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Central Role of the $S_3N_3^-$ and $S_4N_5^-$ Ions in the Deprotonation of Tetrasulfur Tetraimide and in the Reductive or Nucleophilic Degradation of Tetrasulfur Tetranitride

J. BOJES, T. CHIVERS,* I. DRUMMOND, and G. MacLEAN

$K^+S_3N_3^-$ has been isolated and characterized as the major product from the deprotonation of $S_4N_4H_4$ with potassium hydride. Salts of the $S_3N_3^-$ ions are also formed as the final products in the chemical reduction of S_4N_4 with potassium metal in 1,2-dimethoxyethane and in the electrochemical reduction of S_4N_4 in ethanol. The formation of $S_3N_3^-$ in these reduction processes supports an earlier proposal that the initially formed radical anion $S_4N_4^-\cdot$ decomposes by an intramolecular bond rupture. S_4N_4 reacts with liquid ammonia or secondary amines to give salts of the $S_4N_5^-$ ion but in the presence of sodium amide an $S_3N_3^-$ salt is the major product. The reaction of S_4N_4 with potassium cyanide in ethanol or dimethylformamide also produces $K^+S_4N_5^-$, in addition to potassium thiocyanate. Previous claims of sulfur–nitrogen anions derived from S_4N_4 are critically evaluated in the light of these results.

Introduction

The reduction of S_4N_4 with potassium metal in dimethoxyethane at room temperature has been reported by Chapman and Massey to produce a series of color changes attributed to ions of the type $S_4N_4^{n-}$ ($n = 1$–4).[1] A nine-line ESR spectrum was observed and assigned to the radical anion $S_4N_4^-\cdot$.[1] In a subsequent electrochemical study,[2] Meinzer and co-workers observed a *different* nine-line ESR spectrum for the primary reduction product of S_4N_4. Theoretical calculations supported the assignment of this spectrum to $S_4N_4^-\cdot$ with a similar structure to S_4N_4. It was further demonstrated that this radical anion is only stable at temperatures below ca. -25 °C and that, above 0 °C, rapid decomposition occurs. In a more detailed electrochemical investigation, using the techniques of controlled-potential electrolysis and cyclic voltammetry, Prater and co-workers conclusively identified the $S_4N_4^-\cdot$ radical and showed that it decays by a first-order rate law.[3] The activation energy for this process was estimated to be ca. 11 kcal mol^{-1} and it was suggested that decomposition takes place via an intramolecular bond rupture.

Investigations of the deprotonation of $S_4N_4H_4$ are also relevant to a discussion of S–N anions derived from S_4N_4. For example, the orange-red product of the reaction of $S_4N_4H_4$ with triphenylmethyl sodium is claimed to be the sodium salt of the $S_4N_4^{4-}$ anion, although the evidence presented is unconvincing.[4] Similarly, the color changes observed in the deprotonation of $S_4N_4H_4$ with n-butyllithium have been attributed to ions of the type $S_4N_4H_{4-n}^{n-}$ ($n = 1$–4).[5] It is difficult to reconcile these claims with the demonstrated instability of $S_4N_4^-\cdot$.

Very recent studies of S–N anions by Scherer and Wolmershäuser[6a,b] and by the present authors[7] have led to the structural characterization of the $S_4N_5^-$[6b] and $S_3N_3^-$[7c] ions. These are the only binary S–N anions whose structures are known, although the dark blue S_4N^- anion has been isolated as its tetra-n-butylammonium salt.[8] Scherer and Wolmershäuser have referred to the ubiquitous presence of $S_4N_5^-$ among the products of reactions of various sulfur compounds with ammonia.[9] In a preliminary communication,[7a] we referred to the likely formation of $S_3N_3^-$ in the

electrochemical reduction of S_4N_4. In this paper we discuss in detail the role of $S_3N_3^-$ in the chemical and electrochemical reduction of S_4N_4 and in the deprotonation of $S_4N_4H_4$. We also describe the formation of this ion and $S_4N_5^-$ in a variety of reactions of S_4N_4 with nucleophiles. The results of these studies necessitate a reconsideration, and in most cases a reinterpretation, of previous work related to S–N anions derived from S_4N_4.

Experimental Section

Reagents and General Procedures. Absolute ethanol was refluxed with magnesium turnings and a few crystals of iodine for 4 h and distilled immediately prior to use. Absolute methanol was distilled from Drierite. 1,2-Dimethoxyethane was distilled from Drierite, then refluxed over sodium for 6 h, and finally distilled into a flask containing freshly cut sodium. n-Pentane (Caledon laboratories) was distilled from calcium hydride, and tetrahydrofuran (Fisher) and diethyl ether (Mallinckrodt) were distilled from LiAlH$_4$. Methylene chloride (Fisher) was distilled from P$_2$O$_5$. Anhydrous ammonia (Matheson) was distilled from sodium directly into the reaction tube. All distillations of solvents and reactions and manipulation of $S_3N_3^-$ salts were carried out in flame-dried apparatus under N$_2$ (99.99% purity) passed through Ridox and silica gel.

