transfers. Indeed simulation[19] of the observed response gave a best fit for two individual one-electron transfers with $\Delta E^{\circ\prime} = 56 \pm 3$ mV, indicating a weak metal–metal interaction in the complex.[20,21] The weakness of the metal–metal interaction can be attributed to the ability of the complex to rotate about the 4′–4″ bond which links the two $Ru(bpy)_3^{2+}$ subunits, thereby disrupting the overlap of the π systems of the subunits. This is similar to the recently reported[8] noninteracting dimer of $Ru(terpy)_2^{2+}$ units but is in marked contrast to a recently reported[22] strongly interacting binuclear complex containing a bridging tetraiminobiphenyl ligand that also has the potential for free rotation between the bridged components. Although the metal–metal interaction is not strong in **3**, there is extensive electronic coupling between the two bpy groups of the bridging ligand, as evidenced by the large separation between the potentials of the first and subsequent one-electron reductions in **3** and the 210-mV difference in the first reduction potentials of **2** and **3**.[21] This first reduction of **3** is assigned as quaterpyridine-centered by comparison with related literature data.[23]

The electronic absorption spectrum of mononuclear complex **2** is also similar to that of $Ru(bpy)_3^{2+}$ with a maximum at 455 nm ($\epsilon = 1.2 \times 10^4$) in acetonitrile (cf. 451 nm for $Ru(bpy)_3^{2+}$). Binuclear complex **3** showed maxima at 471 nm ($\epsilon = 2.2 \times 10^4$) and 445 nm ($\epsilon = 2.0 \times 10^4$), corresponding to d–$\pi^*$ MLCT transitions into the quaterpyridine and bpy ligands respectively, as well as the usual intense π–π^* absorptions at 287 nm ($\epsilon = 1.1 \times 10^5$) and 244 nm ($\epsilon = 5.2 \times 10^4$). The small red shift of the lowest energy MLCT absorption relative to $Ru(bpy)_3^{2+}$ confirms the weak metal–metal interaction, as binuclear complexes with strong metal–metal interactions usually exhibit much greater red

shifts. Thus the electrochemical and spectroscopic data show that the new ligand, **1**, has the intended similar π-orbital energy to bpy, exhibits electronic coupling between the two bpy subunits, and permits weak metal–metal interactions.

Meyer and co-workers[24] very recently reported a structurally related complex in which the rutheniums are bridged by a ligand containing bpy groups linked through C4 by an ethenyl group. Relative to **3**, this complex has a greater intermetal separation and an extra rotational degree of freedom and, not surprisingly, a weaker metal–metal interaction. However, electronic delocalization in the bridging ligand was observed, and this was proposed to account for the unexpectedly long excited-state lifetime of the complex. In accord with this, a long excited-state lifetime was also observed in a recently reported highly conjugated but noninteracting diruthenium complex containing bpy units linked through a 1,4-diethenylbenzene bridge.[21] Our more strongly interacting complex, **3**, which dispenses completely with the bridging moiety, emits at $\lambda_{max} = 685 \pm 5$ nm with a surprisingly long excited state lifetime of 2.0 ± 0.2 μs (acetonitrile, 295 K). Hence, **1** is a new example of a binucleating ligand that leads to enhanced excited state lifetimes by way of electron delocalization. Furthermore this lifetime is much longer than those reported for strongly interacting binuclear ruthenium complexes with bridging diazine ligands such as 2,2′-bipyrimidine and 2,3-bis(2-pyridyl)pyrazine.

In summary, the new binucleating ligand **1** has been prepared and its diruthenium(II) complex (**3**) shown to display a weak metal–metal interaction. Electron transfer into the bridging ligand results in extended delocalization and an increased excited-state lifetime. Further studies of other complexes of **1**, including heterobinuclear examples and complexes of higher nuclearity, are in progress.

