by the nitrogen nuclei, although this is unclear. However, the i.r. and analytical data suggest the formation of the required compound, $[ClSNSeCl][AsF_6]$.

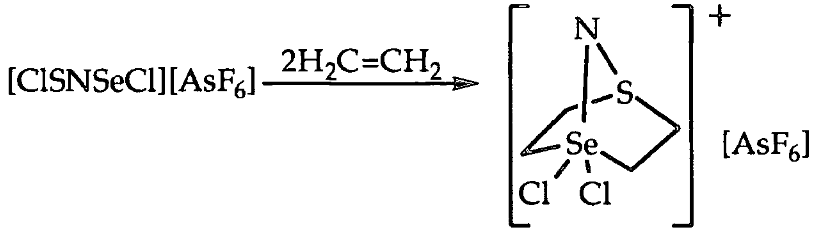
A.3 Reaction of $[ClSNSeCl][AsF_6]$ with ethylene

It is known that the $[N(SCl)_2]$ cation can undergo cycloaddition reactions in a similar manner to the dechlorinated analogue, $[SNS]^+$ [10]. The reactions of $[N(SCl)_2]^+$ are less extensive than those of $[SNS]^+$, presumably because it has frontier orbitals which are higher in energy than those of $[SNS]^+$ [10]. The reactions of $[N(SCl)_2]^+$ with ethylene are shown in Scheme A.1.



Scheme A.1

Mixing a solution of $[\mathrm{ClSNSeCl}][\mathrm{AsF_6}]$ with a solution containing ethylene produced an immediate colour change from yellow to scarlet. Stirring for 5 minutes gave an orange solution from which an orange solid was recovered (after washing with methylene chloride). This analysed well (C,H,N,S) as the product corresponding to the addition of two equivalents of ethylene, but with no loss of chlorine. The proposed reaction is shown in Eqn A.4.



Eqn A.4

Obviously there are several canonical forms that such a cation may possess. This is unusual since the analogous reaction with the sulfur-containing cation yields the four co-ordinate sulfur species shown in Scheme A.1. However, the analysis is very good for the formation of the six co-ordinate selenium species (see section A.4.2). The chlorine atoms are probably on the selenium atom rather than the sulfur atom because six co-ordination is preferred as Group VI is descended.

For both compounds it proved to be difficult to grow crystals which were suitable for single crystal X-ray diffraction. Numerous attempts were made to grow crystals including solvent evaporation, diffusion and layering. However, the extreme solubility of $[\mathrm{ClSNSeCl}][\mathrm{AsF_6}]$ in sulfur dioxide hampered all efforts.

Obviously, an X-ray structure determination would prove the identity of the cations unambiguously. It would also show whether the flexibility observed in the different salts of the $[\mathrm{N(SeCl)_2}]$ cation [8-9] is mirrored when just one selenium atom is present in the cation; no flexibility is observed for the sulfur analogue.

A.4 Experimental

A.4.1 Preparation of [ClSNSeCl][AsF_6]

$(NSCl)_3$ (81mg, 1mmol), $AgAsF_6$ (297mg, 1mmol), Se (39mg, 0.5mmol), and $SeCl_4$ (110mg, 0.5mmol) were placed, together with a magnetic follower, in one limb of a two-limbed reaction vessel. SO_2 was condensed onto the solids. Stirring for 18 hours produced a red/orange solution over a white precipitate. The solution was filtered and the solid washed with back-condensed sulfur dioxide two or three times. The sulfur dioxide was removed *in vacuo* and the soluble solid washed with methylene chloride. Methylene chloride was removed *in vacuo* and the yellow/orange target compound (332mg, 86%) extracted from a trace of very fine silver chloride using sulfur dioxide in a closed extractor.

Found	C	0.18	N	3.81	S	7.92	As	19.17
Calculated	C	0.00	N	3.64	S	8.33	As	19.48

I.R. (ν_{max}/cm^{-1}) 1154w, 1082w, 1024w, 945sh, 919m, 700vs, 570m, and 544m.

A.4.2 Reaction of [ClSNSeCl][AsF_6] with $H_2C=CH_2$

[ClSNSeCl][AsF_6] (128mg, 0.33mmol) was placed, together with a magnetic follower, in the rear limb of a two-limbed reaction vessel with a magnetic stirrer. SO_2 was condensed on, the limb sealed and the other limb cooled to -78°C. One atmosphere of $H_2C=CH_2$ was let into the system, which was then allowed to warm to room temperature. Some SO_2 was condensed into the front limb and then filtered back onto the orange solution. The solution immediately became scarlet in colour. After stirring (5 minutes) the solution was filtered and the solvent removed to give a scarlet oily material. Washing with methylene chloride gave an orange solid which analysed well as the chlorinated norbornane product, [$C_4H_8SNSeCl_2$][AsF_6] (yield 104mg, 71%).

Found	C	10.77	H	1.84	N	3.44	S	7.44
Calculated	C	10.89	H	1.83	N	3.18	S	7.27

I.R. (ν_{max}/cm^{-1}) 1690w, 1655w, 1590w, 1300w, 1253w, 1203w, 1153w, 1072w, 1016w, 965w, 946w, 844sh, 820w, 775w, 700vs, 626sh, 569w, 459w, 390ms.

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Appendix B

The structure of a fluorinated dithiadiazolyl radical, $[C_5NF_4.CNSSN]_2$

B.1 Introduction.

The 7π 1,2,3,5-dithiadiazolyl radical systems have received considerable attention because of the possibility of "one-dimensional stacking" of eclipsed rings in the solid state, section 1.2.1. The crystal structures of this class of compounds are of great importance in helping to explain the physical phenomena observed for these species.

To date, the required stacking arrangement of the heterocyclic rings has not been observed, although diverse structural types have been seen. The more interesting of these contain cyanophenyl derivatives [1-6], including some selenium analogues of these systems.

Both [*m*, and *p*-$NC.C_6H_4.CNSSN]_2$ contain dimers of spin-paired dithiadiazolyl rings, with secondary interactions between the sulfur atoms of the heterocycle and the nitrile group of a neighbouring dimer pair, Figure B.1 [1]. For the *meta*- substituted case, this leads to planar sheets which are close in structure to that required for one-dimensional packing, although the distance between dimer units is too long for significant interactions between rings at 4.26(5)Å (4.15(5)Å in the selenium analogue [1]). Therefore, there is no electron hopping along the direction of the stacks.

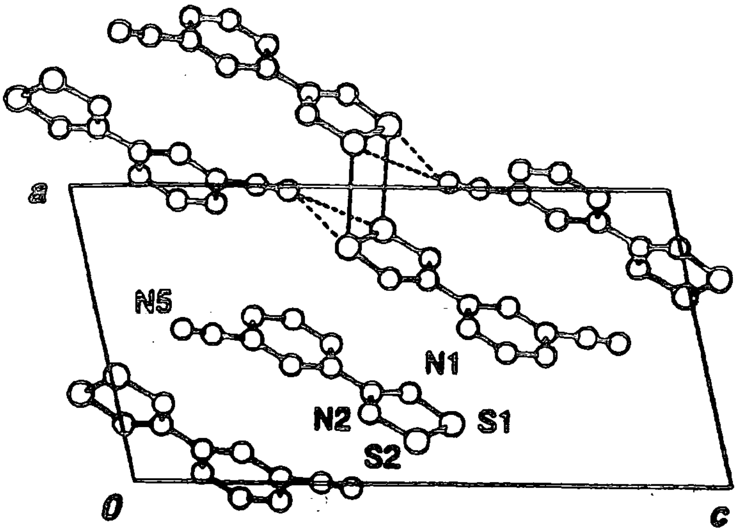

Figure B.1 The S...N interactions in [*m*-$NC.C_6H_4.CNSSN]_2$.

The substitution of hydrogen by fluorine, to give systems based on the cyanotetrafluorophenyl derivatives, has a profound influence on the stacking observed for these compounds. For example, [*p*-$NC.C_6F_4.CNSSN$] exists in two crystalline forms [7], both possessing dominant interactions between the sulfur atoms of the ring and the nitrogen atom of the nitrile functionality. There is no spin-pairing of the heterocyclic ring in these two phases, which contain the first dithiadiazolyl system which is monomeric (and therefore paramagnetic) in the solid state. A view of the α-phase is shown, Figure B.2.

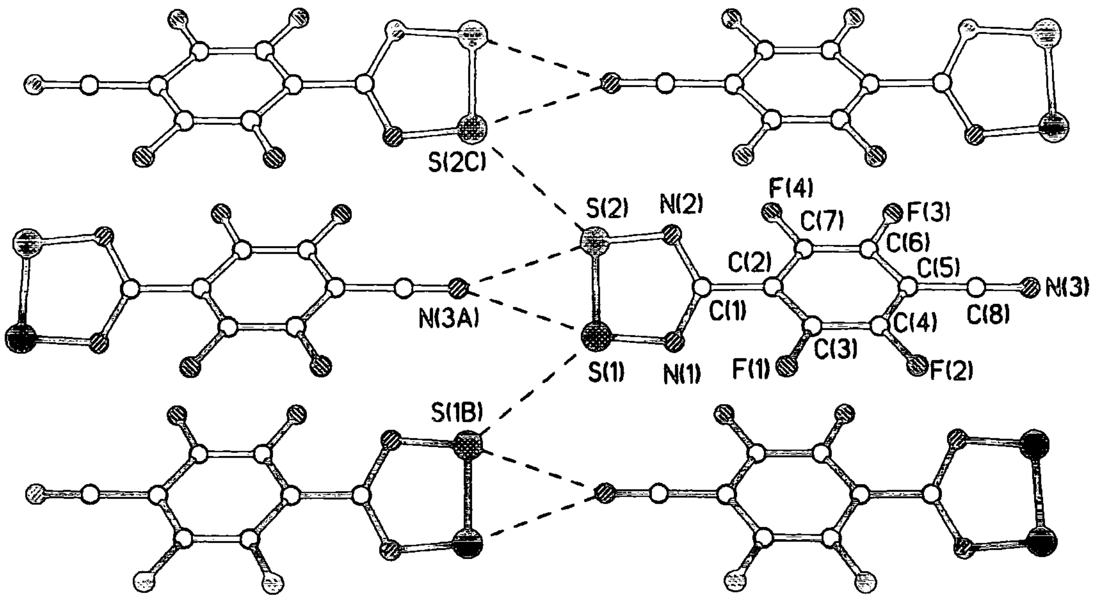

Figure B.2 Showing the S..N interactions responsible for the monomeric stacking seen in [*p*-NC.C$_6$F$_4$.CNSSN].

B.2 The structure of [C$_5$NF$_4$.CNSSN]$_2$.

In view of the unique stacking observed in [*p*-NC.C$_6$F$_4$.CNSSN], the related fluorinated pyridyl radical, [C$_5$NF$_4$.CNSSN]$_2$, was examined. The compound was prepared (by Miss C.M. Aherne) from the chloride precursor in a similar manner to other dithiadiazolyl radical species. Crystals were grown by slow vacuum sublimation to give blue blocks. The colour is quite unusual since the majority of radicals are red/green dichroic in nature. The observed shift is presumably due to the electronic influence of the pyridyl ring, with some spin-leakage occurring at the carbon node, as discussed in section 1.2.7.

There were no unusual problems associated with the data collection for this crystal structure determination, the details of which are in Table B.1. The refinement was carried out in the space group I2/a, rather than C2/c, in order to minimise directional correlations, see Table B.1.

Figure B.3 shows the numbering scheme used for [C$_5$NF$_4$.CNSSN]$_2$, which has one half of the radical pair in the asymmetric unit. Bond lengths and angles for the dithiadiazolylium ring are shown in Table B.2. Atomic co-ordinates, displacement parameters, and a full description of bond lengths and angles are quoted in section B.4.

Table B.1 Crystal data and structure refinement for $[C_5NF_4.CNSSN]_2$.

Empirical formula	$C_6F_4N_3S_2$
Formula weight	254.21
Temperature, K	150
Mean Wavelength, $\bar{\lambda}$, Å	0.71073
Crystal system	Monoclinic
Space group	I2/a
Unit cell dimensions, Å and °	a = 11.420(4) $\alpha = 90$ b = 9.654(4) $\beta = 94.06(1)$ c = 14.563(4) $\gamma = 90$
Volume, $Å^3$	1602(1)
Z	8
Density (calc), gcm^{-3}	2.109
Absorption coefficient, mm^{-1} ($\bar{\lambda}$)	0.698
F(000)	1000
Crystal size, mm	0.65 x 0.60 x 0.55
2θ range for data collection, °	5.0 to 50.0
Index ranges	$-13<h<11$ $-11<k<1$ $-17<l<11$
Reflections collected	1768
Independent reflections	1416, $R_{int} = 0.0236$
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	1.0000 and 0.9593
Refinement method	Full-matrix least-squares on F^2
Data, restraints, parameters	1414, 0, 136
Goodness-of-fit on F^2	1.072
Final R indices, $I>2\sigma(I)$	R1 = 0.0261 wR2 = 0.0704
R indices, all data	R1 = 0.0340 wR2 = 0.0791
Largest diff. peak and hole, $eÅ^{-3}$	0.409 and -0.373

Table B.2 Selected bond lengths, Å, and angles, °, for $[C_5NF_4.CNSSN]_2$.

N(1)-C(1)	1.335(2)	C(1)-N(1)-S(1)	113.4(1)
N(1)-S(1)	1.640(2)	N(1)-S(1)-S(2)	94.55(6)
S(1)-S(2)	2.100(1)	N(2)-S(2)-S(1)	94.51(6)
S(2)-N(2)	1.636(2)	C(1)-N(2)-S(2)	113.5(1)
N(2)-C(1)	1.337(2)	N(1)-C(1)-N(2)	124.0(2)
C(1)-C(2)	1.484(2)	N(1)-C(1)-C(2)	118.2(2)
		N(2)-C(1)-C(2)	117.8(2)

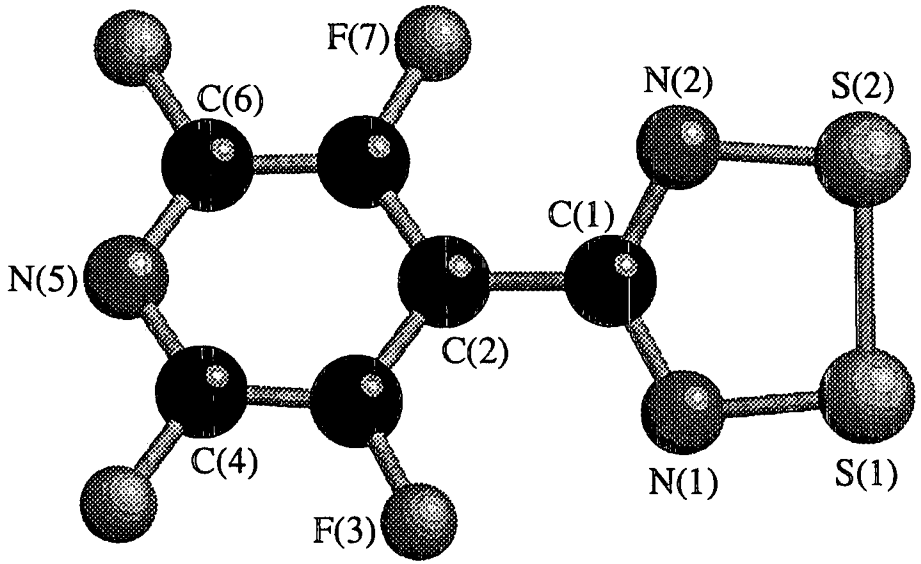

Figure B.3 Numbering scheme in $[C_5NF_4.\overline{CNSSN}]_2$.

The structure of $[C_5NF_4.CNSSN]_2$ exists in an array of spin-paired radicals arranged in a cis-oid formation. This dimerisation of two heterocyclic rings in the solid state is observed for all other characterised systems in the solid state except [*p*-$NC.C_6F_4.CNSSN$]. $[C_5NF_4.CNSSN]_2$ has ring geometries which are very similar to other known radical systems [8]. The Rms deviation from the mean plane of the heterocyclic ring is 0.007Å.

The S..S distance between the rings is 3.111(1)Å. This is longer than in $[C_6F_5.CNSSN]_2$, see Table B.3, and there is also a large twist between the pyridyl and heterocyclic rings of 31.93(4)°.

Table B.3 A comparison of S-S and S...S interactions in selected radicals.

Compound	S-S bond, Å	S...S, Å	Ref
$[C_6F_5.CNSSN]_2$	2.097(1)	3.067(1)	[9]
$[C_5NF_4.CNSSN]_2$	2.100(1)	3.111(1)	[7]
$[C_6H_5.CNSSN]_2$ †	2.095, 2.096 2.080, 2.086	3.097, 3.186 3.116, 3.038	[10]
[*p*-$NC.C_6F_4.CNSSN$]	2.090(1)	-	[7]

† distances quoted with no estimated standard deviations.

The dimer pairs are arranged in a head-to-tail columnar fashion, held together by interactions between the sulfur atoms and the nitrogen of the pyridyl group, see Figure B.4 and Table B.4. The large twist between the heterocyclic ring and the pyridyl ring is responsible for the slight asymmetry observed in the S...N interactions, see Table B.4. The columns of spin-paired radicals are held together by some weak S...F interactions, Table B.4.

Table B.4 Secondary contacts, Å, in $[C_5NF_4.CNSSN]_2$.

S'(1) ... S(2)	3.111(1)	S"(1) ... N(5)	3.266(2)
S"(2) ... N(5)	3.309(2)	S"(1) ... F(7)	3.304(1)
S"(2) ... F(3)	3.148(1)		

S(1)' is related to S(1) by 0.5-x, y, 1-z
S(1)" is related to S(1) by x, y-1, z
S(1)"' is related to S(1) by x-0.5, -y, z

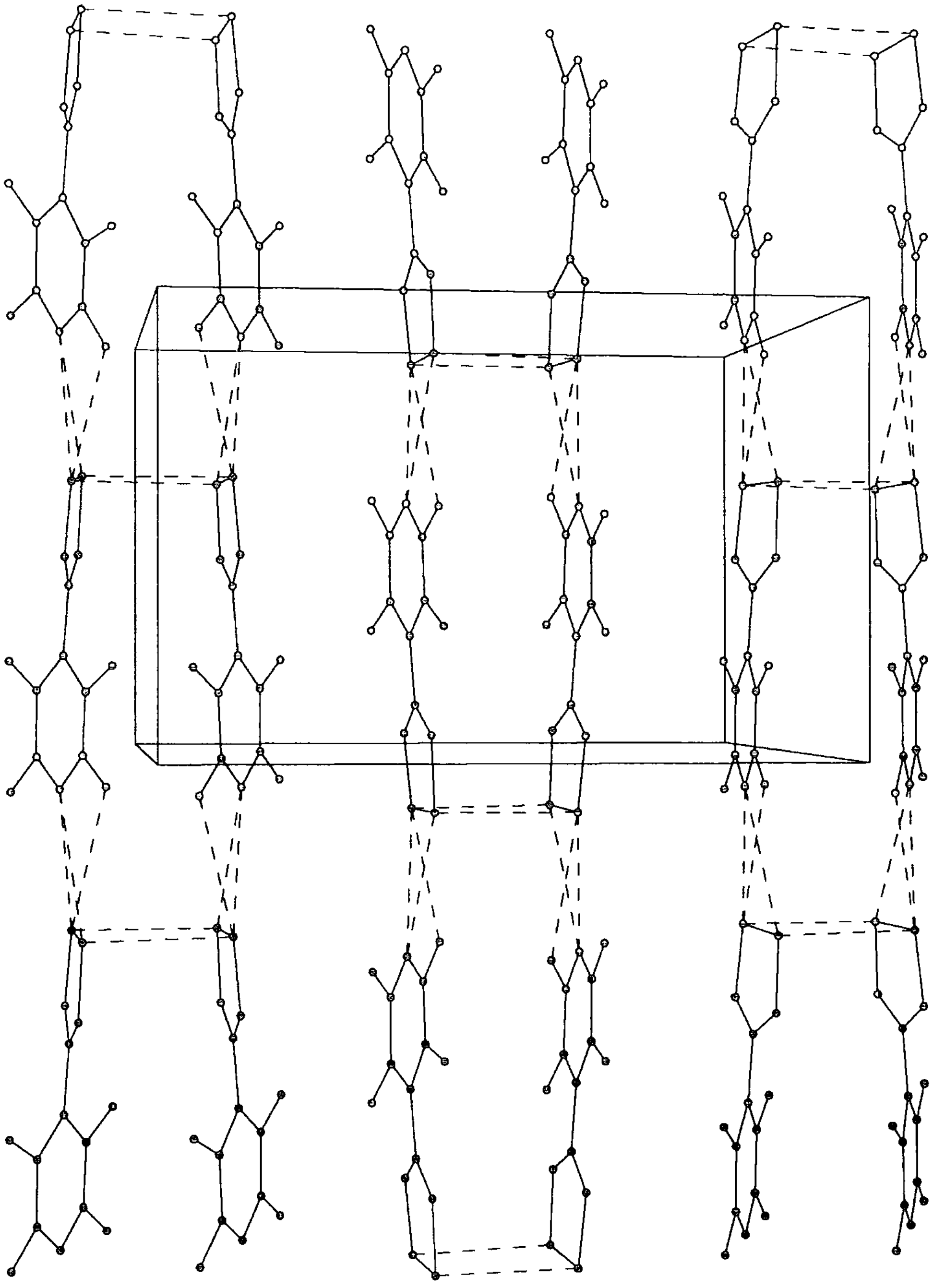

Figure B.4 Packing view of $[C_5NF_4.\overline{CNSSN}]_2$.

