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RECENT STUDIES OF SULFUR-NITROGEN COMPOUNDS

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Paper presented at:
Proceedings of the 1966
Princeton Sulfur Conference

UCRL-17172

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract W-7405-eng-48

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William L. Jolly

September 1966

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By William L. Jolly

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

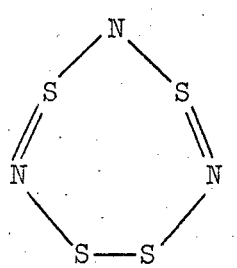
Sulfur-nitrogen chemistry is a fascinating area of study because it has not yet been systematized. With our present understanding, it is very difficult, or impossible, to predict the structures and reactions of sulfur-nitrogen compounds. In this chapter several examples of recent research aimed at determining the structures and systematizing the reactions of these compounds are discussed.

Sulfur-Nitrogen-Chlorine Compounds

Who would have predicted that a solid compound of formula S_4N_3Cl would form upon heating S_4N_4 with S_2Cl_2?

$$3S_4N_4 + 2S_2Cl_2 \rightarrow 4S_4N_3Cl$$

This is just one of many similar reactions[1,2] which defy rationalization. Perhaps even more remarkable than this synthesis is the structure of S_4N_3Cl. A large number of metathetical reactions carried out in solvents such as formic acid and sulfuric acid show that the compound is just one member of a series of salts of general formula $S_4N_3^+X^-$. Two x-ray diffraction studies of the nitrate, $S_4N_3NO_3$, have shown that the $S_4N_3^+$ cation is a nearly planar seven-membered ring with the structure shown below.[3]



Concurrent with the x-ray studies, we used ^{15}N nmr to study the structure of the $S_4N_3^+$ ion.[4] Although the nmr method yielded nowhere near as much structural information as the x-ray studies, this work will be discussed here because the method is relatively simple and is potentially applicable to a large number of nitrogen compounds.

Initially we tried ^{14}N nmr on a solution of normal S_4N_3Cl. However the quadrupole broadening of the ^{14}N nuclei was so great that only an extremely broad, useless band was observed. It was clear that it would be necessary to use ^{15}N nuclei, which have spin 1/2 and no quadrupole moment. Therefore we synthesized the ^{15}N-enriched compound, and ran the ^{15}N nmr spectrum. The spectrum consisted of two relatively sharp signals with intensities in a 1:2 ratio. (See Figure 1.)

The weaker signal was a triplet, as expected from coupling to two equivalent nitrogen atoms, and the stronger signal was a doublet, as expected from coupling to a unique nitrogen atom. The spectrum was thus entirely consistent with the structure shown above, and inconsistent with any structures having three equivalent nitrogens or three nonequivalent nitrogens.

The synthesis of the ^{15}N-enriched S_4N_3Cl presented some problem, because synthesis from S_4N_4 and S_2Cl_2 would require the preparation of ^{15}N-enriched S_4N_4, and preparation of the latter compound from S_2Cl_2 and $^{15}NH_3$ would be very wasteful of NH_3. We developed a relatively efficient process for preparing S_4N_3Cl from ^{15}N-enriched NH_4Cl and S_2Cl_2. The first step of the procedure involved the refluxing of a mixture of the reagents, using an air condenser. NSCl vapor was evolved, and this combined with the cool S_2Cl_2 in the air condenser to form crystals of $S_3N_2Cl_2$.

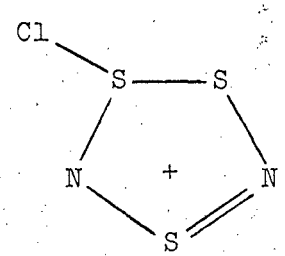
$$NH_4Cl + 2S_2Cl_2 \rightarrow NSCl + 3S + 4HCl$$

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

The reaction pot was then replaced with a flask containing carbon tetrachloride and S_2Cl_2, and by refluxing this mixed solvent, the $S_3N_2Cl_2$ crystals were converted to S_4N_3Cl.

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

By stopping the procedure after the initial refluxing of S_2Cl_2 with NH_4Cl, it was possible to isolate the crystalline $S_3N_2Cl_2$. Some of these crystals were submitted to Drs. Zalkin, Hopkins and Templeton, who determined the crystal structure by x-ray diffraction.[5] Here again the structure is quite remarkable and was completely unanticipated. The compound is a salt with an $S_3N_2Cl^+$ cation and a Cl^- anion. The cation contains a five-membered ring, as shown below.



