Nitrogen-14 Nuclear Magnetic Resonance Studies on Sulphur–Nitrogen Compounds

Ivan P. Parkin and J. Derek Woollins *
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY
Peter S. Belton
AFRC, Norwich NR4 7AU

The ^{14}N n.m.r. spectra of a variety of sulphur–nitrogen heterocycles and metal–sulphur–nitrogen complexes have been recorded and the observed shifts correlated with bonding type. The utility of ^{14}N n.m.r. spectroscopy as a mechanistic tool in sulphur–nitrogen chemistry is illustrated for reactions in liquid ammonia.

The chemistry of sulphur–nitrogen compounds is a broad one with a great diversity of structural types and bonding.[1,2] This field of chemistry has grown rapidly in the past ten years partly as a result of the availability of *X*-ray crystallography. However, the general absence of an easily accessible n.m.r. nucleus in sulphur–nitrogen systems has hampered expansion of mechanistic and structural studies. Nitrogen-15 n.m.r. spectroscopy has been used to probe sulphur–nitrogen systems and the narrow linewidths and coupling information (^{15}N, $I = \frac{1}{2}$) have proved useful in some structural investigations, but the low natural abundance (0.36%) and the long relaxation times (typically 30 s repetition delay between scans) makes the measurements difficult except for very concentrated or ^{15}N-labelled compounds.[3,4] This latter technique is expensive and often involves multi-step procedures from the most commonly available enriched compound $^{15}NH_4Cl$.[3]

Early work on ^{14}N n.m.r. spectroscopy using low-field instruments reported some data on sulphur–nitrogen complexes but did not establish the technique.[5–7] We have shown recently that the quadrupolar ^{14}N nucleus ($I = 1$, 99.6% abundant) although having broad lines and consequent loss of scalar-coupling information can give useful spectra in a wide variety of systems.[8] High signal-to-noise ratio spectra are obtainable because very short pulse delays are possible due to the short spin–lattice relaxation times often observed for the quadrupolar ^{14}N nucleus. The problems of signal loss, from fast relaxation, due to the wide lines can be reduced by the use of a high-power, wide band-width probe associated with a pulse sequence for the elimination of probe ring down.[9]

The actual linewidths observed using ^{14}N n.m.r. spectroscopy (*ca.* 500 in non-metal and 1 000 Hz in metal–sulphur–nitrogen complexes) are not great compared with the chemical shift range (800 p.p.m., 17.3 kHz at 7.0 T). Thus, in principle, a large amount of structural information can be gleaned from shift data. It is also generally true that the symmetry of the atomic environment is related to the linewidth.[6]

In this work we report the ^{14}N n.m.r. spectra of a wide variety of non-metal–sulphur–nitrogen compounds together with metal–sulphur–nitrogen compounds recently prepared by us.[10–15] These new data, together with those previously reported,[5–10] are correlated to give a diagnostic chemical-shift range for SN molecules. The usefulness of ^{14}N n.m.r. spectroscopy as a mechanistic probe is illustrated for the study of sulphur–nitrogen compounds in liquid ammonia[10] and has very recently been demonstrated for liquid SO_2.[10] Furthermore, as part of our studies into reactions in liquid ammonia, we have measured the ^{15}N–^{14}N exchange of 100% ^{15}N-isotopically enriched $[S_4N_3]Cl$ and S_4N_4 in liquid ammonia.

Experimental

Metal–sulphur–nitrogen complexes [(**1**)—(**12**)] were prepared as described by us previously.[11–15] The compounds [(**13**)—(**28**)] and standard sulphur–nitrogen reagents were prepared by the literature methods[16–35] referenced in Tables 3 and 4 respectively. All these compounds had satisfactory microanalytical data, mass and i.r. spectra. The n.m.r. solvents were dried as previously described[11] and degassed with argon prior to use.

Spectral Measurements.—Nitrogen-14 spectral measurements were performed on a Bruker CXP 300 spectrometer operating at 7.05 T using a vertical non-spinning sample and a RIDE[9] programme for the elimination of ring down. The resonance frequency for ^{14}N was 21.682 MHz. The temperature of the measurements was typically 295 K except for those involving liquid ammonia which were controlled using a Bruker BVT1000 temperature controller. The shifts are relative to anhydrous ammonia at 0 p.p.m.

