groups alternate with E*Ph* groups around the peripheries of the complex ions. The D_2 structures have clashing pairwise arrangements of E*Me* and E*Ph* groups, consistent with the upfield chemical shifts observed for the E*Me* groups in the D_2 diastereomers. The equilibrium diastereoselectivities observed for the arsenic derivatives are lower than those observed for the phosphorus derivatives for copper(I) and gold(I), although silver(I) shows slightly higher discrimination with the arsenic ligand under the standard conditions employed. The greatest diastereoselectivity was found in the copper(I)–phosphorus system (D_2:S_4 = 1:6). Unfortunately, there are no solid-state structural data on the present series of complexes and data that are available on related complexes may not be applicable to these systems. Copper–donor atom bond lengths in $[Cu(Ph_2PCH_2CH_2PPh_2)_2]CF_3SO_3{\cdot}CH_3C_6H_5$ (2.31, 2.35 Å)[16] are shorter than those in $[Cu(1,2\text{-}C_6H_4(AsMe)_2)]PF_6$ (2.36 Å);[17] both structures have irregular interligand geometries. There are no structural data available for silver(I) complexes of bis(tertiary arsines) or bis(tertiary phosphines). The Au–P bond length in $[Au(Ph_2PCH_2CH_2PPh_2)_2]SbF_6{\cdot}Me_2CO$ is 2.40 Å;[18] in $[Au(1,2\text{-}C_6H_4(AsMe_2)_2)_2][Au(C_6F_5)_2]$ the Au–As bond length is 2.47 Å.[19] The well-known propensity of copper(I) for tetrahedral four-coordination and of gold(I) for linear two-coordination[20] may be the most important factor in the determination of diastereoselectivity and stability in these complexes. Thus, the greatest diastereoselectivities in solution would be expected for copper(I) systems, where discriminating steric effects would be maximized by four-coordination, particularly with chelating bis(tertiary phosphines).

Experimental Section

Proton NMR spectra of 0.06 M solutions were recorded on Bruker CXP-200 and Jeolco FX 200 spectrometers under the conditions stated. Optical rotations were measured on the specified solutions in 1-dm cells at 293 K with a Perkin-Elmer Model 241 polarimeter. Conductivity measurements were made at 293 K on 10^{-3} M solutions of the substances in acetonitrile with use of a Wissenschaftlich-Technische Werkstatten (D-8120 Weilheim, FRG) conductivity bridge. Elemental anlayses were performed by staff within the Research School of Chemistry.

The isolation of diastereomers and enantiomers of 1,2-phenylenebis(methylphenylphosphine)[6] and of the corresponding bis(tertiary arsine)[7] were carried out as previously described. Tetrakis(acetonitrile)copper(I) hexafluorophosphate hemihydrate was prepared by the method of Kubas.[9]

[*T*-4-[*R*-(*R,*R**)]]-Bis[1,2-phenylenebis(methylphenylphosphine)]copper(I) Hexafluorophosphate Hemiacetone Solvate: (−)-[Cu([R-(*R**,*R**)]-diph)$_2$]PF$_6$·0.5Me$_2$CO.** A suspension of $[Cu(MeCN)_4]PF_6{\cdot}0.5H_2O$ (0.29 g) and [*S*-(*R**,*R**)]-diph (0.50 g)[14] in deoxygenated acetonitrile was stirred until a clear solution resulted. The colorless solution was filtered, and the filtrate was evaporated to dryness; recrystallization of the residue from an acetone–diethyl ether mixture gave the product as colorless needles, yield 0.55 g (83%).

[*T*-4-[*R*-(*R,*R**)]]-Bis[1,2-phenylenebis(methylphenylphopshine)]silver(I) Hexafluorophosphate, (−)-[Ag([*R*-(*R**,*R**)]-diph)$_2$]PF$_6$.** Silver(I) nitrate (0.13 g) was reacted with [*S*-(*R**,*R**)]-diph (0.50 g) in 95% ethanol (50 mL). The solution was evaporated to dryness, and the residue was redissolved in dichloromethane (50 mL). The dichloromethane solution was then treated with an aqueous NH_4PF_6 solution (1 g of NH_4PF_6, 20 mL of H_2O); the mixture was vigorously shaken, the layers were separated, and the organic layer was dried over $MgSO_4$. After filtration, the dried solution was taken to dryness and the colorless residue was recrystallized from an acetone–diethyl ether mixture. The product formed colorless needles, yield 0.58 g (82%).

The remaining compounds were obtained in high yields as colorless crystalline solids by following similar procedures. Details are given in the tables.

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Contribution from the Laboratoire de Chimie-Physique (UA 253 du CNRS),
HEI, 13, rue de Toul, 59046 Lille Cédex, France

Chemical Species in Sulfur–Ammonia Solutions: Influence of Amide Addition

P. Dubois, J. P. Lelieur,* and G. Lepoutre

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The acidity of sulfur–ammonia solutions has been modified by the introduction of an alkali-metal amide, and the chemical composition of the solution has been studied by using UV–visible spectrophotometry and Raman spectroscopy. It is shown that the progressive introduction of an alkali-metal amide makes the oxidized species more oxidized and the reduced species more reduced. It is found that, in sulfur–ammonia solutions, a chemical species less oxidized than S_4N^- exists in solution, which is neither S_7N^- nor a polysulfide; it is suggested that this species is a neutral form of sulfur. It is shown that the concentration of S_4N^- can be increased after amide addition by a factor of about 3 for a 10^{-2} M solution. Other oxidized forms of sulfur that have been observed are assigned to S_3N^- and S_2N^-. Very slow kinetics are observed for the modifications of the species induced by the introduction of the alkali-metal amide.

Introduction

Recent works related to sulfur–ammonia solutions have shown that the solutions contain the NH_4^+ cation and are therefore acidic.[1-5] It was shown that sulfur is solubilized in ammonia by a redox disproportionation mechanism, for which the following equations[1] have been proposed:

$$10S + 4\,NH_3 \rightarrow S_4N^- + S_6^{2-} + 3NH_4^+ \tag{1}$$

$$S_6^{2-} \rightleftarrows 2S_3^- \tag{2}$$

It was found later[2] that eq 1 does not describe completely the chemical species in sulfur–ammonia solutions; the existence of another oxidized species, S_3N^-, has been established by Raman spectroscopy. However eq 1 led us to investigate the influence of amide addition on the concentration of S_4N^- and of S_6^{2-}. It was found that the chemical species in solution can be modified and replaced by other species. In the present paper, the pH dependence of chemical species in solution is demonstrated, and the chemical species are tentatively identified. The increase of

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the pH of the solution was obtained through gradual addition of sodium amide or potassium amide, and the modifications of the absorption spectrum and the Raman spectrum were subsequently monitored.

