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Investigations on Organo–Sulfur–Nitrogen Rings and the Thiocyanogen Polymer, $(SCN)_x$

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Abstract: The synthesis and full characterisation of a series of 1,2,4-thiadiazoles is reported. $(SCN)_x$ has been studied by a variety of techniques and the data compared with 1,2,4-thiadiazole and 1,2,4-dithiazoles. The observed data suggest that the polymer consists of 1,2,4-dithiazole rings linked by nitrogen atoms. For $(SCN)_x$, the MALDI-TOF mass spectroscopy showed a parent ion at 1149 and a series of peaks with $(SCN)_2$ repeat units (116 m/z); this result implies that $(SCN)_2$ may be the monomer unit of the polymer. Its IR spectrum shows a very broad peak with maximum at 1134 cm^{-1} consisting of several overlapping peaks in the same region as ring vibrations for 1,2,4-thiadiazole and 1,2,4-dithiazole compounds. Peaks in the Raman spectrum in the range 400–480 cm^{-1} support the presence of disulfide units within the polymer. The solid-state ^{13}C NMR (99% ^{13}C-labelled) spectrum is dominated by two singlets of equal intensity at approximately 187 and 184 ppm with low intensity peaks in the range 152–172 ppm, in approximately the same range as both 1,2,4-thiadiazoles and 1,2,4-dithiazoles. The solid-state ^{15}N NMR (99% ^{15}N labelled) spectrum displays two major peaks of similar intensity at 236.9 and 197.2 ppm, which are clearly very different environments to those observed in bis(3-bromo-1,2,4-thiadiazol-5-yl) disulfide, but similar to 1,2,4-dithiazoles. The X-ray structures of seven C-S-N systems are reported. Preliminary studies on $(SeCN)_x$ suggest that literature references to this polymer may be in error with the red solid actually being red selenium.

Keywords: nitrogen heterocycles · polymers · structure elucidation · sulfur heterocycles

Introduction

Polythiocyanogen (or parathiocyanogen) with the empirical formula $(SCN)_x$ was first reported in 1919 by Soderback,[1] who observed that thiocyanogen $(SCN)_2$ was thermally unstable and spontaneously polymerised to give an orange/brick-red solid product. It can also be prepared by chemical or electrical oxidation of thiocyanates in melts or solution[2,3] or, in the solid state, by passing chlorine gas over alkali metal thiocyanates.[4] Though all of these routes probably involve forming $(SCN)_2$ at some stage, it should be noted that the method in reference [4] may give rise to material contaminated with NaCl, since the reported yield is 135%. The published work on polythiocyanogen reports that the material is a semiconductor,[5] though thin films appear to be insulators,[6] that it is photoactive[7] and it has been used in photocatalytic systems.[8] Several groups have proposed that the mechanism for polymerisation is a radical process involving $SCN^{\bullet}$ and that the polymer has a conjugated double-bond structure. The spectroscopic data published for polythiocyanogen is limited and some of it is of quite poor quality,[4,9–13] for example, Cataldo has illustrated two completely different solution-state ^{13}C NMR spectra, the first[11] with a S/N ratio of approximately 1.6 was assigned with $\delta_C = 144$ ppm and second[12] has $\delta_C = 189$ ppm and is remarkable for the absence of any solvent (DMF) resonances, especially when one considers that $(SCN)_x$ is almost completely insoluble. A number of speculative structures have been proposed in the literature. An early hypothesis was that the structure could be composed of 1,3,5-triazine rings linked by disulfide bridges formed by the trimerisation of the nitrile groups in thiocyanogen (Figure 1).[9,10] An alternative proposal was that polythiocyanogen has a linear structure analogous to that of polythiazyl $(SN)_x$ (Figure 1b).[4,11] The most recent structure proposed by Cataldo et al. consists of polyazome-

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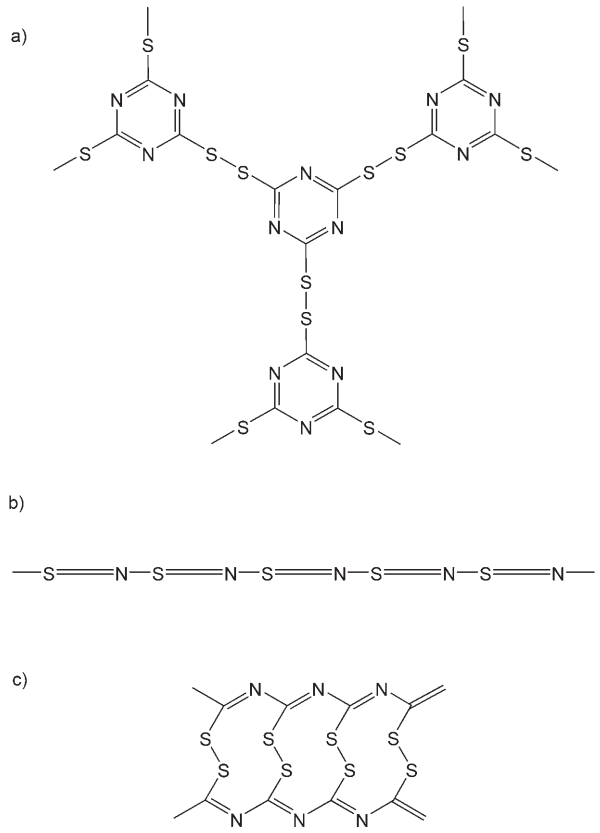
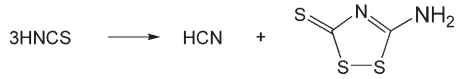


Figure 1. Proposed structures for polythiocyanogen a) 1,3,5-triazine structure, b) linear structure and c) polyazomethine chain.

thine chains analogous to those in polycyanogen $(CN)_x$ but cross-linked by disulfide bridges (Figure 1c).[12,13] Cataldo has also speculated[13] that a cross-linked polycyanogen structure, with S_z bridges, can be used to rationalise the structures of a new series of polymers $[S_z(CN)_2]_x$ ($z=1$–4), though this work has to be treated with some skepticism since 1) the S_zCl_2 starting materials do not appear to have been distilled and so are probably a mixture of S_2Cl_2 and SCl_2 and 2) the new polymers have only been characterised by their (very broad) IR spectra and no analytical data is included in the report.

In preliminary work in collaboration with Knoll Micro-Check into the biological activity of SCN containing species, we carried out some studies on polythiocyanogen $(SCN)_x$. In these studies, UV/VIS, Raman and ^{14}N NMR spectroscopy suggested to us that the polymer may be based on five-membered rings. The literature further supports this proposal. It was reported in 1821 by Wohler that concentrated solutions of isothiocyanic acid HNCS deposited isoperthiocyanic acid $(SCN)_2HS_2$ (Scheme 1).[14–16]



Scheme 1. Synthesis of isoperthiocyanic acid.[14–16]

Hordvic confirmed the 3-amino-5-thione-1,2,4-dithiazole structure by X-ray crystallography, which clearly showed the presence of two adjacent sulfur atoms in a five membered ring.[17] Of the two possible tautomers Hordvic proposed structure **I**, with the both hydrogen atoms located on the exocyclic nitrogen (Figure 2). This structure was further sup-

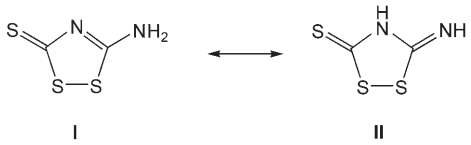
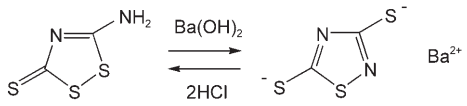


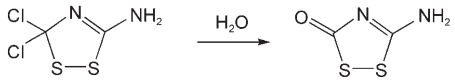
Figure 2. Possible tautomers of isoperthiocyanic acid.

ported by IR data published by Emeleus et al. confirming that an NH_2 group is present.[18] Isoperthiocyanic acid is readily converted into the barium salt of perthiocyanic acid by treatment with barium hydroxide.[19] The isomerisation can be reversed by treatment of the barium salt of perthiocyanic acid with hydrochloric acid (Scheme 2).



Scheme 2. Reaction of isoperthiocyanic acid with barium hydroxide.[19]

Furthermore Soderback reported that reaction of thiocyanogen with HCl in ethereal solution yields two products: a colourless crystalline compound of formula $(SCN)_2{\cdot}2HCl$ and a yellow solid with molecular formula $(SCN)_4Cl_2$.[19,20] The reaction of $(SCN)_2{\cdot}2HCl$ with water yields $(SCN)_2{\cdot}H_2O$ (Scheme 3).[21]



Scheme 3. Speculative structures of the species involved in the reaction of $(SCN)_2{\cdot}2HCl$ with water.[21]

The 1,2,4-dithiazole structure of $(SCN)_2{\cdot}H_2O$ was confirmed by X-ray crystallography;[22] this result led to structure **III** being proposed for $(SCN)_2{\cdot}2HCl$ (Figure 3). The as-

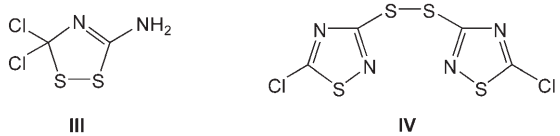
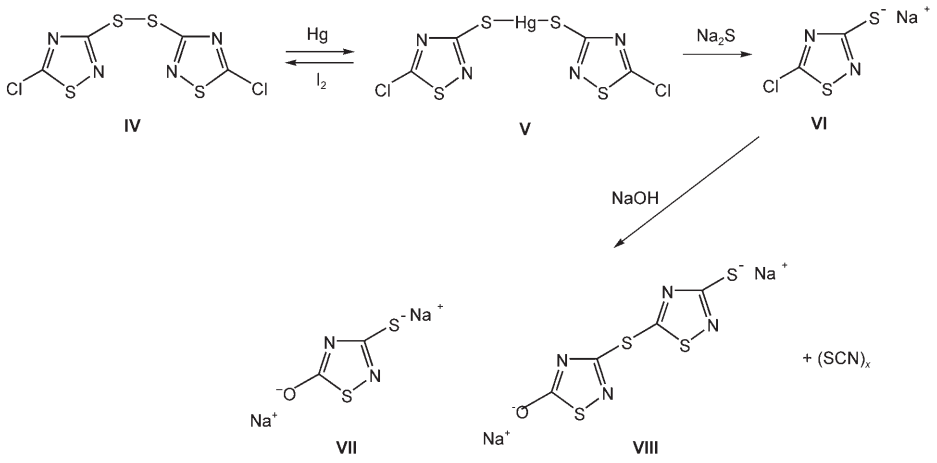


Figure 3. Proposed structure for $(SCN)_2{\cdot}2HCl$ and $(SCN)_4Cl_2$.[18]

signment of structure **III** was further supported by comparison of the IR spectra of $(SCN)_2{\cdot}H_2O$ and $(SCN)_2{\cdot}2HCl$.[18]

A 1,2,4-thiadiazol-3-yl disulfide structure (**IV**) has been suggested for the second product $(SCN)_4Cl_2$.[19,20] Some similarities of the IR spectra with perthiocyanic acid and its barium salt have been observed,[23] but the spectroscopic evidence is not conclusive. Soderback reported that reduction of $(SCN)_4Cl_2$ with mercury gives a compound $Hg[(SCN)_2Cl]_2$ that can be reconverted to $(SCN)_4Cl_2$ by reaction with iodine (Scheme 4).[19,20] Treatment of the mercury compound (**V**) with sodium sulfide was reported to give a highly unstable sodium salt which was proposed to be of 5-chloro-3-thio-1,2,4-thiadiazole.[19,20]

It was reported that reaction of this sodium salt (**VI**) with sodium hydroxide yields a mixture of polythiocyanogen, the disodium salt of 5-hydroxy-3-thio-1,2,4-thiadiazole (**VII**) and a by-product with molecular formula $C_4N_4OS_4Na_2$ (Scheme 4).[19,20] Structure **VIII** was suggested for $Na_2[C_4N_4OS_4]$, since this compound can also be prepared by the reaction of the sodium salt **VI** with **VII**.[19,20]



Scheme 4. Proposed reactions of $(SCN)_4Cl_2$.[19,20]

Though often unsupported by modern spectroscopic methods, the literature clearly illustrates the diversity of heterocyclic five-membered C-S-N rings. Therefore we thought it is quite possible that polythiocyanogen could be composed of such rings. We considered two possible structures for $(SCN)_x$. Firstly a structure based on 1,2,4-thiadiazole rings with sulfur bridges and secondly 1,2,4-dithiazole rings linked by exocyclic nitrogen atoms (Figure 4). In both structures the SCN topology is retained.

Clearly, this is a very confused and difficult area with many different speculative structures for $(SCN)_x$ and a paucity of spectroscopic/structural data for five membered C-S-N heterocycles. Here we report the synthesis and spectroscopic characterisation of polythiocyanogen (including ^{13}C and ^{15}N labeling experiments). Furthermore, the literature structures in Schemes 3 and 4 led us to synthesise a series of 1,2,4-thiadiazoles for spectroscopic comparison with $(SCN)_x$.