(19) Feldberg, S. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1969, Vol. 3, p. 199.
(20) In strongly interacting complexes[3,4] with bridges such as 2,2′-bipyrimidine, two well-resolved separate oxidation waves are observed, whereas noninteracting systems[5,6] produce exactly superimposed one electron waves.
(21) Shaw, J. R.; Webb, R. T.; Schmehl, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 1117.
(22) Auburn, P. R.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 2553.
(23) It is likely that the second reduction also involves the bridging ligand since it occurs at a potential that best correlates with the recently proposed relationship betwen $\Delta E^{\circ\prime}$ and the number of bonds in the bridging ligand; see ref 4. In agreement with this the third reduction, which must be bpy-based, occurs at the same potential as the second reduction of $Ru(bpy)_3^{2+}$.

(24) Boyde, S.; Strouse, G. F.; Jones, W. E.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7395.

Department of Chemistry
University of Canterbury
Christchurch 1, New Zealand

Alison J. Downard*
Gene E. Honey
Leon F. Phillips
Peter J. Steel*

Articles

Absorption Bands of the S3- and S6(2-) Polysulfide Ions in Liquid-Ammonia Solutions

V. Pinon and J. P. Lelieur*

The absorption spectra of Li_2S_6–NH_3 solutions have been resolved at various temperatures and concentrations. It has been shown previously that in these solutions S_6^{2-} is not disproportionated but is in equilibrium with S_3^-. In various previous studies, S_3^- and S_6^{2-} were characterized by a single absorption band in the visible range at 610 and 440 nm, respectively. It is shown that the radical S_3^- also has an absorption band at 268 nm, while S_6^{2-} absorbs also at 330, 288, and 244 nm. The molar extinction coefficient of these bands was determined. The value of the equilibrium constant between S_6^{2-} and S_3^- was determined; this value confirms previous determinations.

Introduction

The identification of the S_3^- radical anion was clarified about 15 years ago.[1] This radical has been observed in many solutions.

It has been found in alkali-metal polysulfides in solution in various solvents (HMPA,[2,3] DMF,[3] NH_3,[4–6] amines[7]). It was also ob-

(1) Chivers, T. *Nature (London)* **1974**, *252*, 32.

(2) Chivers, T.; Drummond, I. *Inorg. Chem.* **1972**, *11*, 2525.
(3) Seel, F.; Guttler; H. J.; Simon, G.; Wieckowski, A. *Pure Appl. Chem.* **1977**, *49*, 45.

served in solutions of sulfur in HMPA,[8] NH$_3$,[9,10] and several amines[11] and in the electrochemical reduction of sulfur in several solvents in which sulfur is not disproportionated.[12-14] The S$_3^-$ radical is found in equilibrium with the polysulfide S$_6^{2-}$ according to

$$S_6^{2-} \rightleftharpoons 2S_3^- \qquad (1)$$

The temperature dependence of this equilibrium has been investigated in DMF[3] and in ammonia[5,6,10] and was shown to be strong. The S$_3^-$ radical is characterized by an absorption band located between 610 and 620 nm. The S$_6^{2-}$ polysulfide has usually been characterized by an absorption band located at ca. 450 nm. It has also been characterized by another absorption band located at 340 nm[12] or at 345 nm.[14] The values published in the literature for the molar extinction coefficient of S$_3^-$ at ca. 610 nm are somewhat dispersed: 4450 M^{-1} cm^{-1} in HMPA,[2] 4850 M^{-1} cm^{-1} in DMF[3], 3900 M^{-1} cm^{-1} in acetonitrile,[12] 3800 M^{-1} cm^{-1} in DMA,[14] 5100 M^{-1} cm^{-1} in ammonia.[5,6] A strong dispersion is also observed for the molar extinction coefficient of S$_6^{2-}$ at ca. 450 nm and for the equilibrium constant of the dissociation of S$_6^{2-}$ into S$_3^-$ (eq 1).