S_4N_4 (mp 179 °C) was prepared according to the literature,[10] recrystallized twice from benzene, and checked for the absence of c-S$_8$ by mass spectroscopy. $S_4N_4H_4$ (mp 151 °C) was prepared by the literature method.[11] CCl$_3$COCl (Eastman), mercury (Johnson, Matthey and Mallory), mercurous chloride (BDH, >99.6%), potassium chloride (Baker, 99.7%), and dimethylamine (Matheson, anhydrous) were used as received. Potassium hydride (Alfa, 22.7% in mineral oil) was handled using the procedure described by Brown.[12] Potassium metal (BDH) was washed with dry n-pentane and cut in a drybox to expose the clean metal surface. Anhydrous Me$_4$NCl was prepared by the neutralization of Me$_4$NOH (Eastman, 25% in methanol) by 6.0 M aqueous HCl, followed by drying in vacuo (50 °C (10^{-2} mmHg) for 24 h). Piperidine (Fisher) was stored over 4-Å molecular sieves and distilled before use. Piperidyllithium was obtained as a white solid from the reaction of n-butyllithium with piperidine in n-hexane.

Instrumentation. Infrared spectra (4000–250 cm^{-1}) were recorded as Nujol mulls (CsI optics) on a Perkin-Elmer 467 spectrophotometer. Mass spectra were recorded on a Varian CH5 instrument operating at 70 eV. Electrochemical reductions were performed in a two-compartment, three-electrode cell using a PAR 176 potentiostate/galvanostat. UV–visible spectra were obtained in a 1-cm cell, with

provision for an inert atmosphere, using a Cary 15 spectrophotometer. Microanalyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Müllheim, West Germany.

Reaction of S$_4$N$_4$H$_4$ with Potassium Hydride. S$_4$N$_4$H$_4$ (1.85 g, 9.85 mmol) was added as a solid in small increments to a stirred slurry of potassium hydride (0.315 g, 7.88 mmol) in tetrahydrofuran (100 mL). Quite vigorous evolution of a gas (presumably H$_2$), accompanied by formation of a yellow precipitate, was evident immediately. After 1 h of stirring, the solution was a dark greenish blue. After 24 h, the solution was royal blue and showed peaks at 590, 460, and 360 nm in the UV–visible spectrum. Addition of *n*-pentane (80 mL) precipitated a brown solid, which was separated by decantation, washed with *n*-pentane (30 mL), and dried at 23 °C (10^{-2} mmHg). This solid was extracted with absolute ethanol (60 mL) and filtered, and addition of *n*-pentane (100 mL) to the filtrate precipitated a bright yellow solid. This product was separated by decantation, washed with *n*-pentane (30 mL), and dried at 23 °C (10^{-2} mmHg) for 24 h. An infrared spectrum showed bands at 925 (s), 640 (vs), and 385 (m) cm^{-1} typical for a salt of the S$_3$N$_3$$^-$ ion.[7b] The product was further purified by dissolution in a 1:4 ethanol–methanol mixture (40 mL), filtration, and reprecipitation by addition of diethyl ether. This process was repeated several times to give analytically pure K$^+$S$_3$N$_3$$^-$ (0.60 g, 3.39 mmol). Anal. Calcd for KN$_3$S$_3$: K, 22.05; N, 23.70; S, 54.24. Found: K, 21.80; N, 23.58; S, 54.10.

Several reactions in which the molar ratio of potassium hydride to S$_4$N$_4$H$_4$ was varied were also carried out. In all reactions in which the molar ratio exceeded 1:1, unreacted potassium hydride was still present after 2.5 days. In these reactions, 2-propanol was used to extract the crude reaction product with subsequent addition of methanol to increase the solubility of K$^+$S$_3$N$_3$$^-$, the major solid product. *c*-S$_8$ was identified by mass spectroscopy as a minor reaction product in the residue after evaporation of solvent from the alcoholic extracts.

Reaction of S$_4$N$_4$ with Potassium Metal. S$_4$N$_4$ (0.403 g, 2.19 mmol) and potassium metal (0.171 g, 4.39 mmol) were stirred vigorously in 1,2-dimethoxyethane (70 mL). The solution changed color from deep red (1 h) to royal blue (18 h) to deep purple (48 h). The solution was decanted from the small pieces of unreacted potassium, and the volume was reduced to ca. 15 mL under vacuum. Addition of *n*-pentane (100 mL) precipitated a rust red solid, which was washed with *n*-pentane (30 mL), dried in a stream of N$_2$, and extracted with anhydrous ethanol (50 mL). Addition of *n*-pentane (75 mL) precipitated a yellow solid which, after decantation, washing with *n*-pentane, and drying, consisted mainly of K$^+$S$_3$N$_3$$^-$ with minor amounts of K$^+$S$_4$N$_5$$^-$ (infrared spectrum).[7b] *c*-S$_8$ was identified (mass spectrum) in the residue after evaporation of the ethanol extract.
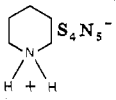
A slurry of the crude product (0.145 g) in methylene chloride (40 mL) was treated with trichloroacetyl chloride (1 mL) in methylene chloride (10 mL) to give a bright yellow solution. After 5 h, potassium chloride was removed by filtration, and solvent and unreacted CCl$_3$COCl were removed under vacuum. The yellow product was recrystallized twice from *n*-pentane/methylene chloride (4:1) to give pure CCl$_3$CONS$_3$N$_2$ (0.100 g, 0.352 mmol) with an infrared spectrum identical with that reported in the literature.[13]