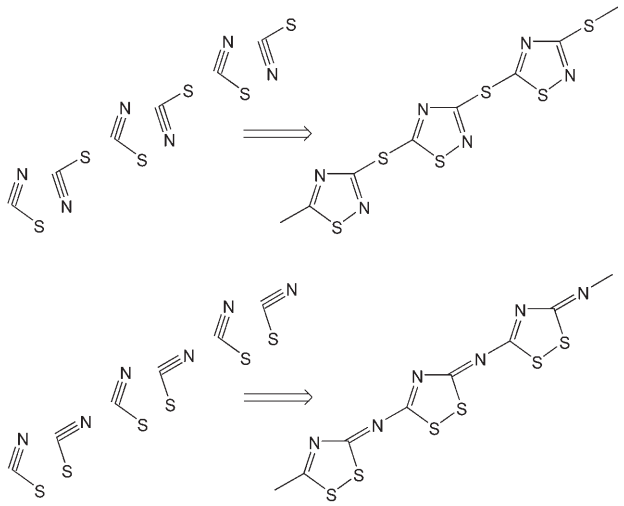


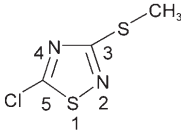
Figure 4. Our proposed structures of polythiocyanogen based on 1,2,4-thiadiazole (top) and 1,2,4-dithiazoles (bottom).

Although some of these 1,2,4-thiadiazoles have been synthesised before, the spectroscopic data is very limited[19,24–26] and only one compound has published ^{13}C NMR data.[27] We also report the synthesis of model compounds composed of two 1,2,4-thiadiazole rings linked by a sulfur bridge. Selected examples have been studied by X-ray crystallography. The spectroscopic data obtained for polythiocyanogen has also been compared to a series of known 1,2,4-dithiazole compounds and we conclude that the structure of $(SCN)_x$ is based upon 1,2,4-dithiazole rings linked by nitrogen atoms.

Experimental Section

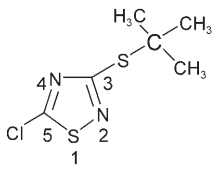
Unless otherwise stated, all operations were carried out under an oxygen-free nitrogen atmosphere by using standard Schlenk techniques. All solvents and reagents were purchased from Aldrich, Alfa Aesar, BOC, BDH, Fisons and Strem. We are grateful to Johnson Matthey PLC for the loan of precious metal salts. Diethyl ether and THF were purified by reflux over sodium/benzophenone and distillation under nitrogen. Hexane was purified by reflux over sodium and distillation under an atmosphere of nitrogen. Dichloromethane was heated to reflux over powdered calcium hydride and distilled under nitrogen. Chloroform (99 atom % d), and CD_2Cl_2 (99.6+ atom D) were used as received. Labelled (99%) ^{15}N and ^{13}C KNCS came from Aldrich. Dipotassium cyanodithioimidocarbonate was prepared by the reaction of cyanamide with carbon disulfide and potassium ethoxide.[28] Potassium methyl cyanodithioimidocarbonate was prepared by reaction of dipotassium cyanodithioimidocarbonate with methyl iodide.[29] *S*-Methylisothiourea hydrochloride and *S*-

tert-butylisothiourea hydrochloride were prepared by the reaction of thiourea, HCl and methanol or *tert*-butanyl alchohol, respectively.[30] [$PtCl_2$(dppe)] (dppe = bis(diphenylphosphino)ethane) was prepared by the addition of a stoichiometric quantity of the diphosphine to a solution of [$PtCl_2$(cod)] (cod = cycloocta-1,5-diene) in dichloromethane. Chlorine (BOC) was dried by passing the gas over phosphorus pentoxide. Ammonium hydroxide, bromine, copper(I) chloride, ferric acetylacetonate, lithium triethylborohydride 1 M in THF, *N*-methylpyrrolidone, methylmagnesium bromide, potassium thiocyanate, sodium hydroxide, sodium methoxide, sodium thiomethoxide, sulfuryl chloride, trichloromethylsulfenyl chloride were used as received. Silver thiocyanate was prepared by mixing equimolar quantities of potassium thiocyanate with silver nitrate in water. Infrared and Raman spectra were recorded (IR spectra as KBr discs unless otherwise stated) on a Perkin–Elmer System 2000 FT/IR/Raman spectrometer. ^{31}P, ^{13}C and ^{1}H NMR spectra were recorded using a JEOL DELTA GSX 270 FT NMR spectrometer. Microanalysis was performed by the University of St. Andrews service. Mass spectra were recorded by both the University of St. Andrews mass spectrometry service and the Swansea mass spectrometry service. The ^{13}C and ^{15}N solid-state NMR spectra were recorded using a 500 MHz triple channel Varian Infinityplus spectrometer operating at 125.76 and 50.68 MHz, respectively. The samples were packed in a 4 mm ZrO_2 rotor with vespel drive tip and teflon spacers. The direct-polarisation magic angle spinning (DP-MAS) NMR spectra were recorded with 10 kHz spinning using a 90° pulse duration of 4 μs and a recycle delay of 500 s. The ^{13}C and ^{15}N spectra were referenced to adamantane (38.4 ppm) and ammonium nitrate (−5.1 ppm).

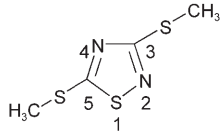


Synthesis of compound 1: *S*-Methylisothiourea hydrochloride (20.000 g, 0.158 mol) was suspended in dichloromethane (200 cm^3). A small volume of water (4 cm^3) was added and the mixture cooled to −10 °C. Trichloromethylsulfanyl chloride (29.364 g, 0.158 mol) in diethyl ether (50 cm^3) and sodium hydroxide (25.273 g, 0.632 mol) in water (50 cm^3) were added dropwise over 1 h, while the mixture was kept at −10 °C. The mixture was then stirred for a further 2 h at room temperature followed by the addition of ammonium hydroxide (5 cm^3). The organic layer was then extracted with dichloromethane (2 × 150 cm^3). The solvent was then removed in vacuo. The product was then isolated by distillation in vacuo at 50 °C by using Kugelrohr apparatus. The product was found to be a pale yellow oil, which upon cooling became a pale yellow crystalline solid. Crystals suitable for X-ray diffraction were obtained. Yield 15.830 g (60 %); elemental analysis calcd (%) for $C_3H_3ClN_2S_2$: C 21.62, H 1.81, N 16.81; found: C 21.80, H 1.84, N 16.51; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 173.1 (s, C5), 171.8 (s, C3), 14.8 ppm (s, CH_3); ^1H NMR (CD_2Cl_2): δ = 2.58 ppm (s, 3H; SCH_3); ES^+ MS: *m*/*z*: 167 $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 3002 (w), 2928 (m), 2783 (w), 2511 (vw), 1606 (w), 1452 (s), 1347 (m), 1334 (w), 1316 (m), 1216 (s), 1065 (s), 977 (m), 907 (s), 807 (w), 722 (w), 538 (w), 508 (w), 489 (m), 442 (w), 344 cm^{-1} (w).

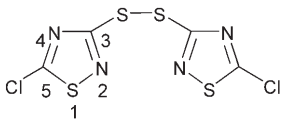
Synthesis of compound 2: This compound was prepared in the same fashion as compound **1** by using *S*-*tert*-butylisothiourea hydrochloride (20.000 g, 0.119 mol), trichloromethylsulfanyl chloride (22.039 g, 0.119 mol) and sodium hydroxide (18.968 g, 0.474 mol). The product was then isolated by distillation in vacuo at 70 °C by using Kugelrohr apparatus. This gave the product as a yellow oil. Yield 18.743 g (76 %); elemental analysis calcd (%) for $C_6H_9ClN_2S_2$: C 34.52, H 4.35, N 13.42; found: C 34.07, H 4.59, N 13.01; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 171.8 (s, C5), 171.2 (s, C3), 48.1 (s, $C(CH_3)_3$), 30.3 ppm (s, $C(CH_3)_3$); ^1H NMR (CD_2Cl_2): δ = 1.56 ppm (s, 9H; $C(CH_3)_3$); ES^+ MS: *m*/*z*: 152.9 $[M+H-tBu]^+$; IR (KBr): $\tilde{\nu}$ = 2992 (s), 2964 (s), 2925 (s), 2865 (s), 2777 (m), 2745 (w), 2717 (w), 2507 (w), 1602 (m), 1476 (s), 1448 (s), 1393 (s), 1365 (s), 1344 (s), 1321 (s), 1222 (s), 1197 (s), 1156 (s), 1063 (s), 1037 (m), 1027 (m), 957 (w), 934 (m), 908 (s), 807 (m), 740 (w), 713 (w), 688 (s), 589 (m), 538 (m), 524 (m), 484 (s), 436 (w), 409 (w), 374 (w), 306 cm^{-1} (w); Raman (glass capillary): $\tilde{\nu}$ = 2970 (s), 2927 (vs), 1452 (w), 1347 (s), 1200 (w), 1162 (w), 936 (vw), 911 (vw), 809 (w), 687 (s), 591 (m), 411 (m), 309 cm^{-1} (s).



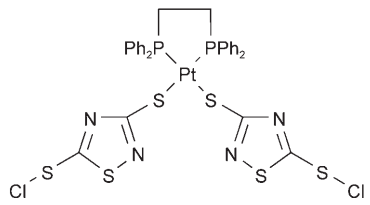
Synthesis of compound 3: Compound **1** (1.000 g. 6.00 mmol) was dissolved in methanol (40 cm^3). Sodium thiomethoxide (0.421 g, 6.00 mmol) was added as a solid in one portion. The resultant solution was heated to 40 °C for 24 h. The solvent was removed in vacuo and dichloromethane (50 cm^3) added. The resultant mixture was filtered through a celite pad to remove precipitated NaCl. The solvent was then removed in vacuo to give the product as a yellow oil. Yield 0.883 g (83 %); elemental analysis calcd (%) for $C_4H_6N_2S_3$: C 26.95, H 3.39, N 15.71; found: C 26.93, H 3.36, N 15.64; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 189.1 (s C5), 171.5 (s, C3), 16.8 (s, C5SCH_3), 15.1 ppm (s, C3SCH_3); ^1H NMR (CD_2Cl_2): δ = 2.59 (s, 3H; C3SCH_3), 2.53 ppm (s, 3H; C5CH_3); ES^+ MS: *m*/*z*: 178 $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 3000 (w), 2927 (m), 2845 (vw), 2413 (vw), 2282 (vw), 1591 (w), 1526 (m), 1424 (s), 1371 (w), 1348 (m), 1314 (m), 1218 (s), 1091 (w), 1067 (s), 1050 (s), 968 (s), 932 (w), 908 (s), 802 (m), 736 (w), 714 (w), 684 (m), 588 (vw), 546 (w), 508 (vw), 489 (w), 470 (w), 443 (w), 383 (w), 331 cm^{-1} (vw); Raman (glass capillary): $\tilde{\nu}$ = 3001 (w), 2929 (vs), 1426 (w), 1372 (m), 1350 (s), 1316 (m), 1219 (w), 910 (w), 803 (w), 721 (m), 683 (m), 672 (m), 448 (m), 409 (vw), 384 (w), 335 (w), 302 (w), 261 cm^{-1} (w).



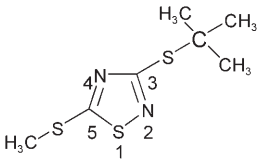
Synthesis of compound 4: Compound **2** (1.000 g, 4.79 mmol) was dissolved in dichloromethane (30 cm^3) and cooled to 0 °C. Chlorine gas (excess) was bubbled slowly through the solution for 20 min. The dichloromethane and excess chlorine were removed under reduced pressure. The residue was then dissolved in THF (30 cm^3) and copper(I) chloride (0.474 g, 4.79 mmol) was added. The resultant solution was stirred in the dark for 2 h. Reaction was observed to be complete when the green copper (I) chloride was converted to brown copper(II) chloride. The solvent was removed in vacuo and the residue dissolved in dichloromethane (30 cm^3). The mixture was filtered through celite and the solvent removed in vacuo. The product was isolated by column chromatography on silica eluting with a 50:50 mixture of dichloromethane/hexane. The product was obtained as a cream powder. Yield 0.256 g (35 %); elemental analysis calcd (%) for $C_4Cl_2N_4S_4$: C 15.84, N 17.82; found: C 15.68, N 18.27; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 174.9 (s, C5), 167.5 (s, C3); ES^+ MS: *m*/*z*: 325 $[M+Na]^+$, 303 $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 2764 (w), 1442 (s), 1436 (s), 1379 (w), 1360 (w), 1339 (m), 1213 (s), 1203 (s), 1082 (s), 1072 (s), 1007 (br s), 905 (s), 801 (w), 685 (m), 674 (m), 539 (m), 486 (m), 471 (m), 380 (m), 348 (m), 302 (w), 282 (w), 271 cm^{-1} (w); Raman (glass capillary): $\tilde{\nu}$ = 1359 (m), 1341 (m), 1211 (w), 907 (w), 805 (w), 693 (vs), 547 (m), 473 (w), 443 (m), 318 (vs), 271 (vw), 241 cm^{-1} (s).



