Figure 4. Proposed stepwise mechanism for the dissociation of Cu-$(3,2,3\text{-tet})^{2+}$ in strongly acidic media.

10^4–10^5 under these conditions (Tables II and IV).

The cleavage of the first Cu–N bond of $Cu(cyclam)^{2+}$ is dominantly via the protonation pathway, while the cleavage of the first Cu–N bond of $Cu(3,2,3\text{-tet})^{2+}$ is mainly via the solvation pathway. As pointed out by Read and Margerum,[11] if the donor is unrestricted and able to move easily out of the first coordination sphere, the presence of acid has little effect. However, if the movement of the donor away from the metal ion is hindered in some way, acid can enhance the rate of dissociation. Thus the

Table VI. Rate Constant Ratios Representing the Relative Importance of the Pathways for the Dissociation Reactions of Copper(II) Tetraamine Complexes

ML^{2+}	k_{1H}/k_{1d}, M^{-1}	k_{2H}/k_{2d}, M^{-1}
$Cu(cyclam)^{2+}$	very large	0.096
$Cu(tet\ a)(red)^{2+}$	very large	0.023
$Cu(3,2,3\text{-tet})^{2+}$	0.081	

ratio k_{1H}/k_{1d} increases with the degree of restriction of the coordinate polydentate ligand, preventing the donor atom from moving out of the first coordination sphere. For the cleavage of the first Cu–N bond of $Cu(cyclam)^{2+}$, the restrictions imposed by the ligand cyclization serve to hold the donor in the first coordination sphere, making $Cu(cyclam)^{2+}$ far less susceptible to solvent attack than $Cu(3,2,3\text{-tet})^{2+}$, which has a much smaller restriction of the chelate ring to prevent the donor from moving smoothly out of the first coordination sphere. As a result, the ratio k_{1H}/k_{1d} for $Cu(cyclam)^{2+}$ is much larger than that for $Cu(3,2,3\text{-tet})^{2+}$, as shown in Table VI.

For the dissociation of $Cu(3,2,3\text{-tet})^{2+}$, the cleavage of the first Cu–N bond involves the formation of an intermediate (4 in Figure 4) with the donor group displaced from the normal chelation position. The metal ion becomes solvated, and there is protonation and rotation of the leaving donor group. In this reaction, solvent and acid assist the dissociation by solvation and protonation of the intermediate (4 in Figure 4), and stabilize it relative to the fully coordinated form. Thus, the cleavage of the first Cu–N bond becomes rate determining at high acid concentrations. In contrast, for the reaction of $Cu(cyclam)^{2+}$, after the breaking of the first Cu–N bond, the macrocyclic ligand twists or folds instead of internally rotating the leaving group. Due to the constraints of the cyclic structure of cyclam the uncoordinated amine group and the metal ion are very close to each other, and the solvation of the metal ion and the protonated amine group is sterically hindered to a very large extent, with the result that k_{-1} is larger than k_2. Therefore, the cleavage of the second Cu–N bond becomes rate determining.

Identification and Characterization of Ammonium Polysulfides in Solution in Liquid Ammonia

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

Ammonium polysulfides $((NH_4)_2S_n)$ in ammonia solutions have been identified by using UV–visible spectrophotometry and Raman spectroscopy. They have been prepared by reducing sulfur–ammonia solutions with hydrogen sulfide or hydrazine monohydrochloride. The radical anion S_3^- is always observed in equilibrium with S_6^{2-} for $n > 1$. The existence of S_4^{2-} in solution is shown, and it is found that this species is disproportionated. The results of this work are compared with those obtained for Li_2S_n–NH_3 solutions. For $n \leqslant 4$, the disproportionation of polysulfides is systematically higher for $(NH_4)_2S_n$ solutions than for Li_2S_n solutions. This results from the fact that in the presence of NH_4^+, HS^- is the most reduced species, while S^{2-} is the most reduced in the presence of Li^+. Ammonium polysulfide solutions, with $2 \leqslant n \leqslant 6$, can be prepared with concentrations at least equal to 6 M. It is shown that S_6^{2-} is the least reduced polysulfide in the medium and that the determination of the equilibrium constant between S_6^{2-} and S_3^- is the source of the difficulties which are discussed.

Introduction

The purpose of this paper is to identify the ammonium polysulfides in solution in liquid ammonia. This work also aims at giving a better characterization of chemical species in sulfur–ammonia solutions. It was recently shown[1,2] that sulfur is solu-

bilized in liquid ammonia with a redox disproportionation mechanism. After Chivers and Lau,[3] we have observed[1,2] the oxidized species S_4N^- and the reduced species S_3^- in sulfur–ammonia solutions. It was shown[2] that S_3^- is in equilibrium with

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S_6^{2-}. This led us to propose[1,2] that the solubilization equation for sulfur in ammonia can be written

$$10S + 4NH_3 \rightarrow S_4N^- + S_6^{2-} + 3NH_4^+ \qquad (1)$$

with

$$S_6^{2-} \rightleftharpoons 2S_3^- \qquad (2)$$
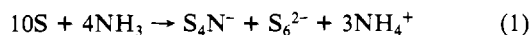
Later, it was observed by Raman spectroscopy, under resonance conditions, for temperatures below $-40\ ^\circ C$, that these solutions also contain another oxidized form of sulfur, S_3N^-. This means that the above equation does not completely describe the sulfur–ammonia solutions. In order to have a better identification of the reduced species of sulfur in ammonia solutions, first the lithium polysulfides in ammonia solutions have been studied.[4] Now the ammonium polysulfides in ammonia solutions are analyzed, because it was suspected that the disproportionation of polysulfides could be modified by the acidity. A simple test is to compare solutions of Li_2S_n and $(NH_4)_2S_n$. This is the main purpose of this paper.
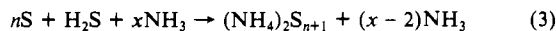
It is thought that this is the first spectroscopic identification of ammonium polysulfides in ammonia. Some old papers[5-7] are related to the synthesis of ammonium polysulfides. More recently, Lautenbach[8] has studied ammonium polysulfides in ammonia solutions, using liquid chromatography, in order to understand the sulfur–ammonia solutions.

In the present work, $(NH_4)_2S_n–NH_3$ solutions have been prepared with well-defined values of the stoichiometry n and the concentration. The absorption and the Raman spectra of these solutions have been recorded versus temperature, for various values of n and the concentration. The identification of polysulfides in solution is based on some species that are considered as well-known. In particular, the radical anion S_3^- has been well identified in solution;[9,10] it is characterized by an absorption band located at 610 nm, and its Raman spectrum displays[9] an intense line at 535 cm^{-1}, corresponding to a symmetrical stretching vibration (ν_1), and a smaller line at 232 cm^{-1}. Resonance Raman spectra are easily obtained[11] for S_3^-. It was found in several media[12,15] that S_3^- is in equilibrium with S_6^{2-}. The oxidized species, S_4N^-, was identified by Chivers et al.[16] and is characterized by an absorption band at 580 nm and by Raman lines at 570, 590, 710, and 898 cm^{-1}. It was shown that S_4N^-, in liquid ammonia, is photosensitive.[1,2]

The study of polysulfides in solution is made more difficult by their possible disproportionation. The disproportionation of a given polysulfide produces a less reduced and a more reduced form of sulfur. In the study of lithium polysulfides in solution in liquid ammonia,[4] it was found that S_4^{2-} and S_6^{2-} are partly disproportionated. It will be shown in the present work that the acidic character of ammonium polysulfide solutions influences the disproportionation.

