Table IV. Chemical Analysis (mol %) Related to B = 1

calcd for	molar ratios N:B	N	C	H	S	B	C_2H_5
	1:0.98	1.01	5.7	17	4.2	1	0.65
	1:1.0	0.98	4.9	14	3.1	1	0.5
	1:1.27	0.8	3.6	11	3.0	1	0.2
	1:3.02	0.6	2.7	9	3.0	1	0.15
	1:2.85	0.6	3.2	10	3.1	1	0.4
	1:8.3	0.5	3.3	10	3.3	1	0.65
I		0.67	3.0	11	2.67	1	0.33
II		0.33	2.67	8	2.33	1	0.67

$B(SC_2H_5)_3$ it is facilitated. This different behavior can only be explained by the bulkiness of the SC_2H_5 ligand.

In B–S chemistry, the formation of six-membered rings comprised of three alternating B and three S atoms is more common than for B–O compounds. For example, thioboric acid is a cyclic trimer,[16] while orthoboric acid is a monomer with strong hydrogen bonds. Among the borates, only the less common triborates have six-membered ring structures analogous to the known alkali metal thioborates; for example, $NaBS_2$ is better represented by the formula $Na_3B_3S_6$.[17]

More highly condensed S-containing ring systems similar to the spiranlike pentaborates are not formed despite the utilization of an up to eightfold excess of $B(SC_2H_5)_3$. This result can be explained by the fact that, as in the case of thioboric acid,[16] the endocyclic B–S bonding distances are smaller than the endocyclic ones. Since the sulfur atoms are larger than the oxygen atoms, the formation of two spiranlike rings at one boron atom as in the pentaborates is unlikely in the B–S chemistry.

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Registry No. I·2[$N(CH_3)_4$], 68550-24-3; II·[$N(CH_3)_4$], 68474-91-9; $H_2S·BCl_3$, 68474-69-1; BCl_2SH, 39130-80-8; BBr_3, 10294-33-4; BBr_2SH, 39130-81-9; $BBr(SH)_2$, 40679-99-0; $(-BBr-S-)_3$, 18495-45-9; $B(SC_2H_5)_3$, 998-26-5; $N(CH_3)_4SH$, 10408-32-9; $N(C_2H_5)_4SH$, 10408-33-0; $N(CH_3)_4[BCl_3SH]$, 15820-64-1; $N(CH_3)_4[BBr_3SH]$, 68474-92-0; $N(C_2H_5)_4[BCl_3SH]$, 15649-93-1; $N(C_2H_5)_4[BBr_3SH]$, 68474-93-1; BCl_3, 10294-34-5; H_2S, 7783-06-4.

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Reactions of Tetrasulfur Tetranitride with Bromine. Reaction in Carbon Disulfide Solution To Give $CS_3N_2Br_2$

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The products of the reaction of tetrasulfur tetranitride depend strongly on the reaction conditions. Recently it has been shown that gas-phase bromination of solid S_4N_4 causes polymerization to conducting $(SNBr_{0.4})_x$ while reaction with liquid bromine leads to a stable tribromide $S_4N_3Br_3$.[4] In contrast the reaction of S_4N_4 with bromine in carbon disulfide solution results in a mixture of $S_4N_3Br_3$, S_4N_3Br, and a novel ionic compound $CS_3N_2Br_2$.

As part of a continuing study of the bromination of S_4N_4,[2,4] the products of bromination in solution have been investigated. We previously reported the reaction of bromine vapor with solid S_4N_4 which gives $(SNBr_{0.4})_x$,[2,3] a highly conducting solid, very similar in its physical properties to brominated $(SN)_x$. The reaction of S_4N_4 with liquid bromine gives the ionic compound $S_4N_3^+Br_3^-$,[4,5] which contains stacks of alternating planar $S_4N_3^+$ rings and asymmetric Br_3^- cations. The bromination of S_4N_4 in CS_2 was first reported by Clever and Muthman in 1896.[6] These authors describe their reaction product as bronze crystals which they assumed to be $S_4N_4Br_4$, similar to the known chlorination product $S_3N_3Cl_3$. Later Becke-Goehring[7] formulated the compound as a polymer $(SNBr)_x$, largely on the basis of its insolubility in nonpolar organic solvents. Heal[8] repeated the synthesis and analyzed the product to be $S_3N_2Br_2$ analogous to the known compound $S_3N_2Cl_2$.[9] In another study Zborilova et al.[10] concluded the bronze crystals were actually a mixture of S_4N_3Br and $S_3N_2Br_2$. In this paper data will be presented which show that the bronze crystals are indeed a mixture, but of $S_4N_3^+Br^-$, its corresponding tribromide, and $CS_3N_2Br_2$ rather than $S_3N_2Br_2$.