The only previous results concerning the reaction of potassium amide with sulfur in liquid ammonia have been obtained by Bergstrom,[6] who studied this reaction for highly concentrated solutions at −33 °C and at room temperature. Bergstrom proposed several reaction equations between sulfur and potassium amide. These equations depend on the ratio between sulfur and amide and follow the chemical analysis of the products obtained after the evaporation of ammonia. Bergstrom suggested that there is sulfide formation when the amide is in excess and polysulfide formation when sulfur is in excess.

The present work is rather different from that of Bergstrom because our main aim was to identify the chemical species in solution and because we were interested in the influence of amide even for dilute solutions and for low values of the ratio NH_2^-/S.

Experimental Section

The absorption and Raman spectra have been recorded as previously described.[2,7,8] The Raman spectra have been recorded with the Raman spectrometers of the Laboratoire de Spectroscopie Infrarouge et Raman (LASIR) de l'Université de Lille 1. The Raman spectra have been obtained for solutions more concentrated than about 10^{-2} M. These solutions were prepared with a given NH_2^-/S ratio. For these experiments, potassium amide, much more soluble in liquid ammonia than sodium amide, was used. Potassium (Alfa, >97%), and sulfur (Fluka, >99.999%) were used without further purification; they were weighed with a precision of ±0.1 mg in a glovebox. Ammonia, dried on potassium, was controlled volumetrically, and condensed on sulfur and potassium amide at the temperature of liquid nitrogen. The sample was then sealed off and kept for at least 3 days at room temperature before recording the Raman spectra.

The UV–visible spectrophotometry experiments have been performed with solutions less concentrated than about 10^{-2} M. These experiments used a two-compartment cell, one end (A) being a quartz optical cell (0.5 mm optical path length for most of the experiments), the other end (B) being a 8-mm-i.d. cylindrical Pyrex tube about 5 cm long. These ends were separated by a frit. Sulfur was weighed with a precision of ±0.01 mg and introduced in the optical cell (end A). Sodium amide (Alfa, >97%) was weighed with a precision of ±0.1 mg in a glovebox and introduced in the Pyrex tube (end B) inside the glovebox. Ammonia, controlled volumetrically, was condensed on sulfur at dry ice temperature. The sample was then sealed off and kept for at least 3 days at room temperature to obtain the complete solubilization of sulfur in ammonia. The temperature of sodium amide (end B) was kept slightly higher than that of the sulfur–ammonia solution (end A) in order to prevent the distillation of ammonia from end A to end B. For a given sample, the first absorption spectrum recorded was therefore related to an amide-free sulfur–ammonia solution. The influence of sodium amide on the absorption spectrum of the solution was then studied in the following way. (i) An amount of ammonia was distilled from end A to end B on the sodium amide. The amount of distilled ammonia was determined from its gaseous volume, and the amount of sodium amide solubilized in distilled ammonia was then obtained. Sodium amide was used in these experiments because it is much less soluble than potassium amide. The solubility of sodium amide in liquid ammonia was taken as 2.34×10^{-2} M at 293 K.[9] Our experimental procedure allows the addition of very small quantities of sodium amide in the sulfur–ammonia solutions, and the changes of the absorption spectrum versus NH_2^-/S can then be followed even for dilute solutions. (ii) Distilled ammonia, saturated with sodium amide was poured down back from end B to end A. The absorption spectrum was then recorded at room temperature until it remained invariant. The procedure to add more sodium amide to the solution could then be repeated.

By use of this experimental procedure, the true ammonium (or amide) concentration in the solution cannot be ascertained. Consequently, the variations of the absorption bands are presented on a NH_2^-/S scale, and not on a pH scale (Figure 3).

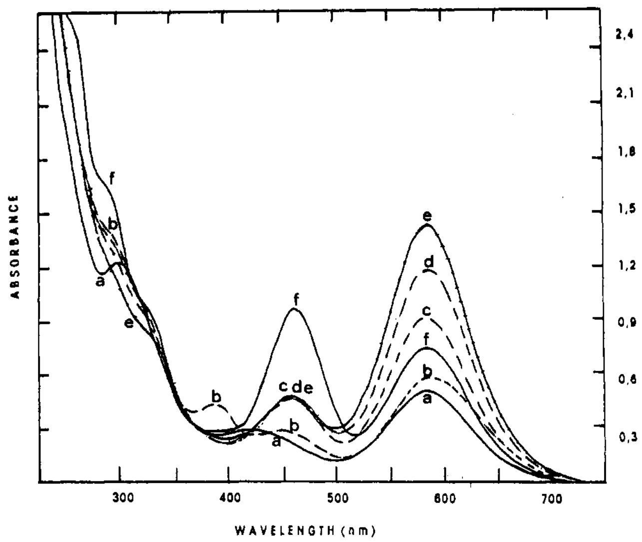

Figure 1. Absorption spectra of a sulfur–ammonia solution (2.4×10^{-2} M) at room temperature: (a) reference spectrum ($A = NH_2^-/S = 0$); (b) spectrum recorded about 15 min after the first amide addition ($A = 0.4 \pm 0.1$); (c) spectrum recorded 24 h after the first amide addition; (d) spectrum recorded at equilibrium, 150 h after the first amide addition; (e) spectrum recorded at equilibrium, after the second amide addition ($A = 0.5 \pm 0.15$); (f) spectrum recorded at equilibrium after the third amide addition ($A = 0.6 \pm 0.2$). Optical path length = 0.5 mm.

