added, the solution was stirred for 30 min. At this point the product had been formed and a nitrogen atmosphere was no longer maintained. The solution was evaporated under reduced pressure to an oil, 40 mL of hot hexanes (~65 °C) was added, and the solution was filtered and evaporated to dryness (or an oil). The product was then dissolved in ~5 mL of pentanes and passed through a Florisil chromatography column (2 × 20 cm) using pentanes as the eluent. The product fraction was isolated and evaporated to dryness (or an oil), dissolved in carbon disulfide (~5 mL) and passed through a small Florisil chromatography column (0.5 × 7 cm) to remove the excess phosphorus ligands which adhere to the Florisil when CS_2 is the eluent. The product fraction was isolated and evaporated to dryness (L = $P(OMe)_3$, $P(n\text{-}Bu)_3$ gave liquids) with an average yield of ~80%. These products were identified by comparison of their IR spectra with known[6] *trans*-$W(CO)_4(CS)L$ derivatives. The x-ray structural determination of the *trans*-$W(CO)_4(CS)(CNC_6H_{11})$ has been reported.[16]

***cis*-$W(CO)_4(CS)L$ (L = $P(OCH_3)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(4\text{-}CH_3C_6H_4)_3$, $P(n\text{-}C_4H_9)_3$, CNC_6H_{11}, 4-$CH_3C_5H_4N$).** The *cis*-$W(CO)_4(CS)L$ complexes were formed by heating the trans isomer in cyclohexane (1.5 mM) at 65.0 ± 0.1 °C until the infrared carbonyl stretching spectrum no longer changed (25–70 h), indicating the cis–trans mixture was at equilibrium. The solution was then passed through a Florisil chromatography column (2 × 5 cm) using pentanes as the eluent. The *cis*-$W(CO)_4(CS)L$–*trans*-$W(CO)_4(CS)L$ product fraction was evaporated to dryness and used in the IR and ^{13}C NMR studies. To ensure that no isomerization occurred on the Florisil column, the cis/trans ratio of $W(CO)_4(CS)[P(C_6H_5)_3]$, determined by ^{13}C NMR, was found to be the same within experimental error (±~10%) before and after chromatography on the Florisil column.

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Registry No. I (L = **1**), 14040-11-0; I (L = **2**), 23306-41-4; I (L = **3**), 23306-42-5; I (L = **4**), 17000-16-7; I (L = **5**), 15444-65-2; I (L = **6**), 17000-19-0; I (L = **7**), 17000-14-5; I (L = **8**), 15603-77-7; I (L = **9**), 14911-74-1; I (L = **10**), 15131-04-1; I (L = **11**), 14911-58-1; II (L = **1**), 50358-92-4; II (L = **2**), 66007-56-5; II (L = **3**), 65969-64-4; II (L = **4**), 65969-63-3; II (L = **5**), 50358-94-6; II (L = **6**), 65969-62-2; II (L = **7**), 65969-61-1; II (L = **8**), 61509-59-9; II (L = **9**), 58569-44-1; II (L = **10**), 58569-42-9; II (L = **11**), 56030-99-0; III (L = **2**), 65969-60-0; III (L = **3**), 66007-60-1; III (L = **4**), 66007-59-8; III (L = **5**), 58617-28-0; III (L = **6**), 66007-58-7; III (L = **7**), 65969-65-5; III (L = **8**), 66007-57-6; $[Et_4N]W(CO)_5Br$, 14780-94-0; $Bu_4N[W(CO)_4(CS)I]$, 56031-00-6; ^{13}C, 14762-74-4.

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Investigation of the Hydride Impurity of $(SN)_x$. Formation of $(SN)_x$ in the Presence of Water

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An investigation of the origin and the nature of the hydride species of $(SN)_x$ is described. The vapor-phase hydride species has a molecular weight of 220 ± 12 and results from a reaction involving water during the synthesis of $(SN)_x$. Reaction with water occurs following S_2N_2 crystal formation and prior to $(SN)_x$ sublimation. The hydride species has been found to comprise up to 20% of the vapor species in some $(SN)_x$ samples, with more typical values being 5–10%. Experimental results are presented which suggest that formation of the hydride species may be the first step of a hydrolysis process.

