Characterization of the $S_2N_2H^-$ Ion by ^{14}N and ^{15}N NMR Spectroscopy

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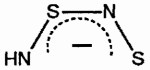
^{14}N and ^{15}N NMR spectroscopy shows that the deprotonation of S_7NH by potassium amide in liquid ammonia proceeds *via* the sequential formation of S_7N^-, S_4N^-, and S_3N^- to give $S_2N_2H^-$, which subsequently decomposes to $S_3N_3^-$; the $S_2N_2H^-$ ion is also produced by treatment of $S_4N_4H_4$ with 2 mol equiv. of potassium amide in liquid ammonia.

The binary sulphur–nitrogen anions $S_4N_5^-$,[1] $S_3N_3^-$,[2] $SSNSS^-$,[3] $SSNS^-$,[4] and SN_2^{2-},[5] are well characterized. The existence of the $S_2N_2H^-$ ion (**1**) has been inferred from the preparation of $L_nMS_2N_2H$ complexes, in which (**1**) acts as a chelating ligand, *via* the deprotonation of $S_4N_4H_4$ in the presence of a metal halide.[6,7] However, the deprotonation of $S_4N_4H_4$ with potassium hydride yields $S_3N_3^-$ as the final isolated product.[8] No direct evidence for (**1**) has been obtained, although the unstable product of the reaction of $S_4N_4H_4$ with 2 mol equiv. of Ph_3CNa has been tentatively characterized as $Na_2N_4S_4H_2$.[9] ^{14}N and/or ^{15}N NMR spectroscopy is an excellent technique for monitoring the formation of sulphur–nitrogen anions.[10–14] We report here a $^{14}N/^{15}N$ NMR investigation of the deprotonation of S_7NH and $S_4N_4H_4$ by KNH_2 in liquid ammonia which provides the first spectroscopic characterization of the thermally unstable $S_2N_2H^-$ ion.



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We have already shown that the ^{14}N NMR spectrum of a deep blue solution of S_7NH in liquid ammonia at 25 °C (after equilibrium has been reached) shows a major resonance at +107 ppm (S_4N^-)†[12] and a weak resonance at −324 ppm for

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† All ^{14}N and ^{15}N NMR chemical shifts are given relative to external $MeNO_2(l)$ at 0 ppm using the downfield positive convention.

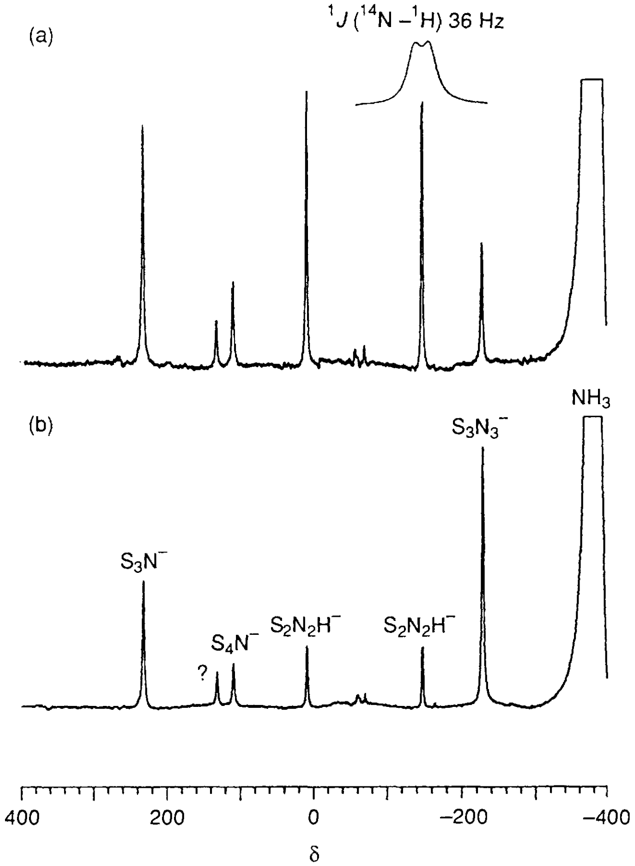


Figure 1. The ^{14}N NMR spectrum of a KNH_2–S_7NH (3 : 1) solution in liquid ammonia at 25 °C after (a) 2 h, (b) 10 days in a thick-walled 10 mm glass tube sealed under vacuum. Spectra were acquired on a Bruker AM 400 spectrometer operating at 28.915 MHz for ^{14}N and were run unlocked. A pulse length of 20 μs provided a *ca.* 90° tip angle and 8 K data points were collected. Typically 5 000—15 000 scans were co-added for a total acquisition time of 10—40 min. Chemical shifts are with respect to external $MeNO_2(l)$.

