^{14}N and ^{15}N NMR Characterization and the Identification in Sulphur–Ammonia Solutions of the S_7N^- Ion

Tristram Chivers,*[a] Deane D. McIntyre,[b] Kenneth J. Schmidt,[a] and Hans J. Vogel[b]

Departments of Chemistry[a] and Biological Sciences[b], The University of Calgary, Calgary, Alberta T2N 1N4, Canada

The cyclic sulphur imide, S_7NH, and the thermally unstable S_7N^- ion have been characterized by ^{14}N and ^{15}N NMR spectroscopy; the existence of S_7N^-, in addition to S_4N^- and small amounts of S_3N^-, in sulphur–ammonia solutions is demonstrated by ^{14}N NMR spectroscopy.

The existence of the S_7N^- anion has been inferred from alkylation studies.[1,2] It decomposes above *ca.* −50 °C to give S_4N^- (and sulphur).[3] We have invoked the initial formation of S_7N^- to explain the production of S_4N^- in sulphur–ammonia solutions (SAS).[4] Subsequently Prestel and Schindewolf estimated from UV-VIS spectra that 36 ± 4% of the dissolved sulphur in ammonia is in the form of S_7N^-.[5] By contrast, Lelieur *et al.* found no evidence for S_7N^- in SAS by UV-VIS or Raman spectroscopy.[6] ^{14}N and/or ^{15}N NMR spectroscopy is an excellent technique for the analysis of complex mixtures of sulphur–nitrogen anions,[7,8] but the S_7N^- anion has not been characterized by this method. We demonstrate here by ^{14}N and ^{15}N NMR spectroscopy that S_7N^- gives rise to a resonance at *ca.* −320 ppm,† while S_7NH exhibits a resonance at −364 ppm. The S_7N^- ion is also shown to be the major N-containing species in SAS at 25 °C. These results are at variance with a recent study in which this species was identified as S_7NH.[9]

The natural abundance ^{15}N NMR spectrum of a 1 M solution of S_7NH in tetrahydrofuran (THF) at −80 °C displays a doublet [$^1J(^{15}N-^1H)$ 97 Hz] at −364 ppm [Figure 1(a)]. Upon addition of an equimolar amount of Bu^{n}Li in hexane to this solution at −80 °C, this doublet disappears completely and instead a singlet at −318.8 ppm is observed. No other resonances are observed with the exception of dissolved N_2 at −71.5 ppm.[10] Therefore we attribute the resonance at −319 ppm to the S_7N^- anion.

The ^{14}N NMR spectrum of S_7NH in THF exhibits a broad resonance centred around −364 ppm. No $^1J(^{14}N-^1H)$ can be observed due to the linewidth ($\nu_{\frac{1}{2}} \approx 700$ Hz). After addition of an equimolar amount of Bu^{n}Li in hexane to this solution at −80 °C, the chemical shift of the resonance due to S_7N^- could not be determined accurately owing to its broadness. At 25 °C, however, a resonance at *ca.* −327 ppm ($\nu_{\frac{1}{2}} \approx 1000$ Hz) was observed in addition to the signal for S_4N^- at +106 ppm [*cf.* $\delta(^{14}N)$ +106 ppm for $(Ph_3P)_2N^+S_4N^-$ in MeCN].[8] The concentrations of S_7N^- and S_4N^- are approximately equal after one day at 25 °C.

The formation of sulphur–nitrogen anions in solutions of S_7NH in liquid ammonia has been demonstrated by UV-VIS[5,11] and Raman spectroscopy.[11] 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 ($\nu_{\frac{1}{2}}$ 110 Hz) due to S_4N^- and a weak resonance at −324 ppm ($\nu_{\frac{1}{2}}$ 280 Hz) for S_7N^- [*cf.* −331 ppm for S_7NH in $NH_3(l)$][9]† consistent with previous findings.[5,11] The production of sulphur–nitrogen anions in SAS was also monitored by ^{14}N NMR spectroscopy. After 2 h major resonances at −323 and +109 ppm attributable to S_7N^- and S_4N^-, respectively, and a very weak resonance at +231 ppm assigned to S_3N^-, [*cf.* $\delta(^{14}N)$ +235 ppm for $(Ph_3P)_2N^+S_3N^-$ in MeCN],[8] are apparent (Figure 2). Surprisingly, S_7N^- accounts for *ca.* 80% of the nitrogen-containing species and this increases to 88% after 5 days. By contrast, Woollins *et al.* have attributed resonances at −329, −38, +105, and +192 ppm† to S_7NH, an unidentified species, S_4N^- and NS^+, respectively.[9] The existence of the extremely electrophilic NS^+ cation[12] in liquid ammonia solutions is highly unlikely.