Experimental Section

The ammonium polysulfides in ammonia solutions have been prepared by reduction of sulfur–ammonia solutions by hydrogen sulfide

$$nS + H_2S + xNH_3 \rightarrow (NH_4)_2S_{n+1} + (x-2)NH_3 \qquad (3)$$

It was also shown, during this work, that hydrazine monohydrochloride

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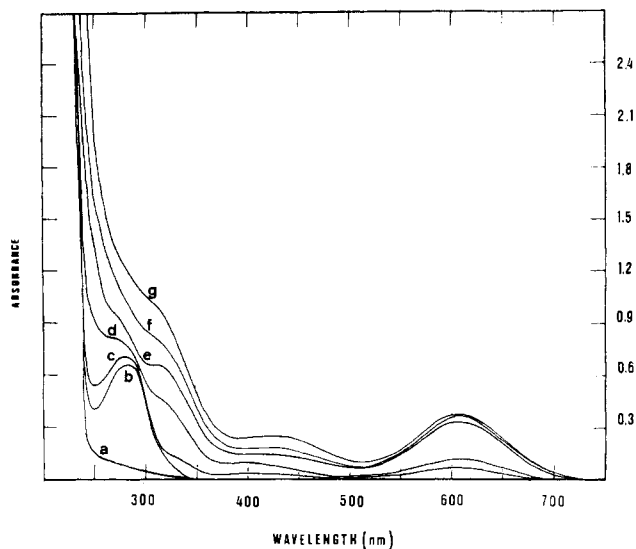(16) Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1980**, *102*, 5773.

Figure 1. Absorption spectra at 293 K: (a) pure NH_3; (b) H_2S in NH_3 (9.7×10^{-4} M); (c) $(NH_4)_2S_2$ (d) $(NH_4)_2S_4$; (e) $(NH_4)_2S_6$; (f) $(NH_4)_2S_8$; (g) $(NH_4)_2S_{10}$. Optical path length = 0.1 cm. Solutions c–g have the same concentration, 9.7×10^{-4} M.
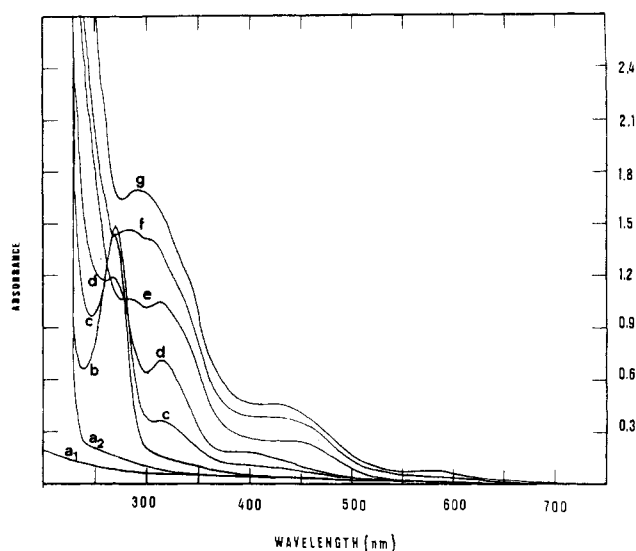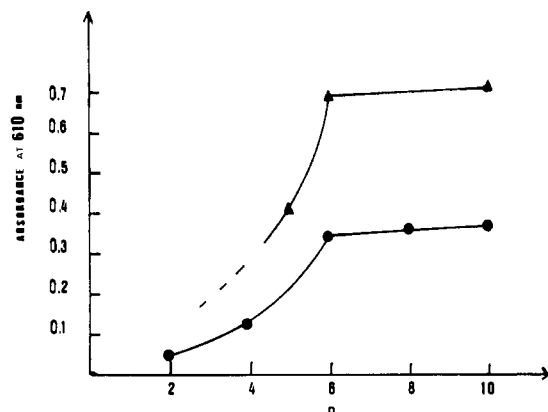

Figure 2. Absorption spectra at 200 K: (a_1) empty cryostat; (a_2) pure ammonia; (b) H_2S in NH_3 (1.15×10^{-3} M); (c) $(NH_4)_2S_2$; (d) $(NH_4)_2S_4$; (e) $(NH_4)_2S_6$; (f) $(NH_4)_2S_8$; (g) $(NH_4)_2S_{10}$. Optical path length = 0.1 cm. Solutions c–g have the same concentration, 1.15×10^{-3} M.

can be used to reduce sulfur–ammonia solutions, and ammonium polysulfides in ammonia are then prepared according to

$$nS + 2N_2H_4, HCl + xNH_3 \rightarrow$$
$$(NH_4)_2S_n + N_2 + 2NH_4Cl + (x-2)NH_3 \qquad (4)$$
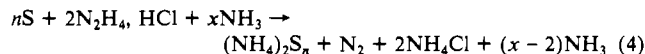
All the experimental results given in the present paper have been obtained with solutions prepared according to eq 3. For the preparation of the solutions, sulfur (Fluka, >99.999%) was used without further purification. Hydrogen sulfide (Air liquide, 99.7%) and ammonia (Air liquide, >99.96%) have been controlled volumetrically and condensed on sulfur at the temperature of liquid nitrogen.

Ammonia was dried on potassium. It must be emphasized that there is no decomposition in the preparation of these solutions, because alkali metals are not the reducing agent. The volumetric determination of hydrogen sulfide allows an accurate determination of the stoichiometry n (Δn smaller than 0.1) and the preparation of rather dilute solutions ($10^{-3}–10^{-4}$ M).

After ammonia and hydrogen sulfide had been condensed on sulfur, the sample was sealed off and kept for at least 3 days either at room temperature or at 0 °C. This was found necessary in order to get completion of the reaction described by eq 3 or 4.

The absorption and Raman spectra have been recorded under the same conditions as previously described.[2,4] The Raman experiments have

Figure 3. Absorbance at 610 nm (S_3^-), at 293 K, versus n [in $(NH_4)_2S_n$]. Optical path length = 0.1 cm. Experimental values in curve A_1 (●) are for 9.7×10^{-4} M solutions. Experimental values in curve B (▲) are for 4.3×10^{-3} M solutions.

been recorded with Raman spectrometers of the Laboratoire de Spectroscopie Infrarouge et Raman (LASIR) de l'Université de Lille 1.

It was found that the $(NH_4)_2S_n$–NH_3 solutions can be prepared directly (without evaporation of ammonia) with a concentration at least equal to 6 M, for $2 \leqslant n \leqslant 6$.

Results

I. Spectrophotometric Observation of S_3^- in $(NH_4)_2S_n$–NH_3 Solutions.
The absorption spectra recorded at room temperature for $(NH_4)_2S_n$–NH_3 solutions, with n = 2, 4, 6, 8, and 10, and for a H_2S–NH_3 solution are given in Figure 1. The absorption spectra recorded at 200 K for the same solutions are given in Figure 2. It is observed that the H_2S–NH_3 solution does not absorb at 610 nm, while the $(NH_4)_2S_n$–NH_3 solutions display, at room temperature, an absorption band at 610 nm, which disappears at 200 K. This band is assigned to the radical anion S_3^-. This interpretation is confirmed by the Raman spectra obtained for the same solutions, but for higher concentrations. In fact, other experiments have shown that S_3^- is observed for $n > 1$, i.e. when sulfur traces are introduced in $H_2S + xNH_3$ (eq 3).