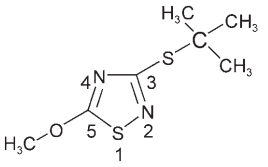
Synthesis of compound 5: Compound **4** (0.046 g, 0.151 mmol) was dissolved in THF (10 cm^3). The solution was cooled to −40 °C and a solution of $LiBEt_3H$ (1.0 M; 0.032 g, 0.30 mmol) in THF was added dropwise. The



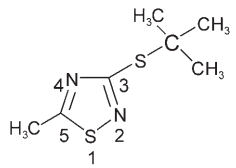
clear solution was observed to change to pale yellow on addition of $LiBEt_3H$. The reaction mixture was then stirred for a further hour at −40 °C then $[PtCl_2(dppe)]$ (0.100 g, 0.15 mmol) was added as a solid in one portion with a further portion of THF (10 cm^3). The solution was allowed to warm to room temperature and stirred for 24 h. The solvent was then removed under reduced pressure and the residue dissolved in dichloromethane (30 cm^3). The resultant mixture was filtered through a celite pad (to removed precipitated LiCl) and the solvent removed in vacuo to give the product as a pale yellow powder. Crystals suitable for X-ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.098 g (73%); elemental analysis calcd (%) for $C_{30}H_{24}Cl_2P_2PtN_4S_4$: C 39.18, H 2.63, N 6.09; found: C 38.93, H 2.36, N 5.70; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 46.3$ ppm ($^1J(^{195}Pt,^{31}P) = 3045$ Hz); ^1H NMR ($CDCl_3$): δ7.83–7.27 (m, 20H; aromatic), 2.61–2.21 ppm (m, 4H; PCH_2CH_2P); EI^+ MS: m/z: 919 $[M+Na]^+$; IR (KBr): $\tilde{\nu} = 3050$ (w), 2920 (w), 2851 (w), 2179 (w), 1478 (m), 1445 (s), 1436 (s), 1308 (wm) 1183 (m), 1164 (m), 1105 (m), 1051 (m), 1027 (w), 999 (w), 897 (w), 882 (w), 817 (w), 749 (w), 705 (m), 690 (m), 534 (m), 487 (w), 282 cm^{-1} (w).



Synthesis of compound 6: This compound was prepared in the same fashion as compound **3** but with compound **2** (2.000 g, 9.58 mmol) and sodium thiomethoxide (0.672 g, 9.59 mmol) to give the product as a yellow oil. Yield 1.475 g (70%); elemental analysis calcd (%) for $C_7H_{12}N_2S_3$: C 38.15, H 5.49, N 12.71; found: C 38.56, H 5.48, N 12.89; $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 187.6 (s C5), 170.5 (s, C3), 47.9 (s, $C(CH_3)_3$), 30.5 (s, $C(CH_3)_3$), 16.6 ppm (s, C5SCH_3); ^1H NMR ($CDCl_3$): $\delta = 2.62$ (s, 3H; C5SCH_3), 1.50 (s, 9H; C-$(CH_3)_3$); ES^+ MS: m/z: 243 $[M+Na]^+$; IR (KBr): $\tilde{\nu} = 2992$ (m), 2963 (s), 2923 (s), 2864 (m), 2715 (vw), 1587 (w), 1526 (m), 1475 (m), 1456 (m), 1427 (brs), 1391 (m), 1364 (s), 1347 (m), 1313 (m), 1230 (s), 1199 (brs), 1157 (s), 1063 (s), 1050 (s), 969 (m), 934 (m), 910 (s), 800 (m), 738 (m), 706 (w), 686 (m), 590 (w), 547 (w), 521 (w), 485 (w), 466 (w), 411 (w), 376 cm^{-1} (w); Raman (glass capillary): 2996 (w), 2967 (m), 2922 (vs), 1454 (w), 1374 (w), 1349 (s), 1316 (w), 1201 (w), 1160 (vw), 912 (w), 808 (w), 711 (w), 685 (m), 675 (m), 593 (m), 489 (w), 414 (w), 353 (w), 312 (m), 226 cm^{-1} (w).

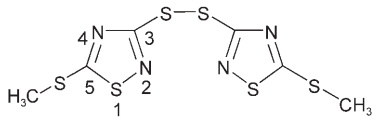


Synthesis of compound 7: This compound was prepared in the same fashion as compound **3**, but by using compound **2** (0.500 g, 2.39 mmol) and sodium methoxide (0.129 g, 4.05 mmol). The solution was heated under reflux for 24 h. This gave the product as yellow oil. Yield 0.412 g (84%); elemental analysis calcd (%) for $C_7H_{12}N_2OS_2$: C 41.15, H 5.92, N 13.71; found: C 40.88, H 5.80, N 14.10; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 190.3$ (s C5), 166.7 (s, C3), 60.4 (s, OCH_3), 47.6 (s, $C(CH_3)_3$), 30.1 ppm (s, $C(CH_3)_3$); ^1H NMR (CD_2Cl_2): $\delta = 4.10$ (s, 3H; OCH_3), 1.55 ppm (s, 9H; $C(CH_3)_3$); ES^+ MS: m/z: 227 $[M+Na]^+$; IR (KBr): $\tilde{\nu} = 2994$ (m), 2963 (s), 2923 (s), 2866 (m), 2757 (w), 1528 (s), 1476 (m), 1434 (brs), 1401 (s), 1389 (s), 1364 (s), 1230 (brs), 1181 (s), 1158 (s), 1065 (w), 1031 (m), 975 (m), 935 (m), 792 (m), 779 (m), 738 (w), 689 (m), 591 (m), 492 (w), 407 (m), 377 cm^{-1} (m); Raman (glass capillary): 2964 (s), 2925 (vs), 1528 (w), 1456 (m), 1436 (m), 1403 (w), 1224 (w), 1157 (w), 935 (w), 810 (m), 782 (m), 690 (w), 591 (s), 494 (w), 427 (w), 409 (m), 376 (w), 307 cm^{-1} (w).

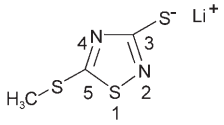


Synthesis of compound 8: Compound **2** (1.00 g, 4.791 mmol) was dissolved in THF (35 cm^3) with *N*-methylpyrrolidone (3.5 cm^3) and a catalytic amount of $[Fe(acac)_3]$ (0.077 g, 0.24 mmol). A solution of methyl magnesium bromide (3.0 M in diethyl ether, 1.76 cm^3, 5.27 mmol) was added dropwise to the resultant red solution. This caused the colour to change to brown. After 10 min when the colour had changed to dark purple, the reaction mixture was diluted with diethyl ether (40 cm^3) and quenched by the addition of hydrochloric acid (1.0 M, 2 cm^3). After extraction of the organic phase the product was isolated by column chromatography on silica eluting with a 50:50 mixture of dichloromethane/hexane. This gave the product as a pale yellow oil. Yield 0.632 g (70%). elemental analysis calcd (%) for $C_7H_{12}N_2S_2$: C 44.65, H 6.42, N 14.88; found: C 44.42, H 6.11, N 14.31; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 185.6$ (s C5), 170.1 (s, C3), 47.5 (s, $C(CH_3)_3$), 30.3 (s, $C(CH_3)_3$), 16.6 ppm (s, C5CH_3); ^1H NMR (CD_2Cl_2): $\delta = 2.68$ (s, 3H; C5CH_3), 1.54 ppm (s, 9H; $C(CH_3)_3$); ES^+ MS: m/z: 211 $[M+Na]^+$; IR (KBr): $\tilde{\nu} = 2993$ (m), 2962 (s), 2923 (s), 2865 (s), 2715 (w), 1611 (w), 1488 (s), 1448 (s), 1393 (m), 1377 (s), 1364 (s), 1343 (m), 1234 (s), 1207 (s), 1159 (s), 1065 (m), 1035 (w), 1025 (w), 993 (w), 935 (m), 909 (w), 852 (w), 810 (m), 695 (m), 675 (w), 587 (m), 533 (w), 493 (w), 424 (w), 378 cm^{-1} (w); Raman (glass capillary): $\tilde{\nu} = 2967$ (m), 2928 (s), 1454 (w), 1395 (w), 1380 (m), 1346 (w), 1216 (w), 1163 (w), 933 (w), 813 (m), 677 (m), 596 (m), 496 (w), 425 (w), 378 (vw), 338 (w), 307 (vw), 279 cm^{-1} (vw).

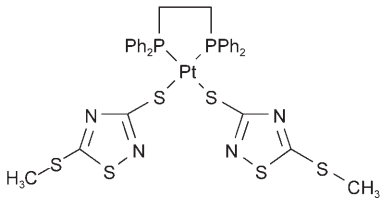
Synthesis of compound 9: Compound **6** (1.000 g, 4.54 mmol) was dissolved in dichloromethane (30 cm^3) and cooled to 0 °C. Chlorine gas (excess) was bubbled slowly through the solution for 20 min. The dichloromethane and excess chlorine were removed under reduced pressure to yield a yellow oil. The product was isolated by column chromatography on silica eluting with a 50:50 mixture of dichloromethane/hexane. The product was obtained as an off white solid. Yield 0.191 g (13%); elemental analysis calcd (%) for $C_6H_6N_4S_6$: C 22.07, H 1.85, N 17.16; found: C 21.74, H 1.81, N 16.89; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 190.0$ (s C5), 167.7 (s, C3), 16.8 ppm (s, C5CH_3); ^1H NMR (CD_2Cl_2): $\delta = 2.67$ (s, 3H; C5CH_3); ES^+ MS: m/z: 349 $[M+Na]^+$; IR (KBr): $\tilde{\nu} = 3000$ (vw), 2926 (w), 2913 (w), 2853 (w), 1595 (w), 1518 (w), 1433 (m), 1415 (s), 1357 (w), 1337 (m), 1317 (w), 1211 (s), 1151 (w), 1089 (w), 1067 (m), 1020 (s), 974 (m), 966 (w), 910 (m), 801 (m), 715 (w), 682 (w), 671 (w), 543 (w), 461 (w), 385 (w), 278 (w), 258 cm^{-1} (w).



Synthesis of compound 10: Compound **9** (0.100 g, 0.31 mmol) was dissolved in THF (20 cm^3). The solution was cooled to −40 °C and a solution of $LiBEt_3H$ (1.0 M; 0.065 g, 0.61 mmol) in THF was added dropwise. The clear solution was observed to change to pale yellow on addition of $LiBEt_3H$. The reaction mixture was then allowed to warm to room temperature and stirred for a further hour. The solvent was evaporated in vacuo to yield the product as a yellow powder. Yield 0.064 g (63%); elemental analysis calcd (%) for $C_3H_3N_2S_3Li$: C 21.17, H 1.77, N 16.45; found: C 20.91, H 1.46, N 16.32; ES^-MS: m/z: 163 $[M]^-$, 131 $[M-S]^-$; IR (KBr): $\tilde{\nu} = 3038$ (w), 2970 (w), 2928 (w), 2902 (s), 2182 (w), 1509 (w), 1399 (s), 1316 (w), 1306 (m), 1179 (s), 1167 (s), 1097 (w), 1078 (m), 980 (w), 957 (w), 923 (w), 805 (w), 728 (w), 697 (m), 668 (w), 495 (w), 438 (w), 381 (w), 323 cm^{-1} (w).

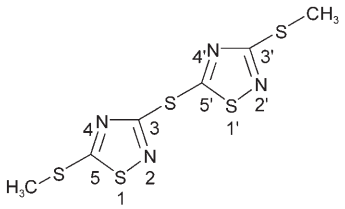


Synthesis of compound 11: This compound was prepared in the same fashion as **5** by using **9** (0.049 g, 0.15 mmol), a solution of $LiBEt_3H$ (1.0 M; 0.032 g, 0.30 mmol) in THF and $[PtCl_2(dppe)]$ (0.100 g, 0.15 mmol) to give the product as a pale yellow powder. Yield 0.107 g (78%); elemental analysis calcd (%) for $C_{32}H_{30}P_2PtN_4S_6$: C 41.78, H 3.29, N 6.09; found: C 41.42, H 2.89, N 6.23; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 46.2$ ppm ($^1J(^{195}Pt,^{31}P) =$ 047 Hz); ^1H NMR ($CDCl_3$): $\delta = 7.81$–7.23 (m, 20H; aromatic), 2.70–2.16 ppm (m, 4H; PCH_2CH_2P); EI^+ MS: m/z: 942 $[M+Na]^+$; IR (KBr):



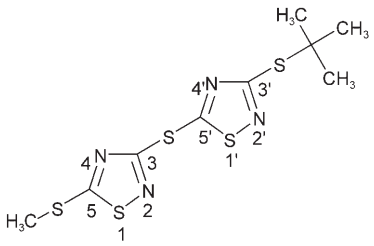
$\tilde{\nu}$ = 3050 (w), 2961 (w), 2920 (w), 2866 (w), 1483 (w), 1435 (m), 1412 (s), 1309 (m), 1262 (m), 1175 (s), 1103 (s), 1042 (m), 1027 (m), 997 (m), 966 (w), 898 (w), 879 (w), 817 (m), 802 (m), 748 (m), 714 (m), 704 (m), 690 (s), 660 (w), 532 (s), 485 (m), 397 cm^{-1} (w).