B.3 References.

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[10] A. Vegas, A. Pérez-Salazar, A.J. Banister & R.G. Hey, *J Chem Soc Dalton Trans,* (1980) 1812.

B.4 Full structural data for $[C_5NF_4.CNSSN]_2$.

Table B.5 Atomic coordinates and equivalent isotropic displacement parameters for $[C_5NF_4.CNSSN]_2$. U(eq) is defined as one third of the trace of the orthogonalised Uij tensor.

	x	y	z	U(eq)
N(1)	0.3316(1)	-0.0518(2)	0.3773(1)	0.021(1)
S(1)	0.3198(1)	0.1168(1)	0.3869(1)	0.023(1)
S(2)	0.1379(1)	0.1133(1)	0.3997(1)	0.023(1)
N(2)	0.1277(1)	-0.0556(2)	0.3940(1)	0.021(1)
C(1)	0.2298(1)	-0.1185(2)	0.3821(1)	0.017(1)
C(2)	0.2298(1)	-0.2717(2)	0.3744(1)	0.017(1)
C(3)	0.3253(1)	-0.3530(2)	0.4077(1)	0.017(1)
F(3)	0.4220(1)	-0.2954(1)	0.4482(1)	0.023(1)
C(4)	0.3176(1)	-0.4952(2)	0.4033(1)	0.018(1)
F(4)	0.4079(1)	-0.5714(1)	0.4390(1)	0.026(1)
N(5)	0.2255(1)	-0.5643(2)	0.3691(1)	0.020(1)
C(6)	0.1360(2)	-0.4892(2)	0.3356(1)	0.019(1)
F(6)	0.0425(1)	-0.5580(1)	0.3001(1)	0.025(1)
C(7)	0.1338(1)	-0.3462(2)	0.3359(1)	0.018(1)
F(7)	0.0386(1)	-0.2822(1)	0.2981(1)	0.026(1)

Table B.6 Bond lengths, Å, and angles, °, in $[C_5NF_4.CNSSN]_2$.

N(1)-C(1)	1.335(2)	N(1)-S(1)	1.640(2)
S(1)-S(2)	2.010(1)	S(2)-N(2)	1.636(2)
N(2)-C(1)	1.337(2)	C(1)-C(2)	1.484(2)
C(2)-C(7)	1.395(2)	C(2)-C(3)	1.403(2)
C(3)-F(3)	1.335(2)	C(3)-C(4)	1.377(3)
C(4)-N(5)	1.313(2)	C(4)-F(4)	1.341(2)
N(5)-C(6)	1.319(2)	C(6)-F(6)	1.331(2)
C(6)-C(7)	1.381(3)	C(7)-F(7)	1.334(2)

C(1)-N(1)-S(1)	113.4(1)	N(1)-S(1)-S(2)	94.55(6)
N(2)-S(2)-S(1)	94.51(6)	C(1)-N(2)-S(2)	113.5(1)
N(1)-C(1)-N(2)	124.0(2)	N(1)-C(1)-C(2)	118.2(2)
N(2)-C(1)-C(2)	117.8(2)	C(7)-C(2)-C(3)	114.9(2)
C(7)-C(2)-C(1)	122.7(2)	C(3)-C(2)-C(1)	122.4(2)
F(3)-C(3)-C(4)	118.9(2)	F(3)-C(3)-C(2)	121.2(2)
C(4)-C(3)-C(2)	119.7(2)	N(5)-C(4)-F(4)	116.2(2)
N(5)-C(4)-C(3)	124.8(2)	F(4)-C(4)-C(3)	119.0(2)
C(4)-N(5)-C(6)	116.1(2)	N(5)-C(6)-F(6)	116.7(2)
N(5)-C(6)-C(7)	124.2(2)	F(6)-C(6)-C(7)	119.1(2)
F(7)-C(7)-C(6)	118.4(2)	F(7)-C(7)-C(2)	121.4(2)
C(6)-C(7)-C(2)	120.1(2)		

Table B.7 Anisotropic displacement parameters for $[C_5NF_4.CNSSN]_2$; taking the form :$-2\pi^2[h^2a^{*2}U11+...+2hka^*b^*U12]$

	U11	U22	U33	U23	U13	U12
N(1)	0.025(1)	0.013(1)	0.026(1)	-0.01(1)	0.06(1)	-0.01(1)
S(1)	0.030(1)	0.013(1)	0.026(1)	-0.01(1)	0.07(1)	-0.03(1)
S(2)	0.025(1)	0.014(1)	0.029(1)	-0.01(1)	-0.04(1)	0.04(1)
N(2)	0.021(1)	0.016(1)	0.027(1)	-0.01(1)	-0.05(1)	0.01(1)
C(1)	0.021(1)	0.016(1)	0.014(1)	0.01(1)	-0.02(1)	0.01(1)
C(2)	0.019(1)	0.017(1)	0.015(1)	0.00(1)	0.01(1)	-0.01(1)
C(3)	0.016(1)	0.018(1)	0.018(1)	-0.02(1)	0.01(1)	-0.01(1)
F(3)	0.018(1)	0.020(1)	0.031(1)	-0.02(1)	-0.06(1)	-0.02(1)
C(4)	0.018(1)	0.018(1)	0.019(1)	0.01(1)	0.01(1)	0.04(1)
F(4)	0.023(1)	0.018(1)	0.037(1)	0.02(1)	-0.05(1)	0.06(1)
N(5)	0.023(1)	0.015(1)	0.022(1)	-0.02(1)	0.03(1)	0.00(1)
C(6)	0.019(1)	0.019(1)	0.018(1)	-0.04(1)	0.01(1)	-0.04(1)
F(6)	0.022(1)	0.022(1)	0.031(1)	-0.06(1)	-0.04(1)	-0.07(1)
C(7)	0.017(1)	0.019(1)	0.017(1)	0.01(1)	-0.02(1)	0.02(1)
F(7)	0.021(1)	0.022(1)	0.032(1)	0.01(1)	-0.010(1)	0.03(1)

Table B.8 Torsion angles, °, in $[C_5NF_4.CNSSN]_2$.

C(1)-N(1)-S(1)-S(2)	-0.6(1)	N(1)-S(1)-S(2)-N(2)	1.13(8)
S(1)-S(2)-N(2)-C(1)	-1.5(1)	S(1)-N(1)-C(1)-N(2)	-0.3(2)
S(1)-N(1)-C(1)-C(2)	-180.0(1)	S(2)-N(2)-C(1)-N(1)	1.4(2)
S(2)-N(2)-C(1)-C(2)	-179.0(1)	N(1)-C(1)-C(2)-C(7)	-148.9(2)
N(2)-C(1)-C(2)-C(7)	31.5(2)	N(1)-C(1)-C(2)-C(3)	33.0(2)
N(2)-C(1)-C(2)-C(3)	-146.7(2)	C(7)-C(2)-C(3)-F(3)	-178.4(1)
C(1)-C(2)-C(3)-F(3)	-0.1(2)	C(7)-C(2)-C(3)-C(4)	-2.0(2)
C(1)-C(2)-C(3)-C(4)	176.3(2)	F(3)-C(3)-C(4)-N(5)	176.8(2)
C(2)-C(3)-C(4)-N(5)	0.4(3)	F(3)-C(3)-C(4)-F(4)	-0.7(2)
C(2)-C(3)-C(4)-F(4)	-177.2(1)	F(4)-C(4)-N(5)-C(6)	178.8(1)
C(3)-C(4)-N(5)-C(6)	1.2(3)	C(4)-N(5)-C(6)-F(6)	179.5(1)
C(4)-N(5)-C(6)-C(7)	-0.9(3)	N(5)-C(6)-C(7)-F(7)	178.7(2)
F(6)-C(6)-C(7)-F(7)	-1.7(2)	N(5)-C(6)-C(7)-C(2)	-0.9(3)
F(6)-C(6)-C(7)-C(2)	178.7(1)	C(3)-C(2)-C(7)-F(7)	-177.3(2)
C(1)-C(2)-C(7)-F(7)	4.4(2)	C(3)-C(2)-C(7)-C(6)	2.3(2)
C(1)-C(2)-C(7)-C(6)	-176.0(2)		

Table B.9 Secondary contacts, Å, in $[C_5NF_4.CNSSN]_2$.

S′(1)...S(2)	3.111(1)	S″(1)..N(5)	3.266(2)
S″(2)..N(5)	3.309(2)	S‴(1)..F(7)	3.304(1)
S‴(2)..F(3)	3.148(1)		

S(1)′ is related to S(1) by 0.5-x, y, 1-z
S(1)″ is related to S(1) by x, y-1, z
S(1)‴ is related to S(1) by x-0.5, -y, z

Angle between planes of the two rings = 31.93 (4)

Appendix C

Crystallographic data for the compounds discussed in chapter 3

Table C.1 Atomic coordinates and equivalent isotropic displacement coefficients, Å^2, for [*p*-Cl.C_6H_4.CNSSN]Cl, see Figure 3.9.

	x	y	z	U(eq)
S	0.7457(2)	0.1278(2)	0.4518(2)	0.052(1)
N	0.5099(7)	0.1098(6)	0.3603(5)	0.052(2)
C(1)	0.4080(12)	0.2500	0.3227(7)	0.043(3)
C(2)	0.1887(12)	0.2500	0.2392(8)	0.043(3)
C(3)	0.0845(9)	0.1031(8)	0.1988(6)	0.051(2)
C(4)	-0.1178(10)	0.1039(8)	0.1156(7)	0.059(2)
C(5)	-0.2164(13)	0.2500	0.0721(8)	0.055(3)
Cl(1)	-0.4615(4)	0.2500	-0.0440(3)	0.082(1)
Cl(2)	0.1495(3)	0.2500	0.6141(2)	0.057(1)

Table C.2 Bond lengths, Å, for [*p*-Cl.C_6H_4.CNSSN]Cl.

S-N	1.592(4)	S-S'	2.007(3)
N-C(1)	1.336(6)	C(1)-C(2)	1.469(10)
C(2)-C(3)	1.395(7)	C(3)-C(4)	1.379(8)
C(4)-C(5)	1.381(8)	C(5)-Cl(1)	1.740(8)
C(3)-H(3)	0.91(7)	C(4)-H(4)	0.95(7)

Table C3 Bond angles, °, for [*p*-Cl.C_6H_4.CNSSN]Cl.

N-S-S'	95.3(2)	S-N-C(1)	115.1(4)
N-C(1)-C(2)	120.4(3)	N-C(1)-N'	119.1(6)
C(2)-C(1)-N'	120.4(3)	C(1)-C(2)-C(3)	120.1(3)
C(3)-C(2)-C(3')	119.8(7)	C(2)-C(3)-C(4)	119.8(6)
C(4)-C(3)-H(3)	119(4)	C(3)-C(4)-C(5)	120.0(6)
C(4)-C(5)-Cl(1)	119.7(4)	C(4)-C(5)-C(4')	120.5(7)
C(2)-C(3)-H(3)	120(4)	C(3)-C(4)-H(4)	121(4)
C(5)-C(4)-H(4)	118(4)		

Table C.4 Anisotropic displacement coefficients, Å^2, for [*p*-Cl.C_6H_4.CNSSN]Cl.

S	0.037(1)	0.038(1)	0.076(1)	0.000(1)	-0.007(1)	0.003(1)
N	0.040(2)	0.034(3)	0.076(3)	-0.003(2)	-0.003(2)	0.001(2)
C(1)	0.035(4)	0.042(5)	0.049(4)	0.000	0.003(3)	0.000
C(2)	0.035(4	0.046(5)	0.049(4)	0.000	0.011(3)	0.000
C(3)	0.041(3)	0.046(4)	0.064(3)	-0.002(3)	0.001(3)	-0.002(3)
C(4)	0.042(3)	0.056(4)	0.074(4)	-0.007(3)	0.001(3)	-0.010(3)
C(5)	0.031(4)	0.075(7)	0.053(5)	0.000	-0.005(3)	0.000
Cl(1)	0.046(1)	0.100(2)	0.090(2)	0.000	-0.020(1)	0.000
Cl(2)	0.046(1)	0.043(1)	0.075(1)	0.000	-0.010(1)	0.000

Table C.5 Hydrogen-atom coordinates and isotropic displacement coefficients, Å^2, for [*p*-Cl.C_6H_4.CNSSN]Cl.

H(3)	0.14(1)	0.01(1)	0.231(6)	0.08
H(4)	-0.19(1)	0.01(1)	0.089(6)	0.08

Atom S′ is related to S by the operation x, 0.5-y, z.

Table C.6 Bond lengths, Å, and angles, °, for the secondary contacts in [*p*-Cl.C_6H_4.CNSSN]Cl.

S...Cl	2.916(2)	S...Cl...S′	40.3(1)
		S′...S...Cl	69.9(0)

Atom S′ is related to S by the operation x, 0.5-y, z.

Table C.7 Atomic coordinates and equivalent isotropic displacement coefficients, Å^2, for [(p-Cl.C_6H_4.CNSSN)$_2$Cl][S_3N_3], see Figure 3.12.

	x	y	z	U(eq)
N(1A)	0.6896(3)	0.9953(3)	0.8060(2)	0.033(1)
S(1A)	0.5199(1)	0.8847(1)	0.7679(1)	0.034(1)
S(2A)	0.4743(1)	0.8584(1)	0.5892(1)	0.037(1)
N(2A)	0.6378(3)	0.9665(3)	0.6024(2)	0.036(1)
C(1)	0.7327(3)	1.0279(3)	0.7142(3)	0.031(1)
C(2)	0.8835(3)	1.1312(3)	0.7374(3)	0.033(1)
C(3)	0.9802(4)	1.1985(3)	0.8539(3)	0.042(1)
C(4)	1.1195(4)	1.2984(4)	0.8754(4)	0.050(2)
C(5)	1.1606(4)	1.3311(3)	0.7813(4)	0.045(1)
ClA	1.3336(1)	1.4588(1)	0.8090(1)	0.073(1)
C(6)	1.0685(4)	1.2661(4)	0.6658(4)	0.051(2)
C(7)	0.9287(4)	1.1648(4)	0.6432(3)	0.045(1)
N(1B)	-0.2491(3)	0.4064(3)	0.6401(2)	0.038(1)
S(1B)	-0.1157(1)	0.5034(1)	0.6051(1)	0.040(1)
S(2B)	0.0194(1)	0.6035(1)	0.7768(1)	0.038(1)
N(2B)	-0.0944(3)	0.5197(3)	0.8358(2)	0.037(1)
C(8)	-0.2235(3)	0.4235(3)	0.7561(3)	0.033(1)
C(9)	-0.3346(3)	0.3366(3)	0.7984(3)	0.032(1)
C(10)	-0.3003(4)	0.3421(3)	0.9184(3)	0.043(1)
C(11)	-0.4031(4)	0.2589(4)	0.9577(3)	0.046(1)
C(12)	-0.5425(4)	0.1698(3)	0.8765(3)	0.037(1)
ClB	-0.6713(1)	0.0648(1)	0.9264(1)	0.055(1)
C(13)	-0.5795(4)	0.1623(3)	0.7566(3)	0.038(1)
C(14)	-0.4763(4)	0.2454(3)	0.7179(3)	0.037(1)
Cl(3)	0.1898(1)	0.7126(1)	0.6315(1)	0.057(1)
S(01)	0.3506(1)	0.3382(1)	0.4346(1)	0.054(1)
N(01)	0.4274(3)	0.3848(3)	0.3387(3)	0.053(1)
S(02)	0.0809(1)	0.1721(1)	0.2407(1)	0.051(1)
N(02)	0.1803(4)	0.2301(3)	0.3800(3)	0.051(1)
S(03)	0.3491(1)	0.3241(1)	0.2006(1)	0.054(1)
N(03)	0.1755(4)	0.2186(3)	0.1553(2)	0.048(1)

Table C.8 Bond lengths, Å, for $[(p\text{-}Cl.C_6H_4.CNSSN)_2Cl][S_3N_3]$.

N(1A)-S(1A)	1.603(2)	N(1A)-C(1)	1.355(5)
S(1A)-S(2A)	2.047(1)	S(2A)-N(2A)	1.610(3)
N(2A)-C(1)	1.339(3)	C(1)-C(2)	1.471(4)
C(2)-C(3)	1.397(4)	C(2)-C(7)	1.395(6)
C(3)-H(3A)	0.935(44)	C(3)-C(4)	1.382(5)
C(4)-H(4A)	0.852(42)	C(4)-C(5)	1.373(7)
C(5)-ClA	1.735(3)	C(5)-C(6)	1.375(5)
C(6)-H(6A)	0.923(55)	C(6)-C(7)	1.391(5)
C(7)-H(7A)	0.937(32)	N(1B)-S(1B)	1.610(3)
N(1B)-C(8)	1.334(4)	S(1B)-S(2B)	2.049(1)
S(2B)-N(2B)	1.613(3)	N(2B)-C(8)	1.356(3)
C(8)-C(9)	1.473(5)	C(9)-C(10)	1.387(5)
C(9)-C(14)	1.398(4)	C(10)-H(10A)	0.916(26)
C(10)-C(11)	1.380(6)	C(11)-H(11A)	0.897(41)
C(11)-C(12)	1.382(4)	C(12)-ClB	1.739(4)
C(12)-C(13)	1.380(5)	C(13)-H(13A)	0.905(31)
C(13)-C(14)	1.378(5)	C(14)-H(14A)	0.909(34)
S(01)-N(01)	1.612(4)	S(01)-N(02)	1.586(3)
N(01)-S(03)	1.578(4)	S(02)-N(02)	1.608(3)
S(02)-N(03)	1.601(4)	S(03)-N(03)	1.599(3)

Table C.9 Angles, °, for $[(p\text{-}Cl.C_6H_4.CNSSN)_2Cl][S_3N_3]$.

