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THE NITROGEN-15 NUCLEAR MAGNETIC RESONANCE SPECTRUM OF THE $S_4N_3^+$ ION

Norman Logan and William L. Jolly

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Contribution from the Department of Chemistry of the University of California and the Inorganic Materials Research Division of the Lawrence Radiation Laboratory, Berkeley, California 94720

The Nitrogen-15 Nuclear Magnetic Resonance Spectrum of the $S_4N_3^+$ Ion

By Norman Logan¹ and William L. Jolly

Nitrogen-15 nuclear magnetic resonance spectra have recently been observed for compounds containing the ^{15}N isotope at natural abundance (0.36%) and also for ^{15}N -enriched samples.^{2,3,4} However, the utility of ^{15}N n.m.r. as a structural tool for the detection of nitrogen atoms in nonequivalent environments has not been demonstrated previously for inorganic systems. We have obtained the ^{15}N spectrum of the thiotrithiazyl cation $S_4N_3^+$ (97.2% ^{15}N) and find it to be consistent with the structure

which has recently been determined by X-ray analysis.⁵

The relatively stable chloride, S_4N_3Cl , was used in the present work. This compound was synthesized from ammonium chloride (97.2% enriched in ^{15}N) and disulfur dichloride. Because of the inherently

low sensitivity of nitrogen resonances (1×10^{-3} that of ^1H at constant field) it was necessary to use a solution more concentrated than 1 M in $\text{S}_4^{15}\text{N}_3^+$ in order to obtain a favorable signal-to-noise ratio. The salt undergoes rapid decomposition in water and is insoluble in most organic solvents. However, $\text{S}_4\text{N}_3\text{Cl}$ dissolves in 70% HNO_3 to the extent of 3-4 molar, forming a solution which is stable for at least one day at room temperature.

The ^{15}N spectrum of a 3.1 M solution of $\text{S}_4\text{N}_3\text{Cl}$ (97.2% ^{15}N) in 70% HNO_3 shows two resonances with an overall intensity ratio of 1:2, corresponding to the N' atom and the two equivalent N'' atoms shown in the structure. Both resonances exhibit spin-spin splitting. The weaker resonance, due to N' , is a 1:2:1 triplet, and the stronger resonance, due to the N'' atoms, is a 1:1 doublet. The triplet and doublet occur at 343 and 355 ± 1 ppm., respectively, downfield from the $^{15}\text{NH}_4^+$ resonance. The ^{15}N - ^{15}N coupling constant is 7 ± 1 c.p.s. and the half-width of individual components of the multiplets is approximately 7 c.p.s.

No particular significance can be attached to the magnitude of the chemical shifts; however, some qualitative observations can be made. Paramagnetic effects associated with electronic asymmetry are considered to provide the dominant contribution to nitrogen chemical shifts.² Unshared electron pairs cause an upfield shift, whereas electronegative substituents and multiple bonding cause a downfield shift. S_4N_3^+ occupies an approximately central position in the range of ^{15}N chemical shifts,² between the highly symmetrical ammonium ion (for which the paramagnetic term is at a minimum) and the nitrite ion (-584 ppm relative to ammonium ion). This is consistent with the fact that, in comparison to its

environment in NO_2^- , each nitrogen atom in S_4N_3^+ is involved in less multiple bonding and is attached to atoms of lower electronegativity. The occurrence of the triplet absorption slightly to high field of the doublet in the spectrum of S_4N_3^+ is indicative of slightly less π -bonding and slightly more unshared electron density around N' compared to N'' . This in turn is reasonably consistent with the observed bond lengths⁵ and with fractional bond orders and formal charges calculated from statistical considerations, assuming a sulfur-sulfur single bond and a total of two double bonds per ring.

The observed ^{15}N - ^{15}N coupling constant of 7 c.p.s. is the first to be reported for a system containing ^{15}N atoms two bonds removed from each other. The only other ^{15}N - ^{15}N coupling constant in the literature is that found for the directly bonded nitrogen atoms in trans-azoxybenzene, and has the value 14 ± 1 c.p.s.^{2,3}

No ^{14}N resonances attributable to the S_4N_3^+ ion were observed for solutions of $\text{S}_4\text{N}_3\text{Cl}$ (not enriched in ^{15}N) in either 80% H_2SO_4 (1 M S_4N_3^+) or 70% HNO_3 (3 M S_4N_3^+). It is well known, however, that the quadrupole interaction of ^{14}N ($I = 1$) may broaden signals to such an extent as to make them indistinguishable from the background.⁶ This effect is particularly serious when the nuclei are in unsymmetrical environments, as is the case for the nitrogen atoms in S_4N_3^+ . Spin-spin coupling in ^{14}N systems is also largely obscured by quadrupole effects.³ The above complications in ^{14}N spectra are eliminated by the use of ^{15}N ($I = 1/2$) which does not possess a quadrupole moment.