Recently, some progress has been made in the identification of polysulfides in liquid ammonia.[5,6] It has been shown that S$_6^{2-}$ is the least reduced polysulfide in this solvent; it is disproportionated in acidic solutions ((NH$_4$)$_2$S$_6$), but it is not in neutral solutions (Li$_2$S$_6$). Consequently, the only polysulfides in Li$_2$S$_6$-NH$_3$ solutions are S$_6^{2-}$ and S$_3^-$ and the analysis of the absorption spectra of these solutions was, therefore, expected to be much easier than for other Li$_2$S$_n$-NH$_3$ solutions.

The purpose of the present paper is to report the resolution of the absorption spectra of Li$_2$S$_6$-NH$_3$ solutions between 230 and 800 nm at various temperatures and concentrations and determine the various absorption bands of S$_6^{2-}$ and S$_3^-$. This characterization of S$_6^{2-}$ and S$_3^-$ is undoubtedly a prerequisite for the full characterization of the other polysulfides in solution and the interpretation of the absorption spectra of polysulfides in various solvents.

Experimental Section

The preparation of Li$_2$S$_6$-NH$_3$ solutions was done as previously described,[5] by reducing sulfur by lithium in liquid ammonia. The samples used in the present work were rather dilute solutions (ca. 10^{-3} M). The preparation of the samples was done in two steps to obtain a satisfactory accuracy for the stoichiometry of the polysulfide (6 ± 0.1). The completion of the reaction was done at 0 °C. The samples were kept at this temperature for about 1 week before recording an absorption spectrum. Quartz optical cells that could sustain ammonia vapor pressure at room temperature were used. These cells have an optical path length of 0.1, 0.5, 1, or 5 mm.

All the electronic absorption spectra were recorded with a Cary 2200 spectrophotometer. The spectra were recorded from 800 to 220 nm. At 800 nm, the absorbance is negligible, while at ca. 220 nm the absorbance is due to the solvent and is high. The value of the absorbance was recorded at 1-nm intervals at various temperatures between 295 and 200 K with an Oxford Instruments DN 704 cryostat. The temperature of the sample was regulated within ±0.1 °C. The data were recorded with the Varian data station (DS15) and transferred to a PC-AT microcomputer.

Results

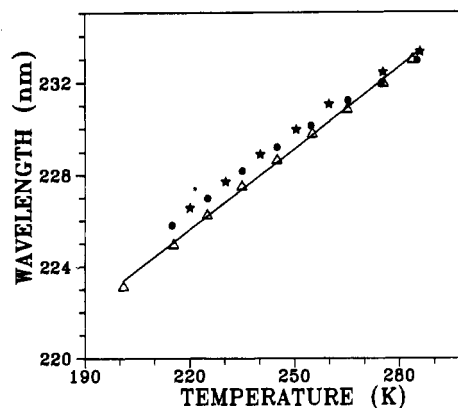The resolution of the spectra was done with a nonlinear least-squares method using a FORTRAN program first proposed

Figure 1. Variation of the wavelength versus the temperature at a given absorbance: (△) NH$_3$, Abs = 1.7; (●) Li$_2$S$_6$-NH$_3$, 0.82 × 10^{-3} M, Abs = 1.7; (★) Li$_2$S$_6$-NH$_3$, 1.15 × 10^{-3} M, Abs = 2.4. The optical path length is 0.05 cm. The slope of the linear variation for NH$_3$ is equal to 0.116 nm K^{-1}.

by Dye and Nicely.[15] An asymmetric Gaussian (or log-normal) profile was assumed for all the bands, and the resolution was performed on the energy scale. These choices lead to the most satisfactory results. The well-known absorption band of S$_3^-$ at 610 nm is only slightly perturbed by the absorption band of S$_6^{2-}$ at 440 nm, and its profile can, therefore, by easily analyzed and was shown to be log-normal. The following equation of the log-normal profile was considered:[16]

$$y = a \exp\left\{(-\log 2)\left[\left(\log\left(1 + \frac{2d(x - b)}{\Delta x}\right)\right)\frac{1}{d}\right]^2\right\} \qquad (2)$$

