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

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

By Norman Logan 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. 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 thiotritihiazyl cation $S_4N_3^+$ (97.2% $^{15}N$) and find it to be consistent with the structure.

\[
\begin{array}{c}
S \quad \text{N'} \quad S \\
\text{N} \quad \text{S} \quad \text{N''} \\
S \quad \text{S} \\
\end{array}
\]

which has recently been determined by X-ray analysis.

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 x 10^{-3} that of $^1$H at constant field) it was necessary to use a solution more concentrated than 1 M in $S_4^{15}N_3$ 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, $S_4^3N_3Cl$ 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 $S_4^3N_3Cl$ (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 ± 1 ppm., respectively, downfield from the $^{15}NH_4^+$ 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. $S_4^3N_3^+$ 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 NO₂⁻, each nitrogen atom in S₄N₃⁺ 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 S₄N₃⁺ 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 ¹⁵N–¹⁵N coupling constant of 7 c.p.s. is the first to be reported for a system containing ¹⁵N atoms two bonds removed from each other. The only other ¹⁵N–¹⁵N 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 ¹⁴N resonances attributable to the S₄N₃⁺ ion were observed for solutions of S₄N₃Cl (not enriched in ¹⁵N) in either 80% H₂SO₄ (1 M S₄N₃⁺) or 70% HNO₃ (3 M S₄N₃⁺). It is well known, however, that the quadrupole interaction of ¹⁴N (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 S₄N₃⁺. Spin-spin coupling in ¹⁴N systems is also largely obscured by quadrupole effects.³ The above complications in ¹⁴N spectra are eliminated by the use of ¹⁵N (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$_4$Cl, 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

$$SCl_2 + S_3N_2Cl_2 \rightleftharpoons 2NSCl + S_2Cl_2$$

Our best results were obtained by using a modest excess of $S_2Cl_2$ ($S_2Cl_2/\text{NH}_4\text{Cl}$ 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 $\text{NH}_4\text{Cl}$) was obtained. It was reported earlier\(^8\) 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$_4$Cl (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 (14N) or 6.080 (15N) 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 ~$10^{-4}$ 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$_4$Cl 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$_4$Cl 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 CCl₄ and 30 ml S₂Cl₂. The mixture was refluxed over the S₃N₂Cl₂, 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 ¹⁵NH₄Cl)

Anal. Calcd. for S₄¹⁵N₃Cl: N, 21.56; S, 61.41; Cl, 16.98.
Found: N, 20.07; S, 60.69; Cl, 17.35.

When NH₄Cl was refluxed with a mixture of equal volumes of S₂Cl₂ and CCl₄, reaction was very slow and little S₃N₂Cl₂ 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 NH₄Cl with excess S₂Cl₂ in a sealed tube at 130° for three days. In a similar experiment conducted at 170° for four days, the NH₄Cl 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 S₄N₃Cl obtained from the modified reflux procedure described above may therefore be attributable to the oxidation of a significant proportion of NH₄Cl to elementary nitrogen.
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