Electrochemical Reduction of S$_4$N$_4$. A stirred slurry of S$_4$N$_4$ (0.80 g, 4.35 mmol) in ethanol (160 mL) containing tetramethylammonium chloride (0.1 M) was subjected to a potential of −0.70 V (vs. SCE) for ca. 6.5 h. The color of the solution changed from greenish yellow to orange-red during this time and some unreacted S$_4$N$_4$ and a significant amount of black precipitate, identified as HgS,[14] were apparent on the surface of the mercury. The electrolyzed solution was filtered and reduced in volume to ca. 30 mL under vacuum. Addition of *n*-pentane (100 mL) precipitated a yellow solid which, after decantation, was Soxhlet extracted with *n*-pentane (to remove S$_4$N$_4$) and dried at 23 °C (10^{-2} mmHg) for 18 h. The infrared spectrum showed this solid to be a mixture of Me$_4$NCl and Me$_4$N$^+$S$_3$N$_3$$^-$.

A slurry of this mixture in methylene chloride (40 mL) was treated dropwise with trichloroacetyl chloride (1 mL) in methylene chloride (10 mL). After 1 h, the solution was bright yellow and tetramethylammonium chloride was removed by filtration. Solvent and unreacted CCl$_3$COCl were removed under vacuum to give a sticky yellow solid, which was recrystallized from *n*-pentane/methylene chloride to give pure CCl$_3$CONS$_3$N$_2$, identified by its infrared spectrum.[13]

Reaction of S$_4$N$_4$ with Liquid Ammonia. Anhydrous ammonia (30 mL) was condensed into a reaction tube containing S$_4$N$_4$ (0.70 g, 3.80

Table I. Infrared Spectra (1200-200 cm^{-1}) of Salts of S$_4$N$_5$$^-$

Li$^+$S$_4$N$_5$$^-$	1020 w, 940 vs, 910 vs, 750 m, 700 s, 670 s, 625 w, 600 s, 530 s, 510 m, 440 s, 410 m, 345 w, 310 m, 300 sh
NH$_4$$^+S_4N_5$$^-$	1010 m, 940 vs, 910 vs, 735 s, 725 s, 685 s, 663 s, 620 w, 600 s, 530 s, 500 s, 435 s, 405 m, 335 w, 300 w
(piperidinium) S$_4$N$_5$$^-$	1025 m, 945 vs, 910 vs, 735 s, 725 s, 685 s, 670 s, 652 s, 625 m, 600 s, 532 s, 503 s, 435 s, 400 m, 335 w, 305 m

mmol) at −78 °C. On warming to −33 °C, all of the S$_4$N$_4$ dissolved to give a red solution. Evaporation of the ammonia in a stream of N$_2$ (2 h) gave a brick red solid, which was washed with diethyl ether (150 mL) and *n*-pentane (100 mL) and then extracted with absolute ethanol (30 mL). The red ethanol solution was filtered; addition of *n*-pentane (80 mL) to the filtrate precipitated a pale yellow solid which, after decantation, was washed with *n*-pentane and purified by Soxhlet extraction with *n*-pentane (to remove S$_4$N$_4$ or *c*-S$_8$) for 18 h. After drying of the solid at 25 °C (10 mmHg) for 24 h, the infrared spectrum of the product showed bands typical of an S$_4$N$_5$$^-$ salt (Table I).[7b,9] Elemental analyses confirmed the identity of the product as NH$_4$$^+S_4N_5$$^-$ (0.30 g, 1.39 mmol). Anal. Calcd for H$_4$N$_6$S$_4$: H, 1.87; N, 38.86; S, 59.28. Found: H, 1.92; N, 38.60; S, 58.72.

Reaction of S$_4$N$_4$ with Sodium Amide in Liquid Ammonia. Anhydrous ammonia (30 mL) was condensed into a reaction tube containing S$_4$N$_4$ (0.85 g, 4.62 mmol) and sodium amide (0.28 g, 7.18 mmol) at −78 °C. The red color of the solution became more intense as it warmed up to −33 °C. Evaporation of the ammonia in a stream of nitrogen gave a brick red residue which was washed with diethyl ether (100 mL), purified by Soxhlet extraction with *n*-pentane, and dried at 23 °C (10^{-2} mmHg). An infrared spectrum of the red product showed bands at 920 (m), 638 (s), and 377 (m) cm^{-1} characteristic of an S$_3$N$_3$$^-$ salt,[7b] together with weaker bands attributable to S$_4$N$_5$$^-$.

