The B^{11} n.m.r. spectrum of μ-$(CH_3)_2NB_2H_5$, for example, is found at *higher field* than that of B_2H_6.[34,35] Note that when a nitrogen bridge is formed four electrons are utilized as compared with a two-electron three-centered bridge hydrogen situation. In contrast, when an R_3N group occupies a terminal position, as in $B_{12}H_{11}N(CH_3)_3^-$,[16] the boron resonance is shifted to lower field (the boron resonance of $B(NR_2)_4^-$ is predicted[27] to be at considerably lower field than that of BH_4^-). In this case the number of bonding electrons remains constant; thus nitrogen and hydrogen as bridges differ in kind while nitrogen and hydrogen as terminal substituents differ only in degree.

The substitution of a bridge oxygen for a bridge hydrogen would also feed more bonding electrons into the neighboring boron environments, which in turn would be expected to lead to increased shielding and a shift to higher field. The shift to higher field of two boron nuclei[36] (dotted arrows in Figure 3) fits well with the observed spectrum. We conclude that Hawthorne and Miller prepared $C_2H_5OB_{10}H_{13}$, wherein the C_2H_5O group occupies a bridge position; a single pair of optical isomers is quite likely and an X-ray study would be most useful.

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[36] Substitution of a hydrogen bridge by an oxygen bridge introduces two additional electrons; greater shielding and a shift to higher field results.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
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The Nitrogen-15 Nuclear Magnetic Resonance Spectrum of the $S_4N_3^+$ Ion

BY NORMAN LOGAN[1] AND WILLIAM L. JOLLY

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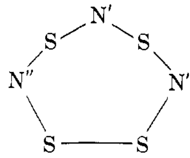
Nitrogen-15 nuclear magnetic resonance spectra have recently been observed for compounds containing the ^{15}N isotope at natural abundance (0.36%) and also for ^{15}N-enriched samples.[2-4] However, the utility of ^{15}N n.m.r. as a structural tool for the detection of nitrogen atoms in nonequivalent 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]

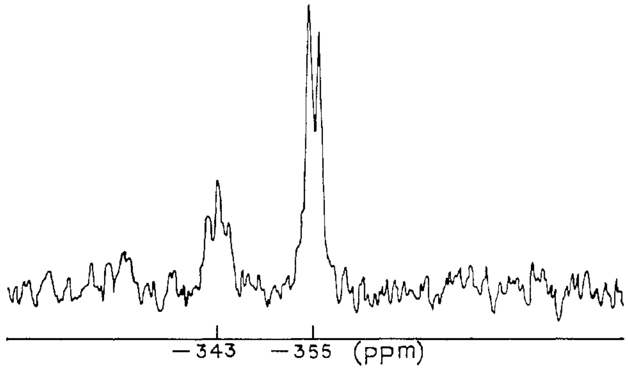


Figure 1.—The ^{15}N n.m.r. spectrum of $S_4N_3^+$ in 70% nitric acid. Chemical shifts relative to $^{15}NH_4^-$.

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 $S_4{}^{15}N_3^+$ 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_4N_3Cl dissolves in 70% HNO_3 to the extent of 3–4 *M*, forming a solution which is stable for at least 1 day at room temperature.

The ^{15}N spectrum of a 3.1 *M* solution of S_4N_3Cl (97.2% ^{15}N) in 70% HNO_3 is shown in Figure 1. The two resonances have an over-all 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 p.p.m., 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

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[1] Miller Research Fellow, University of California, Berkeley, 1964–1965.

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nitrogen chemical shifts.[2] Unshared electron pairs cause an upfield shift, whereas electronegative substituents and multiple bonding cause a downfield shift. The $S_4N_3^+$ ion 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 p.p.m. 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 lengths[5] 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 S_4N_3Cl (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]

$$3S_3N_2Cl_2 + S_2Cl_2 \longrightarrow 2S_4N_3Cl + 3SCl_2$$

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

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

Our best results were obtained by using a modest excess of S_2Cl_2 (S_2Cl_2/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% over-all yield of S_4N_3Cl (based on NH_4Cl) 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, but under the present conditions the yield of S_4N_3Cl was unaffected.

Experimental

Reagents.—Eastman Kodak Practical Grade S_2Cl_2 was used without further purification. The $^{15}NH_4Cl$ (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./sec. and 14,100 gauss. Solutions (minimum volume 2 ml.) were contained in 15-mm. o.d. Pyrex tubes. It was necessary to use low radiofrequency power levels in the case of ^{15}N because of the rather long relaxation times of this nucleus. 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 $\sim$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 min. of the commencement of refluxing. After refluxing for 11 hr., 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 hr., 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. of CCl_4 and 30 ml. of S_2Cl_2. The mixture was refluxed over the $S_3N_2Cl_2$, 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 hr.). 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 $^{15}NH_4Cl$).

Anal. Calcd. for $S_4{}^{15}N_3Cl$: 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 $S_3N_2Cl_2$ 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 3 days. In a similar experiment conducted at 170° for 4 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

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S_4N_3Cl obtained from the synthetic procedure described above may therefore be attributable to the oxidation of a significant proportion of NH_4Cl to elementary nitrogen.

