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PREPARATION OF DISULFUR DINITRIDE, S_2N_2, AND ITS REACTIONS WITH LEWIS ACIDS

Robert Lyle Patton
(Ph. D. Thesis)

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PART I.

PREPARATION OF DISULFUR DINITRIDE, S_2N_2, AND ITS REACTIONS WITH LEWIS ACIDS

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ABSTRACT

The preparation of S_2N_2 by thermally splitting S_4N_4 has been examined, and the reaction found to be catalyzed by silver sulfide, not silver as was previously believed. The reactions of S_2N_2 with antimony pentachloride, boron trifluoride, and boron trichoride in dichloromethane solutions have been studied and the products characterized. Reaction of S_2N_2 with $SbCl_5$ (in excess) yields a diadduct $S_2N_2(SbCl_5)_2$ which reacts further with S_2N_2 to form a monoadduct $S_2N_2SbCl_5$. Treatment with $SbCl_5$ reconverts $S_2N_2SbCl_5$ to the diadduct. With S_2N_2, $S_2N_2SbCl_5$ reacts irreversibly to form both the previously characterized $S_4N_4SbCl_5$ and a less reactive material $(S_4N_4SbCl_5)_x$. With BF_3, S_2N_2 yields only $S_4N_4BF_3$, but with BCl_3 any one of the compounds $S_4N_4BCl_3$, $S_2N_2(BCl_3)_2$ or the apparently polymeric $(S_2N_2BCl_3)_x$ can be produced as the principal product. The loss of BCl_3 from $S_2N_2(BCl_3)_2$ at 0° to form the simple adduct $S_2N_2BCl_3$ is reversed by treatment with BCl_3 at -78°. Whereas $SbCl_5$ displaces BCl_3 from $S_2N_2BCl_3$ to form $S_2N_2(SbCl_5)_2$, the polymeric $(S_2N_2BCl_3)_x$ is inert toward both BCl_3 and $SbCl_5$. The properties of $S_2N_2SbCl_5$, $S_2N_2(SbCl_5)_2$, $S_2N_2BCl_3$, and $S_2N_2(BCl_3)_2$ indicate that the S_2N_2 ring remains intact. A single crystal X-ray diffraction study has yielded the structure of $S_2N_2(SbCl_5)_2$. The tetragonal space group is $I\bar{4}2d$ with Z = 8.

signals. The signal from the cationic species produced in sulfuric acid was similar to that from S_4N_4. In 1966, Warn and Chapman[6] published their determination and analysis of the infrared spectrum of S_2N_2, with the interesting conclusion that S_2N_2 exists as a planar 4-membered ring with alternating sulfur and nitrogen atoms. This was the first evidence supporting the existence of any X_2Y_2 molecule in this configuration.

As part of a continuing interest in this laboratory in sulfur-nitrogen ring compounds, further study of disulfur dinitride was begun with particular interest in its reactions with the Lewis acids antimony pentachloride, boron trifluoride, and boron trichloride. Our interest was two fold: (1) we wished to make a comparison with the known reactions of S_4N_4 with these Lewis acids[7] in which the nitrogen atoms act as donors in donor-acceptor complexes and to study the effects of this coordination on the stability and structure of the S_2N_2 ring, and (2) we hoped to isolate an adduct involving an intact S_2N_2 molecule stable enough to allow confirmation of the proposed S_2N_2 ring structure by X-ray crystallography.

The results of this study follow. Section II describes an investigation into the preparation of S_2N_2 and its behavior. Section III consists of two papers as submitted to Inorganic Chemistry: "Reactions of Disulfur Dinitride with Antimony Pentachloride" and "Reactions of Disulfur Dinitride with Boron Trifluoride and Boron Trichloride" with an appendix containing infrared spectra pertinent to these papers. Finally, Section IV contains the paper submitted to Inorganic Chemistry "The Crystal and Molecular Structure of $S_2N_2(SbCl_5)_2$," which is the result of an X-ray crystal structure study of a compound whose preparation is described in Section III.

II. THE PREPARATION AND BEHAVIOR OF DISULFUR DINITRIDE

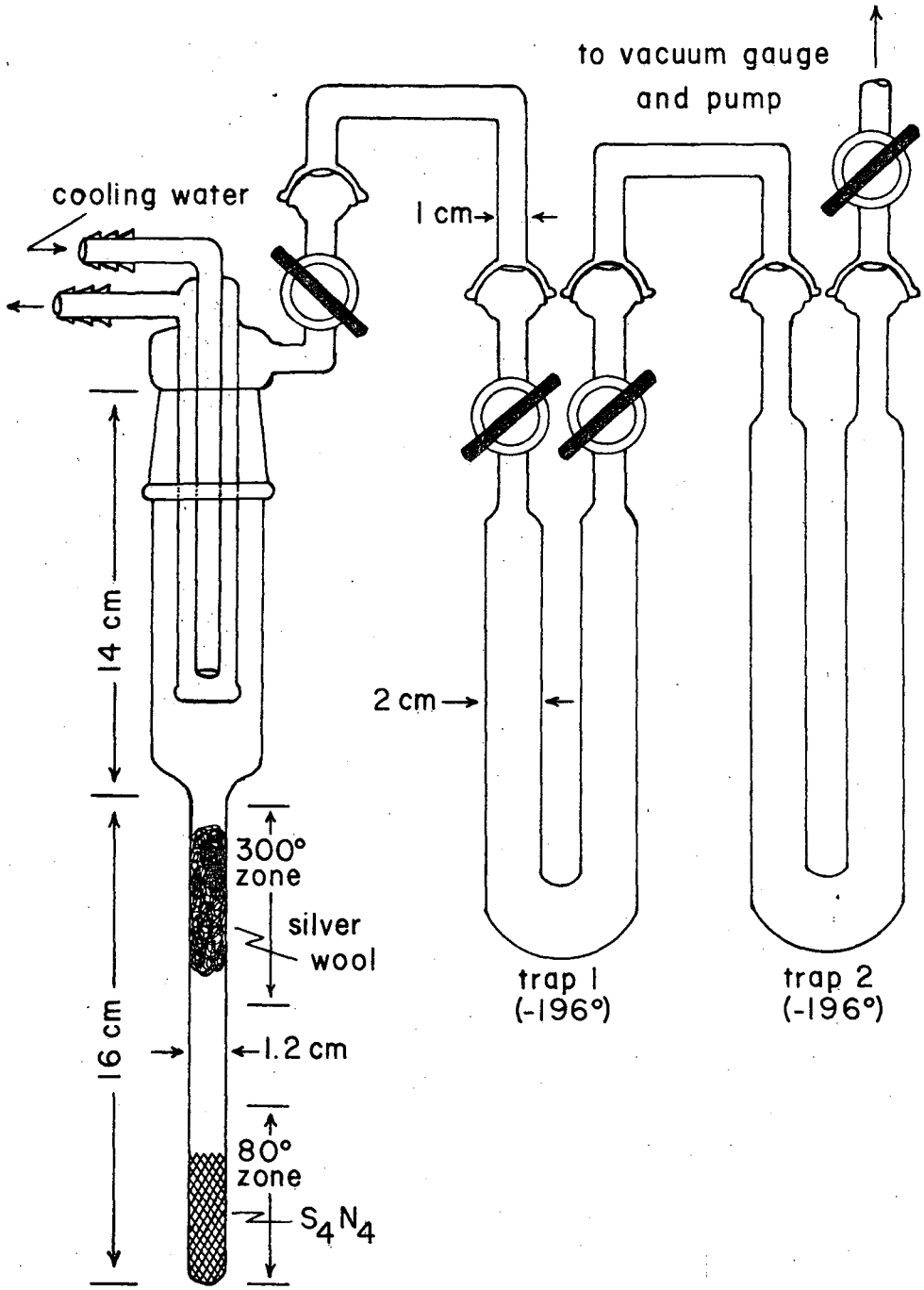
A. Introduction

The preparation of S_2N_2 was carried out using essentially the method described by Becke-Goehring in Inorganic Syntheses.[4] Although an S_2N_2 yield of 80% from S_4N_4 was claimed by this method, the same author reported 50-58% yields in earlier papers,[1,2] and Warn and Chapman,[6] using this method, stated that "yields of S_2N_2 were low at all times". In hopes of optimizing the S_2N_2 yield and gaining further insight into the nature of this thermal splitting of S_4N_4, a quantitative investigation of the preparation was made giving particular attention to the effect of varying the amount of silver wool used.

B. Experimental

1. General

The apparatus used to prepare S_2N_2 is shown in Fig. 1. After S_4N_4, prepared by the method of Villena-Blanco and Jolly,[8] and fine silver wool (Englehard Industries Inc.) were weighed and placed in the appropriate parts of the reactor and trap 1 evacuated and weighed, the parts were assembled and the system evacuated. All joints and stopcocks were lubricated with Kel-F No. 90 grease (3-M Co.) except the stopcocks of trap 1 which were sealed with Kel-F polymer wax to allow its repeated use as a tared vessel. A heating tape wrapped around aluminum foil against the glass tube was used to maintain the zone containing the silver wool at 290-305° (as measured by a copper-constantan thermocouple placed between the glass and the foil). Cold water was then passed through the cold finger and the traps were cooled with liquid nitrogen to -196°, after



XBL 693-297

Fig. 1 Apparatus for the preparation of S_2N_2 (Section II)

which the preparation was started by raising an oil bath at 80-95° around the S_4N_4. The apparatus differs from that of Becke-Goehring,[4] in that the reactor is pyrex, not quartz; the furnaces and traps are different in design; and trap 1 is held at -196° instead of -80°.

2. Preparation of S_2N_2 Using Ag Wool

0.178 g of S_4N_4 and 4.390 g of silver wool were placed in the reactor and the heating begun. The line pressure (normally 0-2μ) soon rose to ~25μ as N_2 was evolved, then slowly dropped to ~ 15μ through the course of the reaction. After 1-1/2 hour a blue-black film began forming on the cold finger and a white film appeared in trap 1. During the 20 hrs required for the S_4N_4 to sublime, the blue-black film thickened and became bronze-colored in places and spread over the cooler walls of the reactor as well as the cold finger. The white film in trap 1 increased, and a blue-black ring formed at its warmer edge. After all the S_4N_4 had sublimed, the system returned to its base pressure. The reactor was then opened, and the blue-black-bronze film was scraped out and weighed (33mg); the silver wool plug, covered with black silver sulfide, was carefully removed and weighed (wt. gain =391 mg) and trap 1 was weighed (wt. gain = 123 mg). Trap 1 was then opened on a vacuum line, and, at 20°, all of the white material slowly distilled into a closely placed -196° trap. Only the blue-black ring, which increased in size while the material was at 20°, remained (wt. = 11 mg). From the descriptions of Becke-Goehring,[2,4] the material on the cold foot and the white and blue-black contents of trap 1 were assumed and later proved to be $(SN)_x + S_4N_4$, S_2N_2, and $(SN)_x$ respectively. Considering all of the trap 1 contents to be S_2N_2, a yield based on the original S_4N_4 of 17.1% was obtained: the $(SN)_x + S_4N_4$ accounted for 4.6%; and the weight gained by the silver wool

(attributed to formation of Ag_2S by the reaction: $S_4N_4 + 8\ Ag \rightarrow 4\ Ag_2S + 2N_2$) accounted for all the remaining 78.4% of the original S_4N_4 (60% of the silver was converted to Ag_2S).

A second preparation was attempted using 0.744 g of S_4N_4 and a much smaller plug of Ag wool (1.129 g). Again the pressure rose to ~ 20 μ but $(SN)_x$ on the cold foot and S_2N_2 in trap 1 appeared after only 5-10 minutes. After several hours the pressure steadily dropped to 0-5μ and remained at this level until the S_4N_4 had all sublimed (21 hrs). The weight gain of the Ag wool (155 mg) corresponded to a 92.4% conversion of the Ag to Ag_2S, which together with the $(SN)_x + S_4N_4$ (57 mg) and the S_2N_2 (460 mg) accounted for the original S_4N_4 as Ag_2S, 30.0%; $(SN)_x + S_4N_4$, 7.7%; and S_2N_2, 61.8% (total = 99.5%).

The plug of Ag_2S + Ag from the above reaction was then used as the hot zone material through which 0.927 g of S_4N_4 was sublimed. Disulfur dinitride began appearing immediately and although the pressure rose briefly to 20μ it returned to base level after one hour. At completion, the plug had been completely converted to Ag_2S, and an 86% yield (0.797 g) of S_2N_2 had resulted. Other runs performed in the same manner followed, each using a fresh plug of silver wool. The results of these and of the above preparations are tabulated in Table I.

In some runs, the effect of varying the temperature of the hot zone was noted. Below 280° a substantial amount of unreacted S_4N_4 passed through the hot zone to the cold finger. If the temperature was raised above 305°, the line pressure rose and a red-orange tint appeared in the S_2N_2 trap. This is presumably S_4N_2 which Becke-Goehring observed as a normal by product,[2] although enough never appeared in our preparations

TABLE I. RESULTS FROM S_2N_2 PREPARATIONS USING SILVER WOOL.

Run No.	S_4N_4 (g)	Silver wool (g)	[a] $\frac{\text{moles Ag}}{8\ (\text{moles } S_4N_4)}$	wt. gained through Ag_2S formation (mg)	Silver converted to Ag_2S (%)	S_4N_4 Accounted For As: Ag_2S+N_2 (mg)	Ag_2S+N_2 (%)	$(SN)_x+S_4N_4$ (mg)	$(SN)_x+S_4N_4$ (%)	S_2N_2 (g)	S_2N_2 (%)	Unfound S_4N_4 (mg)	Unfound S_4N_4 (%)
1	0.718	4.390	1.360	391	59.9	561	78.4	33	4.6	0.123	17.1	1	0.1
2	0.744	1.129	0.324	155	92.4	221	30.0	57	7.7	0.460	61.8	6	0.1
3	0.927	(0.086)[b]	(0.020)[b]	18	100	26	2.8	85	9.2	0.797	86.1	19	2.0
4	2.012	0.707	0.075	96	91.5	139	6.9	172	8.6	1.689	84.0	12	0.6
5	1.570	0.642	0.087	85	89.3	123	7.8	116	7.4	1.325	84.4	6	0.4
6	1.341	0.624	0.099	78	84.4	112	8.4	127	9.5	1.088	81.0	14	1.0
7	1.414	0.622	0.094	90	97.5	130	9.2	110	7.8	1.161	82.2	13	0.9

a. this ratio represents the amount of silver used compared to the amount needed for complete reaction of all the S_4N_4 via the reaction $8\ Ag + S_4N_4 \rightarrow 4\ Ag_2S + N_2$.

b. In this run the plug of silver wool was used which had been converted to 92.4% Ag_2S in the previous run.

to be separated and positively identified. In fact, the small amounts we observed usually disappeared slowly when the S_2N_2 trap was warmed to 20°.

The $(SN)_x + S_4N_4$ mixtures scraped off the cold finger were examined by washing with carbon disulfide; several leachings were required before yellowing of the solvent ceased. Evaporation of the CS_2 yielded S_4N_4 crystals as identified by its infrared spectrum and melting point of 182° (lit : 187°);[8] small amounts of sulfur were also occasionally found. After this extraction only papery blue-black flakes or thicker bronze particles remained. A sample (43.1 mg) was sealed in a tube and held at 250° for 1 hr whereupon it decomposed to sulfur and 0.466 mmole of nitrogen (Calcd. for $(SN)_x$: 0.468 mmole).

3. Examination of S_2N_2

The S_2N_2 was stored in trap 1 at -196° and withdrawn as needed by room temperature vacuum sublimation into another vessel at -196°. The amount of black $(SN)_x$ in the trap increased with each warming to 20° and, as sublimation was slow, also increased steadily during this process. Final weighing of trap 1 after removal of all the volatile S_2N_2 usually showed that 5-15% of the original S_2N_2 had polymerized. In one case 11 mg of $(SN)_x$ left in the trap was treated with 0.5 atm. of chlorine for 8 hrs. at 0° which resulted in complete disappearance of the black solid and formation of a gas, identified by its infrared spectrum as NSCl,[9] by the reaction $2/x\ (SN)_x + Cl_2 \rightarrow 2\ NSCl$. The indentity and purity of S_2N_2 prepared and transferred in this manner were determined by its infrared spectrum[6] (as a Nujol mull and in carbon disulfide), its molecular weight by vapor pressure lowering of dichloromethane (observed, 93; calcd. 92.1), and by an analysis performed by heating a sample (59.5

mg, 0.646 mmole) 1 hr in a sealed tube at 250° during which it decomposed to sulfur and 0.646 mmole of nitrogen. When heated slowly (1-2°/min) after distilling into and sealing off in a melting point capillary, the coversion rate of white S_2N_2 to black $(SN)_x$ visibly increased with temperature until only $(SN)_x$ was seen at 80°; no detonation occured, but at 160° the $(SN)_x$ rapidly decomposed to gaseous sulfur and nitrogen. Also, 0.077 mmole of S_2N_2 reacted for one day at 25° with 0.786 mmole of Cl_2 produced NSCl and $(NSCl)_3$ as identified by their infrared spectra[9] and used 0.078 mmole of Cl_2 in agreement with the equation $S_2N_2 + Cl_2 \rightarrow 2NSCl$.

To examine the thermal stability of S_2N_2 vapor a tube of S_2N_2 was connected to a U-tube, heated with an oil bath, containing a glass wool plug and evacuated through a -196° trap. Repeated passes of several milligrams of S_2N_2 through the glass wool at temperatures from 120-300° were made. At each temperature only white S_2N_2 collected in the -196° trap; no nitrogen evolution or formation of $(SN)_x$ occurred. The experiment was then repeated with the glass wool replaced by silver wool. Above 150° nitrogen evolution was detected by a vacuum gauge and became quite substantial above 200°. Silver sulfide was formed and a blue ring of $(SN)_x$ as well as white S_2N_2 collected in the -196° trap.

4. Preparation With Other Hot Zone Materials

The usual preparation of S_2N_2 was altered by replacing the silver wool or silver sulfide plug with pyrex wool. No nitrogen evolution occured and no S_2N_2 resulted. Approximately 5-10% of the original S_4N_4 was collected on the cold finger as $(SN)_x$ along with the remaining unreacted S_4N_4 as a partly crystalline bronze layer. In a separate experiment the water cooled cold finger was replaced with a liquid nitrogen cooled cold finger at -196°.

As S_4N_4 sublimed over the 300° glass wool a dark red-orange layer formed on the closely placed cold finger. When slowly warmed in vacuo to room temperature, a rapid color change to yellow (S_4N_4) and blue-black ($(SN)_x$) occurred while a minute amount of the red-orange material sublimed to a closely placed -196° cold spot (this also formed S_4N_4 and $(SN)_x$ when warmed). No nitrogen was evolved unless the glass wool was above 335°. A normal S_2N_2 preparation was then attempted with a plug of 100% Ag_2S from a previous run placed on top of the glass wool plug and both heated to 300°. The run proceeded as if only Ag_2S had been used with 12% of the original S_4N_4 found as $(SN)_x$ + S_4N_4 and 87% as S_2N_2.

The silver wool was also replaced with fine copper turnings (10.77 mmoles) at 300° and S_4N_4 (5.01 mmoles) sublimed through it. The pressure quickly rose to ~ 40 μ and remained with no $(SN)_x$, S_4N_4 or S_2N_2 appearing until ~ 40% of the S_4N_4 had sublimed. The pressure then dropped slightly and leveled off with attendant appearance of some $(SN)_x$ and sulfur at the cold finger and slight formation of S_2N_2. At completion, the black crumbly copper turnings were weighed (observed, 1.007 g; calcd. for 10.77 mmoles of CuS, 1.029 g) which corresponded to removal of 50% of the S_4N_4 via the reaction $S_4N_4 + 4Cu \rightarrow 4CuS + 2N_2$. The remaining S_4N_4 was decomposed to a slight amount of $(SN)_x$ mixed with a large quantity of sulfur coated on the cold finger, walls, and outlet tube of the reactor and to 76 mg of impure S_2N_2 (reddened presumably with S_4N_2) in trap 1 corresponding to a yield of ~8%.

C. Results and Discussion

It is seen from the descriptions and the results of the S_2N_2 preparations (Table I) that the use of a large amount of silver wool resulted in nearly complete decomposition of the S_4N_4 of the sort

$$S_4N_4 + 8\ Ag \rightarrow 4\ Ag_2S + 2\ N_2 \qquad (1)$$

and only a small amount of S_2N_2; whereas the use of small amounts of silver wool resulted in nearly complete initial conversion of the silver to silver sulfide via reaction 1 followed by conversion of the remaining S_4N_4 to S_2N_2 and small amounts of $(SN)_x$. Thus, it is silver sulfide, not silver, which catalyzes the thermal splitting

$$S_4N_4 \xrightarrow[300°]{Ag_2S} 2\ S_2N_2 \qquad (2)$$

That any S_2N_2 results at all while silver is still left is due to the layer of Ag_2S which slowly builds up and protects more and more of the S_4N_4 from the buried silver. This also explains why total conversion of Ag to Ag_2S was usually not attained. We cannot, in fact, deny that silver might also catalyze the splitting of S_4N_4 to S_2N_2 but this is academic as we have seen that S_2N_2 itself reacts with hot silver via

$$S_2N_2 + 4Ag \rightarrow 2\ Ag_2S + N_2 \qquad (3)$$

The Ag_2S surface is needed to catalyze the splitting to S_2N_2, however as no S_2N_2 was produced when glass wool was used at the same temperature; thus the splitting is not simply a thermal reaction. The side reaction

$$S_4N_4 \rightarrow 4/x\ (SN)_x$$

may however be simply a thermal reaction as 5-10% conversion to $(SN)_x$ was noted with both glass wool and Ag - Ag_2S surfaces. Further, the lack of decomposition to sulfur and nitrogen of either S_4N_4 or S_2N_2 over 300° glass wool shows that the decomposition is the result of the direct reactions 1 or 3 and not the thermal decomposition

$$S_4N_4 \xrightarrow[\Delta]{} 4S + 2N_2$$

$$(\text{or } S_2N_2 \xrightarrow[\Delta]{} 2\,S + N_2)$$

followed by the reaction

$$S + 2\,Ag \rightarrow Ag_2S\ .$$

The red-orange unstable volatile material trapped on a -196° cold finger after passing S_2N_2 through glass wool at 300° may have been a form of SN radical or short chain. This interesting species together with the mechanism of the thermal splitting of S_4N_4 and the effectiveness of Ag_2S as a catalyst in comparison with other materials could certainly be the worthwhile subject of a future thorough study.

It was reported[2,4] that only small yields of S_2N_2 were obtained using copper in the hot zone. Considering the possibility that copper sulfide might be a catalyst but that previous researchers had used too much copper and converted all the S_4N_4 to copper sulfide and nitrogen, we attempted a preparation using an S_4N_4/Cu ratio such that all the copper would be converted to CuS by the first 50% of the S_4N_4. Indeed, only nitrogen emerged from the hot zone during the first half of the sublimation after which S_2N_2 began appearing and the final weight of the plug indicated complete reaction of the sort $4\,Cu + S_4N_4 \rightarrow 4\,CuS + 2\,N_2$. However, the principle reaction after this conversion was the decomposition of S_4N_4 to sulfur and nitrogen. The red color in the S_2N_2 trap in this and in Ag_2S reactions above 305° was presumably S_4N_2 possibly formed in the vapor phase reaction

$$S_2N_2 + 2S \rightarrow S_4N_2$$

$$\text{or } 2S_2N_2 \rightarrow S_4N_2 + N_2.$$

Our observation that this red color disappeared slowly at 20° is consistent with a report that S_4N_2 decomposes to sulfur and S_4N_4 under the influence of light.[10]

In preparing S_2N_2 we normally used small plugs of silver wool just large enough to provide a good Ag_2S surface after most of the silver had been used in reaction 1. Allowing for this initial reaction and the usual formation of a 5-10% yield of $(SN)_x$ + S_4N_4, all further S_4N_4 was converted to S_2N_2. Reuse of old Ag_2S plugs was troublesome as this material was very brittle and easily crumbled when handled, making it difficult to efficiently suspend in the subliming S_4N_4 vapor. For this reason, we also recommend a small wad of glass wool be placed between the silver and the S_4N_4 (glass wool having been shown to have no effect on the yield); S_4N_4 is known to explode violently at temperatures above 150° and the prospect of a vibration jarring a brittle piece of 300° Ag_2S into the S_4N_4 is frightening.

The thermal stability of S_2N_2 was pleasantly suprising in view of previous reports that detonation occurred on warming above 30°. Not only were the vapors unaffected by glass wool at 300°, but in the several times we warmed the solid above 30° only a faster polymerization, not detonation, was observed. The previous work, however, had been done using crystals of S_2N_2 after recrystallization from ether; the added constraints of the crystalline state or the possible presence of ether residues may have added to its instability.

The quantitative decomposition of S_2N_2 to the elements and the quantitative reaction of S_2N_2 with chlorine to produce NSCl are noteworthy as further correlations with known but slower reactions of S_4N_4.[2,9]

Being convinced that slow but reasonably safe quantitative transfer of pure S_2N_2 to a desired reaction vessel was possible by room temperature

vacuum sublimation from a tared storage vessel, we proceeded to the investigation of its reactions with Lewis acids described in the next section.

REFERENCES TO SECTIONS I AND II

(1). M. Goehring and D. Voigt, Naturwiss., 40, 482 (1953).

(2). M. Goehring and D. Voigt, Z. Anorg. Allgem. Chem., 285, 181 (1956).

(3). M. Becke-Goehring and R. Schwarz, Z. Anorg. Allgem. Chem., 296, 3 (1958).

(4). M. Becke-Goehring, Inorg. Syntheses, 6, 123 (1960).

(5). D. Chapman and A. G. Massey, Trans. Faraday Soc, 58, 1291 (1962).

(6). J. R. W. Warn and D. Chapman, Spectrochim Acta., 22, 1371 (1966).

(7). K. J. Wynne and W. L. Jolly, Inorg. Chem., 6, 107 (1967).

(8). M. Villena-Blanco and W. L. Jolly, UCRL Report No. 11294, Jan. 1964.

(9). O. Glemser and H. Richert, Z. Anorg. Allgem. Chem., 307, 313 (1961).

(10). D. Chapman and A. G. Massey, Chem. and Ind., 1962 (2088).

III. REACTIONS OF DISULFUR DINITRIDE WITH LEWIS ACIDS

A. Paper: "Reactions of Disulfur Dinitride With Anitmony Pentachloride"

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

Reactions of Disulfur Dinitride with Antimony Pentachloride

By R. Lyle Patton and William L. Jolly

ABSTRACT

Solutions of S_2N_2 in dichloromethane react with antimony pentachloride (in excess) to form a diadduct $S_2N_2(SbCl_5)_2$ which can further react with S_2N_2 to form a monoadduct $S_2N_2SbCl_5$. The monoadduct can be reconverted to the diadduct by treatment with $SbCl_5$. The physical and chemical properties of these compounds indicate that the S_2N_2 ring structure is maintained intact. The monoadduct $S_2N_2SbCl_5$ reacts irreversibly with S_2N_2 to form both the previously characterized $S_4N_4SbCl_5$ and, in lower yields, a less reactive material $(S_4N_4SbCl_5)_x$. Antimony pentachloride acts as a catalyst for the dimerization of S_2N_2.

Tetrasulfur tetranitride reacts with many Lewis acids such as antimony pentachloride,[1] boron trichloride[2] and boron trifluoride[2] to form 1:1 adducts in which the Lewis acid is coordinated to a nitrogen atom of S_4N_4. Although a change in the configuration of the S_4N_4 results, the basic 8-membered ring structure remains intact.[3,4] Of the dozen or so known adducts, only two have two molecules of Lewis acid associated with each molecule of S_4N_4. These are $S_4N_4(SO_3)_2$[5] and $BCl_3 \cdot S_4N_4 \cdot SbCl_5$[2] (which may have the ionic structure $[BCl_2S_4N_4]^+ [SbCl_6]^-$). Apparently when one of the nitrogen atoms of S_4N_4 is coordinated, the donor ability of the remaining nitrogens is markedly decreased. In this investigation, we have studied the reactions of disulfur dinitride, a planar four-membered ring with alternating S-N atoms,[6] with antimony pentachloride. Of particular interest to us was the ability of the S_2N_2 nitrogens to act as donor atoms and the effect of this donation on the stability and structure of the S_2N_2 ring.

Experimental Section

General.- The moisture-sensitivity of the materials required their manipulation in a vacuum line or in a polyethylene glove bag flushed with nitrogen or argon. Infrared spectra were recorded in the 400-4000 cm^{-1} range with Perkin Elmer Infracord spectrometers (Models 137 and 137B). Solid samples were prepared as Nujol mulls pressed between KBr plates; solution spectra were run in a 0.1-mm KBr cavity cell.

Melting points were obtained in argon-filled, sealed capillaries. Analyses for N, S, and Cl were performed in the microanalytical laboratory of this department by V. Tashinian.

Antimony pentachloride (J. T. Baker Co.) was purified by vacuum-line fractional condensation and was found to melt at 3° (literature,[7] 2.8°). Dichloromethane was refluxed over P_2O_5 for 6-10 hrs., distilled, and stored in a nitrogen atmosphere. Disulfur dinitride was prepared by subliming S_4N_4 through a plug of silver wool at 300° using a technique like that described by Becke-Goehring.[8] It was found that the best results were obtained using a 0.5-g. plug of silver wool in a 10-mm. i.d. glass tube. Initially almost all the silver reacted with S_4N_4 to form silver sulfide and nitrogen; the silver sulfide then acted as a catalyst for the conversion of S_4N_4 to S_2N_2 and small amounts of $(SN)_x$. The S_2N_2 was identified by its infrared spectrum[6] and its molecular weight in dichloromethane (observed, 93; calcd. 92.1). The material was observed to slowly polymerize to $(SN)_x$ and small amounts of S_4N_4 at room temperature.[9] A sample of S_2N_2 (0.059 g, 0.646 mmole) was held in a sealed tube at 250° for 1 hr, whereupon it decomposed to sulfur and 0.646 mmole of nitrogen.

The $SbCl_5$ and S_2N_2 were stored in tared bulbs equipped with stopcocks lubricated with Kel-F wax. Disulfur dinitride was measured out from its tared storage bulb by room-temperature vacuum sublimation into a reaction vessel held at -196°. This method of transfer also served as a purification method for S_2N_2, because the common contaminants, $(SN)_x$ and S_4N_4, are nonvolatile at room temperature. Enough CH_2Cl_2 was distilled into the reaction vessel to dissolve the S_2N_2 when warmed to 20°; then the solution was transferred to a glove bag. The formation of flocculent blue-black particles of $(SN)_x$ (always less than 1 mg) on dissolution necessitated filtration of these S_2N_2 solutions immediately before use. Because S_2N_2 polymerizes appreciably in the solid state at 20° and is reportedly

shock-sensitive, direct handling of the solid in the glove bag was avoided. Solutions of known amounts of $SbCl_5$ were prepared in a similar manner. Products were normally characterized by their infrared spectra and physical properties.