Trichloroacetyl chloride (1 mL) in methylene chloride (20 mL) was added dropwise to a stirred slurry of the red product in methylene chloride (30 mL). After 24 h, removal of solvent by vacuum transfer gave a sticky yellow solid which was purified by repeated recrystallizations from CH$_2$Cl$_2$/pentane (4:1) to give CCl$_3$CONS$_3$N$_2$ (0.40 g, 1.41 mmol).

Reaction of S$_4$N$_4$ with Piperidine. S$_4$N$_4$ (1.00 g, 5.43 mmol) and piperidine (1.86 g, 21.7 mmol) were stirred in ethanol (20 mL). The solution was bright orange after stirring for 4 h. Addition of *n*-pentane (100 mL) precipitated a flocculent yellow solid which, after decantation, was extracted (Soxhlet) with *n*-pentane for 18 h. The product was then dissolved in ethanol (10 mL) and reprecipitated with *n*-pentane (60 mL). After filtration and washing with *n*-pentane, the yellow solid was dried at 25 °C (10^{-2} mmHg) for 36 h and was shown to be [C$_5$H$_{10}$NH$_2$]$^+$S$_4$N$_5$$^-$ (0.60 g, 2.11 mmol) by its infrared spectrum (Table I)[7b] and elemental analyses. Anal. Calcd for C$_5$H$_{12}$N$_6$S$_4$: C, 21.10; H, 4.26; N, 29.55; S, 45.08. Found: C, 21.07; H, 4.16; N, 29.47; S, 44.94. The original ethanol/*n*-pentane filtrate on evaporation gave colorless crystals of dipiperidyl sulfide, identified by comparison of the infrared spectrum with that of an authentic sample.

Reaction of S$_4$N$_4$ with Piperidyllithium. A solution of piperidyllithium (0.407 g, 4.39 mmol) in tetrahydrofuran (10 mL) was added dropwise to a stirred slurry of S$_4$N$_4$ (1.23 g, 6.68 mmol) in tetrahydrofuran (25 mL). The solution became dark orange-red immediately and a yellow precipitate appeared after stirring for 1 h. Addition of diethyl ether (100 mL) precipitated more yellow solid which, after decantation, was washed with ether (20 mL) and extracted (Soxhlet) with *n*-pentane for 18 h. The product was then dissolved in methanol (10 mL), reprecipitated with ether (100 mL), filtered, washed with ether, and dried at 25 °C (10^{-2} mmHg) for 24 h. It was identified as Li$^+$S$_4$N$_5$$^-$ (0.40 g, 1.95 mmol) by the infrared spectrum (Table I) and by elemental analyses. Anal. Calcd for LiN$_5$S$_4$: Li, 3.38; N, 34.13; S, 62.49. Found: Li, 3.32; N, 34.22; S, 62.23.

Reaction of S$_4$N$_4$ with Potassium Cyanide. A slurry of S$_4$N$_4$ (1.20 g, 6.52 mmol) and potassium cyanide (0.850 g, 13.0 mmol) was stirred in ethanol (50 mL) for 20 h at 23 °C. No evolution of gas was observed and the solution became dark red. Addition on *n*-pentane (250 mL) precipitated an orange-red solid. The infrared spectrum of this solid showed bands attributable to SCN$^-$ at 2050 (vs), 970 (m), 750 (m), 490 (m), and 470 (w) cm^{-1}, and also the bands expected

for $S_4N_5^-$ (Table I). A third product was evident from strong infrared bands at 2160, 1171, and 802 cm^{-1}. The mixture was extracted (Soxhlet) with n-hexane for 3 days, but no elemental sulfur or S_4N_4 was recovered from the hexane extracts. The orange-red mixture was dissolved in water (20 mL), filtered, and treated with an excess of Bu$_4$NOH (20 mL of a 0.25 M aqueous solution). A yellow precipitate was filtered off, washed with water (10 mL) and diethyl ether (20 mL), and dried. An infrared spectrum showed that this yellow solid was pure Bu$_4$N$^+$S$_4$N$_5^-$. Thin-layer chromatography of the orange-red mixture on silica using acetone as eluant gave a clear separation of the red product from KCNS and K$^+$S$_4$N$_5^-$. However, several attempts to isolate the red product by preparative-scale chromatography resulted in decomposition.
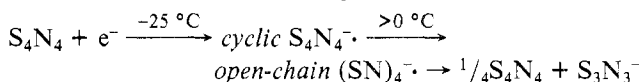
Results and Discussion