S(1A)-N(1A)-C(1)	114.7(2)	N(1A)-S(1A)-S(2A)	95.3(1)
S(1A)-S(2A)-N(2A)	94.9(1)	S(2A)-N(2A)-C(1)	115.1(3)
N(1A)-C(1)-N(2A)	120.0(3)	N(1A)-C(1)-C(2)	119.9(2)
N(2A)-C(1)-C(2)	120.1(3)	C(1)-C(2)-C(3)	120.2(3)
C(1)-C(2)-C(7)	120.1(3)	C(3)-C(2)-C(7)	119.7(3)
C(2)-C(3)-H(3A)	115.2(18)	C(2)-C(3)-C(4)	120.1(4)
H(3A)-C(3)-C(4)	124.7(18)	C(3)-C(4)-H(4A)	115.5(37)
C(3)-C(4)-C(5)	119.3(3)	H(4A)-C(4)-C(5)	124.5(36)
C(4)-C(5)-ClA	119.0(3)	C(4)-C(5)-C(6)	122.0(3)
ClA-C(5)-C(6)	119.0(4)	C(5)-C(6)-H(6A)	123.4(23)

C(5)-C(6)-C(7)	119.2(4)	H(6A)-C(6)-C(7)	117.3(23)
C(2)-C(7)-C(6)	119.8(3)	C(2)-C(7)-H(7A)	121.5(24)
C(6)-C(7)-H(7A)	118.7(24)	S(1B)-N(1B)-C(8)	115.5(2)
N(1B)-S(1B)-S(2B)	94.6(1)	S(1B)-S(2B)-N(2B)	95.5(1)
S(2B)-N(2B)-C(8)	114.0(2)	N(1B)-C(8)-N(2B)	120.3(3)
N(1B)-C(8)-C(9)	120.1(2)	N(2B)-C(8)-C(9)	119.6(3)
C(8)-C(9)-C(10)	120.9(2)	C(8)-C(9)-C(14)	120.5(3)
C(10)-C(9)-C(14)	118.6(3)	C(9)-C(10)-H(10A)	121.7(26)
C(9)-C(10)-C(11)	120.8(3)	H(10A)-C(10)-C(11)	117.5(26)
C(10)-C(11)-H(11A)	117.0(23)	C(10)-C(11)-C(12)	119.5(3)
H(11A)-C(11)-C(12)	123.5(23)	C(11)-C(12)-ClB	119.3(3)
C(11)-C(12)-C(13)	120.8(3)	ClB-C(12)-C(13)	119.8(2)
C(12)-C(13)-H(13A)	122.2(27)	C(12)-C(13)-C(14)	119.4(3)
H(13A)-C(13)-C(14)	118.4(27)	C(9)-C(14)-C(13)	120.8(3)
C(9)-C(14)-H(14A)	116.9(18)	C(13)-C(14)-H(14A)	122.3(18)
N(01)-S(01)-N(02)	115.0(2)	S(01)-N(01)-S(03)	124.4(2)
N(02)-S(02)-N(03)	114.6(2)	S(01)-N(02)-S(02)	125.1(3)
N(01)-S(03)-N(03)	116.1(2)	S(02)-N(03)-S(03)	124.2(2)

Table C.10 Anisotropic displacement parameters, Å^2, for $[(p\text{-Cl.C}_6\text{H}_4\text{.CNSSN})_2\text{Cl}][\text{S}_3\text{N}_3]$.

N(1A)	0.033(1)	0.031(1)	0.036(1)	0.008(1)	0.014(1)	0.010(1)
S(1A)	0.033(1)	0.036(1)	0.037(1)	0.010(1)	0.017(1)	0.011(1)
S(2A)	0.030(1)	0.041(1)	0.035(1)	0.008(1)	0.008(1)	0.013(1)
N(2A)	0.034(1)	0.039(1)	0.036(1)	0.011(1)	0.012(1)	0.015(1)
C(1)	0.029(1)	0.032(2)	0.036(2)	0.013(1)	0.013(1)	0.014(1)
C(2)	0.030(1)	0.032(2)	0.040(2)	0.013(1)	0.012(1)	0.015(1)
C(3)	0.041(2)	0.037(2)	0.043(2)	0.007(1)	0.013(2)	0.013(1)
C(4)	0.039(2)	0.042(2)	0.056(2)	0.006(2)	0.008(2)	0.009(2)
C(5)	0.032(2)	0.032(2)	0.074(3)	0.010(1)	0.023(2)	0.017(2)
ClA	0.045(1)	0.043(1)	0.030(1)	0.003(1)	0.041(1)	0.019(1)
C(6)	0.044(2)	0.055(2)	0.065(3)	0.015(2)	0.030(2)	0.028(2)
C(7)	0.041(2)	0.054(2)	0.045(2)	0.014(2)	0.018(2)	0.021(2)
N(1B)	0.040(1)	0.033(1)	0.041(1)	0.008(1)	0.020(1)	0.011(1)

S(1B)	0.045(1)	0.038(1)	0.040(1)	0.011(1)	0.023(1)	0.011(1)
S(2B)	0.030(1)	0.040(1)	0.044(1)	0.011(1)	0.012(1)	0.015(1)
N(2B)	0.034(1)	0.039(1)	0.039(1)	0.012(1)	0.013(1)	0.017(1)
C(8)	0.035(2)	0.030(1)	0.038(2)	0.015(1)	0.016(1)	0.013(1)
C(9)	0.036(2)	0.032(2)	0.036(2)	0.016(1)	0.015(1)	0.013(1)
C(10)	0.041(2)	0.044(2)	0.034(2)	0.005(2)	0.008(1)	0.009(1)
C(11)	0.051(2)	0.050(2)	0.033(2)	0.007(2)	0.017(2)	0.012(2)
C(12)	0.040(2)	0.036(2)	0.041(2)	0.013(1)	0.019(1)	0.012(1)
ClB	0.051(1)	0.057(1)	0.057(1)	0.006(1)	0.028(1)	0.021(1)
C(13)	0.034(2)	0.038(2)	0.038(2)	0.010(1)	0.009(1)	0.006(1)
C(14)	0.040(2)	0.045(2)	0.029(2)	0.018(1)	0.012(1)	0.012(1)
Cl(3)	0.040(1)	0.066(1)	0.058(1)	0.002(1)	0.024(1)	0.013(1)
S(01)	0.069(1)	0.048(1)	0.037(1)	0.028(1)	0.002(1)	0.006(1)
N(01)	0.029(1)	0.032(2)	0.086(2)	0.003(1)	0.013(1)	0.012(2)
S(02)	0.030(1)	0.034(1)	0.080(1)	0.006(1)	0.010(1)	0.013(1)
N(02)	0.065(2)	0.058(2)	0.065(2)	0.038(2)	0.045(2)	0.040(2)
S(03)	0.065(1)	0.055(1)	0.070(1)	0.030(1)	0.045(1)	0.038(1)
N(03)	0.056(2)	0.055(2)	0.031(1)	0.030(2)	0.005(1)	0.004(1)

Table C.11 Hydrogen coordinates and isotropic displacement coefficients, Å^2, for [(p-Cl.C_6H_4.CNSSN)$_2$Cl][S_3N_3].

	x	y	z	U
H(3A)	0.9447(43)	1.1690(35)	0.9127(32)	0.045(10)
H(4A)	1.1658(57)	1.3431(46)	0.9470(42)	0.076(15)
H(6A)	1.0978(54)	1.2819(44)	0.6016(41)	0.078(15)
H(7A)	0.8695(40)	1.1178(33)	0.5646(32)	0.038(9)
H(10A)	-0.2090(41)	0.4003(33)	0.9744(30)	0.037(9)
H(11A)	-0.3740(44)	0.2659(36)	1.0362(34)	0.048(10)
H(13A)	-0.6717(45)	0.1063(36)	0.7022(32)	0.049(11)
H(14A)	-0.4957(36)	0.2435(29)	0.6398(28)	0.028(8)

Table C.12 Secondary contacts, Å, for [(*p*-Cl.C_6H_4.CNSSN)$_2$Cl][S_3N_3].

Chloride...Dithiadiazolylium Contacts			
Cl(3)...S(1a)	2.967(1)	Cl(3)...S(2b)	2.882(2)
Cl(3)...S(2a)	2.941(1)	Cl(3)...S′(1b)	3.226(2)
Cl(3)...S(1b)	3.039(1)	Cl(ba)...S(1a)	3.467(1)
Contacts involving the Trisulfur Trinitride anion			
Cl(1a)..S(03)	3.308(2)	S′(2b)...S(02)	2.916(2)
S(1a)...S(03)	2.940(2)	S′(1b)...N(02)	3.173(2)
S(2a)...S(01)	3.116(2)	S′(2b)...N(03)	3.230(2)
S′(1b)...S(01)	3.173(2)		

Atom S′ is related to S by the operation -x, -y+1, -z+1.

Table C.13 Atomic coordinates and equivalent isotropic displacement coefficients, Å^2, for [*p*-Cl.C_6H_4.CNSSN]$_6Cl_2$, see Figure 3.15.

	x	y	z	U(iso)
Cl(4)	0.8797(5)	-0.0787(2)	0.4158(2)	0.0456 *
Cl(11)	0.7387(5)	0.5188(2)	0.0614(2)	0.0546 *
Cl(21)	1.8203(5)	0.2522(2)	-0.1034(2)	0.0498 *
Cl(31)	0.7036(5)	0.7175(2)	0.2402(2)	0.0446 *
S(11)	0.0440(4)	0.1506(2)	0.3857(1)	0.0325 *
S(12)	0.3776(5)	0.0789(2)	0.3908(1)	0.0322 *
S(21)	0.9562(4)	0.0072(2)	0.2592(1)	0.0338 *
S(22)	1.2563(5)	-0.0834(2)	0.2762(2)	0.0364 *
S(31)	0.1395(5)	0.2791(2)	0.5288(2)	0.0354 *
S(32)	0.4793(5)	0.2139(2)	0.5196(2)	0.0354 *
N(11)	0.128(1)	0.2314(5)	0.3194(4)	0.026(2)
N(12)	0.494(1)	0.1485(6)	0.3203(5)	0.029(2)
N(21)	1.072(1)	0.0629(6)	0.1826(5)	0.031(2)
N(22)	1.410(1)	-0.0379(6)	0.2007(5)	0.035(2)
N(31)	0.202(1)	0.3751(6)	0.4755(5)	0.034(2)
N(32)	0.582(1)	0.3013(6)	0.4646(4)	0.029(2)
C(11)	0.353(2)	0.2227(7)	0.2915(6)	0.028(2)
C(12)	0.444(1)	0.2913(4)	0.2320(3)	0.027(2)
C(13)	0.3038(8)	0.3762(4)	0.2137(4)	0.029(2)
C(14)	0.392(1)	0.4463(4)	0.1597(4)	0.044(3)
C(15)	0.621(1)	0.4314(4)	0.1239(3)	0.037(3)
C(16)	0.7612(8)	0.3465(4)	0.1421(4)	0.034(3)
C(17)	0.6731(9)	0.2764(4)	0.1962(4)	0.026(2)
C(21)	1.297(2)	0.0371(7)	0.1601(5)	0.027(2)
C(22)	1.422(1)	0.0884(4)	0.0945(3)	0.025(2)
C(23)	1.3133(8)	0.1716(5)	0.0581(4)	0.032(2)
C(24)	1.435(1)	0.2213(4)	-0.0042(4)	0.043(3)
C(25)	1.665(1)	0.1879(5)	-0.0300(3)	0.034(3)
C(26)	1.7737(8)	0.1047(5)	0.0064(4)	0.042(3)
C(27)	1.652(1)	0.0549(4)	0.0687(4)	0.033(2)
C(31)	0.430(2)	0.3764(7)	0.4464(6)	0.030(2)

C(32)	0.497(1)	0.4585(4)	0.3949(3)	0.029(2)
C(33)	0.3358(8)	0.5398(4)	0.3861(4)	0.030(2)
C(34)	0.3982(9)	0.6194(4)	0.3373(4)	0.035(3)
C(35)	0.622(1)	0.6176(4)	0.2973(4)	0.035(3)
C(36)	0.7834(8)	0.5363(4)	0.3061(4)	0.035(3)
C(37)	0.7210(9)	0.4567(4)	0.3549(4)	0.034(3)

* U(eq) values for atoms refined with anisotropic displacement parameters.

Table C.14 Bond lengths, Å, for $[p\text{-Cl.C}_6\text{H}_4\text{.CNSSN}]_6\text{Cl}_2$.

Cl(11)-C(15)	1.712(5)	C(12)-C(17)	1.390 †
Cl(21)-C(25)	1.720(5)	C(13)-C(14)	1.390 †
Cl(31)-C(35)	1.721(5)	C(14)-C(15)	1.390 †
S(11)-S(12)	2.079(4)	C(15)-C(16)	1.390 †
S(11)-N(11)	1.615(8)	C(16)-C(17)	1.390 †
S(12)-N(12)	1.628(8)	C(21)-C(22)	1.46(1)
S(21)-S(22)	2.064(4)	C(22)-C(23)	1.390 †
S(21)-N(21)	1.594(8)	C(22)-C(27)	1.390 †
S(22)-N(22)	1.616(8)	C(23)-C(24)	1.390 †
S(31)-S(32)	2.066(4)	C(24)-C(25)	1.390 †
S(31)-N(31)	1.616(8)	C(25)-C(26)	1.390 †
S(32)-N(32)	1.612(8)	C(26)-C(27)	1.390 †
N(11)-C(11)	1.33(1)	C(31)-C(32)	1.45(1)
N(12)-C(11)	1.34(1)	C(32)-C(33)	1.390 †
N(21)-C(21)	1.33(1)	C(32)-C(37)	1.390 †
N(22)-C(21)	1.36(1)	C(33)-C(34)	1.390 †
N(31)-C(31)	1.36(1)	C(34)-C(35)	1.390 †
N(32)-C(31)	1.33(1)	C(35)-C(36)	1.390 †
C(11)-C(12)	1.44(1)	C(36)-C(37)	1.390 †
C(12)-C(13)	1.390 †		

† bonds are constrained equal to 1.39Å.

Table C.15 Bond angles, °, for [p-Cl.C_6H_4.CNSSN]$_6Cl_2$.

N(11)-S(11)-S(12)	94.2(3)	C(22)-C(21)-N(21)	121.4(9)
N(12)-S(12)-S(11)	93.4(3)	C(22)-C(21)-N(22)	120.0(8)
N(21)-S(21)-S(22)	94.0(3)	C(23)-C(22)-C(21)	120 †
N(22)-S(22)-S(21)	94.9(3)	C(27)-C(22)-C(21)	120 †
N(31)-S(31)-S(32)	94.6(3)	C(27)-C(22)-C(23)	120 †
N(32)-S(32)-S(31)	94.3(3)	C(24)-C(23)-C(22)	120 †
C(11)-N(11)-S(11)	117.1(7)	C(25)-C(24)-C(23)	120 †
C(11)-N(12)-S(12)	116.8(6)	C(24)-C(25)-Cl(21)	120.1(4)
C(21)-N(21)-S(21)	117.6(7)	C(26)-C(25)-Cl(21)	119.8(4)
C(21)-N(22)-S(22)	114.9(7)	C(26)-C(25)-C(24)	120 †
C(31)-N(31)-S(31)	115.7(8)	C(27)-C(26)-C(25)	120 †
C(31)-N(32)-S(32)	116.8(6)	C(26)-C(27)-C(22)	120 †
N(12)-C(11)-N(11)	118.3(8)	N(32)-C(31)-N(31)	118.7(8)
C(12)-C(11)-N(11)	121.1(9)	C(32)-C(31)-N(31)	118.7(9)
C(12)-C(11)-N(12)	120.6(8)	C(32)-C(31)-N(32)	122.5(8)
C(13)-C(12)-C(11)	120 †	C(33)-C(32)-C(31)	120 †
C(17)-C(12)-C(11)	120 †	C(37)-C(32)-C(31)	120 †
C(17)-C(12)-C(13)	120 †	C(37)-C(32)-C(33)	120 †
C(14)-C(13)-C(12)	120 †	C(34)-C(33)-C(32)	120 †
C(15)-C(14)-C(13)	120 †	C(35)-C(34)-C(33)	120 †
C(14)-C(15)-Cl(11)	121.1(4)	C(34)-C(35)-Cl(31)	120.1(4)
C(16)-C(15)-Cl(11)	118.9(4)	C(36)-C(35)-Cl(31)	119.8(4)
C(16)-C(15)-C(14)	120 †	C(36)-C(35)-C(34)	120 †
C(17)-C(16)-C(15)	120 †	C(37)-C(36)-C(35)	120 †
C(16)-C(17)-C(12)	120 †	C(36)-C(37)-C(32)	120 †
N(22)-C(21)-N(21)	118.6(8)		

† angles are constrained equal to 120°.

Table C.16 Anisotropic displacement coefficients, $Å^2$, for $[\text{p-Cl.C}_6\text{H}_4\text{.CNSSN}]_6\text{Cl}_2$.

	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Cl(4)	0.044(2)	0.045(2)	0.048(2)	0.007(1)	0.002(1)	-0.005(2)
Cl(11)	0.059(2)	0.052(2)	0.061(2)	0.011(2)	0.017(2)	-0.007(2)
Cl(21)	0.054(2)	0.062(2)	0.041(2)	0.001(1)	0.004(1)	-0.018(2)
Cl(31)	0.043(2)	0.047(2)	0.044(2)	0.001(1)	0.002(1)	-0.008(1)
S(11)	0.030(2)	0.038(2)	0.031(2)	-0.004(1)	-0.003(1)	-0.005(1)
S(12)	0.031(2)	0.041(2)	0.027(1)	-0.003(1)	-0.003(1)	-0.007(1)
S(21)	0.031(2)	0.041(2)	0.033(2)	-0.000(1)	-0.008(1)	-0.003(1)
S(22)	0.039(2)	0.040(2)	0.032(2)	-0.007(1)	-0.001(1)	-0.004(1)
S(31)	0.033(2)	0.046(2)	0.033(2)	-0.011(1)	0.002(1)	-0.008(1)
S(32)	0.034(2)	0.044(2)	0.032(2)	-0.007(1)	-0.002(1)	-0.007(1)

Table C.17 Hydrogen atom coordinates and isotropic displacement coefficients, $Å^2$, for $[p\text{-Cl.C}_6\text{H}_4\text{.CNSSN}]_6\text{Cl}_2$.

	x	y	z	U(iso)
H(131)	0.1465	0.3864	0.2383	0.0346
H(141)	0.2952	0.5047	0.1471	0.0526
H(161)	0.9186	0.3363	0.1175	0.0408
H(171)	0.7698	0.2180	0.2087	0.0315
H(231)	1.1550	0.1946	0.0758	0.0382
H(241)	1.3605	0.2786	-0.0292	0.0511
H(261)	1.9320	0.0816	-0.0113	0.0501
H(271)	1.7265	-0.0023	0.0937	0.0397
H(331)	0.1819	0.5411	0.4137	0.0363
H(341)	0.2872	0.6753	0.3313	0.0421
H(361)	0.9373	0.5350	0.2785	0.0415
H(371)	0.8320	0.4008	0.3609	0.0414

Table C.18 Secondary contacts, Å, for $[p\text{-Cl.C}_6\text{H}_4\text{.CNSSN}]_6\text{Cl}_2$.

S...Cl interactions within molecular unit			
Cl(4)...S'(21)	2.839(4)	Cl(4)...S'(11)	3.376(4)
Cl(4)...S(31)	2.882(4)	Cl(4)...S(12)	3.420(4)
Cl(4)...S(32)	3.009(3)	Cl(4)...S(11)	3.462(4)
Cl(4)...S(22')	3.033(4)	Cl(4)...S'(12)	3.728(4)
S...Cl interactions between molecular units			
Cl(4)..S''(12)	3.486(4)		
S....S perpendicular interactions			
S(11)...S(21)	3.019(3)	S(11)...S(31)	3.111(3)
S(12)...S(22)	3.130(3)	S(12)...S(32)	2.995(3)

Atom S' is related to S by the operation -x, -y, -z.