Synthesis of compound 12: Compound **9** (0.100 g, 0.306 mmol) was dissolved in THF (20 cm^3). The solution was cooled to −40 °C and a solution



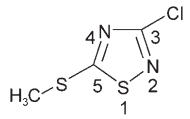
of $LiBEt_3H$ (1.0 M; 0.065 g, 0.61 mmol) in THF was added dropwise. The clear solution was observed to change to pale yellow on addition of $LiBEt_3H$. The reaction mixture was then stirred for a further hour. Compound **1** (0.102 g, 0.61 mmol) was then added as a solid in one portion. The resulting solution was stirred for 24 h. The solvent was evaporated in vacuo and the remaining solid was extracted with dichloromethane (20 cm^3). The mixture was filtered through a celite pad to remove precipitated LiCl and washed through with additional dichloromethane (30 cm^3). The filtrate was evaporated to dryness in vacuo to give a cream powder. Crystals suitable for X-ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.120 g (67 %); elemental analysis calcd (%) for $C_6H_6N_4S_5$: C 24.47, H 2.05, N ;19.03 found: C 24.72, H 1.64, N 18.63; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 191.9 (s, C5), 180.8 (s, C5′), 170.5 (s, C3′), 163.4 (s, C3), 17.0 (s, C5S*C*H_3), 14.7 ppm (s, C3′S*C*H_3); ^1H NMR (CD_2Cl_2): δ = 2.80 (s, 3H; C5SCH_3), 2.65 ppm (s, 3H; C3′SCH_3); ES$^+$ MS: *m*/*z* .317 $[M+Na]^+$; IR (KBr): $\tilde{\nu}$ = 2996 (w), 2966 (w), 2924 (w), 1443 (m), 1416 (s), 1367 (w), 1343 (w), 1331 (m), 1308 (m), 1249 (s), 1217 (s), 1094 (w), 1066 (m), 1058 (m), 977 (w), 966 (w), 916 (w), 906 (w), 801 (m), 681 (m), 482 (w), 420 (w), 387 (w), 285 cm^{-1} (w); Raman (glass capillary): $\tilde{\nu}$ = 3004 (w), 2928 (s), 1421 (w), 1370 (w), 1346 (s), 1334 (m), 1310 (w), 1252 (m), 1227 (w), 919 (w), 808 (m), 724 (m), 694 (s), 524 (m) 422 (w), 313 (w), 268 cm^{-1} (w).

Synthesis of compound 13: This compound was prepared in the same way as compound **12** by using **9** (0.050 g, 0.15 mmol), $LiBEt_3H$ (0.065 g, 0.306 mmol) and compound **2** (0.032 g, 0.31 mmol) to give a cream powder. Crystals suitable for X-ray diffraction were obtained by vapour diffusion from chloroform/hexane. Yield 0.053 g (51 %); elemental analysis calcd (%) for $C_9H_{12}N_4S_5$: C 32.11, H 3.59, N 16.65; found: C 31.88, H

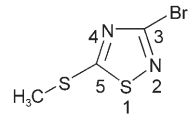


3.15, N 16.42; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 191.8 (s, C5), 179.4 (s, C5′), 169.4 (s, C3′), 163.6 (s, C3), 47.9 (s, *C*(CH_3)$_3$), 30.3 (s, C(*C*H_3)$_3$), 17.0 ppm (s, C5S*C*H_3); ^1H NMR (CD_2Cl_2): δ = 2.80 (s, 3H; C5SCH_3), 1.59 ppm (s, 9H; C(CH_3)$_3$); ES$^+$ MS: *m*/*z*: 359 $[M+Na]^+$; IR (KBr): $\tilde{\nu}$ = 2959 (w), 2920 (w), 2858 (w), 1475 (w), 1459 (w), 1436 (s), 1427 (s), 1362 (m), 1342 (w), 1244 (m), 1221 (m), 1208 (m), 1159 (m), 1074 (m), 1061, 971 (w), 917 (w), 797 (w), 675 (w), 501 (w), 475 (w), 402 (w), 278 cm^{-1} (w); Raman (glass capillary): $\tilde{\nu}$ = 2999 (w), 2965 (m), 2915 (s), 1458 (w), 1435 (w), 1362 (w), 1339 (s), 1323 (w), 1222 (w), 1212 (vw), 1166 (vw), 932 (vw), 919 (w), 812 (w), 801 (w), 714 (w), 676 (s), 598 (m), 490 (w), 478 (m), 443 (w), 383 (w), 368 (w), 319 cm^{-1} (m).

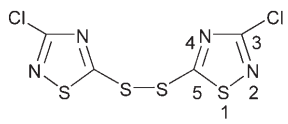
Synthesis of compound 14: A slurry of potassium methyl cyanodithioimidocarbonate (1.257 g, 7.38 mmol) in dichloromethane (30 cm^3) was stirred at 0 °C, while sulfuryl chloride (1.267 g, 9.39 mmol) was added dropwise. The resultant mixture was stirred for a further 24 h at room temperature. The mixture was filtered to remove precipitated KCl then the solvent was then removed in vacuo to give the product as a pale yellow crystalline solid. Yield 1.048 g (85 %); elemental analysis calcd (%) for $C_3H_3N_2S_2Cl$: C 21.62, H 1.81, N 16.81; found: C 21.74, H 1.42, N 16.99; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 191.9 (s, C5), 156.1 (s, C3), 16.5 ppm (s, CH_3); ^1H NMR (CD_2Cl_2): δ = 2.70 (s, 3H; C5CH_3); ES$^+$ MS: *m*/*z*: 167 $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 2990 (w), 2959 (vw), 2922 (w), 2854 (w), 1433 (s), 1425 (s), 1363 (w), 1345 (m), 1330 (w), 1229 (s), 1174 (w), 1073 (s), 1050 (m), 977 (m), 969 (m), 919 (m), 897 (w), 804 (m), 711 (w), 678 (m), 550 (w), 535 (w), 482 (w), 376 cm^{-1} (w); Raman (glass capillary): $\tilde{\nu}$ = 3006 (w), 2995 (m), 2921 (s), 1365 (w), 1347 (vs), 1327 (w), 1233 (w), 918 (w), 806 (w), 715 (w), 680 (vs), 421 (vs), 380 (w), 258 cm^{-1} (w).



Synthesis of compound 15: This compound was prepared in the same fashion as compound **14** using potassium methyl cyanodithioimidocarbonate (4.330 g, 0.025 mol) and bromine (4.063 g, 0.025 mol) to give the product as a pale yellow crystalline solid. Yield 5.043 g (95 %); elemental analysis calcd (%) for $C_3H_3BrN_2S_2$: C 17.36, H 1.43, N 13.27; found: C 17.07, H 1.01, N 13.45; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 191.6 (s, C5), 144.3 (s, C3), 16.6 ppm (s, CH_3); ^1H NMR ($CDCl_3$): δ = 2.73 ppm (s, 3H; C5CH_3); ES$^+$ MS: *m*/*z*: 213 $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 2989 (w), 2918 (w), 1561 (w), 1491 (w), 1415 (s), 1354 (m), 1332 (m), 1324 (m), 1208 (br s), 1192 (s), 1096 (w), 1071 (s), 1048 (m), 974 (m), 968 (m), 894 (s), 786 (m), 712 (w), 667 (m), 547 (w), 456 (m), 378 (w), 305 (w), 250 cm^{-1} (w); Raman (glass capillary): $\tilde{\nu}$ = 3004 (w), 2993 (w), 2920 (s), 1423 (vw), 1354 (m), 1347 (m), 1322 (s), 1210 (w), 891 (m), 714 (m), 673 (s), 381 (m), 307 (s), 228 cm^{-1} (w).



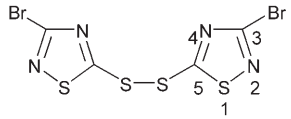
Synthesis of compound 16: A slurry of dipotassium cyanodithioimidocarbonate (7.535 g, 0.04 mol) in dichloromethane (40 cm^3) was stirred at



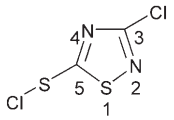
−40 °C, while chlorine (5.498 g, 0.08 mol) in dichloromethane (50 cm^3) was slowly added. The reaction mixture was stirred for 1 h at 0 °C then suction filtered. The dichloromethane was then removed in vacuo to give the product as a yellow crystalline solid. Yield 4.748 g (81 %); elemental analysis calcd (%) for $C_4N_4Cl_2S_4$: C 15.84, N 18.48; found: C 15.99, N 18.45; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 188.5 (s, C5), 158.0 ppm (s, C3); EI$^+$ MS: *m*/*z*: 302 $[M]^+$; IR (KBr): $\tilde{\nu}$ = 2757 (w), 2423 (w), 1606 (w), 1435 (s), 1362 (m), 1342 (s), 1216 (br s), 1096 (w), 1061 (s), 951 (w), 806 (s), 677

(m), 555 (w), 542 (w), 481 (m), 418 (w), 410 (w), 373 (m), 357 cm^{-1} (w); Raman (glass capillary): $\tilde{\nu}$ = 1436 (w), 1365 (m), 1342 (vs), 1223 (w), 915 (m), 809 (m), 681 (m), 560 (w), 538 (w), 471 (w), 419 (m), 376 (w), 360 cm^{-1} (w).

Synthesis of compound 17: A slurry of dipotassium cyanodithioimidocarbonate (2.00 g, 0.01 mol) in dichloromethane (20 cm^3) was stirred at −40 °C, while bromine (3.289 g, 0.02 mol) in dichloromethane (10 cm^3)



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



Synthesis of compound 18: Compound **16** (1.000 g, 3.30 mmol) was dissolved in dichloromethane and cooled to 0 °C. Chorine gas (excess) was bubbled through the solution. The solution was then stirred for a further hour at room temperature then the solvent was removed in vacuo to give the product as a yellow solid. Yield 1.041 g (84 %); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ(C) 180.2 (s, C5), 155.9 ppm (s, C3).

Synthesis of compound $(SCN)_x$ 19

Method A: Thiocyanogen was allowed to warm to room temperature resulting in spontaneous polymerisation to give polythiocyanogen as a brick red solid. Yield 0.672 g (58 %). elemental analysis calcd (%) for $(SCN)_x$: C 20.68, N 4.12; found: C 20.44, N 23.89 (2); ^{13}C DP-MAS NMR (75.4 MHz): δ = 186.8 ppm (broad slightly asymmetric signal with low intensity spinning side bands); MALDI-TOF MS: *m*/*z*: 1149 $[S_{20}C_{20}N_{19}]^+$, 1030 $[S_{18}C_{18}N_{17}]^+$, 914 $[S_{16}C_{16}N_{15}]^+$, 798 $[S_{14}C_{14}N_{13}]^+$, 682 $[S_{12}C_{12}N_{11}]^+$, 566 $[S_{10}C_{10}N_9]^+$, 450 $[S_8C_8N_7]^+$, 334 $[S_6C_6N_5]^+$, 218 $[S_4C_4N_3]^+$, 102 $[S_2C_2N]^+$; Selected IR data (KBr): $\tilde{\nu}$ = 1206 cm^{-1} (vbrs); Raman (glass capillary): $\tilde{\nu}$ = 1508 (m), 1207v (brs), 1155(shs), 994 (w), 652 (vbrm), 473 (s), 453 (shbrm), 400 (shbrm), 289 (m), 229 cm^{-1} (m).

Method B: Potassium thiocyanate (0.500 g, 5.145 mmol) was ground to a very fine powder and added to a flask. Chlorine gas (excess) was then passed through the powder for 30 s. The mixture was then heated using a heat gun for approximately 1 min. Reaction was observed to have occurred by the mixture turning a brick red colour. Once cool the mixture was ground to a fine powder and the process of chlorination followed by heating then grinding was repeated 5 times to ensure complete reaction. The resulting mixture was washed with water (30 cm^3) and filtered to remove KCl and any residual KNCS. The red powder collected was washed with methanol (20 cm^3) followed by diethyl ether (20 cm^3) then dried in vacuo. Yield 0.202 g (68 %). The analytical and spectroscopic data for $(SCN)_x$ **19** synthesised by this method were identical to those found in material produced by method A. ^{13}C and ^{15}N-labelled samples of $(SCN)_x$ were prepared by this method using 99 % ^{13}C and 99 % ^{15}N labelled KNCS respectively.

