(2) S. F. Mason and B. J. Peart, *J. Chem. Soc., Dalton Trans.*, 949 (1973), and references therein.
(3) V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 207 (1972).
(4) K. Ohkawa, J. Fujita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **38**, 66 (1965).
(5) F. P. Dwyer and F. L. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).
(6) F. M. Jaeger and L. Bijkerk, *Z. Anorg. Allg. Chem.*, **233**, 101 (1933).
(7) H. Aoi, M. Ishimori, S. Yoshikawa, and T. Tsuruta, *J. Organomet. Chem.*, **85**, 241 (1975).
(8) A. W. Adamson, *J. Am. Chem. Soc.*, **78**, 4260 (1956).
(9) V. M. Miscowski and H. B. Gray, *Inorg. Chem.*, **14**, 401 (1975).
(10) The elemental analyses of cyano complexes have been reported to be difficult, and the presence of perchlorate was confirmed by the observation of white precipitate formation from aqueous solution upon addition of aqueous tetraphenylarsonium chloride and by strong absorption at ca. 1100 cm^{-1} in the infrared spectra.
(11) S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 3184 (1969).
(12) H. Yoneda, U. Sakaguchi, and K. Maeda, *Chem. Lett.*, 107 (1975).
(13) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **18**, 101 (1962).
(14) H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).
(15) J. A. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 4260 (1968).
(16) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).
(17) K. Kashiwabara (née Konya), T. Yamanaka, K. Saito, N. Komatsu, H. Hamada, H. Nishikawa, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **48**, 3631 (1975).
(18) R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966).
(19) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 202 (1965).
(20) H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **40**, 2584 (1967).
(21) H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 1286 (1969).
(22) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **26**, 1076 (1970).
(23) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc., Chem. Commun.*, 49 (1965).
(24) K. Ogino, K. Uchida, T. Nishide, J. Fujita, and K. Saito, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1968).

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Preparation of the Binary Sulfur–Nitrogen Anions $S_3N_3^-$ and $S_4N_5^-$ from Tetrasulfur Tetranitride and Azides and the Vibrational Spectra of $S_3N_3^-$

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The reaction of tetrasulfur tetranitride, S_4N_4, with alkali metal or tetraalkylammonium azides in ethanol produces either the tetrasulfur pentanitride anion, $S_4N_5^-$ (Li^+, Na^+, K^+), the trisulfur trinitride anion, $S_3N_3^-$ (Cs^+, Me_4N^+, Et_4N^+, n-Pr_4N^+, n-Bu_4N^+), or a mixture of $S_4N_5^-$ and $S_3N_3^-$ (Rb^+). Infrared and Raman spectra of the cesium salt suggest a cyclic structure with C_{3v} symmetry for $S_3N_3^-$, which is an "electron-rich aromatic" (10π) system according to earlier postulates for binary sulfur–nitrogen species. The $S_3N_3^-$ anion is also formed from the reaction of excess sodium sulfide with S_4N_4 in ethanol, but $S_4N_5^-$ is produced when excess S_4N_4 is present. The reaction of $Bu_4N^+S_3N_3^-$ with S_4N_4 produces $Bu_4N^+S_4N_5^-$. A mechanism is proposed for the formation of $S_3N_3^-$ and $S_4N_5^-$ in these reactions.

Introduction

Recent interest in the metallic properties and superconductive behavior of polymeric sulfur nitride, $(SN)_x$,[1] has focused attention on binary sulfur–nitrogen compounds. The central character in this chemistry is the intriguing molecule S_4N_4. Reactions of S_4N_4 with different inorganic oxidizing agents have led to the isolation and characterization of a number of binary sulfur–nitrogen cations, e.g., $S_3N_2^+$,[2,3] $S_4N_3^+$,[4] $S_4N_4^{2+}$,[5] $S_5N_5^+$,[6] and $S_6N_4^{2+}$.[7] Such versatile behavior suggests that a wide variety of structural types might also pertain for binary sulfur–nitrogen anions. An indication of this possibility came from the report of the unexpected isolation of a salt of the $S_4N_5^-$ ion[8] and the subsequent structural characterization of this anion by x-ray crystallography.[9] We have recently isolated and characterized the dark blue salt $Bu_4N^+NS_4^-$ [10] and later discovered that the reaction of azides with elemental sulfur in hexamethylphosphoramide is a convenient source of the NS_4^- anion.[11] Prompted by the proposed structure for $S_4N_5^-$,[8] we have investigated the reaction of azides of S_4N_4 and found that this reaction provides an easy route to salts of the $S_4N_5^-$ anion[12] or of the novel $S_3N_3^-$ ion.[13] Here we report the full details of these syntheses and of the characterization of $S_3N_3^-$, and we discuss the interrelationship of the $S_3N_3^-$ and $S_4N_5^-$ ions.