In summary, we have characterized the thermally unstable S_7N^- anion by ^{14}N and ^{15}N NMR spectroscopy and shown that it is a major component of sulphur–ammonia solutions at room temperature. Raman and UV-VIS spectroscopy are more sensitive methods for the detection of S–N anions, but

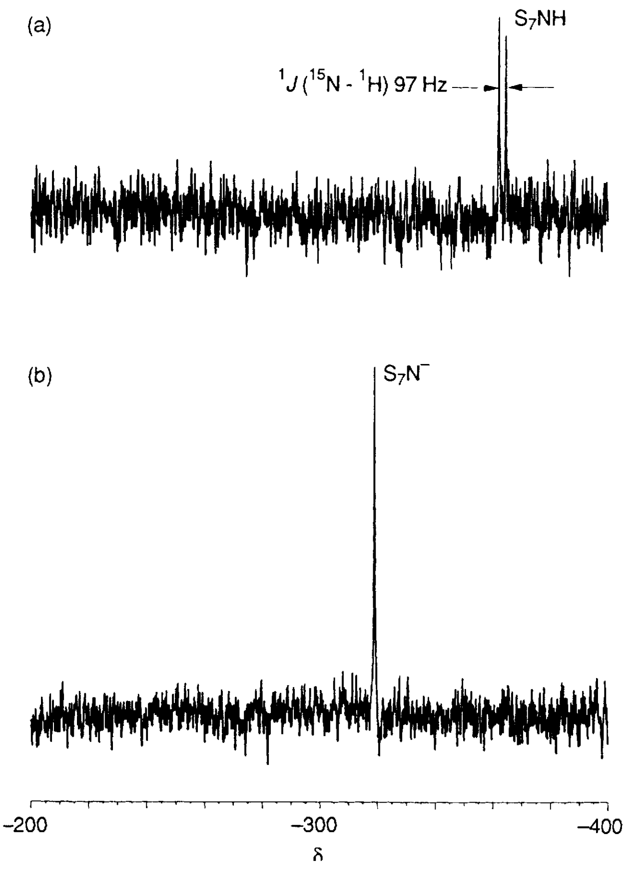

Figure 1. The ^{15}N NMR spectrum (natural abundance) of (a) a 1 M solution of S_7NH in THF at −80 °C (2.5 h acquisition), (b) the same solution at −80 °C after the addition of 1 mol of Bu^{n}Li in hexane per mol of S_7NH (2 h acquisition). Spectra were recorded at 40.56 MHz on a Bruker AM-400 wide-bore spectrometer using a 20 mm broadband probe (10 ml sample size). A pulse length of 40 μs provided a *ca.* 45° tip angle, and a 2.5 s repetition time was used. The spectral width was 25 000 Hz, and 16 K of data points were collected. The chemical shifts are referenced to $MeNO_2(l)$ at 0 ppm using the downfield positive convention.

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† Nitrogen NMR chemical shifts (in ppm) are quoted here with reference to external $MeNO_2(l)$ using the downfield positive convention. ^{14}N NMR chemical shifts in ref. 9 were given relative to $NH_3(l)$ [$\delta(NH_3)(l)$ = −380 ppm *vs.* $MeNO_2(l)$].