X-ray crystallography: Table 1 gives the details of the data collections and refinements. Intensities were corrected for Lorentz polarisation and for absorption. Data for **1, 14** and **16** were collected at 93 K by using $Mo_{K\alpha}$ radiation from a high brilliance Rigaku MM007 generator and a Rigaku Mercury ccd detector; for **5** and **12** at 93 K by using $Mo_{K\alpha}$ radiation from a high brilliance Rigaku MM007 generator and a Rigaku Saturn70 ccd detector; for **13** at 173 K by using $Cu_{K\alpha}$ radiation from a high brilliance Rigaku MM007 generator and a Rigaku Saturn92 ccd detector; and for **17** at 125 K by using $Mo_{K\alpha}$ radiation and a Bruker SMART ccd. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were done by full-matrix least squares based on F^2 using SHELXTL.[37] CCDC 290200–290206 (**1**,**5**,**12**,**13**,**14**,**16**, and **17**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

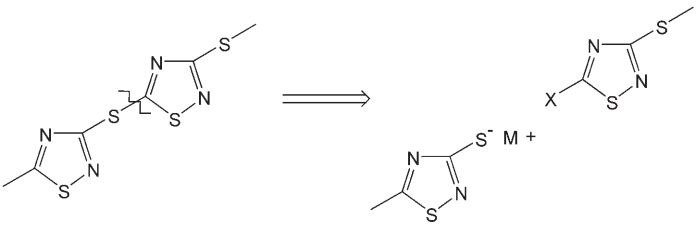
Results and Discussion

As mentioned above there was a need to clarify the data for a range of C-S-N heterocycles in order to understand both heterocyclic and polymer chemistry in this area.

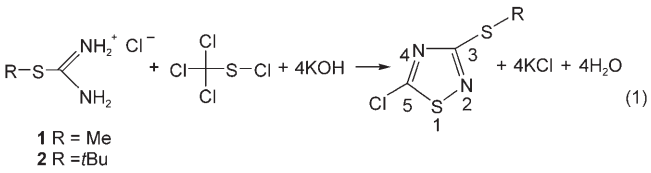
Table 1. Details of X-ray data collections and refinements.

	1	**5**	**12**	**13**	**14**	**16**	**17**
formula	$C_3H_3ClN_2S_2$	$C_{30}H_{24}Cl_2N_4P_2PtS_4$	$C_6H_6N_4S_5$	$C_9H_{12}N_4S_5$	$C_3H_3ClN_2S_2$	$C_4Cl_2N_4S_4$	$C_4Br_2N_4S_4$
crystal dimensions [mm]	0.2 × 0.2 × 0.05	0.1 × 0.03 × 0.01	0.1 × 0.03 × 0.01	0.18 × 0.1 × 0.01	0.2 × 0.05 × 0.05	0.2 × 0.1 × 0.05	0.1 × 0.1 × 0.01
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_12_12_1$	$P2_1/m$	$P2_1$	$P2_1/n$	$P2_1/c$
a [Å]	7.615(2)	29.675(2)	3.9232(11)	9.5487(8)	3.9264(3)	11.3849(13)	5.8977(11)
b [Å]	9.474(4)	8.5789(7)	8.451(3)	6.9794(5)	9.6948(9)	8.1655(10)	7.1476(13)
c [Å]	8.961(4)	25.351(2)	33.094(11)	10.8821(18)	8.2410(6)	11.7320(14)	25.310(5)
α [°]	90	90	90	90	90	90	90
β [°]	106.938(10)	94.429(4)	90	91.592(3)	101.8476(10)	111.840(9)	95.044(3)
γ [°]	90	90	90	90	90	90	90
V [Å^3]	618.4(4)	6434.5(9)	1097.2(6)	724.95(14)	307.02(4)	1012.4(2)	1062.8(3)
Z	4	8	4	2	2	4	4
M_r	166.64	896.70	294.45	336.53	166.64	303.22	392.14
ρ_{calcd} [g cm^{-3}]	1.790	1.851	1.782	1.542	1.803	1.989	2.451
μ [mm^{-1}]	1.176	4.916	1.025	7.272	1.184	1.426	8.375
measured reflns	3097	20800	6257	9453	1632	4752	4388
independent reflns (R_{int})	1017(0.0277)	5626(0.0445)	1807(0.0354)	1311(0.0510)	937(0.0236)	1694(0.1449)	1513(0.0304)
final *R*1/*wR*2 [$I > 2\sigma(I)$]	0.0240/0.0557	0.0451/0.0867	0.0322/0.0643	0.0364/0.0984	0.0228/0.0491	0.0936/0.2082	0.0293/0.0686

1,2,4-Thiadiazoles: Using a retrosynthetic approach (Scheme 5) we attempted to prepare 1,2,4-thiadiazole monomer units that could be linked together by nucleophilic substitution at C5 to form dimers and higher oligomers. The 3-alkylsulfanyl-5-chloro-1,2,4-thiadiazoles **1** and **2** were prepared by the reaction of the appropriate *S*-alkylisothiourea hydrochloride with trichloromethylsulfanyl chloride and potassium hydroxide in a mixture of dichloromethane and water [Eq. (1)].



Scheme 5. Retrosynthetic approach for the preparation of 1,2,4-thiadiazole model compounds.



1 R = Me
2 R = *t*Bu

(1)

After dichloromethane extraction of the organic phase followed by removal of the solvent **1** or **2** was isolated by distillation in vacuo by using a Kugelrohr apparatus at 50 °C or 70 °C, respectively, which was a small modification to the literature preparation of **1** and **2** in water followed by steam distillation,[31] though only melting point and IR spectroscopy were mentioned in this report. More recently the ^{13}C NMR of **1** was reported by Morel et al.[27] Compound **1** is a pale yellow oil which upon cooling slightly became a pale yellow crystalline solid. Compound **2** is a yellow oil. Microanalysis and mass spectroscopy gave the expected results for both species and the C–H stretching bands were noted in the region 2865–3002 cm^{-1}. The ring vibrations were observed at 1452 and 1216 cm^{-1} in **1** and 1447 and 1222 cm^{-1} in **2** (Goerdeler et al. reported[31] the ring stretching bands for 3-alkylsulfanyl-1,2,4-thiadiazoles in the ranges 1435–1445 and 1220–1255 cm^{-1}). In the ^{13}C{^{1}H} NMR spectrum of **1** the shifts for the ring carbons were observed at $\delta = 173.1$ and 171.8 ppm and these are assigned as C5 and C3, respectively (c.f. Morel et al.[27] $\delta = 173.2$ (C5) and 172 ppm (C3)). Our assignment was confirmed by H-C HMBC and H-C HSQC experiments. For compound **2** signals assigned to C5 and C3 were noted at $\delta = 171.8$ and 171.2 ppm, respectively. A single-crystal X-ray diffraction study confirmed the structure of **1** (Figure 5, Table 2). The X-ray structures of the various heterocycles will be considered together (vide infra).

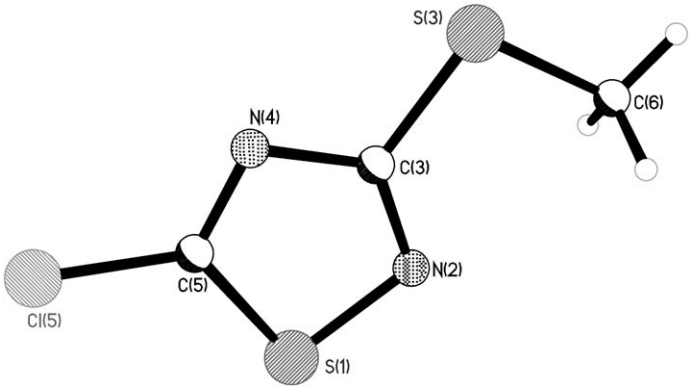


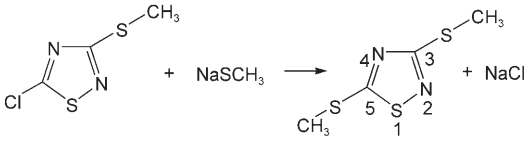
Figure 5. X-ray crystal structure of **1**.

Reaction of **1** with sodium thiomethoxide in methanol [Eq. (2)] gives 3,5-bis-methylsulfanyl-1,2,4-thiadiazole **3** in excellent yield and the disulfide **4** was prepared from **2** according to [Eq. (3)].

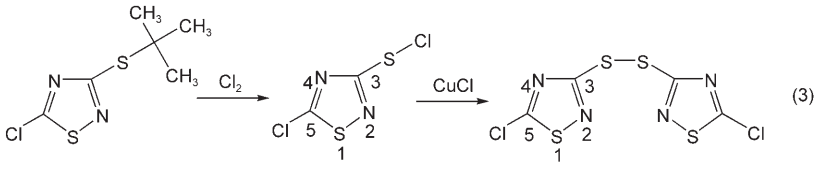
Compound **2** was dissolved in dichloromethane and excess chlorine gas was passed through the solution at 0 °C

Table 2. Selected bond lengths [Å] and angles [°] for **1**, **5**, **12** and **13**.

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



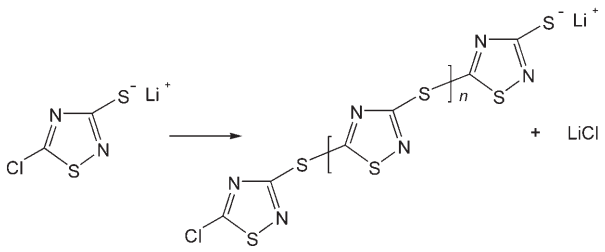
(2)



(3)

to give a mixture of products including the desired sulfenyl chloride. The $^{13}C\{^1H\}$ NMR spectrum of the mixture showed signals assigned to C5 and C3 of the sulfenyl chloride at $\delta =$ 175.2 and 166.9 ppm, respectively. Due to the air sensitive nature of the sulfenyl chloride no attempt was made to isolate this species. Instead the reaction mixture was used as obtained for the next stage. Compound **4** was obtained pure after column chromatography, the ν(S–S) vibration in **4** is assigned as the peak at 471 cm^{-1}.

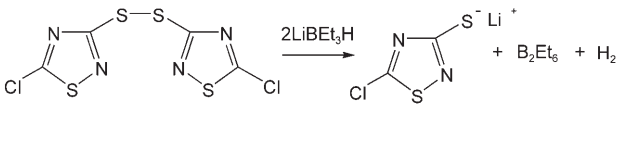
In an attempt to reductively cleave the disulfide bridge and lead to spontaneous polymerisation, $LiBEt_3H$ was added to the disulfide **4** in THF at −40 °C, whereupon the solution turned yellow. After stirring for an hour the yellow solution was allowed to slowly warm to room temperature and as the solution warmed a pale yellow solid precipitated. This solid was insoluble in all common solvents and water. Solid-state ^{13}C NMR did not yield any useful data. We speculate that at −40 °C the lithium salt is formed, but at higher temperatures it reacts with itself to give an oligomeric/polymeric material (Scheme 6) though the colour difference between this and $(SCN)_x$ indicates that this is not the "normal" polymer. We believe that this reaction yields a new isomer of $(SCN)_x$ and are currently making efforts to optimise the reaction and isolate enough material for detailed study.



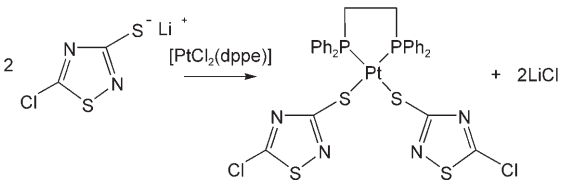
Scheme 6. Proposed polymerisation of the lithium salt of 5-chloro-1,2,4-thiadiazole-3-thiol.

To confirm that the lithium salt was formed at low temperature we trapped the anion as a platinum complex. $LiBEt_3H$ was added to the disulfide **4** in THF at −40 °C and the solution was maintained at −40 °C whilst $[PtCl_2(dppe)]$ was added. This resulted in the formation of $[Pt(C_2N_2S_2Cl_2)_2(dppe)]$ (**5**) [Eq. (4)].

The microanalysis and mass spectral data for **5** were acceptable. The ring stretches were observed at 1436 and 1183 cm^{-1} in the IR spectrum. The $^{31}P\{^1H\}$ NMR spectrum of **5** consists of a sharp singlet at 46.3 ppm with platinum satellites ($^1J(^{195}Pt,^{31}P) = 3045$ Hz). The X-ray structure confirms the connectivity of the compound (Figure 6). Due to the reactivity of the 1,2,4-thiadiazole ring at C5, we replaced chlorine with SMe, OMe, and Me in **6**, **7** and **8**, respectively (Scheme 7) enabling us to obtain a stable lithium salt.