Experimental Section

General Procedures. Absolute ethanol was refluxed with magnesium and a crystal of iodine for 4 h and freshly distilled before use. Absolute methanol was distilled from Drierite. Both solvents were stored under N_2 in flame-dried septum-sealed flasks. n-Pentane (Burdick and Jackson) was distilled from CaH_2 and diethyl ether (Mallinckrodt) from $LiAlH_4$. The distillation of solvents, the reactions of azides with S_4N_4, and subsequent handling of $S_3N_3^-$ and $S_4N_5^-$ salts were carried out under N_2 (99.99% purity passed through Ridox and silica gel).

S_4N_4 (mp 179 °C) was prepared according to the literature,[16] recrystallized twice from benzene, and checked for the absence of c-S_8 by mass spectrometry. Sodium azide (Fisher), potassium azide (Eastman), rubidium and cesium azides (Alfa 99.9%), anhydrous lithium and sodium sulfides (Alfa), and trichloroacetyl chloride (Eastman) were used as received. Tetraalkylammonium hydroxides were obtained as solutions in water (R = Et, Pr) or methanol (R = Me, n-Bu) (Eastman). Tetraalkylammonium and lithium azides were prepared by the neutralization of a 10% solution of hydrazoic acid, generated by passing a sodium azide solution over Amberlite IR-120 (H) ion-exchange resin, with the appropriate tetraalkylammonium or lithium hydroxide.[17] The previously described procedure[17] for the purification of these azides was found to be unsatisfactory, and we therefore include a description of our purification procedure for the crude products. Me_4NN_3 was slurried twice with acetonitrile, and the white solid residue, after filtration, was dissolved in the minimum amount of methanol and precipitated with diethyl ether. Et_4NN_3 was dissolved in the minimum amount of acetonitrile and precipitated with diethyl ether (twice). n-Pr_4NN_3 was dissolved in the minimum amount of absolute ethanol and precipitated with diethyl ether (twice). Crude n-Bu_4NN_3 was obtained as a sticky solid and was slurried twice with diethyl ether/acetone (150:5 mL) to give a white powder after filtration. The azides were dried in an Abderhalden pistol at ca. 65 °C and 10^{-2} mmHg (Me_4N^+, Et_4N^+, n-Pr_4N^+) and at 25 °C (Li^+, n-Bu_4N^+) and were then found to be analytically pure (Table I).

Instrumentation. Infrared spectra (4000–250 cm^{-1}) were recorded as Nujol mulls (CsI optics) on a Perkin-Elmer 467 spectrophotometer, and far-infrared spectra (665–40 cm^{-1}, polyethylene windows) were measured using a Digilab FTS 16 instrument. Raman spectra were obtained on a sample of $Cs^+S_3N_3^-$ in a capillary tube using an argon laser operating at 514.5 nm and a Jarrel-Ash spectrophotometer. Mass spectra were recorded on a Varian CH5 instrument operating at 70 eV. UV–visible spectra were recorded in a 1-cm Airless-ware cell on a Cary 15 spectrophotometer. Microanalyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Müllheim, West Germany.

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Table I. Analytical Data for Tetraalkylammonium Azides and Salts of the $S_3N_3^-$ and $S_4N_5^-$ Ions