The variations of the absorbance at 610 nm, $A(610)$, recorded at room temperature for $(NH_4)_2S_n$–NH_3 solutions, are plotted versus n in Figure 3. The slope of this curve changes (Figure 3) at n = 6. This happens because S_6^{2-} is the least reduced ammonium polysulfide (vide infra), and the solutions with $n >$ 6 must be viewed as solutions of sulfur and ammonium hexasulfide in liquid ammonia. This is confirmed by the observation (Figure 2), at 200 K, for $(NH_4)_2S_{10}$–NH_3 solution of the absorption band of S_4N^- at 580 nm.

The absorption spectra of a $(NH_4)_2S_6$ solution (10^{-3} M), at various temperatures are given in Figure 4. It is seen on this figure that the absorbance at 610 nm decreases as the temperature is lowered. The absorbance of the absorption band located between 400 and 450 nm increases simultaneously. Similar variations are displayed on the absorption spectra of $(NH_4)_2S_2$, $(NH_4)_2S_4$, and $(NH_4)_2S_{10}$ solutions. For these solutions, the absorbance at 610 nm decreases as the temperature is lowered and gives evidence of S_3^-.

II. Characterization of S_6^{2-}. a. Visible Spectra.
After the observation of S_3^- in $(NH_4)_2S_n$–NH_3 solutions, it can be assumed that S_6^{2-} is in equilibrium with S_3^-, as has been shown in several studies.[2,4,13–15] The higher relative concentration of S_6^{2-} and the best conditions for its observation are met in $(NH_4)_2S_6$–NH_3 solutions. In Figure 4 the absorption spectra of a $(NH_4)_2S_6$ solution (10^{-3} M) recorded at various temperatures are given, and it is seen that when the temperature decreases, the absorption band located at 610 nm decreases, while the absorbance between about 250 and 500 nm increases. In this wavelength range, a poorly shaped absorption band is observed between 400 and 450 nm; a rather intense absorption band is observed at 315 nm, while shoulders are seen at about 285 and 330 nm.

The absorption spectra of $(NH_4)_2S_6$ and Li_2S_6 solutions, at 200 and 293 K are compared in Figure 5. It is found that the
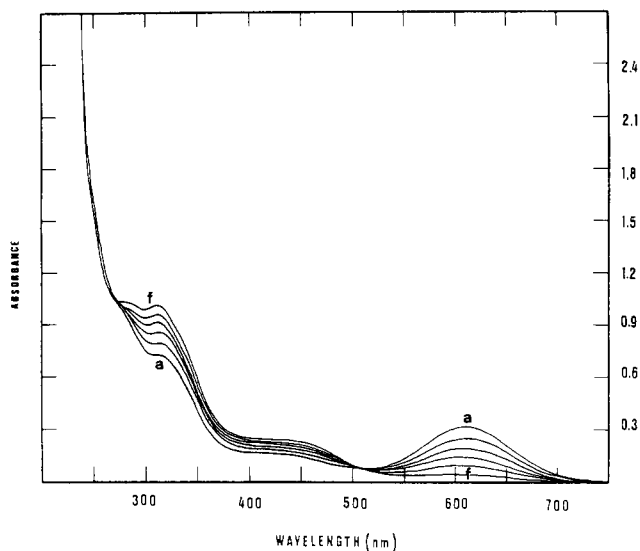

Figure 4. Absorption spectra of a $(NH_4)_2S_6$ solution (9.7×10^{-4} M at 293 K; optical path length = 0.1 cm) for various temperatures: (a) 280.6 K; (b) 270.5 K; (c) 260.4 K; (d) 251.5 K; (e) 239 K; (f) 225 K.
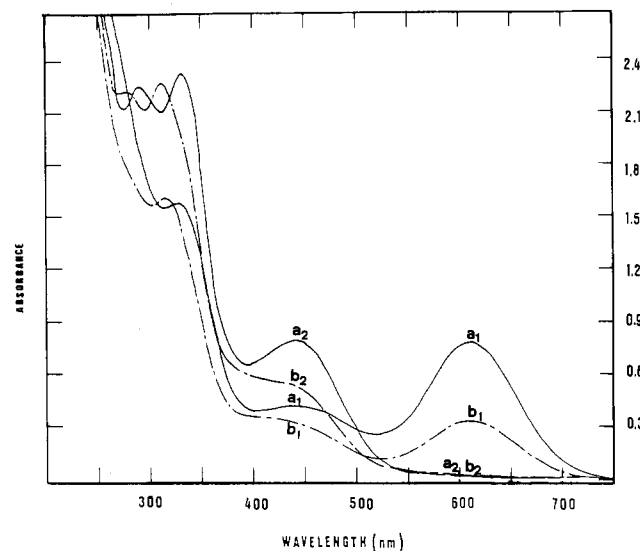

Figure 5. Absorption spectra of Li_2S_6 and $(NH_4)_2S_6$ solutions of the same concentration (4.3×10^{-3} M): (a_1) Li_2S_6 at 293 K; (a_2) Li_2S_6 at 200 K; (b_1) $(NH_4)_2S_6$ at 293 K; (b_2) $(NH_4)_2S_6$ at 200 K.
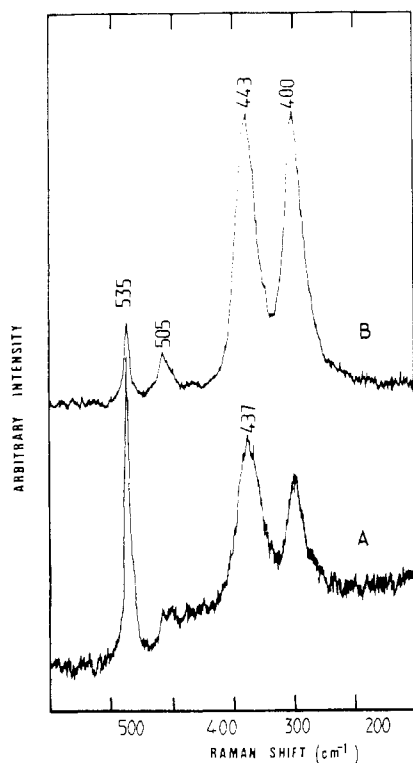
absorbances of a $(NH_4)_2S_6$ solution at 610 nm and around 450 nm are smaller than the corresponding absorbances of a Li_2S_6 solution of the same concentration. These differences are related to difficulties arising in the determination of the equilibrium constant between S_6^{2-} and S_3^- (vide infra).

Figure 5 shows that the band at 450 nm assigned to S_6^{2-} in Li_2S_6 is well-defined; for $(NH_4)_2S_6$, the corresponding absorption band is not well-defined. This suggests that the absorbance between 400 and 450 nm could be due to more than one species and could result from a disproportionation of S_6^{2-}. The species S_6^{2-} was found to be disproportionated in Li_2S_6, because S_4N^- was observed by Raman spectroscopy in this solution.[4] The species S_4N^- was not observed in $(NH_4)_2S_6$ solutions, but this is not a proof that S_6^{2-} is not disproportionated, because the disproportionation (and the disproportionation products) of S_6^{2-} could depend on the acidity of the solution. It will therefore be considered that the absorption band of S_6^{2-} in $(NH_4)_2S_6$ solutions is located in the visible range at 450 nm and that the absorbance between 400 and 450 nm is an indication of the disproportionation of S_6^{2-}. Other independent evidence of a possible disproportionation of S_6^{2-} will be given below.