Electrochemical and Chemical Reduction of S_4N_4. In preliminary studies of the electrochemical reduction of S_4N_4,[7a] we reported the formation of solutions which exhibited a smooth absorption band at 360 nm, characteristic of the $S_3N_3^-$ anion.[7b] The formation of the $S_3N_3^-$ ion as the final product of the electrochemical reduction of S_4N_4 in ethanol, at a potential slightly more negative than the first polarographic half-wave potential, has now been confirmed by preparative-scale experiments. Me$_4$N$^+$S$_3$N$_3^-$ was unambiguously characterized by its infrared spectrum and, since it was not possible to separate it from the excess of supporting electrolyte (Me$_4$NCl), by conversion to the trichloroacetyl derivative, S$_3$N$_3$COCCl$_3$.[13] In previous electrochemical studies of S_4N_4 at -25 °C, the initial reduction step has been shown to be a one-electron process by cyclic voltammetry[3] and by coulometry.[15] In this investigation, coulometric n values obtained at 23 °C were consistently in the range 1.3–1.4 suggesting that the overall electrochemical process can be represented as

$$3S_4N_4 + 4e^- \rightarrow 4S_3N_3^- \tag{1}$$

The formation of mercury(II) sulfide during the chemical reduction probably results from the slow reaction of $S_3N_3^-$ with mercury, since it was shown in a separate experiment that S_4N_4 itself does not react with mercury under these conditions.

The identification of $S_3N_3^-$ as the final product of the electrolytic reduction of S_4N_4 lends support to the suggestion that the initially formed anion radical, $S_4N_4^-\cdot$, decomposes via intramolecular bond rupture.[3] It seems reasonable to propose the formation of an open-chain anion radical from which $S_3N_3^-$ could be formed by cyclization. Thus, the formation of $S_3N_3^-$ would involve the following steps:

$$S_4N_4 + e^- \xrightarrow{-25\ °C} \text{cyclic } S_4N_4^-\cdot \xrightarrow{>0\ °C}$$
$$\text{open-chain } (SN)_4^-\cdot \rightarrow \ ^1/_4 S_4N_4 + S_3N_3^-$$

Similarly, we found that the chemical reduction of S_4N_4 with potassium metal in a 1:2 molar ratio in dimethoxyethane invariably led to the formation of K$^+$S$_3$N$_3^-$ as the major product, usually mixed with smaller amounts of K$^+$S$_4$N$_5^-$.

Gleiter has proposed[16] that the dianion, $S_4N_4^{2-}$, should have a cyclic structure with only one transannular S---S interaction; cf. S$_8^{2+}$.[17] This species would be a 14π electron Hückel aromatic system according to the postulates of Banister.[18] Our studies of the reduction of S_4N_4 indicate, however, that the formation of a stable salt of the $S_4N_4^{2-}$ ion is very unlikely. Indeed, a cyclic voltammetric study of S_4N_4 in acetonitrile at -25 °C showed that the second reduction step is characterized by an ill-defined and totally irreversible wave.[3]

Deprotonation of $S_4N_4H_4$. The reaction of $S_4N_4H_4$ with potassium hydride in various stoichiometries (1:1, 1:2, 1:4, 4:5) in tetrahydrofuran always produced K$^+$S$_3$N$_3^-$. This *potassium* salt has not previously been reported. Like other $S_3N_3^-$ salts it is explosive when subjected to heat or pressure.[7b] A blue species, λ_{max} 590 nm, is also formed in solution. We believe that the blue color can be attributed to the S_4N^- anion,[8] since we have shown in a separate experiment that the $S_3N_3^-$ ion

Scheme I. Central Role of $S_3N_3^-$ in the Reduction and Nucleophilic Degradation of S_4N_4 and in the Deprotonation of $S_4N_4H_4$
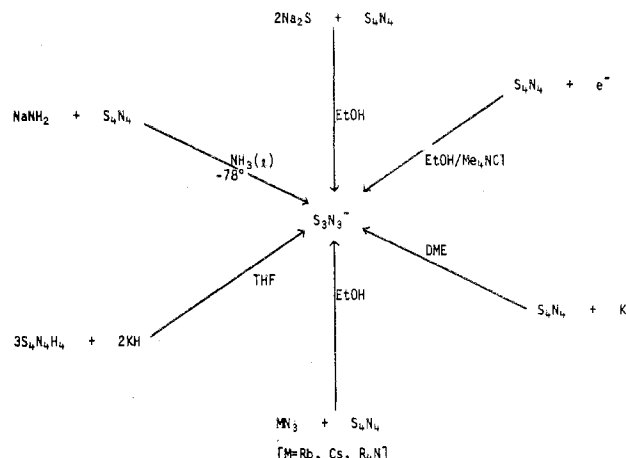
reacts with elemental sulfur (which is also a product of the deprotonation of $S_4N_4H_4$ with potassium hydride) to produce deep blue solutions of the S_4N^- ion in tetrahydrofuran.

