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ADDUCES OF SULFUR NITRIDE WITH BORON TRIHALIDES AND ANTIMONY PENEACHLORIDE

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ADDUCTS OF SULFUR NITRIDE WITH  
BORON TRIHALIDES AND ANTIMONY PENTACHLORIDE

Kenneth J. Wynne and William L. Jolly

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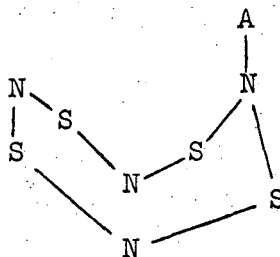
Adducts of Sulfur Nitride with  
Boron Trihalides and Antimony Pentachloride

Kenneth J. Wynne and William L. Jolly

Abstract

Sulfur nitride in methylene chloride reacts with  $\text{BF}_3$  to form burgundy-colored crystals of  $\text{S}_4\text{N}_4 \cdot \text{BF}_3$  and with  $\text{BCl}_3$  to form red-orange needles of  $\text{S}_4\text{N}_4 \cdot \text{BCl}_3$ . The  $\text{BF}_3$  adduct decomposes reversibly to  $\text{S}_4\text{N}_4$  and  $\text{BF}_3$  when heated, whereas the  $\text{BCl}_3$  adduct sublimes with slight decomposition. The properties of the adducts are consistent with structures involving B-N bonds, as in  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$ . The boron trifluoride in  $\text{S}_4\text{N}_4 \cdot \text{BF}_3$  may be displaced by  $\text{BCl}_3$  or  $\text{SbCl}_5$ . In an attempt to displace  $\text{BCl}_3$  from  $\text{S}_4\text{N}_4 \cdot \text{BCl}_3$  with  $\text{SbCl}_5$ , the adduct  $\text{S}_4\text{N}_4 \cdot \text{BCl}_3 \cdot \text{SbCl}_5$  formed. This reaction was unexpected because no di-adducts were found in the reaction of  $\text{S}_4\text{N}_4$  with either excess  $\text{BCl}_3$  or  $\text{SbCl}_5$ . The conversion of  $\text{S}_4\text{N}_4 \cdot \text{BCl}_3$  to  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  may be effected by treating  $\text{S}_4\text{N}_4 \cdot \text{BCl}_3$  with  $\text{SbCl}_5$  to give  $\text{S}_4\text{N}_4 \cdot \text{BCl}_3 \cdot \text{SbCl}_5$ , followed by heating this substance in vacuo to  $90^\circ$  to form  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  and  $\text{BCl}_3$ .

The following adducts of  $S_4N_4$  with Lewis acids have been prepared:  $S_4N_4 \cdot SbCl_5$ ,<sup>1,2</sup>  $2S_4N_4 \cdot SnCl_4$ ,<sup>1,2</sup>  $S_4N_4 \cdot TiCl_4$ ,<sup>1,2</sup>  $S_4N_4 \cdot 2SO_3$ ,<sup>3</sup>  $S_4N_4 \cdot 4SO_3$ ,<sup>3</sup>  $S_4N_4 \cdot TeBr_4$ ,<sup>4</sup>  $S_4N_4 \cdot 4SbF_5$ ,<sup>5</sup> and  $4S_4N_4 \cdot BF_3$ .<sup>6</sup> Only for  $S_4N_4 \cdot SbCl_5$  is definite structural information available. An x-ray study<sup>7</sup> has shown this adduct to have a structure of type I shown below,



I.

where  $A$  represents the coordinated Lewis acid.

The unusual stoichiometry reported for the  $BF_3$  adduct, and the lack of information regarding the other boron trihalide adducts, led us to a systematic study of the reaction of  $S_4N_4$  with the boron trihalides.

### Experimental Section

General. Moisture-sensitive materials were handled in a nitrogen-filled polyethylene glove bag or a standard vacuum line. Analyses were performed in the microanalytical laboratory of this department by V. Tashinian and F. Balistreri.

Infrared spectra were recorded in the  $700-4000\text{ cm}^{-1}$  range with a Perkin-Elmer Infracord Model 137B, in the  $400-700\text{ cm}^{-1}$  range with a Perkin-Elmer Infracord Model 137 equipped with a KBr prism, and in the  $33-400\text{ cm}^{-1}$  range with a Beckman IR-11 grating spectrophotometer. Samples

were generally prepared in a nitrogen atmosphere as Nujol mulls, and then pressed between either KBr or polyethylene plates. Methylene chloride solution spectra were run in a 0.1 mm. KBr cavity cell.

