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REACTIONS OF DISULFUR DINITRIDE WITH BORON TRIFLUORIDE AND BORON TRICHLORIDE

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Contribution from the Department of Chemistry of the
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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 tarred 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 tarred 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

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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 $\text{S}_4\text{N}_4\text{BF}_3$ on the basis of its infrared spectrum,⁴ its melting point of 145° (literature,⁴ $145\text{--}147^\circ$) and its characteristic of slowly losing BF_3 when pumped on at room temperature. Complete conversion of S_2N_2 to $\text{S}_4\text{N}_4\text{BF}_3$ requires 0.355 mmoles of BF_3 (observed, 0.358 mmole), forming 83 mg of $\text{S}_4\text{N}_4\text{BF}_3$.

$\text{S}_2\text{N}_2\text{-BCl}_3$ 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

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of the solution was then unaffected by warming to 20° or cooling to -78°. The reaction mixture was held at -78° while BCl₃ was distilled off in vacuo and then warmed to 0° while removing the remaining CH₂Cl₂. A slight amount of N₂ (0.017 mmole) was evolved in the reaction. No precipitation occurred during the solvent removal, but as the last of the CH₂Cl₂ 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 (S₂N₂BCl₃)_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 N₂, CH₂Cl₂, BCl₃, and slight traces of

Table I. Reactions of S₂N₂ with BCl₃ at 0°

S ₂ N ₂ (mmoles)	BCl ₃ S ₂ N ₂	N ₂ evolved (mmoles)	Product wt (mg)	Calculated for (S ₂ N ₂ BCl 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

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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 $670-1350\text{ cm}^{-1}$ 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

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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

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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 $\text{S}_2\text{N}_2(\text{SbCl}_5)_2$.¹ Extraction of the product with dichloromethane yielded a solution from which pure $\text{S}_2\text{N}_2(\text{SbCl}_5)_2$ was obtained (identified by its infrared spectrum¹) and left some residue with the appearance and infrared spectrum of $(\text{S}_2\text{N}_2\text{BCl}_3)_x$.

The creamy white products of composition $\text{S}_2\text{N}_2\text{BCl}_3$ 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

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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 spectrum⁴ 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.

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(SN)_x - BCl₃ Reaction. - A sample of (SN)_x was obtained as a by-product from several S₂N₂ preparations. It was separated from S₄N₄ 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 tarred 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 BCl₃ and 3 ml of CH₂Cl₂ 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 (S₂N₂BCl₃)_x. Upon heating in a sealed capillary the yellow solid behaved like (S₂N₂BCl₃)_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 BCl₃ were placed in a tarred 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 BCl₃ were removed by pumping, first at -80° and then while warming to 0°, until all volatiles had been removed.

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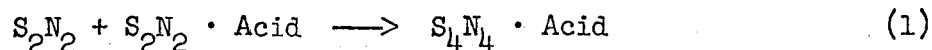
Nitrogen (0.080 mmole) was collected in the Toepler pump buret, and 124 mg of an orange-yellow solid remained. If we assume that the small amount of evolved nitrogen corresponded to the decomposition of some $(SN)_x$ to the elements and that the principal product was $(S_2N_2BCl_3)_x$, we calculate that 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,

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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:



In the case of $\text{S}_2\text{N}_2\text{SbCl}_5$, 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 $\text{S}_2\text{N}_2\text{BF}_3$, the equilibrium concentration of S_2N_2 is high enough for the reaction to proceed and to prevent the isolation of $\text{S}_2\text{N}_2\text{BF}_3$.

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 $(\text{S}_2\text{N}_2\text{BCl}_3)_x$ 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 $(\text{S}_2\text{N}_2\text{BCl}_3)_x$ 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 $\text{S}_4\text{N}_4\text{BCl}_3$.² Thus it appears that $(\text{S}_2\text{N}_2\text{BCl}_3)_x$ 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, $(\text{SN})_x$, with boron trichloride gives a material having the same properties and approximately the same composition as the $(\text{S}_2\text{N}_2\text{BCl}_3)_x$ prepared from S_2N_2 and BCl_3 at 0°. However