On the basis of these results, previous claims of the synthesis of $S_4N_4^{4-}$ and $S_4N_4H_n^{n-4}$ ($n = 1$–3) anions must be considered to be erroneous, since it appears that the removal of only one proton from $S_4N_4H_4$ results in the formation of $S_3N_3^-$. It could be argued that the standard preparation of $S_4N_4H_4$ from S_4N_4 (by reduction with SnCl$_2$ in ethanol)[11] might involve a 4e reduction to give $S_4N_4^{4-}$ followed by protonation to give $S_4N_4H_4$. Our results suggest that, if reduction of S_4N_4 occurs, then $S_3N_3^-$ should be formed. We have been unable, however, to identify $S_3N_3^-$ as a product of the reaction of S_4N_4 with SnCl$_2$ in ethanol and we have also shown that the protonation of $S_3N_3^-$ does not produce cyclic sulfur imides. Therefore, we conclude that a mechanism which does not involve sulfur–nitrogen anions must obtain for the reduction of S_4N_4 to $S_4N_4H_4$ by tin(II) chloride, e.g., protonation followed by electron transfer.

Reactions of S_4N_4 with Liquid Ammonia and Sodium Amide. Scherer and Wolmershäuser have shown that S_4N_4 reacts with liquid ammonia to give NH$_4$$^+S_4N_5^-$ in at least 26% yield.[9] The formation of this anion could account for the reported conductivity of S_4N_4 in liquid ammonia.[19] However, Nelson and Lagowski have described the appearance of a band at 360 nm shortly after the preparation of solutions of S_4N_4 in NH$_3$(l). This absorption could well be due to the $S_3N_3^-$ anion,[7a,b] and we set out to verify this suggestion. Our observations for the S_4N_4/NH$_3$(l) system (37% yield of NH$_4$$^+S_4N_5^-$) were essentially the same as those reported by Scherer and Wolmershäuser, except for the presence of small amounts of $S_3N_3^-$ (IR spectrum) in the crude product. We discovered, however, that the reaction of S_4N_4 with sodium amide in liquid ammonia resulted in the predominant formation of $S_3N_3^-$, and thus this species is undoubtedly responsible for the 360-nm band observed for solutions of S_4N_4 in liquid ammonia.

Central Role of the $S_3N_3^-$ Ion. The results described above and in earlier reports[7a,b] demonstrate that the $S_3N_3^-$ anion plays a central role in the reactions of S_4N_4 (see Scheme I). The mechanism proposed for the formation of $S_3N_3^-$ from S_4N_4 with either reducing agents or nucleophiles is similar, viz., the initial formation of a "linear" S–N chain followed by cyclization to give $S_3N_3^-$. In addition to lattice-energy effects, the driving force for the formation of $S_3N_3^-$ in these reactions may, in part, result from the stabilization energy derived from its planar structure.[7c] It is interesting to note that the formation of a "linear" bent-chain (SN)$_4$ molecule in the vapor phase obtained from heating (SN)$_x$ at 100–160 °C has been proposed
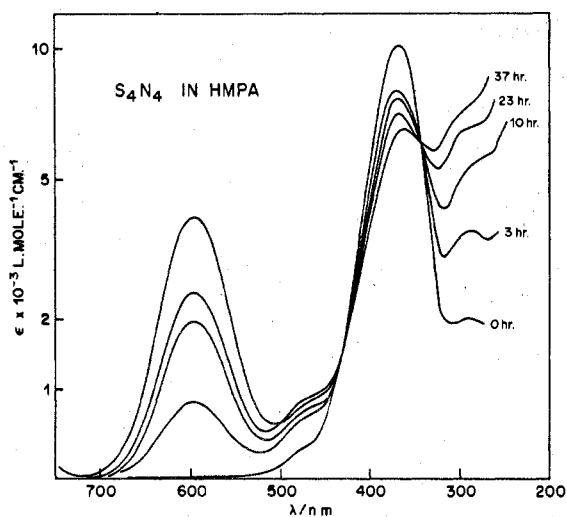
Figure 1. UV–visible spectra of a solution of S_4N_4 (6×10^{-5} M) in HMPA (containing dimethylamine) as a function of time.
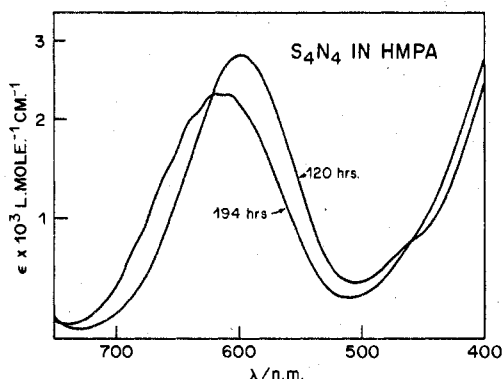

Figure 2. UV–visible spectra of a solution of S_4N_4 (6×10^{-5} M) in HMPA (containing dimethylamine) as a function of time.

on the basis of mass spectroscopic studies.[21]

Reactions of S_4N_4 with Secondary Amines. Earlier literature reports describe the formation of thiobis(amines) from S_4N_4 and secondary amines.[22] We have observed that S_4N_4 in impure hexamethylphosphoramide (HMPA, containing traces of dimethylamine) is a strong electrolyte ($\Lambda_0 = 19.5$ Ω^{-1} cm² mol⁻¹) and exhibits a smooth band at 360 nm in the infrared spectrum. During the course of 1 week, additional bands at 590 nm (NS_4^-)[8] and 620 nm (S_3^-)[23] appeared in the UV–visible spectrum. We have previously observed that elemental sulfur is reduced by dimethylamine in HMPA to give S_3^-,[24] and so it seemed likely that the formation of the 360-nm band in solutions of S_4N_4 in HMPA was due to reduction of S_4N_4 by dimethylamine.

