The Reactions of Sulphur–Nitrogen Species in Liquid Ammonia

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^{14}N N.m.r. spectroscopy reveals that liquid ammonia solutions of [S_4N_3]Cl or [S_3N_2Cl]Cl contain $S_3N_3^-$ whilst solutions of S_4N_4 contain $S_3N_3^-$ and $S_4N_5^-$ and traces of other species such as $S_2N_2^{2-}$; the usefulness of these liquid ammonia solutions in synthesis has been established in several cases with two new complexes being characterised by *X*-ray crystallography.

Currently, there is interest in the constitution of liquid ammonia solutions of sulphur and sulphur–nitrogen compounds. To date, u.v.–visible[1,2] and vibrational[3] spectroscopy have been used to probe the nature of the species in solution. We have shown that ^{14}N n.m.r. spectra of sulphur–nitrogen species are obtainable with a good chemical shift range and only moderate linewidths.[4] Here, we report on ^{14}N n.m.r. investigations into the nature of the interaction of liquid ammonia with [S_3N_2Cl]Cl (**1**), [S_4N_3]Cl (**2**), and S_4N_4 (**3**).

When (**1**) or (**2**) is dissolved in liquid ammonia the ^{14}N n.m.r. spectrum consists of signals due to the liquid ammonia and an additional resonance at 147 p.p.m. Dissolution of (**3**) in liquid ammonia gives a spectrum (Figure 1) containing a large peak at 147 p.p.m. and two smaller peaks at 51 and 137 p.p.m. together with a number of weak signals with higher chemical shifts. Comparison of these chemical shifts with reported ^{15}N data[5] for $S_3N_3^-$ and $S_4N_5^-$ in $CHCl_3$ (δ 148.4 and 138.7, 53.3 p.p.m. respectively) and the spectrum of [PPh_4][S_3N_3] in CH_2Cl_2 (δ 146 p.p.m.) enables the major species in solution to be unequivocally identified as $S_3N_3^-$ and $S_4N_5^-$. To our knowledge, this is the first application of ^{14}N n.m.r. spectroscopy for the study of liquid ammonia solutions. The species responsible for the minor peaks (δ 223, 281, 289, and 349 p.p.m.) cannot be unequivocally assigned as yet. However, the nitrogen atoms in sulphur di-imides generally give resonances at *ca.* 320—350 p.p.m.,[4] the $S_2N_2H^-$ ligand has signals (*vide infra*) in this range and at *ca.* 220 p.p.m., and in the ^{15}N spectrum of S_4N^- δ 213 p.p.m. It seems likely that the weak signals are due to $S_2N_2^{2-}$, S_4N^-, and S_3N^- present at low levels in equilibrium with the $S_3N_3^-$ anion. Integration of the ^{14}N spectrum in Figure 1 allows an estimate of the sensitivity of the measurement. The overall concentration of sulphur–nitrogen species is *ca.* 0.5 M with the weaker peaks representing *ca.* 3 mM concentrations; *i.e.*, we are able to detect less than 3 mg of SN species in under 10 min.

The ease of spectral acquisition allowed us to make measurements on solutions of (**2**) and (**3**) at various time intervals and temperatures. Even freshly prepared solutions which had not been allowed to warm beyond −40 °C contained only $S_3N_3^-$ and upon warming to room temperature (spectra being recorded at 10 °C intervals needing *ca.* 5 min to collect data) and standing for 24 h no significant change was

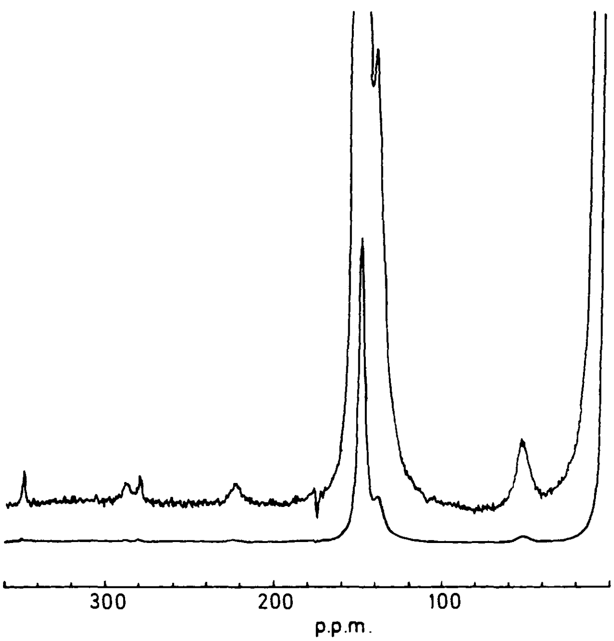

Figure 1. ^{14}N N.m.r. spectrum of a 0.5 M solution of S_4N_4 (**3**) in liquid ammonia. Spectra were acquired on a Bruker CXP300 Spectrometer in a 7 T magnetic field. The ^{14}N resonance frequency was 21.682 MHz. Samples were placed in a 10 mm tube in a high power saddle coil arrangment giving a 90° pulse length of 12.5 μS. Where necessary the RIDE (ring down elimination) sequence was used; no proton decoupling was used. Typically 10 000 scans were co-added with a recycle time of 52 ms giving a total acquisition time of *ca.* 520 s. Samples were thermostated by a liquid nitrogen cryostat arrangment coupled with a Bruker BVT1000 temperature control to within ±1 K. Chemcial shifts are with respect to liquid ammonia at 0 p.p.m.