Formation of $S_4N_4SbCl_5$.- Antimony pentachloride (4.7 mmoles) in 10 ml of CH_2Cl_2 was slowly dripped into a solution of S_2N_2 (3.16 mmoles) in 40 ml of CH_2Cl_2. The reaction mixture immediately became red-black and opaque, and remained so throughout the $SbCl_5$ addition. After 1/2 hour at 20°, the suspension slowly cleared and lightened to a deep red solution over a dark red-brown solid. Filtration of this mixture yielded almost pure crystals of $S_4N_4SbCl_5$ as identified by its infrared spectrum[2] and melting point (observed, 160°; literature,[2] 160-2°). Evaporation of the solution to dryness also resulted in $S_4N_4SbCl_5$. The total yield was 93%.

Formation of $S_2N_2(SbCl_5)_2$.- The dropwise addition at 20° of a solution of S_2N_2 (1.72 mmoles) in 25 ml of CH_2Cl_2 to $SbCl_5$ (7.8 mmoles) in 10 ml of CH_2Cl_2 resulted in the immediate formation of fine yellow-white crystals which increased in quantity with continued S_2N_2 addition. Filtration of the mixture yielded 272 mg of extremely moisture-sensitive yellow-white crystals which quickly turned yellow, then black in moist air. Anal. Calcd. for $S_2N_2(SbCl_5)_2$: N, 4.06; S, 9.29; Cl, 51.37. Found: N, 3.96; S, 9.17; Cl, 51.36.

Cooling the filtrate to -15° yielded a further 522 mg of $S_2N_2(SbCl_5)_2$; the total yield was 67%. Evaporation of the final filtrate to dryness *in vacuo* produced only this diadduct; no $S_4N_4SbCl_5$, as observed when the reactants were mixed in the reverse order, was found. The diadduct is also formed (in 95-100% yields) when a frozen mixture of $SbCl_5$, S_2N_2 and

CH_2Cl_2 is slowly warmed to and held at 20°, followed by vacuum removal of the solvent and excess $SbCl_5$. The glove bag preparation, however, is more convenient.

The solubility of $S_2N_2(SbCl_5)_2$ in dichloromethane is ca. 1.5 g/100 ml at 20°, and it may be readily recrystallized by cooling a saturated solution. No decomposition on long standing in solution was detected, provided moisture was carefully excluded. The crystals slowly become opaque and red-black above 120°, before melting at 130-131° with decomposition. The infrared spectrum of $S_2N_2(SbCl_5)_2$ shows absorptions (in cm^{-1}) at 461 (s), 818 (s), and 898 (vw).

Formation of $S_2N_2SbCl_5$.- Disulfur dinitride (1.95 mmoles) in 30 ml of CH_2Cl_2 was slowly dripped into a solution of $SbCl_5$ (2.0 mmoles) in 10 ml of CH_2Cl_2. After addition of 4 ml of S_2N_2 solution, fine yellow-white crystals appeared which increased in quantity until half of the S_2N_2 solution had been added. As the remaining S_2N_2 was added, the crystals slowly dissolved, and the solution changed from light yellow to light orange in color. Complete addition of the S_2N_2 resulted in complete disappearance of the crystals. Concentration of this solution to 10 ml by distilling off CH_2Cl_2 *in vacuo* followed by cooling to -15° yielded long (up to 1 cm), clear, light orange needles of $S_2N_2SbCl_5$, of which 100 mg was filtered off. Further concentration and filtration, followed by final evaporation to dryness, yielded a total of 700 mg of this product which contained slight $S_2N_2(SbCl_5)_2$ contamination. Anal. Calcd. for $S_2N_2SbCl_5$: N, 7.16; S, 16.39; Cl, 45.32; mol wt, 391.2. Found: N, 7.26; S, 16.08; Cl, 45.38, mol wt (by vapor pressure lowering in CH_2Cl_2), 402.

The monoadduct $S_2N_2SbCl_5$ is very soluble in CH_2Cl_2 at 20°: ca. 10g/100 ml. These solutions may be heated briefly to 40° with no apparent decomposition. Darkening of solutions is observed, however, even at 20° on long standing. In a sealed capillary, $S_2N_2SbCl_5$ crystals turn black at 100°, then melt with decomposition at 108-109°. The crystals immediately blacken in moist air. The infrared spectrum shows the following peaks; 1005 (m), 922 (vw), 800 (s), 723 (mw), 627 (w), and 459 (s) cm^{-1}.

A sample of $S_2N_2SbCl_5$ (0.83 mmole) was placed in a vacuum sublimator with a water-cooled cold finger and heated while evacuating through a -196° trap with a Toepler pump. Above 55° a white material collected on the cold finger. After 4 hours at 70°, the products were examined. An orange-brown residue of $S_4N_4SbCl_5$ (0.12 mmole) remained in the sublimator. Nitrogen (0.008 mmole) was found in the Toepler pump buret, $SbCl_5$ (0.02 mmole) was found in the -196° trap, and a yellow-white solid was found on the cold finger. The infrared absorptions of this material corresponded to ca. 90% $S_2N_2SbCl_5$ and 10% $S_2N_2(SbCl_5)_2$. A slower sublimation at 60° produced proportionately much less $S_4N_4SbCl_5$ and $S_2N_2(SbCl_5)_2$.

Pyrolysis of $S_2N_2(SbCl_5)_2$.- When $S_2N_2(SbCl_5)_2$ (0.25 mmole) was heated at 90° for 1 hour in a vacuum sublimator with a 20° cold finger, $SbCl_5$ (0.22 mmole) was evolved, and yellow-white $S_2N_2SbCl_5$ (with slight $S_2N_2(SbCl_5)_2$ contamination) collected on the cold finger. A slight residue of $S_4N_4SbCl_5$ (0.01 mmole) remained in the sublimator.

Addition of S_2N_2 to $S_2N_2SbCl_5$ and $S_2N_2(SbCl_5)_2$.- Addition of S_2N_2 to $S_2N_2SbCl_5$ solutions in equimolar amounts yielded an opaque greenish-black suspension; precipitation began with the first drops of S_2N_2 added. On standing at 20° for 1-2 hours, the suspension gradually cleared and lightened

to an orange-red solution above a dark red-orange solid. Examination of this solid and that left after evaporation of the solvent showed it to be $S_4N_4SbCl_5$ slightly contaminated with a greenish-yellow substance. The $S_4N_4SbCl_5$ was identified by its infrared spectrum and melting point of 160° (literature,[2] 160-2°) after recrystallization from CH_2Cl_2. No S_2N_2 or S_4N_4 was recovered.

Addition of S_2N_2 to $S_2N_2(SbCl_5)_2$ solutions resulted in an initial color change corresponding to formation of $S_2N_2SbCl_5$ which, with further S_2N_2, again became dark and opaque followed by slow clearing to a red-orange solution and precipitation of $S_4N_4SbCl_5$. Addition of S_2N_2 in excess of the amount required to convert all the $S_2N_2SbCl_5$ to $S_4N_4SbCl_5$ resulted in a mixture of S_4N_4 and $S_4N_4 \cdot SbCl_5$ in the relative amounts expected from conversion of the excess S_2N_2 to S_4N_4. Tetrasulfur tetranitride was recrystallized from dichloromethane and identified by its infrared spectrum[10] and melting point of 182° (literature,[11] 187-187.5°). To test the catalytic effect of $S_4N_4SbCl_5$ on the dimerization of S_2N_2, 1.02 mmoles of disulfur dinitride was slowly added to a solution of 0.15 mmole of $S_4N_4SbCl_5$. The solution remained orange-red. Infrared analysis indicated that after 2 hrs approximately equal amounts of S_4N_4 and S_2N_2 were in the solution, and that after 15 hours only 10% of the original S_2N_2 remained.

A small amount (5-10%) of the greenish-yellow substance was always formed as a by-product of these reactions in which $S_4N_4SbCl_5$ was formed. The characterization of this material is described below.

<u>$(S_4N_4SbCl_5)_x$</u>.- The small amount of greenish-yellow material formed in the above reactions was found to be insoluble in CH_2Cl_2 and could be isolated free of contamination by $S_4N_4SbCl_5$ and S_4N_4 by using enough solvent

to keep all the expected $S_4N_4SbCl_5$ and S_4N_4 in solution. When the opaque suspension cleared, as much as 50 mg of this microcrystalline substance remained and was filtered off. Although the color of different samples varied from yellow to a dull green, each sample melted at 193-194° (the green samples becoming yellow at 100-110°) and exhibited the same infrared absorptions at 1160 (m), 1115 (m), 975 (vw), 725 (w), and 535 (m) cm^{-1}.

In an attempt to prepare a large quantity of this material, S_2N_2 (3.64 mmoles) in 45 ml of CH_2Cl_2 was added with a dropping funnel during 1 hr. to a rapidly stirred solution of $SbCl_5$ (1.58 mmoles) in 5 ml of CH_2Cl_2. When half of the S_2N_2 had been added, the solution became dark and opaque; it cleared to a deep red solution above an orange-yellow solid only after the addition was complete. Several overnight leachings of the solid with CH_2Cl_2 removed all the $S_4N_4SbCl_5$ and left 200 mg of yellow solid having only the above infrared absorptions and a 193-193.5° m.p. Anal. Calcd. for $(S_4N_4SbCl_5)_x$: N, 11.6; S, 26.5; Cl, 36.7; Sb, 25.2. Found: N, 11.8; S, 26.1; Cl, 37.0; Sb (by difference), 25.1.

Approximately the same amounts of S_2N_2 and $SbCl_5$ as above, each in 40 ml of CH_2Cl_2, were mixed during 1 hr in the same manner as above but with the $SbCl_5$ slowly dripped into the S_2N_2 solution. In this reaction only a 1% yield of $(S_4N_4SbCl_5)_x$ was obtained, in contrast to the 26% yield resulting from the addition performed in the opposite order.

Like $S_4N_4SbCl_5$, $(S_4N_4SbCl_5)_x$ is stable to short exposure to moist air; however, its infrared spectrum, melting point, and insolubility in CH_2Cl_2 do not correspond to $S_4N_4SbCl_5$ or to any other known compound. When heated *in vacuo*, no sublimation of $(S_4N_4SbCl_5)_x$ occurred; slow decomposition began at 162°, and after several hours at 170° N_2, S_4N_4, $SbCl_3$, NSCl, and $S_3N_2Cl_2$

were found among the decomposition products. The infrared spectrum of the remaining residue showed only $(S_4N_4SbCl_5)_x$, with no evidence of thermal rearrangement to $S_4N_4SbCl_5$. $(S_4N_4SbCl_5)_x$ was also unaffected by treatment with liquid $SbCl_5$ at 20°.

Several attempts were made to filter the opaque suspensions which formed immediately after mixing solutions of S_2N_2 and $S_2N_2SbCl_5$. In each case, regardless of order or speed of mixing, a dull green-black powder was isolated whose infrared spectrum showed only weak bands due to $(S_4N_4SbCl_5)_x$. When heated <u>in vacuo</u> above 100°, this material became orange-yellow and evolved nitrogen and sulfur. In moist air, the green color slowly changed to yellow. Neither treatment significantly changed the infrared spectrum. All these properties indicate that the isolated solid was a mixture of $(S_4N_4SbCl_5)_x$ and $(SN)_x$.

Results and Discussion

<u>Reactions of S_2N_2 with $SbCl_5$</u>.- The addition of disulfur dinitride to excess antimony pentachloride in dichloromethane results in rapid, complete formation of the diadduct $S_2N_2(SbCl_5)_2$. When S_2N_2 is added to an equimolar amount of $SbCl_5$, $S_2N_2(SbCl_5)_2$ precipitates during the first half of the addition. This $S_2N_2(SbCl_5)_2$ then reacts with the S_2N_2 as it is added during the second half of the addition to form the monoadduct $S_2N_2SbCl_5$. The reactions may be written:

$$S_2N_2 + 2SbCl_5 \rightarrow S_2N_2(SbCl_5)_2 \qquad (1)$$

$$S_2N_2 + S_2N_2(SbCl_5)_2 \rightarrow 2S_2N_2SbCl_5 \qquad (2)$$

Addition of S_2N_2 to an equimolar amount of $S_2N_2SbCl_5$ in dichloromethane yields the previously-characterized adduct $S_4N_4SbCl_5$.

$$S_2N_2 + S_2N_2SbCl_5 \rightarrow S_4N_4SbCl_5 \qquad (3)$$

A relatively insoluble greenish-yellow material, having the empirical formula $(S_4N_4SbCl_5)_x$ but possessing physical properties entirely different from those of ordinary $S_4N_4SbCl_5$, forms as a significant by-product of reaction 3. This incompletely characterized material is definitely worthy of further study. During the course of reaction 3, the formation of a dark-colored intermediate is apparent. Inasmuch as attempts to isolate this intermediate yielded only the $(S_4N_4SbCl_5)_x$ by-product contaminated with what appeared to be $(SN)_x$, we tentatively suggest that the intermediate is an open-chain isomer of S_4N_4 or S_2N_2, perhaps coordinated to $SbCl_5$. This intermediate may be a precursor of $(S_4N_4SbCl_5)_x$.

When S_2N_2 is added to $S_2N_2SbCl_5$ in greater than a 1:1 ratio, the excess S_2N_2 is quickly converted to S_4N_4. Obviously some species in the reaction system catalyzes the dimerization of S_2N_2. The adduct $S_4N_4SbCl_5$ does catalyze the dimerization, but relatively inefficiently. Possibly the dark intermediate discussed above is involved in the rapid dimerization.

The adduct $S_4N_4SbCl_5$ is inert toward $SbCl_5$;[2] consequently this adduct is formed whenever $SbCl_5$ is added to a solution of S_2N_2, regardless of the final S_2N_2: $SbCl_5$ ratio. The fact that $S_2N_2SbCl_5$ in dichloromethane solution does not decompose to $S_4N_4SbCl_5$ proves that the following equilibria lie far to the left.

$$S_2N_2SbCl_5 \rightleftharpoons S_2N_2 + SbCl_5 \qquad (4)$$

$$2S_2N_2SbCl_5 \rightleftharpoons S_2N_2 + S_2N_2(SbCl_5)_2 \qquad (5)$$

Otherwise $S_4N_4SbCl_5$ would form irreversibly by reaction 3. Thus we conclude that S_2N_2 is a strong base toward $SbCl_5$, and that $S_2N_2SbCl_5$ is considerably weaker base. The principle reactions observed in dichloromethane solutions are summarized in the following diagram.

$$S_2N_2 + SbCl_5 \longrightarrow S_2N_2SbCl_5 \underset{S_2N_2}{\overset{SbCl_5}{\rightleftharpoons}} S_2N_2(SbCl_5)_2$$

$$\Big\downarrow (1 + x)S_2N_2$$

$$S_4N_4 + SbCl_5 \longrightarrow S_4N_4SbCl_5 + x/2\ S_4N_4$$

The inertness of $S_4N_4SbCl_5$ toward $SbCl_5$, the interconvertibility of $S_2N_2SbCl_5$ and $S_2N_2(SbCl_5)_2$, and the observed molecular weight of $S_2N_2\ SbCl_5$ support the formulation of the latter compounds as adducts of S_2N_2, not S_4N_4.

Thermal Stability of S_2N_2 Adducts.- The adduct $S_2N_2SbCl_5$ sublimes *in vacuo* at 60-70° with slight decomposition corresponding to reaction 6.

$$2S_2N_2SbCl_5(s) \xrightarrow{60\text{-}70^\circ} S_4N_4SbCl_5(s) + SbCl_5(g) \qquad (6)$$

The sublimed $S_2N_2SbCl_5$ is contaminated with $S_2N_2(SbCl_5)_2$ which forms by reaction 7 on the cold finger.

$$SbCl_5(g) + S_2N_2SbCl_5(s) \xrightarrow{20^\circ} S_2N_2(SbCl_5)_2(s) \qquad (7)$$

The adduct $S_2N_2(SbCl_5)_2$ dissociates *in vacuo* at 90° via the reaction

$$S_2N_2(SbCl_5)_2(s) \longrightarrow S_2N_2SbCl_5(g) + SbCl_5(g)\ . \qquad (8)$$

The slight impurity of $S_2N_2(SbCl_5)_2$ found in the condensed $S_2N_2SbCl_5$ probably resulted from recombination of $S_2N_2SbCl_5$ and $SbCl_5$ on the cold finger rather than from direct sublimation of $S_2N_2(SbCl_5)_2$.

The low sublimation temperature of $S_2N_2SbCl_5$ supports the formulation as an S_2N_2 adduct, because an $S_4N_4(SbCl_5)_2$ adduct would be expected to be much less volatile.

Crystals of $S_2N_2SbCl_5$ are stable indefinitely at -15°, but slowly darken at 20°, becoming black after 1-2 weeks. Crystals of $S_2N_2(SbCl_5)_2$ undergo no change on standing at 20° for several months in sealed ampules after an initial surface yellowing, presumably from reaction with traces of moisture present on the glass. The stability of these adducts, compared to the appreciable polymerization of S_2N_2 above -30°, indicates that the S_2N_2 ring is stabilized by coordination with Lewis acids. The rapid reaction of $S_2N_2SbCl_5$ with S_2N_2, however, shows that this coordination somehow increases the reactivity toward attack by S_2N_2.

Infrared Spectra.- The infrared spectrum and chemical properties of S_2N_2 have led to its formulation as a four-membered planar ring with alternating S-N atoms (D_{2h} point group).[6] The prediction of three infrared-active modes agrees with the observed absorptions at 795 (s), 663 (w), and 474 (s) cm^{-1}. In the adducts, modes due to the donor $SbCl_5$ groups are expected to lie below 400 cm^{-1}. Therefore structural changes in the S_2N_2 caused by coordination should be reflected in changes in the spectrum above 400 cm^{-1}.

The two strong bands at 818 and 461 cm^{-1} in the infrared spectrum of $S_2N_2(SbCl_5)_2$ correspond closely in shape and position to the two strong S_2N_2 bands. The very weak band at 898 cm^{-1} is possibly an overtone of the band at 460 cm^{-1}. The similarity of the absorptions to those of S_2N_2 and the number of modes (2 or 3) observed indicate that the S_2N_2 ring remains

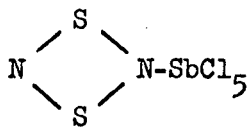
intact and planar (puckering of the ring to C_{2v} symmetry should result in five observed modes) with symmetric arrangement of the two $SbCl_5$ groups.

$S_2N_2SbCl_5$ exhibits strong absorption at 800 and 459 cm^{-1} and a weak band at 627 cm^{-1} corresponding closely in intensity, shape, and position to the S_2N_2 modes. The additional observed bands at 1005 (m), 922 (vw) (possibly an overtone of the 459 cm^{-1} band), and 723 (mw) cm^{-1} are expected from the lowering of symmetry resulting from the non-equivalence of the nitrogen atoms. Distinction between the possible configurations of the S_2N_2 group: planar ring (C_{2v}), puckered ring (C_s), or chain ($C_{\infty v}$, C_s or C_1), is not possible inasmuch as five or six infrared-active modes are predicted for each configuration. That the ring is broken (chain), however, is unlikely because of the ease of interconversion of $S_2N_2SbCl_5$ and $S_2N_2(SbCl_5)_2$, the similarity to the S_2N_2 modes, and the lack of higher frequency bands expected for terminal N-S groups. The 1005 cm^{-1} band can be reasonably assigned to an S-N ring system, because bands have been observed[2] for the S-N ring system in $S_4N_4SbCl_5$ in the same region (at 1060 and 968 cm^{-1}).

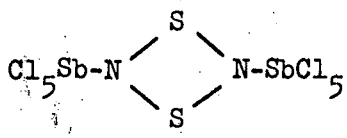
The possibility that the compounds $S_2N_2(SbCl_5)_2$ and $S_2N_2SbCl_5$ are tetra- and diadducts of S_4N_4 was considered. However, the observed bands showed no correlation with those of S_4N_4 or $S_4N_4SbCl_5$, and the forms of highest symmetry for $S_4N_4(SbCl_5)_4$ (planar ring, D_{4h}) and $S_4N_4(SbCl_5)_2$ (planar ring D_{2h}), predict four and eight observed modes, respectively. The lack of correlation in frequency and number of observed modes makes these formulations unlikely.

The infrared and chemical evidence support the formulation of $S_2N_2SbCl_5$ and $S_2N_2(SbCl_5)_2$ as adducts of the difunctional Lewis base

S_2N_2 with the structures:



(puckered or planar ring)



(planar ring) .

A recent x-ray diffraction study of $S_2N_2(SbCl_5)_2$ confirms the second of these predicted structures.[12]

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References

(1) H. Wöbling, Z. Anorg. Allgem. Chem., 57, 281 (1908).

(2) K. J. Wynne and W. L. Jolly, Inorg. Chem., 6, 107 (1967).

(3) D. Neubauer and J. Weiss, Z. Anorg. Allgem. Chem., 303, 28 (1960).

(4) M. G. B. Drew, D. H. Templeton, and A. Zalkin, Inorg. Chem., 6, 1906 (1967).

(5) M. Goehring, H. Hohenschutz, and R. Appel, Z. Naturforsch., 9b, 678 (1954).

(6) J. R. W. Warn and D. Chapman, Spectrochim. Acta, 22, 1371 (1966).

(7) C. D. Hodgman (Editor), "Handbook of Chemistry and Physics," 44th Edition, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1963, pp. 537.

(8) M. Becke-Goehring, Inorg. Syntheses, 6, 123 (1960).

(9) M. Goehring and D. Voight, Z. Anorg. Allgem. Chem., 285, 181 (1956).

(10) E. R. Lippincott and M. C. Tobin, J. Chem. Phys., 21, 1559 (1953).

(11) M. Villena-Blanco, "A Study of the Reactions Between Gaseous Ammonia and Sulfur Chlorides," M.S. Thesis, University of California, Berkeley, California, October, 1963.

(12) Unpublished work of R. L. Patton and K. N. Raymond.

B. Paper: "Reactions of Disulfur Dinitride With Boron Trifluoride and Boron Trichloride"

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Reactions of Disulfur Dinitride with Boron Trifluoride and Boron Trichloride

by R. Lyle Patton and William L. Jolly

Abstract

Disulfur dinitride reacts with boron trichloride in dichloromethane to form the following compounds (each of which can be obtained as the principal product by suitable choice of reaction conditions): $S_4N_4BCl_3$, $S_2N_2(BCl_3)_2$, and an apparently polymeric material $(S_2N_2BCl_3)_x$. At 0°, $S_2N_2(BCl_3)_2$ loses BCl_3 to form a simple adduct $S_2N_2BCl_3$ which can be reconverted to the diadduct by treatment with BCl_3 at -78°. Whereas $SbCl_5$ displaces BCl_3 from $S_2N_2BCl_3$ to form $S_2N_2(SbCl_5)_2$, the polymeric material $(S_2N_2BCl_3)_x$ is inert toward both BCl_3 and $SbCl_5$. The properties of $S_2N_2BCl_3$ and $S_2N_2(BCl_3)_2$ indicate that the S_2N_2 ring structure remains intact. Reaction of S_2N_2 with BF_3 yields only $S_4N_4BF_3$.

In a study of the reactions of S_2N_2 with $SbCl_5$ we have shown that S_2N_2 forms the adducts $S_2N_2SbCl_5$ and $S_2N_2(SbCl_5)_2$, in which the S_2N_2 ring remains intact.[1] To further explore the reactions of S_2N_2 as a Lewis base and the effects of coordination upon its stability, this study has been extended to include boron trifluoride and boron trichloride.

Experimental Section

General. The methods for the manipulation and characterization of volatile and moisture-sensitive materials and for the preparation of S_2N_2 have been described.[1] Boron trichloride and boron trifluoride (Matheson) and antimony pentachloride (J. T. Baker Co.) were purified by vacuum-line fractional condensation. The observed 0° vapor pressure of the BCl_3 was 477 mm (literature,[2] 477 mm). The observed -111.6° vapor pressure of BF_3 was 310 mm (literature,[3] 312 mm). Boron trifluoride was measured by pressure-volume methods, and BCl_3, $SbCl_5$, and S_2N_2 by weight loss of tared storage bulbs after distillation *in vacuo* into reaction vessels.

Reactions were normally carried out in a vacuum-line reactor consisting of a small Erlenmeyer flask attached by a 14/20 ground joint (sealed with Kel-F wax) to a Delmar-Urry 0-4 mm O-ring stopcock. The absence of grease prevented absorption of solvents and allowed use of the reactor as a tared vessel for determining solid product weights. In a typical study, S_2N_2 and CH_2Cl_2 were distilled into the reactor and warmed to 20° to dissolve the S_2N_2, and then rapidly frozen at -196°. The volatile Lewis acid was then distilled in, and the reactor was warmed to the desired reaction

temperature. The solvent and volatile products were removed and separated *in vacuo*, and the remaining non-volatile solids were weighed and then removed in the glove bag. Antimony pentachloride and BF_3 could be cleanly fractionated from CH_2Cl_2 and directly measured, whereas BCl_3 could not and was determined by hydrolysis and titration of the boric acid with standard NaOH in the presence of mannitol.

Reaction of S_2N_2 with BF_3.- Disulfur dinitride (0.71 mmole), BF_3 (3.175 mmoles), and CH_2Cl_2 (4 ml) were distilled into a reactor at -196°. Upon warming to -78°, a white suspension formed which became yellow at -45°, brown at 0°, and slowly formed an intense burgundy solution at 20°. The CH_2Cl_2 and excess BF_3 (2.817 mmoles) were pumped off, leaving 84 mg. of a burgundy solid which was identified as $S_4N_4BF_3$ on the basis of its infrared spectrum,[4] its melting point of 145° (literature,[4] 145-147°) and its characteristic of slowly losing BF_3 when pumped on at room temperature. Complete conversion of S_2N_2 to $S_4N_4BF_3$ requires 0.355 mmoles of BF_3 (observed, 0.358 mmole), forming 83 mg of $S_4N_4BF_3$.

S_2N_2-BCl_3 Reaction at 0°.- Disulfur dinitride (1.55 mmoles), BCl_3 (4.97 mmoles), and CH_2Cl_2 (10 ml) were frozen together in a reactor at -196°. The mixture was held at -78° for 2 hrs. while the CH_2Cl_2 melted and the solution above the white solid became slightly yellow. The mixture was then warmed slowly to 0° while stirring. Only slight darkening of the suspension occurred until the temperature reached -35°, above which the suspension turned, in rapid succession, yellow, grey, grey-green, black, brown, and yellow. Then with brief effervescence, a dark red solution formed. During one half hour at 0° this solution slowly turned light orange, and a slight film of an orange plastic material appeared. The appearance

of the solution was then unaffected by warming to 20° or cooling to -78°. The reaction mixture was held at -78° while BCl_3 was distilled off *in vacuo* and then warmed to 0° while removing the remaining CH_2Cl_2. A slight amount of N_2 (0.017 mmole) was evolved in the reaction. No precipitation occurred during the solvent removal, but as the last of the CH_2Cl_2 distilled off, the solution darkened to orange-brown and finally left 0.314 g. of a solid plastic-like layer. (Calculated for 1.55 mmoles $(S_2N_2BCl_3)_x$: 0.324 g.) Repeated cooling to -196° and warming to 0° broke up this solid, but no further gases were evolved.

Several similar reactions were run with variations in the time held at -80°, the rate of warming, and the time held at 0°. The visual observations of the reactions and products were the same. All the results are summarized in Table I. Only N_2, CH_2Cl_2, BCl_3, and slight traces of

Table I. Reactions of S_2N_2 with BCl_3 at 0°

S_2N_2 (mmoles)	$\frac{BCl_3}{S_2N_2}$	N_2 evolved (mmoles)	Product wt (mg)	Calculated for $(S_2N_2BCl_3)_x$(mg)
0.54	5.1	trace	108	113
0.77	4.8	0.003	161	161
1.16	2.6	0.011	240	242
1.42	3.2	0.015	300	297
1.55	3.2	0.017	314	324
2.90	3.2	trace	607	607

S_2Cl_2 were distilled from the reactions, leaving a product of composition $(S_2N_2BCl_3)_x$.

Nujol mulls of these products all absorbed strongly throughout the region 670-1350 cm^{-1} with prominences on this general broad absorption occurring at 1300, 1240, 1080, 970, and 730 cm^{-1}. Broad absorptions also occurred at 640 and 510 cm^{-1}. These absorption maxima differed slightly in different samples in position and relative intensity.

After removal from the reactor, the product did not redissolve in either CH_2Cl_2 or CCl_4 at 20°, although some darkening of the solvent and S_2Cl_2 evolution occurred. Distillation of CH_2Cl_2 back into the reactor once resulted in slight coloring of the solvent and release of S_2Cl_2 and, in another case, in vigorous N_2 evolution at -10°.

In a sealed capillary the $(S_2N_2BCl_3)_x$ remained solid on heating to 360° - becoming brown above 120° and shrinking with evolution of a yellow liquid above 160°. When $(S_2N_2BCl_3)_x$ was held at 20° for 4 weeks or at 55° for 4 days, considerable decomposition occurred, with formation of BCl_3, S_2Cl_2, N_2 and traces of SCl_2. Pyrolysis at 90° or higher yielded S_2Cl_2, SCl_2, N_2, and only traces of BCl_3. The relative amounts of the volatile products and the empirical composition of the residue did not correspond to any unique stoichiometry.

Liquid boron trichloride (10.70 mmoles) was distilled onto 161 mg. of $(S_2N_2BCl_3)_x$, and the mixture was held at 0° for 2 hours, then cooled to -78° and held for one hour before pumping off the BCl_3 at that temperature. Exactly 10.70 mmoles of BCl_3 was recovered, indicating that no BCl_3 uptake by $(S_2N_2BCl_3)_x$ occurred at -78°. Antimony pentachloride (3.11 mmoles) was

then distilled onto the $(S_2N_2BCl_3)_x$, and the mixture was twice held at 20° for 30 min. followed by cooling to -78° and pumping. No gases were removed. The reactor was then warmed to 20° while pumping to remove all the free $SbCl_5$. No BCl_3 or other gases were removed and the product weight remained 161 mg. Antimony pentachloride obviously did not displace BCl_3 from or add to the $(S_2N_2BCl_3)_x$.