A conductometric titration of S_4N_4 in HMPA with piperidyllithium showed a sharp break at 1:1.98 ($\Lambda_0 = 28.5$ Ω^{-1} cm² mol⁻¹ (S_4N_4)) (Figure 3). In preparative-scale reactions of piperidine or piperidyllithium with S_4N_4, the piperidinium and lithium salts, respectively, of $S_4N_5^-$ were isolated. When anhydrous dimethylamine was bubbled into ethanol solutions of S_4N_4, the dimethylammonium salt of $S_4N_5^-$ was formed (IR spectrum) but decomposed to S_4N_4 during attempted purification by Soxhlet extraction with *n*-pentane. These results can be interpreted in terms of the formation of $S_3N_3^-$ from S_4N_4 and secondary amines in *dilute* solutions, followed by reaction of $S_3N_3^-$ with S_4N_4 to give $S_4N_5^-$[7b] in more concentrated solutions.

Reaction of S_4N_4 with Potassium Cyanide. The reaction of S_4N_4 with KCN has previously been reported to produce potassium thiocyanate and a dianion characterized as a derivative of the dimer of cyanamide $(K^+)_2[N_3S_3N(CN)C-$
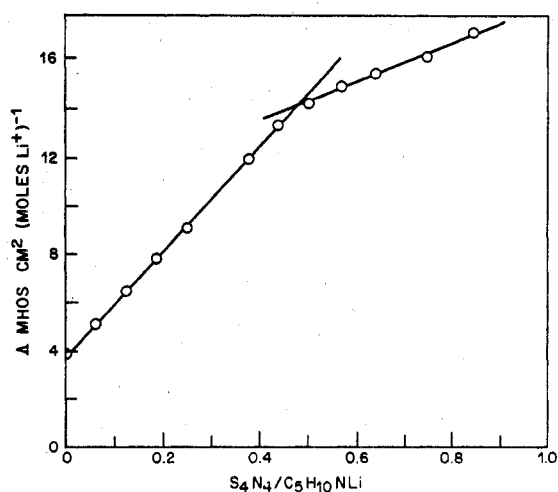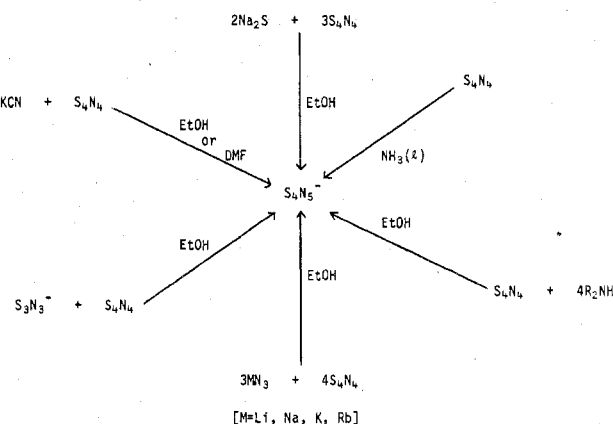

Figure 3. Conductometric titration of S_4N_4 with piperidyllithium in HMPA.

Scheme II. Formation of $S_4N_5^-$ in Reactions of S_4N_4 with Various Nucleophiles

$(N)NS_3N_3]^{2-}$.[25] This product was, however, very poorly characterized and close inspection of the published IR spectrum reveals bands attributable to the $S_4N_5^-$ ion. We, therefore, reinvestigated the reaction of potassium cyanide with S_4N_4 in DMF and in ethanol and were able to isolate pure $Bu_4N^+S_4N_5^-$ after addition of tetra-*n*-butylammonium hydroxide to an aqueous solution of the reaction products. The formation of thiocyanate and an unidentified brick red compound was also evident from the IR spectrum, which indicated that the red product contained a CN group. Several attempts to separate this product from $S_4N_5^-$ and CNS^- were, however, unsuccessful. Nevertheless, the positive identification of the $S_4N_5^-$ ion as a product of the reaction of S_4N_4 with cyanide ion shows that the previous conclusions of Becke-Goehring and co-workers[25] were based on data obtained for a *mixture* of products and must, therefore, be considered erroneous.