Sulfur Nitride-Lewis Acid Adducts

Sulfur nitride, S_4N_4, forms adducts with a wide variety of Lewis acids. The following empirical formulas have been reported: $S_4N_4 \cdot SbCl_5$,[6,7] $2S_4N_4 \cdot SnCl_4$,[6,7] $S_4N_4 \cdot TiCl_4$,[6,7] $S_4N_4 \cdot 2SO_3$,[8] $S_4N_4 \cdot 4SO_3$,[8] $S_4N_4 \cdot TeBr_4$,[9] $S_4N_4 \cdot 4SbF_5$[10] and $4S_4N_4 \cdot BF_3$.[11] The unusual stoichiometry reported for the BF_3 adduct, and a lack of information regarding the other boron trihalide adducts, led us to a systematic study of the reaction of S_4N_4 with boron trihalides.[12]

We found that S_4N_4 in methylene chloride reacts with BF_3 to form burgundy-colored crystals of $S_4N_4 \cdot BF_3$ and with BCl_3 to form red-orange needles of $S_4N_4 \cdot BCl_3$. The properties of the adducts are consistent with structures involving B-N bonds.

The $S_4N_4 \cdot BF_3$ adduct is fairly labile. It decomposes reversibly to S_4N_4 and BF_3 when heated, and the BF_3 in the adduct may be displaced by BCl_3 or $SbCl_5$. On the other hand, the $S_4N_4 \cdot BCl_3$ adduct is much less labile. This adduct, when heated, sublimes with slight decomposition. When we attempted to displace BCl_3 from $S_4N_4 \cdot BCl_3$ by treatment with $SbCl_5$, a completely unexpected result was obtained. Instead of obtaining $S_4N_4 \cdot SbCl_5$, we obtained the adduct $S_4N_4 \cdot BCl_3 \cdot SbCl_5$. This product is remarkable because no di-adducts are found in the reaction of S_4N_4 with either excess BCl_3 or $SbCl_5$. Possibly the mixed adduct can be formulated as $S_4N_4BCl_2^+ \; SbCl_6^-$.

Sulfur Nitride Paramagnetic Anions

Chapman and Massey[13] observed that a series of color changes is obtained when S_4N_4 is reduced with alkali metals in dimethoxyethane, and they observed a nine-line electron spin resonance spectrum, characteristic of a paramagnetic species containing four equivalent nitrogen atoms. They concluded that the spectrum was due to the $S_4N_4^-$ anion, in which the unpaired electron is delocalized over the entire S_4N_4 ring.

More recently, we have observed that several paramagnetic species are formed when a solution of S_4N_4 in tetrahydrofuran is titrated with sodium naphthaleneide.[14] First both a five-line esr signal and a three-line esr signal are observed. The five-line signal is attributable to a species with two equivalent nitrogen atoms, and the three-line signal is due to a species with one nitrogen atom. These two signals disappear as more naphthaleneide is added, and are replaced by a weak nine-line spectrum identical to that observed by Chapman and Massey.

It was very difficult for us to understand how sulfur nitride fragment radicals could form before formation of an $S_4N_4^-$ radical. However, Meinzer and Myers[15] have recently completed an esr study which clarifies this aspect of the problem. They have found that reduction of S_4N_4 in tetrahydrofuran below 0° yields a new nine-line spectrum, with a g value and splitting constant quite different from those of the spectrum first observed by Chapman and Massey. Above 0° this new radical decomposes to give the one- and two-nitrogen radicals and, with further reduction, the four-nitrogen radical of Chapman and Massey. It is believed that the new four-nitrogen species is the $S_4N_4^-$ ion, in which the odd electron is delocalized over the entire molecule, and that the other four-nitrogen species, $S_xN_4^-$, is somehow formed by the combination of smaller fragments.

The esr parameters of all the sulfur nitride radicals which have been observed in tetrahydrofuran are presented in Table 1. The assignment of the new nine-line spectrum to $S_4N_4^-$ is supported by the following evidence: (a) The esr spectrum of the new radical is broadened by the addition of S_4N_4, as would be expected for an electron-exchange reaction. (b) The new radical is formed in high yields at low temperatures, and is a plausible precursor of the fragment radicals which form at higher temperatures. (c) The magnitudes of the A and g values are such as to put the new radical in a different class from the other radicals, indicating a different bonding type. It is suggested that the odd electron is essentially delocalized over all the atoms in $S_4N_4^-$, whereas it is relatively localized on nitrogen atoms in the other radicals.

Acknowledgment. This work was supported by the United States Atomic Energy Commission.