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CONTRIBUTION FROM REACTOR CHEMISTRY AND CHEMISTRY
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Crystal Structures of Rubidium Lithium Fluoride, $RbLiF_2$, and Cesium Lithium Fluoride, $CsLiF_2$[1]

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The existence of $RbLiF_2$ and $CsLiF_2$ was established during thermal analysis studies of molten salt systems by Barton, *et al.*,[2] who showed these to be the only intermediate compounds in the binary systems RbF–LiF and CsF–LiF. The crystal structures of the compounds are of interest because each consists of ions of well-known radii which are expected to pack together in such a manner as to obtain the maximum number of cation–anion contacts consistent with their radius ratios. However, in the component alkali fluorides, for reasons not yet known,[3] the Rb^+ and Cs^+ ions, which are capable of larger coordination numbers, and the Li^+ ion, whose radius is near the lower limit for octahedral coordination, all have the sixfold coordination of the NaCl structure. Thus the present X-ray study was undertaken to determine the type of coordination adopted by the same ions in these difluorides.

Experimental

The compounds $RbLiF_2$ and $CsLiF_2$ melt incongruently at 475 and 495°, respectively, and precipitate as the primary phase from melts within a small range of compositions near 55 mole % RbF (or CsF) and 45 mole % LiF. By slowly cooling melts in this composition range crystals for X-ray study were obtained, along with some of the eutectic mixtures which the difluorides form with RbF or CsF. The resulting material was very hygroscopic, and the separation of crystals from the eutectic mixture was performed by submersion of the products in oil and examination under a microscope. A marked tendency of the material to twin on $\{001\}$ when subjected to a shearing force added to the difficulty of obtaining single crystals. A single crystal of $RbLiF_2$ was obtained, but for $CsLiF_2$ a specimen, about 10% of which was oriented in a twin relationship to the main crystal, was used. The samples selected were sealed in glass capillaries before removal from the oil.

X-Ray precession photographs taken with Mo radiation yielded the following monoclinic crystal data. $RbLiF_2$: $a = 5.83 \pm 0.01$, $b = 11.16 \pm 0.02$, $c = 7.86 \pm 0.02$ Å., $\beta = 94° 55' \pm 5'$; $CsLiF_2$: $a = 6.01 \pm 0.02$, $b = 11.64 \pm 0.02$, $c = 8.18 \pm 0.02$ Å., $\beta = 90° 45' \pm 5'$. The presence of *hkl* only for $h + k = 2n$ and *h0l* only for $l = 2n$ indicated the probable space group C2/c or Cc. There are eight formula weights per unit cell.

On the basis of these data a trial structure for $CsLiF_2$ was obtained by means of a computer program[4] which postulated possible atomic arrangements and evaluated them by comparing calculated and observed structure factors for 13 reflections. Structures were generated by advancing the atoms across a grid of points in the basic asymmetric unit until all acceptable combinations of positions had been obtained. The number of positions scanned was greatly reduced by rejecting those for which some interatomic distances were shorter than the sum of the corresponding ionic radii. Because precession photographs showed that the symmetry of $CsLiF_2$ was very nearly that of the orthorhombic space group Cmca, the number of trial structures to be tested was further reduced by assuming this approximate symmetry.

An estimate of the Coulomb energy was also calculated for each postulated arrangement, and this proved especially useful as a criterion for placing the Li atom, which makes only a small contribution to the structure factor. The best trial structure was nearly that described by the final parameters (space group C2/c) in Table I. Later $RbLiF_2$ was shown to be isostructural with $CsLiF_2$.

TABLE I

PARAMETERS AND STANDARD DEVIATIONS FROM LEAST-SQUARES REFINEMENT

Site	Atom	x $(\sigma)^a$	y $(\sigma)^a$	z $(\sigma)^a$	B $(\sigma)^a$
			$RbLiF_2$		
8(f)	Rb	0.2649 (5)	0.4105 (3)	0.0713 (5)	1.73 (6)
8(f)	Li	0.215 (9)	0.191 (6)	0.351 (8)	2.5
8(f)	F(1)	0.219 (3)	0.362 (2)	0.416 (3)	1.4 (3)
4(e)	F(2)	0	0.116 (2)	$^1/_4$	1.8 (5)
4(c)	F(3)	0	0.682 (2)	$^1/_4$	2.1 (5)
			$CsLiF_2$		
8(f)	Cs	0.2528 (3)	0.4089 (2)	0.0725 (2)	1.96 (5)
8(f)	Li	0.25 (1)	0.209 (4)	0.362 (7)	2.5
8(f)	F(1)	0.244 (3)	0.357 (2)	0.423 (2)	2.2 (3)
4(e)	F(2)	0	0.151 (2)	$^1/_4$	2.4 (4)
4(e)	F(3)	0	0.663 (3)	$^1/_4$	3.0 (5)

[a] The σ applies to the last significant figure for each entry.

The proposed structure was verified by measurement of a sampling of the three-dimensional X-ray reflections. For this purpose a single-crystal orienter was used with the 2θ-scan technique. Mo $K\alpha$ X-rays were detected by a scintillation counter. The inherent accuracy of the equipment was not attained, however, due to the properties of the crystal specimens, namely, irregular shape plus high absorption, presence of oil and glass, and, for $CsLiF_2$, at least, the presence of partial twinning. Some 137 reflections for $RbLiF_2$ and 149 reflections for $CsLiF_2$ were measured, corrected for Lorentz-polarization effects and a spherical absorption factor ($\mu R = 1.46$ for $RbLiF_2$; $\mu R = 1.07$ for $CsLiF_2$), and reduced to structure factors.

The parameters of the trial structure were refined by iterative least squares[5] to the final values in Table I. An isotropic temperature factor was varied for each atom except lithium, for which a constant value was assigned. Atomic form factors and the real and imaginary dispersion corrections were taken from

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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