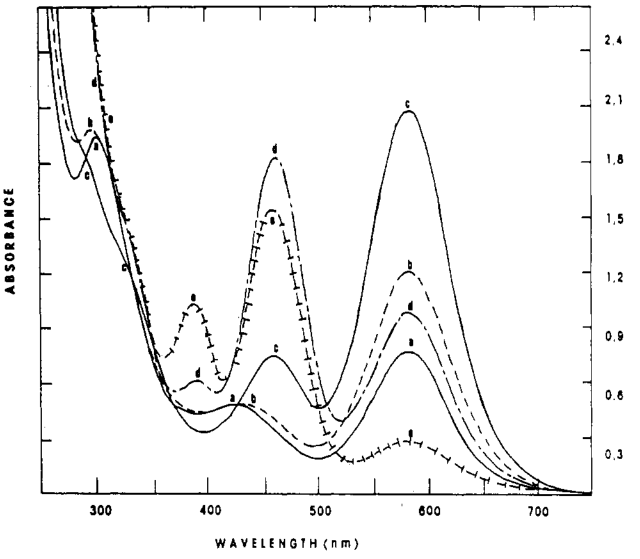

Figure 2. Absorption spectra of a sulfur–ammonia solution (3.6×10^{-2} M) at room temperature. Optical path length = 0.5 mm. Spectra a–e have been recorded at equilibrium and are related to the following value of NH_2^-/S: (a) 0; (b) 0.25; (c) 0.44; (d) 0.6; (e) 0.75. In this experiment, the amide addition was performed in a very accurate manner. Each amide addition gave an increase of NH_2^-/S close to 0.07 ± 0.1; only some of the equilibrium spectra are reported.

Results

Absorption Spectra of Sulfur–Ammonia Solutions with Addition of Amide. The absorption spectra of sulfur-ammonia solutions with various sulfur concentrations, for increasing amide addition, are reported in Figures 1 and 2, together with the absorption spectrum of each solution before the first amide addition (spectrum a of Figures 1 and 2). When amide is added to the solution, very large modifications of the spectra are observed in the visible range and in the UV range. The experiments have shown that the time required to obtain a new equilibrium after an amide addition depends on the change of the ratio NH_2^-/S induced by this amide addition and also depends on the value of this ratio.

As intuitively evident, small changes in the absorption spectra are induced by small changes in NH_2^-/S and the new equilibrium spectra are obtained in shorter times. Practically, the variations

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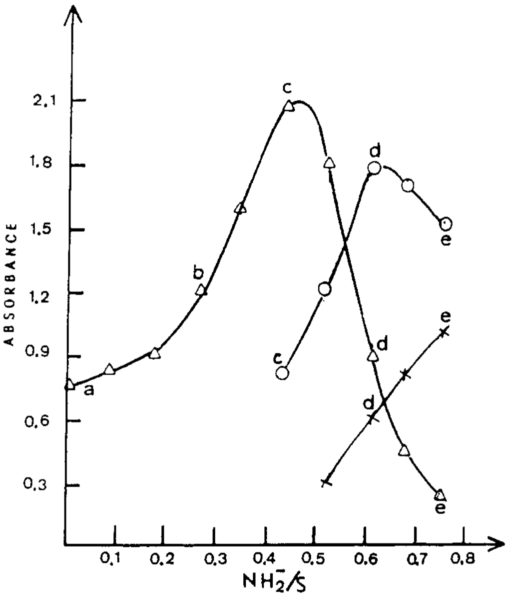

Figure 3. Variations of absorbance at 580 (△), 460 (○) and 390 nm (×) versus NH_2^-/S. These absorbances have been recorded at equilibrium, at room temperature. The absorption spectra (a–e) from Figure 3 are only a fraction of the spectra recorded at equilibrium.

of NH_2^-/S that can be quantitatively estimated with accuracy are on the order of 0.1, when the sulfur concentration is in the 10^{-2} M range, as in Figure 2. It is a general observation that the new equilibrium after amide addition is obtained after a rather long time; the equilibrium often requires several tens of hours.

It was found that upon the addition of a large amount of amide, causing a large variation of NH_2^-/S, transient absorption bands are observed. For instance, in Figure 1, when NH_2^-/S is increased from 0 to about 0.4, an absorption band is observed at 390 nm immediately after the amide additon (Figure 1, spectrum b). After several hours, this peak disappears while the equilibrium is being reached (Figure 1, spectrum d). However, the band at 390 nm is permanently observed at equilibrium for higher values of the NH_2^-/S ratio (Figure 2). The bands at 390 and 460 nm are examples of bands not observed for sulfur–ammonia solutions at equilibrium but only observed after amide addition.

Figures 1 and 2 also show that the variations of absorbance at a given wavelength are nonmonotonic versus NH_2^-/S. For instance, the absorbances at 580 and 460 nm display a well-defined maximum versus NH_2^-/S, as plotted in Figure 3. Indeed, the complex variations of the absorption band upon amide addition already suggest that the chemical species are involved in complex chemical equilibria.

Modifications of Chemical Species upon Amide Addition. The identification of several chemical species in sulfur–ammonia solutions has already been proposed.[1-3] It was shown that the main visible absorption band located at 580 nm results from the absorptions of S_4N^- and S_3^- which are located at 580 and 610 nm, respectively. The S_3^- radical is in equilibrium with S_6^{2-}, which absorbs in the 420–450-nm range. Raman spectroscopy experiments under resonance conditions allowed the identification of another oxidized form of sulfur, S_3N^-, well characterized by its Raman lines at 580, 695, and 898 cm^{-1}.[10,11] The absorption band of this species in acetonitrile was located at 465 nm by Chivers et al..[10,11] This location was confirmed in ammonia by Prestel and Schindewolf.[16] These spectroscopic characterizations will be used for the interpretation of some modifications of the absorption spectra upon amide addition.

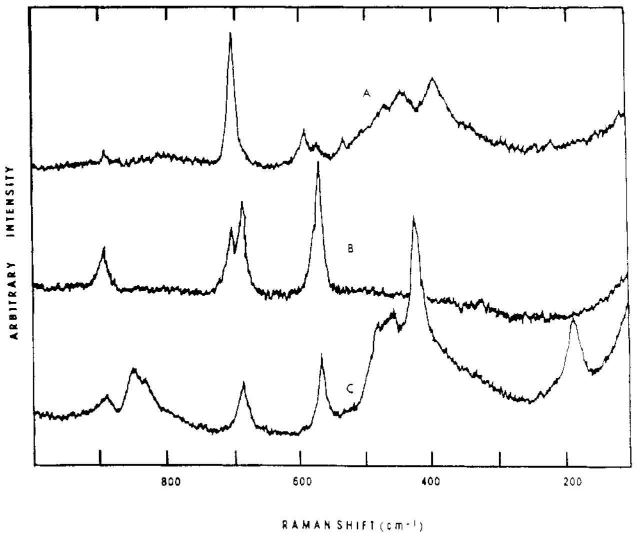

Figure 4. Raman spectra recorded at room temperature with the 514.5-nm excitation line from an argon laser, with a backscattering geometry. Potassium amide was used in these samples: (A) 0.32 M; $NH_2^-/S = 0$; (B) 0.7 M; $NH_2^-/S = 0.45$; (C) 4 M; $NH_2^-/S = 0.6$.