Table 1

Electron Spin Resonance Parameters of

Sulfur Nitride Radicals in Tetrahydrofuran

Radical	Number of lines	g	A (gauss)
$S_xN_2^-$	5	2.0101	5.13
S_xN	3	2.0053	11.2
$S_xN_4^-$	9	2.0065	3.13
e^-(free)		2.0023	
$S_4N_4^-$	9	2.0006	1.20

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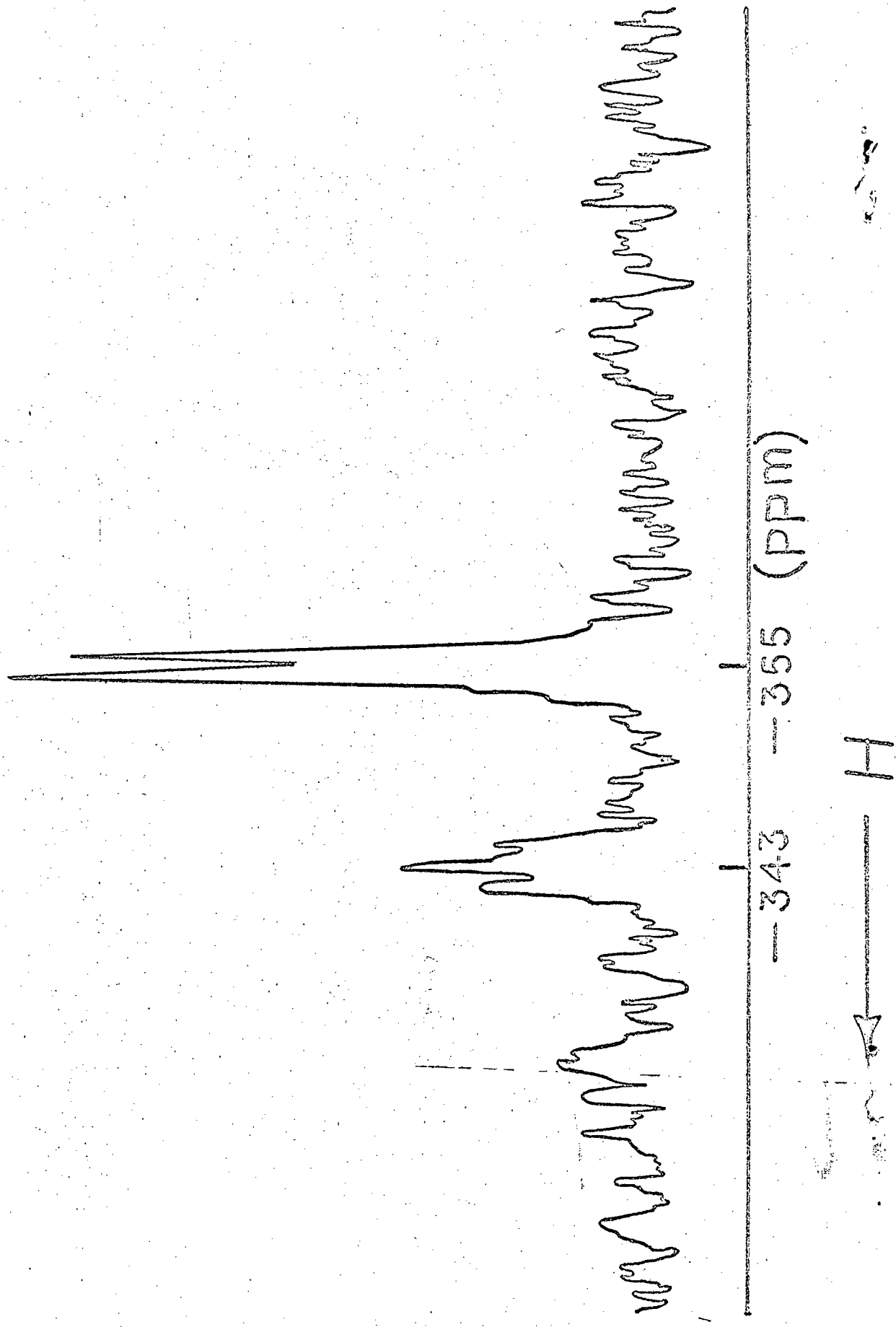
Figure Caption

Figure 1. The Nitrogen-15 N.M.R. Spectrum of $S_4{}^{15}N_3{}^+$. Reproduced from reference 4 with permission of the American Chemical Society.


-343
-355 (ppm)
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