S_2N_2-BCl_3 Reaction at -78°.- When suspensions of S_2N_2, CH_2Cl_2 and excess BCl_3 were held for extended periods at -78° and then subjected to pumping at that temperature to remove the CH_2Cl_2 and excess BCl_3, measurement of the unreacted BCl_3 showed that products approaching the composition $S_2N_2(BCl_3)_2$ were obtained. The reaction times and calculated BCl_3/S_2N_2 ratios for the products for several runs were: 6 hr., 1.67; 15 hr., 1.83; 2.5 days, 1.865; 5 days, 1.96; 6.5 days, 1.83. When the product of the 6.5-day run (containing 0.86 mmole of S_2N_2 and 1.57 mmoles of BCl_3) was warmed slowly while pumping, the creamy white solid evolved 0.70 mmole of BCl_3 between -35 and 0°. Further pumping at 0° for 2 hrs. evolved 1 mg of S_2Cl_2 and no BCl_3. These data correspond to an empirical product composition $S_2N_2 \cdot 1.01\ BCl_3$; the product weight (178 mg) was also in good agreement with that calculated for the formation of $S_2N_2BCl_3$ (179 mg). (In each of the above runs, similar evolution of BCl_3 on warming to 0° left a product composition of $S_2N_2BCl_3$.) The remaining solid was treated with a measured excess of BCl_3 in CH_2Cl_2 at -78° for two hours, and then the reaction mixture was evacuated at that temperature. The product retained 0.625 mmole of the BCl_3, but all of this BCl_3 was evolved when the product was again warmed to 0° *in vacuo*. In a repetition of this

procedure without CH_2Cl_2, 0.615 mmole of BCl_3 was retained at -78° and then evolved at 0°. In a second repetition of the procedure, 0.56 mmole of BCl_3 was retained at -78° and then evolved at 0°. Then the remaining product was treated with 3.90 mmoles of antimony pentachloride at 20° for 1 hour. After cooling to -78° for one half hr., the reactor was evacuated at -78°, and BCl_3 was removed. The reactor (still containing the $SbCl_5$) was twice warmed to 20° and returned to -78° for further BCl_3 removal, then warmed to 20° to pump off the $SbCl_5$. The total BCl_3 removed (0.55 mmole) corresponded to the BCl_3 reversibly absorbed in the previous treatment (0.56 mmole). The weight gain, corrected for the BCl_3 lost, corresponded to the absorption of 1.08 mmoles of $SbCl_5$.

A similar sequence of experiments, in which BCl_3 was absorbed at -78° and removed at 0°, was performed on the product of the 15-hr. run mentioned above containing originally 1.30 mmoles of S_2N_2. The final BCl_3 treatment, in which 1.03 mmoles of BCl_3 was evolved at 0°, was again followed by treatment with excess $SbCl_5$. 0.99 mmole of BCl_3 was evolved while $SbCl_5$ (2.05 mmoles) was retained. The infrared spectrum of the products after treatment with $SbCl_5$ showed the presence of $S_2N_2(SbCl_5)_2$.[1] Extraction of the product with dichloromethane yielded a solution from which pure $S_2N_2(SbCl_5)_2$ was obtained (identified by its infrared spectrum[1]) and left some residue with the appearance and infrared spectrum of $(S_2N_2BCl_3)_x$.

The creamy white products of composition $S_2N_2BCl_3$ yellowed slightly when warmed at 0° during the course of subsequent BCl_3 treatments, and slowly darkened to orange with evolution of S_2Cl_2 when warmed above 0°. However, at -15° in sealed tubes the material remained stable indefinitely

without darkening or change in its infrared absorptions. In a sealed capillary it turned red-orange at 50° before melting at 55° with decomposition.

When dichloromethane was distilled onto $S_2N_2BCl_3$ at -196° and warmed to -78°, the conversion of $S_2N_2BCl_3$ to $(S_2N_2BCl_3)_x$ occurred relatively rapidly, with rapid darkening of the solution. Whenever excess BCl_3 was present, darkening of the solution did not occur until around -35°.

In Nujol mulls, the infrared spectra of fresh samples of $S_2N_2BCl_3$ showed the following peaks (in cm^{-1}): 1115 (ms), 950 (w), 840 (m), 788 (wm), 728 (s-broad), 682 (mw), 610 (ms), and 467 (m). An $S_2N_2BCl_3$ sample was allowed to stand 24 hours at 20° and a Nujol mull taken; the $S_2N_2BCl_3$ absorptions were gone and absorptions characteristic of $(S_2N_2BCl_3)_x$ had appeared.

Addition of BCl_3 to S_2N_2 at 20°.- Slow addition of a BCl_3 (2.20 mmoles) solution to S_2N_2 (1.58 mmoles) in CH_2Cl_2 at 20° in the glove bag resulted in a black, opaque suspension which cleared after several minutes to a dark red solution which finally turned orange-red. Concentration and cooling of this solution yielded pure crystals of $S_4N_4BCl_3$ as shown by its infrared spectrum[4] and melting point of 136° (literature,[4] 137-138°). Infrared spectrometry indicated that the residue from evaporation of the remaining solvent consisted of $S_4N_4BCl_3$, with no S_4N_4 or $S_2N_2BCl_3$ impurity.

$(SN)_x$ - BCl_3 Reaction.- A sample of $(SN)_x$ was obtained as a by-product from several S_2N_2 preparations. It was separated from S_4N_4 and sulfur impurities by repeated extraction with carbon disulfide until no further yellowing of the carbon disulfide occurred. This $(SN)_x$ was then weighed into a tared reactor consisting of an O-ring stopcock attached to a 50 ml Erlenmeyer flask by a joint waxed with Kel-F wax. In one experiment, 1.185 g. of BCl_3 and 3 ml of CH_2Cl_2 were distilled onto 172 mg of $(SN)_x$ in a reactor and held for 2 hours at 0°. No evidence of reaction was observed. The suspension was then warmed to 20° and held 4 days to yield an orange-yellow solid and orange solution together with approximately 10% of the original black particles of $(SN)_x$. The yellow solid was filtered off and the orange filtrate was subjected to pumping at 0° for 1 day to remove the solvent, after which only an orange plastic film remained. Both this orange plastic film and the yellow solid exhibited infrared absorptions very similar to those of $(S_2N_2BCl_3)_x$. Upon heating in a sealed capillary the yellow solid behaved like $(S_2N_2BCl_3)_x$. It did not melt on heating to 360°, but darkened above 100° and shrank with evolution of a yellow liquid above 160°.

In a second experiment, 70 mg of $(SN)_x$ and 1.0445 g of BCl_3 were placed in a tared reactor and held at 0° for 2 days with no reaction. Dichloromethane (5 ml) was distilled into the reactor, and the suspension was held with occasional stirring for 7 days, during which only slight yellowing of the solution occurred. The suspension was then stirred at 20° for 2 days, after which it appeared that all of the black $(SN)_x$ particles had been consumed, leaving an orange solution above a yellow solid. The solvent and excess BCl_3 were removed by pumping, first at -80° and then while warming to 0°, until all volatiles had been removed.

Nitrogen (0.080 mmole) was collected in the Toepler pump buret, and 124 mg of an orange-yellow solid remained. If we assume that the small amount of evolved nitrogen corresponded to the decomposition of some $(SN)_x$ to the elements and that the principal product was $(S_2N_2BCl_3)_x$, we calculate that the residue should have weighed 147 mg. The infrared spectrum of the solid was the same as that of the product of the first reaction.

Results and Discussion

Reaction with Boron Trifluoride.- When disulfur dinitride is added to excess boron trifluoride in dichloromethane, only $S_4N_4BF_3$ is formed,

whereas the analogous reaction with $SbCl_5$ yields an adduct of S_2N_2. We believe the difference may be explained by the relative weakness of BF_3 as a Lewis acid compared with $SbCl_5$ and by the assumption that the S_4N_4 acid adduct is formed by a second-order reaction:

$$S_2N_2 + S_2N_2 \cdot \text{Acid} \longrightarrow S_4N_4 \cdot \text{Acid} \qquad (1)$$

In the case of $S_2N_2SbCl_5$, the equilibrium concentration of S_2N_2 is too low for this reaction to proceed at an appreciable rate unless an excess of S_2N_2 is added to the system. In the case of $S_2N_2BF_3$, the equilibrium concentration of S_2N_2 is high enough for the reaction to proceed and to prevent the isolation of $S_2N_2BF_3$.

Reactions with Boron Trichloride at 0°.- The results of the reactions in which S_2N_2 and BCl_3 were warmed to 0° in dichloromethane show that a product of composition $(S_2N_2BCl_3)_x$ was formed. However, the broad, diffuse, varying infrared spectra of these products showed no correspondence to known S_2N_2, S_4N_4, or BCl_3 adducts. Also, it was not possible to displace BCl_3 from $(S_2N_2BCl_3)_x$ with $SbCl_5$ as might have been expected for a simple adduct inasmuch as $SbCl_5$ is a stronger Lewis acid than BCl_3 and does effect this displacement on $S_4N_4BCl_3$.[2] Thus it appears that $(S_2N_2BCl_3)_x$ is not an adduct involving intact S_2N_2 and BCl_3 units, but rather that some degree of chlorination of the sulfur atoms and some polymerization has occurred. The inability of the product to dissolve after removal of the dichloromethane suggests that the degree of polymerization increased in the solid or highly concentrated state.

The reaction of polymeric sulfur nitride, $(SN)_x$, with boron trichloride gives a material having the same properties and approximately the same composition as the $(S_2N_2BCl_3)_x$ prepared from S_2N_2 and BCl_3 at 0°. However

the $(SN)_x$-BCl_3 reaction must be carried out at temperatures around 20°, and at these temperatures side reactions take place, precluding the isolation of a pure product.

Reactions with Boron Trichloride at -78°.- The data for reactions performed at -78°, in which the solvent and excess BCl_3 were removed at that temperature, indicate the formation of a simple labile diadduct $S_2N_2(BCl_3)_2$ and a small amount of $(S_2N_2BCl_3)_x$. The $S_2N_2(BCl_3)_2$ dissociates reversibly on warming to 0° to BCl_3 and a monoadduct $S_2N_2BCl_3$. The ability of $S_2N_2BCl_3$ to add BCl_3 at low temperatures distinguishes it from $(S_2N_2BCl_3)_x$, which is inert to addition of a second mole of BCl_3. The slight decrease in the BCl_3 reversibly absorbed after each successive BCl_3 replacement was probably caused by a slight amount of the irreversible rearrangement (polymerization) $S_2N_2\ BCl_3 \rightarrow (S_2N_2BCl_3)_x$ occurring at temperatures near 0°. This latter reaction occurs readily in dichloromethane solution whenever excess boron trichloride is absent, even at low temperatures. Apparently the polymerization is blocked when both nitrogens of S_2N_2 are coordinated to BCl_3. The amount of BCl_3 reversibly absorbed is a measure of the monoadduct $S_2N_2BCl_3$ present in a mixture of $S_2N_2BCl_3$ and $(S_2N_2BCl_3)_x$, as evidenced by the displacement, on treatment with $SbCl_5$, of BCl_3 in only the amount equal to that reversibly absorbed in the previous BCl_3 treatment. This displacement of BCl_3 to form the known[1] disulfur dinitride adduct $S_2N_2(SbCl_5)_2$ is in agreement with the relative Lewis acid strengths of $SbCl_5$ and BCl_3 and supports the formulation of $S_2N_2BCl_3$, and $S_2N_2(BCl_3)_2$ as adducts of S_2N_2. The residue of $(S_2N_2BCl_3)_x$ left after washing out the $S_2N_2(SbCl_5)_2$ further confirms its presence as the inert material. The data presented correspond quantitatively

to the reactions:

$$(2 + y)BCl_3 + (1 + y)S_2N_2 \xrightarrow[-78^\circ]{CH_2Cl_2} S_2N_2(BCl_3)_2 + y/x(S_2N_2BCl_3)_x \quad (2)$$

$$S_2N_2(BCl_3)_2 \underset{-78^\circ}{\overset{0^\circ}{\rightleftharpoons}} S_2N_2BCl_3 + BCl_3 \quad (3)$$

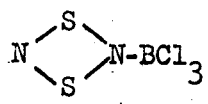
$$S_2N_2BCl_3 \xrightarrow[0^\circ]{(slow)} (S_2N_2BCl_3)_x \quad (4)$$

$$S_2N_2BCl_3 + 2SbCl_5 \rightarrow S_2N_2(SbCl_5)_2 + BCl_3 \quad (5)$$

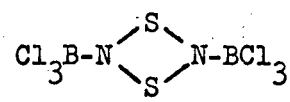
Formation of $S_4N_4BCl_3$.- The formation of $S_4N_4BCl_3$ by the addition of BCl_3 to an S_2N_2 solution is analogous to the formation of $S_4N_4SbCl_5$[1] and $S_4N_4BF_3$ from S_2N_2. In each of these reactions, the mechanism is probably the initial formation of an adduct of the type S_2N_2·Acid, followed by reaction 1.

In adducts in which the boron atom of BCl_3 is bonded directly to the central atom of a Lewis base molecule, a broad infrared absorption envelope characteristic of the BCl_3 portion of the adduct is found with maxima in the 700-800 cm^{-1} region.[5] Also, sulfur-nitrogen compounds usually have strong absorptions in and near this region. For example, S_2N_2,[6] $S_2N_2SbCl_5$,[1] and $S_2N_2(SbCl_5)_2$[1] have absorptions at 795 and 663 cm^{-1}, 800 and 723 cm^{-1}, and 818 cm^{-1}, respectively. It seems likely that all of the infrared absorptions of $S_2N_2BCl_3$ near this region (at 840 (m), 788 (wm), 728 (s-broad) and 682 (mw) cm^{-1}) may result from combinations

of S-N and BCl_3 modes. The remaining $S_2N_2BCl_3$ absorptions (at 1115, 950, 610, and 467 cm^{-1}) correspond closely in position and shape to absorptions in $S_2N_2SbCl_5$. Thus the infrared and chemical evidence support formulation of $S_2N_2BCl_3$ and $S_2N_2(BCl_3)_2$ as adducts of the same type as those of S_2N_2 with $SbCl_5$ with the structures:



and



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References

(1) R. L. Patton and W. L. Jolly, Inorg. Chem., ___, 000 (1969).

(2) A. Stock and O. Pries, Chem. Ber., 47, 3109 (1914).

(3) O. Ruff, A. Braida, O. Bretschneider, W. Menzel and H. Plaut, Z. anorg. allgem. Chem., 206, 59 (1932).

(4) K. J. Wynne and W. L. Jolly, Inorg. Chem., 6, 107 (1967).

(5) K. J. Wynne and J. W. George, J. Am. Chem. Soc., 87, 4750 (1965).

(6) J. R. W. Warn and D. Chapman, Spectrochim. Acta, 22, 1371 (1966).

C. Appendix

The infrared spectra of compounds prepared in parts A and B are presented.

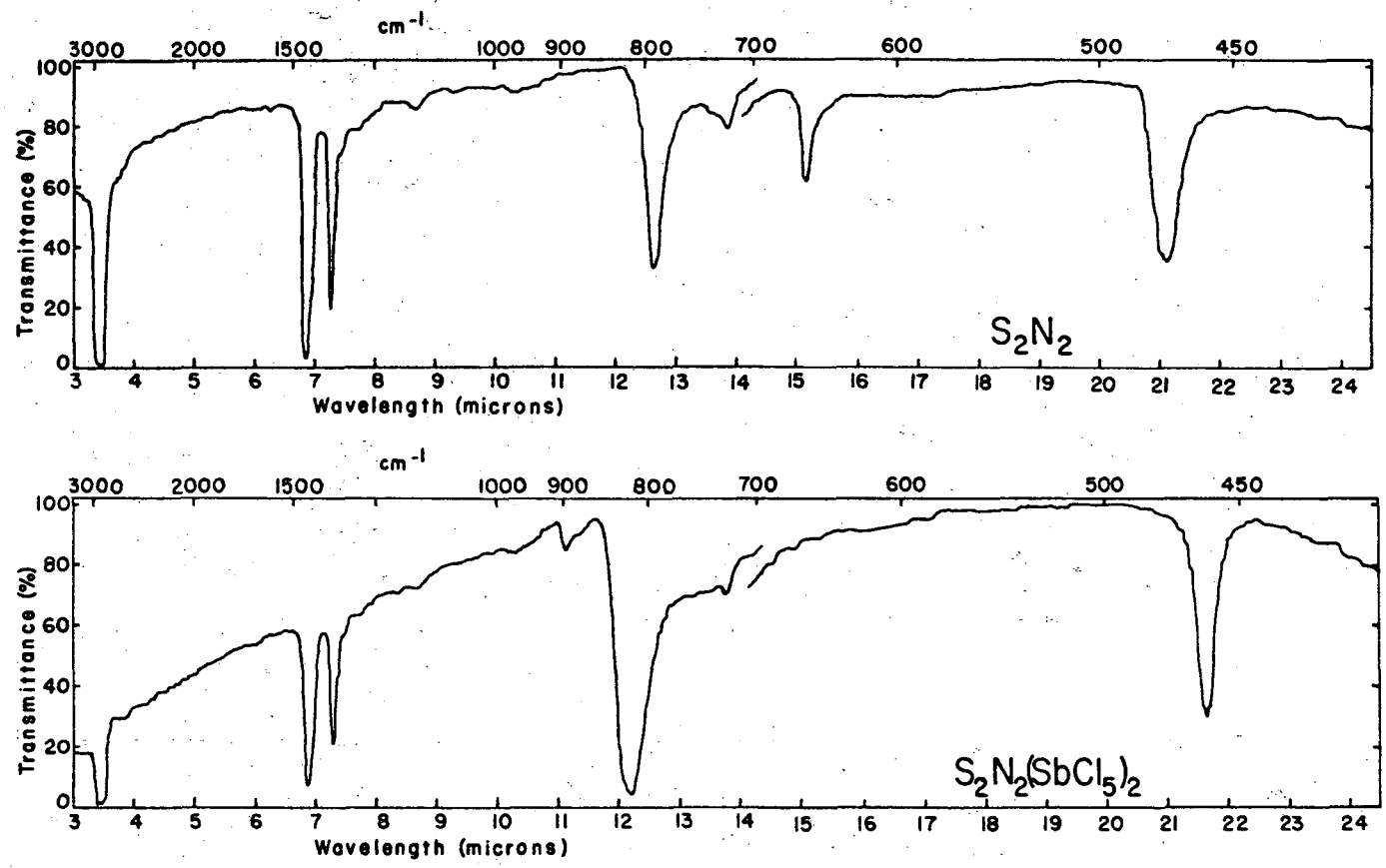
The spectrum of each compound was taken in two overlapping ranges encompassing the entire range of wavelength from 3.0 to 24.5 μ. The spectrum of each compound was taken on the solid suspended in a Nujol mull and also shows the absorptions resulting from the Nujol which occur at 2900 (vs), 1460 (vs), 1370 (s), and 722 (vw) cm^{-1}.

The infrared spectra presented are:

Fig. 1: S_2N_2 and $S_2N_2(SbCl_5)_2$,

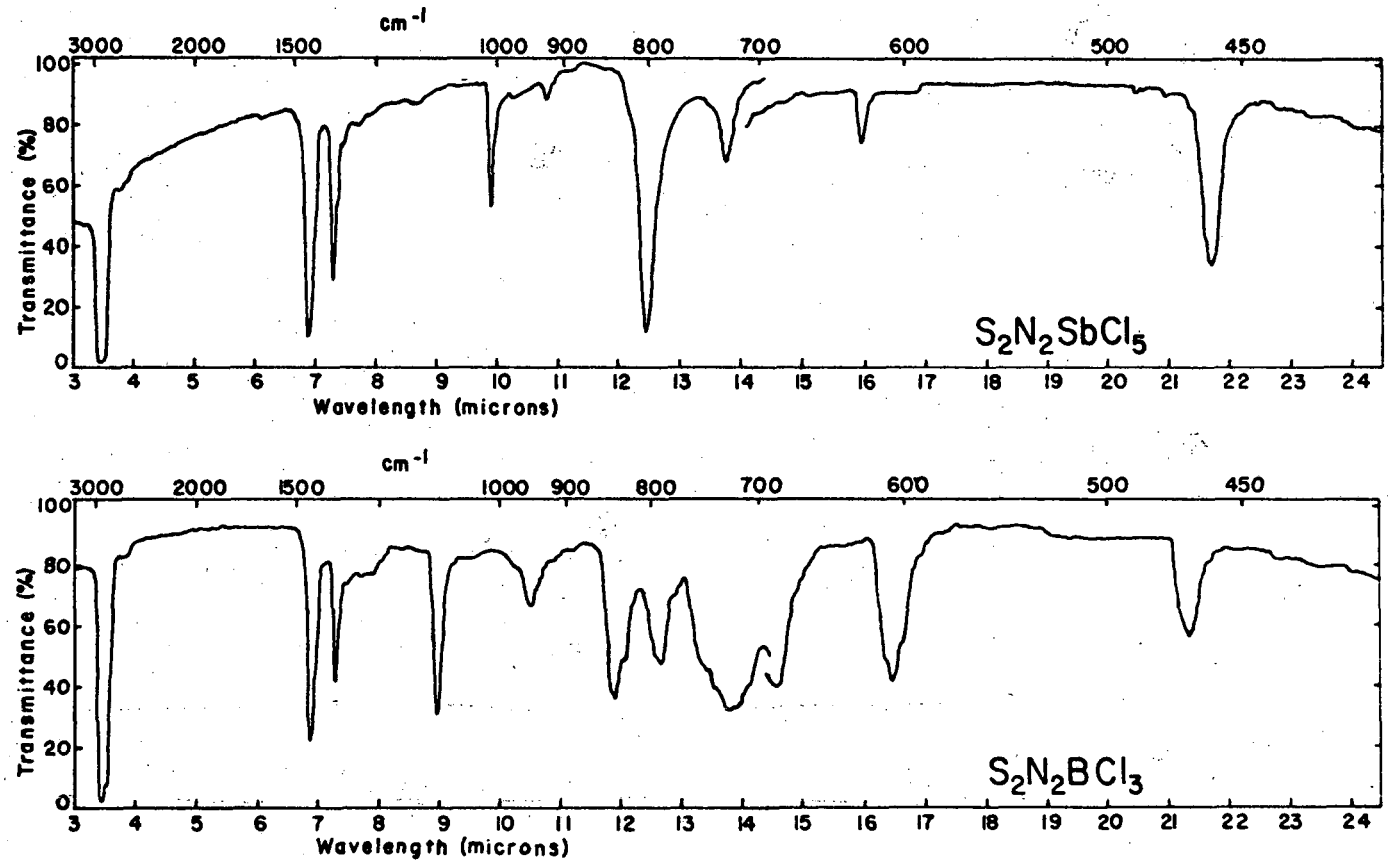
Fig. 2: $S_2N_2SbCl_5$ and $S_2N_2BCl_3$,

Fig. 3: $(S_4N_4SbCl_5)_x$ and $(S_2N_2BCl_3)_x$.



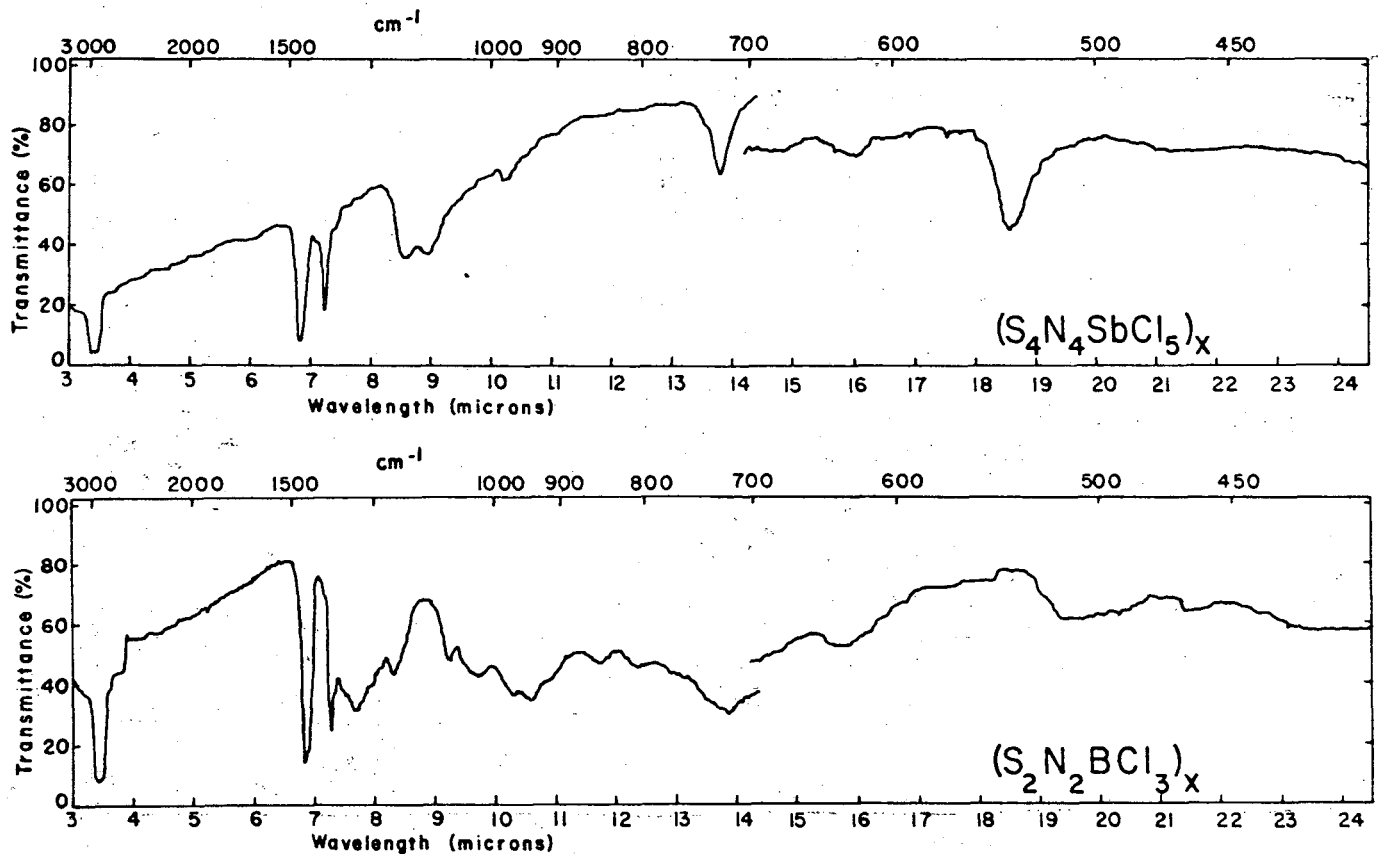
XBL 693-300

Fig. 1 (Section III)



XBL 693-306

Fig. 2 (Section III)



XBL 693-305

Fig. 3 (Section III)

IV. Paper: "The Crystal and Molecular Structure of $S_2N_2(SbCl_5)_2$"

(Note: The work described in this section was performed under the guidance of Professor Kenneth N. Raymond of this department.)

THE CRYSTAL AND MOLECULAR STRUCTURE OF $S_2N_2(SbCl_5)_2$

by

R. Lyle Patton and Kenneth N. Raymond

The crystal structure of the antimony pentachloride diadduct of disulfur dinitride $S_2N_2(SbCl_5)_2$ has been determined from three dimensional X-ray diffraction data. Intensity measurements were made on a manual GE XRD-5 diffractometer using the stationary count method out to a Bragg angle of 50°. Two equivalent forms for each independent reflection were corrected for absorption and then averaged. The material crystallizes in space group $I\bar{4}2d$ of the tetragonal system with 8 molecules in a unit cell of dimensions a = 14.933(3) Å and c = 15.547(3) Å. The calculated density of 2.64 g/cm^3 agrees well with the value 2.70 g/cm^3 measured by flotation. Refinement of the structure on F^2 by least squares methods resulted in a final conventional R factor for F of 3.8%, for 768 independent reflections above background.

The structure consists of a planar S_2N_2 ring with alternating sulfur and nitrogen atoms. An $SbCl_5$ group is bonded via the antimony atom to each nitrogen of the ring. The two antimonys, two nitrogens and two axial chlorines all lie on a crystallographic two-fold axis which passes through the molecule. The two crystallographically independent S-N distances of 1.616(7) and 1.623(8) Å are equal to within the estimated error, as are the two Sb-N distances of 2.281(10) and 2.285(11) Å. The S_2N_2 ring is nearly square with S-N-S angles of 95.4(6) and 94.8(6)° and N-S-N angles of 84.9(4)°.

Introduction

The compound S_2N_2 is obtained as an unstable crystalline material from the thermal cleavage of S_4N_4.[1] On the basis of the infrared spectrum of S_2N_2, a planar ring structure of alternating nitrogen and sulfur atoms was proposed.[2] This was the first example to our knowledge of a tetraatomic molecule of this kind. An x-ray diffraction study of S_2N_2 has not been attempted, however, as the crystals polymerize to $(SN)_x$ when warmed above -80°C. In a recent study of the reactions of S_2N_2 with Lewis acids,[3] a crystalline diadduct of S_2N_2 with antimony pentachloride, $S_2N_2(SbCl_5)_2$, has been prepared which is thermally stable at room temperature. From the chemical properties of $S_2N_2(SbCl_5)_2$ and the similarity of its infrared spectrum to that of S_2N_2, it was proposed that the S_2N_2 ring remained unbroken and planar after coordination by $SbCl_5$. To confirm this proposed structure and show that a planar S_2N_2 ring does indeed exist, the crystal structure of $S_2N_2(SbCl_5)_2$ has been determined by three dimensional X-ray analysis.

Experimental

Yellow crystals of $S_2N_2(SbCl_5)_2$ were prepared as described previously.[3] The crystals had moderately well developed faces and exhibited sharp extinction under the polarizing microscope. As the crystals were extremely moisture sensitive and blackened immediately in room air, several were stuck to the inside of thin-walled quartz capillaries with Kel-F grease in a nitrogen-flushed glove box and the capillaries were sealed. These crystals were then examined under the polarizing microscope and the one whose size, clarity, extinction, and shape seemed most suitable was chosen for further study.

Precession photographs of the $h0\ell$, $0k\ell$, $1k\ell$, $hh\ell$ and $h2h\ell$ zones, and a Weissenberg photograph of the hk0 zone showed 4/mmm symmetry with the systematic absences: $hk\ell$, $h + k + \ell \neq 2n$; and $hh\ell$, $2h + \ell \neq 4n$. These absences are consistent only with the two space groups $I\bar{4}2d$ and $I4_1md$. Preliminary cell constants were measured from the films. The density measured by flotation in a dibromomethane-carbon tetrabromide solution was 2.70(8) compared with the calculated density of 2.64 for eight molecules in the unit cell. Slow decomposition of the compound occurred during the density measurement, hence the large assigned error estimate. Since both possible space groups have sixteen general positions in the cell, the molecules must lie in special positions.

The crystal was mounted on a eucentric goniometer head with the crystal c axis parallel to the spindle direction (ϕ axis) of a General Electric XRD-5 manual goniostat equipped with a scintillation counter, pulse height discriminator and a scaler. Molybdenum radiation ($K\alpha_1$, $\lambda = 0.70926$ Å) at 45 kV and 21 mA was used. The diffracted beams were filtered through 3 mils of Zr foil. The receiving aperture was 10 mm high, 3 mm wide and positioned 15 cm from the crystal. The cell dimensions, a = 14.933(3), c = 15.547(3) Å, were determined by careful measurement at 22°C of the Bragg angles for high-index reflections of the type h00, 0k0 and 00ℓ. The α_1 and α_2 peaks were well resolved in these measurements and were satisfactorily narrow. The standard deviations in the least significant digits are given in parentheses. These were determined from the estimated error in the 2θ angles.