Synthesis of S_4N_3Cl . - When ammonium chloride and disulfur dichloride are refluxed in a vessel fitted with an air condenser, orange crystals of $S_3N_2Cl_2$ collect just above the level of the refluxing liquid. The $S_3N_2Cl_2$ can then be converted quantitatively to S_4N_3Cl by refluxing with a mixture of S_2Cl_2 and CCl_4 .⁷

The usual procedure for preparing $S_3N_2Cl_2$ from ammonium chloride and S_2Cl_2 is designed to maximize the yield based on S_2Cl_2 and therefore involves an excess of ammonium chloride. Because of the high cost of $^{15}NH_4Cl$, we have modified the procedure to maximize the yield based on ammonium chloride. A large excess of S_2Cl_2 is detrimental because, on heating, S_2Cl_2 disproportionates to sulfur and SCl_2 , and the SCl_2 causes destruction of the $S_3N_2Cl_2$ by the reversible reaction

Our best results were obtained by using a modest excess of S_2Cl_2 (S_2Cl_2/NH_4Cl mole ratio of 4:1). Under these conditions, a good crop of $S_3N_2Cl_2$ crystals was formed in the condenser and a 47% overall yield of S_4N_3Cl (based on NH_4Cl) was obtained. It was reported earlier⁸ that addition of sulfur to the reaction mixture reduces the time to the first appearance of $S_3N_2Cl_2$. This was confirmed in the present work, but the yield of S_4N_3Cl was unaffected.

Experimental

Reagents. - Eastman Kodak practical grade S_2Cl_2 was used without further purification. $^{15}NH_4Cl$ (97.2% ^{15}N) was supplied by Volk Radiochemical Co. Reagent grade carbon tetrachloride was dried over

anhydrous calcium sulfate. Merck reagent grade 70% nitric acid (from a freshly opened bottle) was used as a solvent for the n.m.r. study of $S_4^{15}N_3^+$.

Spectra. - N.m.r. spectra were obtained by the side-band method with a Varian V4200A variable frequency spectrometer operated at either 4.334 (^{14}N) or 6.080 (^{15}N) Mc/s and 14,100 gauss. Solutions (minimum volume 2 ml.) were contained in 15 mm. o.d. pyrex tubes. It was necessary to use low r.f. power levels in the case of ^{15}N because of the rather long relaxation times of this nucleus. ^{15}N chemical shifts were measured by the sample replacement method relative to a 5.7 M aqueous solution of $^{15}NH_4Cl$ (97.2% ^{15}N) which was also ~0.1 M in HCl and $\sim 10^{-4}$ M in Fe^{3+} .

Preparation of $S_4^{15}N_3Cl$. - A mixture of 3.29 g. of $^{15}NH_4Cl$, 20 ml of S_2Cl_2 , and 7 g. of sulfur was placed in a 100-ml. round-bottom flask which carried a gas inlet (extending to the bottom of the flask) and a Liebig condenser (28 cm. long and 20 mm. i.d.). The top of the condenser was attached to a calcium sulfate drying tube. A slow stream of argon was passed through the apparatus, and the mixture in the 100 ml. flask was refluxed gently using a heating mantle. Crystals of $S_3N_2Cl_2$ began to form just inside the lower end of the water-jacketed section of the condenser within 5 minutes of the commencement of refluxing. After refluxing for 11 hours, the apparatus was allowed to cool in a stream of argon. Unreacted NH_4Cl adhering to the argon inlet was washed into the reaction mixture by addition of 11 ml. of S_2Cl_2 . Refluxing was continued for a further 7 hours, after which all the NH_4Cl had been

consumed. Heating was stopped and the apparatus was allowed to stand overnight so that most of the liquid adhering to the crystals drained away. The reaction flask was removed and immediately replaced with a 250 ml. flask containing a mixture of 50 ml. CCl_4 and 30 ml. S_2Cl_2 . The mixture was refluxed over the $\text{S}_3\text{N}_2\text{Cl}_2$, which was assisted down into the reflux flask by means of an elongated spatula. The solvent mixture was boiled until all dark material was converted into a bright yellow solid (5 hrs.). Yellow needles crystallized from the solution on cooling. The product was filtered from the solvent mixture on a sintered crucible, washed several times with dry carbon tetrachloride and dried in a vacuum desiccator. Yield, 1.97 g. (47% based on $^{15}\text{NH}_4\text{Cl}$)

Anal. Calcd. for $\text{S}_4^{15}\text{N}_3\text{Cl}$: N, 21.56; S, 61.41; Cl, 16.98.

Found: N, 20.07; S, 60.69; Cl, 17.35.

When NH_4Cl was refluxed with a mixture of equal volumes of S_2Cl_2 and CCl_4 , reaction was very slow and little $\text{S}_3\text{N}_2\text{Cl}_2$ was formed. A crystalline compound containing 10% carbon was isolated from the reaction mixture but was not completely characterized. Little or no reaction occurred on heating NH_4Cl with excess S_2Cl_2 in a sealed tube at 130° for three days. In a similar experiment conducted at 170° for four days, the NH_4Cl was completely consumed and vacuum line analysis showed that it had been quantitatively converted to nitrogen and hydrogen chloride, the only solid product being sulfur. The rather low yield of $\text{S}_4\text{N}_3\text{Cl}$ obtained from the modified reflux procedure described above may therefore be attributable to the oxidation of a significant proportion of NH_4Cl to elementary nitrogen.

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