Figure 5 also shows large differences of the absorption spectra of $(NH_4)_2S_6$ and Li_2S_6 solutions of the same concentration, in the UV range. Surprisingly, the absorbance in the UV range at a
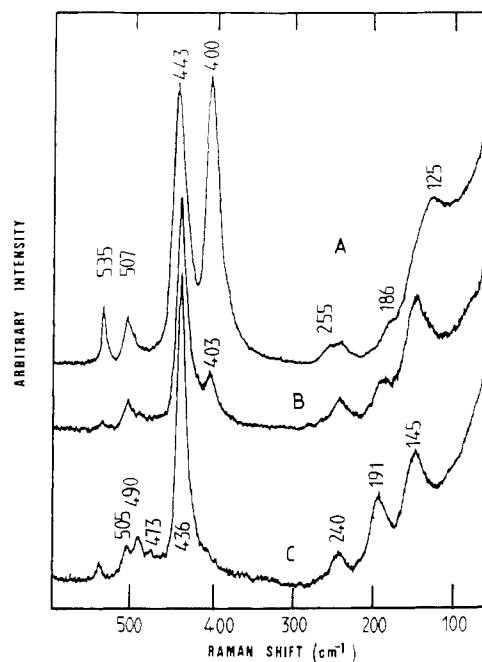
Table I. Raman Lines (cm⁻¹) of M_2S_4 Solids and of M_2S_4 Solutions

	Na₂S₄[28] solid	K₂S₄[29] solid	Cs₂S₄[30] solid	Na₂S₄[31] aq	Na₂S₄ in alcohol[32]	Li₂S₄ in NH₃ at 293 K[4]	Li₂S₄ in NH₃ at 100 K[4]	Na₂S₄ in NH₃ at 293 K[4]	(NH₄)₂S₄ in NH₃ at 213 K[a]
1					535 m ($S_3^{\bullet-}$)	535 w ($S_3^{\bullet-}$)		535 vs ($S_3^{\bullet-}$)	535 w ($S_3^{\bullet-}$)
2							494 w		505 w (S_6^{2-})
3	483 s	485 s	494 ms	484 ms	491 m	490 m	488 m	485 m	490 w
4	469 ms	478 sh	483 ms		475 w	472 m	476 m	469 m	471 w
5	445 vs	434 s	433 s	446 s	450 vvw	430 vs	439 vs	437 vs	437 vs
6			422 s 250 m	410 ms	413 m				400 sh (S_6^{2-})
7	241 w	266 m	240 w	256 w	247 mw	236 vw	235 w		240 m
8	212 m	220 m	209 s 195 s	194 w	195 mw	188 vs	195 vs	191 vs	192 m
9	98 ms		140 m	144 vw	140 w		117 w		145 m

[a] Present work.

Figure 6. Raman spectra of $(NH_4)_2S_6$ solutions for two concentrations, recorded at 200 K, with the 647.1-nm excitation line (backscattering experiment): (A) 3×10^{-2} M; (B) 10^{-1} M.

Figure 7. Raman spectra of various $(NH_4)_2S_n$ solutions of same concentration (1 M), recorded at 200 K, with the 647.1-nm excitation line (backscattering experiment): (A) $(NH_4)_2S_6$; (B) $(NH_4)_2S_5$; (C) $(NH_4)_2S_4$.

given temperature is approximately the same. However the position of the bands is different. The origin of the differences in the UV range is not understood, but could also be related to the disproportionation of S_6^{2-}.

b. Raman Spectra. As was mentioned for the absorption spectrum, the Raman spectrum of S_6^{2-} is observed under the best conditions for $(NH_4)_2S_6$ solutions. The Raman spectra of $(NH_4)_2S_6$ solutions first show that the relative intensities of the two most intense lines, located at about 400 and 443 cm⁻¹, are concentration dependent (Figure 6). The intensity of the line at 400 cm⁻¹ increases faster with concentration than the intensity of the line at about 443 cm⁻¹. Moreover, the position of the latter band is slightly concentration dependent: it is located at 437 cm⁻¹ for a 3×10^{-2} M solution and at 443 cm⁻¹ for a 3×10^{-1} M solution. It will be shown below that S_4^{2-} exists in ammonium polysulfide solutions and has an intense Raman line at 437 cm⁻¹. This is also an indication that S_6^{2-} is disproportionated. The experimental spectra have shown that for concentrations above 3×10^{-1} M, the mentioned lines have the same intensity. This is compatible with the possible disproportionation for S_6^{2-}, because the influence of the disproportionation is expected to be larger for rather dilute solutions. In Figure 6 a weaker line is observed at 507 cm⁻¹. Another line is observed at 535 cm⁻¹ and assigned to S_3^-. The line is even observed at 200 K in Raman spectroscopy

because the temperature of the solution at the impact of the laser beam is likely higher than 200 K and because, with the 647.1-nm excitation line, S_3^- is observed under resonance conditions. It was observed that the intensity of this line, recorded for an average temperature of the sample of 200 K and compared to the intensity of the ν_1 line of NH_3 at 3210 cm⁻¹, does not depend upon the concentration and the stoichiometry of the solution. This suggests that the observation of S_3^- at 200 K corresponds to a small concentration of this species, observed under resonance conditions. The spectrum of a $(NH_4)_2S_6$ solution given in Figure 7 also displays three low-frequency lines.

The Raman spectra obtained for $(NH_4)_2S_6$ solutions can be compared to those of Li_2S_6 solutions.[4] It must be noted that the relative intensities of the two most intense lines of Li_2S_6 solutions, located at 400 and about 440 cm⁻¹ are concentration independent, the line at 400 cm⁻¹ being always slightly more intense than the line at about 440 cm⁻¹. This suggests that the disproportionation of S_6^{2-} is smaller in Li_2S_6 than in $(NH_4)_2S_6$ solutions.

III. Existence of S_4^{2-} in Ammonium Polysulfide Solutions.
a. Observation and Characterization of S_4^{2-} by Raman Spectroscopy. The S_4^{2-} ion is evidenced by Raman spectroscopy because the spectra of $(NH_4)_2S_4$–NH_3 solutions are similar to those of solid alkali-metal tetrasulfides, M_2S_4. The S_4^{2-} ion was similarly identified in Li_2S_4–NH_3 solutions. The Raman spectra recorded for a $(NH_4)_2S_4$ solution with the 647.1- and 514.5-nm excitation lines are given in Figures 7 and 8, respectively. They are compared to the spectra recorded for $(NH_4)_2S_5$ and $(NH_4)_2S_6$ solutions.

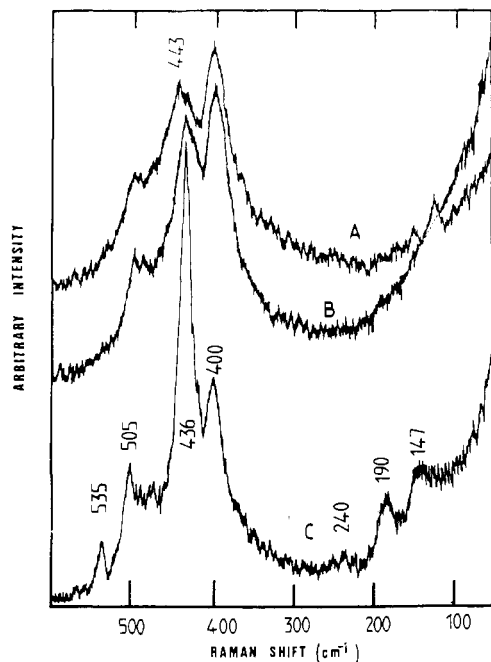**Figure 8.** Raman spectra of various $(NH_4)_2S_n$ solutions of same concentration (1 M), recorded at 200 K, with the 514.5-nm excitation line (backscattering experiment): (A) $(NH_4)_2S_6$; (B) $(NH_4)_2S_5$; (C) $(NH_4)_2S_4$.