Formation of $S_4N_5^-$ in the Reactions of S_4N_4 with Nucleophiles. Scherer and Wolmershäuser have observed the formation of $S_4N_5^-$ in the reactions of ammonia with various sulfur compounds, and they suggest that intermediates of the type R—N=S=NH are involved.[9] In our investigations we have shown that the reactions of S_4N_4 with a variety of nucleophiles (N_3^-, S^{2-}, CN^-, R_2N^-) also result in the formation of $S_4N_5^-$ (Scheme II). The evidence presented here and in a previous report[7b] is consistent with the initial formation of $S_3N_3^-$ in these reactions, followed by reaction of $S_3N_3^-$ with S_4N_4 to give $S_4N_5^-$. This alternative route to $S_4N_5^-$ salts reinforces the earlier suggestion[6b] that the $S_4N_5^-$ ion occupies a key position among sulfur-nitrogen anions.

Conclusions

Both the chemical and electrochemical reduction of S_4N_4 and the deprotonation of $S_4N_4H_4$ lead to the formation of $S_3N_3^-$. This ion is also formed from S_4N_4 and sodium amide in liquid ammonia. The reactions of S_4N_4 with liquid ammonia, secondary amines, or cyanide all produce the $S_4N_5^-$ ion. Thus, the $S_3N_3^-$ and $S_4N_5^-$ ions play a central role in the chemical reactions of S_4N_4 under reducing conditions or with nucleophiles. These two species are the only well-characterized binary S–N anions. Previous claims of the isolation of other S–N anions in the reactions of S_4N_4 with nucleophiles or on reduction should be discounted, since all these reactions have now been shown to lead to the formation of $S_3N_3^-$ and/or $S_4N_5^-$.

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Reduction of (Ethylenediaminetetraacetato)cobaltate(III) and Related Complexes by Titanium(III)

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The kinetics of the reduction of three (ethylenediaminetetraacetato)cobaltate(III) complexes by titanium(III) in aqueous chloride medium have been investigated at 25 °C and ionic strength 1.0 M (HCl + NaCl). The Co(EDTA)$^-$ complex is reduced according to the rate law $-d \ln [Co(EDTA)^-]/dt = a[H^+]^{-1}[Ti(III)]/(1 + K_h[H^+]^{-1}) + c[H^+]^{-1}[Ti(III)]^2$, while the rate law for the reduction of Co(HEDTA)OH$_2$ and Co(HEDTA)Cl$^-$ is of the form $-d \ln [Co(HEDTA)L]/dt = a[H^+]^{-1}[Ti(III)]/(1 + K_h[H^+]^{-1})$. The computed K_h values are similar for all the three oxidizing agents and correspond to the Ti^{3+}(aq) acid dissociation constant. The composite constant a has the values 0.29, 3.0, and 9.0 s^{-1} for the reduction of Co(EDTA)$^-$, Co(HEDTA)OH$_2$, and Co(HEDTA)Cl$^-$. A comparison with other reducing agents is made and the mechanistic implications are discussed.

Introduction

In several kinetic studies (ethylenediaminetetraacetato)cobaltate(III) and related complexes have been used to characterize mechanistic behavior of some transition-metal reducing agents. On the basis of indirect arguments it was shown that Fe^{2+} reduces Co(HEDTA)Cl$^-$ and Co(HETA)-OH$^-$ complexes (HEDTA = monoprotonated EDTA, HETA = *N*-hydroxyethylenediamine-*N,N',N'*-triacetate) by an inner-sphere mechanism with chloro and hydroxo ligands acting as bridges.[1,2] More speculative arguments were used to suggest that Fe^{2+} reduces Co(HEDTA)OH$_2$, Co(HETA)OH$_2$, and hexadentate Co(EDTA)$^-$ by an inner-sphere mechanism, with the carboxylato group of the coordinated acetate acting as a bridge.[2] Inner-sphere reduction of the same series of complexes by Cr^{2+} was proved by analyses of the Cr(III) products, which contained transferred polycarboxylato and (for the Co-(HEDTA)Cl$^-$ reaction) chloro ligands.[3] It was recently elegantly shown, by a comparison of the substitution rates on

the Co(III) centers and the redox rates, that the Fe(CN)$_6^{4-}$ reduction of Co(EDTA)$^-$, Co(EDTA)OH$_2^-$, and Co-(EDTA)Cl^{2-} proceeds through an outer-sphere mechanism.[4]

In view of the preceding literature data it was of interest to study the reactivity of titanium(III) toward EDTA complexes of cobalt(III). Titanium(III) was shown not to exhibit preference toward chloride as a bridge[5,6] and to exhibit preference toward carboxylato groups, including acetato ligand.[7] Here we report a kinetic study on the titanium(III) reduction of Co(EDTA)$^-$, Co(HEDTA)OH$_2$, and Co-(HEDTA)Cl$^-$ at 25 °C in an aqueous chloride medium of 1.0 M ionic strength (HCl + NaCl).

Experimental Section

Materials. The complexes KCo(EDTA)·2H$_2$O and KCo(HED-TA)Cl were prepared according to the method of Dwyer et al.[8,9] The dihydrate KCo(EDTA)·2H$_2$O was dehydrated by heating at 105 °C to constant weight. The identity of the complexes was established from their UV–visible spectra with visible absorption maxima (molar