(4)



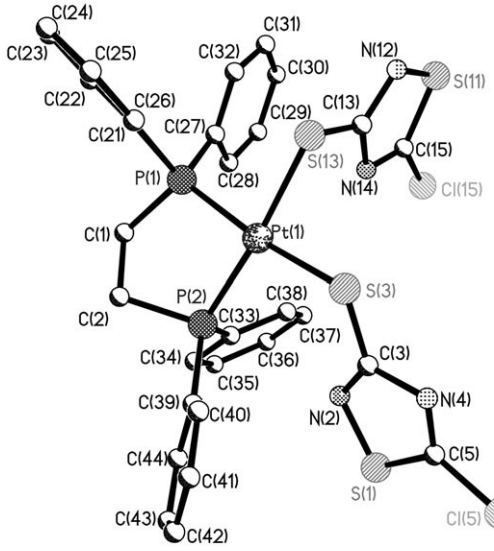
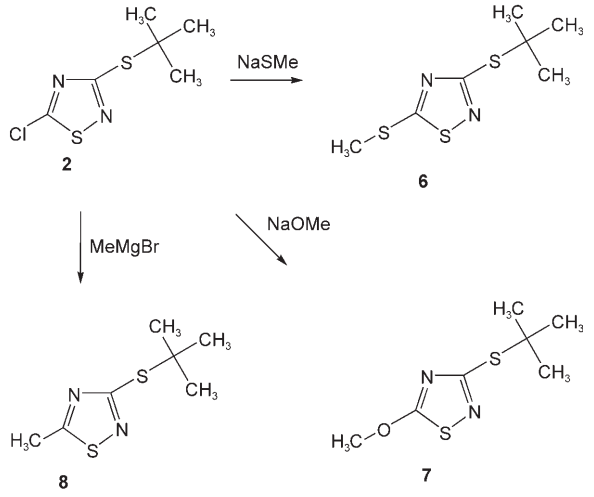


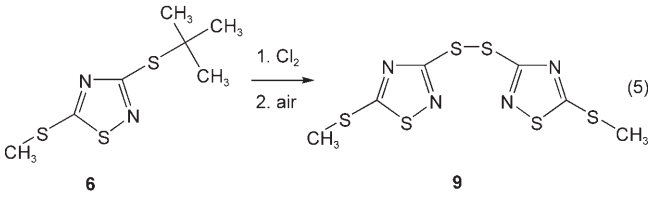
Figure 6. X-ray crystal structure of **5**.

Compound **6** was dissolved in dichloromethane and chlorinated at 0 °C. Further reaction with copper(I) chloride did not successfully convert the sulfenyl chloride to the disulfide. However, we found that if the reaction mixture was

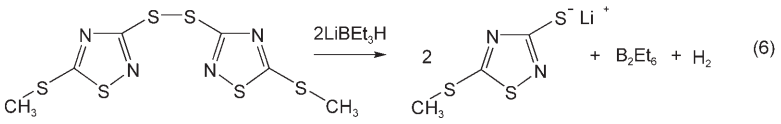


Scheme 7. Synthesis of **6**, **7** and **8**.

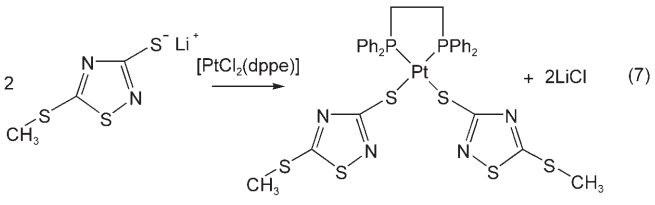
exposed to the atmosphere after chlorination then it was possible to obtain the disulfide **9** in modest yield [Eq. (5)].



In **9** the ν(S–S) vibration was observed at 461 cm^{-1}. Analogous reactions to that shown in Equation (5) were attempted using **7** and **8**, but no disulfides were obtained from these compounds. The lithium salt **10** was synthesised from **9** [Eq. (6)].

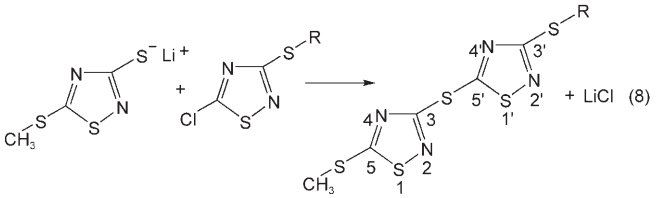


Unfortunately the lithium salt **10** was too insoluble to record ^{13}C NMR data. Therefore platinum complex **11** was prepared in the same way as **5** to confirm the lithium salt had been formed [Eq. (7)].



Complex **11** gave rise to a sharp singlet at $\delta = 46.2$ ppm with a $^1J(^{195}Pt,^{31}P)$ coupling constant of 3047 Hz in its $^{31}P\{^1H\}$ NMR spectrum. As expected the values noted were almost identical to those for **5** ($\delta = 46.3$ ppm, $^1J(^{195}Pt,^{31}P) = 3045$ Hz). The ring stretches were observed at 1412 and 1175 cm^{-1} in the IR spectrum. Microanalysis and mass spectroscopy gave the expected results.

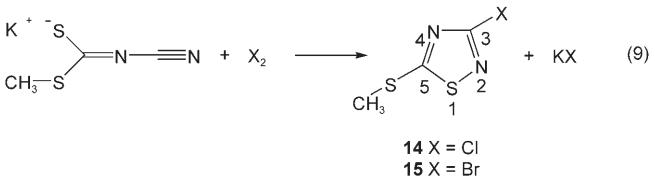
Having successfully synthesised our monomer units [the 3-alkylsulfanyl-5-chloro-1,2,4-thiadiazoles (**1** and **2**) and the lithium salt of 5-methylsulfanyl-1,2,4-thiadiazole-3-thiol (**10**)] the next step was to combine the two species by nucleophilic substitution at C5 to form a model compound [Eq. (8)].



12 R = Me
13 R = *t*Bu

The lithium salt **10** was prepared in situ in THF, a stoichiometric amount of the appropriate 3-alkylsulfanyl-5-chloro-1,2,4-thiadiazole was added and the resulting solution stirred overnight to give after workup both **12** and **13** as cream powders in good yield. In both compounds the microanalysis confirmed the purity of the compounds, mass spectroscopy showed the $[M+Na]^+$ species and the ring vibrations are observed at approximately 1430 and 1230 cm^{-1}. The methyl protons were observed in the ^1H NMR spectrum at $\delta = 2.80$ ($C5SCH_3$) and 2.65 ppm ($C3'SCH_3$) In the $^{13}C\{^1H\}$ NMR spectrum of **12** the methyl carbons were observed at $\delta = 17.0$ ($C5SCH_3$) and 14.7 ppm ($C3'SCH_3$). The signals of the ring carbons were observed at $\delta = 191.9$, 180.8, 170.5, and 163.4 ppm. The peaks at $\delta = 191.9$ and 170.5 ppm are indisputably assigned as C5 and C3′, respectively, by H-C HMBC and H-C HSQC experiments. The peaks at $\delta = 180.8$ and 163.4 ppm were assigned to C5′ and C3, respectively, by comparison with the shifts recorded in the other 1,2,4-thiadiazole compounds. In compound **13** the expected signals were observed in the correct ratio in the ^1H NMR spectrum. In the $^{13}C\{^1H\}$ NMR spectrum the peaks were noted at $\delta = 191.8$, 179.4, 169.4 and 163.6 ppm and were assigned as C5, C5′, C3′ and C3, respectively. H-C HMBC and H-C HSQC experiments confirmed the assignment of C5. The X-ray structures confirm that the monomeric units have been linked together (Figure 7).

The 3-halo-1,2,4-thiadiazoles **14** and **15** were prepared for spectral comparison according to Equation (9).



14 X = Cl
15 X = Br

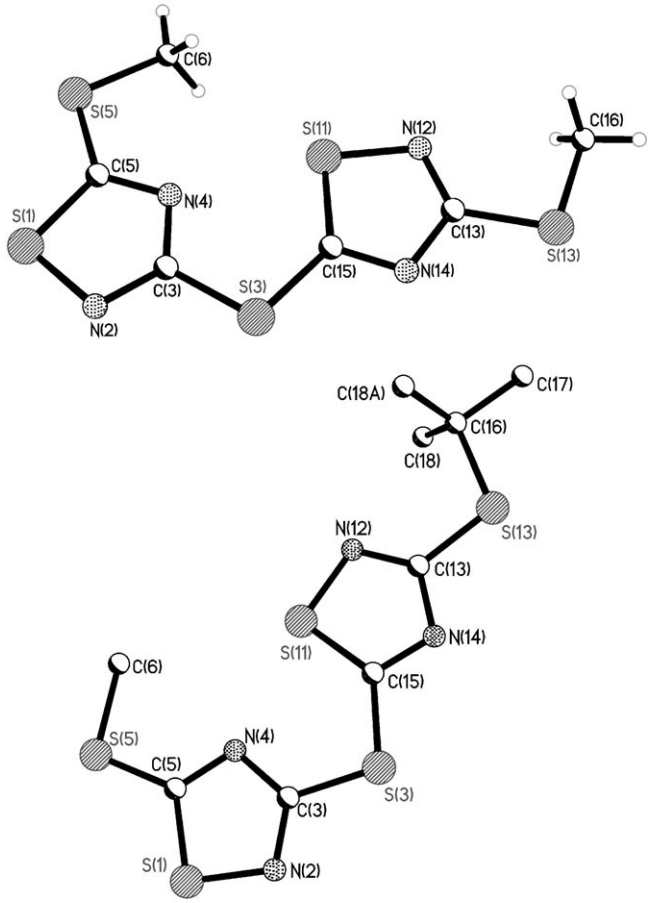


Figure 7. X-ray crystal structures of **12** (top) and **13** (bottom).

Both **14** and **15** gave satisfactory microanalysis and showed the anticipated $[M]^+$ in their mass spectra. The absence of a nitrile band in the region 2000–2200 cm^{-1} confirmed no starting material remained in the samples. Wittenbrook et al. have reported that 3-halo-1,2,4-thiadiazole sulfides have two strong bands in the ranges 1381–1441 and 1175–1232 cm^{-1} assigned as ring vibrations.[29] They noted that different substituents attached to the exocyclic sulfur at C5 do not affect the ring stretches, but different halogen atoms at C3 produce a detectable shift in both bands. They report values for the ring stretches of 1425 and 1228 cm^{-1} for **14** and 1404 and 1202 cm^{-1} for **15**. The change in ring vibrations between **14** and **15** is attributed to chlorine being replaced by bromine. We observe the ring stretching bands at 1425 and 1229 cm^{-1} in **14** and 1415 and 1208 cm^{-1} in **15** with ν(C–S) at 678 and 665 cm^{-1} in **14** and **15**, respectively.

The structure of **14** was confirmed by a single crystal X-ray diffraction study (Figure 8, Table 3).

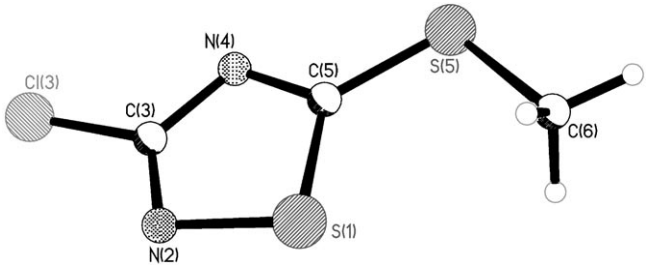
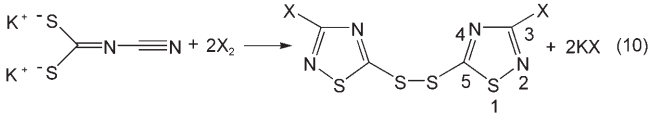


Figure 8. X-ray crystal structure of **14**.

Table 3. Selected bond lengths [Å] and angles [°] for **14**, **16** and **17**.

	14	**16**	**17**
S(1)–N(2)	1.661(2)	1.661(7)	1.659(4)
S(11)–N(12)	–	1.662(7)	1.658(4)
S(1)–C(5)	1.730(3)	1.716(5)	1.719(5)
S(11)–C(15)	–	1.723(8)	1.702(5)
N(2)–C(3)	1.310(4)	1.310(10)	1.313(6)
N(12)–C(13)	–	1.307(10)	1.320(6)
C(3)–N(4)	1.350(4)	1.355(9)	1.358(6)
C(13)–N(14)	–	1.352(10)	1.378(6)
N(4)–C(5)	1.319(3)	1.317(10)	1.321(6)
N(14)–C(15)	–	1.314(10)	1.312(6)
N(2)-S(1)-C(5)	92.29(12)	91.4(4)	91.7(2)
N(12)-S(11)-C(15)	–	91.4(4)	92.1(2)
C(3)-N(2)-S(1)	106.22(18)	106.7(5)	107.1(3)
C(13)-N(12)-S(11)	–	107.2(5)	107.2(3)
N(2)-C(3)-N(4)	122.3(4)	122.3(4)	121.5(4)
N(12)-C(13)-N(14)	–	121.6(7)	120.2(4)
C(5)-N(4)-C(3)	107.2(2)	105.7(6)	106.5(4)
C(15)-N(14)-C(13)	–	106.9(6)	106.5(4)
N(4)-C(5)-S(1)	111.9(2)	113.9(6)	113.2(4)
N(14)-C(15)-S(11)	–	113.0(6)	113.9(4)

Bis(3-halo-1,2,4-thiadiazol-5-yl) disulfides **16** and **17** were prepared by the reaction of potassium cyanodithioimidocarbonate and the appropriate halogen [Eq. (10)].