	% calcd					% found				
Compd	C	H	N	S	M[a]	C	H	N	S	M[a]
Me_4NN_3	41.34	10.43	48.23			40.60	10.05	47.68		
Et_4NN_3	55.76	11.72	32.52			55.61	11.58	32.65		
n-Pr_4NN_3	63.09	12.38	24.53			63.30	12.28	24.51		
LiS_4N_5			34.13	62.49	3.38			34.22	62.23	3.32
NaS_4N_5			31.75	57.59	10.49			31.67	57.95	10.39
KS_4N_5[b]			29.51	54.02	16.47			27.00	49.68	15.07
n-$Bu_4NS_4N_5$	43.59	8.25	19.07	29.09		44.35	8.10	19.03		
CsS_3N_3[c]			15.50	35.48	49.02			14.51	33.58	
$Me_4NS_3N_3$	22.61	5.71	26.38	45.29		22.55	5.59	26.16	45.23	
$Et_4NS_3N_3$	35.78	7.52	20.87	35.82		35.59	7.34	20.69	36.07	
n-$Bu_4NS_3N_3$[d]	50.47	9.55	14.72	25.26		48.46	9.10	13.90	24.05	

[a] Alkali metal. [b] Experimental atomic ratios K:S:N = 1.00:3.97:4.95. [c] An explosion during fusion prevented the determination of the cesium content. The experimental atomic ratio N:S = 1.01. [d] Experimental atomic ratios C:H:N:S = 16.1:36.0:3.96:3.00.

Table II. Infrared Spectra (cm^{-1}) of Alkali Metal Salts of $S_4N_5^-$

$Li^+S_4N_5^-$	1020 w, 940 vs, 910 vs, 750 m, 720 m, 700 s, 670 s, 625 w, 600 s, 530 s, 510 m, 440 s, 410 m, 345 w, 310 m, 300 sh
$Na^+S_4N_5^-$ [12]	1030 b, w, 950 vs, 920 vs, 885 sh, 745 s, 725 s, 725 w, 705 s, 665 vs, 630 w, 590 vs, 530 vs, 500 s, 430 vs, 400 s, 330 w, 300 w
$K^+S_4N_5^-$	1020 w, 940 vs, 910 vs, 870 sh, 730 m, 690 m, 655 s, 620 vw, 600 s, 530 s, 500 m, 435 s, 400 w, 335 vw, 300 w

Synthesis of Salts of the $S_4N_5^-$ Anion. The synthesis of $Na^+S_4N_5^-$ from S_4N_4 and NaN_3 has been described in detail in a preliminary communication.[12] The lithium and potassium salts were prepared in a similar manner. Crude $Li^+S_4N_5^-$ was invariably obtained as a red oil, which was dissolved in methanol (10 mL). The resulting solution was treated with diethyl ether (100 mL) to give a yellow product, which, after Soxhlet extraction with n-pentane followed by reprecipitation from methanol/diethyl ether, gave analytically pure $Li^+S_4N_5^-$ (Table I). n-$Bu_4N^+S_4N_5^-$ was obtained as yellow crystals when n-Bu_4NOH (1 M in methanol) was added to an aqueous solution of $Na^+S_4N_5^-$ and the methanol was allowed to evaporate. The infrared spectra of the lithium and potassium salts are very similar to that of $Na^+S_4N_5^-$ (Table II).

Preparation of $Me_4N^+S_3N_3^-$. S_4N_4 (0.836 g, 4.55 mmol) and Me_4NN_3 (0.396 g, 3.40 mmol) were stirred in ethanol (30 mL). The color of the solution darkened and gas evolution (N_2) occurred within minutes and had ceased after 24 h. The red solution, which contained a yellow precipitate, was filtered and treated with n-pentane (ca. 100 mL) to give a yellow solid. This solid was filtered off, washed with n-pentane (2 × 20 mL), and subjected to Soxhlet extraction with n-pentane (2 days) to remove c-S_8 and unreacted S_4N_4. The final purification of the crude product involved dissolution in ethanol (20 mL) (filtration, if necessary) and reprecipitation with n-pentane (100 mL). The bright yellow powder was filtered off, washed with n-pentane (20 mL), and dried in an Abderhalden pistol (40 °C at 10^{-2} mmHg) for 24 h to give an analytically pure sample of $Me_4N^+S_3N_3^-$ (0.39 g, 40%) (Table I). The initial yellow precipitate from the reaction was shown to contain c-S_8 by mass spectrometry.