Figures 1–3 show that amide addition induces an increase of the concentration of the S_4N^- species. When this species is close to its maximum concentration, an absorption band appears at 460 nm, increases, and goes through a maximum. This absorption band can be assigned to S_3N^-, because of its location and because of the Raman spectrum (Figure 4) of the sulfur–ammonia solutions with amide addition. The Raman spectra of sulfur–ammonia solutions, recorded with the 647.1-nm excitation line, are not modified when the amide addition NH_2^-/S ratio is lower than about 0.4. However, the Raman spectra recorded with the 514.5-nm line are significantly changed and clearly show the Raman lines of S_4N^- and S_3N^- for $NH_2^-/S \sim 0.4$ (Figure 4).

It is therefore concluded that, under progressive amide addition, an increase of the concentration of S_4N^- is followed by an increase of S_3N^- (Figure 3). The maximum concentration of S_4N^- is followed by that of S_3N^-. It is also seen in Figure 3 that the increase of S_3N^- is followed by another peak at 390 nm: the latter will be tentatively assigned to S_2N^- (see below).

The modifications of reduced forms of sulfur (polysulfides) under increasing amide addition are not easy to follow. For absorption spectra, the possible variations of S_6^{2-} are obscured by the large increase of the absorption of S_3N^-, which has an extinction coefficient approximately 5 times larger than that of S_6^{2-}, and the possible variations of S_4^{2-} are similarly obscured by the absorption band at 390 nm, which is assigned to an oxidized species (tentatively S_2N^-). In sulfur–ammonia solutions, the S_6^{2-} Raman lines can be recorded with the 514.5-nm excitation line but not with the 647.1-nm line. However, the Raman lines of S_6^{2-} are not observed with the 514.5-nm line after an amide addition such as $NH_2^-/S = 0.4$ (Figure 4). This results probably from the much higher absorbance of S_3N^- relative to that of S_6^{2-}. Similarly, S_3^- is not observed with the 514.5-nm line, probably because the absorbance of S_4N^- is much higher than that of S_3^-, but S_3^- is observed with 647.1-nm excitation line, for which resonance conditions are better satisfied. For higher amide content ($NH_2^-/S \simeq 0.6$), S_4^{2-} is observed (Figure 4, spectrum C).

It is therefore observed that the modifications of the reduced species with amide addition are not followed as easily as the variations of the oxidized species. However, the overall experimental observations show that the amide addition makes the oxidized species more oxidized and the reduced species more reduced.

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Table I. Absorbance at 580 nm in Sulfur–Ammonia Solutions

10^3C,[a] M	$A(580)/lC$,[b,c] M^{-1} cm^{-1}	$A^M(580)/lC$,[d] M^{-1} cm^{-1}
0.6	1204	
0.9	1130	
1.3	1010	
1.8	824	
2.6	680	990
14.2	483	
23.9	457	1210
35.9	430	1151
36.3	455	

[a] C is the concentration of the solution. [b] l is the optical path length. [c] $A(580)$ is the experimental absorbance at 580 nm at room temperature, without addition of amide. [d] $A^M(580)$ is the experimental absorbance at 580 nm at room temperature, maximized by addition of amide.

Interpretation of the Variations of S_4N^- under Amide Addition. It was shown that the concentration of S_4N^- is increased with increasing amide addition in the solution. This is an unexpected result if eq 1 is considered. It was shown above experimentally that the amide addition makes the oxidized species more oxidized. Consequently, the increase of S_4N^- originates from a species less oxidized that S_4N^-. This will be discussed below but shows a limitation of eq 1 for the description of sulfur–ammonia solutions. From now, the species giving rise to S_4N^- under amide addition will be designated X. X is a stable species formed upon dissolution of sulfur in ammonia. It will be shown that X has a high relative concentration.

It must be noted that the increase of S_4N^- can be rather large, since the ratio of the maximum of the 580-nm absorption band to its initial value is equal to 2.78 for a 3.6×10^{-2} M solution. This enhancement ratio increases with the concentration (Table I). The extinction coefficient of S_4N^- in sulfur–ammonia solutions was found equal to 729 M^{-1} cm^{-1} at 200 K, relative to the sulfur concentration.[2] This value was calculated from the linear part of the Beer's law plot, i.e. for concentrations lower than 1.5×10^{-3} M. For concentrations larger than 1.5×10^{-3} M, there is a deviation of the Beer law, and the apparent extinction coefficient of S_4N^- decreases when the concentration increases. It is noticeable that, upon amide addition, the apparent extinction coefficient of S_4N^- is approximately equal to 1100 M^{-1} cm^{-1}, even in the 10^{-2} M range (Table I). This suggests that, in sulfur–ammonia solutions, the decrease of the apparent extinction coefficient of S_4N^- when the concentration increases is due to an increase of the concentration of X. It is therefore suggested that S_4N^- results from the disproportionation of X. If X gives rise to S_4N^- upon amide addition, the absorption bands of X must decrease. In Figures 1 and 2, the absorbance at about 300 nm decreases upon amide addition. However, this observation does not allow the identification of X. But the possibility that X absorbs at 300 nm is confirmed by the absence of the 300-nm peak in very dilute sulfur–ammonia solutions, because X should be more disproportionated in very dilute solutions.

It can be considered that X gives rise to S_4N^- and that X is less oxidized than S_4N^- and more oxidized than S_6^{2-}. If the oxidation state of nitrogen is taken equal to −3 and does not change, the oxidation state of sulfur in S_4N^- is $+^1/_2$. Therefore the oxidation state of sulfur in X is between $+^1/_2$, and $-^1/_3$ (S_6^{2-}). Since it was shown[7] previously that S_6^{2-} is the least reduced polysulfide in ammonia, the oxidation state of sulfur in X is between 0 and $+^1/_2$. The possible species[13] are the sulfur imide S_7NH, the compounds $S_7N–S_x–S_7N$, and neutral sulfur. The possible existence of $S_7N–S_x–S_7N$ will be related to formation of S_7N^- in solution. Consequently the study of solutions of S_7NH in ammonia was believed to be important for the identification of X, and the results of this study are reported below. This study will show that S_7N^- is not the X species.