Introduction

Polymeric sulfur nitride (polythiazyl), $(SN)_x$, has attracted considerable interest due to its characterization as a strongly anisotropic metal.[1–6] Recently, Smith et al.[5] have studied the vapor-phase species produced upon sublimation of $(SN)_x$ and determined the principal component of the vapors to be an $(SN)_4$ species, probably having a linear, bent-chain structure.[5b] These mass spectrometric studies also revealed the presence of a hydride impurity which has an estimated concentration on the order of 1–4 atom % hydrogen.[5] All other detectable impurities[7] were due to surface-related processes and were negligible after heating under vacuum for a few hours.[5]

The magnitude of the hydrogen concentration of $(SN)_x$ is rather surprising, especially since $(SN)_x$ crystals have often been reported to be "analytically pure". This finding, which has since been confirmed by other workers,[8] immediately gave rise to questions concerning the effect of the hydride impurity on the conductivity of $(SN)_x$ and the temperature at which $(SN)_x$ becomes a superconductor. For example, a hydride impurity might be expected to lower the temperature at which the highly anisotropic $(SN)_x$ crystals become superconducting if hydrogen acts as an $(SN)_x$ chain-terminator. Alternately, the hydride impurity might raise the superconducting temperature of $(SN)_x$. Indeed, the absorption of hydrogen into certain metals (e.g., Pt) is known to increase the superconducting temperature. It has also been recently reported that the addition of bromine to $(SN)_x$ decreases the hydride impurity to less than one-tenth its normal level in this material.[10] Additionally, the hydride impurity, or its precursor, may play a role in the solid-state polymerization of S_2N_2 to $(SN)_x$. For these reasons, and the possible implications for experimental measurements of electronic properties of $(SN)_x$, a further study of this hydride impurity has become imperative.

In the present report we detail our efforts, using a variety of mass spectrometric techniques, to identify the origin and nature of the hydride species detected in the $(SN)_x$ vapors. In the course of this study we have examined $(SN)_x$ samples prepared in this laboratory, as well as at two other laboratories

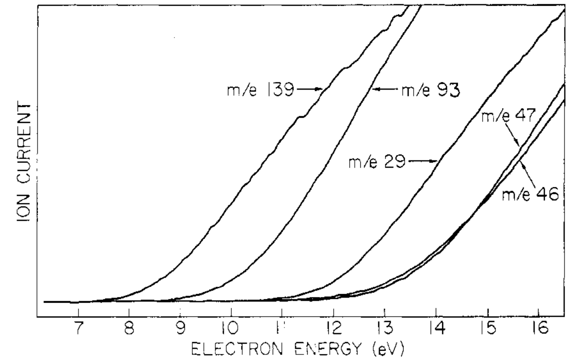

Figure 1. Time-averaged ion current vs. electron energy curves for *m/e* 29, 46, 47, 93, and 139.

Table I. Appearance Potentials for Various Ionic Species Observed for $(SN)_x$ Vapors

Species	AP, eV	Species	AP, eV
$S_4N_4^+$	9.8[a]	SNH^+	13.6
$S_3N_3H^+$	8.4	SN^+	13.3
$S_3N_3^+$	9.5	N_2H^+	12.0
$S_2N_2H^+$	12.0	$HNSO^+$	11.4
$S_2N_2^+$	11.2		

[a] Probably results from a small contribution of the cyclic tetrasulfur tetranitride formed by isomerization of $(SN)_4$; see ref 5.

presently involved in the study of $(SN)_x$.[11] The results of the present study suggest the steps which may be taken to allow the synthesis of hydride-free $(SN)_x$.

Experimental Section

The Knudsen cell and modulated-beam mass spectrometer used in this work have been described previously.[5] The present study has employed $(SN)_x$ crystals synthesized at the Naval Research Laboratory by the method of Mikulski et al.[1d] $(SN)_x$ crystals prepared elsewhere,[11] using similar methods, have also been examined and yielded essentially identical results. All $(SN)_x$ samples were studied by heating several crystals to between 70 and 160 °C and directing an effusive molecular beam through the mass spectrometer ionization region.[5]

The use of modulated-beam techniques eliminates background contributions and allows the application of phase-angle spectrometry.[5,12] In the latter technique the distance between the molecular beam chopper and the ionization region is lengthened to approximately 20 cm, and the mass-dependent phase shift is used to provide an approximate value of the molecular weight of the vapor species. Electron impact spectra were recorded at various electron energies between 9 and 70 eV; unless otherwise noted, the spectra discussed refer to 14-eV electron energies.