Experimental Section. Reaction of Bromine with S_4N_4 in CS_2

All manipulations were carried out under vacuum or in a dry argon atmosphere with purified reagents and dried solvents. A total of 2.5 mL of bromine was added to 1.75 g (9.5 mmol) of S_4N_4 dissolved in 200 mL of CS_2. After 24 h olive brown crystals were collected on a frit and thoroughly washed with CS_2 until the washings were only slightly yellow. The product was then dried under vacuum to give a yield of 3.75 g. This product was then further extracted with liquid SO_2 for 7 days until the washings were almost colorless. The yield of the SO_2-insoluble fraction was 1.03 g. Anal. Calcd for $CS_3N_2Br_2$: C, 4.06; S, 32.48; N, 9.46; Br, 53.99. Found: C, 4.24; S, 31.80; N, 9.94; Br, 53.35.

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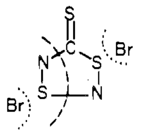
Discussion

Clever and Muthmann[6] did not report the conditions for their reaction of Br_2 with S_4N_4 in CS_2; however, following the procedure described by Becke-Goehring[7] small olive brown crystals were obtained. The analysis of this product varies, particularly in bromine content, depending on the amount of bromine used and the washing and drying conditions. In our experience, the sulfur:nitrogen ratio is 1.3:1 rather than 1:1 as reported by previous workers. The presence of the $S_4N_3^+$ cation[2a,11] is clearly shown from IR data, and thus the variable bromine content can be explained by the presence of a mixture of Br^- and Br_3^- counterions as we reported previously in our investigation of $S_4N_3Br_3$.[4] The IR spectra also clearly show the presence of at least one other compound besides the S_4N_3Br–$S_4N_3Br_3$ mixture. These latter compounds were removed by extraction with liquid SO_2 leaving a moisture-sensitive microcrystalline powder $CS_3N_2Br_2$ with an IR spectrum identical with that of "$S_2N_2Br_2$" reported by Zborilova et al.[10] This result shows that the CS_2 solvent was involved in the reaction. An overall reaction for the formation of $CS_3N_2Br_2$ consistent with all the observed products is given in reaction 1 where the numbers in parentheses refer to the

$$5S_4N_4 + 4CS_2 + 6(10)Br_2 \rightarrow 4CS_3N_2Br_2 + 4S_4N_3Br_{(3)} \tag{1}$$

formation of the tribromide. This reaction is in good agreement with the ratio of $S_4N_3Br_{(3)}$ and $CS_3N_2Br_2$ observed from IR data by comparison with an authentic 1:1 mixture of the pure compounds. No other side products have to be postulated in order to account for this product distribution. Indeed no substantial amount of any additional compound as postulated by Zborilova et al.—besides some hydrolysis product—was observed.

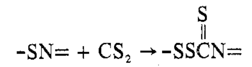
Modulated molecular beam mass spectrometric techniques and conventional chemical ionization mass spectrometry[12] also support these results. Comparison of the pure $CS_3N_2Br_2$ with the $CS_3N_2Br_2$ and $S_4N_3Br_{(3)}$ mixtures shows $CS_3N_2Br_2$ to volatilize with decomposition under vacuum in a Knudsen cell[12] at less than 110 °C while S_4N_3Br volatilizes at higher temperatures. The mass spectral results show that $CS_3N_2Br_2$ decomposes by two apparently competing pathways, reactions 2 and 3, with reaction 3 accounting for over 80% of the products.



$\dashrightarrow$ NSBr + CS_2NBr (2)

$\dashrightarrow$ CS_3N_2 + Br_2 (3)

Though the $CS_3N_2Br_2$ is insoluble in nonpolar solvents it is very slightly soluble in liquid SO_2 and dissolves with decomposition in sulfuric acid. As shown by the Knudsen cell studies, attempts to sublime it lead to decomposition. This lack of solubility and volatility suggests the structure is polymeric or more probably ionic. Its insolubility made it impossible to determine its molecular weight or grow crystals for molecular structure determination. Nevertheless, useful information about the possible structure of $CS_3N_2Br_2$ is obtained from the IR and mass spectra. The presence of a –C=S bond is indicated by a strong IR band at 1316 cm^{-1}. This could arise from the known tendency of CS_2[13] to insert in SN compounds according to reaction 2. In view of the



$$\text{-SN=} + CS_2 \rightarrow \text{-SS}\overset{\overset{S}{\|}}{C}\text{N=} \tag{4}$$