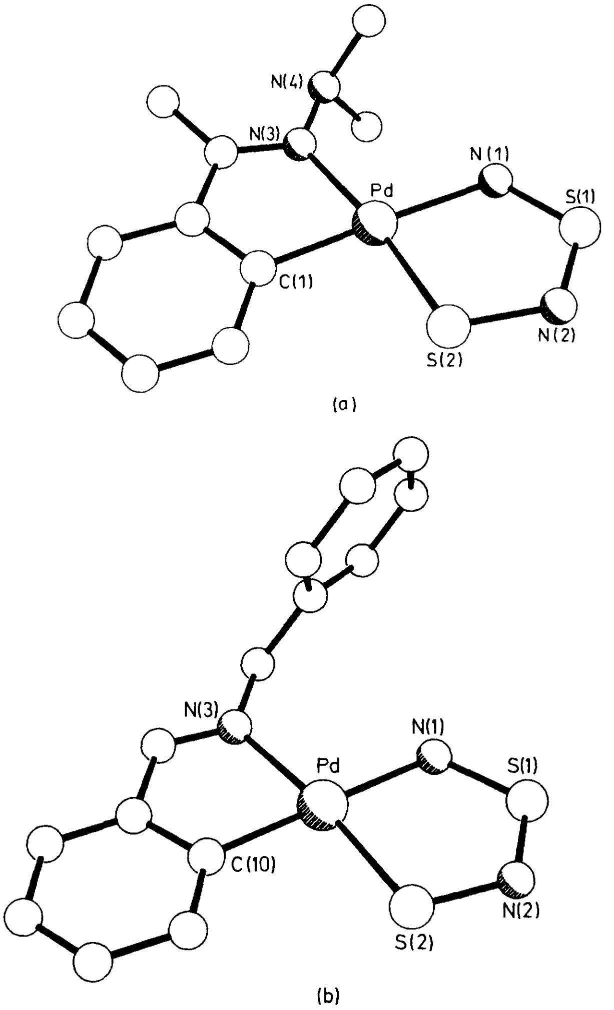

Figure 2. The *X*-ray crystal structures of $Pd(S_2N_2H)(L–L')$. $(L–L')$ = (a) acetophenone *N*,*N*-dimethylhydrazone (**4**) and (b) *N*-benzylidenebenzylamine (**5**). Selected bond lengths and angles: parameters for (**4**) are for one of the independent molecules only [compound (b) in brackets]: Pd–N(1) 2.104(6) [2.064(6)], Pd–S(2) 2.237(3) [2.219(2)], Pd–C(1) 1.984(7) [2.004(7)], Pd–N(3) 2.092(6) [2.084(6)], N(1)–S(1) 1.579(7) [1.592(6)], S(1)–N(2) 1.566(7) [1.546(7)], N(2)–S(2) 1.665(8) [1.664(7)], N(3)–N(4) 1.435(8) Å; N(1)–Pd–S(2) 85.3(2) [86.2(2)], C(1)–Pd–N(3) 80.0(3) [80.7(3)], Pd–N(1)–S(1) 118.0(3) [118.3(3)], N(1)–S(1)–N(2) 110.8(4) [109.4(3)], S(1)–N(2)–S(2) 119.3(5) [120.8(4)], Pd–S(2)–N(2) 106.6(3) [105.3(2)]°.

noted. On the basis of the above n.m.r. data it is possible to propose the equilibria of the type shown in equations (1) and (2). An interesting feature of our measurements is the observation that in the spectra of (**3**) the intensity of the peaks at 51 and 137 p.p.m. was of the order of 10—20% of the intensity of the peaks at 147 p.p.m. This represents a molecular ratio of $S_4N_5^-$ to $S_3N_3^-$ of 0.07 and 0.14 to 1; substantially less than those expected from workup of the reaction or the simple equilibrium in equation (3) which is claimed[5] to give up to 37% $[NH_4][S_4N_5]$. We detected no change in the proportions of $S_4N_5^-$ and $S_3N_3^-$ with time. However, if ^{15}N-labelled S_4N_4 is used in the above reactions and the ammonia (which is in *ca.* 1000 fold excess) evaporated off, mass spectroscopy allows determination of the ^{15}N content in the recovered S_4N_4. This diminishes steadily with time; after a reaction of 1 h *ca.* 42% ^{15}N label remains whilst after 56 h 5% label is present as S_4N_4. Apart from the species observed by n.m.r. spectroscopy, minor amounts of other SN species are probably present in a complex set of equilibria.