Atom S'' is related to S by the operation x-1, y, z.

Table C.19 Atomic coordinates and equivalent isotropic displacement coefficients, Å^2, for $[(p\text{-Cl.C}_6\text{H}_4\text{.CNSSN})_2\text{Br}][\text{Br}_3]$, see Figure 3.19.

	x	y	z	U[iso]
Br(2)	0.38832(14)	0.61486(10)	0.07772(3)	0.0298(3)
Br(1)	0.50671(15)	0.60980(11)	0.15089(3)	0.0340(3)
Br(3)	0.2512(2)	0.62797(13)	0.00584(3)	0.0456(3)
Br(4)	0.80989(14)	0.93591(10)	0.05466(3)	0.0284(3)
Cl(2)	1.0948(4)	0.9441(3)	0.21698(9)	0.0395(7)
N(1)	0.3293(11)	0.9908(8)	0.0801(2)	0.027(2)
S(1)	0.2586(4)	0.9980(3)	0.03468(8)	0.0285(6)
S(2)	0.3493(4)	1.1940(3)	0.02582(8)	0.0344(7)
N(2)	0.4298(12)	1.2164(8)	0.0708(2)	0.035(2)
C(1)	0.4145(13)	1.1058(10)	0.0957(3)	0.025(2)
C(2)	0.4875(12)	1.1123(10)	0.1372(3)	0.020(2)
C(3)	1.5120(13)	0.9896(10)	0.1587(3)	0.027(2)
H(3)	1.4814(13)	0.9028(10)	0.1461(3)	0.032
C(4)	0.9191(13)	0.4937(10)	0.3016(3)	0.030(2)
H(4)	0.8991(13)	0.4103(10)	0.2864(3)	0.036
C(5)	0.8798(12)	0.6226(11)	0.2844(3)	0.029(2)
Cl(1)	0.7977(4)	0.6272(3)	0.23424(7)	0.0359(6)
C(6)	0.9027(13)	0.7452(10)	0.3059(3)	0.027(2)
C(7)	0.5337(13)	0.2396(10)	0.1551(3)	0.024(2)
N(3)	1.0121(10)	0.5964(7)	0.1456(2)	0.023(2)
S(3)	0.9569(4)	0.7260(2)	0.11904(8)	0.0266(6)
S(4)	0.8757(3)	0.6169(3)	0.06926(7)	0.0255(6)
N(4)	0.9208(10)	0.4717(7)	0.0892(2)	0.021(2)
C(8)	0.9865(12)	0.4737(9)	0.1283(3)	0.021(2)
C(9)	1.0225(12)	0.3445(9)	0.1495(3)	0.018(2)
C(10)	1.0908(12)	0.3450(9)	0.1893(3)	0.024(2)
C(11)	1.1117(13)	1.2210(10)	0.2104(3)	0.028(2)
C(12)	1.0709(13)	1.0971(9)	0.1908(3)	0.029(2)
C(13)	1.0066(12)	1.0972(9)	0.1511(3)	0.029(2)
C(14)	0.9824(13)	1.2186(9)	0.1305(3)	0.030(3)

Table C.20 Bond lengths, Å, for $[(p\text{-Cl.C}_6\text{H}_4\text{.CNSSN})_2\text{Br}][\text{Br}_3]$.

Br(2)-Br(1)	2.543(2)	N(3) - S(3)	1.576(8)
Br(2) - Br(3)	2.547(2)	C(7) - C(6)	1.357(12)
Cl(2) - C(12)	1.725(9)	C(7) - C(2)	1.402(12)
N(1) - C(1)	1.361(11)	N(3) - C(8)	1.330(11)
N(1) - S(1)	1.573(8)	N(3) - S(3)	1.576(8)
S(1) - S(2)	2.030(4)	S(3) - S(4)	2.028(3)
S(2) - N(2)	1.594(9)	S(4) - N(4)	1.582(7)
N(2) - C(1)	1.362(12)	N(4) - C(8)	1.362(11)
C(1) - C(2)	1.455(12)	C(8) - C(9)	1.455(12)
C(2) - C(3)	1.394(12)	C(9) - C(10)	1.390(12)
C(3) - C(4)	1.390(13)	C(9) - C(14)	1.396(12)
C(3) - C(2)	1.394(12)	C(10) - C(11)	1.397(12)
C(4) - C(3)	1.390(13)	C(11) - C(12)	1.392(13)
C(4) - C(5)	1.397(13)	C(11) - C(10)	1.397(12)
C(5) - C(6)	1.393(13)	C(12) - C(13)	1.376(13)
C(5) - Cl(1)	1.746(9)	C(13) - C(14)	1.369(13)
C(6) - C(7)	1.357(12)	C(14) - C(9)	1.396(12)

Table C.21 Angles, Å, for $[(p\text{-Cl.C}_6\text{H}_4\text{.CNSSN})_2\text{Br}][\text{Br}_3]$.

Br(1) - Br(2) - Br(3)	176.37(6)	C(8) - N(3) - S(3)	116.3(6)
C(1) - N(1) - S(1)	116.8(7)	N(3) - S(3) - S(4)	95.6(3)
N(1) - S(1) - S(2)	95.2(3)	N(4) - S(4) - S(3)	94.3(3)
N(2) - S(2) - S(1)	95.4(3)	C(8) - N(4) - S(4)	116.3(6)
C(1) - N(2) - S(2)	115.4(7)	N(3) - C(8) - N(4)	117.5(8)
N(1) - C(1) - N(2)	117.2(9)	N(3) - C(8) - C(9)	122.7(8)
N(1) - C(1) - C(2)	122.2(9)	N(4) - C(8) - C(9)	119.8(8)
N(2) - C(1) - C(2)	120.6(9)	C(10) - C(9) - C(14)	119.3(8)
C(3) - C(2) - C(7)	120.7(8)	C(10) - C(9) - C(8)	120.4(8)
C(3) - C(2) - C(1)	118.7(9)	C(14) - C(9) - C(8)	120.2(8)
C(7) - C(2) - C(1)	120.5(9)	C(9) - C(10) - C(11)	120.1(8)
C(4) - C(3) - C(2)	119.6(9)	C(12) - C(11) - C(10)	119.3(9)
C(3) - C(4) - C(5)	118.1(9)	C(13) - C(12) - C(11)	120.2(8)
C(6) - C(5) - C(4)	122.3(9)	C(13) - C(12) - Cl(2)	120.5(7)

C(6) - C(5) - Cl(1)	119.8(8)	C(11) - C(12) - Cl(2)	119.3(8)
C(4) - C(5) - Cl(1)	117.9(8)	C(14) - C(13) - C(12)	120.7(9)
C(7) - C(6) - C(5)	119.0(9)	C(13) - C(14) - C(9)	120.3(10)
C(6) - C(7) - C(2)	120.2(9)		

Table C.22 Anisotropic displacement coefficients, Å^2, for $[(p\text{-Cl.C}_6\text{H}_4\text{.CNSSN})_2\text{Br}][\text{Br}_3]$.

	U11	U22	U33	U23	U13	U12
Br(2)	0.0236(5)	0.0273(5)	0.0384(6)	-0.0024(5)	0.0015(5)	-0.0023(5)
Br(1)	0.0350(6)	0.0257(6)	0.0405(7)	0.0010(5)	-0.0104(5)	-0.0007(5)
Br(3)	0.0467(7)	0.0604(8)	0.0296(6)	-0.0028(6)	0.0010(6)	-0.0130(6)
Br(4)	0.0316(6)	0.0285(5)	0.0245(5)	0.0007(5)	-0.0038(5)	0.0010(5)
Cl(2)	0.036(2)	0.030(1)	0.053(2)	0.017(1)	0.006(1)	0.003(1)
N(1)	0.022(5)	0.032(5)	0.028(5)	-0.005(4)	-0.001(4)	-0.004(4)
S(1)	0.028(2)	0.028(1)	0.029(2)	-0.002(1)	-0.002(1)	-0.007(1)
S(2)	0.052(2)	0.028(1)	0.023(1)	0.005(1)	-0.006(1)	-0.009(1)
N(2)	0.048(6)	0.031(5)	0.027(5)	0.004(4)	-0.001(5)	-0.004(4)
C(1)	0.024(5)	0.023(5)	0.029(6)	-0.004(5)	0.007(5)	0.000(5)
C(2)	0.019(5)	0.028(5)	0.013(5)	0.003(5)	0.009(4)	0.001(4)
C(3)	0.015(5)	0.031(6)	0.033(7)	-0.008(5)	-0.008(5)	-0.007(4)
C(4)	0.020(6)	0.028(6)	0.041(7)	-0.005(5)	0.001(5)	-0.002(4)
C(5)	0.017(5)	0.048(6)	0.023(5)	0.003(6)	0.006(4)	-0.005(5)
Cl(1)	0.044(2)	0.042(2)	0.022(2)	-0.001(1)	-0.000(1)	0.001(1)
C(6)	0.031(6)	0.030(6)	0.021(6)	-0.004(5)	-0.006(5)	0.003(5)
C(7)	0.022(6)	0.027(6)	0.023(6)	-0.002(4)	-0.003(5)	-0.001(4)
N(3)	0.028(5)	0.022(5)	0.019(5)	-0.005(4)	0.002(4)	0.001(4)
S(3)	0.038(2)	0.018(1)	0.024(1)	-0.001(1)	-0.003(1)	0.001(1)
S(4)	0.026(1)	0.024(1)	0.026(1)	0.001(1)	-0.003(1)	-0.001(1)
N(4)	0.019(4)	0.010(4)	0.033(5)	-0.002(3)	-0.001(4)	0.000(3)
C(8)	0.019(6)	0.026(6)	0.018(6)	-0.003(4)	-0.005(4)	0.001(4)
C(9)	0.014(5)	0.021(5)	0.019(5)	-0.002(4)	-0.002(4)	-0.003(4)
C(10)	0.020(5)	0.018(5)	0.033(6)	0.001(4)	-0.004(5)	0.004(4)
C(11)	0.020(6)	0.030(6)	0.034(6)	0.002(5)	-0.002(5)	0.002(5)
C(12)	0.023(5)	0.021(6)	0.043(7)	0.011(5)	0.008(5)	0.007(4)

C(13)	0.017(5)	0.016(5)	0.054(7)	-0.003(5)	0.004(5)	0.005(4)
C(14)	0.030(6)	0.019(5)	0.040(7)	0.001(5)	0.001(5)	0.000(4)

Table C.23 Hydrogen atomic coordinates and equivalent isotropic displacement coefficients, Å^2, for [(*p*-Cl.C_6H_4.CNSSN)$_2$Br][Br_3].

H(3)	1.481(1)	0.903(1)	0.1461(3)	0.032
H(4)	0.899(1)	0.410(1)	0.2864(3)	0.036
H(6)	0.874(1)	0.832(1)	0.2934(3)	0.033
H(7)	0.520(1)	0.323(1)	0.1397(3)	0.029
H(10)	1.124(1)	0.4307(9)	0.2022(3)	0.028
H(11)	1.154(1)	1.221(1)	0.2382(3)	0.034
H(13)	0.979(1)	1.0113(9)	0.1378(3)	0.035
H(14)	0.938(1)	1.2173(9)	0.1029(3)	0.036

Table C.24 Secondary contacts, Å, for [*p*-Cl.C_6H_4.CNSSN)$_2$Br][Br3].

Bromide contacts			
S(1)...Br(4)	3.059(3)	S(2)...Br(4)	3.127(3)
S(3)...Br(4)	3.103(3)	S(4)...Br(4)	3.160(3)
Br(4)...*S*′(1)	3.327(3)		
Tribromide contacts			
Br(2)...*S*″(3)	3.556(3)	Br(2)...*S*″(4)	3.631(3)
Br(3)...*S*″(4)	3.461(3)	Br(3)...*S*‴(4)	3.535(3)
Br(3)...*S*⁗(2)	3.511(3)		

Atom S′ is related to S by the operation x-1, y, z.

Atom S″ is related to S by the operation x+1, y, z.

Atom S‴ is related to S by the operation 1-x, 1-y, -z.

Atom S⁗ is related to S by the operation 1-x, 2-y, -z.

Appendix D

Crystallographic data for the complexes discussed in chapter 5

Table D.1 Atomic coordinates and equivalent isotropic displacement parameters, Å^2, for $[\mathrm{Pt(SNCPhNS}\text{-}S,S)(\mathrm{PPh_3})_2]\cdot\mathrm{MeCN}$, see Figure 5.2.

	x	y	z	U(eq)
Pt(1)	0.1934(1)	0.3246(1)	0.4274(1)	0.013(1)
S(1)	0.1548(2)	0.1922(2)	0.6033(2)	0.013(1)
S(2)	0.1291(2)	0.4847(2)	0.4098(2)	0.011(1)
P(1)	0.1269(2)	0.1823(2)	0.4562(2)	0.015(1)
P(2)	0.1395(2)	0.3776(2)	0.1476(1)	0.014(1)
N(1)	0.1381(6)	0.3096(6)	0.6573(5)	0.013(2)
N(2)	0.1954(5)	0.4575(6)	0.5102(5)	0.011(2)
C(1)	0.3001(6)	0.3759(6)	0.6093(6)	0.018(2)
C(11)	0.3817(6)	0.3585(7)	0.6786(6)	0.015(2)
C(12)	0.4438(7)	0.4276(8)	0.6415(7)	0.030(2)
C(13)	0.5263(8)	0.405(1)	0.7026(8)	0.039(2)
C(14)	0.5463(8)	0.315(1)	0.8018(8)	0.045(3)
C(15)	0.4839(9)	0.145(1)	0.8431(8)	0.046(3)
C(16)	0.4016(7)	0.1668(8)	0.7822(7)	0.032(2)
C(21)	0.0152(6)	0.1449(6)	0.3541(6)	0.016(2)
C(22)	0.0172(6)	0.1815(7)	0.1969(6)	0.013(2)
C(23)	-0.0497(7)	0.1399(8)	0.1169(7)	0.019(2)
C(24)	-0.1316(7)	0.3628(8)	0.1934(7)	0.035(2)
C(25)	-0.1355(7)	0.4279(8)	0.1504(6)	0.016(2)
C(26)	-0.0582(6)	0.3678(7)	0.3305(6)	0.014(2)
C(31)	0.0456(6)	0.1437(7)	0.5808(6)	0.019(2)
C(32)	-0.0733(7)	0.1082(7)	0.5889(6)	0.014(2)
C(33)	-0.1322(7)	0.1800(8)	0.6849(6)	0.019(2)
C(34)	-0.0728(8)	0.0885(8)	0.7746(7)	0.033(2)
C(35)	0.0472(8)	0.0138(8)	0.7692(7)	0.019(2)
C(36)	0.1049(7)	0.0511(7)	0.6737(6)	0.016(2)
C(41)	0.1386(6)	0.0189(7)	0.4644(6)	0.018(2)
C(42)	0.1103(7)	-0.0675(7)	0.4838(6)	0.015(2)
C(43)	0.1976(8)	-0.1828(7)	0.4890(7)	0.032(2)
C(44)	0.4119(7)	-0.2052(7)	0.4771(6)	0.015(2)
C(45)	0.4416(7)	-0.1130(8)	0.4617(7)	0.030(2)
C(46)	0.3549(7)	0.0047(7)	0.4542(6)	0.012(2)
C(51)	0.3918(6)	0.3443(6)	0.1112(6)	0.017(2)
C(52)	0.4334(6)	0.3503(7)	0.1090(6)	0.011(2)
C(53)	0.5468(7)	0.3326(7)	0.0789(6)	0.014(2)
C(54)	0.6190(7)	0.3096(8)	0.1493(7)	0.019(2)
C(55)	0.5787(7)	0.3010(9)	0.1513(7)	0.037(2)
C(56)	0.4657(7)	0.3193(8)	0.1812(7)	0.017(2)
C(61)	0.1600(6)	0.5460(6)	0.1752(5)	0.015(2)

C(62)	0.0420(6)	0.6032(7)	0.1996(6)	0.019(2)
C(63)	-0.0222(7)	0.7298(7)	0.1468(6)	0.013(2)
C(64)	0.0188(7)	0.8015(7)	0.0715(6)	0.014(2)
C(65)	0.1464(7)	0.7461(7)	0.0505(7)	0.030(2)
C(66)	0.1118(7)	0.6187(7)	0.1018(6)	0.017(2)
C(71)	0.1189(6)	0.3096(6)	0.1706(6)	0.015(2)
C(72)	0.1849(7)	0.1828(7)	0.1958(6)	0.014(2)
C(73)	0.1818(7)	0.1243(8)	0.1381(6)	0.015(2)
C(74)	0.1111(7)	0.1949(8)	0.0501(7)	0.030(2)
C(75)	0.1439(7)	0.3220(8)	0.0132(7)	0.030(2)
C(76)	0.1476(7)	0.3778(7)	0.0842(6)	0.012(2)
C(81)	0.6082(8)	0.0071(9)	0.1228(9)	0.048(3)
C(82)	0.6774(8)	0.0135(8)	0.1258(9)	0.038(2)
N(83)	0.7328(8)	0.0338(8)	0.0503(8)	0.054(2)

Table D.2 Bond lengths, Å, for [Pt(SNCPhNS-*S*,*S*)$(PPh_3)_2$]·MeCN.

Pt(1) - S(1)	2.294(2)	Pt(1) - S(2)	2.309(2)
Pt(1) - P(1)	2.311(2)	Pt(1) - P(2)	2.322(2)
S(1) - N(1)	1.628(7)	S(2) - N(2)	1.648(7)
P(1) - C(21)	1.823(8)	P(1) - C(31)	1.832(8)
P(1) - C(41)	1.818(7)	P(2) - C(51)	1.833(7)
P(2) - C(61)	1.832(7)	P(2) - C(71)	1.827(7)
N(1) - C(1)	1.36(1)	N(2) - C(1)	1.33(1)
C(1) - C(11)	1.49(1)	C(11) - C(12)	1.38(1)
C(11) - C(16)	1.41(1)	C(12) - C(13)	1.38(1)
C(13) - C(14)	1.36(1)	C(14) - C(15)	1.39(1)
C(15) - C(16)	1.38(1)	C(21) - C(26)	1.39(1)
C(21) - C(22)	1.39(1)	C(22) - C(23)	1.38(1)
C(23) - C(24)	1.39(1)	C(24) - C(25)	1.40(1)
C(25) - C(26)	1.38(1)	C(31) - C(32)	1.38(1)
C(31) - C(36)	1.40(1)	C(32) - C(33)	1.39(1)
C(33) - C(34)	1.36(1)	C(34) - C(35)	1.39(1)
C(35) - C(36)	1.37(1)	C(41) - C(46)	1.40(1)
C(41) - C(42)	1.41(1)	C(42) - C(43)	1.38(1)
C(43) - C(44)	1.37(1)	C(44) - C(45)	1.38(1)
C(45) - C(46)	1.40(1)	C(51) - C(56)	1.37(1)
C(51) - C(52)	1.40(1)	C(52) - C(53)	1.39(1)
C(53) - C(54)	1.37(1)	C(54) - C(55)	1.38(1)
C(55) - C(56)	1.38(1)	C(61) - C(66)	1.38(1)
C(61) - C(62)	1.40(1)	C(62) - C(63)	1.38(1)
C(63) - C(64)	1.38(1)	C(64) - C(65)	1.38(1)
C(65) - C(66)	1.39(1)	C(71) - C(76)	1.38(1)

C(71) - C(72)	1.39(1)	C(72) - C(73)	1.37(1)
C(73) - C(74)	1.40(1)	C(74) - C(75)	1.39(1)
C(75) - C(76)	1.39(1)	C(81) - C(82)	1.45(2)
C(82) - N(83)	1.14(1)		

Table D.3 Angles, °, for [Pt(SNCPhNS-*S*,*S*)(PPh$_3$)$_2$]·MeCN.