The other tetraalkylammonium salts of $S_3N_3^-$ were prepared in a similar manner. It is preferable to use a slight (5–10%) excess of S_4N_4 in these reactions to avoid contamination of the product by unreacted azide. In the case of n-$Bu_4N^+S_3N_3^-$ it is necessary to cool the red solution to −10 °C before addition of n-pentane in order to prevent the formation of an oily product. $Cs^+S_3N_3^-$ is only slightly soluble in ethanol and thus the initial precipitate formed in the reaction of S_4N_4 with cesium azide was combined with the yellow precipitate obtained after addition of n-pentane to the decanted red solution. After Soxhlet extraction (n-pentane), the yellow product was dissolved in the minimum amount of methanol (ca. 100 mL) and precipitated as a light yellow solid by the addition of diethyl ether (175 mL). The infrared and Raman spectra of $Cs^+S_3N_3^-$ are shown in Figure 2 (see Discussion).

Caution! Like S_4N_4, both the $S_3N_3^-$ and $S_4N_5^-$ salts, particularly those with alkali metal cations, will explode on grinding, scratching, or heating in a melting point capillary tube.[12,13] It is recommended that these syntheses be carried out only on a small scale (ca. 1.0 g) and that appropriate caution be exercised when touching samples with a spatula or when preparing infrared mulls.

Reaction of Sodium Sulfide with S_4N_4. (a) Using Excess S_4N_4. Solid S_4N_4 (0.956 g, 5.19 mmol) was added in small increments to a stirred slurry of sodium sulfide (0.270 g, 3.46 mmol) in ethanol (25 mL). The solution immediately became dark orange-red and was dark red after completion of the addition of S_4N_4. After the solution was stirred for 1/2 h, a yellow precipitate was present, which was filtered off. Addition of n-pentane (100 mL) to the filtrate produced a yellow precipitate, which was filtered off and extracted (Soxhlet) with n-pentane for 1 day. After drying in vacuo, the yellow solid had an infrared spectrum identical with that of $Na^+S_4N_5^-$. A trace of $Na^+S_3N_3^-$ was also present.

The reaction of lithium sulfide (0.146 g, 3.18 mmol) and S_4N_4 (0.877 g, 4.76 mmol) was carried out in a similar manner. The product was obtained by addition of diethyl ether (100 mL) to a methanol solution (10 mL) and was identified as $Li^+S_4N_5^-$ by its infrared spectrum. There was no evidence for the presence of $Li^+S_3N_3^-$.

(b) Using Excess Sodium Sulfide. The addition of S_4N_4 (0.559 g, 3.03 mmol) to a slurry of sodium sulfide (0.473 g, 6.06 mmol) in ethanol (25 mL) produced a deep purple solution after stirring for 1 h. After filtration, addition of n-pentane (175 mL) precipitated a yellow solid which was washed with pentane and dried under vacuum. The infrared spectrum of this solid showed strong bands at ca. 920 (s), 645 (vs), and 380 (s) cm^{-1} characteristic of the $S_3N_3^-$ anion. The reaction of sodium sulfide with S_4N_4 was also carried out using a 1:1 molar ratio of reagents. The yellow solid product was again identified as $Na^+S_3N_3^-$ by its infrared spectrum.

Reaction of $Cs^+S_3N_3^-$ with Trichloroacetyl Chloride. Trichloroacetyl chloride (0.549 g, 3.02 mmol) in methylene chloride (20 mL) was added dropwise to a stirred slurry of $Cs^+S_3N_3^-$ (0.819 g, 3.02 mmol) in methylene chloride (30 mL). After being stirred for 18 h, the solution was dark yellow and a pale yellow precipitate was present, which was filtered off and shown to be cesium chloride (0.49 g, 2.91 mmol). Solvent was removed from the filtrate under vacuum to give bright yellow crystals which were recrystallized from CH_2Cl_2/n-pentane to give CCl_3CON-S_3N_2 (0.73 g, 2.57 mmol, 85% yield), identified by its infrared spectrum which was in excellent agreement with that reported in the literature.[25]

Results and Discussion

Azide Synthesis of $S_3N_3^-$ and $S_4N_5^-$. Previous applications of azides in the synthesis of sulfur–nitrogen compounds include the preparation of $[S_4N_3]^+Cl^-$ from lithium azide and S_2Cl_2 in an inert solvent[14] and the conversion of this cation to S_4N_4 by aluminum azide.[15] We now find that the reaction of S_4N_4 with azides in ethanol provides a convenient source of salts of the binary sulfur–nitrogen anions $S_3N_3^-$ and $S_4N_5^-$. The product isolated depends on the size of the cation. With the smaller alkali metals Li^+, Na^+, and K^+, the $S_4N_5^-$ salt is obtained, whereas cesium or tetraalkylammonium azides yield salts of the novel $S_3N_3^-$ ion. Rubidium azide gives a mixture of $Rb^+S_3N_3^-$ and $Rb^+S_4N_5^-$. Ethanol appears to be the solvent of choice for this reaction, since no reaction occurred when sodium azide and S_4N_4 were stirred for 24 h in tetrahydrofuran, whereas the use of methanol in the synthesis of