Selected $(SN)_x$ samples were subjected to additional study using field ionization (FI) and field desorption (FD) mass spectrometry. The application of FI and FD techniques to $(SN)_x$ have been described previously.[5b]

Results

As reported previously,[5] the mass spectra of $(SN)_x$ vapors show several ion intensities (at *m/e* 29, 47, 93, and 139) which are attributed to the presence of a hydrogen-containing species. The intensities are much greater than isotopic contributions from $S_xN_y^+$ ions due to ^{33}S and ^{15}N. On the basis of the analysis of the mass spectra, these ions have been identified as N_2H^+, SNH^+, $S_2N_2H^+$, and $S_3N_3H^+$. All other hydrogen-containing ions (e.g., $S_3N_2H^+$ and S_2NH^+) have considerably smaller intensities and may be disregarded in the present discussion.

Appearance potentials (AP's) were determined from graphs of ion intensity vs. electron energy, as shown in Figure 1. These curves are the results of signal averaging several hundred sweeps of electron energy, as described previously.[5] AP's for the major ions observed for $(SN)_x$ vapors between 100 and 160 °C are given in Table I.

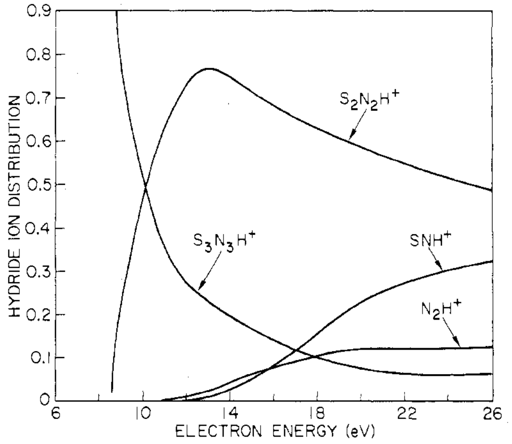

Figure 2. Hydride ion distributions observed as a function of ionizing electron energy. This type of distribution is typical of the fragmentation of a single species.

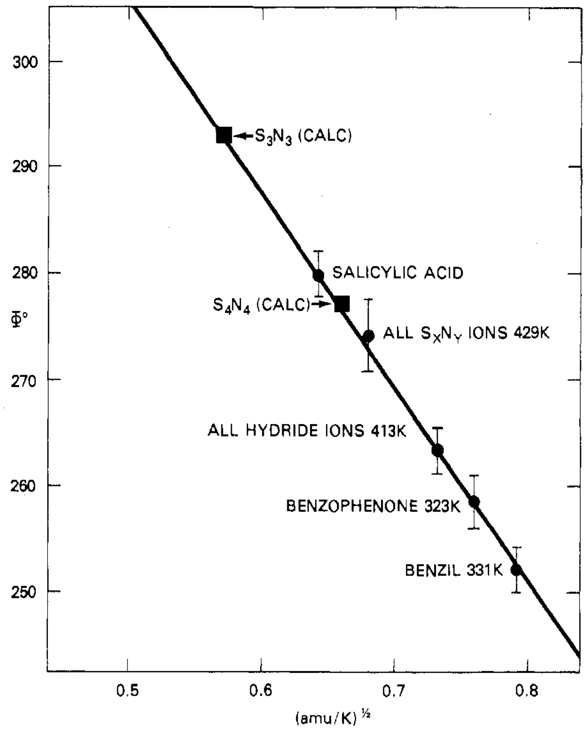

Figure 3. Phase-angle spectrometry results used to determine the molecular weight (220 ± 12) of the vapor-phase hydride species of $(SN)_x$. The phase angle Φ is approximately linear with respect to $(amu/K)^{1/2}$; see ref 12.

The distribution of hydride ions as a function of the average electron energy is given in Figure 2. This breakdown of data clearly shows the effects of increased internal energy on fragmentation of the parent ionic species. These distributions, in cooperation with phase-angle results, support the hypothesis that a single hydride species is responsible for all the hydride ions.