S(1) - Pt(1) - S(2)	86.76(8)	S(1) - Pt(1) - P(1)	87.82(7)
S(2) - Pt(1) - P(1)	170.21(7)	S(1) - Pt(1) - P(2)	172.16(7)
S(2) - Pt(1) - P(2)	85.43(7)	P(1) - Pt(1) - P(2)	100.01(7)
N(1) - S(1) - Pt(1)	115.2(2)	N(2) - S(2) - Pt(1)	115.1(2)
C(41) - P(1) - C(21)	109.3(3)	C(41) - P(1) - C(31)	101.6(3)
C(21) - P(1) - C(31)	104.2(3)	C(41) - P(1) - Pt(1)	115.4(3)
C(21) - P(1) - Pt(1)	110.0(2)	C(31) - P(1) - Pt(1)	115.4(2)
C(71) - P(2) - C(61)	104.3(3)	C(71) - P(2) - C(51)	98.3(3)
C(61) - P(2) - C(51)	104.2(3)	C(71) - P(2) - Pt(1)	122.2(2)
C(61) - P(2) - Pt(1)	110.1(2)	C(51) - P(2) - Pt(1)	115.7(2)
C(1) - N(1) - S(1)	128.4(5)	C(1) - N(2) - S(2)	128.0(6)
N(2) - C(1) - N(1)	129.0(7)	N(2) - C(1) - C(11)	115.5(7)
N(1) - C(1) - C(11)	115.4(7)	C(12) - C(11) - C(16)	118.1(8)
C(12) - C(11) - C(1)	121.2(8)	C(16) - C(11) - C(1)	120.6(7)
C(13) - C(12) - C(11)	121.5(9)	C(14) - C(13) - C(12)	119.9(9)
C(13) - C(14) - C(15)	120.5(9)	C(16) - C(15) - C(14)	119.9(9)
C(15) - C(16) - C(11)	120.1(9)	C(26) - C(21) - C(22)	118.6(7)
C(26) - C(21) - P(1)	115.9(6)	C(22) - C(21) - P(1)	125.4(6)
C(23) - C(22) - C(21)	120.8(7)	C(22) - C(23) - C(24)	120.0(8)
C(23) - C(24) - C(25)	120.1(8)	C(26) - C(25) - C(24)	119.1(7)
C(25) - C(26) - C(21)	121.3(7)	C(32) - C(31) - C(36)	117.6(7)
C(32) - C(31) - P(1)	122.6(6)	C(36) - C(31) - P(1)	119.7(6)
C(31) - C(32) - C(33)	121.3(7)	C(34) - C(33) - C(32)	120.2(8)
C(33) - C(34) - C(35)	119.7(8)	C(36) - C(35) - C(34)	119.9(8)
C(35) - C(36) - C(31)	121.3(8)	C(46) - C(41) - C(42)	119.1(7)
C(46) - C(41) - P(1)	119.5(6)	C(42) - C(41) - P(1)	121.3(6)
C(43) - C(42) - C(41)	119.7(8)	C(44) - C(43) - C(42)	120.8(8)
C(43) - C(44) - C(45)	120.3(7)	C(44) - C(45) - C(46)	119.8(7)
C(45) - C(46) - C(41)	120.2(7)	C(56) - C(51) - C(52)	118.5(7)
C(56) - C(51) - P(2)	121.2(6)	C(52) - C(51) - P(2)	120.3(6)
C(53) - C(52) - C(51)	120.6(7)	C(54) - C(53) - C(52)	120.2(7)
C(53) - C(54) - C(55)	119.2(8)	C(56) - C(55) - C(54)	120.6(8)
C(51) - C(56) - C(55)	120.8(8)	C(66) - C(61) - C(62)	119.0(6)
C(66) - C(61) - P(2)	123.3(6)	C(62) - C(61) - P(2)	117.7(5)
C(63) - C(62) - C(61)	120.0(7)	C(64) - C(63) - C(62)	120.9(7)
C(63) - C(64) - C(65)	119.2(7)	C(64) - C(65) - C(66)	120.5(7)

C(61) - C(66) - C(65)	120.2(7)	C(76) - C(71) - C(72)	117.9(7)
C(76) - C(71) - P(2)	124.1(5)	C(72) - C(71) - P(2)	117.8(6)
C(73) - C(72) - C(71)	122.3(8)	C(72) - C(73) - C(74)	119.0(8)
C(75) - C(74) - C(73)	119.8(8)	C(76) - C(75) - C(74)	119.7(8)
C(71) - C(76) - C(75)	121.2(7)	N(83) - C(82) - C(81)	178.6(9)

Table D.4 Anisotropic displacement parameters, Å^2, for [Pt(SNCPhNS-*S*,*S*)(PPh$_3$)$_2$]·MeCN.

	U11	U22	U33	U23	U13	U12
Pt(1)	0.014(1)	0.012(1)	0.013(1)	-0.005(1)	0.000(1)	-0.006(1)
S(1)	0.029(1)	0.035(1)	0.014(1)	-0.009(1)	0.005(1)	-0.023(1)
S(2)	0.031(1)	0.014(1)	0.020(1)	-0.004(1)	-0.003(1)	-0.013(1)
P(1)	0.014(1)	0.013(1)	0.019(1)	-0.005(1)	-0.002(1)	-0.006(1)
P(2)	0.013(1)	0.014(1)	0.015(1)	-0.004(1)	-0.001(1)	-0.006(1)
N(1)	0.032(4)	0.023(4)	0.013(3)	-0.004(3)	-0.002(3)	-0.014(3)
N(2)	0.025(4)	0.016(3)	0.025(4)	-0.009(3)	0.001(3)	-0.009(3)
C(1)	0.016(4)	0.010(4)	0.024(4)	-0.010(3)	0.000(3)	0.000(3)
C(11)	0.018(4)	0.028(4)	0.030(5)	-0.020(4)	0.003(4)	-0.005(4)
C(12)	0.028(5)	0.040(5)	0.034(5)	-0.027(4)	0.007(4)	-0.016(4)
C(13)	0.033(5)	0.069(7)	0.046(6)	-0.042(6)	0.014(4)	-0.033(5)
C(14)	0.029(5)	0.069(7)	0.052(7)	-0.034(6)	-0.004(5)	-0.020(5)
C(15)	0.052(6)	0.055(6)	0.029(5)	-0.016(5)	-0.017(5)	-0.017(5)
C(16)	0.037(5)	0.039(5)	0.025(5)	-0.015(4)	0.000(4)	-0.019(4)
C(21)	0.019(4)	0.014(4)	0.011(4)	0.000(3)	0.003(3)	-0.010(3)
C(22)	0.019(4)	0.021(4)	0.034(5)	-0.012(4)	0.002(4)	-0.012(3)
C(23)	0.029(5)	0.031(5)	0.031(5)	-0.006(4)	-0.014(4)	-0.016(4)
C(24)	0.030(5)	0.042(6)	0.032(5)	-0.005(4)	-0.011(4)	-0.019(4)
C(25)	0.018(4)	0.024(4)	0.024(5)	-0.004(4)	-0.002(3)	-0.003(4)
C(26)	0.021(4)	0.025(4)	0.025(5)	-0.015(4)	0.007(4)	-0.009(4)
C(31)	0.024(4)	0.016(4)	0.024(4)	-0.008(3)	-0.001(3)	-0.014(3)
C(32)	0.026(5)	0.016(4)	0.024(5)	-0.006(3)	-0.004(4)	-0.007(4)
C(33)	0.025(5)	0.032(5)	0.024(5)	-0.013(4)	0.012(4)	-0.013(4)
C(34)	0.048(6)	0.037(5)	0.028(5)	-0.017(4)	0.010(4)	-0.031(5)
C(35)	0.042(5)	0.031(5)	0.022(5)	-0.006(4)	-0.004(4)	-0.025(4)
C(36)	0.027(4)	0.022(4)	0.023(5)	0.000(4)	-0.008(4)	-0.012(4)
C(41)	0.020(4)	0.017(4)	0.013(4)	-0.005(3)	-0.003(3)	-0.005(3)
C(42)	0.023(4)	0.016(4)	0.029(5)	-0.003(4)	-0.012(4)	-0.005(4)
C(43)	0.039(5)	0.020(4)	0.038(5)	-0.013(4)	-0.010(4)	-0.008(4)
C(44)	0.027(5)	0.013(4)	0.022(4)	-0.010(3)	-0.004(3)	0.007(4)
C(45)	0.011(4)	0.033(5)	0.029(5)	-0.014(4)	-0.007(3)	0.006(4)
C(46)	0.027(4)	0.023(4)	0.017(4)	-0.004(3)	-0.003(3)	-0.014(4)
C(51)	0.020(4)	0.013(4)	0.019(4)	-0.005(3)	0.000(3)	-0.009(3)

C(52)	0.020(4)	0.021(4)	0.018(4)	-0.008(3)	0.001(3)	-0.006(3)
C(53)	0.025(4)	0.025(4)	0.024(4)	-0.013(4)	0.008(4)	-0.014(4)
C(54)	0.027(5)	0.035(5)	0.028(5)	-0.011(4)	0.008(4)	-0.020(4)
C(55)	0.023(5)	0.057(6)	0.039(6)	-0.028(5)	0.001(4)	-0.015(4)
C(56)	0.020(4)	0.033(5)	0.025(5)	-0.015(4)	-0.003(4)	-0.004(4)
C(61)	0.023(4)	0.008(4)	0.08(4)	0.003(3)	-0.001(3)	-0.009(3)
C(62)	0.017(4)	0.021(4)	0.012(4)	-0.003(3)	-0.002(3)	-0.005(3)
C(63)	0.022(4)	0.021(4)	0.020(4)	-0.008(4)	-0.004(3)	-0.005(4)
C(64)	0.030(5)	0.014(4)	0.018(4)	-0.003(3)	-0.004(3)	-0.003(4)
C(65)	0.028(5)	0.023(5)	0.028(5)	-0.003(4)	0.010(4)	-0.013(4)
C(66)	0.017(4)	0.023(4)	0.027(5)	-0.006(4)	0.004(3)	-0.005(4)
C(71)	0.020(4)	0.016(4)	0.016(4)	-0.006(3)	0.001(3)	-0.014(3)
C(72)	0.022(4)	0.025(4)	0.021(4)	-0.006(4)	0.000(3)	-0.010(4)
C(73)	0.024(4)	0.025(4)	0.026(5)	-0.015(4)	-0.002(4)	-0.006(4)
C(74)	0.032(5)	0.032(5)	0.032(5)	-0.021(4)	-0.004(4)	-0.008(4)
C(75)	0.025(4)	0.039(5)	0.024(5)	-0.017(4)	-0.007(4)	-0.006(4)
C(76)	0.023(4)	0.020(4)	0.025(4)	-0.009(4)	0.001(3)	-0.010(3)
C(81)	0.032(5)	0.031(5)	0.069(8)	-0.014(5)	-0.001(5)	-0.009(4)
C(82)	0.024(5)	0.018(5)	0.063(7)	-0.016(5)	-0.008(5)	0.001(4)
N(83)	0.059(6)	0.034(5)	0.069(7)	-0.026(5)	0.006(5)	-0.017(5)

Table D.5 Hydrogen coordinates and isotropic displacement parameters, Å^2, for [Pt(SNCPhNS-*S*,*S*)(PPh$_3$)$_2$]·MeCN.

	x	y	z	U(eq)
H(12A)	0.4282(7)	0.4934(8)	0.5722(7)	0.036
H(13A)	0.5684(8)	0.454(1)	0.6760(8)	0.047
H(14A)	0.6057(8)	0.297(1)	0.8427(8)	0.054
H(15A)	0.4975(9)	0.182(1)	0.9138(8)	0.055
H(16A)	0.3571(7)	0.2202(8)	0.8099(7)	0.038
H(22A)	0.0834(6)	0.0963(7)	0.3130(6)	0.027
H(23A)	-0.0466(7)	0.1950(8)	0.1780(7)	0.035
H(24A)	-0.1851(7)	0.4035(8)	0.1376(7)	0.042
H(25A)	-0.1921(7)	0.5130(8)	0.2340(6)	0.031
H(26A)	-0.0619(6)	0.4117(7)	0.3707(6)	0.028
H(32A)	-0.1165(7)	0.2744(7)	0.5271(6)	0.028
H(33A)	-0.2151(7)	0.2242(8)	0.6884(6)	0.034
H(34A)	-0.1136(8)	0.0699(8)	0.8413(7)	0.039
H(35A)	0.0896(8)	-0.0408(8)	0.8319(7)	0.035
H(36A)	0.1877(7)	0.0056(7)	0.6708(6)	0.031
H(42A)	0.1308(7)	-0.0532(7)	0.4944(6)	0.030
H(43A)	0.2785(8)	-0.2475(7)	0.4991(7)	0.038
H(44A)	0.4718(7)	-0.2850(7)	0.4793(6)	0.030

H(45A)	0.5216(7)	-0.1301(8)	0.4567(7)	0.036
H(46A)	0.3749(7)	0.0694(7)	0.4425(6)	0.026
H(52A)	0.3828(6)	0.3669(7)	0.0596(6)	0.025
H(53A)	0.5747(7)	0.3355(7)	0.0088(6)	0.029
H(54A)	0.6958(7)	0.3024(8)	0.1269(7)	0.035
H(55A)	0.6300(7)	0.2804(9)	0.3021(7)	0.045
H(56A)	0.4376(7)	0.3153(8)	0.3516(7)	0.033
H(62A)	0.0062(6)	0.5541(7)	0.2532(6)	0.023
H(63A)	-0.1034(7)	0.7680(7)	0.1635(6)	0.027
H(64A)	-0.0169(7)	0.8889(7)	0.0334(6)	0.029
H(65A)	0.1835(7)	0.7962(7)	0.0009(7)	0.036
H(66A)	0.2930(7)	0.5806(7)	0.0854(6)	0.032
H(72A)	0.3348(7)	0.1348(7)	0.2555(6)	0.029
H(73A)	0.3256(7)	0.0357(8)	0.1597(6)	0.031
H(74A)	0.2125(7)	0.1569(8)	0.0055(7)	0.037
H(75A)	0.0918(7)	0.3702(8)	-0.0348(7)	0.035
H(76A)	0.1019(7)	0.4658(7)	0.0652(6)	0.027
H(81C)	0.6338(8)	0.0202(9)	0.2728(9)	0.058
H(81B)	0.5266(8)	0.0597(9)	0.2129(9)	0.058
H(81A)	0.6307(8)	-0.0803(9)	0.2467(9)	0.058

Table D.6 Atomic coordinates and equivalent isotropic displacement parameters, Å^2, for [Pt(SNCPhNS-*S*,*S*)(dppe)], see Figure 5.3.

	x	y	z	U(eq)
Pt(1)	0.20380(7)	0.98334(7)	0.15767(4)	0.0274(3)
S(1)	0.1859(6)	1.1681(5)	0.1734(3)	0.040(2)
N(1)	0.417(2)	1.126(2)	0.0881(9)	0.036(5)
C(1)	0.361(2)	1.218(2)	0.094(1)	0.037(6)
C(11)	0.414(2)	1.314(2)	0.058(1)	0.044(6)
C(12)	0.353(3)	1.404(2)	0.043(1)	0.053(7)
C(13)	-0.099()	1.017(3)	-0.009(1)	0.055(7)
C(14)	0.015(3)	1.019(3)	0.011(1)	0.063(8)
C(15)	0.075(3)	1.107(3)	-0.004(1)	0.053(7)
C(16)	0.533(3)	1.306(3)	0.038(1)	0.058(8)
N(2)	0.270(2)	1.248(2)	0.1296(9)	0.037(5)
S(2)	0.3851(5)	1.0055(5)	0.1166(3)	0.036(1)
P(1)	0.0342(5)	0.9425(5)	0.2097(3)	0.028(1)
C(21)	-0.102(2)	1.007(2)	0.1902(9)	0.033(5)
C(22)	-0.205(2)	0.970(2)	0.212(1)	0.044(6)
C(23)	0.691(2)	1.016(3)	0.197(12	0.054(7)
C(24)	0.691(3)	1.109(2)	0.159(1)	0.056(7)
C(25)	0.797(3)	1.148(3)	0.138(1)	0.057(7)
C(26)	-0.102(2)	1.101(2)	0.151(1)	0.037(6)
C(31)	0.056(2)	0.948(2)	0.296(1)	0.035(6)
C(32)	-0.027(2)	0.907(2)	0.339(1)	0.041(6)
C(33)	-0.003(2)	0.404(2)	0.096(1)	0.049(7)
C(34)	0.395(2)	1.066(2)	-0.074(1)	0.046(7)
C(35)	0.184(2)	0.976(2)	0.386(1)	0.050(6)
C(36)	0.162(2)	0.976(3)	0.320(1)	0.058(7)
C(2)	0.009(2)	0.800(2)	0.195(1)	0.030(5)
C(3)	0.118(2)	0.736(2)	0.196(1)	0.038(6)
P(2)	0.2240(5)	0.7993(5)	0.1449(3)	0.030(1)
C(41)	0.361(2)	0.747(2)	0.169(1)	0.036(6)
C(42)	0.427(2)	0.796(2)	0.217(1)	0.043(6)
C(43)	0.526(3)	0.741(3)	0.239(1)	0.053(8)
C(44)	0.558(3)	0.648(3)	0.213(1)	0.060(8)
C(45)	0.498(3)	0.589(3)	0.167(2)	0.08(1)
C(46)	0.400(2)	0.642(2)	0.144(1)	0.044(7)
C(51)	0.198(2)	0.747(2)	0.063(1)	0.031(5)
C(52)	0.111(3)	0.673(3)	0.052(1)	0.058(8)
C(53)	0.090(3)	0.637(4)	-0.012(2)	0.09(1)
C(54)	0.150(2)	0.681(3)	-0.060(1)	0.052(7)
C(55)	0.232(3)	0.764(3)	-0.047(2)	0.068(9)
C(56)	0.257(3)	0.794(3)	0.015(1)	0.061(8)

Table D.7 Bond lengths, Å, for [Pt(SNCPhNS-*S*,*S*)(dppe)]

Pt(1) - P(2)	2.285(6)	Pt(1) - S(2)	2.293(6)
Pt(1) - S(1)	2.300(7)	Pt(1) - P(1)	2.308(6)
S(1) - N(2)	1.66(2)	N(1) - C(1)	1.31(3)
N(1) - S(2)	1.64(2)	C(1) - N(2)	1.34(3)
C(1) - C(11)	1.52(3)	C(11) - C(12)	1.36(4)
C(11) - C(16)	1.44(4)	C(12) - C(13)	1.33(4)
C(13) - C(12)	1.33(4)	C(13) - C(14)	1.38(4)
C(14) - C(15)	1.32(4)	C(15) - C(16)	1.37(4)
C(16) - C(15)	1.37(4)	P(1) - C(2)	1.81(2)
P(1) - C(21)	1.82(2)	P(1) - C(31)	1.83(2)
C(21) - C(22)	1.36(3)	C(21) - C(26)	1.41(3)
C(22) - C(23)	1.37(3)	C(23) - C(22)	1.37(3)
C(23) - C(24)	1.40(4)	C(24) - C(25)	1.39(4)
C(25) - C(26)	1.33(4)	C(26) - C(25)	1.33(4)
C(31) - C(36)	1.38(3)	C(31) - C(32)	1.41(3)
C(32) - C(33)	1.41(4)	C(33) - C(34)	1.33(4)
C(33) - C(32)	1.41(4)	C(34) - C(33)	1.33(4)
C(34) - C(35)	1.35(3)	C(35) - C(34)	1.35(3)
C(35) - C(36)	1.40(4)	C(2) - C(3)	1.49(3)
C(3) - P(2)	1.82(2)	P(2) - C(41)	1.79(3)
P(2) - C(51)	1.87(2)	C(41) - C(42)	1.37(3)
C(41) - C(46)	1.46(4)	C(42) - C(43)	1.47(4)
C(43) - C(44)	1.31(4)	C(44) - C(45)	1.39(4)
C(45) - C(46)	1.41(4)	C(51) - C(56)	1.35(4)
C(51) - C(52)	1.38(4)	C(52) - C(53)	1.44(4)
C(53) - C(54)	1.34(4)	C(54) - C(55)	1.42(4)
C(55) - C(56)	1.39(4)		

