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Authors
Patton, R. Lyle
Jolly, William L.

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R. Lyle Patton and William L. Jolly

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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,\textsuperscript{1} boron trichloride\textsuperscript{2} and boron trifluoride\textsuperscript{2} to form 1:1 adducts in which the Lewis acid is coordinated to a nitrogen atom of S\textsubscript{4}N\textsubscript{4}. Although a change in the configuration of the S\textsubscript{4}N\textsubscript{4} results, the basic 8-membered ring structure remains intact.\textsuperscript{3,4} Of the dozen or so known adducts, only two have two molecules of Lewis acid associated with each molecule of S\textsubscript{4}N\textsubscript{4}. These are S\textsubscript{4}N\textsubscript{4}(SO\textsubscript{3})\textsubscript{2}\textsuperscript{5} and BCl\textsubscript{3}·S\textsubscript{4}N\textsubscript{4}·SbCl\textsubscript{5}\textsuperscript{2} (which may have the ionic structure [BCl\textsubscript{2}8\textsubscript{4}N\textsubscript{4}]\textsuperscript{+} [SbCl\textsubscript{6}]\textsuperscript{3−}). Apparently when one of the nitrogen atoms of S\textsubscript{4}N\textsubscript{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,\textsuperscript{6} with antimony pentachloride. Of particular interest to us was the ability of the S\textsubscript{2}N\textsubscript{2} nitrogens to act as donor atoms and the effect of this donation on the stability and structure of the S\textsubscript{2}N\textsubscript{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 4000-4000 cm\textsuperscript{-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 \(3^\circ\) (literature,\(^7\) 2.8\(^\circ\)). Dichloromethane was refluxed over \(\text{P}_2\text{O}_5\) for 6-10 hrs., distilled, and stored in a nitrogen atmosphere. Disulfur dinitride was prepared by subliming \(\text{S}_4\text{N}_4\) through a plug of silver wool at 300\(^\circ\) 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 \(\text{S}_4\text{N}_4\) to form silver sulfide and nitrogen; the silver sulfide then acted as a catalyst for the conversion of \(\text{S}_4\text{N}_4\) to \(\text{S}_2\text{N}_2\) and small amounts of \((\text{SN})_x\). The \(\text{S}_2\text{N}_2\) 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 \((\text{SN})_x\) and small amounts of \(\text{S}_4\text{N}_4\) at room temperature.\(^9\) A sample of \(\text{S}_2\text{N}_2\) (0.059 g, 0.646 mmole) was held in a sealed tube at 250\(^\circ\) for 1 hr, whereupon it decomposed to sulfur and 0.646 mmole of nitrogen.

The \(\text{SbCl}_5\) and \(\text{S}_2\text{N}_2\) 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\(^\circ\). This method of transfer also served as a purification method for \(\text{S}_2\text{N}_2\), because the common contaminants, \((\text{SN})_x\) and \(\text{S}_4\text{N}_4\), are nonvolatile at room temperature. Enough \(\text{CH}_2\text{Cl}_2\) was distilled into the reaction vessel to dissolve the \(\text{S}_2\text{N}_2\) when warmed to 20\(^\circ\); then the solution was transferred to a glove bag. The formation of flocculent blue-black particles of \((\text{SN})_x\) (always less than 1 mg) on dissolution necessitated filtration of these \(\text{S}_2\text{N}_2\) solutions immediately before use. Because \(\text{S}_2\text{N}_2\) polymerizes appreciably in the solid state at 20\(^\circ\) 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$_4$N$_4$SbCl$_5$.—Antimony pentachloride (4.7 mmoles) in
10 ml of CH$_2$Cl$_2$ was slowly dripped into a solution of S$_2$N$_2$ (3.16 mmoles)
in 40 ml of CH$_2$Cl$_2$. 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$_4$N$_4$SbCl$_5$ 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$_4$N$_4$SbCl$_5$. The total yield was 93%.