Phase-angle spectrometry[12] was used to determine the approximate mass of the vapor-phase neutral species which forms $S_3N_3H^+$, $S_2N_2H^+$, SNH^+, and N_2H^+ upon ionization. Using benzophenone, benzil, salicycylic acid, and S_4N_4 to calibrate the mass scale, a molecular weight of 220 ± 12 (95% confidence limits) was determined for the neutral precursor of all hydride ions (see Figure 3). This result is somewhat surprising since $S_3N_3H^+$ (*m/e* 139) is the most intense ion observed by low-energy (10-eV) electron impact (Figure 2). Thus, the hydride ions quite clearly arise from a different molecular species than the $S_xN_y^+$ fragments (x, y = 1 to 4), which we have previously identified as $(SN)_4$.[5] Furthermore, the neutral hydride species forms a molecular ion which is unstable under electron impact.

Field ionization (FI) and field desorption (FD) mass spectra of $(SN)_x$ crystals identified as having a relatively large hydride concentrations were also obtained. Because of the relatively high *S*/*N* levels involved in these pulse-counting experiments, minor peaks (<1% of the base peak) must be viewed with considerable uncertainty. However, these spectra do not contain the hydride ions ($S_3N_3H^+$, etc.) nor any ionic species in the *m*/*e* 190–600 range (other than S_8^+). Our failure to observe the hydride species using FI or FD techniques may be attributed to: most probably an unusual fragmentation mechanism (yielding only $S_xN_y^+$ ions); a disparity in the ionization efficiency of the two species; surface-related processes (which are relatively common phenomena in such studies[13]).

A number of additional experiments were undertaken to determine the origin of the hydride species. The complete synthesis of $(SN)_x$ was studied mass spectrometrically, and detailed results of this work will be presented elsewhere.[14] The S_4N_4 starting material was examined and found to be "hydride free". However, upon being immersed in water for extended periods (several days), small intensities of ions indicative of the hydride impurity were observed in the vapors, in addition to NH_3 and SO_3. This reaction is far too slow, however, to be responsible for the hydride species observed in $(SN)_x$.

In addition to S_4N_4, the S_2N_2 intermediate was also studied and found to be "hydride free". S_2N_2 was examined both by immediately following formation, by passing S_4N_4 through heated silver wool, and by vaporization of S_2N_2 crystals. During the synthesis of $(SN)_x$, S_2N_2 is warmed from liquid nitrogen temperatures to form S_2N_2 crystals in an adjacent water-cooled container. As the S_2N_2 was warmed, NH_3, N_3H, HNSO, SNO, and H_2O molecular species were also observed.[14] The water, having a concentration on the order of 10% of S_2N_2, is assumed to result from a combination of outgassing from the glass surfaces and stopcock grease and small leaks in the vacuum systems. Any water which finds its way into the vacuum system is collected efficiently on the liquid N_2 cooled cold finger during the 6–8 h required for the initial steps of the synthesis.[1d] Thus, a considerable quantity of water is present during the S_2N_2 deposition process and is probably included in the S_2N_2 crystal lattice. The other highly volatile species noted above are efficiently removed by several minutes of pumping at −10 °C and are not present in the S_2N_2 crystals used for polymerization.[14] The hydride species is not observed in the vapors until polymerization has occurred and a sample is heated to >75 °C [i.e., when $(SN)_x$ begins to sublime].

These results indicated that the hydride impurity may result from the presence of water during or after polymerization; hence, further experiments were performed to test this hypothesis. In one experiment, $(SN)_x$ crystals were wetted for approximately 1 min, the excess water was removed, and the crystals were quickly placed in a Teflon Knudsen cell under vacuum.[5] The initial mass spectra obtained at 120 °C showed approximately 8 atom % hydrogen.[5] The level of hydride impurity dropped over a 2-h period until it was typical of unwetted crystals (~3 atom %). Another experiment was undertaken to determine the possibility of a gas-phase reaction between $(SN)_4$ and H_2O. A diffuse molecular beam of H_2O was crossed with the diffuse $(SN)_4$ beam from the Knudsen cell. Species undergoing gas-phase collisions are sampled through the "beam skimmer" and are mechanically chopped and ionized in the convention manner.[5] Under conditions in which more than 80% of the $(SN)_4$ molecules undergo at least one collision with H_2O molecules, no change in the hydride impurity level was observed. This experiment rules out a fast bimolecular gas-phase reaction as the source of the hydride impurity.