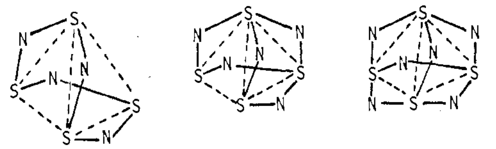


Figure 1. Structures of S_4N_4, $S_4N_5^-$, and $S_4N_6^{2-}$.

$Na^+S_4N_5^-$ and $K^+S_4N_5^-$ resulted in the formation of a white solid, with infrared bands at 1100 cm^{-1} suggestive of >S=O, and only a low yield of $S_4N_5^-$ salt.

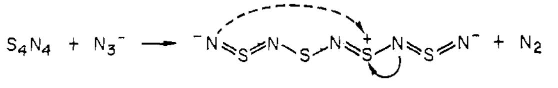
The alkali metal salts of $S_4N_5^-$ were pale yellow and have been characterized by complete elemental analyses (Li^+, Na^+) and by their infrared spectra (Table II). The crystal structure of $S_4N_5^-$ has been solved[9] and is compared in Figure 1 with the known structure of S_4N_4 and the adamantane-like structure expected for the hypothetical $S_4N_6^{2-}$ ion. Banister has pointed out[18] that the S_4N_4 molecule can be considered as a distorted S_4 tetrahedron (two S–S distances at 2.58 Å and four S–S distances at 2.69 Å) in which four of the edges are bridged by a N atom. In $S_4N_5^-$, a fifth edge is N-bridged, but the remarkable feature of the structure of this anion is that the S···S distances fall within the narrow range 2.71–2.75 Å (i.e., an almost undistorted S_4 tetrahedron). We have been unable to make $S_4N_6^{2-}$ by reaction of $S_4N_5^-$ with azide in ethanol. Since $S_4N_5^-$ decomposes to S_4N_4 after several hours in ethanol, this observation may indicate kinetic rather than thermodynamic stability for the $S_4N_5^-$ anion.

The explosive nature of these salts in the solid state is undoubtedly due to the high N content (elimination of N_2), but it is noteworthy that the exocyclic O atom in $S_4N_5O^-$ apparently reduces this explosive tendency.[19]

The $S_3N_3^-$ salts are bright yellow and decompose below 120 °C. The infrared spectra are much simpler than for the $S_4N_5^-$ salts and are characterized by three strong bands at ca. 930, 640, and 380 cm^{-1} (370 cm^{-1} for the Cs^+ salt). The UV–visible spectrum of $Et_4N^+S_3N_3^-$ shows a single peak at λ_{max} 360 nm; this is converted to a species with λ_{max} at 340 nm when air is passed into the solution. Solutions of $S_3N_3^-$ salts in ethanol under an inert atmosphere produce S_4N_4 after several hours, and in the solid state decomposition takes place in air after ca. 15 min.

Reactions of Sulfide with S_4N_4. The effect of cation size on the product isolated from the N_3^-/S_4N_4 reactions at first suggested that the formation of $S_3N_3^-$ was favored by larger cations. It was therefore surprising to discover that the reaction of sodium sulfide with S_4N_4 (3:2 or 1:1 molar ratio) produced $Na^+S_3N_3^-$, predominantly. The products isolated from the sulfide/S_4N_4 reaction are, however, influenced by the stoichiometry of the reagents. With excess S_4N_4, $Na^+S_4N_5^-$ is formed. Subsequently we showed that $Bu_4N^+S_3N_3^-$ reacts slowly with S_4N_4 in ethanol to give $Bu_4N^+S_4N_5^-$.