16 X = Cl
17 X = Br

Both species were prepared in excellent yields. Compounds **16** and **17** have previously been reported in the literature, but only melting point and IR spectroscopy data were recorded.[28] Compounds **16** and **17** showed the anticipated $[M]^+$ ions in their mass spectra with the expected isotopomer distributions and the microanalyses were within the specified limits. In the IR spectra the S–S stretch is observed at 481 and 448 cm^{-1} in **16** and **17**, respectively. The ring vi-

brations are noted at 1435 and 1216 cm^{-1} (lit.:[28] 1435, 1215 cm^{-1}) in **16** and at 1415 and 1208 cm^{-1} (lit.:[28] 1427, 1192 cm^{-1}) for **17**. In the $^{13}C\{^1H\}$ NMR spectrum of **16**, C5 and C3 were observed at $\delta = 188.5$ and 158.0 ppm respectively. Similarly in **17**, C5 and C3 were noted at $\delta = 188.5$ and 145.9 ppm. The ^{14}N NMR spectrum of **17** revealed two broad singlets centred at $\delta = 310.6$ and 278.4 ppm assigned as N2 and N4, respectively. X-ray crystal structures have been determined (Figure 9).

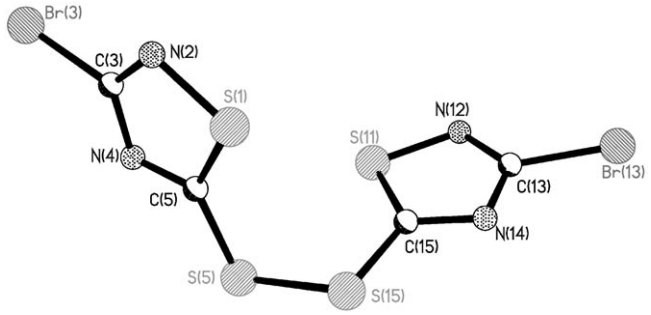
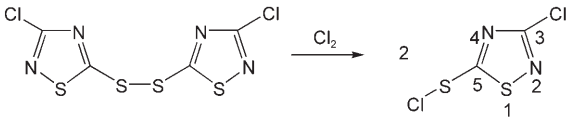


Figure 9. X-ray crystal structure of **17**, the structure of **16** is very similar and is not illustrated.

Compound **16** was readily converted into the sulfenyl chloride **18** by chlorinating with excess Cl_2 [Eq. (11)].[28]

Compound **18** is air sensitive; therefore it was stored



(11)

under nitrogen and no mass spectroscopy, microanalytical or IR data were collected. In the $^{13}C\{^1H\}$ NMR spectrum C5 and C3 were noted at $\delta = 180.2$ and 155.9 ppm respectively.

In summary, all of the 1,2,4-thiadiazole compounds **1**–**17** were found to be pure by microanalysis and the expected ions were observed in the mass spectra. X-ray crystallography has been used to establish the connectivity in selected examples. In the IR and Raman spectra, the ring vibrations are observed at approximately 1400 and 1200 cm^{-1}. The ^{13}C NMR shifts for the ring carbon atoms C5 and C3 are compiled in Table 4; the data reveal that C5 lies in the range $\delta = 180$–192 ppm when bonded to alkyl, alkoxy and thioalkoxy groups and the peak corresponding to C3 is observed at approximately $\delta = 171$ ppm when bonded to thioalkoxy groups.

Parathiocyanogen: We synthesised polythiocyanogen by two different methods. Firstly by allowing thiocyanogen $S_2(CN)_2$, prepared by the reaction of silver thiocyanate with bromine, to slowly warm to room temperature resulting in spontaneous polymerisation to give **19**. The second method involved passing excess chlorine gas through powdered potassium

Table 4. $^{13}C\{^1H\}$ NMR shifts for ring carbon atoms in 1,2,4-thiadiazoles.

	δ [ppm]	
	C5 [C5′]	C3 [C3′]
1	173.1	171.8
2	171.8	171.2
3	189.1	171.5
4	174.9	167.5
6	187.6	170.5
7	190.8	166.7
8	185.6	170.1
9	190.0	167.7
12	191.9 [180.5]	163.4 [170.5]
13	191.8 [179.4]	163.6 [169.4]
14	191.6	156.1
15	191.6	144.3
16	188.5	158.0
17	188.5	145.9
18	180.2	155.9

thiocyanate, followed by heating. We found that chlorinating for approximately 30 s and heating for 1 min then repeating the procedure a further five times optimised the yield of $(SCN)_x$. Using this method we also prepared ^{13}C- and ^{15}N-labelled samples of $(SCN)_x$ from ^{13}C- and ^{15}N-labelled potassium thiocyanate, respectively. Polythiocyanogen obtained by both methods gave identical analytical and spectral data. It is an air stable, brick red, amorphous solid. We made several attempts under variety of conditions and using different samples, but were unable to obtain any powder diffraction whatsoever from $(SCN)_x$; this result is in contrast to Cataldo[12] who observed a broad reflection at about 27° and more in keeping with the observations of Bowmaker et al.[6] The broadness of the one reflection in Cataldo's diffractogram precludes any structural conclusions and may be a background artifact. Conductivity measurements revealed that samples of $(SCN)_x$ prepared in this work were insulators; occasional samples which showed modest conductivity were always found to be contaminated with KCl and we speculate that some literature conductivities may be erroneous because of the presence of ionic impurities. Polythiocyanogen is insoluble in water and all organic solvents, with the exception of dimethyl formamide and dimethyl sulfoxide in which it is very sparingly soluble. Microanalysis of $(SCN)_x$ confirmed the composition of the polymer. MALDI-TOF mass spectra with [3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) as the matrix were recorded several times with the addition of various metal salts (NaI, LiCl, $Cu(NO_2)_2$, $Ag(NO_2)$). The spectrum with addition of LiCl did not yield any useful information; however, the spectra with addition of NaI, $Cu(NO_2)_2$ and $Ag(NO_2)$ showed identical results. As an example the spectrum with $Cu(NO_2)_2$ added is illustrated (Figure 10). It contains the series at m/z 1149 $[S_{20}C_{20}N_{19}]^+$ (most intense peak m/z value cited), 1030 $[S_{18}C_{18}N_{17}]^+$, 914 $[S_{16}C_{16}N_{15}]^+$, 798 $[S_{14}C_{14}N_{13}]^+$, 682 $[S_{12}C_{12}N_{11}]^+$, 566 $[S_{10}C_{10}N_9]^+$, 450 $[S_8C_8N_7]^+$, 334 $[S_6C_6N_5]^+$, 218 $[S_4C_4N_3]^+$, 102 $[S_2C_2N]^+$. The isotope pattern for each set of peaks in the series matches the predicted patterns exactly.

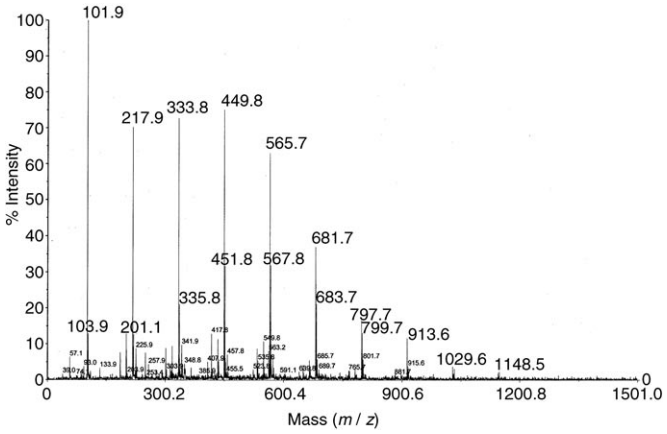


Figure 10. MALDI TOF mass spectrum of polythiocyanogen **19**.

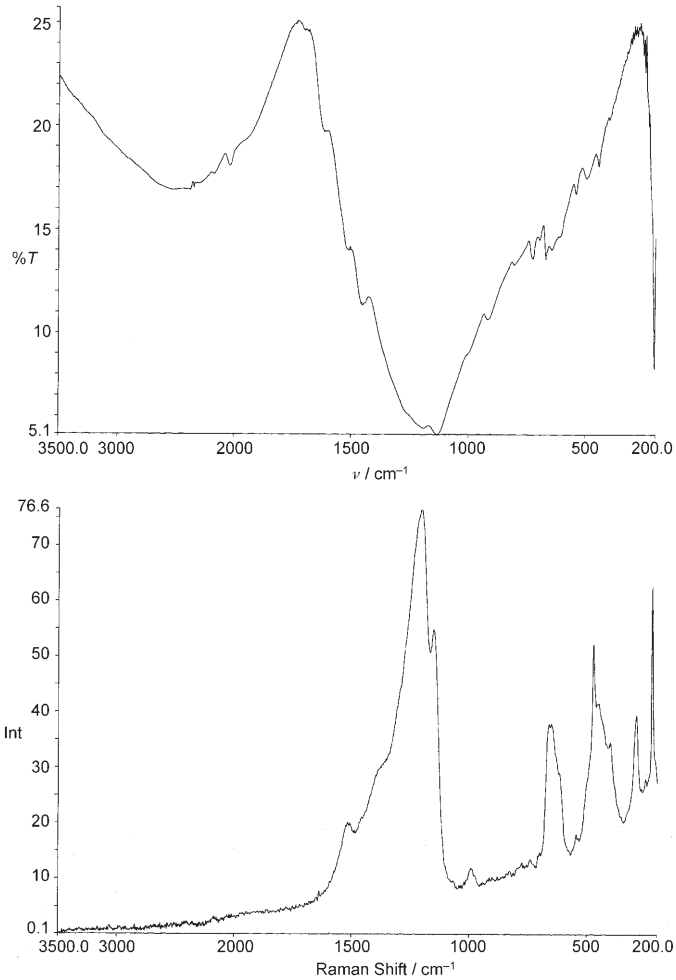


Figure 11. IR spectrum (top) and Raman spectrum (bottom) of $(SCN)_x$ **19**.

The repeat unit of 116 m/z corresponds to $(SCN)_2$, which suggests that this may be the monomeric unit. The $(SCN)_2$ repeat unit fits very well with our proposed structures of linked heterocyclic five-membered rings. The absence of any series with a 58 m/z (SCN) repeat unit is strong evidence against $(SCN)_x$ polymer being composed of linear chains of linked SCN units as proposed in the literature.[4,11]

The IR spectrum of $(SCN)_x$ we obtained is dominated by a very broad peak with a maximum at 1134 cm^{-1} (Figure 11) consisting of several overlapping peaks and is comparable with IR spectra reported in the literature.[4,11–13] The Raman spectrum (Figure 11) was more informative, but there is still considerable broadness caused by overlapping peaks. In the Raman spectra there are no peaks in the range 1600–3500 cm^{-1}; the absence of any bands in the region 2000–2200 cm^{-1} strongly suggests that there are no nitrile groups present in $(SCN)_x$. In the range 800–1600 cm^{-1} there is a small peak at 1508 cm^{-1}, a very broad, intense peak at 1207 cm^{-1} with an evident shoulder, a strong peak at 1155 cm^{-1} and a low intensity peak at 994 cm^{-1}. In the range 200–800 cm^{-1} there are several overlapping peaks at approximately 650 cm^{-1}, several overlapping peaks in the range 400–480 cm^{-1} and two further peaks at 289 and 229 cm^{-1}. We propose that the peak at 650 cm^{-1} is due to ν(C–S) vibrations and we speculate that the peaks in the range 400–480 cm^{-1} may correspond to ν(S–S) vibrations. The IR and Raman spectral data for $(SCN)_x$ is, as expected, very different to the linear small molecules $S_n(CN)_2$ ($n=1, 2, 3$) which show virtually no peaks in the range 800–1600 cm^{-1}. Interestingly the 1,2,4-thiadiazole compounds that we have prepared and 1,2,4-dithiazole compounds[14,15,18,23] show strong ring vibrations in the same region as the large central peak in the IR spectrum of $(SCN)_x$.

We attempted to record the ^{13}C NMR spectrum of $(SCN)_x$ in dimethylformamide, which was reported twice in the literature by Cataldo.[11,12] We found only a trace amount of the polymer dissolved resulting in a faint yellow colour of the solution and no signal was observed (except for dimethylformamide) even with a 99% ^{13}C-labelled sample of $(SCN)_x$ after 29000 scans. Examination of the published literature spectrum is enlightening, since the spectrum illustrated by Cataldo contains no solvent resonance. This seems remarkable and we are inclined to the view that the reported spectra are actually solid state not solution data or due to impurities such as thiourea. We recorded ^{13}C and ^{15}N NMR spectra of normal and labelled $(SCN)_x$ in the solid state. In the $^{13}C\{^1H\}$ DP-MAS NMR of natural abundance and 99% ^{13}C-labelled polythiocyanogen we observed a major resonance at $\delta=186.8$ ppm. The signal is broad and slightly asymmetric with low intensity spinning side bands (Figure 12). As expected the signal-to-noise ratio was substantially improved in the ^{13}C-labelled sample.