Formation of S$_2$N$_2$(SbCl$_5$)$_2$.—The dropwise addition at 20° of a
solution of S$_2$N$_2$ (1.72 mmoles) in 25 ml of CH$_2$Cl$_2$ to SbCl$_5$ (7.8 mmoles)
in 10 ml of CH$_2$Cl$_2$ resulted in the immediate formation of fine yellow-white
crystals which increased in quantity with continued S$_2$N$_2$ 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$_2$N$_2$(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$_2$N$_2$(SbCl$_5$)$_2$;
the total yield was 67%. Evaporation of the final filtrate to dryness in
vacuo produced only this diadduct; no S$_4$N$_4$SbCl$_5$, 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$_2$N$_2$ and
CH$_2$Cl$_2$ 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$_2$N$_2$(SbCl$_5$) 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$_2$N$_2$(SbCl$_5$)$_2$ shows absorptions (in cm$^{-1}$) at 461 (s), 818 (s), and 898 (vw).

**Formation of S$_2$N$_2$SbCl$_5$.** Disulfur dinitride (1.95 mmol) in 30 ml of CH$_2$Cl$_2$ was slowly dripped into a solution of SbCl$_5$ (2.0 mmol) in 10 ml of CH$_2$Cl$_2$. After addition of 4 ml of S$_2$N$_2$ solution, fine yellow-white crystals appeared which increased in quantity until half of the S$_2$N$_2$ solution had been added. As the remaining S$_2$N$_2$ was added, the crystals slowly dissolved, and the solution changed from light yellow to light orange in color. Complete addition of the S$_2$N$_2$ resulted in complete disappearance of the crystals. Concentration of this solution to 10 ml by distilling off CH$_2$Cl$_2$ in vacuo followed by cooling to -15° yielded long (up to 1 cm), clear, light orange needless of S$_2$N$_2$SbCl$_5$, 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$_2$N$_2$(SbCl$_5$)$_2$ contamination. Anal. Calcld. for S$_2$N$_2$SbCl$_5$: 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$_2$Cl$_2$), 402.
The monoadduct \( \text{S}_2\text{N}_2\text{SbCl}_5 \) is very soluble in \( \text{CH}_2\text{Cl}_2 \) 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, \( \text{S}_2\text{N}_2\text{SbCl}_5 \) 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 \( \text{S}_2\text{N}_2\text{SbCl}_5 \) (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 \( \text{S}_4\text{N}_4\text{SbCl}_5 \) (0.12 mmole) remained in the sublimator. Nitrogen (0.008 mmole) was found in the Toepler pump buret, \( \text{SbCl}_5 \) (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% \( \text{S}_2\text{N}_2\text{SbCl}_5 \) and 10% \( \text{S}_2\text{N}_2(\text{SbCl}_5)_2 \). A slower sublimation at 60° produced proportionately much less \( \text{S}_4\text{N}_4\text{SbCl}_5 \) and \( \text{S}_2\text{N}_2(\text{SbCl}_5)_2 \).

**Pyrolysis of \( \text{S}_2\text{N}_2(\text{SbCl}_5)_2 \).** - When \( \text{S}_2\text{N}_2(\text{SbCl}_5)_2 \) (0.25 mmole) was heated at 90° for 1 hour in a vacuum sublimator with a 20° cold finger, \( \text{SbCl}_5 \) (0.22 mmole) was evolved, and yellow-white \( \text{S}_2\text{N}_2\text{SbCl}_5 \) (with slight \( \text{S}_2\text{N}_2(\text{SbCl}_5)_2 \) contamination) collected on the cold finger. A slight residue of \( \text{S}_4\text{N}_4\text{SbCl}_5 \) (0.01 mmole) remained in the sublimator.

**Addition of \( \text{S}_2\text{N}_2 \) to \( \text{S}_2\text{N}_2\text{SbCl}_5 \) and \( \text{S}_2\text{N}_2(\text{SbCl}_5)_2 \).** - Addition of \( \text{S}_2\text{N}_2 \) to \( \text{S}_2\text{N}_2\text{SbCl}_5 \) solutions in equimolar amounts yielded an opaque greenish-black suspension; precipitation began with the first drops of \( \text{S}_2\text{N}_2 \) 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 slightly contaminated with a greenish-yellow substance. The was identified by its infrared spectrum and melting point of 160° (literature, 160-2°) after recrystallization from CH₂Cl₂. No S₂N₂ or S₄N₄ was recovered.