Solutions of S_7NH in Ammonia: Solubilization and Absorption Spectra. The solid compound S_7NH was synthesized by following the method described by Bojes et al.[14] The Raman spectra we have recorded for S_7NH confirm published results.[15] The solubilization process of S_7NH in ammonia is rather fast, at least for the first step of this process. S_7NH dissolves more rapidly than S_8 in liquid ammonia. At −78 °C, S_7NH is solubilized in NH_3 in a few minutes and yields a clear yellow solution with an absorption band at 256 nm, with a wide tail extending to 600 nm (Figure 5). As the solution is heated up to −35 °C, the absorption spectrum changes; after 2 h at −35 °C, the absorption spectrum described by Prestel and Schindewolf was obtained.[16] The changes of the absorption spectrum at −35 °C were followed for 3 days: the absorption at 460 nm goes through a maximum (Figure 5), while the absorbance at 580 nm increases and the shoulder at 300 nm becomes a well-defined band. However the solution is not yet in equilibrium; when the solution is heated up to room temperature, the absorption spectrum changes irreversibly: the absorbance increases at 580 nm but decreases at 460, 300, and 256 nm. These observations show that the equilibrium state of the solution must be carefully checked. It was found that the time to reach equilibrium increases when temperature and concentration decrease.

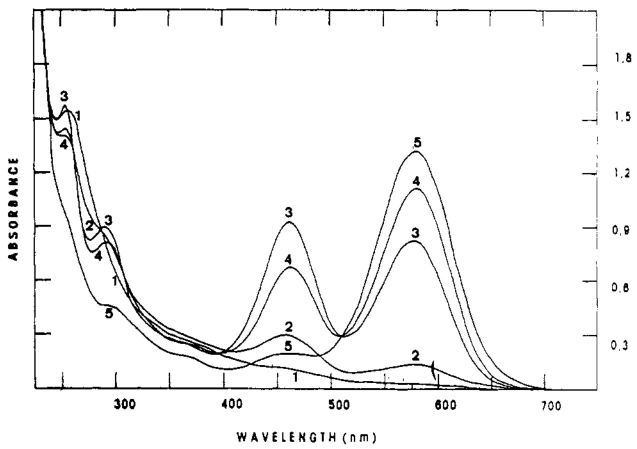

Figure 5. Absorption spectra of a $S_7NH–NH_3$ solution recorded during the solubilization process: (1) T = −35 °C (recorded after approximately 10 min at −35 °C; sample previously kept at −78 °C); (2) T = −35 °C; after 2.5 h at −35 °C; (3) T = −35 °C; after 17 h at −35 °C; (4) T = −35 °C; after 63 h at −35 °C; (5) at equilibrium, at 293 K. Optical path length = 1 mm.

The Raman spectra recorded for $S_7NH–NH_3$ solutions, at room temperature with the 514.5-nm excitation line, show the lines of S_4N^-, which allows the attribution of the absorption band located at 580 nm to this species. The main Raman line of S_3^-, at 535 cm^{-1}, was also observed, but the Raman lines of S_6^{2-} were not observed, so the absorption band located at 460 nm is consequently assigned to S_3N^-. The Raman lines of S_7NH were not observed,[15] which is a first indication of the complete disproportionation of this compound in ammonia. The complete disproportionation could be demonstrated by Raman spectroscopy only by using excitation wavelengths in the 300-nm range. This disproportionation is discussed below.

Disproportionation of S_7N^- in Ammonia. The observation of S_4N^- in either the absorption spectrum or the Raman spectrum of $S_7NH–NH_3$ solutions shows the disproportionation of S_7N^-. However the following question must be considered: Is the disproportionation of S_7N^- in ammonia complete or not? An absorption band is observed at 256 nm in S_7NH–ammonia solutions, as in S_7NH–chloroform solutions. However the absorption band at 256 nm in ammonia cannot be used to estimate the concentration of S_7N^- when the solution has reached its equilibrium state, because the nonmonotonic variations of absorbance at 256 nm during the solubilization process suggest that this band is complex and results from the composition of several bands. The concentration of S_4N^- in $S_7NH–NH_3$ solutions can be estimated through the absorption band of S_4N^-. We have found that the $S_7NH–NH_3$ solutions obey the Beer law, for the absorption band of S_4N^- at 580 nm, up to a concentration at least equal to 2×10^{-2} M and an extinction coefficient of 14 000 M^{-1} cm^{-1} relative to the concentration of S_7NH was obtained. This value is rather close to that (16 000 M^{-1} cm^{-1}) given by Chivers et al. for solutions of $PPN^+S_4N^-$ in acetonitrile.[17] In S_7NH-NH_3 solutions, two oxidized species are detected: S_4N^- (580 nm) and S_3N^- (460 nm) (Figure 5, spectrum 5). Consequently, the concentration of S_4N^- is necessarily lower than the concentration of S_7N^-, and the extinction coefficient of 14 000 M^{-1} cm^{-1} for S_4N^-, relative to the concentration of S_7NH, can only be an underestimated value.

It can be argued that the correct extinction coefficient of S_4N^- in ammonia is close to the value found by Chivers in acetonitrile. The concentration of S_3N^- in the S_7NH-NH_3 solution can only be estimated, because its extinction coefficient is not known. However, on the basis of the observations reported in Figure 3, the extinction coefficient of S_3N^- must be rather close to the extinction coefficient of S_4N^- and is taken to be about 15 000 M^{-1} cm^{-1}. With this hypothesis, the concentration of S_3N^- is approximately equal to 10% of the concentration of S_4N^-. Consequently the extinction coefficient of S_4N^- in ammonia, deduced from the study of S_7NH-NH_3 solutions, is approximately 15 500 M^{-1} cm^{-1} and confirms the value obtained by Chivers in acetonitrile. The present analysis also shows that there is approximately one oxidized species (S_4N^- or S_3N^-) for one S_7N^-. This conclusion shows that the disproportionation of S_7N^- is complete; this is consistent with the absence of the Raman lines of S_7N^- in the solution. It must be said here that S_4N^- is not produced directly from S_7N^-; intermediate steps are observed, involving at least S_3N^-,[18] as found in the study of the solubilization process of S_7NH (or S_8) in liquid ammonia monitored with UV-visible spectrophotometry.