In another series of experiments, the entire apparatus used in the synthesis of $(SN)_x$ was rinsed with D_2O. The resulting $(SN)_x$ crystals produced vapors with approximately equal contributions of SND^+ and SNH^+. These results show that the hydride species results from a reaction involving water. Our study of the synthesis of $(SN)_x$ has shown that significant quantities of water are usually included in the S_2N_2 crystal lattice.[14] In a recent experiment[15] the hydride impurity was reduced to less than 2% of the vapor-phase species by carefully drying the apparatus with Me_3SiCl and allowing a small amount of Me_3SiCl drying agent to be present throughout the synthesis. Obviously, the production of "hydride-free" $(SN)_x$ will require more careful attention to the maintenance of a high-vacuum, moisture-free environment.

Samples of $(SN)_x$ exposed to water and air for longer periods exhibited marked physical and chemical changes. Physically, samples exposed to water for 1 h, followed by exposure to air for several days, became coated with a gray, powder-like material. Samples of $(SN)_x$ exposed to air for extended periods (>3 months), or to both water and air for shorter periods, exhibited an increased thickness of the gray powder surface layer. When these samples were heated for several hours at 160 °C and removed for visual examination, a white solid remained. This material is easily crushed, is white throughout, and when dissolved in water, gives a precipitate upon addition of barium chloride solution, indicating the presence of sulfate and/or sulfite.

The electron impact spectra of the vapors of $(SN)_x$ crystals exposed to water for various lengths of time (>1 day) are quite similar, the major difference being that crystals contaminated for longer periods show a smaller $(SN)_x$ content, which is more quickly removed by heating (at ~160 °C), leaving the residue mentioned above. At 80 °C the major ions are *m*/*e* 17, 18, 48, 64, and 80, which correspond to NH_3^+, H_2O^+, SO^+, SO_2^+ and/or S_2^+, and SO_3^+. At 100 °C additional contributions from S_x^+ ($x = 1$ to 8) ions are also observed. At temperatures between 120 and 160 °C the spectra are characterized by increasing contributions of ions indicative of $(SN)_x$ vapors, the hydride species, and *m*/*e* 63 (possibly $HNSO^+$), as well as the ions noted above.

The FI spectra of the "wet" $(SN)_x$ samples showed major ions at *m*/*e* 17, 18, and 64, and ions indicative of $(SN)_x$ and S_x. Small ion currents were also observed at *m*/*e* 63 (possibly HNSO), *m*/*e* 156 (possibly S_4N_2), and *m*/*e* 239–241 (unidentified).

AP measurements identify *m*/*e* 17 and 18 as NH_3 and H_2O. The SO^+ contribution has a rather high AP (~18 eV) and probably results from SO_2. The *m*/*e* 80 species (SO_3^+) is less intense, and the AP value of 15 eV has a rather large uncertainty (±3 eV), resulting primarily from the $^{34}S^{32}SN^+$ contribution (AP 10.1 eV). Failure to observe an alternative parent species to SO_3^+ at higher *m*/*e* values suggests that SO_3 also exists as a molecular species under the present experimental conditions.

Discussion and Conclusions

As reported previously, the hydrogen atom concentration of the vapors of typical $(SN)_x$ crystals is approximately 2–4 atom %.[5] By exposing $(SN)_x$ crystals to water for brief periods, the H atom concentration was increased to a maximum of 8 atom %. This increased hydrogen concentration may be attributed to either a surface layer of considerable (but undetermined) depth or perhaps a more uniform permeation of the $(SN)_x$ crystals by a mechanism analogous to bromination.[9] By allowing the synthesis of $(SN)_x$ to occur in the presence of additional water vapor, $(SN)_x$ samples of 8 atom % H throughout have been produced.[15]

The hydride species (of molecular weight 220 ± 12) exists as a distinct molecular species in the vapor of $(SN)_x$, independent of the $(SN)_4$ species.[5] The earlier estimates of the atom % hydrogen were based solely on lower mass fragments (which tend to overestimate the hydrogen atom concentration). For example, considering *only* the SNH^+ and SN^+ products and assuming SNH and SN neutral species, a $[SNH^+]/[SN^+]$ (*m*/*e* 47 and 46 corrected for isotopic contributions of ^{15}N and ^{33}S) ratio of 0.20 would result in an estimated 0.17 for the mole fraction of the vapor-phase hydride species, and an estimate of 7.7 atom % H. However, if the vapor-phase hydride species were S_5N_5H, one could estimate a lower value of 2 atom % H (by assuming that SN^+ and SNH^+ were formed with equal efficiency from $(SN)_4$ and S_5N_5H, respectively). However, assuming that the $(SN)_4$ and the hydride species are ionized with equal efficiency to yield $S_xN_y^+$ and $S_xN_yH^+$ ions, then an intensity ratio of 0.20 for all ions would result in an estimate that 17% of the vapor consists of hydride species. This estimate of the molecular contribution of the hydride vapor includes the relatively small errors resulting from mass discrimination and differences in ionization efficiencies and may underestimate the hydride contribution if the H atom resides with the neutral fragment in a significant fraction of the ionization events.