Table 1. Experimental conditions used for data collection

Experimental conditions	Liquid ammonia	Non-metal SN compounds	Metal SN compounds
Spectral width/Hz	25 000	50 000	50 000
Data table	4 096	1 024	1 024
π/2 Pulse length/μs	21.6	21.6	21.6
Number of transients accumulated	5 000	50 000	500 000
Recycle delay/ms	82	102	102
Accumulation time/h	0.167	1	10
Signal-to-noise ratio (for strongest SN signal)	> 100	> 100	> 50

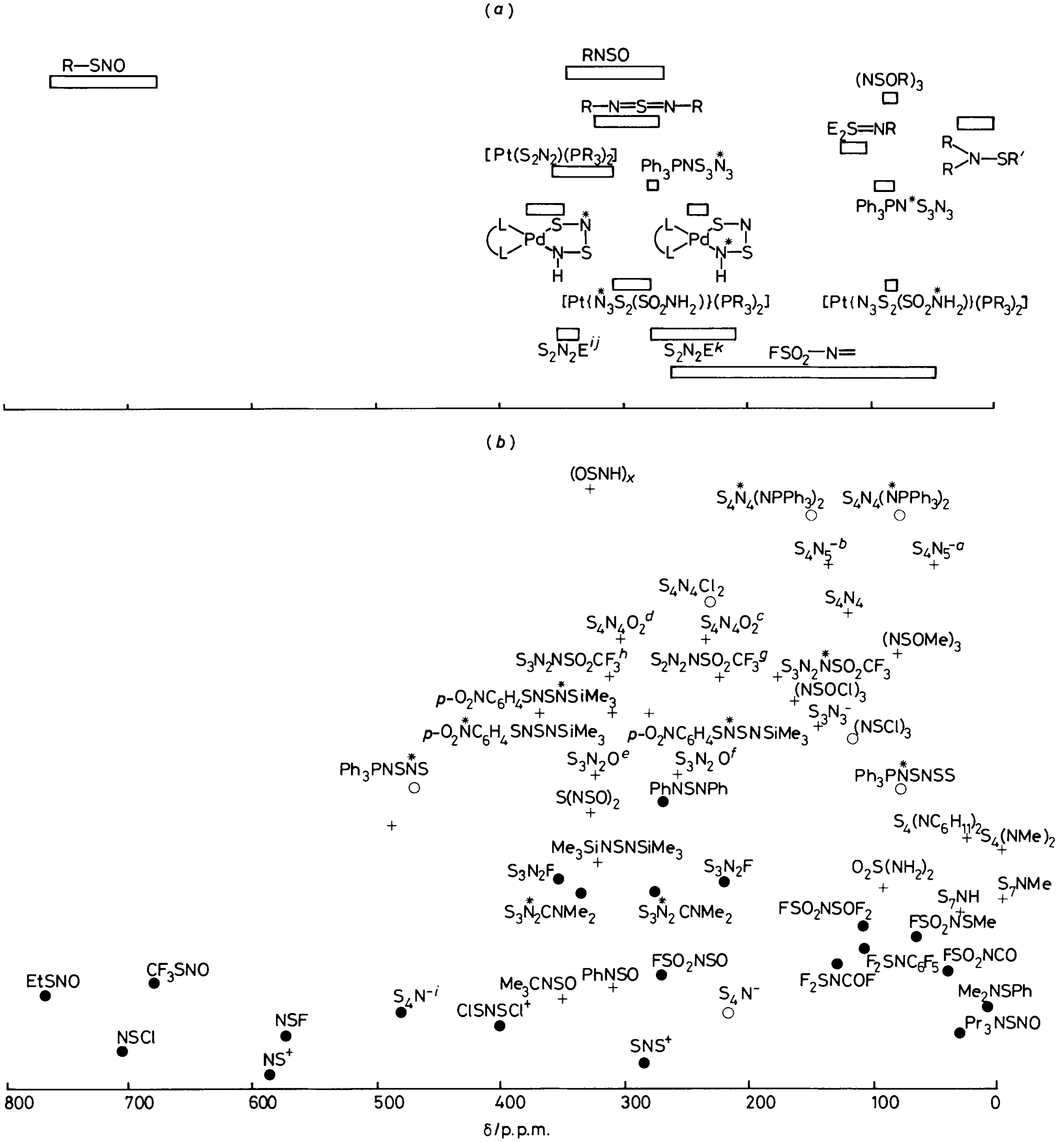

Figure 1. (*a*) A ^{14}N n.m.r. chemical-shift range for sulphur–nitrogen compounds, (*b*) ^{14}N and ^{15}N n.m.r. data for specific SN compounds. Crosses indicate data reported in this work, closed circles previous ^{14}N studies, and open circles previous ^{15}N studies. [a] Apical nitrogen. [b] Four equivalent nitrogens. [c] N_2SO Nitrogens. [d] N_2S Nitrogens. [e] NS_2 Nitrogen. [f] SNS(O) Nitrogen. [g] SNSR Nitrogen. [h] NS_2 Nitrogen. [i] T. Chivers, personal communication. [j] E = SF, SCl, CCH_3, or $CNMe_2$, NS_2 nitrogen. [k] SNSE Nitrogen. There is a discrepancy between the ^{15}N and ^{14}N chemical-shift data for S_4N^-, see footnote on following page.