The disproportionation of S_7N^- gives mainly S_4N^- and one species more reduced than S_7N^-. The identification of this species must be considered, and this identification depends on the identification of X: if X is S_7N^-, this species (more reduced than S_7N^-) will be S_6^{2-}, but if X is not S_7N^-, the disproportionation of S_7N^- gives mainly S_4N^- and X. The experimental results clearly answer this question; there is no indication of S_6^{2-} given by either Raman spectroscopy or by UV-visible spectrophotometry in S_7NH-NH_3 solutions. The main visible absorption band located at 580 nm is more symmetrical for S_7NH solutions than for sulfur solutions, which shows that the contribution of S_3^- to this band is smaller. This is confirmed by the observation of the temperature dependence of the absorption spectrum around 610 nm: this temperature dependence is much less than that for $S-NH_3$ solutions, and the concentration of S_3^- is much smaller than that for $S-NH_3$ solutions. However, S_3^- is observed in S_7NH-NH_3 solutions by Raman spectroscopy under resonance conditions. S_6^- is probably present as a result of the normal S_3^-/S_6^{2-} equilibrium, but below detection limits. In conclusion, it can be said that the disproportionation of S_7N^- produces the species X, which absorbs at 300 nm, and X is not S_6^{2-}. A shoulder is indeed observed at 300 nm in the absorption spectrum of S_7NH-NH_3 solutions at equilibrium; a well-defined band was even observed at 300 nm during the process of reaching equilibrium (Figure 5).

The above-mentioned experiments demonstrate that S_7N^- is completely disproportionated in ammonia, and this shows that the species X in sulfur-ammonia solutions is not S_7N^-. This conclusion is confirmed, since the disproportionation of S_7N^- produces X, and not S_6^{2-}, together with S_4N^-. Consequently the species X in sulfur-ammonia solutions is neutral sulfur. However, X is not cyclic S_8, whose spectrophotometric or Raman characteristics are not observed in $S-NH_3$ solutions.[19,20] Since X is in solution in ammonia, X is now described as S_{am}, involving possibly several sulfur atoms.

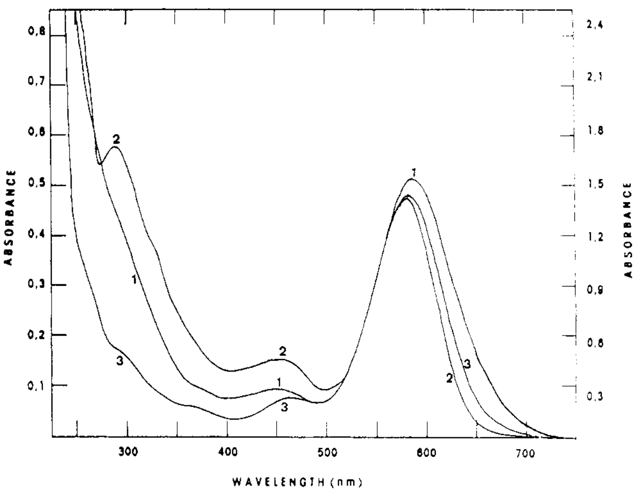

Figure 6. Comparison of the absorption spectra of $S-NH_3$ and S_7NH-NH_3 solutions: (1) $S-NH_3$, 9.9 × 10^{-4} M, 293 K; (2) $S-NH_3$, 9.9 × 10^{-4} M, 200 K; (3) S_7NH-NH_3, 2 × 10^{-4} M, 293 K. Optical path length = 5 mm. The absorbance scale for $S-NH_3$ is on the left side of the plot; the absorbance scale for S_7NH-NH_3 is on the right side of the plot.

Finally, the absorption spectra of S_7NH-NH_3 and $S-NH_3$ solutions are compared in Figure 6. This comparison is done for solutions with the same S_4N^- concentration by the normalization of the absorbances at 580 nm. Very large differences are observed in the UV range, where the absorbance is much higher for $S-NH_3$ solutions and is assigned to a higher concentration of S_{am} and to a much higher concentration of S_6^{2-}.

In conclusion, we have found that the disproportionation of S_7NH in ammonia is complete. When the concentrations of S_3N^- and of S_6^{2-} (and S_3^-) are neglected, this disproportionation can be written, as a first approximation as

$$S_7N^- \rightarrow S_4N^- + S_{am} \qquad (3)$$

where S_{am} is a neutral form of sulfur. This study also shows that S_7N^- is not present in the sulfur ammonia solutions and that S_{am} is present in these solutions.

It has been mentioned above that S_{am} absorbs at about 300 nm. If S_{am} involves several sulfur atoms, it can be thought that this species could be detected by Raman spectroscopy. However the Raman spectra of sulfur-ammonia solutions do not display evidence of S_{am}. Two reasons can be given for the lack of evidence of S_{am} in the Raman spectra. (i) The S-S vibrations of S_{am} should be in the 400-500-cm^{-1} range, where the vibrations of S_6^{2-} are observed. Weak lines from S_{am} can possibly be masked by S_6^{2-} lines. Indeed, small differences in the relative intensity of the Raman lines in the 400-500-cm^{-1} range are systematically found for $S-NH_3$ solutions and for $Li_2S_6-NH_3$ and $(NH_4)_2S_6-NH_3$ solutions. (ii) The Raman spectra of sulfur-ammonia solutions have been obtained with the 488.0-, 514.5, and 647.1-nm excitation wavelengths. Obviously, a UV excitation wavelength in the 300-nm range would be more appropriate for the observation of the Raman spectrum of the S_{am} species.