In the spectrum there is a broad peak centred at $\delta=$ 186.6 ppm with a visible shoulder. Deconvolution yielded two singlets at $\delta=187.1$ (integral intensity 0.88) and $\delta=$ 183.8 ppm (integral intensity 1). Additionally there is a multiplet at $\delta=152$–172 ppm with significantly lower intensity. Deconvolution of the multiplet yielded three singlets at $\delta=$ 156.6 ppm (integral intensity 0.24), $\delta=163.2$ (integral intensity 0.35) and 168.1 ppm (integral intensity 0.16). Thus, the ^{13}C NMR spectrum of $(SCN)_x$ is dominated by two carbon

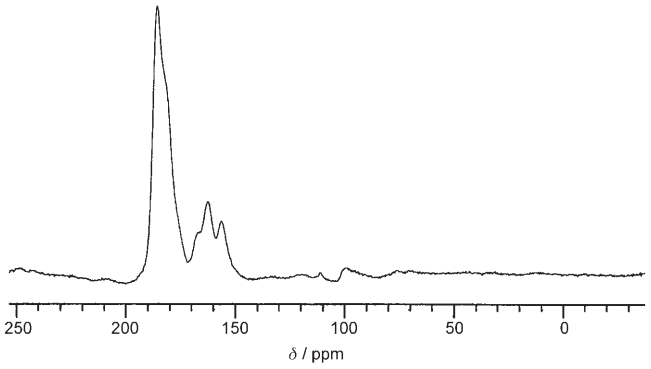


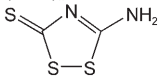
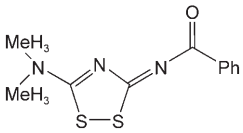
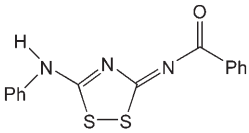
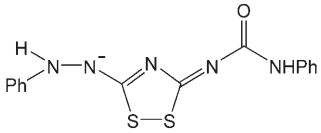
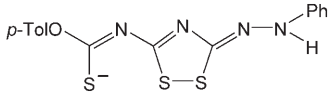
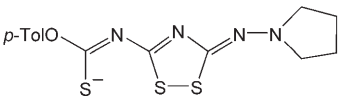
Figure 12. ^{13}C DP-MAS solid-state NMR spectrum of ^{13}C-labelled $(SCN)_x$.

shifts at $\delta = 183.8$ and 187.1 ppm of approximately equal intensity. We attribute these two peaks to the polymer chain and the lower intensity peaks may be due to terminal groups or impurities; the intensities of these latter peaks are in accord with end groups for a "polymer" with a molecular weight of approximately 1000 as determined from mass spectrometry. The carbon environments in the polymer **19** are clearly different to that of KSCN ($\delta = 133.8$ ppm), $S_2(CN)_2$ ($\delta = 108.3$ ppm) and $S(CN)_2$ ($\delta = 100.1$ ppm). The ^{13}C shifts recorded for polythiocyanogen are in the same range as the 1,2,4-thiadiazoles (Table 4) and 1,2,4-dithiazoles.[14,15] In polythiocyanogen the close proximity of the two peaks at $\delta = 183.8$ and 187.1 ppm indicates that the two carbon environments in the polymer are very similar. In the proposed 1,2,4-thiadiazole structure, C5 is bonded to one nitrogen atom and two sulfur atoms, whereas C3 is bonded to two nitrogen atoms and one sulfur atom. We note from Table 4 that typically the C5 signal is observed in the range 180–192 ppm, whereas C3 atom resonates in the range 163–172 ppm. If $(SCN)_x$ had a 1,2,4-thiadiazole structure, the C3 environment in the polymer would be comparable to that of C3 in **12** and **13**, which are observed at approximately 163.5 ppm. In the 1,2,4-thiadiazole model compounds the most downfield shift observed for C3 is 172 ppm. This is strong evidence against a 1,2,4-thiadiazole structure for polythiocyanogen. Furthermore, we note the outcome of the reaction of the lithium salt of bis(5-chloro-1,2,4-thiadiazol-3-yl) disulfide with itself. If the polymer was made of 1,2,4-thiadiazole rings this reaction should result in the formation of polythiocyanogen. Instead it gave a yellow solid which may be, as indicated earlier, an isomeric form of $(SCN)_x$.

Our alternative hypothesis, described above, was that the polymer is based on five-membered rings linked by nitrogen atoms and the ^{13}C NMR data for polythiocyanogen is compatible with a structure composed of 1,2,4-dithiazole rings linked by exocyclic nitrogen atoms; both carbon atoms are in very similar environments bonded to two nitrogen atoms and one sulfur atom. Butler and Glidewell reported that the ^{13}C NMR spectrum of isoperthiocyanic acid (3-amino-5-thione-1,2,4-dithiazole)[32] consists of two peaks at $\delta = 208$ and 183 ppm. We resynthesised isoperthiocyanic acid[33] and obtained almost identical ^{13}C NMR data with the peaks at $\delta = 208.2$ and 183.1 ppm corresponding to C5 and C3, respectively. The C3 atom is bonded to two nitrogen atoms and one sulfur atom and is comparable to the carbon environments in our proposed 1,2,4-dithiazole structure. The value for C3 at $\delta = 183.1$ ppm is very similar to the main peaks observed in $(SCN)_x$ ($\delta = 183.9$ and 187.1 ppm).

Furthermore, Graubaum et al. have prepared several 1,2,4-dithiazole compounds[34,35] in which both carbon atoms in the ring are in environments comparable to the carbon environments in our proposed 1,2,4-dithiazole structure for $(SCN)_x$. The ^{13}C NMR shifts reported are very similar to those which we have recorded for polythiocyanogen and are shown in Table 5.

Table 5. ^{13}C NMR data for 3-amino-5-thione-1,2,4-dithiazole and 1,2,4-dithiazoles reported by Graubaum et al.[34,35]

	δ [ppm]	
	C5	C3
$(SCN)_x$	187.1	183.8
	208.2	183.1
	184.5	180.1
	185.6	178.9
	180.7	174.9
	193.3	180.8
	192.6	183.0

Even more compelling evidence for the nitrogen-linked structure came from the solid-state ^{15}N NMR spectrum of $(SCN)_x$, which we recorded using a 99% ^{15}N-labelled sample (Figure 13). Two peaks of equal intensity are noted at $\delta =$ 236.9 and 197.2 ppm. A lower intensity peak is observed at $\delta = 170.2$ ppm.

These ^{15}N NMR resonances differ considerably from the ^{14}N NMR shifts for the small molecules $S_n(CN)_2$ ($n = 1, 2$), which are observed at approximately $\delta = 290$ ppm indicating the difference between the nitrogen environments in the polymer and the linear small molecules. Furthermore, thiazoles have ^{15}N NMR shifts at approx $\delta = 300$ ppm[36] and the

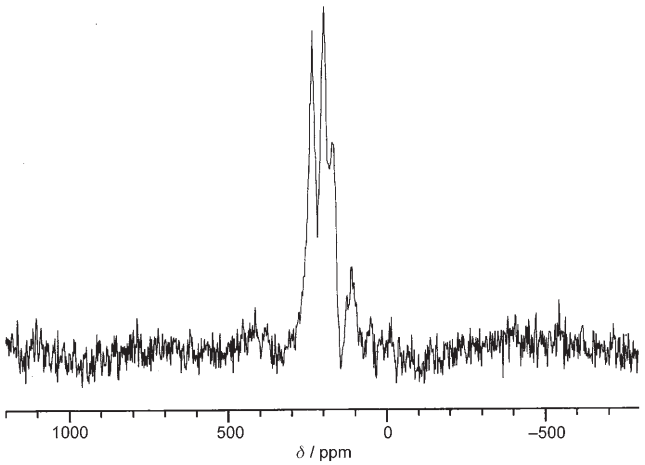
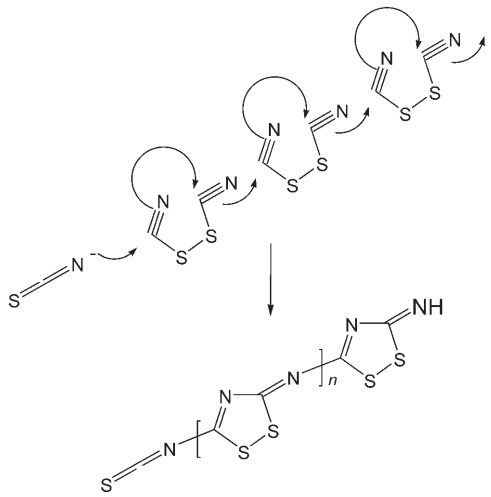


Figure 13. DP-MAS solid-state ^{15}N NMR spectrum of $(SCN)_x$.

^{14}N NMR spectra for bis(3-bromo-1,2,4-thiadiazol-5-yl) disulfide (**17**) displays two shifts at $\delta = 310.6$ and 278.4 ppm assigned as N2 and N4 respectively. Thus the nitrogen NMR data do not support a 1,2,4-thiadiazole structure for $(SCN)_x$. Butler and Glidewell reported that the ^{15}N NMR spectrum of isoperthiocyanic acid (3-amino-5-thione-1,2,4-dithiazole)[32] consists of two peaks; we repeated this experiment and observed two broad peaks at $\delta = 221$ and 106 ppm in the ^{14}N NMR spectrum of isoperthiocyanic acid. The peak at $\delta = 221$ ppm is assigned as N4 and the peak at $\delta =$ 106 ppm corresponds to the exocyclic NH_2. Interestingly ^{15}N NMR shifts for imino groups are observed in the range 170–200 ppm.[36] Our observed solid-state ^{15}N data fit very well with an $(SCN)_x$ structure based on repeating 1,2,4-dithiazole rings linked by =N− imino nitrogen atoms. The structure proposed in Scheme 8 does not rationalise the $[S_z(CN)_2]_x$ polymers claimed by Cataldo;[13] however, as mentioned above, these polymers have only been characterised by IR spectroscopy. The spectra in reference [13] can be readily reconciled with mixtures of $(SCN)_x$ and sulfur impurities. We have repeated the polymerisations as described by Cataldo and the product is invariably contaminated with sulfur (as determined by HPLC analysis) and we do not consider the existence of $[S_z(CN)_2]_x$ to be firmly established.



Scheme 8. Proposed mechanism for polymerisation of $S_2(CN)_2$.

Polyselenocyanogen: Finally, we note that $(SeCN)_x$ has been recently described[38] by Cataldo, who reported that selenocyanogen ($Se_2(CN)_2$) when treated with certain organic solvents (acetone, dimethyl formamide, methanol and triethylamine) spontaneously polymerises to give polyselenocyanogen $(SeCN)_x$. In the same work it was reported that polyselenocyanogen could alternatively be prepared from selenocyanogen by heating in high boiling solvents such as xylenes and decalin. We have examined a number of selenium-containing systems[39–44] and it is reasonable to anticipate that C-Se-N analogues of the C-S-N described here could exist and thus we conducted some preliminary experiments on $(SeCN)_x$ and it is appropriate to include our preliminary observations here.

We added selenocyanogen to acetone and a red solid precipitated as reported.[38] The solid was isolated by suction filtration and dried in vacuo. Analysis of the insoluble red solid showed it was red selenium rather than $(SeCN)_x$. Microanalysis showed 2.25% C and 0.42% N compared to the expected 11.44% C and 13.35% N for $(SeCN)_x$. Positive ion electron impact mass spectroscopy displayed the $[M]^+$ at $m/z = 632$ corresponding to Se_8. Ions at $m/z = 553$ (Se_7), $m/z = 474$ (Se_6), $m/z = 395$ (Se_5), $m/z = 316$ (Se_4), $m/z = 238$ (Se_3), $m/z = 158$ (Se_2) and $m/z = 79$ (Se) were all observed with the expected isotopomer distributions. Raman spectroscopy showed only one vibration at 253 cm^{-1} corresponding to ν(Se−Se). Similar results were obtained from reaction with methanol and by heating in high boiling solvents. Bowmaker et al. have prepared thin films of polythiocyanogen by oxidation of potassium thiocyanate in methanol.[6] When they carried out oxidation of potassium selenocyanate the results were far less conclusive. They obtained a patchy orange red film that exhibited bands due to grey selenium in the Raman spectrum. Within a day the film had decomposed to give grey selenium. On the basis of our evidence and the observations of Bowmaker et al. we have no reason to believe that $(SeCN)_x$ exists.

Conclusion

This work describes a systematic investigation and full characterisation of a series of 1,2,4-thiadiazoles. Furthermore, the data we have collected and the propensity of HNCS and $(SCN)_2$ to form 1,2,4-dithiazole rings leads us to propose that polythiocyanogen has a structure composed of 1,2,4-dithiazole rings linked by nitrogen bridges (Scheme 8). We believe our analysis, based on good quality spectroscopic data, provides a reasonable proposal for the structure of $(SCN)_x$ and we do not believe that compelling evidence for the existence of $[S_z(CN)_2]$ or $(SeCN)_x$ has been presented to date.

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