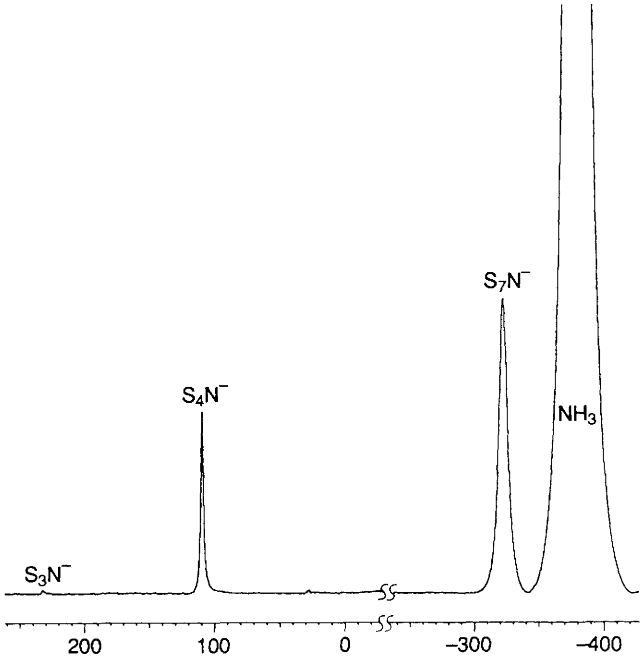

Figure 2. The ^{14}N NMR spectrum of a 1 M (S atom) solution of S_8 in liquid ammonia after 2 h at room temperature (2 h acquisition). The spectrum was obtained at 36.14 MHz on a Bruker AMX-500 spectrometer (equipped with a 16-bit digitizer) using a 10 mm broadband probe. A pulse length of 40 μs provided a *ca.* 90° tip angle, and no delay was used between pulses (acquisition time per pulse was 0.13 s). The spectral width was 30 000 Hz, and 8 K of data points were collected (zero filled to 64 K before processing). The chemical shifts are referenced to $MeNO_2(l)$ at 0 ppm using the downfield positive convention.

the use of ^{14}N NMR spectroscopy as a complementary technique is essential for a complete analysis of reaction mixtures.[8,13] Furthermore, the NMR technique can provide an unambiguous identification of S_7N^- in such mixtures because of the large separation of the ^{14}N chemical shifts of individual sulphur–nitrogen anions.[13]

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References

1 B. A. Olsen and F. P. Olsen, *Inorg. Chem.*, 1969, **8**, 1736; E. M. Tingle and F. P. Olsen, *ibid.*, 1969, **8**, 1741.
2 M. H. Mendelsohn and W. L. Jolly, *J. Inorg. Nucl. Chem.*, 1973, **35**, 95.
3 T. Chivers and I. Drummond, *Inorg. Chem.*, 1974, **13**, 1222.
4 T. Chivers and C. Lau, *Inorg. Chem.*, 1982, **21**, 453.
5 H. Prestel and V. Schindewolf, *Z. Anorg. Allg. Chem.*, 1987, **551**, 21.
6 P. Dubois, J. P. Lelieur, and G. Lepoutre, *Inorg. Chem.*, 1989, **28**, 195.
7 T. Chivers, A. W. Cordes, R. T. Oakley, and W. T. Pennington, *Inorg. Chem.*, 1983, **22**, 2429.
8 T. Chivers, D. D. McIntyre, K. J. Schmidt, and H. J. Vogel, *Can. J. Chem.*, 1989, **67**, 1788.
9 I. P. Parkin, J. D. Woollins, and P. S. Belton, *J. Chem. Soc., Dalton Trans.*, 1990, 511.
10 D. D. McIntyre, A. W. Apblett, P. Lundberg, K. J. Schmidt, and H. J. Vogel, *J. Magn. Reson.*, 1989, **83**, 377, and references therein.
11 P. Dubois, J. P. Lelieur, and G. Lepoutre, *Inorg. Chem.*, 1988, **27**, 3032.
12 A. Apblett, T. Chivers, and J. F. Fait, *Inorg. Chem.*, 1990, **29**, 1643.
13 T. Chivers and K. J. Schmidt, *J. Chem. Soc., Chem. Commun.*, 1990, following communication.