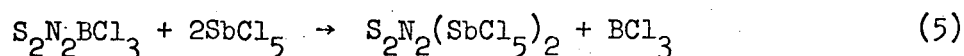
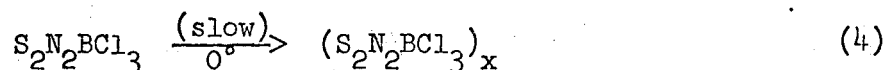
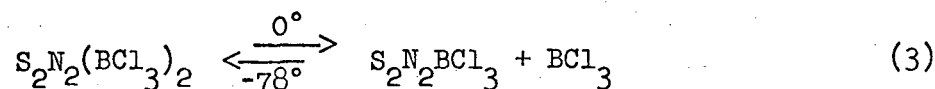
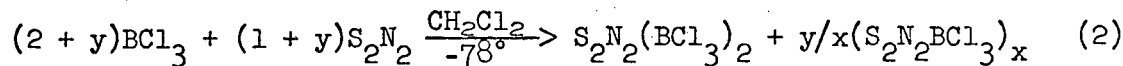
-12-

the $(\text{SN})_x\text{-BCl}_3$ 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 $\text{S}_2\text{N}_2(\text{BCl}_3)_2$ and a small amount of $(\text{S}_2\text{N}_2\text{BCl}_3)_x$. The $\text{S}_2\text{N}_2(\text{BCl}_3)_2$ dissociates reversibly on warming to 0° to BCl_3 and a monoadduct $\text{S}_2\text{N}_2\text{BCl}_3$. The ability of $\text{S}_2\text{N}_2\text{BCl}_3$ to add BCl_3 at low temperatures distinguishes it from $(\text{S}_2\text{N}_2\text{BCl}_3)_x$, 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) $\text{S}_2\text{N}_2\text{BCl}_3 \rightarrow (\text{S}_2\text{N}_2\text{BCl}_3)_x$ 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 $\text{S}_2\text{N}_2\text{BCl}_3$ present in a mixture of $\text{S}_2\text{N}_2\text{BCl}_3$ and $(\text{S}_2\text{N}_2\text{BCl}_3)_x$, 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 known¹ disulfur dinitride adduct $\text{S}_2\text{N}_2(\text{SbCl}_5)_2$ is in agreement with the relative Lewis acid strengths of SbCl_5 and BCl_3 and supports the formulation of $\text{S}_2\text{N}_2\text{BCl}_3$, and $\text{S}_2\text{N}_2(\text{BCl}_3)_2$ as adducts of S_2N_2 . The residue of $(\text{S}_2\text{N}_2\text{BCl}_3)_x$ left after washing out the $\text{S}_2\text{N}_2(\text{SbCl}_5)_2$ further confirms its presence as the inert material. The data presented correspond quantitatively

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to the reactions:

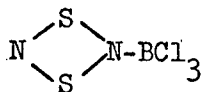


Formation of $S_4N_4BCl_3$.-- The formation of $S_4N_4BCl_3$ by the addition of BCl_3 to an S_2N_2 solution is analogous to the formation of $S_4N_4SbCl_5$ ¹ and $S_4N_4BF_3$ from S_2N_2 . In each of these reactions, the mechanism is probably the initial formation of an adduct of the type $S_2N_2 \cdot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

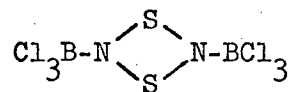
In adducts in which the boron atom of BCl_3 is bonded directly to the central atom of a Lewis base molecule, a broad infrared absorption envelope characteristic of the BCl_3 portion of the adduct is found with maxima in the 700-800 cm^{-1} region.⁵ Also, sulfur-nitrogen compounds usually have strong 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

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of S-N and BCl_3 modes. The remaining $\text{S}_2\text{N}_2\text{BCl}_3$ absorptions (at 1115, 950, 610, and 467 cm^{-1}) correspond closely in position and shape to absorptions in $\text{S}_2\text{N}_2\text{SbCl}_5$. Thus the infrared and chemical evidence support formulation of $\text{S}_2\text{N}_2\text{BCl}_3$ and $\text{S}_2\text{N}_2(\text{BCl}_3)_2$ as adducts of the same type as those of S_2N_2 with SbCl_5 with the structures:



and



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-15-

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