Methylene chloride was refluxed for 3-4 hours over  $P_2O_5$ , distilled, and stored in a nitrogen atmosphere. Sulfur nitride was prepared and purified according to the method described by Villena-Blanco and Jolly.<sup>8</sup>

Sulfur Nitride-Boron Trifluoride Adduct. A slurry of 8.45 g. of sulfur nitride and 135 ml.  $CH_2Cl_2$  was prepared in a flask equipped with a gas inlet tube and an outlet protected with a  $CaSO_4$  drying tube. While stirring with a magnetic stirrer,  $BF_3$  was bubbled at ca. 4-6 bubbles/sec. The solution, initially red-orange, immediately turned dark burgundy. The  $BF_3$  flow was terminated after 40 min., the gas bubbler was removed, and the slurry was filtered yielding 7.89 g of dark burgundy  $S_4N_4 \cdot BF_3$ . A further yield of 3.07 g. of relatively large crystals (ca 3 x 1 x 1 mm.) was obtained by cooling the filtrate to  $-15^\circ$ ; the total yield was 95%. On heating, the product became continually lighter in color above  $90^\circ$  until melting occurred at  $145-7^\circ$ .

Anal. Calcd. for  $S_4N_4 \cdot BF_3$ : S, 50.88; N, 22.23. Found: S, 50.22; N, 22.21.

The Nujol mull infrared spectrum showed the following peaks<sup>9</sup> (in  $cm^{-1}$ ): [1171 m, 1138 m-s, 1117 s, 1070 s, 1040 vs, 1014 m, 949 s, 908 m, 888 s, 840 w-m], 724 vw, 697 vw, 682 vw, 658 m-s, 623 m-s, 567 w, 552 w, 527 s, 502 m, 490 wsh, 420 m-s. In  $CH_2Cl_2$  solution absorptions were at 1121 m, 1058 m-s, 964 m, 933 m, 882 s, 658 sh on solvent, 623 m, 569 w, and 527 s  $cm^{-1}$ .

Anal. Calcd for  $S_4N_4 \cdot BCl_3 \cdot SbCl_5$ : S, 21.36; N, 9.33; Cl 47.2.

Found: S, 21.47; N, 9.58; Cl, 46.8.

The infrared spectrum showed the following peaks<sup>9</sup> (in  $cm^{-1}$ ):  
1317 vw, 1059 vw, 1018 vs, 932 s, 900 vs, 875 w, 840 vs, 811 m, 788 vs,  
748 m, 703 w-m, 691 m-s, 677 s, [552 s, 517 m ], 461 m, [419 m, 407 m-s],  
359 vs, 320 s, 294 m-s, 269 m-s, 241.5 m, 208 s, 181 vs, 78 w, 52 w.

Sulfur Nitride-Boron Tribromide. A solution of 3 ml. (31.7 mmoles) of  $BBr_3$  in 25 ml.  $CH_2Cl_2$  was added slowly to a solution of  $S_4N_4$  (2.35 g., 12.75 mmoles) in 150 ml.  $CH_2Cl_2$ . The solution turned a dark burgundy color, with the separation of a precipitate. Filtration yielded a gooey orange-brown mass. It was washed with 10 ml.  $CH_2Cl_2$  and held in vacuo for 15 hours, yielding 4.2 g. of brown solid. When flushing the glove bag, a distinct odor of bromine was detected. The material imparted a faint orange-yellow coloration when mixed with  $CH_2Cl_2$ .

Anal. Calcd. for  $S_4N_4 \cdot BBr_3$ : S, 29.49; N, 12.89; Br, 55.13.

Found: S, 27.1; N, 12.75; Br, 57.7.

The infrared spectrum showed the following peaks<sup>9</sup> (in  $cm^{-1}$ ):  
[1310 s, 1000 m-s, 820 m, 670 w]. Inasmuch as  $S_4N_4 \cdot BBr_3$  was found to be finely-divided, moisture-sensitive, and insoluble in  $CH_2Cl_2$ , it was not investigated further.