The spectra in liquid ammonia were obtained using thick-walled 10-mm tubes with Teflon in glass Youngs taps which were filled under an argon atmosphere. For the room-

*Nitrogen-*15 *Exchange Reactions in Liquid Ammonia.*—Nitrogen-15 enriched $[S_4N_3]Cl$ and S_4N_4 were prepared by the literature methods.[36]

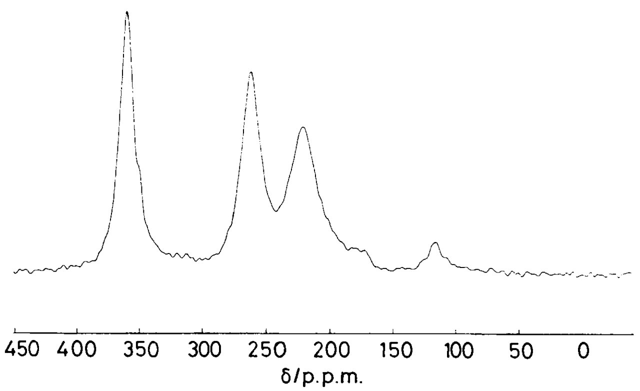

Figure 2. Nitrogen-14 n.m.r. spectrum of $S_3N_2NSO_2CF_3$ in CH_2Cl_2

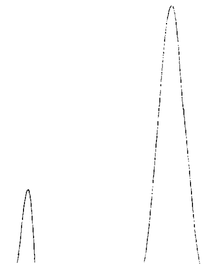

Figure 3. Nitrogen-14 n.m.r. spectrum of $[Pd(S_2N_2H)(Me_2NC_{10}H_6)]$ (4) in CH_2Cl_2

was allowed to evaporate under a stream of argon. Extraction with tetrahydrofuran (thf) (10 cm^3) afforded a red solution which was allowed to evaporate in air leaving a purple-black residue. Further extraction of this residue with thf (10 cm^3) followed by evaporation of the solvent in air gave crystals of S_4N_4. The ^{15}N content was determined by mass spectrometry using a VG 2020 instrument operating in the electron impact mode.

