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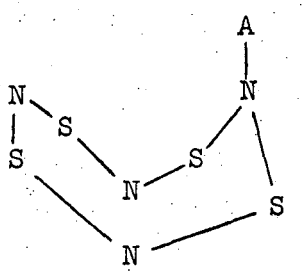
Adducts of Sulfur Nitride with Boron Trihalides and Antimony Pentachloride

Kenneth J. Wynne and William L. Jolly

Abstract

Sulfur nitride in methylene chloride reacts with BF_3 to form burgundy-colored crystals of $S_4N_4 \cdot BF_3$ and with BCl_3 to form red-orange needles of $S_4N_4 \cdot BCl_3$. The BF_3 adduct decomposes reversibly to S_4N_4 and BF_3 when heated, whereas the BCl_3 adduct sublimes with slight decomposition. The properties of the adducts are consistent with structures involving B-N bonds, as in $S_4N_4 \cdot SbCl_5$. The boron trifluoride in $S_4N_4 \cdot BF_3$ may be displaced by BCl_3 or $SbCl_5$. In an attempt to displace BCl_3 from $S_4N_4 \cdot BCl_3$ with $SbCl_5$, the adduct $S_4N_4 \cdot BCl_3 \cdot SbCl_5$ formed. This reaction was unexpected because no di-adducts were found in the reaction of S_4N_4 with either excess BCl_3 or $SbCl_5$. The conversion of $S_4N_4 \cdot BCl_3$ to $S_4N_4 \cdot SbCl_5$ may be effected by treating $S_4N_4 \cdot BCl_3$ with $SbCl_5$ to give $S_4N_4 \cdot BCl_3 \cdot SbCl_5$, followed by heating this substance *in vacuo* to 90° to form $S_4N_4 \cdot SbCl_5$ and BCl_3.

The following adducts of S_4N_4 with Lewis acids have been prepared: $S_4N_4 \cdot SbCl_5$,[1,2] $2S_4N_4 \cdot SnCl_4$,[1,2] $S_4N_4 \cdot TiCl_4$,[1,2] $S_4N_4 \cdot 2SO_3$,[3] $S_4N_4 \cdot 4SO_3$,[3] $S_4N_4 \cdot TeBr_4$,[4] $S_4N_4 \cdot 4SbF_5$,[5] and $4S_4N_4 \cdot BF_3$.[6] Only for $S_4N_4 \cdot SbCl_5$ is definite structural information available. An x-ray study[7] 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 cm^{-1} range with a Perkin-Elmer Infracord Model 137B, in the 400-700 cm^{-1} range with a Perkin-Elmer Infracord Model 137 equipped with a KBr prism, and in the 33-400 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.[8]

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°; the total yield was 95%. On heating, the product became continually lighter in color above 90° until melting occurred at 145-7°.

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[9] (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[9] (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[9] (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[6] 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 $\Delta H^\circ = 15.0$ kcal. mole^{-1} and $\Delta S^\circ = 31$ e.u. for the reaction

$$S_4N_4 \cdot BF_3(s) \longrightarrow S_4N_4(s) + BF_3(g)$$

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

$$S_4N_4 \cdot BF_3 + BCl_3 \xrightarrow{CH_2Cl_2} S_4N_4 \cdot BCl_3 + BF_3$$

$$S_4N_4 \cdot BF_3 + SbCl_5 \xrightarrow{CH_2Cl_2} S_4N_4 \cdot SbCl_5 + BF_3$$

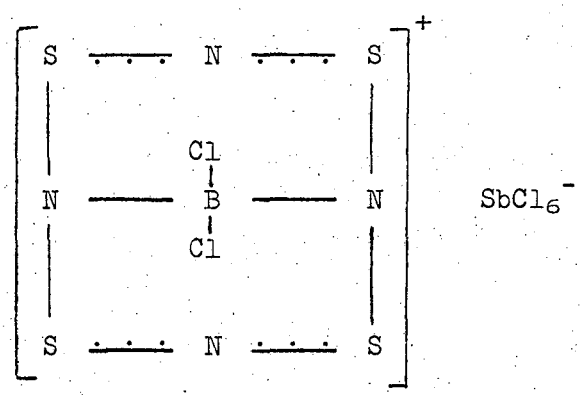
$S_4N_4BF_3$ decomposes at 140° in a sealed tube as follows

$$S_4N_4 \cdot BF_3 \longrightarrow 4S + 2N_2 + BF_3$$

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

<u>$S_4N_4 \cdot BCl_3 \cdot SbCl_5$</u>. 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. $[S_4N_4BCl_2]^+[SbCl_6]^-$, and C. $Cl_3B\text{-}S_4N_4\text{-}SbCl_5$ (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[10,11] 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 hexachoroantimonate(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 cm^{-1}. By analogy with the spectra of other octahedral species,[12] and from a knowledge of the Raman spectrum[13] of the $SbCl_6^-$ ion, these bands are assigned to ν_3, ν_4, and a lattice vibration, respectively.

The $S_4N_4 \cdot SbCl_5$ adduct showed absorptions at 345.5 and 177.5 cm^{-1}, and $S_4N_4 \cdot BCl_3 \cdot SbCl_5$ showed absorptions at 357 and 181 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[14] have reported B-Cl frequencies at 849 and 842 cm^{-1}, and a B-N absorption at 925 cm^{-1}, for $\{[(CH_3)_2NH]_2BCl_2\}Cl$. Possibly the peaks at 840 and 932 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° 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.

$$S_4N_4 \cdot SbCl_5 + 2SbCl_5 \rightarrow S_4N_4Sb_2Cl_{12} + SbCl_3$$

The product (mp 128-9°) exhibited infrared absorptions[9] (in cm^{-1}) at 1060 m-s, 1016 s, 619 w, and [455 m, 426 m]. It was insoluble in CH_2Cl_2 and was not investigated further. The data indicate that a simple di-adduct of S_4N_4 and $SbCl_5$ is not stable under these conditions and that, if it forms, it is rapidly chlorinated by the excess $SbCl_5$.

When $S_4N_4 \cdot BCl_3 \cdot SbCl_5$ was heated to 85-93°, with constant removal of volatiles in a -196° trap, $S_4N_4 \cdot SbCl_5$ and BCl_3 were formed. Thus a conversion of $S_4N_4 \cdot BCl_3$ to $S_4N_4SbCl_5$ may be effected by the following successive reactions.

$$S_4N_4 \cdot BCl_3 + SbCl_5 \xrightarrow{CH_2Cl_2} S_4N_4 \cdot BCl_3 \cdot SbCl_5$$

$$S_4N_4 \cdot BCl_3 \cdot SbCl_5 \xrightarrow{85\text{-}90^\circ} S_4N_4 \cdot SbCl_5 + BCl_3$$

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