While we know that water is involved in formation of the hydride species, the precise point of this reaction is still uncertain. The present and previous results[5] show that H_2O does not react with S_2N_2 either as a vapor or in the crystals *prior* to polymerization. We have also been able to discount the possibility of a fast gas-phase reaction of $(SN)_4$ after vaporization. The remaining possibilities are that H_2O reacts with S_2N_2 during the polymerization or with $(SN)_x$ after polymerization and at any point up to and including the vaporization process. The possibility that H_2O reacts with S_2N_2 during polymerization, or even plays a role in the polymerization process, is of interest since ESR results imply that an ionic mechanism occurs in the presence of water which may interfere with the radical reaction in the absence of water.[16]

An alternative rationalization is that $(SN)_x$ reacts with water. The fact that addition of water to $(SN)_x$ crystals (in the absence of any detectable S_2N_2) causes an increase in the hydride impurity level supports this hypothesis. The porous, fibrous nature of the polymer would explain the fact that several hours of heating at 140 °C were required to remove excess amounts of the hydride species (since the hydrogen penetration obviously extended much deeper than a monolayer).

The molecular weight of the hydride species is 220 ± 12 and, on the basis of its mass spectra, it must contain S_3N_3H. A species containing an oxygen atom is unlikely since no O atom containing fragments are observed (discounting $(SN)_x$ samples exposed to air and/or water for extended periods). Thus, the most likely molecular formulas would be S_5N_4H, S_5N_5H, or $S_5N_5H_2$. While a ten-membered ring, $S_5N_5^+$, is known to exist in the solid phase,[17] such a stable configuration is unlikely in the hydride, since one would expect the $S_5N_5^+$ ion to be stable and to be observed by electron impact or field ionization. Since the structure of $(SN)_4$ has been shown to be linear, a similar bent-chain $(SN)_4SH$, $(SN)_5H$ species, or $H(SN)_5H$ may be reasonable.

A possible by-product of the hydride-forming reaction may be HNSO, which was tentatively identified on the basis of the *m*/*e* 63 ion intensity and its relatively low AP (11.4 ± 0.6 eV). Most of this highly volatile product, if formed, is probably lost from the fibrous polymer prior to mass spectral study. It is interesting that SO_2, NH_3 and, very likely, a series of ammonium salts $[(NH_4)_2SO_3$, $(NH_4)_2S_3O_6$, and $(NH_4)_3S_2O_6]$ are expected from the hydrolysis of HNSO.[18] Similar products $[(NH_4)_2S_2O_3$, $(NH_4)_2SO_3$, and $(NH_4)_2S_3O_6]$ are expected for the hydrolysis of S_4N_4.[18,19] These hydrolysis products resemble those suggested by the mass spectra of samples exposed to water for extended periods (>1 day) and indicate that formation of the hydride species (and SNOH) may be the first step toward these hydrolysis products. The presence of SO_3 in the vapors also suggests the presence of sulfate salts.

The present work has established that the "hydride impurity" of $(SN)_x$ is an important species in the vapors of $(SN)_x$, comprising up to 20% of the gaseous species in some cases. We have also found that this product results from the presence of water during the synthesis of $(SN)_x$ and is probably the first step in the hydrolysis to form $(NH_4)_2S_xO_y$ salts and other unidentified products. The vapor-phase hydride species has a molecular weight of 220 ± 12.

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(11) In addition to $(SN)_x$ crystals prepared at the Naval Research Laboratory, samples were also supplied by Professor A. G. MacDiarmid of the University of Pennsylvania and Dr. G. Bryan Street of IBM (San Jose, Calif.). The hydrogen atom concentration for these samples varied between 2 and 5 atom %, calculated as described in the text.

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