S_7N^-.[13] We now report that the addition of two molar equivalents of potassium amide to this solution results in the partial conversion of S_4N^- into S_3N^- [$\delta(^{14}N)$ +230 ppm][12] and $S_3N_3^-$ [$\delta(^{14}N)$ −230 ppm].[12] The addition of a third molar equivalent of KNH_2 produces two new resonances at +7 and −149 ppm, [Figure 1(a)], which do not correspond to any known sulphur–nitrogen anion. These resonances are associated with the same species since they grow and decay together [Figure 1(b)]. The signal at −149 ppm is a doublet [$^1J(^{14}N-^1H)$ 36 Hz] [Figure 1(a)] indicating that one of the nitrogen atoms is attached to a hydrogen atom.

The same species is generated by treatment of 99% ^{15}N-enriched $S_4N_4H_4$ with two molar equivalents of potassium amide in liquid ammonia (Figure 2). Two resonances are observed at +9 and −148 ppm [$^1J(^{15}N-^1H)$ 55 Hz] in addition to a weak resonance at −230 ppm for $S_3N_3^-$. The ratio $^1J(^{15}N-^1H)/^1J(^{14}N-^1H)$ is 1.53, *cf.* $\gamma(^{15}N)/\gamma(^{14}N) = 1.40$, (where γ = magnetogyric ratio). The coupling between the inequivalent nitrogen atoms was determined for the resonance at +9 ppm to be *ca.* 2.2 Hz‡ [*cf.* $^2J(^{15}N-^{15}N)$ 2.2 Hz for $Ph_3AsNS_3N_3$].[10] These NMR data are uniquely consistent with a species

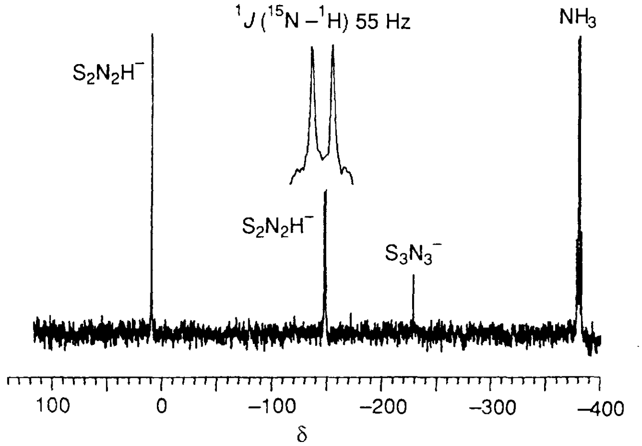
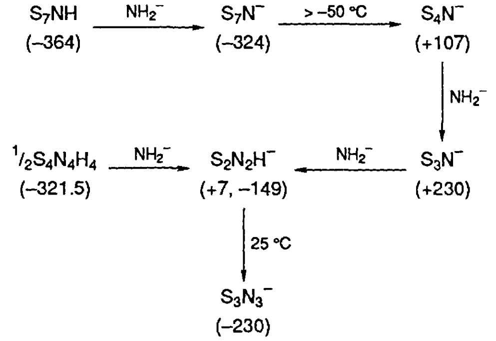


Figure 2. The ^{15}N NMR spectrum of a *ca.* 0.07 M solution of 99% ^{15}N-enriched $S_4N_4H_4$ in liquid ammonia containing two molar equivalents of KNH_2 at 25 °C in a thick-walled 16 mm tube sealed under vacuum. The tube was mounted coaxially within a 20 mm tube and D_2O was added to the outer tube as a lock. Spectra were acquired on a Bruker AM 400 wide bore spectrometer operating at 40.557 MHz for ^{15}N. A pulse length of 40 μs provided a *ca.* 45° tip angle and 16 K data points were collected; 226 scans with 30 s repetition time were used.



Scheme 1. Sulphur-nitrogen anions formed in the deprotonation of S_7NH and $S_4N_4H_4$. Nitrogen NMR chemical shifts (in ppm) are given in parentheses [ref. $MeNO_2(l)$]. The values for the imides are for tetrahydrofuran solutions and those for the anions are for liquid ammonia solutions.

containing the –NSNH group and, in view of previous chemical evidence,[6,7] we attribute these two resonances to the inequivalent nitrogen atoms of (**1**). The co-ordinated $S_2N_2H^-$ ligand exhibits ^{14}N NMR signals at *ca.* −20 and −150 ppm.§ The two resonances for $S_2N_2H^-$ decrease in intensity after several days at 25 °C, while the resonance for $S_3N_3^-$ at −230 ppm grows concomitantly [Figure 1(b)]. This observation is consistent with the isolation of $K^+S_3N_3^-$ as the final product of the deprotonation of $S_4N_4H_4$ by potassium hydride.[8] The transformations that occur upon deprotonation of S_7NH or $S_4N_4H_4$ with potassium amide in liquid ammonia are summarized in Scheme 1.