Reaction Mechanism. The following experimental observations must be accounted for in any proposed mechanism for the reaction of azides with S_4N_4: (a) the formation of substantial amounts of *c*-S_8 in the synthesis of $Na^+S_4N_5^-$; (b) the isolation of $S_3N_3^-$ or $S_4N_5^-$ salts (depending on the cation); and (c) the formation of $Na^+S_3N_3^-$ or $Na^+S_4N_5^-$ (depending on the stoichiometry of the reagents) in the reaction of sodium sulfide with S_4N_4. Observation (a) rules out a mechanism involving attack of N_3^- at a S–S linkage of S_4N_4 followed by loss of N_2 without rupture of the cage structure. We therefore propose that the initial attack of the nucleophile at sulfur results in ring opening to give a poly(sulfur–nitrogen) chain.



The intermediate chain could then cyclize to give $S_3N_3^-$, as indicated, but the process by which a polysulfur chain is built up to give *c*-S_8 is not apparent. Such a mechanism could clearly be applicable to the reactions of S_4N_4 with other nucleophiles. Indeed the ion [NSNSNSNSCN]$^-$ has been proposed as an intermediate in the reaction of S_4N_4 with potassium cyanide, but the final product was formulated as a dimer $K_2(C_2N_{10}S_6)$.[20] In addition, the structural determination of the product $Ph_3P{=}N{-}S_3N_3$ from the reaction of triphenylphosphine with S_4N_4 revealed a six-membered sulfur–nitrogen ring.[21]

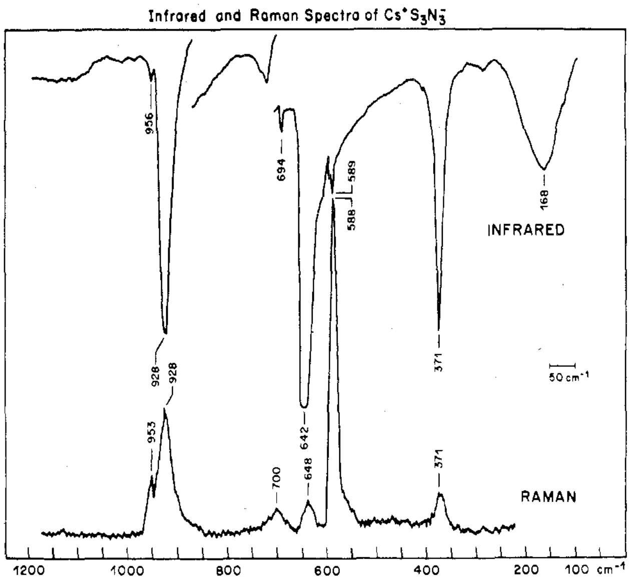
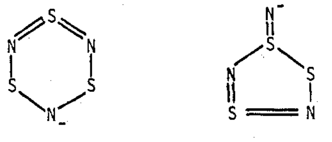


Figure 2. Infrared and Raman spectra of $Cs^+S_3N_3^-$. The weak band at ca. 720 cm^{-1} is due to Nujol.

In the present case, the proposed mechanism implies that $S_4N_5^-$ salts are formed from the reaction of the initially formed $S_3N_3^-$ with S_4N_4. This could explain the observed dependence on stoichiometry of the S^{2-}/S_4N_4 reaction. Furthermore, the effect of cation on the product isolated from the N_3^-/S_4N_4 reactions may be attributed to a dependence of the rate of the $S_3N_3^-/S_4N_4$ reaction on the size of the cation. Solvation of the smaller alkali metal cations by solvent ethanol could result in a more nucleophilic $S_3N_3^-$ ion for Li^+, Na^+, and K^+ compared to the larger cations (Cs^+ and R_4N^+) where ion-pair effects could considerably reduce the nucleophilicity of the anion. In any event the isolation of $Na^+S_4N_5^-$ from the NaN_3/S_4N_4 reaction but $Bu_4N^+S_3N_3^-$ from the Bu_4NN_3/S_4N_4 reaction cannot be attributed to lattice energy effects, since $Na^+S_4N_5^-$ is readily converted to $Bu_4N^+S_4N_5^-$ by Bu_4NOH in methanol.