Results and Discussion

The ^{14}N data from this work are displayed in Tables 2 and 3 and the chemical-shift range, which combines these with those from previously reported ^{14}N and ^{15}N studies,[4—10] is illustrated in Figure 1. There are a number of important features. First, it is clear that the degree of saturation has a marked effect on the chemical shift. Thus, simple singly bonded species such as S_7NH and $S_4(NR)_2$ are observed at *ca.* 0 p.p.m. Alternatively, triply bonded NSF has δ 576 p.p.m.[10] Formal N=S double bonds are observed in di-imides, RNSNR, and the isoelectronic RNSO systems, and these give rise to signals at δ 250—400 p.p.m. It is interesting that the planar, 'pseudo-aromatic'[1,18] species such as $S_3N_3^-$, or $(NSX)_3$ (X = Cl or OR) give chemical shifts intermediate between singly and doubly bonded species. The poorly characterised $(OSNH)_x$ polymer gives δ 330 p.p.m., suggesting a large degree of unsaturation which is not compatable with the currently proposed[1] structure. The diagnostic ability of the technique is well illustrated by the spectrum of $S_4N_5^-$ which consists of two resonances (139, intensity 4 and 52 p.p.m., intensity 1). The larger signal is associated with the four equivalent nitrogens which are in similar environments to those in S_4N_4 (123 p.p.m.), whilst the smaller signal is due to the bridging N^- (isoelectronic with NH) which is not heavily involved in cluster bonding and so has a chemical shift close to that in S_7NH. Furthermore, in $S_3N_2NSO_2CF_3$ (Figure 2), all three nitrogens give well separated signals. The two ring nitrogens are readily assigned 319 and 224 p.p.m.) by comparison with the spectrum of S_3N_2O with the exocyclic nitrogen having δ 179 p.p.m. Compounds (**27**) and (**28**) were formed from the reaction of S_4N_4 and PR_3 (R = PEt_3 or PPh_2Me) and were identified by ^{31}P n.m.r., i.r., and mass spectra. The microanalyses were difficult to perform due to phosphine sulphide impurity, however the observed shifts are similar to the reported ^{15}N n.m.r. spectra of $Ph_3PNS_3N_3$.[4]

We have also obtained useful information on metal–sulphur–nitrogen complexes (Table 2, Figure 3). In MS_2N_2 and MS_2N_2H rings both nitrogens are observed and are readily distinguishable. In these metallacycles the angles at nitrogen deviate substantially from tetrahedral[11,13] and the linewidths are greater than those observed for free di-imides. The assignment of the two resonances in these systems comes from looking at the effect of protonation. Typically, the protonated ligand $S_2N_2H^-$ gives signals at *ca.* 360 and 230 p.p.m. whereas for the $S_2N_2^{2-}$ ligand the lower-frequency signal is shifted to *ca.* 320 p.p.m. We therefore assign the lower-frequency signal to the metal-bound nitrogen. We have also obtained the spectra of some $[Pt\{N_3S_2(SO_2NH_2)\}(PR_3)_2]$ complexes. The NH_2 group is well separated from the broad signal due to the three similar ring nitrogens. This might be expected since the S–N bond lengths show only marginal variation around the ring in this metallacycle.[14]

Table 4 summarises the species observed when a variety of sulphur–nitrogen compounds are dissolved in liquid ammonia. It appears that dissolution of a wide range of SN species in liquid ammonia gives rise to $S_3N_3^-$ with, in addition, in some cases, $S_4N_5^-$. A surprising observation is that although S_7NH disproportionates (to some extent) in solution, $S_4N_4H_4$ does not. The presence of signals at only 52 and 139 p.p.m. when $S_4N_5^-$ is dissolved in liquid ammonia indicates that this species is not in equilibrium with $S_3N_3^-$ and the formation of the latter on dissolution of S_4N_4 thus appears to proceed by a parallel pathway[9] to the formation of $S_4N_4^-$. We believe that dissolution of $S(NSO)_2$ gives NSO^- since the chemical shift (500 p.p.m.) is in the appropriate region [(**12**) occurs at 463 p.p.m.] and we have been able to isolate $[Pt(NSO)_2(PR_3)_2]$ complexes from these solutions.[15] Since in reactions of this solution we have obtained metal complexes containing the $S_2N_2^{2-}$ ligand we have assigned the resonances at 294 and 226 p.p.m. to $S_2N_2^{2-}$. This is in accord with our previous comments about S_4N_4–NH_3(l) solutions.[10] However, $S_3N_3O^-$ has ^{15}N shifts of 289 and 225 p.p.m.[36] and so it is possible that the liquid ammonia solution contains $S_3N_3O^-$ formed by oxidation of $S_3N_3^-$.