Data were collected by the point count method. The intensities of all 1670 space-group-allowed reflections in the +h +k +ℓ octant were measured out to $2\theta = 50°$ by 10 sec counts at the peak maximum with the crystal and counter stationary, and at a takeoff angle of 4°. For all

$hh\ell$, $h0\ell$, $0k\ell$ and 00ℓ reflections, all $hk\ell$ reflections with $2\theta \leq 20°$, and about one third of the reflections with $20° < 2\theta \leq 50°$, individual backgrounds were measured by seeking a minimum on the low 2θ side of the peak. The remaining backgrounds were taken from a plot of background as a function of 2θ for various values of the orientation angles, ϕ and χ. A set of arbitrarily chosen standard reflections which were monitored approximately every 100 measurements showed no trend or change throughout the course of the measurement beyond that expected from counting statistics. The intensities, I, after subtraction of background, were assigned standard deviations according to the formula $\sigma(I) = [I + 0.75B + (0.05I)^2]^{1/2}$ where the background, B, was not the actual background measured for each peak, but instead was estimated by the expression $B = 650 - 10(2\theta) + 0.02\ I$, which was a reasonable representation of the actual background counted. Values of I were then reduced to values of F^2 by application of Lorentz-polarization corrections.[4]

The measured reflections consisted of two sets: the first with $h \leq k$ and the second with $h \geq k$. These two sets are equivalent forms in both $I\bar{4}2d$ and $I4_1md$ since both space groups contain diagonal mirror planes. Comparison of the measured intensities for equivalent reflections in the two sets showed systematic differences due to absorption effects.

The dimensions of the crystal were carefully measured with a micrometer eyepiece attached to a microscope. Each bounding plane of the crystal was indexed and the plane to plane distances determined. The approximate dimensions of the crystal are 0.15 x 0.26 x 0.45 mm. The longest dimension is along c. An absorption correction was then applied to each reflection.[4] For a linear absorption coefficient of 49.7 cm^{-1} the transmission factors of the measured reflections ranged from 0.474 to 0.587. The two forms were then averaged to give 859

independent reflections of which 761 were greater than three times their standard deviation.

Solution and Refinement of the Structure

An unsharpened Patterson function was calculated using the data set which was uncorrected for absorption and had $h \leq k$. An initial solution was attempted in space group $I4_1md$ which contains vertical mirror planes at x = 0, 1/2 and at y = 0, 1/2. Special positions on the mirror planes could be found for two independent Sb atoms separated by $\Delta z = 1/2$ for which peaks corresponded to all predicted Sb-Sb interactions. However, further search for chlorine atom positions from the weaker Sb-Cl vectors always gave some disagreement between predicted and observed peak positions and intensities. Moreover, chlorine positions determined from the Patterson map required chemically unreasonable Sb-Cl bond lengths or Cl-Cl van der Waals contacts. For this reason, space group $I4_1md$ was rejected. The subsequent choice of the remaining possible space group $I\bar{4}2d$ was confirmed as being correct by the successful refinement of the crystal structure.

Analysis of the Patterson map in space group $I\bar{4}2d$ led easily to two unique sets of antimony, chlorine and sulfur positions for which all predicted positions and intensities of Sb-Sb, Sb-Cl, and Sb-S peaks were found in the 88 Patterson peaks with greater than 0.7% of the origin height. Both sets corresponded to the predicted molecular geometry of $S_2N_2(SbCl_5)_2$. This expected geometry has three different possible two-fold axes. The two solutions of the Patterson function corresponded to two of these. In both cases the long axis of the molecule (the Sb-Sb vector) lies in the xy plane, with the x and y coordinates of the Sb atoms

very nearly 0, 1/4; and 1/2, 1/4, respectively. The first solution placed them at z = 3/8. The antimony atoms then occupy the general position 16(e) and are related by the two-fold axis passing between them at 1/4, y, 3/8. As will be shown later, the two N-$SbCl_5$ groups are very nearly related by a non-crystallographic axis in exactly this way. In the second solution the z coordinate is 1/8 and the two N-$SbCl_5$ groups occupy 8(e) with the two-fold axis at x, 1/4, 1/8 passing through both groups, which are then crystallographically independent. These two solutions differ significantly only in the position of the sulfur atoms of the S_2N_2 ring. In the first case these atoms must lie on the two-fold axis, in the second case they are in a general position and the S_2N_2 ring need not be parallel to the xy plane.

Trial parameters for the first solution were refined by least squares techniques using initially the 761 reflections with $h \leq k$ and $F^2 \geq 3\sigma(F^2)$ before correction for absorption. In this and succeeding refinements the function minimized was $\Sigma\, w\, (|F_o| - |F_c|)^2$, in which $|F_o|$ and $|F_c|$ are the observed and calculated structures factors and the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral Sb, Cl, S and N tabulated by Ibers[5] were used together with the values of $\Delta f'$ and $\Delta f''$ for Sb, Cl, and S given by Cromer[6] to include the effects of anomalous dispersion.[7] Four cycles of least squares refinement, in which only the Sb and Cl atoms were assigned anisotropic temperature factors, gave values of $R_1 = \Sigma\, ||F_o| - |F_c|| / \Sigma\, |F_o|$ and of $R_2 = (\Sigma\, w(|F_o - F_c|)^2 / \Sigma\, wF_o^2)^{1/2}$ of 22 and 34%, respectively.

At this point a difference Fourier[4] was computed. Although the highest peak was only 2.1 electrons $Å^3$, considerable fluctuation of

electron density appeared in the circle containing the equatorial chlorines; also, the sulfur atoms were smeared out around the two-fold axis which passed through them. It appeared that either some free rotation or disorder was present or that the trial solution was incorrect. Assuming the latter, the second solution to the Patterson map was tried. All of the atoms were shifted a small distance along x to destroy a false mirror plane which is otherwise generated. The extra pseudosymmetry of the structure (the source of the ambiguous interpretation of the Patterson map described earlier) also caused singularity problems in the refinement when the $SbCl_5$ groups were rotated so that the $Sb\text{-}Cl_{eq}$ bonds were coincident with the crystal axes.

After the correct orientations of the $SbCl_5$ groups were determined, the refinement was straight-forward. Twelve reflections were discarded because of data collection errors or because their very high intensities gave coincidence losses. Several cycles of refinement on F with all atoms assigned anisotropic thermal parameters brought R_1 and R_2 to 4.2 and 6.5% respectively.

The error in an observation of unit weight was 3.06 and was found to vary linearly with F_{obs} as approximately $E = 3.19 - 2.53\ F_o/F_{max}$. The standard deviations were then revised by multiplying them times this quantity. Of 847 remaining reflections 768 had $F^2 > \sigma(F^2)$ and these were used in the final refinements on F^2. After convergence, the final values of R_1 and R_2 on F^2 are 5.6 and 9.7%, respectively, with an error in an observation of unit weight of 0.89.[8] The final values of R_1 and R_2 on F are 3.8 and 4.9%. A final difference Fourier showed a maximum electron density of $0.37/\mathring{A}^3$. Final values of $|F_o|$ and $|F_c|$ (in electrons x 5) are given in Table I. The final values of the atomic parameters

along with their standard deviations estimated from the variance-covariance matrix are given in Table II.

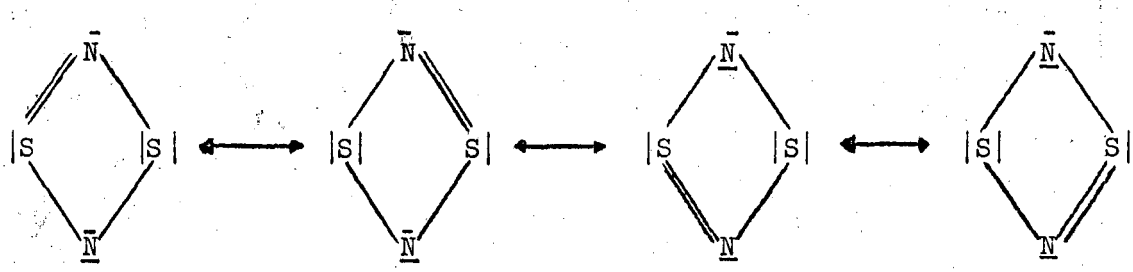
Description and Discussion of the Structure

The unit cell contains eight discrete $S_2N_2(SbCl_5)_2$ molecules, each lying on one of the horizontal two-fold rotation axes in the cell. The bulky $SbCl_5$ groups appear to be the main factor controlling the molecular packing with the S_2N_2 rings fitting into spaces between these groups. None of the intermolecular distances observed are short enough to indicate any unusual association. Several chlorine-chlorine contacts are slightly less than the sum of their van der Waals radii (3.6 Å): Cl_{12}-Cl_{22}, 3.337 Å; Cl_{21}-Cl_{21}, 3.397 Å; Cl_{11}-Cl_{11}, 3.425; and Cl_{13}-Cl_{23}, 3.559. These may be compared with some close intermolecular Cl-Cl contacts found in previous structures involving $SbCl_5$ groups such as: $SbCl_5$, 3.33 Å;[9] $SbCl_5 \cdot SeOCl_2$, 3.33 Å;[10] and $SbCl_5 \cdot POCl_3$, 3.41 Å.[11] All intermolecular distances less than 3.8 Å are listed in Table III.

The molecular structure consists of an S_2N_2 ring formed of alternating sulfur and nitrogen atoms (Figures 1 and 2). Each of the nitrogen atoms is coordinated to an $SbCl_5$ group, and the N-$SbCl_5$ groups are then roughly octahedral. Each molecule lies on a crystallographic two-fold axis which passes through the axial chlorine, antimony, and nitrogen atoms. This two-fold symmetry constrains the S_2N_2 ring to planarity. The S-N bond distances, given in Table IV, are equal to within the experimental error. Their weighted mean is 1.619(5) Å. The internal angles of the ring are 84.9(4)° and 95.1(4)° for the N-S-N and averaged S-N-S angles, respectively. These values are in remarkable agreement with those predicted from the infrared spectrum for the planar S_2N_2 ring itself.[2]

The predicted bond length and angles were 1.62 Å, 85° and 95°. In fact, it is reasonable to assume that the coordination with $SbCl_5$ has not significantly changed the dimensions of the S_2N_2 ring. This is supported by the apparent weakness of the $N \rightarrow SbCl_5$ coordinate bond as evidenced by the ease with which an $SbCl_5$ can be removed,[3] by the similar infrared absorption frequencies of S_2N_2 and $S_2N_2(SbCl_5)_2$[2,3] and by the relatively long Sb-N distance. The much stronger $S_4N_4 \cdot SbCl_5$ adduct is very difficult to dissociate[12] and has a significantly shorter Sb-N bond.[13] However, even in this case the average S-N distance in the eight membered puckered ring remains the same as in S_4N_4 itself.[14]

The S-N distance in $S_2N_2(SbCl_5)_2$ is the same as that determined for S_4N_4, 1.616(10) Å. Using a recent correlation of bond order vs. bond length in S-N compounds,[15] this corresponds to a bond order near 1.3. The most reasonable resonance structures which explain a fractional double bond character and are consistent with equivalent S-N bonds are the set:



These resonance forms correspond directly with a molecular orbital description which uses only the valence s and p orbitals of nitrogen and sulfur. The basic features of such a description are the filled sigma-bonding network (a_g, B_{2u}, b_{1g} and b_{3u}) and the non-bonding unshared electron pairs ($2a_g$, b_{2u} and b_{3u}). In addition, there is one filled π-bonding orbital (b_{1u}) and two filled, rigorously non-bonding π orbitals

(b_{2g} and b_{3g}). Although there is possibly some involvement of the sulfur 3d orbitals in the bonding, similar to that proposed by Craig[16] and by Dewar, Lucken and Whitehead[17] for other S-N and P-N ring systems, this does not fundamentally alter the bonding scheme just described.

Attempts to determine the importance of different resonance forms by correlating them to the indicated bond order must be tempered by the recognition that the bonds are obviously strained in the four-membered ring. This four-membered ring is the smallest in a series of compounds containing rings composed only of sulfur and nitrogen atoms. Examples of other ring sizes are: a five-membered ring in $S_3N_2Cl_2$;[18] a six-membered ring in $(NSCl)_3$;[19] a seven-membered ring in $S_4N_3NO_3$;[20] and an eight-membered ring in S_4N_4.[14]

Coordination with nitrogen has changed the configuration around the antimony from the trigonal bypyramid in crystalline $SbCl_5$[9] to a distorted octahedron with four equatorial chlorine atoms surrounding a linear Cl-Sb-N axis. Although crystallographically independent, the two $NSbCl_5$ groups are chemically equivalent. The Sb_2-Cl_{21} bond is the only one which appears to deviate significantly from the average of 2.305(3) Å. However, this deviation is very dependent on corrections for thermal motion.[23] These bond length corrections and the rms amplitudes of vibration are in Table V.

The S_2N_2 ring is rotated 10.59(21)° out of the xy plane. This and other dihedral angles are in Table VI. By averaging two dihedral angles one can obtain a measure of the rotation of the $SbCl_5$ groups out of the xy plane. This rotation (where 0° would correspond to the equatorial Sb-Cl bonds being in the xz or xy planes) is 6.7(2)° around Sb_1 and 17.8(2)° around Sb_2. These dihedral angles are shown in Figure 3. The ease of

vibrational or librational motion around the long molecular axis can be seen in the shapes of the thermal ellipsoids for the equatorial chlorine atoms, shown in Figures 1 and 3.

The octahedral geometry of the N-$SbCl_5$ groups is distorted by a shift of the equatorial chlorines toward the nitrogen donor atom such that the Cl_{eq}-Sb-N angles are all less than 90° whereas the Cl_{eq}-Sb-Cl_{ax} angles are correspondingly larger than 90°. This tendency of the equatorial chlorines to move in toward the donor atom is characteristic of $SbCl_5$ adducts. For example, $SbCl_5 \cdot SeOCl_2$,[10] $SbCl_5 \cdot S_4N_4$,[13] and $SbCl_5 \cdot CH_3CN$[22] exhibit average Cl_{eq}-Sb-donor atom angles of 86.2°, 89.0° and 84.9° respectively. The average Sb-Cl bond length in $S_2N_2(SbCl_5)_2$, 2.305(3) Å, falls at the short end of the range of distances previously reported for similar adducts. Some of these are $SbCl_5 \cdot SO_2(CH_3)_2$, 2.32 Å;[10] $SbCl_5 \cdot POCl_3$, 2.33 Å;[11] $SbCl_5 \cdot SeOCl_2$, 2.34 Å;[10] $SbCl_5 \cdot PO(CH_3)_3$, 2.34 Å;[11] $SbCl_5 \cdot SO(C_6H_5)_2$, 2.35 Å;[10] $SbCl_5 \cdot CH_3CN$, 2.36 Å;[22] and $SbCl_5 \cdot S_4N_4$, 2.39 Å.[13] The $SbCl_5$ bond lengths reported for solid antimony pentachloride at -30° are 2.29 Å for the three basal chlorines and 2.34 Å for the two apical chlorines (average = 2.31 Å).[9]

We find, then, that in comparison with known structures of similar donor → $SbCl_5$ adducts, $S_2N_2(SbCl_5)_2$ contains the longest Sb-N bond, the shortest Sb-Cl bonds, and the greatest displacement of the equatorial chlorines toward the donor atom (smallest average Cl_{eq}-Sb-donor atom angle). It appears that all three properties are functions of the strength of the adduct, and the data summarized in Table VII show that $S_2N_2(SbCl_5)_2$ is then the weakest such adduct reported to date. This correlation is apparently a general property of electron donor-acceptor complexes. In a recent review of this type of complex, Prout and Wright[23] presented an analogous table of these properties for a series of N → BF_3 adducts which

showed the same trends with increasing donor strength that we describe here for N-$SbCl_5$ adducts.

Table VII

	$S_4N_4 \cdot SbCl_5$ [a]	$CH_3CN \cdot SbCl_5$ [b]	$S_2N_2(SbCl_5)_2$ [c]	$SbCl_5$ [d]
N-Sb dist. Å	2.17	2.23	2.283	
Sb-Cl dist. Å	2.39	2.36	2.305	2.31
Cl_{eq}-Sb-N (°)	89.0	84.9	83.04	

a) Reference 13

b) Reference 22

c) This work

d) Reference 9

Table I. Observed and calculated structure amplitudes (in electron × 5) for $S_2N_2(SbCl_5)_2$

K	L	FO	FC
***** H = 0 *****			
0	0	0	12731
0	12	1714	1608
0	16	746	676
***** H = 1 *****			
0	1	62	55
0	3	245	251
0	5	403	848
0	7	68	90
0	9	79	22
0	13	162	182
1	2	1362	1338
1	6	907	972
1	10	183	171
1	14	252	229
***** H = 2 *****			
0	0	706	657
0	4	959	990
0	8	623	623
0	10	1070	1107
0	12	296	297
0	14	1281	1284
0	18	335	368
1	1	265	230
1	3	283	284
1	5	325	338
1	7	442	442
1	11	119	109
2	4	836	755
2	8	2144	2075
2	12	1699	1668
2	16	537	476
***** H = 3 *****			
1	0	1140	1081
1	2	408	391
1	4	451	453
1	6	329	325
1	8	498	453
1	10	92	73
1	12	253	245
1	14	196	184
1	16	108	97
2	1	331	357
2	3	246	260
2	5	391	429
2	9	366	392
2	11	55	54
2	13	78	81
2	15	73	81
3	2	909	849
3	6	844	852
3	10	245	237
3	14	519	468
***** H = 4 *****			
0	2	130	126
0	4	1825	1875
0	6	649	597
0	8	2130	2176
0	10	373	361
0	12	1111	1118
0	14	204	203
0	16	477	477
1	1	385	363
1	3	384	396
1	5	497	509
1	7	323	325
1	9	168	171
1	11	101	98
1	13	228	249
2	2	1648	1644
2	4	315	297
2	6	2224	2273
2	8	301	236
2	10	901	891
2	12	233	210
2	14	678	840
2	16	70	33
3	1	531	527
3	3	419	426
3	5	313	371
3	7	96	107
3	9	287	299
3	13	187	165
4	0	1126	1059
4	4	762	731
4	8	1066	1045
4	12	704	717
4	16	312	316
***** H = 5 *****			
0	1	1339	1371
0	5	289	293
0	7	315	348
0	9	416	445
0	11	157	174
1	2	1556	1543
1	4	1209	1213
1	6	1427	1478
1	8	1046	1027
1	10	295	330
1	12	374	365
1	14	509	561
1	16	136	131
2	1	341	339
2	3	789	823
2	5	407	471
2	7	720	698
2	9	92	108
2	11	194	179
2	13	177	175
2	15	159	156
3	0	1790	1830
3	2	121	157
3	4	872	835
3	6	346	368
3	8	1241	1203
3	10	121	126
3	12	656	652
3	14	206	166
3	16	204	211
4	1	311	327
4	3	123	123
4	5	260	263
4	7	329	293
4	9	189	211
4	11	200	207
4	13	220	221
4	15	84	94
5	2	1322	1280
5	6	1611	1593
5	10	540	604
5	14	587	575
***** H = 6 *****			
0	0	1482	1548
0	2	2288	2374
0	4	1219	1153
0	6	1959	1978
0	8	413	420
0	10	1014	1043
0	12	315	354
0	14	718	723
1	1	408	423
1	3	255	247
1	7	362	393
1	9	244	230
1	11	210	203
1	13	174	179
1	15	143	97
2	2	942	930
2	4	2176	2209
2	6	625	634
2	8	1446	1460
2	10	159	170
2	12	823	852
2	14	117	114
2	16	308	375
3	1	295	293
3	3	457	467
3	5	263	246
3	7	383	383
3	9	240	173
3	11	90	102
3	13	217	211
3	15	138	145
4	0	658	643
4	2	1603	1549
4	4	532	536
4	6	1316	1275
4	8	286	258
4	10	751	759
4	14	489	465
5	1	760	758
5	3	351	359
5	5	358	328
5	7	316	320
5	9	279	276
5	11	239	237
5	13	117	107
5	15	76	98
6	0	1816	1736
6	4	1775	1738
6	6	1089	1071
6	12	634	658
6	16	265	266
***** H = 7 *****			
0	1	630	614
0	3	469	498
0	5	641	627
0	7	530	535
0	9	190	158
0	11	70	71
0	13	251	239
0	15	197	195
1	0	1528	1919
1	2	1229	1165
1	4	656	565
1	6	1178	1156
1	8	888	869
1	10	353	351
1	12	505	496
1	14	428	409
1	16	234	239
2	1	763	755
2	3	249	221
2	5	476	498
2	7	541	530
2	9	274	265
2	11	263	241
2	13	133	152
2	15	111	113
3	2	1750	1717
3	4	101	84
3	6	1667	1643
3	8	597	528
3	10	646	641
3	12	282	269
3	14	571	562
3	16	146	131
4	1	593	577
4	3	429	433
4	5	568	481
4	7	456	428
4	9	375	368
4	11	166	150
4	13	220	220
4	15	158	140
5	0	2396	2432
5	2	273	267
5	4	1602	1701
5	6	547	506
5	8	1202	1168
5	10	223	223
5	12	782	768
5	14	420	434
5	16	298	299
6	1	752	738
6	3	732	724
6	5	634	606
6	7	393	368
6	9	297	289
6	11	223	229
6	13	239	230
6	15	141	148
7	2	2548	2534
7	6	1811	1750
7	10	473	485
7	14	541	540
***** H = 8 *****			
0	0	1795	1823
0	2	778	753
0	4	1753	1747
0	6	516	548
0	8	1073	1113
0	10	216	222
0	12	737	717
0	14	275	272
0	16	356	352
1	1	276	279
1	3	344	339
1	5	397	392
1	7	316	331
1	9	104	129
1	11	182	177
1	13	73	112
1	15	82	86
2	0	649	671
2	2	2004	2015
2	4	338	299
2	6	1216	1250
2	8	222	242
2	10	815	831
2	12	270	259
2	14	359	367
2	16	88	69
3	1	492	477
3	3	480	471
3	5	80	80
3	7	354	371
3	9	110	104
3	11	202	174
3	13	80	66
4	0	1056	1019
4	2	196	216
4	4	1047	1004
4	6	123	129
4	8	538	538
4	10	97	117
4	12	441	427
4	14	144	165
5	1	185	169
5	3	333	334
5	5	286	261
5	7	221	221
5	11	145	140
5	13	67	101
5	15	114	117
6	0	960	860
6	2	852	798
6	4	624	591
6	6	651	629
6	8	316	316
6	10	543	531
6	12	158	149
6	14	248	238
7	1	504	478
7	3	465	418
7	5	331	362
7	7	422	427
7	9	185	231
7	11	237	230
7	13	107	111
8	0	125	160
8	4	465	433
8	8	366	320
8	14	227	205
***** H = 9 *****			
0	1	729	690
0	3	465	465
0	5	292	278
0	7	542	549
0	9	353	355
0	11	124	125
0	13	258	239
1	0	1331	1287
1	2	790	751
1	4	541	517
1	6	797	811
1	8	563	572
1	10	367	343
1	12	242	231
1	14	395	368
2	1	579	564
2	3	120	130
2	5	617	647
2	7	339	360
2	9	258	274
2	11	86	92
2	13	263	251
2	15	143	136
3	0	863	877
3	2	350	369
3	4	572	534
3	6	492	447
3	8	665	666
3	10	105	118
3	12	454	442
3	14	195	177
4	1	351	351
4	3	162	168
4	5	367	321
4	7	223	233
4	9	220	214
4	11	106	107
4	13	263	248
4	15	80	63
5	2	711	688
5	6	807	817
5	10	560	541
5	14	413	394
6	1	431	414
6	3	175	192
6	5	304	304
6	7	303	298
6	9	245	251
6	11	152	155
6	13	166	167
7	0	1094	1080
7	2	221	232
7	4	979	927
7	6	158	179
7	8	662	669
7	10	124	125
7	12	563	539
8	1	267	276
8	3	172	162
8	5	427	429
8	7	148	201
8	9	200	218
8	11	78	103
8	13	173	165
9	2	756	769
9	6	603	621
9	10	531	502
***** H = 10 *****			
0	0	1392	1410
0	2	341	330
0	4	925	892
0	6	481	464
0	8	798	802
0	10	727	661
0	12	568	483
0	14	225	240
1	1	281	278
1	3	272	285
1	7	256	246
1	9	98	76
1	11	102	95
2	0	93	90
2	2	392	373
2	4	583	568
2	6	621	639
2	8	344	353
2	10	368	289
2	12	295	294
2	14	250	260
3	1	147	153
3	3	82	42
3	5	258	274
3	7	74	101
3	9	168	94
3	11	75	67
3	13	86	67
4	0	283	366
4	2	726	716
4	4	208	222
4	6	401	410
4	8	403	383
4	10	454	429
4	12	281	258
4	14	137	156
5	1	264	192
5	7	90	97
5	9	207	191
5	11	110	135
6	0	401	436
6	2	543	518
6	4	566	561
6	6	378	379
6	8	338	338
6	10	141	165
6	12	195	205
7	1	137	141
7	3	258	264
7	5	292	290
7	7	161	166
7	9	148	143
7	11	130	118
7	13	114	116
8	0	470	454
8	2	459	459
8	4	272	267
8	6	288	293
8	8	138	132
8	10	182	194
8	12	97	86
9	1	258	238
9	3	233	243
9	5	122	132
9	7	172	172
9	9	186	191
9	11	114	108
10	0	242	217
10	4	135	135
10	6	78	72
***** H = 11 *****			
0	1	302	298
0	3	300	303
0	5	160	165
0	7	634	618
0	9	104	105
0	11	245	240
0	13	172	179
1	0	715	715
1	2	265	258
1	4	491	478
1	6	245	238
1	8	538	541
1	10	120	130
1	12	296	302
1	14	163	158
2	1	467	469
2	3	303	295
2	5	339	318
2	7	370	391
2	9	239	260
2	11	227	220
2	13	198	195
3	0	712	720
3	2	568	533
3	4	428	445
3	6	629	621
3	8	300	302
3	10	399	401
3	12	129	146
3	14	249	271
4	1	559	555
4	3	404	395
4	5	292	289
4	7	459	451
4	9	198	190
4	11	229	220
4	13	188	176
5	0	970	977
5	2	195	193
5	4	1019	1602
5	6	99	114
5	8	791	766
5	12	475	470
6	1	467	424
6	3	440	437
6	5	333	312
6	7	451	422
6	9	185	206
6	11	239	227
6	13	187	180
7	0	282	267
7	2	836	824
7	4	177	165
7	6	704	709
7	10	577	550
8	1	425	348
8	3	343	349
8	5	318	318
8	7	314	325
8	9	212	213
8	11	200	199
9	0	703	708
9	2	119	94
9	4	760	763
9	6	66	32
9	8	549	540
10	1	219	214
10	3	256	263
10	5	133	147
10	7	246	240
10	9	69	73
11	2	473	480
11	6	399	431
***** H = 12 *****			
0	0	520	528
0	2	1191	1159
0	4	940	912
0	6	1031	1032
0	8	511	473
0	10	455	454
1	1	302	265
1	5	210	228
1	7	122	135
1	9	114	119
1	13	66	82
2	0	768	698
2	2	340	331
2	4	466	439
2	6	153	177
2	8	530	511
2	10	257	269
2	12	290	367
3	1	162	166
3	3	163	80
3	7	214	192
3	9	157	130
3	13	81	87
4	0	364	371
4	2	650	651
4	4	411	412
4	6	724	711
4	8	136	183
4	10	330	334
4	12	98	167
5	1	317	336
5	3	294	314
5	5	368	368
5	7	269	197
5	9	161	157
5	11	81	86
6	0	369	391
6	2	162	150
6	4	418	442
6	6	112	95
6	8	338	353
6	10	165	167
6	12	260	223
7	1	302	403
7	3	366	361
7	5	290	226
7	7	248	244
7	9	151	153
7	11	158	142
8	2	460	457
8	6	315	310
8	8	109	58
8	10	164	166
9	1	201	309
9	3	203	164
9	5	347	336
9	7	116	160
9	9	173	177
10	0	119	92
10	2	85	81
10	4	121	103
10	6	127	120
10	8	84	43
11	1	127	134
11	3	132	132
11	5	89	86
11	7	112	113
12	0	109	87
***** H = 13 *****			
0	1	679	682
0	3	408	446
0	5	648	682
0	7	409	478
0	9	360	403
0	11	310	277
1	0	351	342
1	2	957	948
1	4	323	330
1	6	692	695
1	8	308	305
1	10	429	424
1	12	190	167
2	1	694	678
2	3	641	647
2	5	366	443
2	7	310	321
2	9	351	353
2	11	240	240
3	0	835	831
3	2	443	443
3	4	754	746
3	6	336	328
3	8	458	467
3	10	217	234
3	12	243	278
4	1	631	633
4	3	443	431
4	5	488	495
4	7	359	330
4	9	265	299
4	11	222	225
5	0	260	246
5	2	1037	1026
5	4	161	158
5	6	733	736
5	10	449	456
6	1	332	325
6	3	282	289
6	5	204	293
6	7	316	317
6	9	225	246
7	0	602	598
7	2	74	66
7	4	659	643
7	6	74	27
7	8	656	659
8	1	303	302
8	3	316	326
8	5	304	295
8	7	307	300
8	9	213	231
9	2	728	713
9	6	559	556
10	1	399	390
10	3	291	293
10	5	273	311
10	7	221	219
11	0	480	466
11	2	192	198
11	4	429	465
12	1	237	248
***** H = 14 *****			
0	0	1320	1287
0	2	552	514
0	4	649	633
0	6	241	242
0	8	569	589
0	10	206	214
1	1	369	369
1	3	183	172
1	5	243	245
1	7	253	257
1	9	148	153
2	0	102	108
2	2	611	600
2	4	228	228
2	6	519	520
2	10	258	266
3	1	226	224
3	3	112	85
3	5	151	159
3	7	210	215
4	0	610	599
4	2	387	377
4	4	458	454
4	6	138	144
4	8	349	372
4	10	113	112
5	1	222	228
5	3	108	128
5	5	152	152
5	7	113	122
5	9	151	135
6	0	78	58
6	2	233	230
6	4	112	105
6	6	263	204
6	8	168	76
7	1	170	194
7	3	204	204
7	5	198	219
7	7	152	165
8	0	238	233
8	4	266	201
8	6	78	49
9	1	228	236
9	3	223	243
9	5	178	190
10	0	196	208
10	4	156	168
***** H = 15 *****			
0	1	144	157
0	3	101	103
0	5	163	290
0	7	94	90
0	9	257	234
1	0	178	197
1	4	281	272
1	8	160	163
2	1	283	274
2	3	314	301
2	5	206	208
2	7	241	245
2	9	178	167
3	0	143	145
3	2	363	359
3	4	226	217
3	6	203	217
3	8	79	105
4	1	464	394
4	3	322	304
4	5	334	336
4	7	163	166
5	0	498	512
5	4	490	476
5	8	204	269
6	1	295	290
6	3	212	226
6	5	281	295
6	7	170	188
7	0	125	126
7	2	436	460
7	6	321	329
8	1	240	247
8	3	260	255
8	5	226	220
9	0	401	410
9	2	86	78
***** H = 16 *****			
0	0	156	145
0	2	312	301
0	4	217	208
0	6	285	295
1	1	139	101
1	3	68	65
1	5	69	64
1	7	245	221
2	0	332	340
2	2	123	125
2	4	241	257
2	6	75	74
3	1	224	225
3	3	73	94
3	5	165	147
3	7	176	172
4	0	77	48
4	2	324	331
4	6	261	263
5	1	197	190
5	3	233	243
5	5	103	92
6	0	396	406
6	2	91	87
6	4	349	355
7	1	213	215
7	3	169	170
***** H = 17 *****			
0	1	81	72
0	3	163	192
0	5	91	82
1	0	65	54
1	4	125	130
2	1	117	119
2	3	167	157
3	0	65	90
3	4	160	160
4	1	65	65
4	3	133	148