The $S_2N_2H^-$ ion is an important ligand in co-ordination chemistry[15,16] and a key member of a growing series of sulphur–nitrogen anions.[1–5,13] The characterization of (**1**) in solution is also significant in view of recent speculation regarding the identity of sulphur–nitrogen anions, *e.g.* $S_2N_2^{2-}$,[14a] $S_2N_2H^-$,[14b] and S_2N^-,[17] present as minor com-

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‡ $^2J(^{15}N-^{15}N)$ was resolved by the application of a convolution-difference algorithm to the ^{15}N NMR data.

§ Literature values were given relative to $NH_3(l)$;[14] the chemical shifts given here have been converted with reference to $MeNO_2(l)$ [$\delta(NH_3)(l) = -380$ ppm].

ponents in ammonia solutions of S_4N_4[14] or sulphur in the presence of amide ion.[17] However, the potassium salt, like $Na_2N_4S_4H_2$[9,18] [$\equiv (Na^+S_2N_2H^-)_2$], is susceptible to explosion if subjected to mild heating or friction. As in the case of other thermally labile sulphur–nitrogen anions, it will be necessary to use large counterions, *e.g.* Ph_4As^+ or $(Ph_3P)_2N^+$,[1–3,19] in order to isolate crystalline salts of this unstable anion.

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References

1 W. Flues, O. J. Scherer, J. Weiss, and G. Wolmershäuser, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 379.
2 J. Bojes, T. Chivers, W. G. Laidlaw, and M. Trsic, *J. Am. Chem. Soc.*, 1979, **101**, 4517.
3 T. Chivers, W. G. Laidlaw, R. T. Oakley, and M. Trsic, *J. Am. Chem. Soc.*, 1980, **102**, 5773.
4 J. Bojes, T. Chivers, W. G. Laidlaw, and M. Trsic, *J. Am. Chem. Soc.*, 1982, **104**, 4837.
5 M. Herberhold and W. Ehrenreich, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 633.
6 R. Jones, P. F. Kelly, C. P. Warrens, D. J. Williams, and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1986, 711.
7 T. Chivers, F. Edelmann, U. Behrens, and R. Drews, *Inorg. Chim. Acta*, 1986, **116**, 1509.
8 J. Bojes, T. Chivers, I. Drummond, and G. MacLean, *Inorg. Chem.*, 1978, **17**, 3668.
9 (a) M. Becke-Goehring, *Adv. Inorg. Chem. Radiochem.*, 1960, **2**, 159; (b) M. Becke-Goehring and R. Schwarz, *Z. Anorg. Chem.*, 1958, **296**, 3.
10 T. Chivers, R. T. Oakley, O. J. Scherer, and G. Wolmershäuser, *Inorg. Chem.*, 1981, **20**, 914.
11 T. Chivers, A. W. Cordes, R. T. Oakley, and W. T. Pennington, *Inorg. Chem.*, 1983, **22**, 2429.
12 T. Chivers, D. D. McIntyre, K. J. Schmidt, and H. J. Vogel, *Can. J. Chem.*, 1989, **67**, 1788.
13 T. Chivers, D. D. McIntyre, K. J. Schmidt, and H. J. Vogel, *J. Chem. Soc., Chem. Commun.*, 1990, preceding communication.
14 (a) P. S. Belton, I. P. Parkin, D. J. Williams, and J. D. Woollins, *J. Chem Soc., Chem. Commun.*, 1988, 1479; (b) I. P. Parkin, J. D. Woollins, and P. S. Belton, *J. Chem. Soc., Dalton Trans.*, 1990, 511.
15 T. Chivers and F. Edelmann, *Polyhedron*, 1986, **5**, 1661.
16 P. F. Kelly and J. D. Woollins, *Polyhedron*, 1986, **5**, 607.
17 P. Dubois, J. P. Lelieur, and G. Lepoutre, *Inorg. Chem.*, 1988, **27**, 3032.
18 T. Chivers, F. Edelmann, and K. J. Schmidt, unpublished results.
19 J. Bojes, T. Chivers, and R. T. Oakley, *Inorg. Synth.*, 1989, **25**, 30; 1989, **25**, 35.