Solutions of S_8 in liquid ammonia have been studied by a number of groups.[36,37] In the ^{14}N n.m.r. spectrum the peak at 485 p.p.m. can be assigned to S_4N^-* and that at 572 p.p.m. to NS^+ (NSF,[10] 576; $NSAsF_6$,[10] 582 p.p.m.), with the major peak at 51 p.p.m. being due to S_7NH, and thus our n.m.r. measurements are in accord with previous u.v.–visible studies.[37,39]

Peaks observed at 283 p.p.m. in the spectrum of $S_3N_3Cl_3$ (Figure 4), $S_4N_4O_2$, and S_5N_5Cl are assignable to SNS^+ since $SNS^+AsF_6^-$ [10] occurs at 289 p.p.m. with the slight difference in

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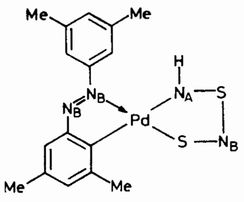
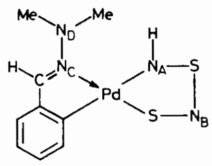
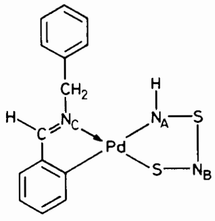
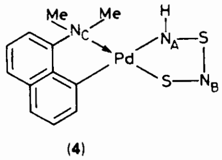
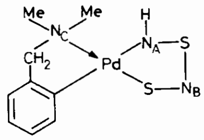
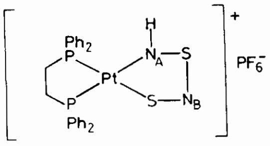
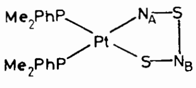
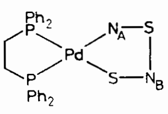
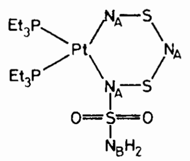
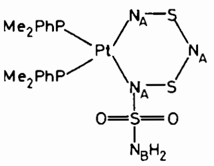
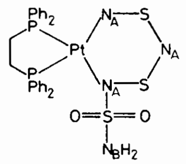
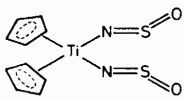
* Although the previous ^{15}N study[4] reported a much lower δ value for S_4N^-, more recently Chivers[38] has measured ^{14}N spectra for S_4N^- and S_3N^- which give shifts of +110 and +237 p.p.m. relative to $MeNO_2$ and +490 and +617 p.p.m. relative to liquid NH_3.

Table 2. Nitrogen-14 n.m.r. spectral data for metal–sulphur–nitrogen compounds

Compound	δ/p.p.m.	$\nu_{\frac{1}{2}}$/Hz
 (1)	A 245 B 371*	1 560 1 170
 (2)	A 228 B 363 C 300 D 20	800 960 1 200 2 000
 (3)	A 236 B 363 C 254	1 300 1 100 1 300
 (4)	A 237 B 354 C 43	690 690 1 600
 (5)	A 237 B 349 C 48	1 280 770 1 200
 (6)	A 236 B 317	1 300 1 300
 (7)	A 323 B 355	1 500 1 500
 (8)	A 310 B 360	1 500 1 500
 (9)	A 306* B 91	1 800 700
 (10)	A 306* B 91	2 300 700
 (11)	A 307* B 91	2 200 700
 (12)	N 463*	600

* Multiple nitrogens.