Vibrational Spectra of $S_3N_3^-$. The infrared and Raman spectra of $Cs^+S_3N_3^-$ are shown in Figure 2. Six of the seven infrared bands have coincidences in the Raman spectrum. A very intense Raman band at 140 cm^{-1} was attributed to a lattice mode as were two broad bands of medium intensity below 100 cm^{-1} in the infrared spectrum. From consideration of isoelectronic species the most likely structural alternatives for $S_3N_3^-$ indicated in Figure 3 are (a) a six-membered ring (cf. S_4N_2[22]) or (b) a five-membered ring with an exocyclic N atom (cf. $S_3N_2Cl^+$[23] or S_3N_2O[24,25]).

Steudel and co-workers[25] have recently described the structure of the compound $CF_3COS_3N_3$, which had previously been assumed to contain a six-membered ring of alternating sulfur and nitrogen atoms.[26] In fact the x-ray structural determination reveals a nonplanar S_3N_2 ring containing an unusually long (2.206 Å) S–S bond.[25] Comparison of the infrared spectra of $CX_3CONS_3N_2$ derivatives (X = F, Cl) with the spectra of S_3N_2O and eight other RNS_3N_2 compounds led these authors to propose that four vibrations at ca. 990, 920,



(a) (b)

Figure 3. Possible structures of the $S_3N_3^-$ ion. Only one resonance form is indicated for (a) and (b).

Table III. Calculated Number of Fundamental Vibrational Modes for Cyclic $S_3N_3^-$

Structure[a]	Symmetry	IR-active modes	Raman-active modes	Coincidences
Planar	D_{3h}	4	6	3
Puckered	C_{3v}	7	7	7
Boat or chair	C_s	12	12	12
Exptl spectra		7	6	6

[a] Assuming alternating S and N atoms.

740, and 660 cm^{-1} (±20 cm^{-1}) are characteristic of the S_3N_2 ring. In addition, a very strong band at 331 cm^{-1} in the Raman spectrum of $CF_3CONS_3N_2$ was assigned to ν(SS).[25] For $S_3N_3^-$, therefore, the small number of observed frequencies and the lack of a strong band in the Raman spectrum attributable to an S–S stretching frequency strongly suggest that structure (b) in Figure 3 can be ruled out. The calculated number of fundamental vibrational modes for various conformations of an S_3N_3 ring are shown in Table III. The experimental data for $S_3N_3^-$ are clearly in best agreement with a structure of C_{3v} symmetry. It should be added, however, that the reaction of $Cs^+S_3N_3^-$ with CCl_3COCl proceeds cleanly to give $CCl_3CON–S_3N_2$ in excellent yield. Presumably a rearrangement from the six-membered ring of $S_3N_3^-$ to a five-membered ring in the product must occur in this reaction.

Electron-Rich Aromatic Species. Banister has described binary sulfur–nitrogen species with $(4n + 2)\pi$ electrons as "electron-rich aromatics".[27] This classification assumes that, in addition to the σ framework electrons (two per atom) and the lone-pair electrons (two per atom), each nitrogen provides one π electron and each sulfur atom supplies two π electrons to the π system. Thus examples of such Hückel systems include the neutral molecules S_2N_2 (6π)[28] and S_4N_2 (10π)[22] and the cations $S_4N_3^+$ (10π)[4] and $S_5N_5^+$ (14π).[6] We can now add to this list the first example of a potentially aromatic binary sulfur–nitrogen anion $S_3N_3^-$, a 10π system according to Banister's classification. It should be noted, however, that the configurations of the rings in the neutral and cationic S–N species referred to above are planar, whereas the vibrational spectra of $S_3N_3^-$ suggest a puckered-ring structure for this anion. Confirmation of this suggestion and further discussion of the bonding in $S_3N_3^-$ must await the results of an x-ray structural determination which is in progress.

Conclusion

The reaction of azides with S_4N_4 provides a convenient source of salts of the $S_3N_3^-$ and $S_4N_5^-$ ions. On the basis of vibrational spectra a six-membered ring structure is proposed for $S_3N_3^-$, which thus bears a close structural relationship to $S_4N_5^-$. $S_3N_3^-$ is the first example of a potentially aromatic sulfur–nitrogen anion and plays a key role in the nucleophilic degradation of S_4N_4.