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Table II

Positional and Thermal Parameters ($\times 10^5$) for $S_2N_2(SbCl_5)_2$

Atom	Position	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb_1	8d	03348(6)	1/4	1/8	305(4)	487(7)	420(6)	0	0	17(8)
Sb_2	8d	48558(6)	1/4	1/8	319(5)	402(6)	457(6)	0	0	21(7)
Cl_{11}	16e	05877(33)	40153(33)	14122(66)	842(26)	411(21)	2294(76)	154(20)	113(45)	7(36)
Cl_{12}	16e	04539(27)	23087(71)	27216(28)	547(17)	2097(69)	476(17)	70(40)	17(14)	181(34)
Cl_{13}	8d	-12118(27)	1/4	1/8	306(17)	1476(57)	708(27)	0	0	51(63
Cl_{21}	16e	46035(33)	39338(40)	16963(55)	648(23)	647(31)	2559(97)	- 1(20)	- 36(32)	-798(42)
Cl_{22}	16e	47346(35)	20357(71)	26555(40)	742(28)	2729(126)	710(31)	-273(37)	-106(20)	657(49)
Cl_{23}	8d	64049(26)	1/4	1/8	299(16)	776(35)	1053(37)	0	0	- 74(51)
S	16e	25907(21)	32866(18)	13913(28)	387(12)	369(13)	973(25)	- 8(12)	7(21)	-139(13)
N_1	8d	18623(70)	1/4	1/8	307(48)	353(70)	424(61)	0	0	- 33(82)
N_2	8d	33258(72)	1/4	1/8	303(48)	375(73)	500(69)	0	0	-170(89)

[a]The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III

Non-Bonded Distances Under 3.8 Å

Intramolecular Distances[a]				Intermolecular Distances		
Cl_{13}-Cl_{11}	3.522(6)	Cl_{23}-Cl_{21}	3.507(6)	Cl_{13}-Cl_{23}	(1)[b]	3.559(6)
Cl_{13}-Cl_{12}	3.392(5)	Cl_{23}-Cl_{22}	3.388(6)	Cl_{13}-S	(2)	3.745(4)
Cl_{11}-Cl_{12}	3.268(11)	Cl_{21}-Cl_{22}	3.209(12)	Cl_{12}-Cl_{23}	(3)	3.703(5)
Cl_{11}-Cl_{12}'	3.225(12)	Cl_{21}-Cl_{22}'	3.228(10)	Cl_{12}-Cl_{21}	(4)	3.758(11)
Cl_{11}-N_1	2.968(8)	Cl_{21}-N_2	2.951(9)	Cl_{12}-Cl_{22}	(5)	3.337(11)
Cl_{12}-N_1	3.121(8)	Cl_{22}-N_2	3.111(9)	Cl_{12}-S	(4)	3.521(6)
Cl_{11}-S	3.183(6)	Cl_{21}-S	3.193(6)	Cl_{11}-Cl_{11}	(6)	3.425(11)
Sb_1-S	3.574(3)	Sb_2-S	3.587(3)	Cl_{21}-Cl_{21}	(7)	3.397(11)
N_1-N_2	2.186(15)			S-Cl_{22}	(8)	3.568(6)
S-S'	2.390(5)					

a) Primed atoms are related to those in Table II by the crystallographic (and molecular) two-fold axis. b) These numbers correspond to the following transformations of the positions given in Table II:

1	x - 1	y	z	7	-x + 1	-y + 1	z
2	y - ½	x	z - ¼	8	½ - y	1 - x	z - ¼
3	½ - y	x - ½	½ - z				
4	y - ½	½ - x	½ - z				
5	½ - x	y	3/4 - z				
6	-x	-y + 1	z				

Table IV

Bond Distances and Angles in $S_2N_2(SbCl_5)_2$

Bond	Distance (Å) Sb_1	Distance (Å) Sb_2	Atoms[a]	Angle (Deg) Sb_1	Angle (Deg) Sb_2
S-N	1.616(7)	1.623(8)	S-N-S'	95.39(59)	94.85(61)
Sb-N	2.281(10)	2.285(11)	N_1-S-N_2	84.88(42)	
Sb-Cl_1	2.308(5)	2.282(5)	Sb-N-S	132.31(30)	132.57(31)
Sb-Cl_2	2.313(4)	2.300(6)	N-Sb-Cl_1	80.58(12)	80.50(12)
Sb-Cl_3	2.310(4)	2.313(4)	N-Sb-Cl_2	85.59(10)	85.49(13)
			N-Sb-Cl_3	180	180
			Cl_1-Sb-Cl_2	90.03(37)	88.91(34)
			Cl_1-Sb-Cl_2'	88.53(36)	89.60(34)

Wtd. Av. Bond Distances

Bond Type	No.	Av. Distance
Sb-Cl	6[b]	2.305(2)
S-N	2	1.619(5)
Sb-N	2	2.283(8)

Wtd. Av. Bond Angles

Angle	No.	Av. Angle
S-N-S	2	95.11(42)
Cl_1-Sb-N	2	80.54(9)
Cl_2-Sb-N	2	85.55(8)
Cl_1-Sb-Cl_2	4	89.26(18)

[a]The primed atoms are related to those in Table II by the two-fold rotation.

[b]This is the number of crystallographically independent bonds; the averaging is over all 10 Sb-Cl bonds.

Table V

Root Mean-Square Amplitudes of Vibration Along Principle Axes

Atom	Axis 1 Å	Axis 2 Å	Axis 3 Å
Sb_1	0.1858(13)	0.2248(19)	0.2365(21)
Sb_2	0.1899(14)	0.2117(17)	0.2378(16)
Cl_{13}	0.1858(52)	0.2937(57)	0.4089(80)
Cl_{23}	0.1837(50)	0.2932(73)	0.3616(69)
Cl_{11}	0.2021(57)	0.3158(50)	0.5309(88)
Cl_{12}	0.2358(44)	0.2483(41)	0.4897(81)
Cl_{21}	0.2018(62)	0.2707(47)	0.5880(109)
Cl_{22}	0.2496(61)	0.2826(56)	0.5804(129)
S	0.1957(36)	0.2093(34)	0.3500(44)
N_1	0.1863(144)	0.1969(229)	0.2303(183)
N_2	0.1722(276)	0.1851(148)	0.2718(236)

Bond Lengths Corrected for Thermal Motion

Bond	Distances, Å[a]	Distances, Å[b]	Distances Å[c]
$S-N_1$	1.616(7)		1.695(7)
$S-N_2$	1.623(8)		1.705(8)
Sb_1-N_1	2.281(10)		2.325(11)
Sb_2-N_2	2.285(11)	2.285(11)	2.329(11)
Sb_1-Cl_{11}	2.308(5)	2.368(5)	2.406(5)
Sb_1-Cl_{12}	2.313(4)	2.358(4)	2.397(4)
Sb_1-Cl_{13}	2.310(4)	2.341(4)	2.388(4)
Sb_2-Cl_{21}	2.282(5)	2.353(6)	2.394(6)
Sb_2-Cl_{22}	2.300(6)	2.372(6)	2.407(6)
Sb_2-Cl_{23}	2.313(4)	2.338(4)	2.382(4)

a - uncorrected for thermal motion
b - corrected for thermal motion - riding model (ref. 22)
c - corrected for thermal motion - independent model (ref. 22)

Table VI

Dihedral Angles Between Planes Defined by Three Atoms

Plane 1	Plane 2	Angle, deg
Cl_{11}-Sb_1-Cl_{13}	Cl_{12}-Sb_1-Cl_{13}	90.76(37)
Cl_{11}-Sb_1-Cl_{13}	Cl'_{12}-Sb_1-Cl_{13}	89.24(37)
Cl_{11}-Sb_1-Cl_{13}	N_1-S-N_2	4.23(34)
Cl_{11}-Sb_1-Cl_{13}	x,y plane	6.36(26)
Cl_{12}-Sb_1-Cl_{13}	Cl_{22}-Sb_2-Cl_{23}	10.49(43)
Cl_{21}-Sb_2-Cl_{23}	Cl_{22}-Sb_2-Cl_{23}	89.65(34)
Cl_{21}-Sb_2-Cl_{23}	Cl'_{22}-Sb_2-Cl_{23}	90.35(34)
N_1-S-N_2	x,y plane	10.59(21)
Cl_{21}-Sb_2-Cl_{23}	N_1-S-N_2	7.36(31)
Cl_{21}-Sb_2-Cl_{23}	x,y plane	17.96(23)
Cl_{22}-Sb_2-Cl_{23}	x,y plane	107.60(27)
Cl_{12}-Sb_1-Cl_{13}	x,y plane	97.12(26)

Legends for Figures

Figure 1. A drawing of the $S_2N_2(SbCl_5)_2$ molecule. The horizontal axis is a; the vertical axis is b. The $SbCl_5$ groups on the left and right contain Sb_1 and Sb_2, respectively. The thermal ellipsoids in this and the following drawings represent 50% probability contours.

Figure 2. A perspective drawing of the S_2N_2 ring in $S_2N_2(SbCl_5)_2$ as viewed normal to the plane of the ring.

Figure 3. A perspective drawing of $S_2N_2(SbCl_5)_2$ which shows the relative orientations of the S_2N_2 ring and the $SbCl_5$ groups. The view is down the a axis, from Sb_2 to Sb_1. The horizontal axis is -c; the vertical axis is +b.

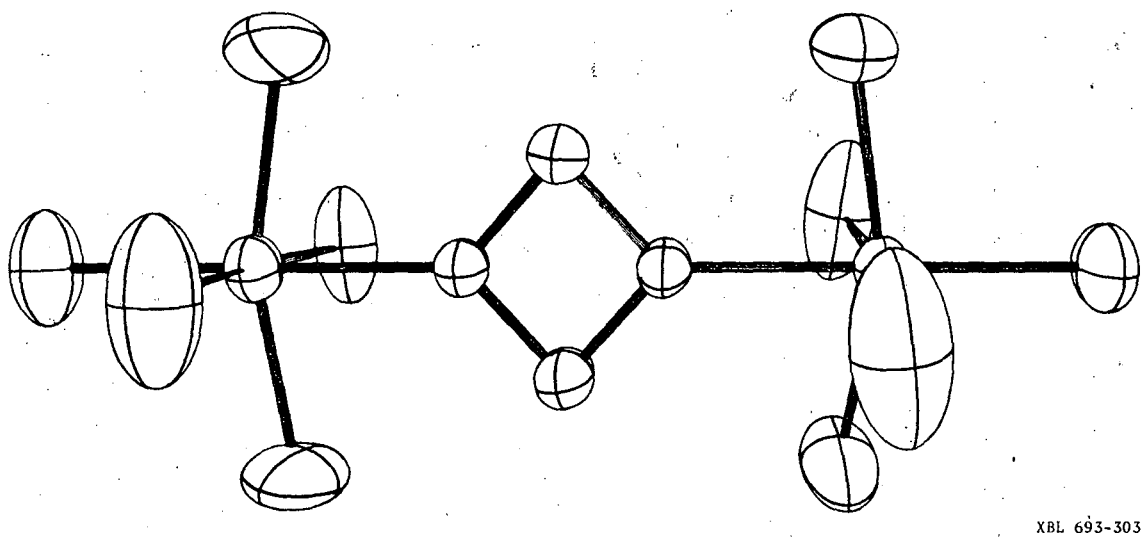

Fig. 1 (Section IV)

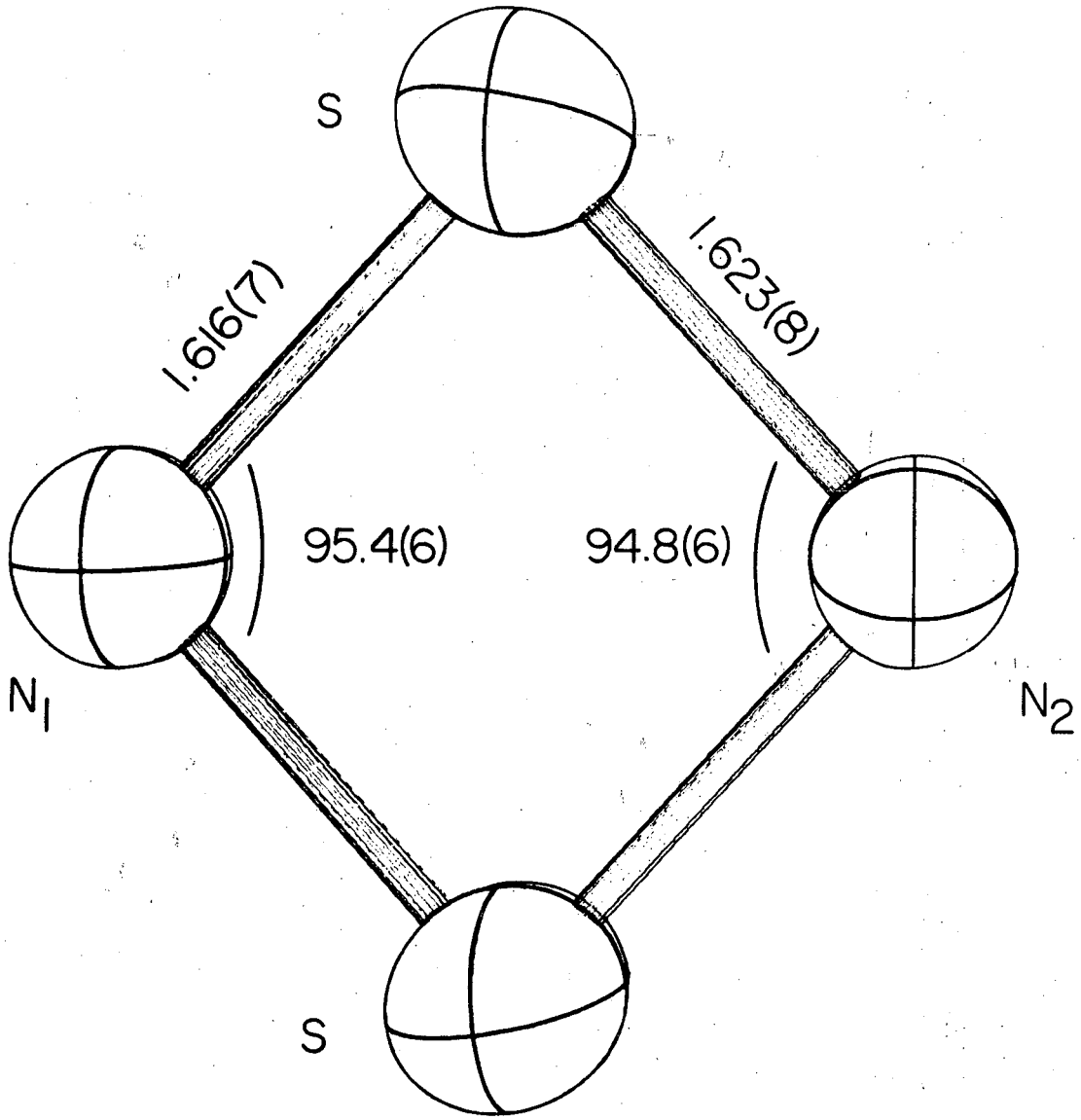

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Fig. 2 (Section IV)

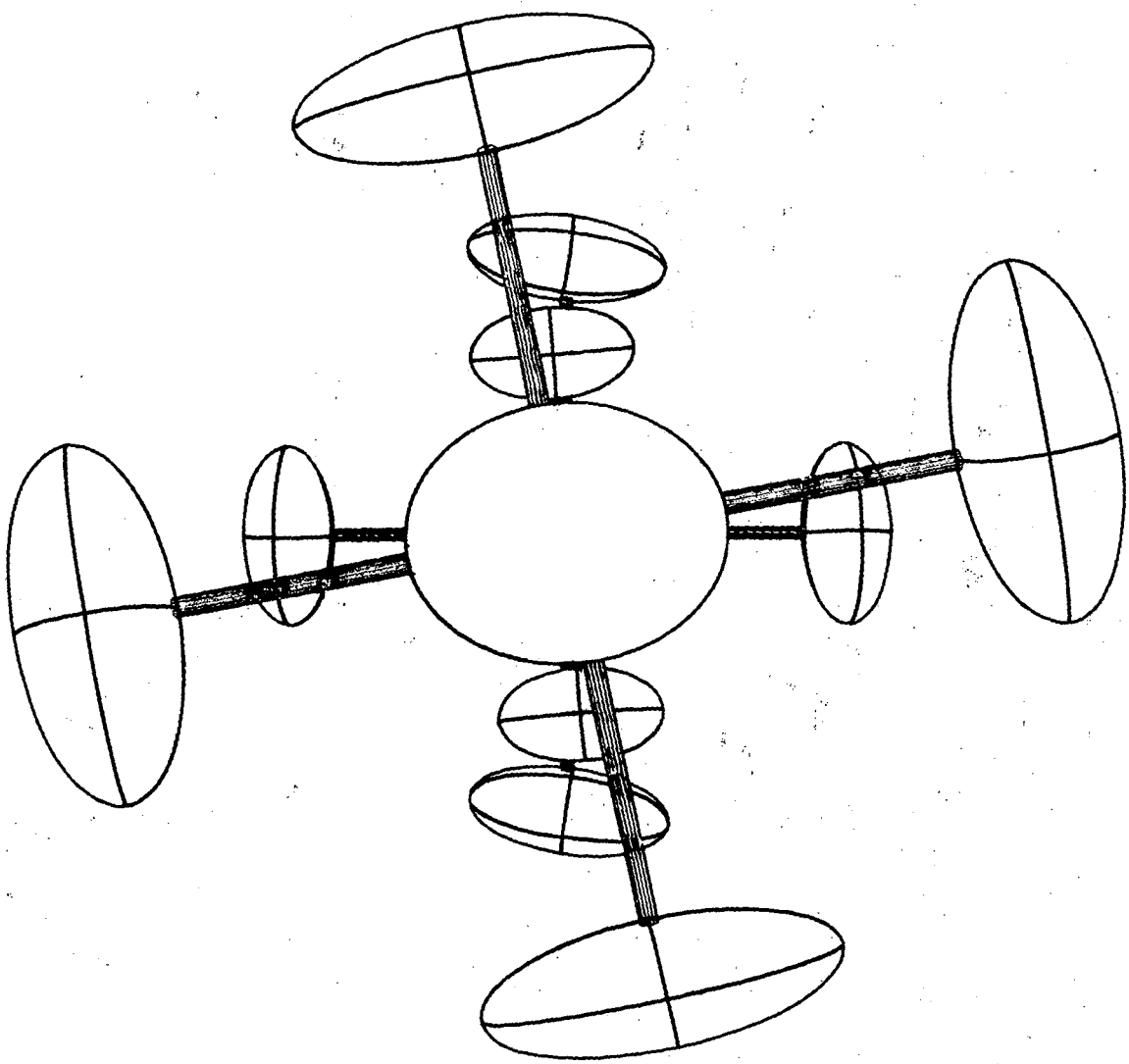

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Fig. 3 (Section IV)

References

(1) M. Becke-Goehring, Inorg. Syntheses, 6, 123 (1960).

(2) J.R.W. Warn and D. Chapman, Spectrochim. Acta, 22, 1371 (1966).

(3) R. L. Patton and W. L. Jolly, submitted for publication to Inorg. Chem., see Abstract 188, American Chemical Society Division of Inorganic Chemistry, San Francisco, California, April, 1968.

(4) Programs for the CDC 6400 computer used in this study were Zalkin's EULERA and AUDIT programs for diffractometer data processing and the FORDAP Fourier program; Hamilton's GONO9 absorption program; Iber's modifications of the Busing-Levy ORFLS least-squares and ORFFE error function program; and Johnson's ORTEP thermal ellipsoid plotting program.

(5) J.A. Ibers, "International Tables for X-ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(6) D.T. Cromer, Acta Cryst., 18, 17 (1965).

(7) J.A. Ibers and W.C. Hamilton, ibid, 17, 781 (1964).

(8) Since $I\bar{4}2d$ lacks a center of symmetry, the intensities of centrosymmetrically related reflections are not identical. The correct assignment of the indices corresponds to a determination of the absolute configuration of the structure, even though the crystal is composed of racemic pairs of $S_2N_2(SbCl_5)_2$ molecules. The two configurations differ only in a rotation of 90° about c. That is, although the structure is its own enantiomorph, the x direction is the mirror image of the y direction. To test the assigned configuration, additional refinements were carried out with the signs of h, k and ℓ reversed. Both R_1 and R_2 were somewhat larger (5.9 and 10.0), indicating that the assigned configuration is correct.

(9) S.M. Ohlberg, J. Am. Chem. Soc., 81, 811 (1959).

(10) Y. Hermodsson, Acta. Chem. Scand., 21, 1313 (1967).

(11) C. I. Brändén and I. Lindquist, Acta. Chem. Scand., 17, 353 (1963).

(12) K. J. Wynne and W. L. Jolly, Inorg. Chem., 6, 107 (1967).

(13) D. Neubauer and J. Weiss, Z. Anorg. Allgem. Chem., 303, 28 (1960).

(14) B. D. Sharma and J. Donohue, Acta. Cryst., 16, 891 (1963).

(15) O. Glemser, A. Müller, D. Böhler, and B. Krebs, Z. Anorg. Allgem. Chem., 357, 184 (1968).

(16) D. P. Craig and N.L. Paddock, Nature, 181, 1052 (1958); D.P. Craig, J. Chem. Soc., 1959, 997.

(17) M.J.S. Dewar, E.A.C. Lucken, and M.A. Whitehead, J. Chem. Soc., 1960, 2423.

(18) A. Zalkin, T.E. Hopkins, and D.H. Templeton, Inorg. Chem., 5, 1767 (1966).

(19) G.A. Wiegers and A. Vos, Acta. Cryst., 20, 192 (1966).

(20) A.W. Cordes, R. F. Kruh, and E. K. Gordon, Inorg. Chem., 4,681 (1965).

(21) W. R. Busing and H.A. Levy, Acta. Cryst., 17, 142 (1964).

(22) H. Binas, Z. Anorg. Allgem. Chem., 352, 271 (1967).

(23) C. K. Prout and J.D. Wright, Angew. Chem. Int. Ed., 7, 659 (1968).

PART II.

STUDIES OF TRITHIAZYL TRICHLORIDE, $S_3N_3Cl_3$

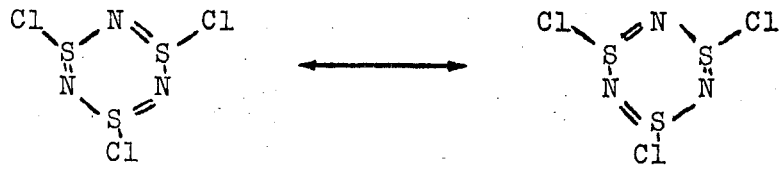
ABSTRACT

The depolymerization to NSCl of its cyclic trimer, $S_3N_3Cl_3$, has been studied and a reversible equilibrium found to exist between the solid trimer and the gaseous monomer at 31 - 60°. The equilibrium NSCl pressure is represented by the equation log P(mm) = -3360/T + 12.321 and for the reaction 1/3 $S_3N_3Cl_3(s) \longrightarrow NSCl(g)$ leads to the values ΔH^o = 15.4 ±0.5 kcal/mole and ΔS^o = 43.2 ±1.6 cal/deg mole. The direct thermal depolymerization of $S_3N_3Cl_3$ has been found to be extremely slow below 55°. Depolymerization into a closed volume shows an initial induction period of random length of very slow pressure rise followed by a rapid depolymerization rate, that is prevented or halted in the presence of chlorine, which again diminishes as the equilibrium NSCl pressure is approached. A reaction sequence explaining these observations in terms of catalysis by a decomposition product is proposed. Using a gas-flow saturation method employing a helium/chlorine carrier gas mixture to prevent depolymerization, the sublimation pressure of $S_3N_3Cl_3$ has been measured at 35 - 50° and is represented by the equation log P(μ) = -5316/T + 17.270 and yields the values ΔH^o = 24.3 ± 1.5 kcal/mole and ΔS^o = 52.1 ± 4.6 cal/deg mole for the sublimation. Combination of the above values yields the quantities ΔH^o = 21.9 ±3.0 kcal/mole and ΔS^o = 77.5 ±9.4 cal/deg mole for the gaseous depolymerization $S_3N_3Cl_3(g) \longrightarrow 3\ NSCl(g)$.

PART II. STUDIES OF TRITHIAZYL TRICHLORIDE

I. INTRODUCTION

Sulfur-nitrogen compounds are an interesting class of substances in which single, double, and triple SN bonds are found; many of these contain rings, some of which have delocalized double bonds and may be thought of as inorganic aromatic compounds. (Several good review articles concerning this class of compounds are listed for further reference.[1,2,3,4]) Most of the known halides have been formed in reactions involving the eight-membered ring S_4N_4 or its derivatives; as early as 1880, Demarcay[5] reported the formation of a yellow solid chloride of empirical composition NSCl during the passing of chlorine through a chloroform suspension of S_4N_4. This compound was first formulated as $S_4N_4Cl_4$[6,7] but a later molecular weight determination,[8] as confirmed finally by an X-ray crystal structure analysis,[9] determined its correct formula, $S_3N_3Cl_3$. The molecule consists of a six-membered ring composed of alternating sulfur and nitrogen atoms in a chair configuration with the three nitrogens 0.18Å below the plane of the sulfurs and one chlorine bonded to each sulfur in an axial position above the ring. Equivalent SN bond distances of 1.605Å[9,10] are consistent with this being an inorganic "aromatic" compound containing delocalized π bonds. These bonds have been proposed to consist of nitrogen p_π - sulfur d_π overlapping delocalized either over the entire ring as in benzene (as proposed by Craig[11]) or over separate three center S-N-S bonds as proposed by Dewar, Lucken and Whitehead.[12] The resonance structures best representing the bonding in $S_3N_3Cl_3$ are[2]



Trithiazyl trichloride may be prepared by the method originally described by Demarcay[5] and most recently revised by Schröder and Glemser[13] of passing chlorine through a suspension of S_4N_4 in an inert solvent resulting in the reaction: $3S_4N_4 + 6Cl \longrightarrow 4S_3N_3Cl_3$, or by the more convenient method recently described by Jolly and Maguire[14] utilizing the reaction:

$$3S_3N_2Cl_2 + 3Cl_2 \longrightarrow 2S_3N_3Cl_3 + 3SCl_2$$

involving chlorination of the solid $S_3N_2Cl_2$, which itself is much easier to prepare than S_4N_4.

In 1961 Glemser and Perl[15] reported that the same greenish-yellow gas which formed when chlorine reacted with NSF in the gas phase also was produced when $S_3N_3Cl_3$ was pyrolyzed <u>in vacuo</u> at 110°. This gas, shown to be NSCl by its molecular weight and analysis, condensed on cooling to a green liquid which quickly repolymerized to $S_3N_3Cl_3$. Microwave spectroscopy[16] has shown NSF to be a bent triatomic molecule with sulfur as the central atom and as the gas phase infrared absorptions of NSCl and NSF are of the same shape and only slightly different frequency[17] NSCl must have an analogous structure.

The intent of this research has been to carefully study the depolymerization of $S_3N_3Cl_3$ to NSCl with respect to the NSCl pressure and decomposition products obtained at various temperatures in hopes of finding and measuring a reversible equilibrium for the reaction

$$S_3N_3Cl_3(s) \rightleftharpoons 3NSCl(g)$$

and further, if possible, to determine whether a stable species $S_3N_3Cl_3(g)$ exists and, if so to measure the equilibria

$$\begin{array}{ccc} S_3N_3Cl_3(s) & \rightleftharpoons & S_3N_3Cl_3(g) \\ & \rightleftharpoons\ 3NSCl(g) & \end{array}$$

over a sufficient temperature range to determine the free energy, heat, and entropy changes of these processes. Thermodynamic data for the class of sulfur-nitrogen compounds we have described above is sadly lacking. To our knowledge, no thermodynamic measurements of reactions between SN compounds have been made; of the cyclic compounds only S_4N_4 has been subjected to calorimetric measurement of its heat of formation;[18,19] heats of formation and bond energies of a few non-cyclic NS compounds have been determined by mass spectrometry;[20] and recently, the thermodynamic functions of NSCl were calculated from its infrared spectrum.[21] Hopefully the results of our work can be combined with available and future thermodynamic data to aid in the understanding and prediction of reactions in sulfur-nitrogen chemistry.

II. EXPERIMENTAL SECTION

A. General

The moisture sensitivity of the materials required their manipulation in a vacuum line or in a polyethylene glove bag flushed with dry nitrogen or argon. Glass stopcocks and joints were lubricated with Kel-F No. 90 grease (3-M Co.) which was inert to the materials handled but tended to absorb some of them, and where this was intolerable either Delmar-Urry 0-4 mm stopcocks or Fischer-Porter needle valve stopcocks employing Teflon plugs seated against glass barrels with Viton o-rings were used.

The intensity and purity of solids were determined by infrared spectrometry with Perkin-Elmer Infracord spectrometers and by melting points taken in argon filled, sealed capillaries on a Mel-Temp apparatus. Volatile materials were identified and checked for purity by infrared spectrometry, mass spectrometry with a Consolidated Engineering Corporation Mass Spectrometer Model 21-620, by vapor pressure measurements, and by molecular weight determinations.