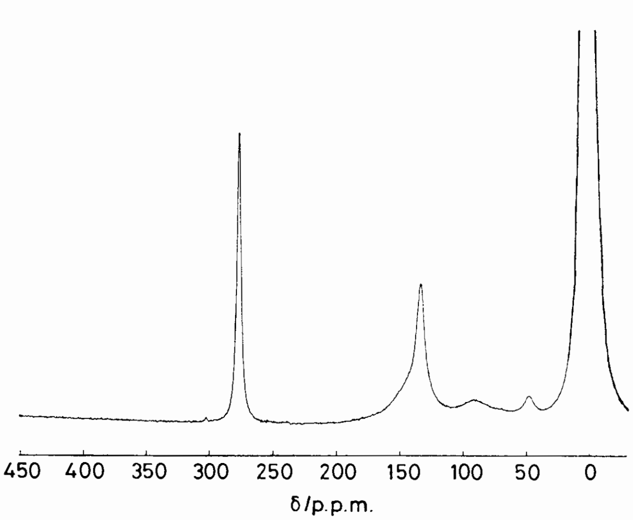


Figure 4. Nitrogen-14 n.m.r. spectrum of $S_3N_3Cl_3$ in liquid ammonia

shift being due to the change in counter ion and solvent. In the spectrum of $S_4N_4O_2$ the main peak at 90 p.p.m. is likely to be of the type R–SO_2–NH_2 as 91—94 p.p.m. is observed for **(9)**—**(11)** and δ 93 p.p.m. for sulphamide.[8] The unidentified species at 97—84 p.p.m. observed for $S_3N_3Cl_3$, S_5N_5Cl, and $SOCl_2$ is also probably of the R–NH_2 type.

Some of the observed liquid ammonia spectra (Table 4) are somewhat time dependent. However, the spectra of $[S_4N_3]Cl$, $[S_3N_2Cl]Cl$, and S_2Cl_2 which only contain peaks due to $S_3N_3^-$ show no change after 1 week at room temperature. In general

Table 3. Nitrogen-14 n.m.r. spectral data for sulphur–nitrogen compounds

Compound	Reference of preparation	δ/p.p.m.	$\nu_{\frac{1}{2}}$/Hz	Solvent
(**13**) $S_4(NC_6H_{11})_2$	16	22	1 500	CH_2Cl_2
(**14**) S_7NH	17	26	780	Benzene
(**15**) $S_3N_3(OMe)_3$	18	88	1 400	CH_2Cl_2
(**16**) $S_3N_3(OEt)_3$	18	93	1 470	CH_2Cl_2
(**17**) $S_3N_3(OPr^i)_3$	18	96	1 560	CH_2Cl_2
(**18**) $S_3N_3(OC_5H_{11})_3$	18	86	1 400	CH_2Cl_2
(**19**) $[PPh_4][S_3N_3]$	19	146	200	CH_2Cl_2
(**20**) $Na[S_4N_5]$	20	139, 52	300, 300	CH_2Cl_2
(**21**) S_3N_2O	21	326, 259	240, 240	Benzene
(**22**) $S(NSO)_2$	22	330	240	Toluene
(**23**) *p*-$MeC_6H_4SO_2NSO$	23	345	390	Toluene
(**24**) *p*-$NO_2C_6H_4SO_2NSO$	23	372, 323	350, 580	Toluene
(**25**) $(OSNH)_x$	24	330	270	CH_2Cl_2
(**26**) $S_3N_2NSO_2CF_3$	25	319, 224, 179	390, 500, 600	CH_2Cl_2
(**27**) $Et_3PNS_3N_3$	26	287, 207, 85	600, 800, 1 300	CH_2Cl_2
(**28**) $Ph_2MePNS_3N_3$	26	287, 206, 126	1 100, 1 200, 600	CH_2Cl_2

Table 4. Nitrogen-14 n.m.r. spectral data for the major sulphur–nitrogen species in liquid ammonia showing the approximate percentage (in brackets) attributable to each peak[a]