The positions of the lines observed for $(NH_4)_2S_4$ solutions are compared, in Table I, with those observed for alkali-metal tetrasulfides in the solid state or in solution. These comparisons show the existence of S_4^{2-} as an ammonium polysulfide.

The Raman spectra of $(NH_4)_2S_4$ solutions (Figures 7 and 8) and their absorption spectra (Figures 1 and 2) show the presence of S_3^-, which proves the disproportionation of S_4^{2-}. However, it was found that the Raman spectra of $(NH_4)_2S_4$ solutions are concentration independent.

The comparison of Figures 7 and 8 shows that the Raman spectra of $(NH_4)_2S_4$ solutions depend on the excitation line. The 514.5-nm excitation line makes possible the observation of a line at 400 cm^{-1}, near an intense line at 437 cm^{-1} due to S_4^{2-}. The line at 505 cm^{-1} is more intense than that with the 647.1-nm excitation line. The line at 400 cm^{-1} is assigned to S_6^{2-}. The absorption band of S_6^{2-} is located near 450 nm, and the S_6^{2-} species is therefore under resonance Raman conditions for the 514.5-nm excitation line, but it is not for the 647.1-nm excitation line. The Raman spectra of $(NH_4)_2S_4$ solutions have a line at about 190 cm^{-1}, which has approximately the same relative intensity as the corresponding line observed for the solids Na_2S_4[28] and K_2S_4.[29] The

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corresponding line has a much larger relative intensity in Li_2S_4 solutions. The variations of the intensity of this line are not understood but could be related to small structural changes of the S_4^{2-} species associated with the change of the cation.

b. UV–Visible Characterization of S_4^{2-}. The absorption spectrum of a $(NH_4)_2S_4$ solution (10^{-3} M) (Figures 1 and 2) shows four bands located at 610 nm, and at about 390, 315, and 270 nm. The first band is assigned to S_3^-. The three other bands increase when the first decreases, i.e. when the temperature decreases. The observation of S_3^- is a consequence of the disproportionation of S_4^{2-}. The absorbance measured at 610 nm at room temperature allows the determination of the concentration of S_3^- in the solution, assuming that $\epsilon(S_3^-) = 4800 \pm 300$ M^{-1} cm^{-1}. It is found that, for the 10^{-3} M solution, the concentration of S_3^- is 2.6×10^{-4} M. This is an indication of the degree of disproportionation of S_4^{2-}. The disproportionation of S_4^{2-} produces one (or more) species less reduced than S_4^{2-}, which can be S_5^{2-} and/or S_6^{2-}. The hexasulfide S_6^{2-} has been characterized by an absorption band located near 450 nm. This band is not observed at low temperatures (200 K); however, a Raman line at 400 cm^{-1} was observed at 200 K for a $(NH_4)_2S_4$ solution under resonance conditions. It must be emphasized that the absorption band located at 390 nm increases without shift or deformation when the temperature decreases. Therefore, it is considered that this band is related to the absorbance of S_4^{2-}. The determination of the extinction coefficient $\epsilon(S_4^{2-})$ will be analyzed in the Discussion.

IV. Study of the $(NH_4)_2S_n$–NH_3 Solutions with $n < 4$. The $(NH_4)_2S_n$–NH_3 solutions with $n < 4$ display rather unexpected results. It will be explained in the Discussion that these results are related to the acidity of the solutions. These solutions are deeply colored, and their color is temperature dependent. They can be highly concentrated (at least 6 M). These crude experimental observations are very different from what was found in the corresponding lithium polysulfides solutions with $n < 4$.

A crucial point in the analysis of these solutions is the identification of the most reduced form of sulfur. In ammonia, this problem has been studied only by Nelson and Lagowski.[18,19] They have recorded the absorption spectra of ammonia solutions of hydrogen sulfide in the concentration range from 1×10^{-4} to 50×10^{-4} M. These solutions exhibit only one band at 271 nm at 196 K. The position of the band maximum is temperature dependent. The apparent extinction coefficient of the band is nonlinear versus concentration above 1×10^{-3} M, and the addition of alkali-metal amide results in an increase of the intensity of the band. The solubilization of H_2S in NH_3 leads to the following chemical equilibra:

$$H_2S + NH_3 \rightleftharpoons HS^- + NH_4^+ \qquad (5)$$

$$HS^- + NH_3 \rightleftharpoons S^{2-} + NH_4^+ \qquad (6)$$
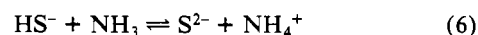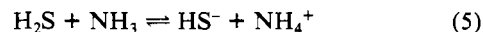
Nelson and Lagowski[19] conclude from their experimental results that the band at 271 nm arises from the presence of sulfide ions rather than hydrosulfide ions. However Nelson and Lagowski suggest that the sulfide ion is probably hydrogen bonded to an ammonium ion, i.e. $S^{2-}\cdots HNH_3^+$, and that this species probably would not be distinguishable from a hydrosulfide ion hydrogen bonded to ammonia, $SH^-\cdots NH_3$. This interpretation is associated with their observation of a single band at 271 nm.

The same problem has been analyzed, in aqueous media, by Giggenbach.[20] His analysis is based on UV spectra recorded for very concentrated NaOH solutions (that did not contain any dissolved oxygen). Giggenbach found near 250 nm an absorbance assigned to S^{2-}; this appeared as a shoulder on the more intense HS^- absorbance located at approximately 230 nm. Therefore, it would appear that the absorption bands of HS^- and S^{2-} are distinguished in aqueous media but not in ammonia. This problem, the so-called second dissociation constant for H_2S, has also been analyzed from the observation of the Raman line of HS^- at 2570 cm^{-1} by Meyer et al.[21]

(32) Eysel, H. H.; Weighardt, G.; Kleinschmager, H.; Weddingen, G. *Z. Naturforsch., B: Inorg. Chem., Org. Chem.* **1976**, *31B*, 415.

We now turn to the description of our experimental data. The Raman spectra obtained for $(NH_4)_2S_n-NH_3$ solutions (1 M or more) always display the band due to HS^- for $n \leqslant 4$, and these spectra are identical with the spectrum of a $(NH_4)_2S_4$ solution, except for the intensity of the lines. The intensity of the S_4^{2-} lines decreases when n decreases, while the intensity of the HS^- line increases. Therefore the Raman spectra for $n \leqslant 4$ indicate that the same chemical species are present in these solutions, but with relative concentrations depending upon n. These results show that S_2^{2-}, S_3^{2-}, and S_4^{2-} are at least partly disproportionated.

The absorption spectra of H_2S-NH_3 (10^{-3} M) and $(NH_4)_2S_2-NH_3$(10^{-3} M) solutions are compared in Figures 1 and 2. They display an absorption band at 268 nm, with approximately the same intensity. From the analysis of Nelson and Lagowski and because the concentration of these solutions is low, the band at 268 nm should instead be assigned to S^{2-}. However the absorbance of $(NH_4)_2S_2-NH_3$ is significantly higher than that of H_2S-NH_3 around 250 nm. This suggests that S_2^{2-} is not completely disproportionated and could absorb around 250 nm, as found in $Li_2S_2-NH_3$ solutions. The disproportionation of S_2^{2-} can be written

$$3S_2^{2-} \rightleftharpoons 2S^{2-} + S_4^{2-} \qquad (7)$$
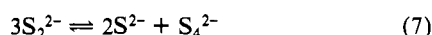
with the sulfide ion in equilibrium with the hydrosulfide ion following eq 6, which explains the observation of HS^-. For concentrated solutions, the hydrosulfide ion will be predominant over the sulfide ion, so that the disproportionation could be written

$$3S_2^{2-} + 2NH_4^+ \rightleftharpoons 2HS^- + S_4^{2-} + 2NH_3 \qquad (8)$$
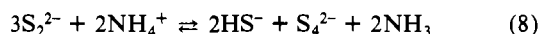
An absorption band at 268 nm can still be observed (Figure 2) for $n = 4$ but is not detected for higher values of n. It must be noted that eq 7 implies that S_3^{2-} does not exist (i.e. is fully disproportionated) in solution.