Addition of S₂N₂ to S₂N₂(SbCl₅)₂ solutions resulted in an initial color change corresponding to formation of S₂N₂SbCl₅ which, with further S₂N₂, again became dark and opaque followed by slow clearing to a red-orange solution and precipitation of S₄N₄SbCl₅. Addition of S₂N₂ in excess of the amount required to convert all the S₂N₂SbCl₅ to S₄N₄SbCl₅ resulted in a mixture of S₄N₄ and S₄N₄·SbCl₅ in the relative amounts expected from conversion of the excess S₂N₂ to S₄N₄. Tetrasulfur tetranitride was recrystallized from dichloromethane and identified by its infrared spectrum and melting point of 182° (literature, 187-187.5°). To test the catalytic effect of S₄N₄SbCl₅ on the dimerization of S₂N₂, 1.02 mmoles of disulfur dinitride was slowly added to a solution of 0.15 mmole of S₄N₄SbCl₅. The solution remained orange-red. Infrared analysis indicated that after 2 hrs approximately equal amounts of S₄N₄ and S₂N₂ were in the solution, and that after 15 hours only 10% of the original S₂N₂ remained.

A small amount (5-10%) of the greenish-yellow substance was always formed as a by-product of these reactions in which S₄N₄SbCl₅ was formed. The characterization of this material is described below.

(S₄N₄SbCl₅)x - The small amount of greenish-yellow material formed in the above reactions was found to be insoluble in CH₂Cl₂ and could be isolated free of contamination by S₄N₄SbCl₅ and S₄N₄ 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 in vacuo 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

Reactions of \(S_2N_2\) with \(SbCl_5\).- 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:

\[
S_2N_2 + 2SbCl_5 \rightarrow S_2N_2(SbCl_5)_2 \tag{1}
\]

\[
S_2N_2 + S_2N_2(SbCl_5)_2 \rightarrow 2S_2N_2SbCl_5 \tag{2}
\]
Addition of \( \text{S}_2\text{N}_2 \) to an equimolar amount of \( \text{S}_2\text{N}_2\text{SbCl}_5 \) in dichloromethane yields the previously-characterized adduct \( \text{S}_4\text{N}_4\text{SbCl}_5 \).

\[
\text{S}_2\text{N}_2 + \text{S}_2\text{N}_2\text{SbCl}_5 \rightarrow \text{S}_4\text{N}_4\text{SbCl}_5
\]  
(3)

A relatively insoluble greenish-yellow material, having the empirical formula \( (\text{S}_4\text{N}_4\text{SbCl}_5)_x \) but possessing physical properties entirely different from those of ordinary \( \text{S}_4\text{N}_4\text{SbCl}_5 \), 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 \( (\text{S}_4\text{N}_4\text{SbCl}_5)_x \) by-product contaminated with what appeared to be \( (\text{SN})_x \), we tentatively suggest that the intermediate is an open-chain isomer of \( \text{S}_4\text{N}_4 \) or \( \text{S}_2\text{N}_2 \), perhaps coordinated to \( \text{SbCl}_5 \).

This intermediate may be a precursor of \( (\text{S}_4\text{N}_4\text{SbCl}_5)_x \).

When \( \text{S}_2\text{N}_2 \) is added to \( \text{S}_2\text{N}_2\text{SbCl}_5 \) in greater than a 1:1 ratio, the excess \( \text{S}_2\text{N}_2 \) is quickly converted to \( \text{S}_4\text{N}_4 \). Obviously some species in the reaction system catalyzes the dimerization of \( \text{S}_2\text{N}_2 \). The adduct \( \text{S}_4\text{N}_4\text{SbCl}_5 \) does catalyze the dimerization, but relatively inefficiently. Possibly the dark intermediate discussed above is involved in the rapid dimerization.

The adduct \( \text{S}_4\text{N}_4\text{SbCl}_5 \) is inert toward \( \text{SbCl}_5 \); consequently this adduct is formed whenever \( \text{SbCl}_5 \) is added to a solution of \( \text{S}_2\text{N}_2 \), regardless of the final \( \text{S}_2\text{N}_2: \text{SbCl}_5 \) ratio. The fact that \( \text{S}_2\text{N}_2\text{SbCl}_5 \) in dichloromethane solution does not decompose to \( \text{S}_4\text{N}_4\text{SbCl}_5 \) proves that the following equilibria lie far to the left.

\[
\text{S}_2\text{N}_2\text{SbCl}_5 \rightleftharpoons \text{S}_2\text{N}_2 + \text{SbCl}_5
\]  
(4)

\[
2\text{S}_2\text{N}_2\text{SbCl}_5 \rightleftharpoons \text{S}_2\text{N}_2 + \text{S}_2\text{N}_2(\text{SbCl}_5)_2
\]  
(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.

$$
S_2N_2 + SbCl_5 \rightarrow S_2N_2SbCl_5 \xrightarrow{SbCl_5^-} S_2N_2(SbCl_5^-)_2 \xrightarrow{(1 + x)S_2N_2} \frac{x}{2} S_4N_4
$$

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 $S_2N_2(SbCl_5^-)_2$ 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.