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References and Notes

(1) (a) V. V. Walatka, M. M. Labes, and J. H. Peelstein, *Phys. Rev. Lett.*, **31**, 1139 (1973); (b) R. L. Green, G. B. Street, and L. J. Suter, *ibid.*, **34**, 577 (1975); (c) R. J. Nowak, H. B. Mark, Jr., A. G. MacDiarmid, and D. Weber, *J. Chem. Soc., Chem. Commun.*, 6 (1977); (d) E. J. Louis, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger, *ibid.*, 426 (1976), and references cited therein.

(2) R. J. Gillespie, P. R. Ireland, and J. E. Vekris, *Can. J. Chem.*, **53**, 3147 (1975).

(3) H. W. Roesky and A. Hamza, *Angew. Chem., Int. Ed. Engl.*, **15**, 226 (1976).

(4) P. Friedman, *Inorg. Chem.*, **8**, 692 (1969), and references cited therein.

(5) R. J. Gillespie, D. R. Slim, and J. D. Tyrer, *J. Chem. Soc., Chem. Commun.*, 253 (1977).

(6) (a) A. J. Banister and H. G. Clarke, *J. Chem. Soc., Dalton Trans.*, 2661 (1972); (b) A. C. Hazell and R. G. Hazell, *Acta Chem. Scand.*, **26**, 1287 (1972); (c) H. W. Roesky, W. G. Böwing, I. Rayment, and H. M. M. Shearer, *J. Chem. Soc., Chem. Commun.*, 735 (1975).

(7) A. J. Banister, H. G. Clarke, I. Rayment, and H. M. M. Shearer, *Inorg. Nucl. Chem. Lett.*, **10**, 647 (1974).

(8) O. J. Scherer and G. Wolmershäuser, *Angew. Chem., Int. Ed. Engl.*, **14**, 485 (1975).

(9) W. Flues, O. J. Scherer, J. Weiss, and G. Wolmershäuser, *Angew. Chem., Int. Ed. Engl.*, **15**, 379 (1976).

(10) T. Chivers and I. Drummond, *Inorg. Chem.*, **13**, 1222 (1974).

(11) J. Bojes and T. Chivers, *J. Chem. Soc., Dalton Trans.*, 1715 (1975).

(12) J. Bojes, P. M. Boorman, and T. Chivers, *Inorg. Nucl. Chem. Lett.*, **12**, 551 (1976).

(13) J. Bojes and T. Chivers, *J. Chem. Soc., Chem. Commun.*, 453 (1977).

(14) O. Glemser, A. Haas, and H. Reinke, *Z. Naturforsch., B*, **20**, 809 (1965).

(15) M. Becke-Goehring and G. Magin, *Z. Naturforsch., B*, **20**, 493 (1965).

(16) M. Villena-Blanco and W. L. Jolly, *Inorg. Synth.*, **9**, 98 (1967).

(17) V. Gutmann, G. Hampel, and O. Leitmann, *Monatsh. Chem.*, **95**, 1034 (1964).

(18) A. J. Banister, *Nature (London), Phys. Sci.*, **239**, 69 (1972).

(19) R. Steudel, P. Luger, and H. Bradaczek, *Angew. Chem., Int. Ed. Engl.*, **12**, 316 (1973), and private communication.

(20) E. Fluck, M. Becke-Goehring, and G. Dehoust, *Z. Anorg., Allg. Chem.*, **312**, 61 (1961).

(21) E. M. Holt and S. L. Holt, *Chem. Commun.*, 1704 (1970).

(22) J. Nelson and H. G. Heal, *J. Chem. Soc.*, A, 136 (1971).

(23) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **5**, 1767 (1966).

(24) H. W. Roesky and H. Wiezer, *Angew. Chem., Int. Ed. Engl.*, **14**, 258 (1975).

(25) R. Steudel, F. Rose, R. Reinhardt and H. Bradaczek, *Z. Naturforsch., B*, **32**, (1977).

(26) W. Lidy, W. Sundermeyer, and W. Verbeek, *Z. Anorg. Allg. Chem.*, **406**, 228 (1974).

(27) (a) A. J. Banister and R. J. Dainty, *J. Chem. Soc., Dalton Trans.*, 2558 (1972); (b) A. J. Banister, *Nature (London), Phys. Sci.*, **237**, 92 (1972).

(28) M. J. Cohen, A. F. Garito, A. J. Heeger, A. G. MacDiarmid, C. M. Mikulski, M. S. Saran, and J. Kleppinger, *J. Am. Chem. Soc.*, **98**, 3844 (1976).