strong tendency of S–N compounds to form cyclic structures rather than chains, the most reasonable structure is shown in Figure 1 together with that of the known compound COS_2N_2.[14] This structure is consistent with the mass spectral data on the gas-phase CS_3N_2 species (confirmed by phase angle mass spectrometry[12]) which shows the major ions to be $CS_3N_2^+$ (*m/e* 136), CS_2N^+ (*m/e* 90), CS_2^+ (*m/e* 76), CSN^+ (*m/e* 80), and SN^+ (*m/e* 46). The IR spectra of $CS_3N_2Br_2$ and COS_2N_2 are given in Table I. Both spectra show corresponding bands. The observed shifts are not unexpected in view of the difference in charge. For $CS_3N_2Br_2$ there are bands at 414 and 394 cm^{-1} in the region of the S–Br stretching vibration (300–450 cm^{-1}).[15] Thus structures such as those shown in Figure 1c cannot be ruled out; however, no SN compounds containing bromine bonded covalently to sulfur are known except the reaction intermediate SNBr.[4] On the other hand, doubly charged SN cations are known only in the presence of much stronger acceptors than bromine.[16]

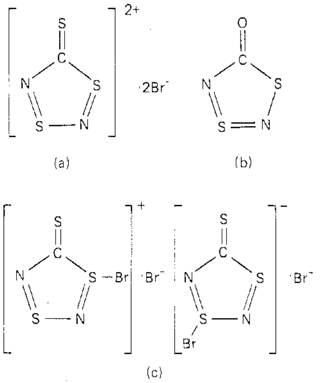


Figure 1. (a) Suggested structure of $CS_3N_2Br_2$. (b) Structure of COS_2N_2.[14] (c) Alternative structures for $CS_3N_2Br_2$.

Table I. Comparison of the IR Spectra (cm^{-1}) of $CS_3N_2Br_2$ and COS_2N_2[a]

$CS_3N_2Br_2$		COS_2N_2[a]	
1334 (w)	760 (vs)	1727 (vs)	725 (s)
1316 (vs)	722 (m)	1172 (w)	640 (w)
1120 (vw)	633 (s)	1158 (w)	520 (w)
970 (vs)	572 (s)	1065 (m)	523 (w)
922 (s)	562 (m)	780 (m)	
882 (s)	414 (vs)		
783 (vw)	394 (m)		

[a] Reference 14.

Reaction of S_4N_4 with Br_2 in inert solvents such as SO_2 leads exclusively to a mixture of S_4N_3Br and $S_4N_3Br_3$ depending on the bromine concentration. When Br_2 is reacted with an S_4N_4 suspension in CCl_4 (a solvent in which it is poorly soluble), the product is a mixture of S_4N_3Br/Br_3 and brominated $(SN)_x$, i.e., $(SNBr_{0.4})_x$. The S_4N_3Br/Br_3 is formed by the bromination of the dissolved S_4N_4, whereas the undissolved S_4N_4 undergoes the previously reported solid-state bromination to $(SNBr_{0.4})_x$.

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Registry No. $CS_3N_2Br_2$, 68423-43-8; S_4N_4, 28950-34-7; CS_2, 75-15-0; bromine, 7726-95-6.

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Vapor Complexes of Samarium(III) and Samarium(II) Chlorides with Aluminum(III) Chloride

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The electronic absorption spectra of vapor-phase compounds formed by reacting $SmCl_3(s)$ and $SmCl_2(s)$ with gaseous Al_2Cl_6 have been measured at temperatures up to 800 K and total pressures up to 13 atm. The spectra of the pale yellow Sm^{III}–Al–Cl gaseous complex(es) were characteristic of the f → f electronic transitions of Sm(III). The spectra of the red-brown Sm^{II}–Al–Cl gaseous complex(es) showed high-intensity, broad bands which are attributed to 4f → 5d transitions of Sm(II). Spectrophotometric measurements have been used to investigate the partial pressures of the vapor complexes at different Al_2Cl_6 pressures. Thermodynamic considerations suggest that the $SmAl_3Cl_{12}$ is the predominant vapor species formed by the trivalent samarium. For the reaction $SmCl_3(s) + {}^3/_2Al_2Cl_6(g) \rightarrow SmAl_3Cl_{12}(g)$ the values of $\Delta H = 6.7$ kcal/mol and $\Delta S = -1.0$ eu have been derived. At 650 K the volatility enhancement of Sm(II) has been estimated to be $\sim 10^{10}$. Rare earth oxides have been halogenated and vapor transported using Al_2Cl_6 or Al_2Br_6. A new method for the preparation of anhydrous rare earth halide crystals is suggested. The data are discussed in terms of the systematics of formation and structure of gaseous lanthanide chloride complexes.