It will now be shown that the differences observed between lithium and ammonium polysulfide solutions are associated with the acidity of the ammonium solutions. This will be approached on a rather general basis.
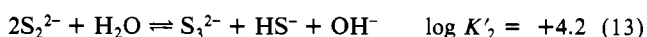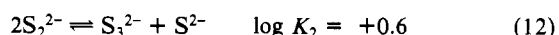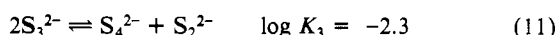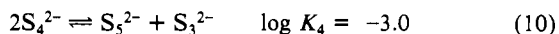
Discussion

I. Sulfides and Polysulfides in Ammonia and in Water: a Semithermodynamic Approach. The value of the equilibrium constant for the second dissociation constant of H_2S in water

$$HS^-_{aq} \rightleftharpoons H^+_{aq} + S^{2-}_{aq} \qquad (9)$$
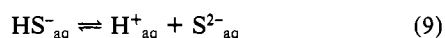
has been subject to much controversy. Recent works by Meyers[22] and Licht and Manassen[23] confirm the results of Giggenbach[20] and Meyer et al.[21] A value of $pK_a = 17.6 \pm 0.3$ for eq 9 can now be considered as reliable.[23] Consequently, the concentration of S^{2-} ions can always be neglected in water with respect to HS^-. The problem is expected to be rather different in ammonia, a solvent much more basic than water. Therefore two questions can be analyzed: Is there, in ammonia, a range of pH where HS^- is replaced by S^{2-}? How do the polysulfides disproportionate into their nearest neighbors, in water an in ammonia? These problems will be approached by the examination of the following points: (a) disproportionation of polysulfides in water; (b) transfer of ions from water to ammonia; (c) disproportionation of polysulfides in ammonia; (d) comparison of pH scales in water and in ammonia. This will lead to the conclusion that, in ammonia, the disproportionation should be pH independent in neutral or basic media, while a pH dependence is expected in acidic media.

a. Disproportionation of Polysulfides in Water. The data of Licht and Manassen[24] can be used to find the constants log K_x of the following disproportionation equilibria in water:

$$2S_4^{2-} \rightleftharpoons S_5^{2-} + S_3^{2-} \qquad \log K_4 = -3.0 \qquad (10)$$

$$2S_3^{2-} \rightleftharpoons S_4^{2-} + S_2^{2-} \qquad \log K_3 = -2.3 \qquad (11)$$

$$2S_2^{2-} \rightleftharpoons S_3^{2-} + S^{2-} \qquad \log K_2 = +0.6 \qquad (12)$$

$$2S_2^{2-} + H_2O \rightleftharpoons S_3^{2-} + HS^- + OH^- \qquad \log K'_2 = +4.2 \qquad (13)$$

These values of log K_x are not compatible with the older thermodynamic data for S_x^{2-} ions,[25] which will not be used. The value of log K'_2 (eq 13) show a higher disproportionation of S_2^{2-} in water, due to its hydrolysis. This is a new reason for asking the first question: Is there a range of pH where the ammonolysis is avoided, HS^- being replaced by S^{2-}?

b. Transfer of Ions from Water to Ammonia. Jolly[26] has used extrathermodynamic assumptions to give a relation between the standard free enthalpies when an ion of charge $\pm n$ is transferred from water to ammonia:[27]

$$\Delta G_f^\circ{}_{am} - \Delta G_f^\circ{}_{aq} = \pm 16n + 2 \text{ kcal mol}^{-1} \qquad (14)$$

This neglects any specific interaction between individual ions and the solvents, with a huge exception for the proton.

c. Disproportionation in Ammonia. Reactions 10, 11, and 12 conserve the numbers of ions and their charges. In such a case, when the ΔG°'s of the reactions are computed, both terms on the right of (14) cancel out. This conclusion is independent of the numerical values in (14) and implies only that the various polysulfides do not interact specifically with either solvent.

The equilibrium constants for (10), (11), and (12) are then identical in ammonia and in water. Obviously the situation is different for (13) to which we will come back below.

d. pK_a in Ammonia and Comparison of pH Scales. In ammonia, (9) becomes

$$HS^- + NH_3 \rightleftharpoons S^{2-} + NH_4^+ \qquad (15)$$
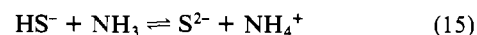
Then, as shown by Jolly,[26] (14) yields

$$pK_a \text{ in ammonia (eq 15)} = pK_a \text{ in water (eq 9)} - 11.8 \qquad (16)$$

Since pK_a in water is equal to 17.6, it results that pK_a in ammonia is equal to 5.8. This is valid for the transfer of any couple AH/A^- from water to ammonia, but it implies all the assumptions made above and the numerical values of (14). The uncertainty in the value of pK_a in ammonia is probably on the order of ± 1.

The following conclusion can therefore be given: whereas the ratio S^{2-}/HS^- is always very small in water, it becomes large in ammonia when the pH is larger than 5.8. Since neutrality in ammonia[26] corresponds to pH $\simeq 16$ at $-33 \,^\circ C$, S^{2-} is the main species in all neutral and basic solutions. Furthermore, the general relation

$$pH = pK_a + \log (\text{base}/\text{acid}) \qquad (17)$$

applied in ammonia as in water for identical values of log (base/acid) shows that (16) can also be written as

$$pH \text{ in ammonia} = pH \text{ in water} - 11.8 \qquad (18)$$

e. Hydrolysis and Ammonolysis of S_2^{2-}. In ammonia, (13) becomes

$$2S_2^{2-} + NH_4^+ \rightleftharpoons S_3^{2-} + HS^- + NH_3 \qquad (19)$$
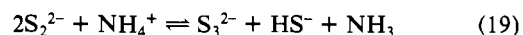
The couple NH_4^+/NH_3 is substituted for H_2O/OH^-, because, according to (16), basic solutions in water correspond to acidic solutions in ammonia.

Figure 9 compares the degrees of disproportionation of the polysulfides in ammonia by using log K_x for (10), (11), and (12) and the quantity $A = \log ([S_3^{2-}][HS^-][S_2^{2-}]^{-2})$ for (19). A is pH dependent and has to be used for all values of pH in water and for pH <5.8 in ammonia.

The main result is that no pH dependence is expected in neutral or basic ammonia solutions. A large dependence is expected in acidic solutions where HS^- is produced instead of S^{2-}. This explains the large differences observed between lithium and ammonium polysulfides solutions for $n \leqslant 4$.

Experiments and calculations similar to those of Giggenbach[20] and Licht et al.[24] in basic solutions could be done in acidic ammonia solutions by varying the NH_4^+ concentration.