Compound	Reference of preparation	δ/p.p.m.	$\nu_{\frac{1}{2}}$/Hz	Principal species
$[S_4N_3]Cl$	27	148(100)	120	$S_3N_3^-$
$[S_3N_2Cl]Cl$	28	148(100)	400	$S_3N_3^-$
S_2Cl_2	*b*	149(100)	240	$S_3N_3^-$
S_4N_4	29	148(90)	120	$S_3N_3^-$
		138(10)	shoulder	$S_4N_5^-$
		52	120	
$[NH_4][S_4N_5]$	30	139(100)	180	$S_4N_5^-$
		52	150	
$S_4N_4H_4$	31	62(100)	700	$S_4N_4H_4$
$S_3N_3O_3Cl_3$	32	98(100)	560	
$S_3N_3Cl_3$	33	283(30)	110	SNS^+
		139(70)	230	$S_4N_5^-$
		52	200	
		97(15)	500	RNH_2
$[S_5N_5]Cl$	34	283(10)	60	SNS^+
		149(70)	110[c]	$S_3N_3^-$
		139(15)		$S_4N_5^-$
		53	300	
		94(5)	200	RNH_2
S_7NH	35	484(50)	120	S_4N^-
		148(20)	100	$S_3N_3^-$
		49(20)	440	S_7NH
		−21(20)	500	?
$SOCl_2$	*b*	502(15)	100	NSO^-
		485(50)	180	S_4N^-
		272(15)	140	
		84(15)	800	$SO(NH_2)_2$?
$S(NSO)_2$	22	500(50)	120	NSO^-
		294(10)	120	$S_2N_2^{2-}$?
		226(10)	120	$S_2N_2^{2-}$?
		149(20)	85	$S_3N_3^-$
S_8	*b*	572(5)	100	NS^+
		485(10)	100	S_4N^-
		352(5)	100	
		51(80)	350	S_7NH
$S_4N_4O_2$	35	283(10)	150	SNS^+
		157(20)	180	
		149(30)	180	$S_3N_3^-$
		137(10)	200	
		90(30)	410	RSO_2NH_2

[a] For $S_4N_5^-$ the area under both peaks has been summed. [b] Aldrich. [c] Overlapping resonance does not allow individual linewidths to be determined with accuracy.

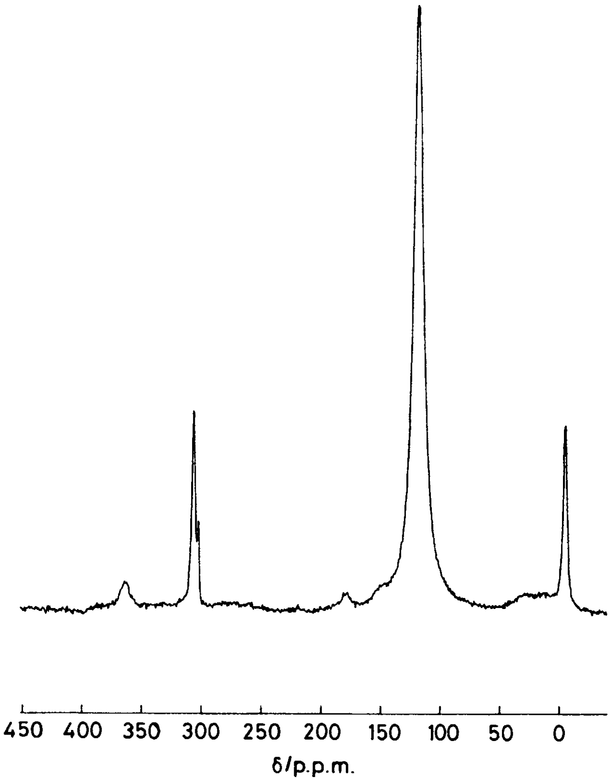


Figure 5. Nitrogen-14 n.m.r. spectrum of a 24 h-old thf solution obtained after bubbling NH_3 through a suspension of $[S_4N_3]Cl$ in thf for 10 min

the change in concentration of the various species in the more complex solutions (*i.e.* $S_4N_4O_2$) show *ca.* 20% change in product distribution after 24 h. Two systems that we have studied in some detail are the reaction between $[S_4N_3]Cl$ and $NH_3(g)$ in thf and the associated process, *i.e.* thf extraction of the $[S_4N_3]Cl–NH_3(l)$ residue (Table 5).

The thf extract from $[S_4N_3]Cl–NH_3(l)$ shows a multitude of different species, no $S_3N_3^-$ or $S_4N_5^-$ salts are observed but initially *ca.* 10% of S_4N_4 (121 p.p.m.)[8] is apparent. The main component of the solution (344, 333 p.p.m.), *ca.* 65%, is a sulphur–di-imide-type species, possibly N_2S^{2-} or $HNSN^-$. After