Introduction

In recent years the formation of vapor complexes of transition metal halides with "acidic" halide vapors (e.g., Al_2Cl_6, Fe_2Cl_6) has been widely investigated by different research groups.[1-6] Spectrophotometric,[2-5] mass spectrometric,[1] and transpiration techniques[1,4,6] have been used to obtain thermodynamic information for these complexes. Very little work, however, has been done for the vapor complexes involving lanthanide or actinide halides. Exceptions are the investigations of Gruen et al.,[7] of Zvarova et al.,[8] and the recent work of Sørlie and Øye.[9] From a practical point of view, the interest in the rare earth–acidic vapor complexes arises from their potential use both as agents for chemical separations of the elements[8] and as gain media in the construction of high-power vapor lasers.[10]

Our present work is a part of a general study of the thermodynamics,[5,11-13] electronic absorption,[11-13] and Raman spectroscopy[14-16] of vapor complexes. The investigation concerns the vapor complexes of Sm(II) and Sm(III) chlorides with aluminum chloride. Spectrophotometric studies have been used to establish the formation of yellow Sm(III) and ceramic-red Sm(II) vapor complexes formed according to the reactions

$$m\mathrm{SmCl_3(s)} + n\mathrm{Al_2Cl_6(g)} \rightarrow m\mathrm{SmCl_3}\cdot n\mathrm{Al_2Cl_6(g)} \quad (1)$$

$$m'\mathrm{SmCl_2(s)} + n'\mathrm{Al_2Cl_6(g)} \rightarrow m'\mathrm{SmCl_2}\cdot n'\mathrm{Al_2Cl_6(g)} \quad (2)$$

From the measurements, the thermodynamics and stoichiometry of reaction 1 are derived. The data are discussed in terms of the electronic spectral properties and possible structure of the vapor complexes. The thermodynamic and structural properties of the Sm(III) complex are compared with the corresponding properties of the Nd(III)[7a] and Ho(III)[17] complexes.

Experimental Section

Anhydrous aluminum chloride was prepared from the corresponding Cerac/Pure Inc. reagent by repeated slow sublimations in fused silica tubes under vacuum.

A new method has been employed for the preparation and purification of samarium(III) chloride. Anhydrous and degassed Sm_2O_3 ($\sim$2 g) was placed in fused silica tubes ($\sim$1 cm i.d. × 20 cm long) containing an excess of aluminum cloride ($\sim$2 g). The evacuated and sealed tube was then placed in a furnace and the temperature was raised slowly (3–4 h) to 300 °C. Near 200 °C the following reaction began:

$$\mathrm{Sm_2O_3(s)} + \mathrm{Al_2Cl_6(g,l)} \rightarrow \mathrm{Al_2O_3(s)} + 2\mathrm{SmCl_3(s)} \quad (3)$$

The chlorination was completed within a few hours and the remaining excess of $Al_2Cl_6(g)$ created a pressure of $\sim$2 atm in the tube. The tube was then placed in a tilted furnace where the lower part of the tube, containing the solids (Al_2O_3 + $SmCl_3$), was at 350 °C and the upper part was near the melting point of aluminum chloride (180 °C). With this thermal gradient, $SmCl_3$ was vapor transported according to reaction 1 and was deposited in the form of small yellow crystals ($\sim$0.1 mm × 1 mm) at the middle of the tube. Within 2 days the vapor transport yielded $\sim$1 g of $SmCl_3$. Reaction 3 appears to be very general for the preparation of lanthanide and actinide halides using aluminum halides. To date, we have prepared and vapor transported $NdCl_3$, $NdBr_3$, $PrCl_3$, $ErCl_3$, YCl_3, $ThCl_4$, UCl_3, and UCl_4 by reacting the corresponding oxide with Al_2Cl_6 or Al_2Br_6. The yields are high and by controlling the rate of vapor transport small single crystals of the halides can be obtained.

Initially the red-brown samarium(II) chloride was prepared[18] by fusing together a 1:2 mixture of samarium metal and samarium(III) chloride at $\sim$750 °C. It was later found, however, that $SmCl_3$ could be reduced at $\sim$250 °C by either Sm or Al metal in fused silica tubes containing an excess of Al_2Cl_6 liquid or gas. The reduction yielded a dark red binary liquid which contained large amounts of Al_2Cl_6. This liquid solidified at $\sim$220 °C and was very stable up to 500 °C; at this temperature, the aluminum chloride began to react with the fused silica tubes. By heating the liquid under vacuum at 300 °C, all Al_2Cl_6 was removed, leaving a red-brown powder whose X-ray patterns showed the presence of $SmCl_2$ plus other unidentifiable samarium chloride compounds. In the presence of excess Al_2Cl_6 vapors, the red-brown liquid was vapor transported to a colder part of the tube. A similar binary liquid was also formed by mixing $SmCl_2$ with Al_2Cl_6. Vapors over these liquids were red-brown giving identical electronic absorption spectra.

The anhydrous materials were handled in evacuated fused-silica tubes or in a helium-atmosphere drybox with a water vapor level <20 ppm.

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