II. Dissociation Equilibrium between S_6^{2-} and S_3^-. The equilibrium between S_6^{2-} and S_3^- is displayed by the absorption spectra of Figure 4. We now turn to the determination of the corresponding equilibrium constant. It will be shown that only an apparent equilibrium constant can be determined. The same method[4] as for Li_2S_6 solutions is used. This method assumes that

Table II. Dissociation Equilibrium between S_6^{2-} and S_3^-

	$(NH_4)_2S_6$			Li_2S_6[4]
concn at 200 K, 10^{-3} M	1.24	5.12	11.9	5.12
concn of S_6^{2-} at 200 K, 10^{-3} M	1.24	5.12	11.9	5.12
$\epsilon(S_6^{2-})$ at 450 nm, M^{-1} cm^{-1}	1840 ± 300	1750 ± 300	1800 ± 300	2300 ± 100
$\epsilon(S_3^-)$ at 610 nm, M^{-1} cm^{-1}	4800 ± 300	4500 ± 300	4800 ± 300	4800 ± 300
K at 273 K, 10^{-4} M	4.12 ± 0.6	2.58 ± 0.4	1.63 ± 0.25	7.8 ± 1.2
ΔH, kJ mol^{-1}	44.6	44.6	44.4	47.3
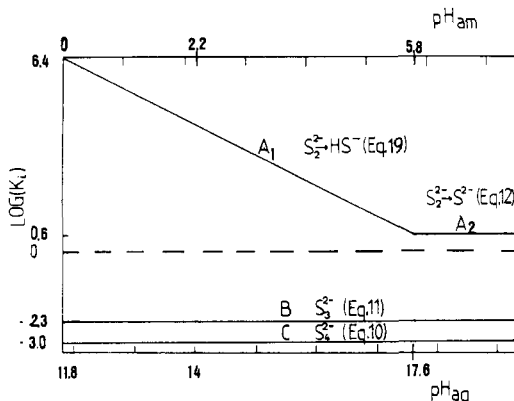
Figure 9. Disproportionations of S_n^{2-}, versus pH in ammonia and in water (A_1) log $([S_3^{2-}][HS^-][S_2^{2-}]^{-2})$; (A_2) log $([S_3^{2-}][S^{2-}][S_2^{2-}]^{-2})$ (B) log $([S_4^{2-}][S_2^{2-}][S_3^{2-}]^{-2})$; (C) log $([S_5^{2-}][S_3^{2-}][S_4^{2-}]^{-2})$.

the absorbance at 450 nm is due only to S_6^{2-}. With this assumption, the absorbances at 450 nm, $A(450)$ and at 610 nm, $A(610)$, are related to the extinction coefficients of S_6^{2-} and S_3^- by

$$A(450) = -\frac{\epsilon(S_6^{2-})}{2\epsilon(S_3^-)}A(610) + C_0d[\epsilon(S_6^{2-})] \qquad (20)$$

where d is the optical path length and C_0 is the total concentration of S_6^{2-} when S_3^- has completely dimerized into S_6^{2-}. A linear relation between $A(450)$ and $A(610)$ is indeed obtained, when the experimental absorbances are corrected for the thermal variations of the density of the solutions. It is assumed that C_0 is equal to the analytical concentration of the solution at 200 K. The extinction coefficients $\epsilon(S_6^{2-})$ and $\epsilon(S_3^-)$ are deduced from eq 20. The apparent equilibrium constant K_D of eq 2 is then calculated from

$$K_D = (S_3^-)^2(S_6^{2-})^{-1} \qquad (21)$$

For several $(NH_4)_2S_6$ solutions of various concentration between about 10^{-3} and 10^{-2} M, log K_D is linear versus $1/T$, with a constant slope. It is also found that K_D decreases when the concentration of the $(NH_4)_2S_6$ solution increases. These results are summarized in Table II. The decrease of K_D when the concentration of the $(NH_4)_2S_6$ solutions increases is empirically correlated with the acidity of the medium. This is a rather large effect (Table II): when the concentration increases by a factor of 10, K_D is reduced by a factor equal to about 2.5.

These results are compared (Table II) to those obtained[4] for Li_2S_6 solutions, for which it was found that the equilibrium constant K_D is concentration independent between 5×10^{-3} and 1.8×10^{-2} M, with a value of 4.3×10^{-3} M at 298 K.

The present results have been directly confirmed by the observation of the influence of the concentration of NH_4Cl introduced in a Li_2S_6 solution (Figure 10). It was found, when the concentration of NH_4Cl increases progressively, that the concentration of S_3^- decreases, while nonmonotonic changes are observed between 300 and 500 nm. The variations of the absorbance around 450 nm are obviously not simply related to the decrease of the absorbance of S_3^- at 610 nm, and this observation shows that NH_4Cl does not simply shift the equilbrium between S_6^{2-} and S_3^- and that S_6^{2-} is likely involved in a disproportionation equilibrium which is NH_4^+ dependent. Consequently, the concentration C_0 of S_6^{2-} at 200 K in a $(NH_4)_2S_6$ solution is lower
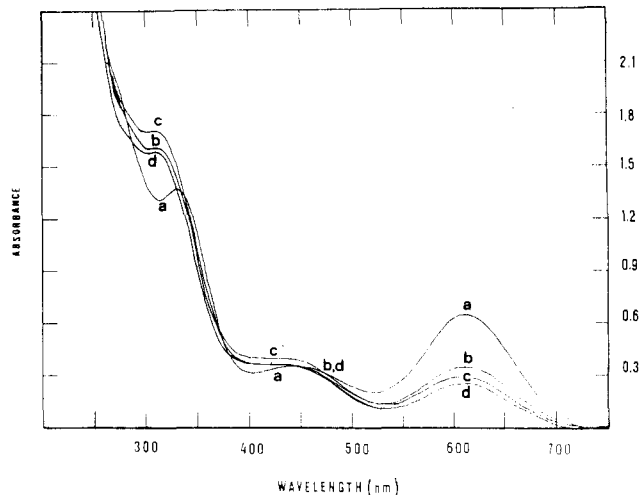
Figure 10. Absorption spectra of a Li_2S_6 solution (4.3 × 10^{-3} M; optical path length = 0.05 cm; 293 K) obtained for various NH_4Cl concentrations: (a) $[NH_4^+] = 0$; (d) $[NH_4^+]/[Li^+] \simeq 90 \pm 5$. The concentration of added NH_4Cl increases from a to d.

than the overall concentration of the solution and is also dependent on NH_4^+. This leads to the observed dependence of K_D with the concentration of $(NH_4)_2S_6$ solution.

It must also be noted that the dependence of K_D with the NH_4^+ concentration explains the differences (for $n > 6$) observed in the slope of $A(610)$ versus n between the $(NH_4)_2S_n$ solutions (Figure 3) and the Li_2S_n solutions.[4] In Li_2S_n solutions, the acidity of the solutions will increase sharply when n becomes larger than 6 (because S_6^{2-} is the least reduced polysulfide), while the corresponding change is much smaller in $(NH_4)_2S_n$ solutions.

Finally, some comments can be given about S_6^{2-} as the least reduced ammonium polysulfide. For Li_2S_n solutions, it was indicated that S_6^{2-} is the least reduced polysulfide. The same arguments can be used for $(NH_4)_2S_n$ solutions. In particular, there is not indication from the visible absorption spectrum that S_8^{2-}, identified in other solvents,[15] could exist in these solutions. It was seen above that there are several indications of a possible disproportionation of S_6^{2-} from the absorption spectrum and the Raman spectrum of $(NH_4)_2S_6$ solutions. A full analysis of the disproportionation of S_6^{2-} is not presently possible. The disproportionation of S_6^{2-} will give, on the more reduced side, S_5^{2-} and/or S_4^{2-}. It is shown below that the existence of S_5^{2-} in solution cannot be ascertained. The disproportionation of S_6^{2-} could give, on the more oxidized side, S_4N^-, which was observed in Li_2S_6 solutions but not in $(NH_4)_2S_6$ solutions. However there are several indications[17] that, in $S-NH_3$ solutions, an oxidized form of sulfur, less oxidized than S_4N^- should exist. This makes the disproportionation of S_6^{2-} in $(NH_4)_2S_6$ solutions compatible with the nonobservation of S_4N^-.