Table 5. The use of ^{14}N n.m.r. spectroscopy in mechanistic studies

Reaction conditions	δ/p.p.m. (% of total)
thf extract from $[S_4N_3]Cl–NH_3(l)$	393, 372, 344, 333, 191, 121, 103, 24
after 1 h	(5) (5) (25) (35) (10) (10) (5) (5)
thf extract from $[S_4N_3]Cl–NH_3(l)$	333, 274, 193, 121, 24
after 24 h	(20) (30) (5) (40) (5)
thf solution from $[S_4N_3]Cl–NH_3(g)$	366, 310, 305, 274, 214, 179, 121, 33
after 1 h	(2) (1) (1) (2) (2) (5) (85) (2)
thf solution from $[S_4N_3]Cl–NH_3(g)$	366, 309, 180, 121, 29
after 1 h	(4) (7) (1) (85) (3)

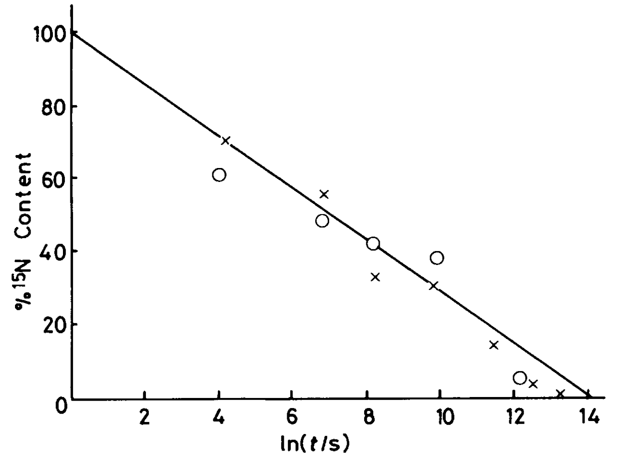


Figure 6. Graph showing the ^{15}N content in the S_4N_4 recovered from solutions of (*a*) $S_4{}^{15}N_4$(×) and (*b*) $[S^{15}N_3]Cl$ (○), where *t* refers to the total time the samples were in liquid ammonia (see Experimental section)

24 h more S_4N_4 is produced and the main peaks initially at 333 and 344 p.p.m. have decreased in magnitude.

The initial thf extract from $[S_4N_3]Cl–NH_3(l)$ is known to react with $[PtCl_2(PR_3)_2]$ to yield $[Pt(S_2N_2)(PR_3)_2]$.[40] From the ^{14}N n.m.r. spectrum it is unlikely that the reaction proceeds in the same way as that of the thf solution of $[S_4N_3]Cl–NH_3(g)$ with $[PtCl_2(PR_3)_2]$ because the same reactive SN species are not detected by ^{14}N n.m.r. spectroscopy. The main product from passing $NH_3(g)$ through a solution of $[S_4N_3]Cl$ in thf is S_4N_4 in *ca.* 85% yield, detected by ^{14}N n.m.r. spectroscopy. This agrees with the current theory that S_4N_3Cl is an intermediate in the synthesis of S_4N_4 from 'SCl_3' and ammonia.[1]

In the light of our n.m.r. measurements we have dissolved ^{15}N-labelled S_4N_4 in liquid ammonia to determine if the nitrogen atoms in the SN heterocycle exchange with the solvent. Figure 6 illustrates the decrease in ^{15}N content of the S_4N_4 with time together with the same results for $[S_4N_3]Cl$. It is clear that the SN species observed by n.m.r. spectroscopy, *i.e.* $S_3N_3{}^-$ is in equilibrium with other SN molecules in reactions which incorporate the solvent nitrogen atoms. The initial $^{15}N–^{14}N$ exchange is very rapid in the $[S_4N_3]Cl$ case and we believe that there are two processes that account for the loss of ^{15}N label from the heterocycle. The formation of the $S_3N_3{}^-$ anion occurs rapidly [equation (1)] and this species is involved in other equilibria which result in further

$$7\,S_4N_3{}^+ + 6\,NH_3 \longrightarrow 9\,S_3N_3{}^- + H_2S + 16\,H^+ \quad (1)$$

exchange of the nitrogen atoms. We have previously speculated[9] on the species that might be involved since we do observe some weak signals (1—2% of the total) in the spectrum of S_4N_4 in liquid ammonia. It seems likely that small amounts of SN anions such as S_3N^-, $S_2N_2{}^{2-}$, $S_2N_2H^-$, and $SN_2{}^{2-}$ may be present.

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