Absorption Spectra of S_7NH-NH_3 Solutions under Amide Addition. The influence of amide addition on a S_7NH-NH_3 solution was examined. This experiment was carried out in the same way as for $S-NH_3$ solutions, and the results are displayed in Figure 7. For the first amide additions, the absorbance is not changed at 580 nm, but increases at 460 nm and decreases at 300 nm. However, for more amide addition, the absorption spectrum undergoes drastic changes, as for sulfur-ammonia solutions: the

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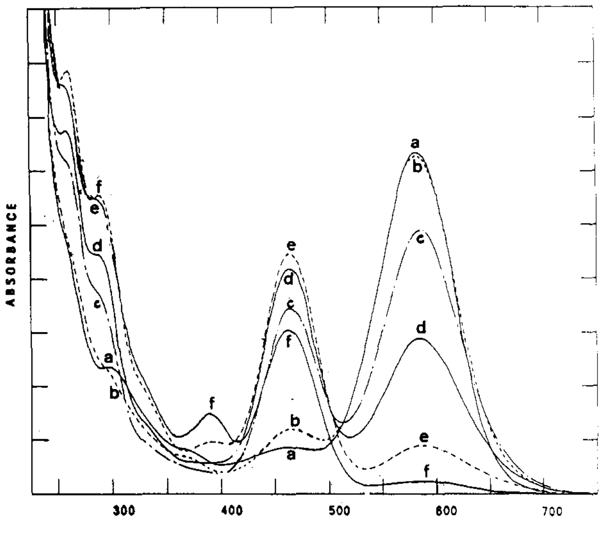

Figure 7. Absorption spectra of S_7NH-NH_3 solutions (1.9×10^{-4} M) at 293 K. Optical path length = 1 mm. Spectrum A was recorded at equilibrium before the first addition of sodium amide. Spectrum B was obtained for an amide addition such as $NH_2^-/S_7NH \simeq 0.3$. Spectra C-F have been obtained at equilibrium with an increasing amount of amide.

absorbance decreases at 580 nm and goes through a maximum at 460 nm, while an absorption band appears at 390 nm. In the UV range, absorption bands appear at 300 and 256 nm that were not observed in $S-NH_3$ solutions, for which a general increase was observed between 350 and 250 nm, under amide addition. It must be noted that the variations of the absorbances with time, after and amide addition, are very slow as in sulfur-ammonia solutions.[24]

The main observation from this experiment is the invariance of S_4N^- after the first amide additions.[24] This observation is consistent with the previous conclusion that S_7N^- is fully disproportionated in liquid ammonia.

Further amide addition (Figure 7) displays a great similarity with the case of $S-NH_3$ solutions. The S_4N^- species is gradually replaced by S_3N^-; the species S_3N^- goes through a maximum concentration, and S_3N^- is itself gradually replaced by a species absorbing at 390 nm, tentatively identified as S_2N^- as in $S-NH_3$ solutions. The modifications observed in the UV range are not interpreted.

Observation of Oxidized Forms of Sulfur in $S-NH_3$ Solutions under Amide Addition. It was shown above that the concentration of S_4N^- in $S-NH_3$ solutions is increased under the first amide addition. The concentration of S_4N^- goes through a maximum and decreases when S_4N^- is gradually replaced by S_3N^-. The further modifications of oxidized species have been tentatively interpreted in the following way.

When the absorption band of S_3N, located at 460 nm, decreases, an absorption band at 390 nm increases (Figures 2 and 3). This latter band is assigned to S_2N^-, which is close to S_3N^- on the increasing oxidation scale of the $S_xN_y^-$ anions. Chivers et al.[12] in an electrochemical study have also identified S_2N^- as the species immediately more oxidized than S_3N^-. However, they have observed that the absorption band of S_2N^- is located at 375 nm in acetonitrile. It was also found (Figure 4, spectrum C) that two Raman lines are observed at 858 and 839 cm^{-1} together with the lines of S_3N^-, and these are assigned to S_2N^-.

When more amide is added to the solution described by spectrum e of Figure 2, a precipitate is observed. Spectrum C_2 of Figure 8 is then obtained, showing absorption bands at 285 and 365 nm. This latter band at 365 nm appears to be an envelope, which could include the absorption due to $S_3N_3^-$. The absorption band of $S_3N_3^-$ in ammonia has been located by Prestel and Schindewolf[16] at 360 nm. The absorption band at 285 nm could be assigned to S^{2-}, which has low solubility in ammonia.[7] However the ctts properties previously found for S^{2-} in neutral ammonia[7,21] have not been displayed by the band observed at 285 nm.

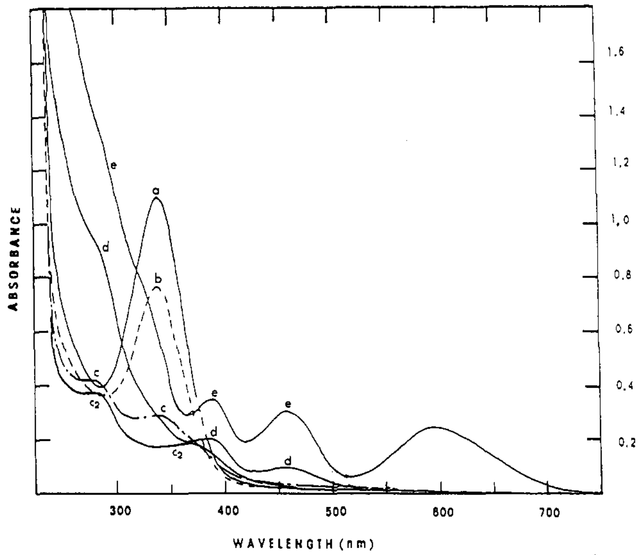

Figure 8. Absorption spectra. Optical path length = 1 mm. Spectrum C_2 results from the addition of amide (approximately $NH_2^-/S \simeq 1$) to a $S-NH_3$ solution (2.5×10^{-3} M). Absorption spectra a-e result from the gradual addition of sulfur to a sample of ammonia initially saturated with sodium amide.

When more amide is added to the solution described by spectrum C_2 of Figure 8, it is not possible to record an absorption spectrum, for experimental reasons due to the large precipitate in the cell; therefore, it was not possible to record the absorption band of NH_2^- with this experimental procedure. Consequently, it must be emphasized that the absorption spectra of Figures 1 and 2 and spectrum C_2 of Figure 8 have not been obtained for basic solutions. Basic solutions were obtained with a different experimental procedure. A solution of liquid ammonia saturated with sodium amide at room temperature was prepared, and sulfur was gradually introduced in the solution. The absorption spectrum of ammonia saturated with sodium amide is displayed in Figure 8, together with the absorption spectra recorded at equilibrium after gradual addition of sulfur to the solution. It was observed that the first addition of sulfur induces a precipitate; however, the absorption band of amide[22] at 337 nm at room temperature is still observed; it is smaller, which is the indication that a chemical reaction has occurred. The subsequent sulfur addition is followed by the appearance of an absorption band at 285 nm; the absorption band of NH_2^- decreases but could include a contribution of $S_3N_3^-$ around 360-365 nm. After the next sulfur addition, the absorption band of NH_2^- is no longer observed, and two absorption bands appear at 390 (S_2N^-) and 460 nm (S_3N^-) together with a shoulder at 290 nm. These observations are therefore consistent with the results obtained with addition of amide to a $S-NH_3$ solution.