$$S_3N_2Cl^+ + NH_3 = S_3N_3^- + 3H^+ + Cl^- \qquad (1)$$

$$7S_4N_3^+ + 6NH_3 = 9S_3N_3^- + H_2S + 16H^+ \qquad (2)$$

$$5S_4N_4 + 2NH_3 = 2S_4N_5^- + 4S_3N_3^- + 6H^+ \qquad (3)$$

The above results clearly demonstrate the ability of ^{14}N n.m.r. spectroscopy to characterise sulphur–nitrogen species in liquid ammonia and it is interesting to compare them with the results of synthetic studies which are in accord with the presence of $S_3N_3^-$, which is known to react to give $S_2N_2^{2-}$ complexes.[6] For example, reaction of $PtCl_2(PR_3)_2$ with S_4N_3Cl/NH_3(liq) gives $Pt(S_2N_2)(PR_3)_2$ quantitatively by ^{31}P n.m.r. (70% isolated, characterised by microanalyses, i.r., and n.m.r.[6,7]). Alternatively, organometallic palladium complexes, $Pd(S_2N_2H)(L–L')$, may be formed by reactions with $(L–L')PdCl_2Pd(L–L')$ [*e.g.*, where the neutral form of the ligand $(HL–L')$ = *N*-benzylidenebenzylamine (**4**) or acetophenone *N*,*N*-dimethylhydrazone (**5**)]. These complexes were characterised by i.r., ^1H n.m.r., and mass spectroscopy, together with ^{14}N n.m.r. spectroscopy [for (**4**) δ 343, 234, 216; (**5**) 343, 280, 208 p.p.m.] with ^{14}N resonances at δ *ca.* 350 and 230 p.p.m. being characteristic of the $S_2N_2H^-$ ligand. The *X*-ray crystal structures of (**4**) and (**5**) are shown in Figure 2.† The compounds exhibit the expected square planar geometry. The N(1) proton was located and refined for both independent molecules in (**4**) whereas in (**5**) the presence of a disordered CH_2Cl_2 molecule meant that the N(1) proton could not be located. However both compounds exhibit the characteristic distances and angles for the $S_2N_2H^-$ rather than the $S_2N_2^{2-}$ ligand.[8]

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References

1 H. Prestel and U. Schindewolf, *Z. Anorg. Allg. Chem.*, 1987, **551**, 21.
2 P. Dubois, J. P. Lelieur, and G. Lepoutre, *Inorg. Chem.*, 1987, **26**, 1897.
3 T. Chivers and C. Lau, *Inorg. Chem.*, 1982, **21**, 453.
4 P. S. Belton and J. D. Woollins, *Magn. Reson. Chem.*, 1986, **24**, 1080.
5 T. Chivers, R. T. Oakley, O. J. Scherer, and G. Wolmershauser, *Inorg. Chem.*, 1981, **20**, 914.
6 P. A. Bates, M. B. Hursthouse, P. F. Kelly, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1986, 2367.
7 R. Jones, P. F. Kelly, D. J. Williams, and J. D. Woollins, *Polyhedron*, 1987, **6**, 1541.
8 R. Jones, P. F. Kelly, D. J. Williams, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1988, 803.

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† *Crystal data*: (**4**), $C_{10}H_{14}N_4S_2Pd$, M = 360.79, monoclinic, a = 17.723(2), b = 9.028(1), c = 18.986(3) Å, β = 116.74(1)°, U = 2713 Å^3, space group $P2_1/c$, Z = 8 (2 crystallographically independent molecules), D_c = 1.77 g cm^{-3}, $\mu(Cu\text{-}K_\alpha)$ = 140 cm^{-1} $F(000)$ = 1440.
(**5**), $C_{14}H_{14}N_3S_2Pd\cdot0.83(CH_2Cl_2)$, monoclinic, M = 465.2, a = 9.538(4), b = 15.549(6), c = 12.364(5) Å, β = 92.11(3)°, U = 1832 Å^3, space group $P2_1/a$, Z = 4, D_c = 1.74 g cm^{-3}, $\mu(Cu\text{-}K_\alpha)$ = 132 cm^{-1}, $F(000)$ = 927. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α radiation using ω-scans. The structures were solved by the heavy-atom method and refined anisotropically using absorption corrected data to give R = 0.046, R_w = 0.053 for 2785 independent observed reflections [$|F_o|>3\sigma(|F_o|)$, $\theta\leqslant55°$] for (**4**) and R = 0.064, R_w = 0.072 for 2185 independent observed reflections [$|F_o|>3\sigma(|F_o|)$, $\theta\leqslant55°$] for (**5**). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.