Table D.8 Angles, °, for [Pt(SNCPhNS-*S*,*S*)(dppe)]

P(2)-Pt(1)-S(2)	88.7(2)	P(2)-Pt(1)-S(1)	178.3(2)
S(2)-Pt(1)-S(1)	91.2(2)	P(2)-Pt(1)-P(1)	85.9(2)
S(2)-Pt(1)-P(1)	171.2(2)	S(1)-Pt(1)-P(1)	93.9(2)
N(2)-S(1)-Pt(1)	116.5(8)	C(1)-N(1)-S(2)	130(2)
N(1)-C(1)-N(2)	132(2)	N(1)-C(1)-C(11)	115(2)
N(2)-C(1)-C(11)	113(2)	C(12)-C(11)-C(16)	119(3)
C(12)-C(11)-C(1)	122(3)	C(16)-C(11)-C(1)	119(3)
C(13)-C(12)-C(11)	120.3)	C(12)-C(13)-C(14)	123(3)
C(15)-C(14)-C(13)	117(3)	C(14)-C(15)-C(16)	124(3)
C(15)-C(16)-C(11)	116(3)	C(1)-N(2)-S(1)	128(1)

N(1)-S(2)-Pt(1)	116.7(8)	C(2)-P(1)-C(21)	104(1)
C(2)-P(1)-C(31)	103(1)	C(21)-P(1)-C(31)	109(1)
C(2)-P(1)-Pt(1)	105.5(8)	C(21)-P(1)-Pt(1)	122.9(8)
C(31)-P(1)-Pt(1)	110.1(8)	C(22)-C(21)-C(26)	118(2)
C(22)-C(21)-P(1)	123(2)	C(26)-C(21)-P(1)	119(2)
C(21)-C(22)-C(23)	124(2)	C(22)-C(23)-C(24)	118(3)
C(25)-C(24)-C(23)	117(3)	C(26)-C(25)-C(24)	125(3)
C(25)-C(26)-C(21)	118(2)	C(36)-C(31)-C(32)	117(2)
C(36)-C(31)-P(1)	120(2)	C(32)-C(31)-P(1)	122(2)
C(31)-C(32)-C(33)	118(3)	C(34)-C(33)-C(32)	123(3)
C(33)-C(34)-C(35)	120(3)	C(34)-C(35)-C(36)	120(3)
C(31)-C(36)-C(35)	122(3)	C(3)-C(2)-P(1)	112(2)
C(2)-C(3)-P(2)	110(2)	C(41)-P(2)-C(3)	106(1)
C(41)-P(2)-C(51)	106(1)	C(3)-P(2)-C(51)	107(1)
C(41)-P(2)-Pt(1)	114.4(9)	C(3)-P(2)-Pt(1)	106.6(9)
C(51)-P(2)-Pt(1)	115.7(7)	C(42)-C(41)-C(46)	120(2)
C(42)-C(41)-P(2)	120(2)	C(46)-C(41)-P(2)	119(2)
C(41)-C(42)-C(43)	116(3)	C(44)-C(43)-C(42)	121(3)
C(43)-C(44)-C(45)	126(4)	C(44)-C(45)-C(46)	114(3)
C(45)-C(46)-C(41)	122(3)	C(56)-C(51)-C(52)	123(3)
C(56)-C(51)-P(2)	117(2)	C(52)-C(51)-P(2)	120(2)
C(51)-C(52)-C(53)	118(3)	C(54)-C(53)-C(52)	120(4)
C(53-C(54)-C(55)	119(3)	C(56)-C(55)-C(54)	121(3)
C(51)-C(56)-C(55)	119(3)		

Table D.9 Anisotropic displacement parameters, Å^2, for [Pt(SNCPhNS-*S,S*)(dppe)]

	U11	U22	U33	U23	U13	U12
Pt1	0.0265(4)	0.0283(4)	0.0275(4)	0.0007(4)	0.0008(3)	-0.0017(4)
S1	0.041(4)	0.030(3)	0.050(4)	-0.004(3)	0.014(3)	-0.005(3)
S2	0.031(3)	0.031(4)	0.047(3)	0.001(3)	0.006(2)	0.002(3)
P1	0.025(3)	0.032(3)	0.027(3)	0.000(3)	0.001(2)	0.001(3)
P2	0.030(3)	0.025(3)	0.034(3)	-0.002(2)	0.002(3)	0.003(3)

Table D.10 Hydrogen coordinates, Å, and isotropic displacement parameters, Å^2, for [Pt(SNCPhNS-*S*,*S*)(dppe)].

	x	y	z	U(eq)
H12	0.2769(26)	1.4108(24)	0.0559(12)	0.063
H13	-0.1435(23)	0.9568(28)	0.0028(12)	0.066
H14	0.0471(25)	0.9615(30)	0.0334(13)	0.076
H15	0.1519(26)	1.1088(25)	0.0083(13)	0.064
H16	0.5773(26)	1.2448(27)	0.0462(13)	0.070
H22	-0.2050(22)	0.9096(21)	0.2390(11)	0.052
H23	0.6226(24)	0.9864(25)	0.2122(12)	0.065
H24	0.6231(26)	1.1436(23)	0.1471(13)	0.067
H25	0.7978(27)	1.2113(25)	0.1139(13)	0.069
H26	-0.0339(21)	1.1283(20)	0.1345(12)	0.044
H32	-0.0983(23)	0.8831(20)	0.3248(12)	0.049
H33	0.0521(24)	0.3788(24)	0.0672(13)	0.059
H34	0.3785(22)	1.0730(23)	-0.0307(12)	0.055
H35	0.2524(22)	1.0048(23)	0.4016(12)	0.060
H36	0.2208(24)	0.9957(26)	0.2923(13)	0.069
H2A	-0.0434(19)	0.7711(19)	0.2267(10)	0.036
H2B	-0.0269(19)	0.7909(19)	0.1534(10)	0.036
H3A	0.1036(21)	0.6615(21)	0.1823(11)	0.046
H3B	0.1472(21)	0.7325(21)	0.2397(11)	0.046
H42	0.3957(22)	0.8605(24)	0.2360(12)	0.051
H43	0.5710(25)	0.7719(25)	0.2704(13)	0.063
H44	0.6274(28)	0.6187(27)	0.2273(14)	0.072
H45	0.5210(31)	0.5203(32)	0.1534(16)	0.096
H46	0.3581(23)	0.6097(22)	0.1108(12)	0.052
H52	0.0662(28)	0.6468(27)	0.0859(14)	0.070
H53	0.0343(34)	0.5845(35)	-0.0199(17)	0.102
H54	0.1386(24)	0.6565(25)	-0.1017(14)	0.062
H55	0.2702(28)	0.7978(28)	-0.0808(15)	0.082
H56	0.3126(27)	0.8466(28)	0.0237(14)	0.073

Table D.11 Atomic coordinates and equivalent isotropic displacement parameters, Å^2, for [Pd(SNCPhNS-*S*,*S*)(dppe)], see Figure 5.4.

	x	y	z	U(eq)
Pd(1)	0.2033(1)	0.9885(1)	0.1561(1)	0.018(1)
S(1)	0.1894(3)	1.1730(2)	0.1728(1)	0.023(1)
N(1)	0.2699(8)	1.2524(7)	0.1291(4)	0.027(2)
C(1)	0.363(1)	1.2263(9)	0.0930(5)	0.024(2)
C(11)	0.4134(9)	1.3183(9)	0.0549(5)	0.027(3)
C(12)	0.0529(1)	1.312(1)	0.0349(5)	0.037(3)
C(13)	0.0577(1)	1.3971)	0.0021(5)	0.038(3)
C(14)	0.0513(1)	1.491(1)	-0.0130(5)	0.048(4)
C(15)	0.0397(1)	1.496(1)	0.0034(5)	0.039(3)
C(16)	0.351(1)	1.410(1)	0.0392(5)	0.036(3)
N(2)	0.4171(7)	1.1311(7)	0.0875(4)	0.023(2)
S(2)	0.3851(2)	1.0122(2)	0.1176(1)	0.025(1)
P(1)	0.0313(2)	0.9463(2)	0.2086(1)	0.021(1)
C(21)	-0.1038(8)	1.0128(9)	0.1905(4)	0.024(2)
C(22)	-0.1070(9)	1.1055(9)	0.1530(6)	0.030(2)
C(23)	-0.212(1)	1.1539(8)	0.1370(5)	0.033(3)
C(24)	-0.311(1)	1.1116(9)	0.1590(6)	0.037(3)
C(25)	-0.312(1)	1.019(1)	0.1973(5)	0.038(3)
C(26)	-0.2088(9)	0.9674(8)	0.2116(5)	0.033(2)
C(31)	0.0546(9)	0.9496(8)	0.2964(5)	0.023(2)
C(32)	0.161(1)	0.980(1)	0.3185(5)	0.037(3)
C(33)	0.187(1)	0.975(1)	0.3841(5)	0.039(3)
C(34)	0.105(1)	0.935(1)	0.4260(5)	0.037(3)
C(35)	-0.000(1)	0.907(1)	0.4046(5)	0.036(3)
C(36)	-0.0281(9)	0.9110(8)	0.3392(5)	0.030(2)
C(2)	0.0029(8)	0.8000(8)	0.1945(5)	0.021(2)
C(3)	0.1164(9)	0.7380(8)	0.1964(5)	0.027(2)
P(2)	0.2230(2)	0.8019(2)	0.1446(1)	0.025(1)
C(41)	0.195(1)	0.7497(8)	0.0634(4)	0.021(2)
C(42)	0.115(1)	0.6690(9)	0.0509(6)	0.037(3)
C(43)	0.091(1)	0.635(1)	-0.0122(6)	0.044(4)
C(44)	0.151(1)	0.682(1)	-0.0601(6)	0.044(4)
C(45)	0.232(1)	0.7622(9)	-0.0507(5)	0.044(4)
C(46)	0.256(1)	0.7960(9)	0.0117(5)	0.038(3)
C(51)	0.3598(9)	0.7423(9)	0.1702(5)	0.027(3)
C(52)	0.397(1)	0.6441(9)	0.1449(6)	0.037(3)
C(53)	0.499(1)	0.599(1)	0.1663(6)	0.056(4)
C(54)	0.560(1)	0.650(1)	0.2148(6)	0.047(4)
C(55)	0.526(1)	0.748(1)	0.2401(6)	0.039(3)
C(56)	0.425(1)	0.794(1)	0.2169(5)	0.035(3)

Table D.12 Bond lengths, Å, for [Pd(SNCPhNS-*S*,*S*)(dppe)].

Pd(1) - S(2)	2.285(3)	Pd(1) - S(1)	2.294(3)
Pd(1) - P(2)	2.312(3)	Pd(1) - P(1)	2.339(3)
S(1) - N(1)	1.629(9)	N(1) - C(1)	1.36(1)
C(1) - N(2)	1.33(1)	C(1) - C(11)	1.50(1)
C(11) - C(16)	1.38(2)	C(11) - C(12)	1.42(2)
C(12) - C(13)	1.36(2)	C(13) - C(14)	1.41(2)
C(14) - C(15)	1.40(2)	C(15) - C(16)	1.40(2)
N(2) - S(2)	1.630(9)	P(1) - C(21)	1.81(1)
P(1) - C(2)	1.85(1)	P(1) - C(31)	1.85(1)
C(21) - C(22)	1.38(2)	C(21) - C(26)	1.42(1)
C(22) - C(23)	1.40(2)	C(23) - C(24)	1.35(2)
C(24) - C(25)	1.39(2)	C(25) - C(26)	1.39(1)
C(31) - C(32)	1.37(1)	C(31) - C(36)	1.40(1)
C(32) - C(33)	1.40(1)	C(33) - C(34)	1.38(2)
C(34) - C(35)	1.36(2)	C(35) - C(36)	1.40(2)
C(2) - C(3)	1.53(1)	C(3) - P(2)	1.82(1)
P(2) - C(51)	1.83(1)	P(2) - C(41)	1.84(1)
C(41) - C(42)	1.38(1)	C(41) - C(46)	1.41(1)
C(42) - C(43)	1.41(1)	C(43) - C(44)	1.35(2)
C(44) - C(45)	1.37(2)	C(45) - C(46)	1.39(1)
C(51) - C(52)	1.38(2)	C(51) - C(56)	1.39(2)
C(52) - C(53)	1.38(2)	C(53) - C(54)	1.38(2)
C(54) - C(55)	1.38(2)	C(55) - C(56)	1.39(2)

Table D.13 Angles, °, for [Pd(SNCPhNS-*S*,*S*)(dppe)].

S(2) - Pd(1) - S(1)	89.6(1)	S(2) - Pd(1) - P(2)	89.8(1)
S(1) - Pd(1) - P(2)	176.8(1)	S(2) - Pd(1) - P(1)	170.5(1)
S(1) - Pd(1) - P(1)	95.0(1)	P(2) - Pd(1) - P(1)	85.1(1)
N(1) - S(1) - Pd(1)	117.6(3)	C(1) - N(1) - S(1)	129.0(8)
N(2) - C(1) - N(1)	129(1)	N(2) - C(1) - C(11)	115(1)
N(1) - C(1) - C(11)	115(1)	C(16) - C(11) - C(12)	118(1)
C(16) - C(11) - C(1)	122(1)	C(12) - C(11) - C(1)	119(1)
C(13) - C(12) - C(11)	119(1)	C(12) - C(13) - C(14)	122(1)
C(15) - C(14) - C(13)	119(1)	C(14) - C(15) - C(16)	118(1)
C(11) - C(16) - C(15)	122(1)	C(1) - N(2) - S(2)	129.9(7)
N(2) - S(2) - Pd(1)	117.4(3)	C(21) - P(1) - C(2)	104.3(5)
C(21) - P(1) - C(31)	108.9(5)	C(2) - P(1) - C(31)	101.8(5)
C(21) - P(1) - Pd(1)	123.2(3)	C(2) - P(1) - Pd(1)	107.1(3)
C(31) - P(1) - Pd(1)	109.3(3)	C(22) - C(21) - C(26)	118.5(9)
C(22) - C(21) - P(1)	120.8(8)	C(26) - C(21) - P(1)	120.7(8)

C(21) - C(22) - C(23)	121(1)	C(24) - C(23) - C(22)	120(1)
C(23) - C(24) - C(25)	121(1)	C(24) - C(25) - C(26)	119(1)
C(25) - C(26) - C(21)	120.1(9)	C(32) - C(31) - C(36)	120(1)
C(32) - C(31) - P(1)	118.1(8)	C(36) - C(31) - P(1)	121.6(8)
C(31) - C(32) - C(33)	121(1)	C(34) - C(33) - C(32)	119(1)
C(35) - C(34) - C(33)	121(1)	C(34) - C(35) - C(36)	121(1)
C(31) - C(36) - C(35)	118(1)	C(3) - C(2) - P(1)	108.9(7)
C(2) - C(3) - P(2)	111.2(7)	C(3) - P(2) - C(51)	104.4(5)
C(3) - P(2) - C(41)	105.9(5)	C(51) - P(2) - C(41)	106.6(5)
C(3) - P(2) - Pd(1)	107.2(4)	C(51) - P(2) - Pd(1)	116.8(4)
C(41) - P(2) - Pd(1)	115.0(3)	C(42) - C(41) - C(46)	119(1)
C(42) - C(41) - P(2)	122.9(8)	C(46) - C(41) - P(2)	118.2(8)
C(41) - C(42) - C(43)	121(1)	C(44) - C(43) - C(42)	117(1)
C(43) - C(44) - C(45)	123(1)	C(44) - C(45) - C(46)	119(1)
C(45) - C(46) - C(41)	119(1)	C(52) - C(51) - C(56)	119(1)
C(52) - C(51) - P(2)	120.6(9)	C(56) - C(51) - P(2)	119.9(9)
C(53) - C(52) - C(51)	120(1)	C(52) - C(53) - C(54)	120(1)
C(55) - C(54) - C(53)	122(1)	C(54) - C(55) - C(56)	118(1)
C(55) - C(56) - C(51)	122(1)		

Table D.14 Anisotropic displacement parameters, Å^2, for [Pd(SNCPhNS-*S,S*)(dppe)]

	U11	U22	U33	U23	U13	U12
Pd(1)	0.019(1)	0.019(1)	0.018(1)	0.000(1)	0.000(1)	-0.001(1)
S(1)	0.023(2)	0.015(1)	0.032(2)	-0.004(1)	0.009(1)	-0.001(1)
N(1)	0.020(6)	0.021(4)	0.041(6)	-0.008(4)	0.008(4)	0.002(4)
C(1)	0.025(6)	0.038(6)	0.009(5)	-0.001(5)	-0.008(5)	-0.011(5)
C(11)	0.023(6)	0.034(6)	0.023(6)	0.001(5)	-0.003(5)	-0.001(5)
C(12)	0.043(8)	0.038(7)	0.029(7)	0.001(6)	0.001(6)	-0.011(7)
C(13)	0.039(7)	0.056(8)	0.021(6)	0.003(6)	0.004(5)	-0.019(7)
C(14)	0.074(9)	0.051(8)	0.021(6)	0.021(7)	0.004(6)	-0.017(9)
C(15)	0.059(8)	0.029(6)	0.030(5)	-0.004(6)	0.006(5)	0.005(7)
C(16)	0.032(7)	0.047(7)	0.031(6)	-0.004(6)	0.008(5)	-0.006(6)
N(2)	0.020(5)	0.026(5)	0.023(5)	-0.002(4)	0.006(4)	-0.001(4)
S(2)	0.020(1)	0.024(1)	0.030(1)	0.001(1)	0.005(1)	-0.001(1)
P(1)	0.020(1)	0.022(1)	0.021(1)	0.000(1)	0.001(1)	-0.004(1)
C(21)	0.021(5)	0.026(6)	0.026(5)	-0.004(5)	-0.001(4)	-0.006(5)
C(22)	0.014(5)	0.040(6)	0.036(6)	-0.007(7)	0.005(6)	-0.001(5)
C(23)	0.028(6)	0.033(6)	0.040(6)	-0.002(5)	-0.013(6)	0.014(6)
C(24)	0.023(6)	0.045(6)	0.042(6)	-0.004(7)	0.001(7)	0.017(6)
C(25)	0.030(7)	0.052(7)	0.032(5)	0.010(6)	0.001(5)	-0.002(7)
C(26)	0.019(5)	0.034(6)	0.045(6)	0.006(5)	0.004(6)	0.005(6)
C(31)	0.024(5)	0.018(5)	0.027(6)	-0.006(5)	-0.005(5)	0.005(4)