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

(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.

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

(7)

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

$$
S_2N_2(SbCl_5^-)_2(s) \rightarrow S_2N_2SbCl_5(g) + SbCl_5(g).
$$

(8)
The slight impurity of \( \text{S}_2\text{N}_2(\text{SbCl}_5)\)\(_2\) found in the condensed \( \text{S}_2\text{N}_2\text{SbCl}_5 \) probably resulted from recombination of \( \text{S}_2\text{N}_2\text{SbCl}_5 \) and \( \text{SbCl}_5 \) on the cold finger rather than from direct sublimation of \( \text{S}_2\text{N}_2(\text{SbCl}_5)\)\(_2\).

The low sublimation temperature of \( \text{S}_2\text{N}_2\text{SbCl}_5 \) supports the formulation as an \( \text{S}_2\text{N}_2 \) adduct, because an \( \text{S}_4\text{N}_4(\text{SbCl}_5)\)\(_2\) adduct would be expected to be much less volatile.

Crystals of \( \text{S}_2\text{N}_2\text{SbCl}_5 \) are stable indefinitely at \(-15^\circ\), but slowly darken at \(20^\circ\), becoming black after 1-2 weeks. Crystals of \( \text{S}_2\text{N}_2(\text{SbCl}_5)\)\(_2\) undergo no change on standing at \(20^\circ\) 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 \( \text{S}_2\text{N}_2 \) above \(-30^\circ\), indicates that the \( \text{S}_2\text{N}_2 \) ring is stabilized by coordination with Lewis acids. The rapid reaction of \( \text{S}_2\text{N}_2\text{SbCl}_5 \) with \( \text{S}_2\text{N}_2 \), however, shows that this coordination somehow increases the reactivity toward attack by \( \text{S}_2\text{N}_2 \).

**Infrared Spectra.** The infrared spectrum and chemical properties of \( \text{S}_2\text{N}_2 \) 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 \( \text{SbCl}_5 \) groups are expected to lie below 400 cm\(^{-1}\). Therefore structural changes in the \( \text{S}_2\text{N}_2 \) 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 \( \text{S}_2\text{N}_2(\text{SbCl}_5)\)\(_2\) correspond closely in shape and position to the two strong \( \text{S}_2\text{N}_2 \) 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 \( \text{S}_2\text{N}_2 \) and the number of modes (2 or 3) observed indicate that the \( \text{S}_2\text{N}_2 \) 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$_2$N$_2$SbCl$_5$ 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$_2$N$_2$ 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$_2$N$_2$ group: planar ring ($C_{2v}$), puckered ring ($C_s$), or chain ($C_{ov}$, $C_s$ 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$_2$N$_2$SbCl$_5$ and S$_2$N$_2$(SbCl$_5$)$_2$, the similarity to the S$_2$N$_2$ 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$_4$N$_4$SbCl$_5$ in the same region (at 1060 and 968 cm$^{-1}$).

The possibility that the compounds S$_2$N$_2$(SbCl$_5$)$_2$ and S$_2$N$_2$SbCl$_5$ are tetra- and diadducts of S$_4$N$_4$ was considered. However, the observed bands showed no correlation with those of S$_4$N$_4$ or S$_4$N$_4$SbCl$_5$, and the forms of highest symmetry for S$_4$N$_4$(SbCl$_5$)$_4$ (planar ring, $D_{4h}$) and S$_4$N$_4$(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$_2$N$_2$SbCl$_5$ and S$_2$N$_2$(SbCl$_5$)$_2$ as adducts of the difunctional Lewis base.
$S_2N_2$ with the structures:

\[
\begin{aligned}
\text{N} & \quad \text{SbCl}_5 \\
\text{S} & \quad \text{S}
\end{aligned}
\]

(puckered or planar ring)

\[
\begin{aligned}
\text{Cl}_5\text{Sb-N} & \quad \text{S} \\
\text{S} & \quad \text{S}
\end{aligned}
\]

(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

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