Frequent pressure measurements of systems containing gases such as Cl_2, S_2Cl_2, SCl_2 and NSCl which react rapidly with mercury necessitated the use of a glass spiral manometer (distributed by Electronic Space Products, Inc., Los Angeles, California) depicted in Fig. 1 with the sample chamber constructed for use with it. The manometer operates on the Bourdon Gauge principle, detecting pressure differentials between the sample chamber and the case by means of a flat spiral of hollow thin-walled glass from which a mirror is suspended. The glass spiral is thin enough that an increase in pressure inside the spiral (connected to the

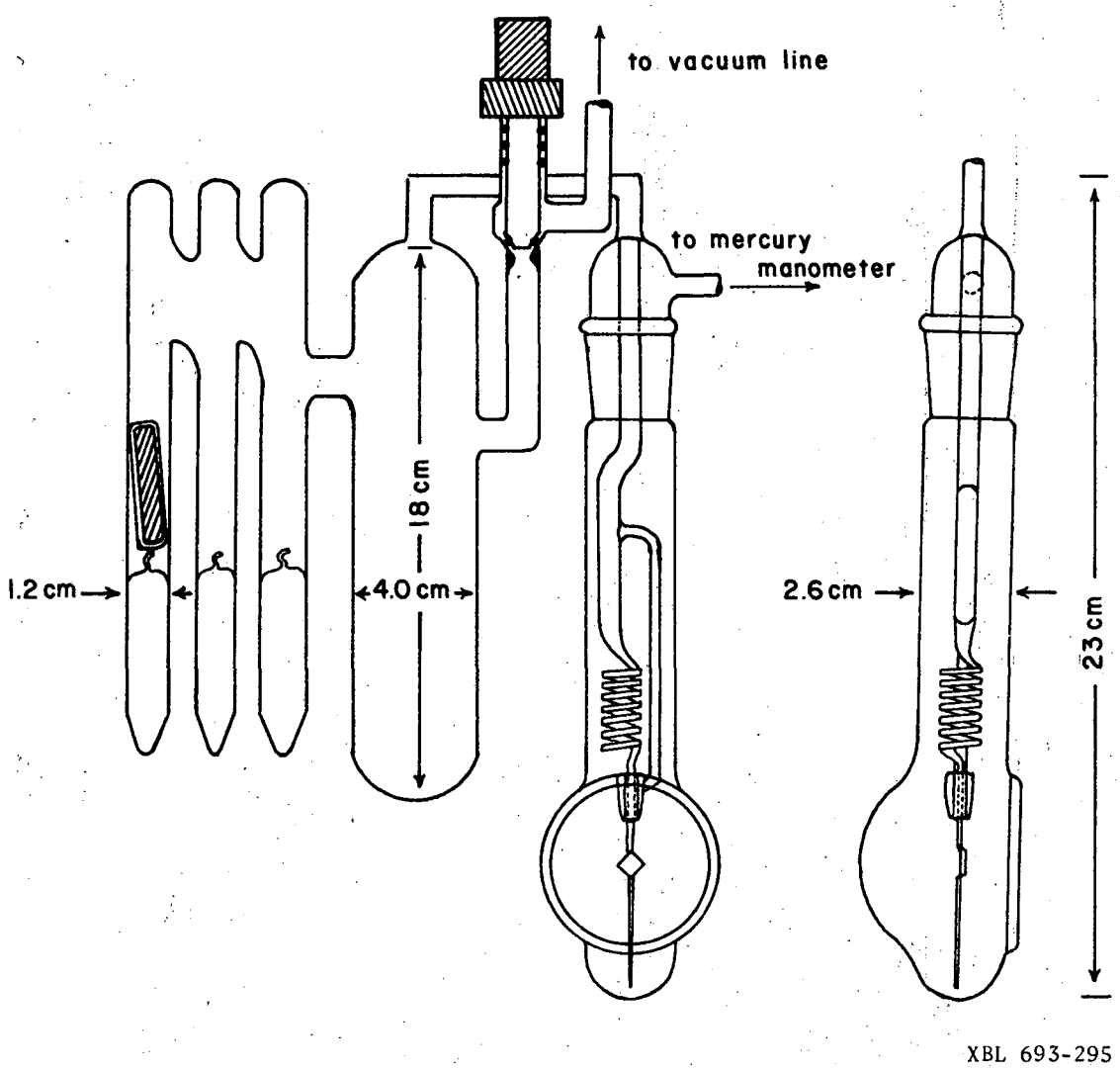


Fig. 1 Glass spiral manometer as used to determine the equilibrium pressure of NSCl.

sample chamber) relative to the case pressure outside the spiral causes the spiral to uncoil, thus turning the mirror. This uncoiling is detected, and the pressure differential causing it is measured, by noting the amount of travel along a frosted glass scale of a narrow light beam that has been reflected from the mirror. The light beam source and scale are of the type used to measure the deflection of a galvanometer. The apparatus is operable with pressures from high vacuum to one atmosphere in either the case or sample chamber. Regardless of the absolute pressure, equal pressure on both sides of the spiral results in the same "null" position of the light beam on the scale, and any deflection from this null point is proportional to and dependent only on the pressure differential. In our apparatus pressure differentials of ≤ 30 mm of Hg produced linear deflections on the scale placed approximately one meter from the mirror of ~ 1 mm/mm of Hg which were readable in a darkened, vibration-free room to ± 0.1 mm. The case pressure itself was measurable at an accuracy of ± 0.1 mm. of Hg with a cathetometer-viewed, mercury manometer constructed of 10 mm i.d. tubing to minimized meniscus effects; thus the sample chamber pressure was measurable to ± 0.2 mm of Hg. Typically, pressure measurements were made by evacuating both sides of the manometer and noting the null point on the scale, introducing (and measuring with the mercury manometer) a small pressure of dry air into either the sample chamber or the case and noting the resultant deflection to obtain a calibration factor, $\underline{f}$ = mm Hg/(mm scale deflection), placing the sample in the chamber, adding dry air to the case to return the light beam approximately to its null point, and reading the mercury manometer and the scale deflection to determine the sample pressure via the formula

$$P_{sample} = P_{case} + (\underline{f}) \times (\text{scale deflection}).$$

Remeasurement of $\underline{f}$ was only necessary when the lamp or manometer was moved or the temperature of the spiral was appreciably changed.

The manometer has the desirable property that the sample volume does not change with pressure and that the manometer, including the entire sample chamber, can be completely immersed in a constant temperature bath. A bath was constructed using a large cylindrical glass jar (8" i.d.× 17" high) surrounded by several inches of vermiculite for insulation in an open topped box with a cardboard tube inserted in a hole cut in the side to allow the light beam to reach the mirror. Suspension of the manometer and connection to the vacuum line was from above to enable raising of the bath around it without disturbance, and the bath was supported in such a way that its raised position, and thus the null point of the manometer, was reproducible (movement of the bath position changed the null point as the curvature of the glass jar wall and the differences in the refractive indices of the glass and bath liquid from that of air caused the light beam to deviate from its straight line path). The bath temperature (both oil and water were used as bath liquids) was controlled by a mercury contact thermometer connected to a mercury switch relay which turned on and off a knife immersion heater. Adjustment of the power input to the heater and, at temperatures $\leq 40°$ in mineral oil baths, addition of copper coils cooled by a constant flow of cold water, controlled fluctuations of the bath temperature to $\leq 0.05°$ as read from a total immersion mercury-in-glass thermometer with 0.1° graduations. In a system check 113.4 mm of helium at 28.7° was closed into the sample chamber of 156.9 cc volume; pressure readings taken at 12 temperatures up to

140° showed a maximum deviation of 0.15 mm from the values predicted from the perfect gas law. Introduction of materials into the sample chamber was made either by transfer from the vacuum line through a Delmar-Urry o-ring valve or by sealing the materials into breakseal-equipped tubes and glassblowing them onto the chamber; the breakseals could then be opened by magnetic manipulation of a breaker to open the sample to the chamber, even after the manometer was in the bath at a desired temperature.

Carbon tetrachloride was refluxed for 6-10 hours over P_2O_5, distilled and stored under an inert gas. Chlorine (Matheson) and S_2Cl_2 (Eastman Kodak Co.) were purified when necessary by vacuum line fractional condensation. Tetrasulfur tetranitride was prepared and purified using the method of Villena-Blanco and Jolly,[22] and S_4N_3Cl, $S_3N_2Cl_2$, and S_3N_2Cl were identified when found during this work by comparing their infrared absorptions, appearance, and thermal properties with those of known samples prepared by the method of Jolly and Maguire.[14]

B. Preparation and Preliminary Investigations of $S_3N_3Cl_3$

Trithiazyl trichloride was prepared once by the method of Schröder and Glemser[13] and thereafter by the method of Jolly and Maguire.[14] The crude product from the chlorination of S_4N_4 melted (with decomposition) at 77-78° (lit[13]:162.5); the crude product from preparations via the chlorination of $S_3N_2Cl_2$ exhibited decomposition points ranging from 76-82° (lit[14]:crude, 75°; recrystallized from CCl_4, 91°). Samples prepared by both methods exhibited the same infrared absorptions including the strongest band at 1015 cm^{-1} reported to be characterisitc of $S_3N_3Cl_3$ by Glemser and Richert[17] and produced yellow solutions in CCl_4 which turned a vivid mintgreen color above 55° but returned to yellow when cooled. The melt-

ing points of $S_3N_3Cl_3$ recrystallized from hot CCl_4 ranged from as high as 93° to as low as 73° (although all samples melted in a 1-2° range) with the highest melting samples crystallizing from solutions that had not been hot enough to produce the green color and the lowest from solutions heated above 60° in which, although the green color disappeared on cooling, an orange-brown hue remained to the previously yellow solution.

In one recrystallization the solution was heated to 65° which resulted in a very vivid, green color and, while maintained at 65°, a stream of chlorine was bubbled through the stirred solution. The green color immediately disappeared, leaving the original yellow color; when cooled, $S_3N_3Cl_3$ with mp = 95-1/4 - 96-1/4° crystallized. All further $S_3N_3Cl_3$ recrystallizations were done with the CCl_4 continually being saturated by passing Cl_2 until the solution was hot enough to dissolve all the $S_3N_3Cl_3$. No green color or other darkening of the solution occurred at < 70° and the crystallized $S_3N_3Cl_3$ consistently melted between 95 and 98°. This higher melting material exhibited the same infrared absorptions as material recrystallized without passage of chlorine. In fact, all samples recrystallized with or without chlorine passage that melted above 80° dissolved completely in CCl_4 and showed the same properties when sublimed or pyrolyzed.

A 100 ml bulb closed with a Delmar-Urry stopcock was held in an 80° oil bath for two hours during which the 100 mg of $S_3N_3Cl_3$ it contained completely vaporized to a green gas. When cooled quickly the gas condensed to a green liquid in which yellow crystals of $S_3N_3Cl_3$ (identified by their infrared spectrum) immediately began growing and soon consumed all the liquid. A similar sample was vaporized at 80° and the bulb

allowed to cool very slowly to 20°. No liquid phase was visible as the green gas slowly disappeared and yellow crystals grew on the walls. The gas remaining was opened to a KBr gas infrared cell and a spectrum was taken which showed NSCl,[17] S_2Cl_2,[23] and SCl_2[23] to be present. The infrared absorptions of the solid in the bulb corresponded to $S_3N_3Cl_3$ and a small amount of $S_3N_2Cl_2$ presumably formed in the reaction

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

The S_2Cl_2 arose from ~10% decomposition of the NSCl in the bulb to N_2 and S_2Cl_2 as detected by measurement of the nitrogen with a Toepler pump. Another 100 mg of $S_3N_3Cl_3$ was pyrolyzed in the same bulb at 80° and, while holding at 60° in a water bath, the bulb was opened to a 7 cm NaCl gas cell mounted on the Infracord while maintaining the cell at 60° with a stream of hot air. Very large NSCl absorptions were observed but none corresponded to $S_3N_3Cl_3$. While maintaining the cell at 60° the bulb was allowed to slowly cool to 20° and then reheated; the NSCl absorptions correspondingly decreased and grew in amounts much greater than simple gas thermal expansion would have caused. The bulb, and then the i.r. cell, was cooled to 20° and disconnected. After 1 day at 20° the NSCl absorptions had only slightly diminshed and even after repeatedly freezing the contents of the cell into a side arm with liquid nitrogen and rewarming to 20° some NSCl remained although each cycle decreased the NSCl peak and increased the size of a solid $S_3N_3Cl_3$ ring where the NSCl had appeared to pass through the liquid state.

The same $S_3N_3Cl_3$ pyrolysis method prepared NSCl which was quickly condensed onto a layer of frozen, degassed CCl_4. When thawed, a greenish yellow solution resulted which showed only large NSCl and no $S_3N_3Cl_3$ infrared absorptions, but after 1 day an $S_3N_3Cl_3$ peak had appeared and the NSCl peak decreased and after one week the $S_3N_3Cl_3$ appeared to be the predominant species present. When scanned while in a cell heated

above 55° a green $S_3N_3Cl_3$ solution did not show NSCl infrared absorptions which in fact, did not appear unless an $S_3N_3Cl_3$ solution had been heated several minutes at 75°. The depolymerization of $S_3N_3Cl_3$ in the 100 ml bulb, both when the bulb was initially evacuated and when initially filled with 1/2 atm. of argon, proceeded slowly enough that larger (~200 mg) samples heated at 1-2°/min were still largely present and melted normally to pools of yellow-brown liquid at 96-98°, the same temperature they had melted at in sealed argon filled capillaries. However, one sample heated under 1/2 atm. of chlorine showed no change until 116° where a brown liquid appeared which wet the solid but went away again quickly at 119° leaving a yellow solid which slowly volatized until it disappeared at 175°. Another sample under chlorine showed no change until 110° where it melted quickly to an orange liquid and completely vaporized. In both cases NSCl and $S_3N_3Cl_3$ were recovered despite > 50% decomposition based on the resultant N_2.

C. Sublimation of $S_3N_3Cl_3$

In a continually evacuated sublimator $S_3N_3Cl_3$ sublimed very slowly at 55° to a water cooled cold finger giving yellow $S_3N_3Cl_3$ on the finger while only traces of NSCl were pumped out. With a water-cooled finger at higher temperatures substantial decomposition and depolymerization resulted but not with a liquid-nitrogen cold finger; even at 80° in an evacuated system no N_2 was evolved while the -196° cold finger was covered with a blue-green solid which, when warmed to 20°, instantly returned to a yellow, completely non-volatile solid with infrared absorptions only of $S_3N_3Cl_3$. However, when ~40 mm pressure of nitrogen or helium was present during closed sublimation at 70-80° to a -196° finger a yellow-white film, and later white-to purple crystals, collected which

virtually all pumped out when warmed to 20° and proved to be NSCl with less than 5% of the material remaining as $S_3N_3Cl_3$. In the presence of nitrogen or helium at 50° however, again only $S_3N_3Cl_3$, not NSCl, sublimed to the -196° cold finger. When sublimed through a 9-inch long, 22° inlet to a mass spectrometer (Consolidated Engineering Corporation Model 21-103C) ionization chamber at 200° using 70 e.v. electrons, even though a parent $S_3N_3Cl_3^+$ peak was not detected, an $S_3N_3^+$ peak 47% as high as the largest peak ($S_2N_2^+$) was found indicating the probable intact presence of $S_3N_3Cl_3(g)$ in the vapor state.

Other species found, listed in order of descending mass, with > 1% abundance relative to $S_2N_2^+$ were:

Species	% relative abundance	Species	% relative abundance	Species	% relative abundance
$S_4N_4^+$	1	$NSCl^+$	9	Cl^+	46
$S_4N_2^+$	86	NS_2^+	7	S^+, O_2^+	79
$S_3N_3^+$	47	SCl^+	2	N_2^+	88
$S_3N_2^+$	5	N_2Cl^+	9	Cl^{++}	5
$SNCl_2^+$	22	S_2^+	6	H_2O^+	57
S_3N^+	7			OH^+	14
S_2Cl^+	3	NS^+	98	O^+	15
$S_2N_2^+$	100	HCl^+	94		

D. Measurement of the Equilibrium $S_3N_3Cl_3(s) \rightleftharpoons 3NSCl(g)$

The equilibrium pressure of NSCl(g) above $S_3N_3Cl_3(s)$ was determined at various temperatures by static pressure measurements in the thermostated constant volume, glass spiral manometer described earlier. Runs were started by glassblowing onto the manometer a breakseal equipped

tube of $S_3N_3Cl_3$ which had been finely ground in a dry bag and weighed, raising the temperature bath into place while evacuating the manometer, recording the null point with both sides evacuated, opening the $S_3N_3Cl_3$ into the sample chamber, and if not already done, setting the bath temperature. An initial sample of 84 mg in 160 ml was held at 45° for one hour but no pressure developed; the temperature was then increased to and held at 55, 60, 65 and 75° for short periods with corresponding pressure rises observed of 0.3, 1.0, 1.8, and 12.6 mm/min until a final pressure of 148 mm was reached when all the $S_3N_3Cl_3$ had vaporized. Cooling to 22° for 2 days dropped the pressure to 16 mm; reheating to 75° returned the pressure to 150 mm; but recooling to 22° lowered the pressure only to 23 mm indicating that other gases besides NSCl, presumably N_2 and other decomposition products, had built up. Another sample of $S_3N_3Cl_3$ was loaded and heated in a similar manner with similar results, and measurement of the noncondensible gas with a Toepler pump showed 15% decomposition to nitrogen had occurred. It was decided to work at 50° or below in hopes that, although slow, depolymerization to an equilibrium value would occur without more decomposition occurring than could be corrected for or ignored. Also we found that cooling of the bath caused crystals of $S_3N_3Cl_3$ to grow everywhere inside the sample chamber as NSCl condensed; some of these grew inside the spiral causing it to clog and give false readings. To prevent this a common infrared heat lamp was mounted outside the temperature bath and aimed at the spiral down a 15 mm glass tube through the insulating box. This constant bathing of only the spiral in a beam of warm infrared radiation throughout all future runs kept it sufficiently warmer than the rest of the sample chamber to prevent crystallization of material in the spiral.

A new loading of $S_3N_3Cl_3$ (0.5 mmoles) was introduced and held at 49.9°. After 24 hours the pressure had only reached 12 mm and after 40 hours was only 21 mm, but 10 hours later it had risen to 84 mm and remained constant after reaching 84.65 mm in four more hours. The temperature bath was then lowered; the sample chamber was cooled with liquid nitrogen to condense the NSCl and volatile decomposition products; and nitrogen corresponding to 0.55 mm pressure in the sample chamber was pumped out and measured with a Toepler pump. The chamber was closed, the bath again raised, and in the 30 minutes required to reheat it to 49.9° the pressure had already risen to 77 mm. After equilibration for 15 hours a constant pressure (unchanged in two hours) of 85.16 mm was present of which 0.57 mm was N_2 as shown by pumping the contents through -196° traps with the Toepler pump. A new loading of 97 mg of $S_3N_3Cl_3$ was made and, at 55° vaporized completely in 16 hours to 117 mm pressure of which 0.97 mm were nitrogen as measured by dropping the bath and freezing the condensible contents into the bottom of the chamber with liquid nitrogen and Toepler pumping out the N_2. The chamber was then closed and the bath raised and reset at a series of lower temperatures. At each temperature the pressure was followed until no change was detected over several hours and the nitrogen then measured by the above technique. The temperatures in the order used where 40.3, 45.1 35.4, 31.0, and 47.2° which in some cases involved the equilibrium being reached from above and in some cases from below its final pressure. The equilibrium was reached in at most 12 hours at each temperature, but an attempt at 26° was aborted when a pressure change of 0.1 mm per hour was still noticed after two days. The raw data, consisting of the total pressure and nitrogen pressure at each temperature, are presented in

Table I together with the NSCl pressure derived from the corrections to be described in the discussion. Two molecular weight determinations were made by carefully weighing $S_3N_3Cl_3$ samples loaded into the manometer and allowing them to completely vaporize, one at 45.1° and one at 49.5°. Found: mw = 81.9 ± 1.0 and 82.0 ± 0.5 respectively; calcd. for NSCl: 81.5.

It was noted that the depolymerization at 49.9° proceeded very slowly at first and then rapidly reached equilibrium. To explore this further a series of experiments were made in which fairly large $S_3N_3Cl_3$ samples were vaporized between 49.4 and 50.0° with the pressure rise followed with respect to time. Reevacuation of the chamber for varying lengths of time, sometimes with cooling to 25° and other times while keeping at the bath temperature, was then followed by closing and beginning another timed run. Each vaporization curve obtained when pressure vs. time was plotted showed the same general "S" shape consisting of an induction period in which the pressure rose very slowly and nearly linearly for a number of hours to somewhere between 1 and 10 mm followed by a period of rate increase to a nearly constant rapid pressure rise, followed by a steady decrease in rate as the equilibrium pressure was approached, and ending in a pressure rise of 0.1 mm/hr presumably resulting only from decomposition as, when checked, an equilibrium NSCl pressure could always be calculated consistent with previous results. It was found that the "induction period" at the beginning was an unpredictable feature of the vaporization in that the same $S_3N_3Cl_3$ sample could show an induction period which varied from less than one hour to longer than 20 hours with its length not seeming to correlate reproducibly with any factor of the solid's history. One sample was vaporized several times, one of which included closing 22 mm of nitrogen into the chamber immediately before the run; the only effect observed was a possible slight

Table I. Results of static NSCl pressure measurements

Run	T (°C)	$P_{tot.}$ (mm)	P_{N_2} (mm)	$P_{previous\ S_2Cl_2}$ (mm)	$P_{Cl_2\ added}$ (mm)	[a]P_{corr} (mm)	$P_{NSCl}=P_{Tot}=P_{Corr}$ (mm)	Used for $\Delta H°$ calc.
C-1	49.9	84.65	0.55	—	—	1.10	83.55	✓
C-2	49.9	85.16	0.57	0.55	—	1.69	83.45	✓
D-2	40.3	41.1	0.1	0.92	—	1.12	40.0	✓
D-3	45.1	59.5	0.23	1.04	—	1.5	58.0	✓
D-4	35.4	29.25	0.04	1.24	—	1.3	27.9	✓
D-6	31.0	20.47	0.01	1.26	—	1.3	19.2	✓
D-7	47.2	69.8	0.3	—	—	0.6	69.2	✓
G-1	49.55	85.3	1.65	—	—	3.3	82.0	✓
H-1	49.4	85.0	1.9	—	—	3.8	81.2	✓
K-2	49.9	93.4	3.2	—	2.8	9.2	84.2	✓
K-3	49.9	102.0	6.6	—	5.35	18.5	83.5	✓
L-2	52.1	100.7	1.65	—	—	3.3	97.4	✓
M-1	58.0	167.7	3.85	—	—	7.7	160.0	
M-2	63.5	257.2	8.9	—	—	17.8	239.4	
M-3	66.7	324.9	15.1	—	—	30.2	294.7	
M-4	70.2	414.9	36.3	—	—	72.6	342.3	
N-1	55.2	129.2	0.95	—	—	1.9	127.3	
N-2	60.0	187.7	1.65	—	—	3.3	184.4	
N-3	60.0	218.7	11.95	—	—	23.9	194.8	
N-4	60.0	261.0	25.7	—	36.4	87.8	173.2	✓
O-1	65.0	381.0	22.85	—	56.3	102.0	279.0	
O-2	60.0	273.5	18.85	—	59.6	97.3	176.2	✓
O-3	57.5	267.7	29.2	—	62.6	121.0	141.7	✓

[a] $P_{corr} = 2P_{N_2} + P_{previous\ S_2Cl_2} + P_{Cl_2\ added}$

reduction in the maximum vaporization rate. Chlorine, however, had a very noticable effect; its introduction (2.3 mm) at the beginning caused an initial 0.5 mm rise in the first 1/4 hour followed by no increase for 20 hours after which the system was evacuated for an hour and reclosed whence the pressure rose reluctantly to only 8 mm in the first 60 hours before beginning the rapid rise portion of the "S" curve. When introduced during the rapid depolymerization period (by breaking a breakseal tube of chlorine already in the chamber) Cl_2 killed the rapid rise and the depolymerization returned to a very low rate; this was done twice at 49.9°: once (with 2.8 mm Cl_2) the rapid rise eventually returned, and the second time (5.35 mm Cl_2) only the slow pressure increase occurred for the 15 days it took the pressure to reach equilibrium. Both times, initially upon adding the chlorine, the pressure rose by the amount added plus an additional 1/2 mm in the next few minutes before leveling off. Both of these runs, however, yielded the same equilibrium NSCl pressure after the chlorine and the decomposition products present were subtracted out. Several graphs are presented (Figs. 2 and 3), together with a description of the sample treatment before each vaporization, which represent the randomness of the induction period. As the runs were of an exploratory nature and only led to general conclusions, the data are sufficiently represented by the graphs and long tables of times and pressures would be unenlightening.

To complete these experiments a series of runs, some with and some without chlorine, was carried out above 50°. All of these were timed to determine the attainment of equilibrium, as continuing decomposition resulted in a constant noticable pressure rise. The final pressure was determined by adding to the final reading the result of multiplying the final rate by the several minutes required to stop a run by opening the

Figure 2

A 700 mg sample of $S_3N_3Cl_3$ was loaded into the glass spiral manometer and the pressure rise into an evacuated 200 ml sample chamber at 49.4° was followed with respect to time.

Curve 1 was started by closing the chamber after initially allowing the pressure to rise to 13 mm and evacuating for 30 minutes.

Curve 2 was begun by closing the chamber after evacuating for one hour following curve 1.

Curve 3 was begun after 9-1/2 hours evacuation following curve 2. (Final equilibration was reached but the last of the curve was not plotted to prevent clutter.)

Curve 4 Was started after evacuation following curve 3 for six hours at 22° and 1/2 hour at 49.4°. Before starting 20 mm of nitrogen pressure were closed into the chamber (this N_2 pressure was subtracted from the total pressure before plotting).

(Only a few of the points taken have been shown to preserve clarity in this and the following figure.)

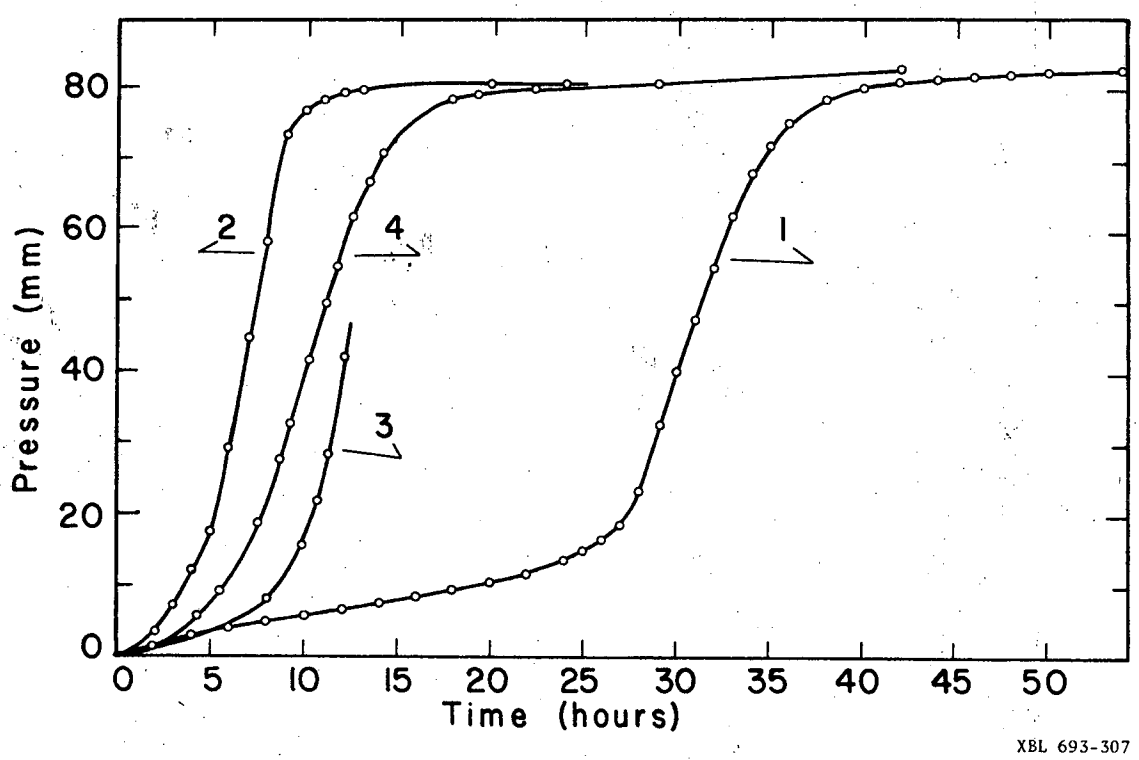

Pressure (mm)
80
60
40
20
0
0
5
10
15
20
25
30
35
40
45
50
Time (hours)
2
4
3
1
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Fig. 2 - Part II

Figure 3

Curve 1 was started after evacuation for two hours following curve 4 of the previous figure. Immediately before closing, 2.3 mm of chlorine pressure were added. No change in pressure resulted after an initial $\frac{1}{2}$ mm rise in the first 20 minutes and the run was ended after 22 hours by evacuation.

Curve 2 was begun after one hour evacuation following curve 1. A new loading of $S_3N_3Cl_3$ was made and chlorine was sealed into breakseal tubes attached to the sample chamber. The system was closed until 85 mm of pressure had developed and then evacuated.

Curve 3 (49.9°) was begun after overnight evacuation. When the pressure was 7.8 mm and rising rapidly a breakseal tube was opened containing 2.3 mm of chlorine (based on total volume and bath temperature). The rapid rise stopped. (The bath overheated for a short time causing some pressure rise which stopped when the temperature returned to 49.9°.) The chlorine was eventually overcome as shown in the graph.

Curve 4 (49.9°) was started after 24 hours evacuation following curve 3 including one hour at 22°. When the pressure was at 27 mm and rising rapidly a breakseal tube was opened to add 5.1 mm of chlorine. The pressure rose only slowly thereafter and was followed until equilibrium was reached after 400 hours. Only the first 80 hours are shown. The pressure rise was 0.1 mm/hr at 100 hours, 0.2 mm/hr at 200 hours, and a maximum of 0.4 mm/hr at 300 hours.