The above experiments suggest that $S_3N_3^-$ is the more oxidized form of sulfur in liquid ammonia. It must be noted that $S_3N_3^-$ is a cyclic compound[23] and is stable in NH_3, in contrast with S_7NH (see above).

Discussion

The main observation in the present work is that addition of amide to a $S-NH_3$ solution makes the oxidized species more oxidized and the reduced species more reduced. This means that disproportionation equilibria are displayed by the addition of amide. This general trend can be tentatively interpreted by

$$S_4N^- \rightleftarrows S_3N^- + S \tag{4}$$

$$3S + 3NH_2^- \rightleftarrows S_3N^- + 2e^- + 2NH_3 \tag{5}$$

$$2S_6^{2-} + 2e^- \rightleftarrows 3S_4^{2-} \tag{6}$$

$$3S_4N^- + 2S_6^{2-} + 3NH_2^- \rightleftarrows 4S_3N^- + 3S_4^{2-} + 2NH_3 \tag{7}$$

where eq 7 results from eq 4-6. Sulfur atoms resulting from eq

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[24] Dubois, P. Thèse de doctorat No. 184, Lille, 1987.

4 are expected to give S_{am}. Equation 4 is based on several experimental observations.[18,24] It was found from the study of the solubilization process of sulfur in ammonia that S_4N^- is formed from S_3N^-. At equilibrium, S_4N^- is the main oxidized species, but a small concentration of S_3N^- is also present. The effect of the first amide additions is to oxidize S_{am} into S_4N^-, and this corresponds to an increase of the S_4N^- concentration (Figure 3). More amide addition oxidizes S_4N^- into S_3N^- and corresponds to the increase of the S_3N^- concentration (Figure 3). This latter step is expected to be described by eq 7. Similar equations can be written for equilibria between S_3N^- and S_2N^- and between S_2N^- and $S_3N_3^-$:

$$2S_3N^- + S_4^{2-} + 3NH_2^- \rightleftarrows 3S_2N^- + 2S_2^{2-} + 2NH_3 \quad (8)$$

$$7S_2N^- + 6NH_2^- \rightleftarrows 3S_3N_3^- + 5S^{2-} + 4NH_3 \quad (9)$$

Equations 7–9 give a qualitative understanding of the main observations of the present work.

An important conclusion from the present work is that, in solutions of sulfur and of heptasulfur imide in ammonia, there is a chemical species (S_{am}) less oxidized than S_4N^-, and this species can only be a species in which sulfur has the zero oxidation state. It is shown below that a large fraction of sulfur in the solution is in this state.

The quantitative determination of the concentration of S_{am} in sulfur–ammonia solutions requires the determination of the concentration of S_4N^-, S_6^{2-} (and S_3^-), and S_3N^- in a solution of known concentration.

(i) The concentration of S_4N^- is obtained in dilute solutions ($<2 \times 10^{-3}$ M) for which Beer's law is obeyed for the 580-nm absorption band. It is also assumed that the correct extinction coefficient of S_4N^- in ammonia is close to 16 000 M^{-1} cm^{-1}. It is then calculated that the concentration of S_4N^- is 22 times smaller than the concentration of the solution. This means that $^4/_{22}$ atoms of sulfur in the solution are involved in S_4N^-.

(ii) The total concentration of S_6^{2-} (including half the concentration of S_3^-) is obtained from the quantitative analysis of the dimerization equilibrium (eq 2). It is found that, for dilute solutions, the concentration of S_6^{2-} is (22 ± 2) times smaller than the concentration of the solution; i.e., about $^6/_{22}$ atoms of sulfur in the solution are in the reduced form of sulfur.

(iii) S_3N^- has been shown to absorb at 460 nm, but its extinction coefficient has not been determined. For the sake of simplicity, its extinction coefficient is assumed to be equal to that of S_4N^-. The variations of absorbance of S_4N^- under amide addition (Figure 3) support this approximation. The absorbance of S_3N^- in a sulfur ammonia solution is estimated by subtracting from the experimental absorbance at 460 nm, the estimated contribution of S_6^{2-} determined with $\epsilon(S_6^{2-}) \simeq 2000$ M^{-1} cm^{-1}.[7] The concentration of S_3N^- is then found to be about 10 times smaller than the concentration of S_4N^-, as was also found in S_7NH–NH_3 solutions.

Finally, the fraction of sulfur atoms of the solution involved in S_4N^-, S_6^{2-}, and S_3N^- is found to be about 50%, and therefore 50% of sulfur is in the S_{am} state. This fraction will even be higher for more concentrated solutions for which Beer's law is not obeyed.[24]

A similar estimation can be made for S_7NH–NH_3 solutions. The determination of the concentration of S_4N^- is done as for sulfur–ammonia solutions. The concentration of S_6^{2-} is neglected. The concentration of S_3N^- is determined with the assumption that the absorbance at 460 nm is due to S_3N^- only. It is found that 50% of the atoms of sulfur of the solution are involved in S_4N^- and about 5% in S_3N^-. Consequently, about 45% of the sulfur atoms in S_7NH–NH_3 solutions are in the S_{am} state.

Conclusion

It is demonstrated in the present work that the chemical species in sulfur–ammonia solutions are modified when the acidity of the solution is decreased. This result shows that, in S–NH_3 solutions, as in S_7NH–NH_3 solutions, several disproportionation equilibria are present and are displaced by the addition of amide to these solutions. The experimental observations after the first amide additions to a sulfur–ammonia solution show the presence of a neutral form of sulfur, S_{am}, with a large relative concentration: this indicates that the redox disproportionation of sulfur in ammonia is a non fully displaced equilibrium. However, in S_7NH–NH_3 solutions, the presence of S_{am} results from the disproportionation of S_7N^-.

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Registry No. S, 7704-34-9; NH_3, 7664-41-7; S_3N^-, 53596-70-6; S_2N^-, 91054-03-4; S_4N^-, 51330-98-4; potassium amide, 17242-52-3; sodium amide, 7782-92-5.