III. Does S_5^{2-} Exist as an Ammonium Polysulfide? In the study of lithium polysulfides, it was said[4] that S_5^{2-} is at least partly disproportionated but that no spectroscopic characterization could be given. For ammonium polysulfides, it is also found that no spectroscopic characterization of S_5^{2-} can be suggested. However two experimental results indicate that the disproportionation of S_5^{2-} should be larger in ammonium solutions than in lithium solutions. (i) For $(NH_4)_2S_5$ solutions, the visible absorption band between about 400 and 430 nm is shifted toward the lower wavelengths and is not so well shaped. (ii) The Raman spectra

of $(NH_4)_2S_5$ solutions depend on the excitation line; this was not the case for Li_2S_5 solutions.

IV. Determination of the Extinction Coefficient of S_4^{2-}. The determination of the extinction coefficient of S_4^{2-} is based on the following assumptions: (i) The disproportionation of S_4^{2-} for the dilute $(NH_4)_2S_n$ solutions studied with UV–visible spectrophotometry can be written

$$2S_4^{2-} \rightleftharpoons 2S_3^- + S_2^{2-} \qquad (22)$$
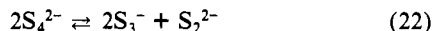
(ii) The absorbance at 390 nm, $A(390)$ is due to S_4^{2-}. (iii) The concentration C_0 of S_4^{2-} at 200 K is equal to the overall concentration of the $(NH_4)_2S_4$ solution. The absorbance $A(390)$ and $A(610)$ are then related by

$$A(390) = -\frac{\epsilon(S_4^{2-})}{\epsilon(S_3^-)}A(610) + C_0 d[\epsilon(S_4^{2-})] \qquad (23)$$

where d is the optical path length. The experimentally measured absorbances $A(390)$ and $A(610)$ are found to be linearly related, when the measured absorbances are corrected for the thermal variations of the density of the solution. For all the $(NH_4)_2S_4$ solutions investigated, it was found that $\epsilon(S_4^{2-}) = 1300 \pm 150$ M^{-1} cm^{-1} and that $\epsilon(S_3^-) = 4600 \pm 400$ M^{-1} cm^{-1}. This value obtained

for $\epsilon(S_3^-)$ is quite compatible with that found in Li_2S_6 or $(NH_4)_2S_6$ solutions. The value obtained for $\epsilon(S_4^{2-})$ has to be compared with the value $\epsilon(S_4^{2-}) = 900$ M^{-1} cm^{-1} given by Martin et al. in DMSO solutions.[12]

A similar analysis was done in Li_2S_4 solutions[4] and gave $\epsilon(S_4^{2-}) = 1100$ M^{-1} cm^{-1} but $\epsilon(S_3^-) \simeq 2000$ M^{-1} cm^{-1}. This suggests that the analysis based on eq 22 and 23 is more realistic in $(NH_4)_2S_4$ solutions; the disproportionation is larger in ammonium solutions, and eq 22 gives more precise results.

Registry No. S, 7704-34-9; NH_3, 7664-41-7; H_2S, 7783-06-4; N_2-$H_4\cdot HCl$, 2644-70-4; $(NH_4)_2S_2$, 113894-22-7; $(NH_4)_2S_4$, 74238-82-7; $(NH_4)_2S_5$, 12135-77-2; $(NH_4)_2S_6$, 113894-04-5; S_3^-, 12597-04-5; S_4^-, 12597-07-8; $(NH_4)_2S_{10}$, 110299-90-6; $(NH_4)_2S_8$, 83682-24-0.

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Synthesis, X-ray Crystal Structure, and Multinuclear NMR Study of the Dynamic Behavior of Tris[dihydrobis(1-pyrazolyl)borato]yttrium(III): A Molecule with Three Three-Center, Two-Electron Bonds

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Reaction of YCl_3 with $K[H_2B(pz)_2]$ (pz = pyrazolyl ring) and $K[H_2B(3,5-Me_2pz)_2]$ yields $[H(\mu-H)B(pz)_2]_3Y$ (**1**) and $[H(\mu-H)B(3,5-Me_2pz)_2]_3Y$ (**2**). The molecular structure of **1** has been determined by single-crystal X-ray diffraction: monoclinic, space group $P2_1/n$, $a = 14.231$ (3) Å, $b = 22.959$ (4) Å, $c = 9.342$ (2) Å, $\beta = 104.06$ (2)°, $V = 2961$ Å³, and $Z = 4$. The six nitrogen donor atoms are arranged in a nearly perfect trigonal prism. Each of the three rectangular faces of the trigonal prism is capped by a three-center B–H⋯Y agostic bond. The observation of B–H stretching bands at low frequencies in the solution IR spectra and the nonequivalence of the BH_2 hydrogen atoms in low-temperature NMR spectra demonstrates these agostic bonds are maintained in solution. Low-temperature ^{13}C NMR spectroscopy shows that the pyrazolyl rings are also nonequivalent, forming a 1/1 set. Thus, the solution structure is different from that of the solid by a twisting of the triangular faces of the trigonal prism toward an octahedral geometry. The molecules are fluxional in solution, both the pyrazolyl rings and BH_2 hydrogen atoms becoming equivalent in ambient-temperature spectra. The barriers to equilibration of the pyrazolyl rings and the BH_2 hydrogen atoms are the same (11.4 kcal/mol from the carbon data), indicating a common dynamic process. This process is proposed to be breaking of the agostic bonds and flipping of the boat arrangement of the six-membered BN_4Y rings, with re-formation of the bridging interactions on the adjacent faces. A common mechanism involving breakage of the agostic interaction is supported by a small isotope effect in the equilibration of the pyrazolyl rings measured in the barrier of **1** and its isotopomer $[D(\mu-D)B(pz)_2]_3Y$. Compound **2** shows similar fluxional behavior in solution with a measured barrier of 11.8 kcal/mol. Resonances in the ^{89}Y NMR spectra at 238.8 ppm for **1** and 105.6 ppm for **2** are observed. These data are best collected by using the INEPT pulsing sequence.

Introduction

We have been exploring the chemistry of polypyrazolylborate complexes of the early transition metals.[1,2] Part of our plan in using this flexible ligand system is to prepare complexes by using the trischelating $[RB(pz)_3]^-$ ligand (pz = pyrazolyl ring) as a six-electron donor and to also prepare similar complexes with the four-electron-donor bischelating $[R_2B(pz)_2]^-$ ligands. If successful, the second series would have potentially two fewer electrons donated to the metal, and this could drastically alter reaction chemistry. We have prepared two sets of complexes of this type.

In both sets, $[HB(3,5-Me_2pz)_3]TaMe_3Cl/[H(\mu-H)B(3,5-Me_2pz)_2]TaMe_3Cl$[1] and $[HB(pz)_3]CpZrCl_2/[H(\mu-H)B(pz)_2]$-$CpZrCl_2$,[2d] the complex prepared with the $[H_2B(pz)_2]^-$ ligand shows an interesting three-center, two-electron B–H⋯metal interaction making the ligand a six-electron donor to the metal. This type of agostic interaction[3] has also been observed with molybdenum–polypyrazolylborate complexes[4] and very recently with ruthenium complexes.[5]

We have recently expanded our study to the chemistry of yttrium.[6] With zirconium and tantalum, we were unable to

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