C(32)	0.046(7)	0.041(7)	0.023(5)	0.001(5)	0.006(5)	-0.004(6)
C(33)	0.044(7)	0.051(7)	0.023(5)	0.004(5)	-0.013(5)	-0.018(7)
C(34)	0.039(7)	0.048(8)	0.024(6)	-0.010(6)	-0.005(5)	0.017(7)
C(35)	0.053(8)	0.036(7)	0.021(6)	0.005(5)	0.012(6)	0.002(6)
C(36)	0.036(6)	0.027(6)	0.026(6)	0.005(6)	0.000(6)	-0.012(5)
C(2)	0.021(5)	0.026(6)	0.015(5)	-0.007(5)	0.010(4)	-0.002(5)
C(3)	0.032(6)	0.023(5)	0.025(6)	-0.002(5)	-0.004(5)	-0.002(5)
P(2)	0.026(2)	0.024(1)	0.026(2)	0.001(1)	-0.002(1)	-0.001(1)
C(41)	0.029(6)	0.021(5)	0.014(5)	0.001(4)	0.007(5)	0.009(6)
C(42)	0.029(6)	0.042(7)	0.039(7)	-0.014(6)	0.002(6)	-0.020(6)
C(43)	0.048(8)	0.050(8)	0.034(7)	-0.023(6)	-0.003(6)	-0.019(7)
C(44)	0.064(10)	0.040(7)	0.029(7)	-0.007(6)	-0.011(6)	-0.002(7)
C(45)	0.076(11)	0.037(6)	0.019(6)	0.007(5)	0.007(6)	-0.012(7)
C(46)	0.064(9)	0.021(6)	0.029(6)	0.001(5)	-0.001(6)	0.001(6)
C(51)	0.021(6)	0.035(6)	0.025(6)	0.012(5)	0.005(5)	0.010(5)
C(52)	0.033(6)	0.037(7)	0.040(8)	0.001(6)	-0.018(6)	0.012(5)
C(53)	0.067(10)	0.059(9)	0.042(9)	-0.008(8)	0.004(8)	0.035(8)
C(54)	0.049(8)	0.055(9)	0.036(8)	0.017(7)	-0.006(7)	0.026(7)
C(55)	0.025(7)	0.061(8)	0.030(7)	0.010(6)	-0.006(6)	-0.001(7)
C(56)	0.033(7)	0.049(8)	0.024(6)	0.000(6)	-0.007(6)	-0.002(6)

Table D.15 Hydrogen coordinates, Å, and isotropic displacement parameters, Å^2, for [Pd(SNCPhNS-*S*,*S*)(dppe)].

	x	y	z	U(eq)
H(12)	0.573(1)	1.250(1)	0.0442(5)	0.044
H(13)	0.653(1)	1.392(1)	-0.0107(5)	0.046
H(14)	0.548(1)	1.550(1)	-0.0337(5)	0.058
H(15)	0.352(1)	1.555(1)	-0.0091(5)	0.047
H(16)	0.275(1)	1.414(1)	0.0528(5)	0.044
H(22)	-0.0388(9)	1.1360(9)	0.1382(6)	0.036
H(23)	-0.213(1)	1.2157(8)	0.1111(5)	0.040
H(24)	-0.380(1)	1.1450(9)	0.1482(6)	0.044
H(25)	-0.381(1)	0.992(1)	0.2133(5)	0.046
H(26)	-0.2088(9)	0.9029(8)	0.2352(5)	0.039
H(32)	0.216(1)	1.005(1)	0.2896(5)	0.044
H(33)	0.258(1)	0.998(1)	0.3991(5)	0.047
H(34)	0.123(1)	0.929(1)	0.4694(5)	0.044
H(35)	-0.056(1)	0.883(1)	0.4339(5)	0.044
H(36)	-0.0999(9)	0.8888(8)	0.3247(5)	0.036
H(2A)	-0.0484(8)	0.7722(8)	0.2274(5)	0.025
H(2B)	-0.0336(8)	0.7901(8)	0.1531(5)	0.025
H(3A)	0.1039(9)	0.6634(8)	0.1826(5)	0.032
H(3B)	0.1450(9)	0.7363(8)	0.2402(5)	0.032

H(42)	0.076(1)	0.6365(9)	0.0849(6)	0.044
H(43)	0.035(1)	0.582(1)	-0.0207(6)	0.053
H(44)	0.137(1)	0.659(1)	-0.1019(6)	0.053
H(45)	0.270(1)	0.7934(9)	-0.0854(5)	0.053
H(46)	0.311(1)	0.8487(9)	0.0193(5)	0.045
H(52)	0.354(1)	0.6088(9)	0.1136(6)	0.044
H(53)	0.526(1)	0.534(1)	0.1481(6)	0.067
H(54)	0.625(1)	0.616(1)	0.2308(6)	0.056
H(55)	0.569(1)	0.783(1)	0.2716(6)	0.046
H(56)	0.401(1)	0.861(1)	0.2330(5)	0.042

Table D.16 Atomic coordinates and equivalent isotropic displacement parameters, Å^2, for $[Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh_3)_4]\cdot 2PhMe$, see Figure 5.8.

	x	y	z	U(eq)
Pt(1)	0.1032(1)	0.0804(1)	0.4050(1)	0.028(1)
Pt(2)	0.0000	0.0000	0.5000	0.028(1)
S(1)	0.0380(4)	0.0879(2)	0.5523(3)	0.033(1)
S(2)	0.1828(3)	0.0036(2)	0.4934(3)	0.029(1)
P(1)	-0.0116(4)	0.1472(2)	0.3341(3)	0.031(1)
P(2)	0.1948(4)	0.0586(2)	0.2838(3)	0.032(1)
N(1)	0.138(1)	0.0858(6)	0.6499(9)	0.032(3)
N(2)	0.254(1)	0.0179(5)	0.603(1)	0.032(3)
C(1)	0.221(1)	0.0537(7)	0.662(1)	0.037(5)
C(11)	0.296(2)	0.0587(8)	0.764(1)	0.041(5)
C(12)	0.261(2)	0.0835(8)	0.840(1)	0.042(5)
C(13)	0.325(2)	0.0879(9)	0.931(1)	0.052(6)
C(14)	0.428(2)	0.0672(8)	0.948(1)	0.048(5)
C(15)	0.468(2)	0.0443(9)	0.874(2)	0.060(6)
C(16)	0.398(2)	0.0381(8)	0.779(1)	0.046(5)
C(21)	-0.097(1)	0.1770(7)	0.411(1)	0.031(4)
C(22)	-0.095(2)	0.2314(8)	0.432(1)	0.046(5)
C(23)	-0.165(2)	0.2530(9)	0.488(1)	0.051(6)
C(24)	-0.230(2)	0.2212(9)	0.524(2)	0.058(6)
C(25)	-0.235(2)	0.1669(9)	0.506(1)	0.049(5)
C(26)	-0.169(1)	0.1456(7)	0.446(1)	0.034(4)
C(31)	0.058(2)	0.2045(8)	0.295(1)	0.042(5)
C(32)	0.016(2)	0.2369(6)	0.216(1)	0.037(5)
C(33)	0.074(2)	0.2816(8)	0.199(2)	0.053(6)
C(34)	0.170(2)	0.2916(8)	0.247(2)	0.049(5)
C(35)	0.216(2)	0.2604(7)	0.328(2)	0.050(5)
C(36)	0.157(2)	0.2170(8)	0.351(1)	0.044(5)
C(41)	-0.116(2)	0.0729(7)	0.192(1)	0.042(5)
C(42)	-0.115(1)	0.1247(7)	0.230(1)	0.031(4)
C(43)	-0.188(2)	0.0562(8)	0.115(2)	0.053(6)
C(44)	-0.272(2)	0.0868(9)	0.075(1)	0.052(6)
C(45)	-0.280(2)	0.1380(9)	0.113(1)	0.052(6)
C(46)	-0.206(2)	0.1570(8)	0.192(1)	0.043(5)
C(51)	0.338(1)	0.0736(7)	0.316(1)	0.036(4)
C(52)	0.401(1)	0.0809(9)	0.245(2)	0.052(5)
C(53)	0.511(2)	0.085(1)	0.273(2)	0.066(7)
C(54)	0.563(2)	0.080(1)	0.366(2)	0.066(6)
C(55)	0.504(2)	0.074(1)	0.439(2)	0.077(8)
C(56)	0.391(1)	0.0696(8)	0.415(1)	0.047(5)

C(61)	0.155(1)	0.0905(7)	0.163(1)	0.033(5)
C(62)	0.090(1)	0.0602(8)	0.083(1)	0.043(5)
C(63)	0.054(2)	0.0862(9)	-0.007(1)	0.055(6)
C(64)	0.081(2)	0.1388(7)	-0.020(1)	0.045(5)
C(65)	0.143(2)	0.1677(8)	0.055(1)	0.047(5)
C(66)	0.179(2)	0.1429(8)	0.147(1)	0.044(5)
C(71)	0.186(1)	-0.0114(7)	0.257(1)	0.033(4)
C(72)	0.102(2)	-0.0422(7)	0.271(1)	0.033(4)
C(73)	0.093(2)	-0.0961(7)	0.252(1)	0.043(5)
C(74)	0.180(2)	-0.1235(8)	0.229(1)	0.049(5)
C(75)	0.269(2)	-0.0932(8)	0.216(2)	0.069(7)
C(76)	0.275(2)	-0.0403(8)	0.234(2)	0.056(6)
C(1S)	0.465(2)	0.184(1)	0.731(2)	0.091(9)
C(2S)	0.413(4)	0.172(2)	0.625(4)	0.19(2)
C(3S)	0.412(7)	0.202(4)	0.572(7)	0.42(7)
C(4S)	0.435(5)	0.247(3)	0.591(5)	0.26(3)
C(5S)	0.475(4)	0.273(2)	0.676(4)	0.17(2)
C(6S)	0.506(6)	0.244(3)	0.759(7)	0.28(3)
C(7S)	0.530(5)	0.238(3)	0.835(4)	0.34(5)

Table D.17 Bond lengths, Å, in $[Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh_3)_4]\cdot 2PhMe$.

Pt(1) - P(1)	2.300(5)	Pt(1) - P(2)	2.301(4)
Pt(1) - S(1)	2.367(4)	Pt(1) - S(2)	2.387(4)
Pt(1) - Pt(2)	2.865(1)	Pt(2) - S(1)	2.332(5)
Pt(2) - S(2)	2.344(4)	S(1) - N(1)	1.66(1)
S(2) - N(2)	1.64(1)	P(1) - C(41)	1.82(2)
P(1) - C(31)	1.82(2)	P(2) - C(71)	1.79(2)
P(1) - C(21)	1.83(2)	P(2) - C(61)	1.83(2)
P(2) - C(51)	1.82(2)	N(1) - C(1)	1.31(2)
N(2) - C(1)	1.34(2)	C(11) - C(16)	1.38(2)
C(1) - C(11)	1.53(3)	C(12) - C(13)	1.36(2)
C(11) - C(12)	1.38(2)	C(14) - C(15)	1.36(2)
C(13) - C(14)	1.38(3)	C(21) - C(26)	1.37(2)
C(15) - C(16)	1.44(3)	C(22) - C(23)	1.40(3)
C(21) - C(22)	1.39(2)	C(24) - C(25)	1.38(3)
C(23) - C(24)	1.33(3)	C(31) - C(36)	1.37(3)
C(25) - C(26)	1.40(2)	C(32) - C(33)	1.42(2)
C(31) - C(32)	1.38(2)	C(34) - C(35)	1.39(3)
C(33) - C(34)	1.33(3)	C(41) - C(43)	1.35(3)
C(35) - C(36)	1.39(2)	C(42) - C(46)	1.42(2)
C(41) - C(42)	1.41(2)	C(44) - C(45)	1.39(3)
C(43) - C(44)	1.34(3)	C(51) - C(52)	1.40(2)

C(45) - C(46)	1.37(3)	C(52) - C(53)	1.38(3)
C(51) - C(56)	1.40(2)	C(54) - C(55)	1.39(3)
C(53) - C(54)	1.33(3)	C(61) - C(66)	1.38(2)
C(55) - C(56)	1.41(3)	C(62) - C(63)	1.40(3)
C(61) - C(62)	1.45(2)	C(64) - C(65)	1.37(3)
C(63) - C(64)	1.38(3)	C(71) - C(72)	1.36(2)
C(65) - C(66)	1.40(3)	C(72) - C(73)	1.37(2)
C(71) - C(76)	1.43(2)	C(74) - C(75)	1.41(3)
C(73) - C(74)	1.39(3)	C(75) - C(76)	1.35(3)
C(1S) - C(6S)	1.61(8)	C(1S) - C(2S)	1.52(5)
C(2S) - C(4S)	1.98(9)	C(2S) - C(3S)	1.1(1)
C(4S) - C(5S)	1.34(7)	C(3S) - C(4S)	1.2(1)
C(6S) - C(7S)	1.1(1)	C(5S) - C(6S)	1.34(9)

Table D.18 Angles, Å, in $[Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh_3)_4]\cdot 2PhMe$.

P(1) - Pt(1) - P(2)	103.3(2)	P(1) - Pt(1) - S(1)	90.5(2)
P(2) - Pt(1) - S(1)	166.2(2)	P(1) - Pt(1) - S(2)	165.3(2)
P(2) - Pt(1) - S(2)	87.8(2)	S(1) - Pt(1) - S(2)	78.8(2)
P(1) - Pt(1) - Pt(2)	113.3(1)	P(2) - Pt(1) - Pt(2)	121.3(1)
S(1) - Pt(1) - Pt(2)	51.9(1)	S(2) - Pt(1) - Pt(2)	52.1(1)
S(1) - Pt(2) - S'(1)	180.0	S(1) - Pt(2) - S(2)	80.4(2)
S'(1) - Pt(2) - S(2)	99.6(2)	S(1) - Pt(2) - S'(2)	99.6(2)
S'(1) - Pt(2) - S'(2)	80.4(2)	S(2) - Pt(2) - S'(2)	180.0
S(1) - Pt(2) - Pt(1)	53.0(1)	S'(1) - Pt(2) - Pt(1)	127.0(1)
S(2) - Pt(2) - Pt(1)	53.4(1)	S'(2) - Pt(2) - Pt(1)	126.6(1)
Pt(1) - Pt(2) - Pt'(1)	180.0	N(2) - S(2) - Pt(2)	109.3(5)
N(2) - S(2) - Pt(1)	113.2(5)	Pt(2) - S(2) - Pt(1)	74.5(1)
N(1) - S(1) - Pt(2)	107.4(6)	N(1) - S(1) - Pt(1)	111.1(5)
Pt(2) - S(1) - Pt(1)	75.1(1)	C(31) - P(1) - C(42)	108.7(8)
C(31) - P(1) - C(21)	103.5(8)	C(42) - P(1) - C(21)	99.6(8)
C(31) - P(1) - Pt(1)	113.3(7)	C(42) - P(1) - Pt(1)	113.8(6)
C(21) - P(1) - Pt(1)	116.6(5)	C(71) - P(2) - C(51)	105.6(8)
C(71) - P(2) - C(61)	104.1(8)	C(51) - P(2) - C(61)	102.2(8)
C(71) - P(2) - Pt(1)	111.3(5)	C(51) - P(2) - Pt(1)	113.7(6)
C(61) - P(2) - Pt(1)	118.6(5)	C(1) - N(2) - S(2)	123(1)
C(1) - N(1) - S(1)	126(1)	N(1) - C(1) - N(2)	132(2)
N(1) - C(1) - C(11)	114(2)	N(2) - C(1) - C(11)	114(2)
C(16) - C(11) - C(12)	119(2)	C(16) - C(11) - C(1)	120(2)
C(12) - C(11) - C(1)	121(2)	C(13) - C(12) - C(11)	122(2)
C(12) - C(13) - C(14)	120(2)	C(15) - C(14) - C(13)	121(2)
C(14) - C(15) - C(16)	119(2)	C(11) - C(16) - C(15)	119(2)
C(26) - C(21) - C(22)	118(2)	C(26) - C(21) - P(1)	120(1)

C(22) - C(21) - P(1)	122(1)	C(21) - C(22) - C(23)	121(2)
C(24) - C(23) - C(22)	120(2)	C(23) - C(24) - C(25)	122(2)
C(24) - C(25) - C(26)	118(2)	C(21) - C(26) - C(25)	121(2)
C(36) - C(31) - C(32)	118(2)	C(36) - C(31) - P(1)	117(2)
C(32) - C(31) - P(1)	125(2)	C(31) - C(32) - C(33)	121(2)
C(34) - C(33) - C(32)	118(2)	C(33) - C(34) - C(35)	123(2)
C(36) - C(35) - C(34)	118(2)	C(31) - C(36) - C(35)	122(2)
C(43) - C(41) - C(42)	121(2)	C(41) - C(42) - C(46)	118(2)
C(41) - C(42) - P(1)	121(1)	C(46) - C(42) - P(1)	121(1)
C(44) - C(43) - C(41)	122(2)	C(43) - C(44) - C(45)	119(2)
C(46) - C(45) - C(44)	122(2)	C(45) - C(46) - C(42)	119(2)
C(52) - C(51) - C(56)	119(2)	C(52) - C(51) - P(2)	122(1)
C(56) - C(51) - P(2)	118(1)	C(53) - C(52) - C(51)	120(2)
C(54) - C(53) - C(52)	123(2)	C(53) - C(54) - C(55)	119(2)
C(54) - C(55) - C(56)	121(2)	C(55) - C(56) - C(51)	119(2)
C(66) - C(61) - C(62)	119(2)	C(66) - C(61) - P(2)	122(2)
C(62) - C(61) - P(2)	119(1)	C(63) - C(62) - C(61)	118(2)
C(64) - C(63) - C(62)	121(2)	C(65) - C(64) - C(63)	121(2)
C(64) - C(65) - C(66)	119(2)	C(61) - C(66) - C(65)	122(2)
C(72) - C(71) - C(76)	115(2)	C(72) - C(71) - P(2)	123(1)
C(76) - C(71) - P(2)	121(1)	C(71) - C(72) - C(73)	124(2)
C(72) - C(73) - C(74)	119(2)	C(73) - C(74) - C(75)	118(2)
C(76) - C(75) - C(74)	121(2)	C(75) - C(76) - C(71)	122(2)
C(2S) - C(1S) - C(6S)	119(5)	C(3S) - C(2S) - C(1S)	118(8)
C(3S) - C(2S) - C(4S)	30(7)	C(1S) - C(2S) - C(4S)	89(4)
C(2S) - C(3S) - C(4S)	124(10)	C(3S) - C(4S) - C(5S)	133(9)
C(3S) - C(4S) - C(2S)	26(6)	C(5S) - C(4S) - C(2S)	107(5)
C(4S) - C(5S) - C(6S)	120(7)	C(7S) - C(6S) - C(5S)	156(10)
C(7S) - C(6S) - C(1S)	97(8)	C(5S) - C(6S) - C(1S)	105(7)

Atom S′ is related to atom S by the operation -x,-y,-z+1.

Table D.19 Anisotropic displacement parameters, Å^2, for $[Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh_3)_4]\cdot 2PhMe$.