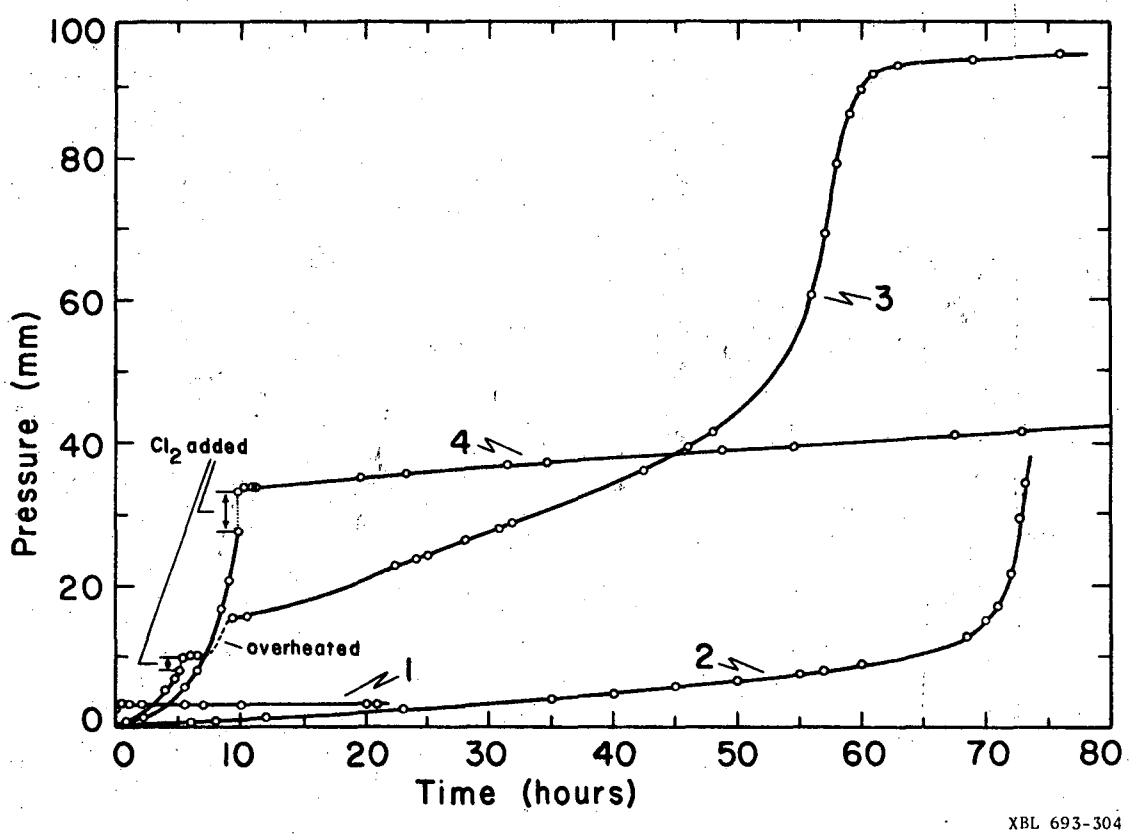
100
80
60
40
20
0
Pressure (mm)
0
10
20
30
40
50
60
70
80
Time (hours)
Cl_2 added
overheated
1
2
3
4
XBL 693-304

Fig. 3 - Part II

chamber to the Toepler pump and lowering the bath. In each run the $S_3N_3Cl_3$ was pretreated with chlorine for several hours at 40° as previous runs indicated that Cl_2 possibly removed some impurity. These results are also presented in Table I. Following the non-chlorine runs above 52.1° dark greenish-brown solids, which disappeared if chlorine was introduced, contaminated the $S_3N_3Cl_3$ left in the chamber and showed infrared absorptions corresponding to S_3N_2Cl and S_4N_3Cl impurities.[14] Chlorine runs at $\leq 60°$ left a yellow solid which showed only $S_3N_3Cl_3$ absorptions and non-Cl_2 runs at $< 52.1°$ left yellow or orange-yellow solids with infrared absorptions of only $S_3N_3Cl_3$ and occasionally $S_3N_2Cl_2$.[14] Also in non-chlorine runs the vaporization, though naturally faster at higher temperatures, still followed the "S" curve behavior, while Cl_2 runs still subdued this behavior except at 65°, allowing only a fairly moderate, steady depolymerization rate.

E. Measurement of the Sublimation Pressure of $S_3N_3Cl_3$

The equilibrium pressure of $S_3N_3Cl_3(g)$ above $S_3N_3Cl_3(s)$ was determined by a saturated gas-flow method using helium and chlorine as the carrier gas mixture. The apparatus used finally is diagrammed in Fig. 4. Runs were made by passing a fixed flow of helium (set with a pressure regulator and needle valve) through a large tube packed with Drierite and magnesium perchlorate followed by a liquid nitrogen trap to remove any water; it was then mixed with a stream of chlorine (10.3-12.6% of the total flow) from a needle-valve equipped Matheson lecture bottle. The He + Cl_2 mixture then flowed through a coiled length of tube for temperature equilibration and into a saturator tube packed with ~50 g of $S_3N_3Cl_3$ in the constant-temperature water bath described previously.

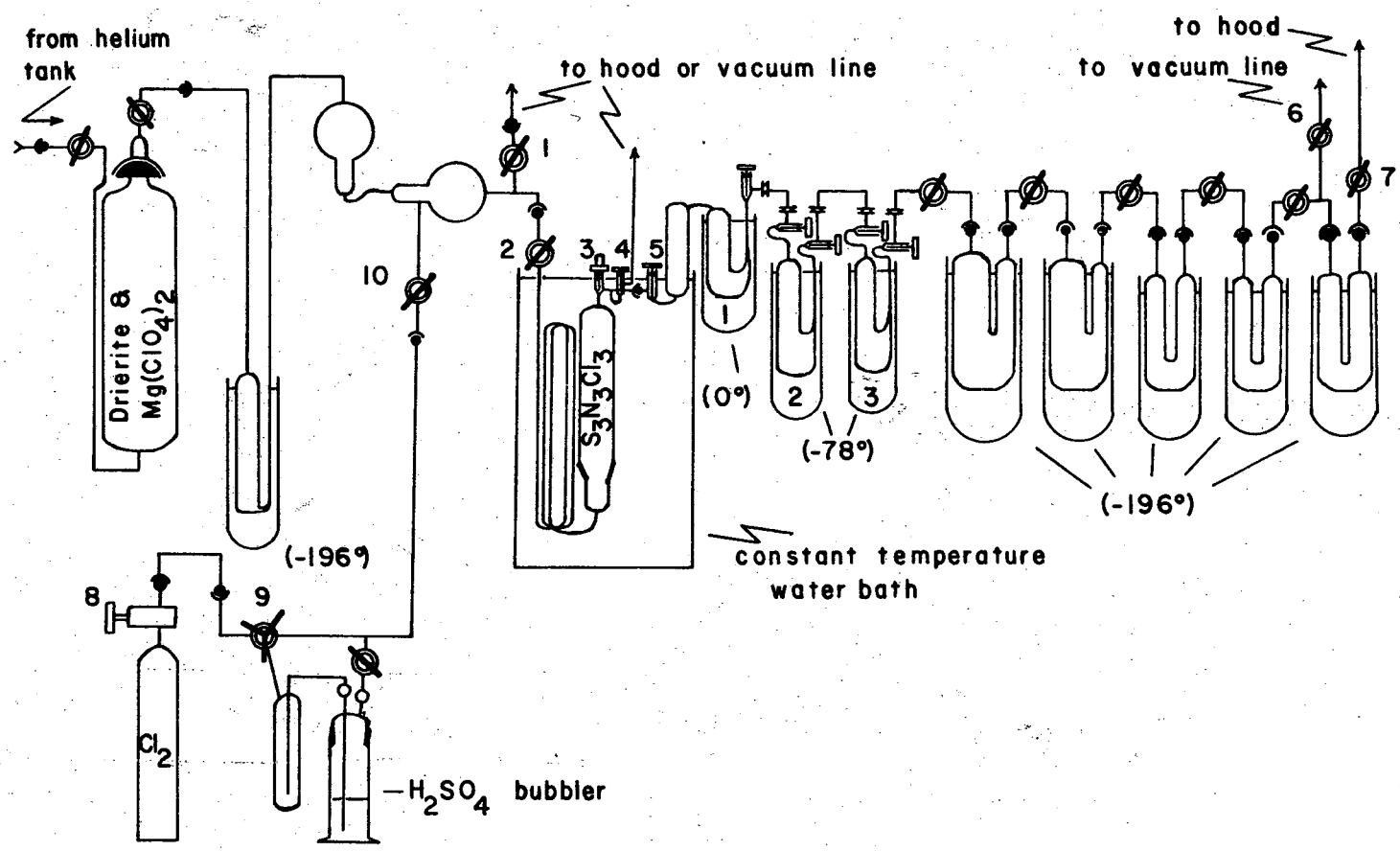

Fig. 4 Saturated gas-flow apparatus used to determine the sublimation pressure of $S_3N_3Cl_3$.

XBL 693-296

The tube had a Kel-F waxed 24/40 joint at the bottom for loading and was closed at the exit side by a Delmar-Urry o-ring stopcock whose exit led underwater through a 12/5 ball joint couple, well clamped and sealed with Kel-F wax, into a tared trap which cooled passing gasses first to room temperature (~20°), and later to 0°, in a Dewar of ice water. Both the trap entrance and a bypass tube leading to the vacuum line between the saturator and the trap were closed with Fischer-Porter 0-1 mm needle valves, and both they and the Delmar-Urry stopcock were positioned such that all gas flow was under the bath liquid while the stem openings and handles were out of the water. Both sides of this and the two following traps, which were cooled to -78° with dry ice/acetone baths, were closed with Fischer-Porter needle valves and connected with o-rings joints to allow their easy use as tared vessels. The passing gas then exited to the hood through a series of -196° traps.

The gas mixture was saturated with $S_3N_3Cl_3$(g) which then was completely trapped out (as shown by no $S_3N_3Cl_3$ collected in Trap 2 when a -22° bath was placed around it for part of a run) in the 22°/0° first trap; and NSCl which formed was collected in the -78° traps (as shown by collection of a large amount of NSCl in Trap 2 at -78° and only some SCl_2 in Trap 3 held at -196° in a run without chlorine); and the chlorine was removed in the -196° traps. Runs were started, with stopcock 1 open and vented to the hood and stopcock 2 closed, by setting the He flow to its desired rate by measurements with a soapfilm flowmeter attached either before the drying tube or at stopcock 1 (no difference in flowrates was detected). The chlorine flow from the preweighed bottle was started and the time noted and its flowrate quickly adjusted to the approximate desired value by estimating its magnitude from its rate of bubbling through a sulfuric acid

bubbler (a previous volume vs. bubbles/minute calibration had been made). When all flowrates had stabilized at desired levels and stopcocks 3 and 4 had been opened to evacuate the $S_3N_3Cl_3$, which was stored between runs under an atmosphere of chlorine, the vacuum line was closed; the sulfuric acid bubbler was switched out of the system; stopcock 1 was closed; 2 was opened; and the vacuum line was vented to the hood after the He + Cl_2 had filled the system to 1 atm. The flow through the saturator by-passed the traps for at least six hours after heating the bath to temperature to purge the saturator and stabilize the system. The evacuated trap system with all baths in place was filled backwards to 1 atm. with helium from another tank and vented to the hood, and the actual run begun by closing 4 opening 5. Periodically the bath fluids were replenished; the constancy of the chlorine flow checked by switching in the sulfuric acid bubbler; the drying tube closed and the helium measured by momentarily passing it through the flowmeter; the back-pressure in the line (always $\leq$ 1 mm) checked by opening 1 to an open backed U-tube of mercury; and the room atmosphere pressure measured.

When a measurable amount of $S_3N_3Cl_3(s)$ had collected in Trap 1 the run was stopped by venting through 4 to the hood and closing 5 and 7, opening 6 to vacuum, cooling the bath to ~22°, closing off and measuring the He flow again while Cl_2 filled the saturator, and opening 1 to the hood and closing 4, 3, 2, 8, 9, and 10 successively before removing and weighing the chloring tank. Traps 1, 2 and 3 were weighed after evacuation (traps 2 and 3 took as much as 8 hours pumping at -78° to remove liquid chlorine which had condensed during the flow) to determine the weights of $S_3N_3Cl_3$ and NSCl collected.

The gas volumes of chlorine passed and $S_3N_3Cl_3$ and NSCl collected were calculated at S.T.P. from their weights by assuming them to be

perfect gases. The chlorine flowrate in cc/min. (S.T.P.) was then calculated from the total time flowed. The helium flowrate was also converted to S.T.P. and added to the chlorine to obtain the total flowrate. After determining the average carrier gas pressure (atmospheric) during the run, and assuming the $S_3N_3Cl_3$ to have saturated the flowstream at the bath temperature, the sublimation pressure of $S_3N_3Cl_3$ was calculated using the formula:

$$\frac{\text{Pressure of He} + Cl_2\text{(mm)}}{\text{Volume of He} + Cl_2\ \text{(S.T.P.)}} \times S_3N_3Cl_3\text{(g) (S.T.P.)} \times 10^3 = P_{S_3N_3Cl_3}\ \text{(microns)}\ .$$

The average pressure of NSCl formed was calculated similarly.

Eleven good runs (listed in Table II) were done using flowrates ranging from 59 to 195.2 cc/min and temperatures from 35.0 to 55.0°. The weights of $S_3N_3Cl_3$ collected, ranging from 29 to 42 mg, took as long as 13 days to collect at 35.0° and were weighed in trap 1 to ± 1.0 mg placing an error limit of ± 3% on each pressure, which ranged from 1.0 to 8.0 microns. The maximum chlorine flowrate fluctuation was ±10% during a run creating a possible maximum total flowrate fluctuation of ±1.0% but the several hundred grams of Cl_2 flowed were weighted to ±0.2 grams giving an accurate average chlorine flowrate. The maximum helium flowate fluctuation of ± 0.5% and the maximum atmospheric pressure uncertainty of ± 0.3% are negligible relative to the $S_3N_3Cl_3$ weight uncertainty which limits the accuracy.

A series of preliminary runs was also performed in which the -196° drying trap on the helium line was absent; the chlorine was bubbled constantly through the H_2SO_4 (which was the only flow measurement) from an

Table II. Results of gas-flow saturation experiments

Run	T (°C)	flowrate (cc/min STP)	Cl_2 (%)	Time (min)	total flow ℓ(STP)	Ave P (mm Hg)	$S_3N_3Cl_3$ (mg)	$S_3N_3Cl_3$ cc(STP)	$S_3N_3Cl_3$ P(μ)[b]	NSCl mg	NSCl ave P(μ)
1[a]	45.0	104.7	12.6	5739	599.5	755	32	2.94	3.69(12)	26	9.0
2	45.0	132.4	11.5	6365	842.0	756	40	3.67	3.29(08)	30	7.8
3[a]	45.0	172.3	10.3	5010	864.0	753	31.5	2.89	2.52(08)	34	8.1
4	45.0	59.0	11.5	14243	840.0	755	42	3.85	3.46(08)	294	72.6
5	40.0	100.2	10.4	9306	933.0	755	26.5	2.43	1.97(07)	58	12.6
6	35.0	101.6	10.0	8855	899	756					
		101.2	11.0	10085	1021	756					
(2 part run)		(101.4)	(10.6)	(18940)	(1920)	(756)	29	2.66	1.05(04)	27	3.0
7	45.0	100.4	10.3	7040	706.5	758	35	3.21	3.44(10)	111	32.7
8[a]	50.0	101.0	10.6	3745	378.0	765	30	2.76	5.58(19)	70	39.0
9	55.0	100.9	11.6	2775	279.6	761	32	2.94	8.01(25)	332	249.3
10[a]	50.0	146.1	11.7	2605	380.6	757	36.5	3.35	6.67(18)	60	33.0
11	50.0	195.2	11.8	2277	444.0	760	41.5	3.80	6.50(14)	75	36.0

[a] Denotes run beginning after recrystallization of $S_3N_3Cl_3$ bed.

[b] Numbers in parentheses are errors in last reported digits corresponding to uncertainties of ±1 mg in the $S_3N_3Cl_3$ weight

unpurified, unweighable tank; and the lead-in tube to trap 1 from the saturator was of larger volume leading out of the bath and was kept warmer than the bath by continual flow of warm air. Eight runs at 40-50° and total flowrates of 80-180 cc/min with chlorine percentages of 2.15-13% were performed with the results of two runs being identical to the values from comparable final runs but with all of them ranging from 0 to 3 microns high in calculated pressure. Using an empty saturator, 20-hour blank runs followed at 45° and ~100 cc/min; only the -80° trap collected material, mostly water, in amounts of 2.5 mg with helium only and 18.5 mg with 10% chlorine. To remove the water the system was changed to its final form and a lecture bottle of Matheson chlorine was purified by vacuum line fractionation quickly several times through a -112° trap (keeping what remained) followed by slowly pumping the chlorine out of a bulb held at -78° and discarding the last 10% of the liquid; the chlorine was returned to the flamed and evacuated bottle that thereafter was used as a tare. Blank 20 hours runs with and without chlorine then gave less than 1 mg of material in following traps. The impurity of the chlorine may have accounted for the high results of preliminary runs by reacting to form impurities non-volatile at 0°; and corresondingly, the two preliminary runs with lowest chlorine percentage were two agreeing with later results. In the final runs it was possible to remove all the material in trap 1 by immersing it in a 55° bath forl2 hour periods and briefly pumping out all the depolymerized $S_3N_3Cl_3$ in the form of NSCl.

The earlier runs also showed the correlation that more NSCl resulted with both lower chlorine percentages and lower total flowrates. In fact, one run tried without chlorine increased the NSCl production by a factor of 200. In the final runs the chlorine percentage was made as

high as possible without clogging the -80° trap, and the tube leading from the saturator to trap 1 was put under the bath to minimize the volume and time the $S_3N_3Cl_3(g)$ saturated stream had to travel after leaving the bed before being trapped, hopefully to insure the $S_3N_3Cl_3$ did not depolymerize after it could no longer be replaced. This volume was ~3 ml while the dead space within the $S_3N_3Cl_3$ bed was ~60 ml. The NSCl production seemed to increase somewhat as the bed got older so the $S_3N_3Cl_3$ was recrystallized occasionally and the runs with fresh samples are noted in the table.

III. RESULTS AND DISCUSSION

A. Preparation of $S_3N_3Cl_3$

Jolly and Maguire[14] prepared $S_3N_3Cl_3$ with a melting point of 91° which a molecular weight determination and analysis showed to be good $S_3N_3Cl_3$ while Schröder and Glemser[13] reported a melting point of 162.5° for S_3N_3-Cl_3 prepared differently. The possiblity that two forms of $S_3N_3Cl_3$ exist is unlikely as we have found the materials from both preparations to have the properties reported by Jolly and Maguire,[14] including melting point.

We observed $S_3N_3Cl_3$ to melt with decomposition sharply (1-2° ranges) at temperatures from 75 to 98° and even higher in the presence of chlorine. This is characteristic of decomposition catalyzed by small impurities, which also occurs in S_4N_4,[24] rather than a lowering from large amounts of impurities. As $S_3N_3Cl_3$ depolymerizes rapidly above 70° to NSCl which also decomposes appreciably at higher temperatures to N_2 and S_2Cl_2 the observed melting process is probably the dissolution or reaction of $S_3N_3Cl_3$ in NSCl or S_2Cl_2 rather than formation of $S_3N_3Cl_3(\ell)$, and impurities catalyzing the depolymerization would lower the melting point. We observed in hot CCl_4 solutions a green color, not NSCl, which probably corresponded to some step in the thermal decomposition process and added to $S_3N_3Cl_3$ recrystallized from these solutions impurities that likely were responsible for catalyzing depolymerization. Chlorine in the solution may have resulted in higher melting samples by preventing formation of this green species and subsequent buildup of the catalytic impurities.

The very high melting observed in a bulb of chlorine was possibly

due to its removal <u>via</u> reaction: $S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$ of any S_2Cl_2 which built up through the NSCl decomposition and thus prevented S_2Cl_2 from reacting with, or in some way catalyzing the depolymerization of, $S_3N_3Cl_3$. It's difficult to believe that the melting point of 162.5° reported by Schröder and Glemser[13] could have been $S_3N_3Cl_3$ heated slowly in a sealed tube; if they actually used a sealed tube it was possibly a compound such as S_4N_3Cl they saw melting as we have often seen, as did Maguire, Smith and Jolly,[25] the appearance of other yellow solids soon after the $S_3N_3Cl_3$ melted which, it will be shown later, can decompose to form S_4N_3Cl which, when pure, melts with decomposition at 180-200°.

The experiments involving depolymerization in a bulb of $S_3N_3Cl_3$ and observing the NSCl, both visually and thru infrared spectrometry, indicated that the depolymerization is a reversible process, with or without solvent, in which moderate amounts of NSCl are possible even near room temperature. It was also evident that NSCl(ℓ) is unstable with respect to $S_3N_3Cl_3$(s) and NSCl(g), thus any equilibrium pressure of NSCl obtained statically would be a measure of the gas-solid equilibrium: $S_3N_3Cl_3 \rightleftharpoons 3NSCl(g)$.

B. <u>Sublimation of $S_3N_3Cl_3$</u>

The results of sublimations of $S_3N_3Cl_3$ show that, though its equilibrium pressure is very low, $S_3N_3Cl_3$(g) is a stable species relative to depolymerization even over the time required to pass through an inert gas to the cold finger $\leq 55°$. At 70-80° with a -196° cold finger however, vacuum sublimation gave a blue-green material which changed back to yellow $S_3N_3Cl_3$ when warmed, but sublimation in the presence of an inert gas resulted in nearly complete depolymerization to NSCl.

Two descriptions of 70-80° $S_3N_3Cl_3(g)$ are possible: (1) it is a stable species, the green color resulting only from an excited state, with respect to a potential energy barrier; and depolymerization requires further energy transfer from collision with another body, M, to excite it over this barrier; or (2) it is a thermally unstable intermediate decomposing spontaneously to NSCl but with short lifetime, t. Process (1) is represented by the sequence:

$$S_3N_3Cl_3(g) + M \rightarrow S_3N_3Cl_3^*(g) + M$$

$$S_3N_3Cl_3^*(g) \rightarrow 3NSCl$$

in which N_2 or helium is the species M not available *in vacuo*. In process (2) the depolymerization is merely the step

$$S_3N_3Cl_3^*(g) \rightarrow 3NSCl$$

but *in vacuo* the time required to reach the cold finger was short compared to t and it was trapped before decomposing while N_2 or He kept it from reaching the cold finger long enough for it to decompose. Since very little NSCl formed at $\leq 55°$, even in a gas, process (1) seems more likely for if (2) were the case at 70-80°, then at 55° it should not be too difficult for a gas M to provide the energy for process (1) to occur as the energy difference between the initially vaporized species at 55° and at 70° should be small. Regardless of the actual process, direct gas phase depolymerization must have a high activation energy barrier and be very slow at lower temperatures.

C. Measurement of the Equilibrium Pressure of NSCl

The data presented in Table I from the vaporization of $S_3N_3Cl_3$ into a closed system until a constant pressure is reached, and the observations made during their accumulation indicate that NSCl(g) does exist

in a measurable, reversible equilibrium with $S_3N_3Cl_3(s)$ which may be reached either from above or below the equilibrium NSCl pressure. However, those data consist of total pressures and pressures of nitrogen present from decomposition. To determine the actual NSCl(g) pressure it is necessary to know how much of the total pressure represented gaseous decomposition products. (The low volatility of $S_3N_3Cl_3$ and the gas molecular weight determinations indicate that any $S_3N_3Cl_3(g)$ present is less than the uncertainty of the measurements and may be ignored).

Analysis of the decomposition products of NSCl showed, at various times, the gases S_2Cl_2, SCl_2 and Cl_2 and the solids $S_3N_2Cl_2$, S_3N_2Cl, and S_4N_3Cl with the last two solids only being found in runs at > 52.1° without chlorine present, and at > 60° with chlorine. Considering that the decomposition reaction to form nitrogen has the stoichiometry corresponding to:

$$2NSCl(g) \rightarrow N_2(g) + S_2Cl_2(g) \qquad (1)$$

we can account for the presence of all the products formed from known reactions of the starting materials: NSCl, $S_3N_3Cl_3$, and S_2Cl_2. These consist of the sulfur-chlorine equilibria:

$$S_2Cl_2(g) \rightleftharpoons S(s) + SCl_2(g) \qquad (2a)$$

$$S_2Cl_2(g) \rightleftharpoons 2S(s) + Cl_2(g) \qquad (3a)$$

which may also be written as:

$$S_2Cl_2(g) + Cl_2(g) \rightleftharpoons 2SCl_2(g) \qquad (2b)$$

$$SCl_2(g) \rightleftharpoons S(s) + Cl_2(g) \qquad (3b)$$

and several reactions involving sulfur-nitrogen chlorides. Jolly, Maguire, and Rabinovich[26] mentioned that vapors of S_2Cl_2 and NSCl formed

$S_3N_2Cl_2$ in a condenser *via* in the reaction:

$$S_2Cl_2(g) + 2NSCl(g) \rightarrow S_3N_2Cl_2(s) + SCl_2(g) \qquad (4a)$$

for which Smith[27] later found evidence indicating it may only occur substantially in condensed phases so it might be better written for our system as:

$$S_2Cl_2(g) + S_3N_3Cl_3(s) \rightarrow S_3N_2Cl_2(s) + NSCl(g) + SCl_2(g) \qquad (4b)$$

Further, $S_3N_2Cl_2$ reacts with chlorine at room temperature to reform NSCl:[25]

$$S_3N_2Cl_2(s) + Cl_2(g) \rightarrow 2NSCl(g) + SCl_2(g) \qquad (5)$$

At higher temperatures $S_3N_2Cl_2$ is reported to decompose *in vacuo*[25] (80-100°) *via* the reaction:

$$3S_3N_2Cl_2(s) \rightarrow 3S_3N_2Cl(s) + 2NSCl(g) + SCl_2(g) \qquad (6)$$

which we have observed actually begins below 70°. With S_2Cl_2 in refluxing CCl_4 (77°) $S_3N_2Cl_2$ also reacts to form S_4N_3Cl *via* the reaction[14]

$$S_3N_2Cl_2(s) + S_2Cl_2(g) \rightarrow S_4N_3Cl(s) + 3SCl_2(g) \qquad (7)$$

which also is reported to proceed without added S_2Cl_2 and may actually involve S_3N_2Cl as an intermediate product which itself decomposes to produce S_4N_3Cl at 130-150°.[26]

Examination shows that all the reactions which occur at lower temperatures (2 through 5) form exactly one mole of gas for each mole of gas consumed(with the exception of NSCl and $S_3N_3Cl_3$ which can reequilibrate). Therefore, once reaction 1 produces two moles of decomposition products, all further reactions occurring at lower temperatures result in no net change in the moles of gaseous decomposition products of which N_2 is exactly one-half. The equilibrium pressure of NSCl may therefore

be derived from the total pressure and the nitrogen pressure by the equation

$$P_{NSCl} = P_{total} - 2P_{N_2}$$

provided no reactions have been overlooked and the higher temperature reactions (6 and 7) to form S_3N_2Cl do not occur as these reactions produce an increase in the gaseous decomposition products and would result in a high calculated P_{NSCl}. Reactions 6 and 7 require $S_3N_2Cl_2$ which itself is destroyed by chlorine in reaction 5 and is formed in reaction 4 with S_2Cl_2 which also is removed by chlorine in reaction 2b; thus, chlorine should hinder reactions 6 and 7.

We have applied the above correction to the data in Table I and find, indeed, that (1) the four points at 49.9° (two with and two without Cl_2), whose total pressures ranged from 84.65 to 102.0 mm, yield the same P_{NSCl}, and (2) when log P_{NSCl} is plotted vs. 1/T(°K) the data fall on a good straight line, with the exception of the runs without chlorine above 52.1° and with chlorine above 60° which are all to high corresponding to occurrence of the higher temperature reactions, 6 and 7 as was indicated by the presence of S_3N_2Cl and S_4N_3Cl in remaining residues. This straight line (Fig. 5) can be represented by the equation :

$$\log P \text{ (mm)} = -3360\ (1/T) + 12.321$$

to the accuracy shown in Table III and is a necessary condition for the pressure of a gas in equilibrium with a solid as log P is related to 1/T by the linear equation

$$\log P = -\Delta H^\circ(\text{vap})/(2.303RT) + \text{constant}$$

(to the approximation that ΔH° (vap) is constant and NSCl is an ideal gas in the measured temperature range), and a plot of log P vs. (1/T)

Table III

P_{NSCl} data used to determine the equation

$$\log P\ (mm) = -\ 3360(1/T) + 12.321$$

for the equilibrium $S_3N_3Cl_3(s) \rightleftharpoons NSCl(g)$

T (°C)	P_{obs} (mm)	P_{calc} (mm)	$\Delta = P_{obs} - P_{calc}$ (mm)
31.0	19.2	18.9	+ 0.3
35.4	27.9	27.2	+ 0.7
40.3	40.0	40.3	- 0.3
45.1	58.0	58.3	- 0.3
47.2	69.2	68.4	+ 0.8
49.4	81.2	80.7	+ 0.5
49.55	82.0	81.7	+ 0.3
49.9	83.6	83.8	- 0.2
49.9	83.5	83.8	- 0.3
49.9	84.2	83.8	+ 0.4
49.9	83.5	83.8	- 0.3
52.1	97.4	98.4	- 1.0
57.5	141.7	145.2	- 3.5
60.0	173.2	173.0	+ 0.2
60.0	176.2	173.0	+ 3.2

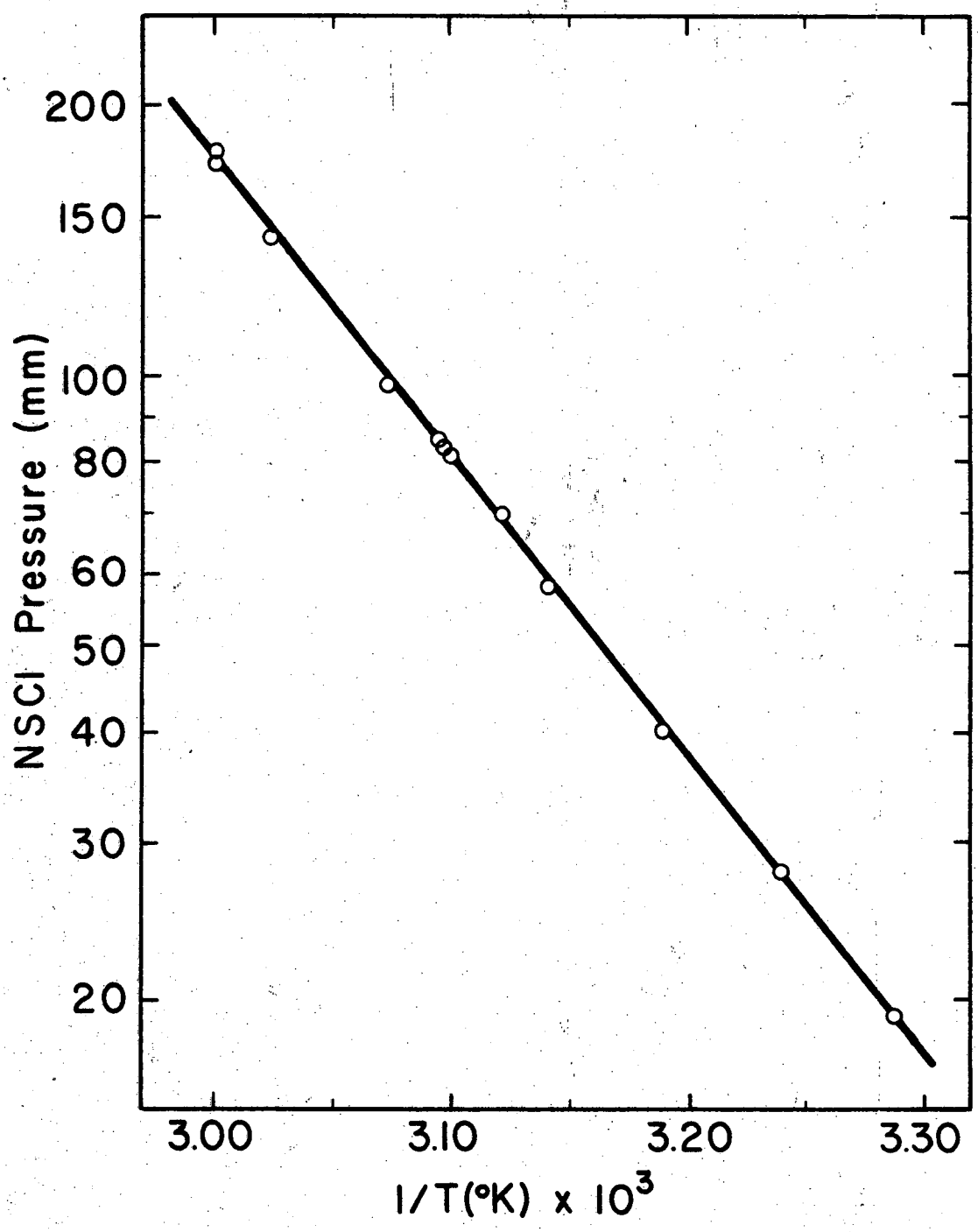

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Fig. 5 Plot of log P_{NSCl} vs 1/T

must be a straight line with slope = $(-\Delta H^\circ(\text{vap})/(2.303R)$.