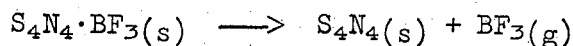
### Results and Discussion

$S_4N_4 \cdot BF_3$ . Whereas we found that bubbling  $BF_3$  into a suspension of  $S_4N_4$  in  $CH_2Cl_2$  gives an almost quantitative yield of a material of composition  $S_4N_4 \cdot BF_3$ , Glemser and Ludemann<sup>6</sup> found that a material of overall composition  $4S_4N_4 \cdot BF_3$  formed in a direct reaction of  $BF_3$  gas



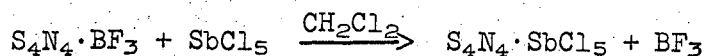
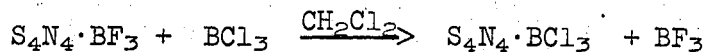
with solid  $S_4N_4$  at room temperature. Perhaps incomplete reaction was responsible for the unusual stoichiometry observed by these investigators.

The lability of the adduct is shown by the facts that passage of nitrogen through a  $CH_2Cl_2$  solution for 12-14 hours, or evaporation of solvent in vacuo or heating the solid in vacuo, cause loss of  $BF_3$  and formation of  $S_4N_4$ . The dissociation pressure of the adduct was measured in an immersible tensimeter over the temperature range 30-70°C. The combined data for two runs are presented in Table I, where the observed pressures may be compared with those calculated from the equation  $\log P_{mm} = 10.82 - 3270/T$ . From this equation we calculate the values  $\Delta H^\circ = 15.0 \text{ kcal. mole}^{-1}$  and  $\Delta S^\circ = 31 \text{ e.u.}$  for the reaction

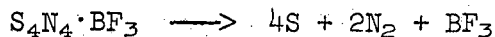


In the absence of the heats of sublimation for  $S_4N_4$  and  $S_4N_4 \cdot BF_3$ , we cannot compare the base strength of  $S_4N_4$  with that of any other Lewis base.

In  $CH_2Cl_2$  solution,  $BF_3$  in the adduct may be replaced by  $BCl_3$  or  $SbCl_5$  as shown by the following equations



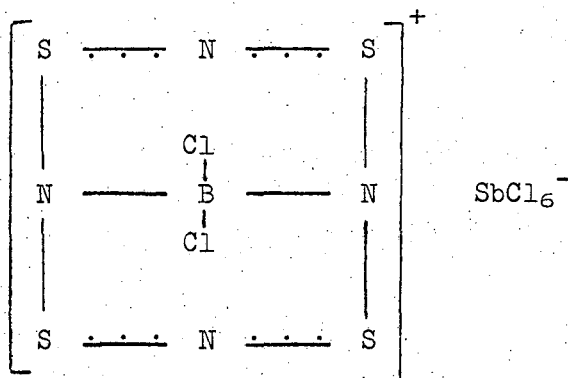
$S_4N_4BF_3$  decomposes at 140° in a sealed tube as follows



By analogy with the structure of  $S_4N_4 \cdot SbCl_5$ ,<sup>7</sup>  $S_4N_4 \cdot BF_3$  is believed to have a structure of type I, with a B-N bond.

$S_4N_4 \cdot BCl_3 \cdot SbCl_5$ . In an attempt to displace the  $BCl_3$  from  $S_4N_4 \cdot BCl_3$  with  $SbCl_5$  in  $CH_2Cl_2$ , a yellow precipitate of  $S_4N_4 \cdot BCl_3 \cdot SbCl_5$  formed.

Three possible structural formulations were considered for the di-adduct: A.  $[S_4N_4 \cdot SbCl_5]^+ [BCl_4]^-$ , B.  $[S_4N_4 BCl_2]^+ [SbCl_6]^-$ , and C.  $Cl_3B-S_4N_4-SbCl_5$  (B-N and Sb-N bonds). For B one can conceive of the  $BCl_2^+$  group being either monovalent, as in structure type I, or divalent, as in structure II, below.



II.

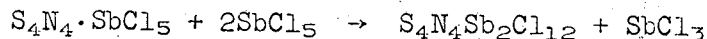
Formulation A may be eliminated on the basis that the characteristic  $BCl_4^-$  absorption envelope<sup>10,11</sup> is not observed in the infrared spectrum.