	U11	U22	U33	U23	U13	U12
Pt(1)	0.028(1)	0.029(1)	0.027(1)	0.002(1)	0.006(1)	0.000(1)
Pt(2)	0.028(1)	0.027(1)	0.028(1)	0.000(1)	0.007(1)	-0.001(1)
S(1)	0.038(3)	0.037(3)	0.026(2)	-0.005(2)	0.009(2)	0.000(2)
S(2)	0.023(2)	0.028(2)	0.034(2)	0.001(2)	0.003(2)	0.005(2)
P(1)	0.032(3)	0.030(3)	0.030(3)	0.001(2)	0.005(2)	-0.001(2)
P(2)	0.025(3)	0.038(3)	0.032(3)	0.004(2)	0.006(2)	0.004(2)
N(1)	0.020(8)	0.040(9)	0.032(8)	-0.004(7)	0.001(6)	0.005(7)
N(2)	0.029(8)	0.030(8)	0.039(9)	-0.006(7)	0.013(7)	0.001(6)

C(1)	0.03(1)	0.04(1)	0.05(1)	0.016(9)	0.014(9)	-0.002(9)
C(11)	0.04(1)	0.05(1)	0.03(1)	0.007(9)	0.002(9)	-0.00(1)
C(12)	0.04(1)	0.05(1)	0.03(1)	-0.02(1)	0.005(9)	0.00(1)
C(13)	0.04(1)	0.09(2)	0.03(1)	-0.03(1)	0.011(9)	-0.01(1)
C(14)	0.05(1)	0.06(2)	0.03(1)	-0.01(1)	0.006(9)	0.00(1)
C(15)	0.05(1)	0.07(2)	0.06(1)	0.01(1)	0.01(1)	0.03(1)
C(16)	0.04(1)	0.06(1)	0.03(1)	-0.01(1)	0.01(1)	0.00(1)
C(21)	0.03(1)	0.04(1)	0.026(9)	0.005(8)	-0.001(8)	0.011(8)
C(22)	0.05(1)	0.05(1)	0.04(1)	-0.01(1)	0.02(1)	0.01(1)
C(23)	0.06(2)	0.05(1)	0.03(1)	0.00(1)	-0.00(1)	-0.00(1)
C(24)	0.06(2)	0.06(2)	0.07(2)	-0.01(1)	0.02(1)	0.00(1)
C(25)	0.03(1)	0.07(2)	0.04(1)	-0.00(1)	0.001(9)	-0.01(1)
C(26)	0.03(1)	0.03(1)	0.04(1)	0.004(8)	0.003(9)	0.001(8)
C(31)	0.04(1)	0.05(1)	0.04(1)	0.00(1)	0.03(1)	-0.01(1)
C(32)	0.05(1)	0.02(1)	0.04(1)	0.001(8)	0.007(9)	-0.015(9)
C(33)	0.06(2)	0.04(1)	0.07(2)	0.01(1)	0.03(1)	0.01(1)
C(34)	0.04(1)	0.03(1)	0.08(2)	0.00(1)	0.02(1)	-0.01(1)
C(35)	0.06(1)	0.03(1)	0.07(1)	0.01(1)	0.02(1)	-0.01(1)
C(36)	0.04(1)	0.05(1)	0.05(1)	-0.01(1)	0.01(1)	-0.02(1)
C(41)	0.04(1)	0.02(1)	0.06(1)	0.001(9)	0.01(1)	-0.002(9)
C(42)	0.03(1)	0.04(1)	0.018(9)	0.011(8)	0.008(8)	-0.012(9)
C(43)	0.04(1)	0.05(1)	0.07(2)	-0.01(1)	0.00(1)	-0.01(1)
C(44)	0.04(1)	0.06(2)	0.05(1)	-0.02(1)	0.01(1)	-0.03(1)
C(45)	0.06(1)	0.06(2)	0.04(1)	0.01(1)	0.00(1)	0.00(1)
C(46)	0.04(1)	0.05(1)	0.04(1)	0.01(1)	0.005(9)	0.02(1)
C(51)	0.03(1)	0.03(1)	0.05(1)	-0.009(9)	0.008(9)	-0.017(9)
C(52)	0.03(1)	0.07(2)	0.06(1)	0.01(1)	0.03(1)	0.01(1)
C(53)	0.05(2)	0.07(2)	0.08(2)	-0.01(2)	0.04(1)	0.00(1)
C(54)	0.04(1)	0.08(2)	0.08(2)	0.01(2)	0.01(1)	-0.01(1)
C(55)	0.05(2)	0.012(2)	0.06(2)	0.01(2)	0.00(1)	-0.02(2)
C(56)	0.03(1)	0.06(2)	0.05(1)	0.01(1)	0.003(9)	-0.01(1)
C(61)	0.05(1)	0.04(1)	0.023(9)	0.018(8)	0.015(8)	0.025(9)
C(62)	0.03(1)	0.07(2)	0.03(1)	0.001(1)	0.014(9)	-0.01(1)
C(63)	0.07(2)	0.07(2)	0.03(1)	0.01(1)	0.02(1)	-0.01(1)
C(64)	0.07(1)	0.04(1)	0.03(1)	0.01(1)	0.01(1)	0.01(1)
C(65)	0.06(1)	0.04(1)	0.05(1)	0.00(1)	0.04(1)	0.01(1)
C(66)	0.05(1)	0.04(1)	0.04(1)	0.01(1)	0.02(1)	0.00(1)
C(71)	0.04(1)	0.03(1)	0.03(1)	0.002(8)	0.013(9)	0.003(9)
C(72)	0.04(1)	0.03(1)	0.03(1)	0.003(8)	0.013(9)	0.004(9)
C(73)	0.04(1)	0.04(1)	0.05(1)	0.001(9)	0.01(1)	0.004(9)
C(74)	0.06(2)	0.03(1)	0.05(1)	0.00(1)	0.01(1)	0.01(1)
C(75)	0.08(2)	0.03(1)	0.11(2)	0.00(1)	0.04(2)	0.04(1)
C(76)	0.07(2)	0.04(1)	0.07(2)	-0.01(1)	0.04(1)	0.01(1)

Table D.20 Hydrogen coordinates and isotropic displacement parameters, Å^2, for [$Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh_3)_4$]·2PhMe.

	x	y	z	U(eq)
H(12A)	0.189(2)	0.0975(8)	0.829(1)	0.080
H(13A)	0.300(2)	0.1054(9)	0.983(1)	0.080
H(14A)	0.472(2)	0.0694(8)	1.013(1)	0.080
H(15A)	0.542(2)	0.0324(9)	0.885(2)	0.080
H(16A)	0.422(2)	0.0195(8)	0.727(1)	0.080
H(22A)	-0.046(2)	0.2540(8)	0.408(1)	0.080
H(23A)	-0.165(2)	0.2909(9)	0.499(1)	0.080
H(24A)	-0.274(2)	0.2363(9)	0.566(2)	0.080
H(25A)	-0.284(2)	0.1445(9)	0.532(1)	0.080
H(26A)	-0.173(2)	0.1082(7)	0.430(1)	0.080
H(32A)	-0.055(2)	0.2288(6)	0.178(1)	0.080
H(33A)	0.044(2)	0.3039(8)	0.137(2)	0.080
H(34A)	0.211(2)	0.3216(8)	0.231(2)	0.080
H(35A)	0.286(2)	0.2681(7)	0.366(2)	0.080
H(36A)	0.186(2)	0.1954(8)	0.407(1)	0.080
H(41A)	-0.054(2)	0.0494(7)	0.220(1)	0.080
H(43A)	-0.181(2)	0.0214(8)	0.088(2)	0.080
H(44A)	-0.327(2)	0.0734(9)	0.023(2)	0.080
H(45A)	-0.339(2)	0.1604(9)	0.083(1)	0.080
H(46A)	-0.214(2)	0.1912(8)	0.220(1)	0.080
H(52A)	0.366(2)	0.0834(9)	0.177(2)	0.080
H(53A)	0.552(2)	0.090(1)	0.224(2)	0.080
H(54A)	0.640(2)	0.081(1)	0.383(2)	0.080
H(55A)	0.541(2)	0.072(1)	0.507(2)	0.080
H(56A)	0.351(2)	0.0638(8)	0.466(1)	0.080
H(62A)	0.071(2)	0.0236(8)	0.093(1)	0.080
H(63A)	0.011(2)	0.0672(9)	-0.061(1)	0.080
H(64A)	0.058(2)	0.1555(7)	-0.083(1)	0.080
H(65A)	0.159(2)	0.2046(8)	0.046(1)	0.080
H(66A)	0.223(2)	0.1630(8)	0.199(1)	0.080
H(72A)	0.045(2)	-0.0246(7)	0.294(1)	0.080
H(73A)	0.028(2)	-0.1149(7)	0.255(1)	0.080
H(74A)	0.179(2)	-0.1617(8)	0.223(1)	0.080
H(75A)	0.327(2)	-0.1108(8)	0.193(2)	0.080
H(76A)	0.340(2)	-0.0212(8)	0.231(2)	0.080
H(1SA)	0.476(2)	0.158(1)	0.782(2)	0.080
H(2SA)	0.393(4)	0.135(2)	0.609(4)	0.080
H(3SA)	0.382(7)	0.192(4)	0.505(7)	0.080
H(4SA)	0.424(5)	0.274(3)	0.540(5)	0.080

H(5SA)	0.494(4)	0.309(2)	0.691(4)	0.080
H(7SA)	0.543(5)	0.276(3)	0.837(4)	0.080
H(7SB)	0.482(5)	0.230(3)	0.878(4)	0.080
H(7SC)	0.596(5)	0.219(3)	0.855(4)	0.080

Appendix E

Lectures and conferences attended.

The following research conferences were attended during the period of tuition for this Thesis:

December 1992	British Crystallographic Association Charge Density Meeting, University of Durham.
March 1993	British Crystallographic Association Intensive School of Crystallography, University of Aston.
December 1993	British Crystallographic Association Charge Density Meeting, University of Cardiff.
March 1994	British Crystallographic Association Annual Spring Meeting, University of Newcastle.
August 1994	IRIS VII, Banff, Canada.

The following is a list of colloquia, lectures and seminars from invited speakers to the Department of Chemistry, University of Durham, during the period of this research. An asterisk indicates those lectures which were attended by the author of this Thesis.

<u>1991</u>

October 17	Dr. J.A. Salthouse, University of Manchester. Son et Lumiere - a demonstration lecture.
October 31	Dr. R. Keeley, Metropolitan Police Forensic Science. Modern forensic science.
November 6	Prof. B.F.G. Johnson , Edinburgh University. * Cluster-surface analogies.
November 7	Dr. A.R. Butler, St. Andrews University. * Traditional Chinese herbal drugs: a different way of treating disease.
November 13	Prof D. Gani, St. Andrews University. The chemistry of PLP-dependent enzymes.
November 20	Dr. R. More O'Ferrall, University College, Dublin. Some acid-catalysed rearrangements in organic chemistry.
November 28	Prof. I.M. Ward, IRC in Polymer Science, University of Leeds. * The SCI lecture: the science and technology of orientated polymers.

December 4	Prof. R. Grigg, Leeds University. Palladium-catalysed cyclisation and ion-capture processes.
December 5	Prof. A.L. Smith, ex Unilever. * Soap, detergents and black puddings.
December 11	Dr. W.D. Cooper, Shell Research. * Colloid science: theory and practice.

1992

January 22	Dr. K.D.M. Harris, St. Andrews University. Understanding the properties of solid inclusion compounds.
January 29	Dr. A. Holmes, Cambridge University. * Cycloaddition reactions in the service of the synthesis of piperidine and indolizidine natural products.
January 30	Dr. M. Anderson, Sittingbourne Research Centre, Shell Research. * Recent Advances in the Safe and Selective Chemical Control of Insect Pests.
February 12	Prof. D.E. Fenton, Sheffield University. * Polynuclear complexes of molecular clefts as models for copper biosites.
February 13	Dr. J. Saunders, Glaxo Group Research Limited. * Molecular Modelling in Drug Discovery.
February 19	Prof. E.J. Thomas, Manchester University. * Applications of organostannanes to organic synthesis.
February 20	Prof. E.Vogel, University of Cologne. The Musgrave Lecture: Porphyrins: Molecules of Interdisciplinary Interest.
February 25	Prof. J.F. Nixon, University of Sussex. * The Tilden Lecture: Phosphaalkynes: new building blocks in inorganic and organometallic chemistry.
February 26	Prof. M.L. Hitchman, Strathclyde University. Chemical vapour deposition.

March 5	Dr. N.C. Billingham, University of Sussex. * Degradable Plastics - Myth or Magic?
March 11	Dr. S.E. Thomas, Imperial College. Recent advances in organoiron chemistry.
March 12	Dr. R.A. Hann, ICI Imagedata. * Electronic Photography - An Image of the Future.
March 18	Dr. H. Maskill, Newcastle University. Concerted or stepwise fragmentation in a deamination-type reaction.
April 7	Prof. D.M. Knight, Philosophy Department, University of Durham. Interpreting experiments: the beginning of electrochemistry.
May 13	Dr. J-C Gehret, Ciba Geigy, Basel. Some aspects of industrial agrochemical research.
October 15	Dr M. Glazer & Dr. S. Tarling, Oxford University & Birbeck College. * It Pays to be British! - The Chemist's Role as an Expert Witness in Patent Litigation.
October 20	Dr. H. E. Bryndza, Du Pont Central Research. Synthesis, Reactions and Thermochemistry of Metal (Alkyl) Cyanide Complexes and Their Impact on Olefin Hydrocyanation Catalysis.
October 22	Prof. A. Davies, University College London. * The Ingold-Albert Lecture: The Behaviour of Hydrogen as a Pseudometal.
October 28	Dr. J. K . Cockcroft, University of Durham. * Recent Developments in Powder Diffraction.
October 29	Dr. J. Emsley, Imperial College, London. * The Shocking History of Phosphorus.
November 4	Dr. T. P. Kee, University of Leeds. * Synthesis and Co-ordination Chemistry of Silylated Phosphites.
November 5	Dr. C. J. Ludman , University of Durham. * Explosions, A Demonstration Lecture.

November 11	Prof. D. Robins, Glasgow University. Pyrrolizidine Alkaloids: Biological Activity, Biosynthesis and Benefits
November 12	Prof. M. R. Truter, University College, London. * Luck and Logic in Host - Guest Chemistry.
November 18	Dr. R. Nix, Queen Mary College, London. * Characterisation of Heterogeneous Catalysts.
November 25	Prof. Y. Vallee, University of Caen. Reactive Thiocarbonyl Compounds.
November 25	Prof. L. D. Quin, University of Massachusetts, Amherst. * Fragmentation of Phosphorous Heterocycles as a Route to Phosphoryl Species with Uncommon Bonding.
November 26	Dr. D. Humber , Glaxo, Greenford. AIDS - The Development of a Novel Series of Inhibitors of HIV.
December 2	Prof. A. F. Hegarty , University College, Dublin. Highly Reactive Enols Stabilised by Steric Protection.
December 2	Dr. R. A. Aitken, University of St. Andrews. * The Versatile Cycloaddition Chemistry of $Bu_3P.CS_2$.
December 3	Prof. P. Edwards , Birmingham University. * The SCI Lecture - What is Metal?
December 9	Dr. A. N. Burgess, ICI Runcorn. The Structure of Perfluorinated Ionomer Membranes.

<u>1993</u>

January 20	Dr. D. C. Clary , University of Cambridge. Energy Flow in Chemical Reactions.
January 21	Prof. L. Hall , Cambridge. NMR - Window to the Human Body.
January 27	Dr. W. Kerr, University of Strathclyde. Development of the Pauson-Khand Annulation Reaction: Organocobalt Mediated Synthesis of Natural and Unnatural Products
January 28	Prof. J. Mann , University of Reading.

	Murder, Magic and Medicine.
February 3	Prof. S. M. Roberts, University of Exeter. Enzymes in Organic Synthesis.
February 10	Dr. D. Gillies, University of Surrey. NMR and Molecular Motion in Solution.
February 11	Prof. S. Knox , Bristol University. The Tilden Lecture: Organic Chemistry at Polynuclear Metal Centres.
February 17	Dr. R. W. Kemmitt, University of Leicester. Oxatrimethylenemethane Metal Complexes.
February 18	Dr. I. Fraser , ICI Wilton. Reactive Processing of Composite Materials.
February 22	Prof. D. M. Grant , University of Utah. Single Crystals, Molecular Structure, and Chemical-Shift Anisotropy.
February 24	Prof. C. J. M. Stirling, University of Sheffield. Chemistry on the Flat-Reactivity of Ordered Systems.
March 10	Dr. P. K. Baker , University College of North Wales, Bangor. * Chemistry of Highly Versatile 7-Coordinate Complexes.
March 11	Dr. R. A. Y. Jones , University of East Anglia. * The Chemistry of Wine Making.
March 17	Dr. R. J. K. Taylor , University of East Anglia. Adventures in Natural Product Synthesis.
March 24	Prof. I. O. Sutherland, University of Liverpool. Chromogenic Reagents for Cations.
May 13	Prof. J. A. Pople , Carnegie-Mellon University, Pittsburgh, USA. * The Boys-Rahman Lecture: Applications of Molecular Orbital Theory.
May 21	Prof. L. Weber, University of Bielefeld. * Metallo-phospha Alkenes as Synthons in Organometallic Chemistry.

June 1	Prof. J. P. Konopelski, University of California, Santa Cruz. Synthetic Adventures with Enantiomerically Pure Acetals.
June 2	Prof. F. Ciardelli, University of Pisa. Chiral Discrimination in the Stereospecific Polymerisation of Alpha Olefins.
June 7	Prof. R. S. Stein , University of Massachusetts. Scattering Studies of Crystalline and Liquid Crystalline Polymers.
June 16	Prof. A. K. Covington, University of Newcastle. Use of Ion Selective Electrodes as Detectors in Ion Chromatography.
June 17	Prof. O. F. Nielsen, H. C. 0rsted Institute, University of Copenhagen. Low-Frequency IR - and Raman Studies of Hydrogen Bonded Liquids.
September 13	Prof. Dr. A.D. Schluter, Freie Universitat Berlin, Germany. Synthesis and Characterisation of Molecular Rods and Ribbons.
September 13	Dr. K.J. Wynne, Office of Naval Research, Washington, USA. Polymer Surface Design for Minimal Adhesion.
September 14	Prof. J.M. DeSimone, University of North Carolina, USA. Homogeneous and Heterogeneous Polymerisations in Environmentally Responsible Carbon Dioxide.
September 28	Prof. H. Ila, North Eastern Hill University, India. Synthetic Strategies for Cyclopentanoids via Oxoketene Dithioacetals.
October 4	Prof. F.J. Feher, University of California, Irvine, USA. * Bridging the Gap between Surfaces and Solution with Sessilquioxanes.
October 14	Dr. P. Hubberstey , University of Nottingham. Alkali Metals: Alchemist's Nightmare, Biochemist's Puzzle and Technologist's Dream.

October 20	Dr. P. Quayle , University of Manchester. * Aspects of Aqueous ROMP Chemistry.
October 21	Prof. R. Adams , University of South Carolina, USA. * Chemistry of Metal Carbonyl Cluster Complexes: Development of Cluster Based Alkyne Hydrogenation Catalysts.
October 27	Dr. R.A.L. Jones , Cavendish Laboratory, Cambridge. Perambulating Polymers.
November 10	Prof. M.N.R. Ashfoldt, University of Bristol. High Resolution Photofragment Translational Spectroscopy: A New Way to Watch Photodissociation.
November 17	Dr. A. Parker, Rutherford Appleton Laboratory, Didcot. Applications of Time Resolved Resonance Rarnan Spectroscopy to Chemical and Biochemical Problems.
November 24	Dr. P.G. Bruce , University of St. Andrews. * Structure and Properties of Inorganic Solids and Polymers.
November 25	Dr. R.P. Wayne , University of Oxford. The Origin and Evolution of the Atmosphere.
December 1	Prof. M.A. McKervey, Queen's University, Belfast. Synthesis and Applications of Chemically Modified Calixarenes.
December 8	Prof. O. Meth-Cohn , University of Sunderland. Friedel's Folly Revisited - A Super Way to Fused Pyridines.
December 16	Prof. R.F. Hudson, University of Kent. Close Encounters of the Second Kind.

1994

January 26	Prof. J. Evans , University of Southampton. Shining Light on Catalysts.
February 2	Dr. A. Masters, University of Manchester. Modelling Water Without Using Pair Potentials.

February 9	Prof. D. Young, University of Sussex. Chemical and Biological Studies on the Coenzyme Tetrahydrofolic Acid.
February 16	Prof. K.H. Theopold, University of Delaware, USA. * Paramagnetic Chromium Alkyls: Synthesis and Reactivity.
February 23	Prof. P.M. Maitlis , University of Sheffield. * Across the Border: From Homogeneous to Heterogeneous Catalysis.
March 2	Dr. C. Hunter, University of Sheffield. * Noncovalent Interactions between Aromatic Molecules.
March 9	Prof. F. Wilkinson, Loughborough University of Technology. Nanosecond and Picosecond Laser Flash Photolysis.
March 10	Prof. S.V. Ley, University of Cambridge. New Methods for Organic Synthesis.