With the additional relations that $\Delta F^\circ_T = -RT \ln P$

$$\text{and} \quad \Delta S^\circ_T = \frac{\Delta H^\circ_T - \Delta F^\circ_T}{T}$$

we calculate for the reaction

$$1/3\ S_3N_3Cl_3(s) \rightarrow NSCl(g)$$

the values $\Delta H^\circ_{31\text{-}60^\circ} = 15.4 \pm 0.5$ kcal/mole

and $\Delta S^\circ_{31\text{-}60^\circ} = 43.2 \pm 1.6$ cal/deg.mole

The uncertainty represents the maximum deviation in slope, from that of the best straight line, of the possible lines drawn after applying the experimental uncertainties of P ± 0.2 mm and T ± 0.1° to all points.

D. The Depolymerization Process

Near 50° $S_3N_3Cl_3$ depolymerized by a process involving an initial indefinite induction period of little pressure rise (0-1 mm/hr) followed by a rate increase for several hours to a maximum of 10-15 mm/hr which then fell off until the final pressure was reached. Chlorine was found to extend the induction period indefinitely and to halt the rapid vaporization process, while the pressure of an inert gas had negligible effect.

The extremely low initial rate and the final fall-off are understandable: near the equilibrium pressure the repolymerization process, which may be simply

$$3NSCl(g) \rightarrow S_3N_3Cl_3(g)$$

will become most important; while sublimation experiments have shown first, that vaporization to $S_3N_3Cl_3(g)$ is slow but much more favorable

than the direct solid depolymerization:

$$S_3N_3Cl_3(s) \rightarrow 3NSCl(g)$$

and second, that the thermal splitting:

$$S_3N_3Cl_3(g) \rightarrow 3\ NSCl(g)$$

is extremely slow at $\leq 50^\circ$ which would predict only a very slow depolymerization.

The rate of gas phase depolymerization at $\leq 50^\circ$ is too slow to account for the fast depolymerization observed, thus a second depolymerization mechanism must occur. The rate is, in fact, so fast that attack by some species X upon $S_3N_3Cl_3(s)$, not $S_3N_3Cl_3(g)$, is involved as the maximum depolymerization rate used ~ 10 mg of $S_3N_3Cl_3$ per hour while sublimation into vacuum could only produce ~ 2 mg per hour of $S_3N_3Cl_3(g)$ from a similar quantity of solid. This second process does not occur initially or predictably so X must be initially formed in the system by a random process or its amount be controlled by a random impurity, and the nature of the rate increase suggests that X is autocatalytic. The chlorine results are enlightening: if added initially no measurable depolymerization occurred over 20 hours showing not only that the second process was prevented but that thermal depolymerization was so slow as to be unmeasurable; if added later, chlorine almost, but not completely, stopped the pressure rise which was able to very slowly recover. The conclusion drawn is that chlorine reacts with X, which is not NSCl (or chlorine would not have stopped the process when added after large NSCl pressures were present) but is possibly created from NSCl.

It is possible to write a reaction sequence using only previously discussed reactions to explain all these effects:

$$S_3N_3Cl_3(s) \underset{1'}{\overset{1}{\rightleftharpoons}} S_3N_3Cl_3(g)$$

$$S_3N_3Cl_3(g) \underset{2'}{\overset{2}{\rightleftharpoons}} 3NSCl(g)$$

$$2NSCl(g) \xrightarrow{3} N_2(g) + S_2Cl_2(g)$$

$$S_2Cl_2(g) + S_3N_3Cl_3(s) \xrightarrow{4} S_3N_2Cl_2(s) + NSCl(g) + SCl_2(g)$$

$$2SCl_2(g) \underset{5'}{\overset{5}{\rightleftharpoons}} S_2Cl_2(g) + Cl_2(g)$$

$$Cl_2(g) + S_3N_2Cl_2(s) \xrightarrow{6} 2NSCl(g) + SCl_2(g)$$

$$S_2Cl_2(g) + S_3N_3Cl_3(s) \xrightarrow{4} S_3N_2Cl_2(s) + NSCl(g) + SCl_2(g)$$

Each of these reactions has been justified earlier. The mechanism proceeds as follows: 1 and 1' produce a low equilibrium $S_3N_3Cl_3(g)$ pressure, which very slowly depolymerizes to NSCl (2), which itself very slowly decomposes to N_2 and S_2Cl_2 (3) Then S_2Cl_2 reacts quickly (4)with $S_3N_3Cl_3(s)$ to produce NSCl, SCl_2, and an $S_3N_2Cl_2(s)$ impurity. Reaction 4 does produce NSCl(g) from $S_3N_3Cl_3(s)$, but the sum of 3 and 4 is

$$NSCl(g) + S_3N_3Cl_3(s) \xrightarrow{3+4} S_3N_2Cl_2(s) + N_2(g) + SCl_2(g)$$

which is still limited by 2. However, once sufficient $SCl_2(g)$ has built up, its disproportionation (5)followed by the resulting $Cl_2(g)$ and $S_2Cl_2(g)$ undergoing 6 and 4 gives the desired net reaction:

$$S_3N_3Cl_3(s) \xrightarrow{4+5+6} 3NSCl(g)$$

in which NSCl(g) is produced from $S_3N_3Cl_3(s)$ by a process not involving $S_3N_3Cl_3(g)$ and using S_2Cl_2, Cl_2 and $S_3N_2Cl_2$ together as a catalyst. This process explains the observed autocatalytic behavior by the enhanced occurrence of 3 with buildup of NSCl(g). The observed rapid, smooth rate decrease to zero at the equilibrium NSCl pressure corresponds to the $(NSCl)^3$ term in the rate of 2'.

The sequence would be stopped (as observed) by addition of Cl_2 by removal of S_2Cl_2 through 5'; addition after some NSCl had built up would initially halt the sequence but it would recover (as observed) after enough S_2Cl_2 had been formed by continuation of 3 to override the amount of chlorine added; addition initially would cause the virtually permanent halt noticed, as any NSCl for 3 must then first come from slow procedure of 2. (Direct decomposition to S_2Cl_2 and nitrogen of $S_3N_3Cl_3(s)$ is unimportant relative to 3 as shown by no measureable formation of nitrogen in the 20 hours the pressure remained constant with chlorine above $S_3N_3Cl_3(s)$, whereas several millimeters of N_2 resulted in less time in pressure measurements of NSCl).

The induction period, then, is the time required for S_2Cl_2 to build up via 2 and 3, and the randomness could be caused either (1) by removal of S_2Cl_2 by small amounts of chlorine occluded in the solid during the recrystallization process, or (2) by the presence of slight $S_3N_2Cl_2$ impurities in the $S_3N_3Cl_3$ which, besides enhancing 6, might also form slight amounts of NSCl and SCl_2 to start the catalytic process by the slow decomposition:

$$3S_3N_2Cl_2(s) \rightarrow 2S_3N_2Cl(s) + 2NSCl(g) + SCl_2(g)$$

This decomposition is not measurable at 50° but may occur sufficiently as $S_3N_2Cl_2$ is reported to decompose even at room temperature on long standing.[14] The presence of $S_3N_2Cl_2$ is supported by the slight (~ 1/2 mm) pressure rises observed just following addition of chlorine presumably resulting from 6.

This mechanism is probably not the only one which can qualitatively explain the observed effects, as the presence and involvement of small

amounts of many unknown and known species which would react with chlorine or $S_3N_3Cl_3(s)$ is possible; however, its use of only known reactions and species known to be present is in its favor.

E. The Sublimation Pressure of $S_3N_3Cl_3$

We have previously presented evidence that production of NSCl from $S_3N_3Cl_3$ occurs only slowly at $\leqslant 50°$ by the direct thermal depolymerization:

$$S_3N_3Cl_3(g) \rightarrow 3NSCl(g) \qquad (1)$$

and very rapidly by a catalytic process, presumably involving a direct attack on the solid, that is prevented or greatly retarded by chlorine. The gas-flow system was used in hopes that a constant high concentration of chlorine would suppress this catalytic process enough that any NSCl produced would indicate the extent reaction 1 had occurred. The experimental problem was one of flowing the carrier gas slow enough that it became saturated with $S_3N_3Cl_3(g)$ over the bed, slow enough that it could be trapped efficiently in a small, weighable trap, but fast enough that reaction 1 would not measurably remove $S_3N_3Cl_3(g)$ after leaving the bed and before it could be trapped out for weighing.

The data presented in Table II all refer to runs with a similar high chlorine concentration and variations only in flowrate and temperature. Runs 1 - 4 were preformed at 45.0° in hopes of finding a flowrate giving maximum saturation and trapping and minimum depolyermization as indicated by a maximum $S_3N_3Cl_3(g)$ content. Indeed a maximum was found at ~ 100 cc/min indicating that the faster flows were not saturated or, less likely, not trapped. The NSCl was also considered; if only reaction 1 occurred then the NSCl should be inversely proportional to the flowrate. This is not the case as higher flowrates gave comparable NSCl pressures and the

lower flowrate (Run 4) gave a 10-fold increase in NSCl with only a slight $S_3N_3Cl_3$ decrease; thus, a substantial part of the NSCl found, though miniscule compared with amounts found without chlorine, still resulted from the catalytic process rather then from reaction 1; and a buildup of catalytic impurities in the bed with its use was also indicated. The $P_{S_3N_3Cl_3}$ at 59.0 cc/min is only slightly lower than the 100 cc/min value (Run 1) and, in fact, is comparable to a later 100 cc/min value (Run 7); but as the reactions depolymerizing $S_3N_3Cl_3(s)$ might also affect $S_3N_3Cl_3(g)$ with a different rate, though to a much smaller extent, the large NSCl pressure makes the value uncertain.

The 100 cc/min run (1) yielded a $P_{S_3N_3Cl_3}$ of 3.69 (12) microns and NSCl corresponding to a maximum depolymerization of $S_3N_3Cl_3(g)$ or 3.0μ. If reaction 1 did produce all of this then the ratio of depolymerization after and before leaving the bed would be the ratio of flow times through or volumes of each area while saturated, or 1:20; this would imply that the measured $P_{S_3N_3Cl_3}$ was $3.0 \times (1/20) = 0.15\mu$ low (an acceptable error) from depolymerization, but presumably was even less affected as apparently some of this NSCl resulted from catalytic depolymerization of the solid.

As 100 cc/min seemed to be the fastest flowrate unaffected by saturation problems it was used in lower temperature 40.0 and 35.0° runs where reaction 1 is presumably completely negligible. At 50.0° runs at 101, 146, and 195 cc/min were made with the 101 cc/min result substantially lower than the nearly equal faster flowrate results. Presumably reaction 1 is faster at this temperature and proceeded sufficiently to be noticable so the faster flowrates were used to reduce this effect. The results indicate the saturation, expected to be easier at higher temperatures was achieved. (Glass wool was packed in trap 1 to insure efficient

TABLE IV

$P(S_3N_3Cl_3)$ data used to determine the equation

$$\log P(\mu) = -5316\ (1/T) + 17.270$$

for the equilibrium $S_3N_3Cl_3(s) \rightleftharpoons S_3N_3Cl_3(g)$

T (°C)	P_{obs} (μ)	P_{calc} (μ)	$\Delta = P_{obs} - P_{calc}$ (μ)
35.0	1.05	1.05	0.00
40.0	1.97	1.97	0.00
45.0	3.69	3.65	+0.04
45.0	3.44	3.65	-0.21
50.0	6.67	6.62	+0.07
50.0	6.50	6.62	-0.12

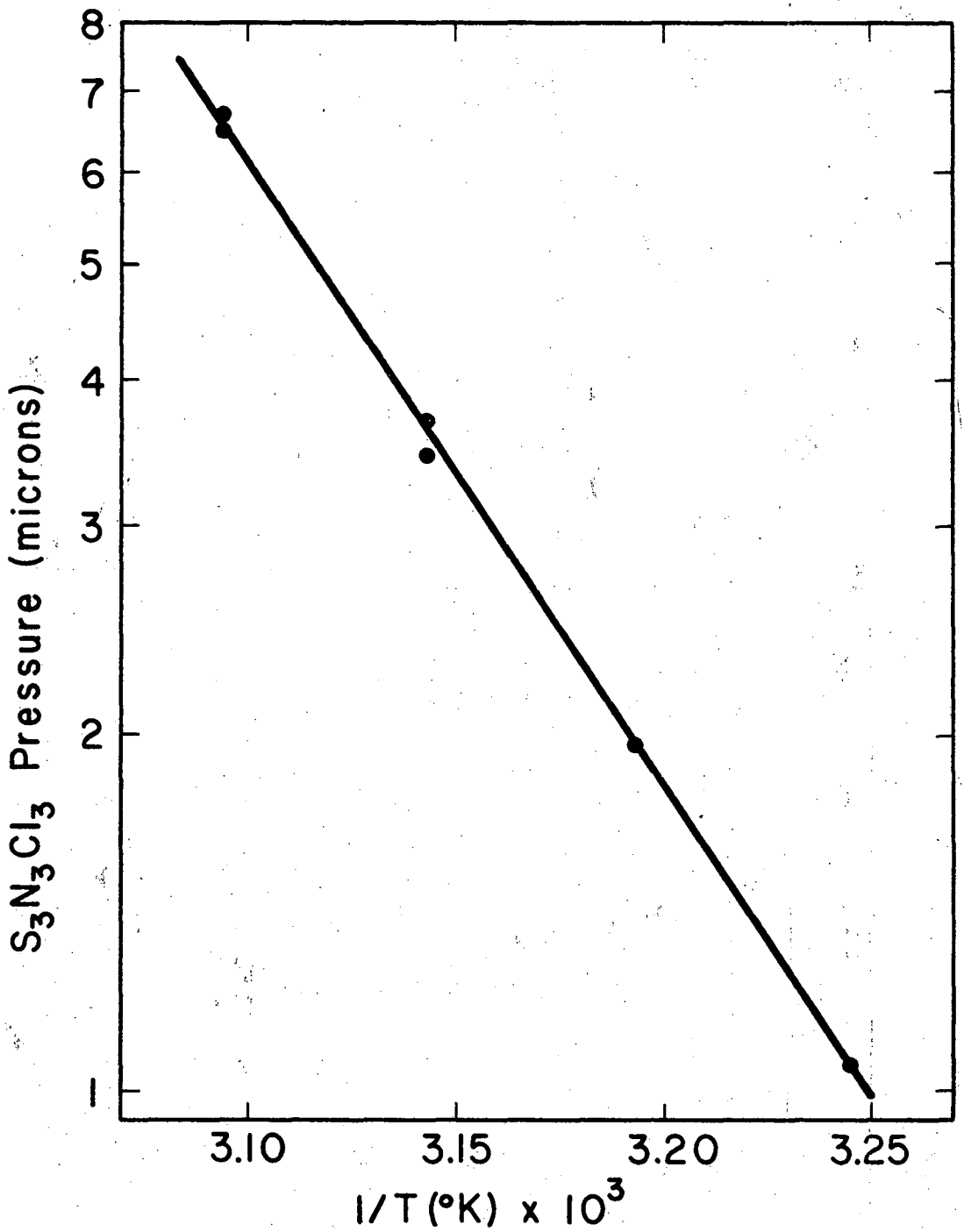

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Fig. 6 Plot of log $P_{S_3N_3Cl_3}$ vs 1/T

$S_3N_3Cl_3$ trapping at the highest flowrate.) At 55.0° and 100 cc/min a substantial depolymerization and darkening of the $S_3N_3Cl_3$ bed indicated that reliable data were unobtainable.

Considering the 100 cc/min results at 45, 40, and 35° and the faster flowrates at 50° to be the most reliable, these were plotted (Fig. 6) as log P vs. (1/T) and gave a quite resonable fit as indicated in Table IV to a straight line of equation $\log P(\mu) = -5.316\ (1/T) + 17.270$. Having passed this test the data were interpreted as representing the equilibrium pressure of $S_3N_3Cl_3(g)$ above the solid and treated in the manner earlier described for the NSCl(g) pressures.

We thus obtain for the sublimation

$$S_3N_3Cl_3(s) \rightarrow S_3N_3Cl_3(g)$$

the values $\Delta H^\circ_{35-50^\circ} = 24.3 \pm 1.5$ kcal/mole

and $\Delta S^\circ_{35-50^\circ} = 52.1 \pm 4.6$ cal/deg.mole

By combining these values with those obtained for the reaction:

$$S_3N_3Cl_3(s) \rightarrow 3NSCl(g)$$

we derive the results for the gaseous depolymerization reaction:

$$S_3N_3Cl_3(g) \rightarrow 3NSCl(g)$$

which are $\Delta H^\circ_{35-50^\circ} = 21.9 \pm 3.0$ kcal/mole

$\Delta S^\circ_{35-50^\circ} = 77.5 \pm 9.4$ cal/deg. mole

(The uncertainties represent the sum of the uncertainties of the individual measurements.)

F. Discussion of Thermodynamic Values

The derived results are summarized in the diagram below:

$$\Delta H^\circ = 24.3 \pm 1.5 \text{ kcal/mole}$$

$$\Delta S^\circ = 52.1 \pm 4.6 \text{ cal/deg.mole}$$

$$S_3N_3Cl_3(s) \longrightarrow S_3N_3Cl_3(g)$$

$\Delta H^\circ = 46.2 \pm 1.5$ $\quad$ $\Delta H^\circ = 21.9 \pm 3.0$

$\Delta S^\circ = 129.6 \pm 4.8$ $\quad$ $\Delta S^\circ = 77.5 \pm 9.4$

$$\searrow \quad 3NSCl(g) \quad \swarrow$$

The ΔH° values are primarily dependent on the strengths of the bonds broken, about which little is known, but the entropy changes are determined primarily by the process involved and should be similar to those found in depolymerizations of other trimeric six-membered ring compounds.

The closest analogy to the trimeric solid → monomeric gas process for which data are available is the vaporization of the ice-like form of SO_3, γ-SO_3, which exists in the solid as a trimeric six-membered ring composed of alternating sulfur and oxygen atoms in a chair configuration with two terminal oxygens bonded to each sulfur.[28] Both the structure and the molecular weight of the solid are very similar to $S_3N_3Cl_3(s)$. Measurement of the vapor pressure of $SO_3(g)$ above the solid has yielded an entropy change of $\Delta S^\circ = 122.1$ e.u. (all entropies to be referred to are in cal/deg.mole = e.u.) for the reaction:

$$(SO_3)_3(s) \rightarrow 3SO_3(g).^{29}$$

Not only is this value quite similar to the ΔS° of 129.6 e.u. we have determined for the corresponding $S_3N_3Cl_3$ process; but when these values are combined with the spectroscopically determined 25° absolute entropies, $S^\circ_{SO_3(g)} = 61.24$ e.u.[29] and $S^\circ_{NSCl(g)} = 63.66$ e.u.,[21] the calculated trimeric solid entropies, $S^\circ_{(SO_3)_3(s)} = 61.6$ e.u. and $S^\circ_{S_3N_3Cl_3(s)} = 61.4$ e.u., are virtually identical.

It is difficult to obtain suitable analogies for the trimer(s) → trimer(g) process. Although the major contribution to the entropy change is from the translational contributions of the resulting gaseous molecule, the greater the intermolecular association in the crystalline lattice and the greater the internal motion or lack of rigidity of the gaseous molecule the greater will be the entropy change in the process. A substantial amount of interaction in $S_3N_3Cl_3$(s) has been proposed to explain some significantly close (compared to van der Waal's radii) intermolecular contacts and the presence of two distinct S-Cl bond lengths found in its crystal structure,[9] but nothing is known about the rigidity of gaseous $S_3N_3Cl_3$. In fact very little sublimation pressure data are available for compounds of similar structure and high molecular weight; one possible analogy is $(PNCl_2)_3$ with a ΔS°(subl) = 38.0 e.u., calculated from reported sublimation pressures,[30] which is somewhat lower than our value of 52.1 e.u. for $S_3N_3Cl_3$ sublimation. However, the ring in $(PNCl_2)_3$ is planar; correlation with the ΔS°(subl) = 45.3 e.u. calculated from the heat of fusion (7.6 kcal/mole)[31] and heat of vaporization (15.5 kcal/mole), boiling point (325.5°), and melting point (123.5°)[32] of the puckered ring compound $(PNCl_2)_4$ may be more applicable.

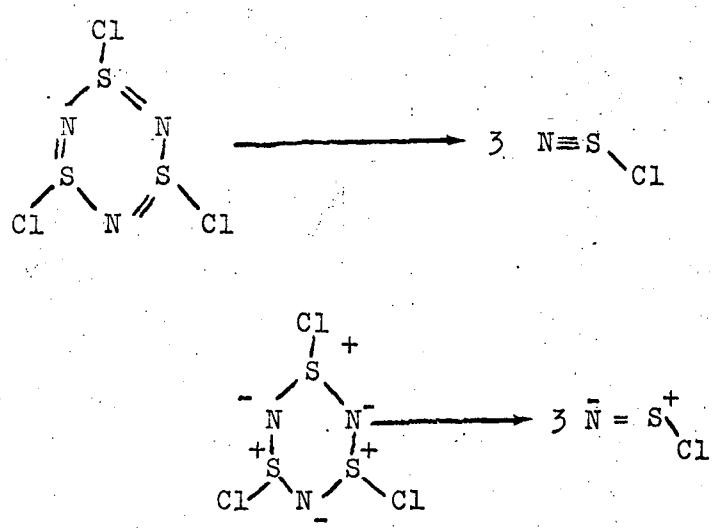
Of more applicability may be a comparison of the entropy changes in the trimer(g) → 3 monomer(g) processes for six-membered ring compounds. The major term in the entropy of a gas is from translational and rotational contributions; as each depolymerization forms three molecules with exactly one-third the molecular weight of the parent molecule, the ΔS contributed by this term to any gaseous trimerization reaction will be similar. Again there are contributions from vibration and free internal rotation, or "rigidity", which will not be the same for

depolymerization of different compounds, but consideration only of six-membered ring depolymerizations involving breaking of six ring bonds to form three bonds of higher order should minimize the differences. Calculation from reported ideal gas $S^{\circ}_{25^{\circ}}$ values of ΔS for detrimerizations even of markedly different molecules, provided the general six-membered ring breaking process is the same, leads to a suprisingly small range of values. Some of these are:

Trimer(g)	S°(e.u.)	Monomer(g)	S°(e.u.)	ΔS° for Trimer(g) → Monomer(g)
$B_3O_3H_3$	69.7[33]	HBO	50.24[33]	81.0
$B_3O_6H_3$	83.05[33]	HOBO	57.27[33]	88.8
$B_3O_3Cl_3$	91.37[33]	ClBO	56.72[33]	78.8
$B_3O_3F_3$	81.8 [33]	FBO	57.3 [33]	90.1
C_6H_6 (benzene)	64.34[34]	C_2H_2 (acetylene)	48.0 [34]	79.7
C_9H_{12} (mesitylene)	92.12[34]	C_3H_4 (propyne)	59.30[34]	85.8
C_6H_{12} (cyclohexane)	71.28[34]	C_2H_4 (ethylene)	52.54[34]	86.3
C_6F_6	91.4 [35]	C_2F_2	60.25[33]	89.3
Be_3O_3	65.3 [33]	BeO	47.2 [33]	76.3

This 76-90 e.u. range includes, and thus adds plausibility to, the 77.5 ± 9.4 e.u. value determined for the depolymerization of $S_3N_3Cl_3$(g).

The ΔH° value of 21.9 kcal/mole for the reaction $S_3N_3Cl_3(g) \rightarrow 3NSCl(g)$ corresponds to the breaking of six and forming of three SN bonds of orders somewhere between the two extremes represented by the forms:



The most recently published bond order assignments for SN compounds[20] listed the SN bond order in $S_3N_3Cl_3(s)$ as 1.4 and that in NSCl(g) as 2.2, but these resulted from a somewhat arbitrary correlation of bond distances, force constants, and orders of which many were estimated and are at best only approximate. Regardless, the order of the bonds approximately doubles with depolymerization and the relation between their energies may be approximated by the measured ΔH using the formula

$$\Delta H^\circ/3 = 2D(N\text{-}S)_{S_3N_3Cl_3(g)} - D(N\text{-}S)_{NSCl(g)} = 7.3 \text{ kcal/mole}$$

which gives the reasonable result that the bond which is twice the order of the other is nearly twice the strength, and is valid to the extent that the S-Cl bond energy remains constant.

A very approximate bond energy might be estimated from the calorimetrically determined D(S-N) in S_4N_4 of 73.5 kcal/mole,[19] but this is an upper limit as S-S interactions of which there is evidence were ignored in the calculation. The S-N distance in $S_3N_3Cl_3(s)$[9] is only 0.14Å shorter than in S_4N_4[36] so their bond energies should be similar. Assuming this to hold in $S_3N_3Cl_3(g)$ also, gives an upper limit for the bond energy in

NSCl of around 130 kcal. This value is in the range of 115 ± 25 crudely determined spectroscopically for SN(g),[31] which by analogy with NO should have a bond order of 2.5.

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REFERENCES TO PART II.

1. M. Becke-Goehring, Angew. Chem. 73, 589 (1961).
2. O. Glemser, Angew. Chem. Internat. Edit., 2. 530 (1963).
3. M. Becke-Goehring and E. Fluck, Developments in the Inorganic Chemistry of Compounds Containing the Sulphur-Nitrogen Bond, Elsevier Pub. Co., Amsterdam, 1965.
4. M. Becke-Goehring, Sulphur Inst. J., Spring 1966, 2, and Summer 1966 9.
5. E. Demarcay, C. R. Hebd. Séances Acad. Sci., 91, 854 (1880).
6. A. Andreacci, Z. Anorg. Allgem. Chem., 14, 246 (1897).
7. W. Muthmann and E. Seitter, Ber. Dtsch. Chem. Ges., 30, 627 (1897).
8. A. Meuwsen, Ber. Dtsch Chem. Ges., 64, 2311 (1931).
9. G. A. Wiegers and A. Vos, Acta Crystallogr., 20, 192 (1966).
10. $S_3N_3Cl_3$ crystalizes in space groups $P2_1/m$ or $P2_1$; a = 5.49Å; b = 11.14Å, c = 6.05Å; β = 98.4°; Z = 2; N-S-N angle = 113.4°; S-N-S angle = 123.8°; N-S-Cl angle = 113.8°; S-Cl distance = 2.150 and 2.084Å.
11. D. P. Craig and N. L. Paddock, Nature, 181, 1052 (1958); D. P. Craig, J. Chem. Soc., 1959, 997.
12. M.J.S. Dewar, E. A. C. Lucken, and M. A. Whitehead, J. Chem. Soc., 1960, 2423.
13. H. Schröder and O. Glemser, Z. Anorg. Allgem. Chem., 298, 78 (1959).
14. W. L. Jolly and K. D. Maguire, Inorg. Syntheses, 9, 102 (1967).
15. O. Glemser and H. Perl, Naturwissenshaften, 48, 620 (1961).
16. W. H. Kirchhoff, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1962.
17. O. Glemser and H. Richert, Z. Anorg. Allgem. Chem., 307, 313 (1961).

18. M. Berthelot and P. Vieille, Ann. Chim. Phys., 27, 202 (1882).

19. C. K. Barker, A. W. Cordes and J. L. Margrave, J. Phys. Chem., 69 334 (1965).

20. O. Glemser, A. Müller, D. Bohler and B Krebs, Z. Anorg. Allgem. Chem. 357, 184 (1968).

21. A. Müller, G. Nagarajan, O. Glemser, S. F. Cyvin and J. Wegener, Spectrochim. Acta, 23A, 2683 (1967).

22. M. Villena-Blanco and W. L. Jolly, UCRL Report No. 11294, January 1964.

23. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, Inc., New York, 1963.

24. M. Villena-Blanco, "A Study of the Reactions Between Gaseous Ammonia and Sulfur Chlorides," M.S. Thesis, University of California October, 1963.

25. K. D. Maguire, J. J. Smith, and W. L. Jolly, Chem. Ind., 1963, 1589.

26. W. L. Jolly, K. D. Maguire, and D. Rabinovich, Inorg. Chem., 2, 1304 (1963).

27. J. J. Smith, "Reactions of Active Nitrogen with Sulfur Compounds", Ph.D. Thesis, University of California, January, 1965.

28. R. Westrich and C. H. MacGillavry, Rec. Trav. Chim. Pays-Bas, 60, 794 (1941).

29. F. Rossni, D. Wagman, W. Evans, S. Levine, and I. Jaffe, National Bureau of Standards Circular 500, 1952.

30. R. Steinman, F. B. Schirmer, Jr., and L. F. Audrieth, J. Amer. Chem. Soc., 64, 2377 (1942).

31. S. B. Hartley, N. L. Paddock, and H. T. Searle, J. Chem. Soc., 1961, 430.

32. H. Moureu and A. de Ficquelmont, C. R. Acad. Sci., Paris, 213, 306 (1941).

33. JANAF Thermochemical Tables, the Dow Chemical Company, Midland, Michigan, March 31, 1965.

34. F. D. Rossini et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds" Research Project 44, American Petroleum Institute, Carnegie Press, Pittsburgh, 1953.

35. D. R. Douslin, H. L. Finke, W. D. Good, and D. W. Scott, Quarterly Technical Summary Report No. 20, Bureau of Mines, U. S. Dept. of the Interior, Bartlesville, Oklahoma, Dec. 31, 1963.

36. B. D. Sharma and J. Donohue, Acta. Cryst., 16, 891 (1963).

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