The far-infrared spectra of  $KSbCl_6$  and  $S_4N_4 \cdot SbCl_5$  were obtained to determine if significant differences in Sb-Cl frequencies would be found, corresponding to the different coordination around antimony. Potassium hexachloroantimonate(V) was prepared by stirring KCl and  $SbCl_5$  in  $CH_2Cl_2$  for 47 hours. The infrared spectrum, not previously reported, showed absorptions at 349, 181, and  $72 \text{ cm}^{-1}$ . By analogy with the spectra of other octahedral species,<sup>12</sup> and from a knowledge of the Raman spectrum<sup>13</sup> of the  $SbCl_6^-$  ion, these bands are assigned to  $\nu_3$ ,  $\nu_4$ , and a lattice vibration, respectively.

The  $S_4N_4 \cdot SbCl_5$  adduct showed absorptions at  $345.5$  and  $177.5 \text{ cm}^{-1}$ , and  $S_4N_4 \cdot BCl_3 \cdot SbCl_5$  showed absorptions at  $357$  and  $181 \text{ cm}^{-1}$ . The small differences in the respective Sb-Cl frequencies in all three cases does not allow a choice between formulations B and C for the di-adduct. Absorptions in the B-Cl and B-N region slightly favor formulation B, with structure II. Nöth and Lukas<sup>14</sup> have reported B-Cl frequencies at  $849$  and  $842 \text{ cm}^{-1}$ , and a B-N absorption at  $925 \text{ cm}^{-1}$ , for  $[(CH_3)_2NH]_2BCl_2 \cdot Cl$ . Possibly the peaks at  $840$  and  $932 \text{ cm}^{-1}$  of the di-adduct correspond to the B-Cl and B-N frequencies, respectively, expected for tetravalent boron.

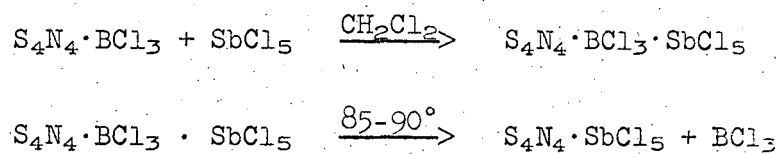
The formation of the mixed adduct was surprising because di-adducts of  $BCl_3$  and  $SbCl_5$  were not formed even though excess  $BCl_3$  and  $SbCl_5$  were present in the preparation of the corresponding mono-adducts.

Boron trichloride, in tenfold excess, was heated in a sealed tube with  $S_4N_4 \cdot BCl_3$  in  $CH_2Cl_2$  at  $34^\circ$  for 57 hours in an attempt to form a di-adduct. The pressure released upon opening the flask, presumably due to nitrogen, and the presence of  $S_2Cl_2$  among the products, indicated that if a di-adduct formed it was unstable under these conditions. A small amount of light yellow solid was also produced in the reaction, but was not investigated further. Under similar conditions  $S_4N_4 \cdot SbCl_5$  was treated with a tenfold excess of  $SbCl_5$ . After 72 hours, a yellow solid which analyzed for  $S_4N_4Sb_2Cl_{12}$  was produced. In the absence of a solvent this yellow material formed in only 2 hours. A white volatile solid, presumably  $SbCl_3$ , was obtained from the latter reaction, and its quantity determined by uptake of  $Cl_2$ . The calculated stoichiometry of the reaction of  $SbCl_5$  with  $S_4N_4 \cdot SbCl_5$  is shown by the following equation.



The product (mp 128-9°) exhibited infrared absorptions<sup>9</sup> (in  $\text{cm}^{-1}$ ) at 1060 m-s; 1016 s, 619 w, and [455 m, 426 m]. It was insoluble in  $\text{CH}_2\text{Cl}_2$  and was not investigated further. The data indicate that a simple di-adduct of  $\text{S}_4\text{N}_4$  and  $\text{SbCl}_5$  is not stable under these conditions and that, if it forms, it is rapidly chlorinated by the excess  $\text{SbCl}_5$ .

When  $\text{S}_4\text{N}_4 \cdot \text{BCl}_3 \cdot \text{SbCl}_5$  was heated to 85-93°, with constant removal of volatiles in a -196° trap,  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  and  $\text{BCl}_3$  were formed. Thus a conversion of  $\text{S}_4\text{N}_4 \cdot \text{BCl}_3$  to  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  may be effected by the following successive reactions.



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