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

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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 eight-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 and 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 Data.—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° (lit.[7] mp 2.8°). Dichloromethane was refluxed over P_2O_5 for 6–10 hr, 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 of 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 (obsd, 93; calcd, 92.1). The material was observed to polymerize slowly 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 mmol) was held in a sealed tube at 250° for 1 hr, whereupon it decomposed to sulfur and 0.646 mmol 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 mmol) in 10 ml of CH_2Cl_2 was slowly dripped into a solution of S_2N_2 (3.16 mmol) 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 0.5 hr 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 of 160° (lit.[2] ml 160–162°). 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 mmol) in 25 ml of CH_2Cl_2 to $SbCl_5$ (7.8 mmol) 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 and 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

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(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, Ed., "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1963, p 537.

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

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

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 at 461 (s), 818 (s), and 898 (vw) cm^{-1}.

Formation of $S_2N_2SbCl_5$.—Disulfur dinitride (1.95 mmol) in 30 ml of CH_2Cl_2 was slowly dripped into a solution of $SbCl_5$ (2.0 mmol) 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.* 10 g/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° and then melt with decomposition at 108–109°. The crystals immediately blacked in moist air. The infrared spectrum shows peaks at 1005 (m), 922 (vw), 800 (s), 723 (mw), 627 (w), and 459 (s) cm^{-1}.

A sample of $S_2N_2SbCl_5$ (0.83 mmol) 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 hr at 70°, the products were examined. An orange-brown residue of $S_4N_4SbCl_5$ (0.12 mmol) remained in the sublimator. Nitrogen (0.008 mmol) was found in the Toepler pump buret, $SbCl_5$ (0.02 mmol) 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 mmol) was heated at 90° for 1 hr in a vacuum sublimator with a 20° cold finger, $SbCl_5$ (0.22 mmol) 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 mmol) 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 hr, 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° (lit.[2] mp 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 of 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° (lit.[11] mp 187–187.5°). To test the catalytic effect of $S_4N_4SbCl_5$ on the dimerization of S_2N_2, 1.02 mmol of disulfur dinitride was slowly added to a solution of 0.15 mmol of $S_4N_4SbCl_5$. The solution remained orange-red. Infrared analysis indicated that after 2 hr approximately equal amounts of S_4N_4 and S_2N_2 were in the solution and that after 15 hr 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.

$(S_4N_4SbCl_5)_x$.—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 of 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 mmol) 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 mmol) 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 of the $S_4N_4SbCl_5$ and left 200 mg of yellow solid having only the above infrared absorptions and a melting point of 193–193.5°. *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 a sublimator equipped with a water-cooled cold finger and evacuated through −45 and −196° traps with a Toepler pump, no sublimation of $(S_4N_4SbCl_5)_x$ occurred. Slow decomposition began at 162°, and after several hours at 170°, S_4N_4 was found on the cold finger, $SbCl_3$ in the −45° trap, and N_2 in the Toepler pump buret. After warming to 20°, NSCl and SCl_2 were distilled from the −196° trap leaving a residue of $S_3N_2Cl_2$. The NSCl,[12] SCl_2,[13] $S_3N_2Cl_2$,[14] and S_4N_4[10] were identified by their infrared spectra, and the $SbCl_3$ was identified by its appearance and its melting point of 71–72° (lit.[7] mp 73.4°). 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

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

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(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

(14) The infrared absorptions were identical with those of an $S_3N_2Cl_2$ sample prepared by the method of W. L. Jolly and K. D. Maguire, *Inorg. Syn.*, **9**, 102 (1967).

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 of 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

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

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

Addition of S_2N_2 to an equimolar amount of $S_2N_2SbCl_5$ in dichloromethane yields the previously characterized adduct $S_4N_4SbCl_5$, as shown by

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

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 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, bur 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 equilibria 4 and 5 lie far to the left. Otherwise S_4N_4-

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

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

$SbCl_5$ 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 a considerably weaker base.

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 $S_2N_2SbCl_5$ 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. The sub-

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

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

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

adduct $S_2N_2(SbCl_5)_2$ dissociates *in vacuo* at 90° *via* reaction 8. The slight impurity of $S_2N_2(SbCl_5)_2$ found in

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

the condensed $S_2N_5SbCl_5$ 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 ampoules 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 and 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}.

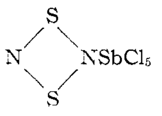
The two strong bands at 818 and 461 cm^{-1} in the infrared spectrum of $S_2N_2(SbCl_5)_2$ correspond closely in shape and position to the two strong S_2N_2 bands. The very weak band at 898 cm^{-1} is possibly an overtone of the band at 460 cm^{-1}. The similarity of the absorptions to those of S_2N_2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

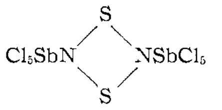
and 723 (mw) cm^{-1} are expected from the lowering of symmetry resulting from the nonequivalence of the nitrogen atoms. Distinction between the possible configurations of the S_2N_2 group [planar ring (C_{2v}), puckered ring (C_s), or chain ($C_{\infty v}$, C_s, or C_1)] is not possible inasmuch as 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 evidences 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.[15]

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[15] R. L. Patton and K. N. Raymond, unpublished work.

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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 explore further 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 Data.—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 (lit.[2] 477 mm). The observed −111.6° vapor pressure of BF_3 was 310 mm (lit.[3] 312 mm). Boron trifluoride was measured by pressure–volume methods, and BCl_3, $SbCl_5$, and S_2N_2 were measured 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, 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 nonvolatile 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 mmol), BF_3 (3.175 mmol), 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 mmol) were pumped off, leaving 84 mg

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[1] R. L. Patton and W. L. Jolly, *Inorg. Chem.*, **8**, 1389 (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).