In the present case, y is the absorbance at energy x, a the maximum absorbance, b the position of the maximum, and d the asymmetry parameter. The Δx parameter is connected to the bandwidth at half-height, c, by the relation

$$c = (\Delta x)\frac{\sinh d}{d} \qquad (3)$$

Before the beginning of the resolution procedure, it was necessary to substract the solvent contribution. This contribution cannot be compensated for by a double-beam experiment with a pure solvent cell in the reference beam because the absorption band of the solvent in a solution is shifted relative to its position in the pure solvent. Indeed, the absorbance of liquid ammonia increases abruptly for wavelengths shorter than 250 nm, and only the steep rise of the absorbance can be recorded. The absorbance cutoff in liquid ammonia is located at 240 nm at room temperature, and it has been observed to be shifted toward shorter wavelengths when the temperature decreases. By the use of optical cells with a path length of 0.1 mm, the absorbance of liquid ammonia down to 220 nm at various temperatures between 290 and 200 K has been measured. When the temperature decreased, a given absorbance, A was found at a shorter wavelength, λ_1 (Figure 1). The variations of λ_1 versus T are linear with a slope equal to 0.116 nm K^{-1}. This is the first time that the shift of the absorption band of liquid ammonia with temperature has been quantitatively determined.

In Li$_2$S$_6$-NH$_3$ solutions, and in other polysulfide solutions, we have observed that the absorption band of the solvent is shifted toward longer wavelengths when the concentration of the solution increases. Such an observation has already been made by Burrow and Lagowski for iodide solutions,[17] by Corset and Lepoutre for amide solutions,[18] and by Koehler et al. for polyselenide and polytelluride solutions.[19,20] We have observed that the temperature

(4) Bernard, L.; Lelieur, J. P.; Lepoutre, G. *Nouv. J. Chim.* **1985**, *9*, 199.
(5) Dubois, P.; Lelieur, J. P.; Lepoutre, G. *Inorg. Chem.* **1988**, *27*, 1883.
(6) Dubois, P.; Lelieur, J. P.; Lepoutre, G. *Inorg. Chem.* **1988**, *27*, 73.
(7) Daly, F. P.; Brown, C. W. *J. Phys. Chem.* **1975**, *79*, 350.
(8) Chivers, T.; Drummond, I. *Chem. Commun.* **1971**, 1623.
(9) Chivers, T.; Lau, C. *Inorg. Chem.* **1982**, *21*, 453.
(10) Dubois, P.; Lelieur, J. P.; Lepoutre, G. *Inorg. Chem.* **1987**, *26*, 1897.
(11) Daly, F. P.; Brown, C. W. *J. Phys. Chem.* **1973**, *77*, 1859.
(12) Martin, R. P.; Doub, W. H.; Roberts, J. L.; Sawyer, D. T. *Inorg. Chem.* **1973**, *12*, 1921.
(13) Fujinaga, T.; Kuwamoto, S.; Okazaki, S.; Hojo, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2851.
(14) Paris, J.; Bosser, G.; Plichon, V. *Electrochim. Acta* **1986**, *31*, 457.

(15) Dye, J. L.; Nicely, V. A. *J. Chem. Educ.* **1971**, *48*, 443.
(16) Fraser, R. D. B.; Suzuki, E. *Anal. Chem.* **1969**, *41*, 37.
(17) Burrow, D. F.; Lagowski, J. J. *Adv. Chem. Ser.* **1965**, *50*, 125.
(18) Corset, J.; Lepoutre, G. *J. Chim. Phys.* **1966**, *63*, 659.
(19) Sharp, K. W.; Koehler, W. H. *Inorg. Chem.* **1977**, *16*, 2258.

dependence of the absorption band of the solvent in very dilute solutions is the same as in the pure solvent, even when the absorption band is shifted (Figure 1). Figure 1 shows that for a very dilute solution (8.2 × 10⁻⁴ M), the absorption band of the solvent is identical with that of the pure solvent. In this case, the contribution of the solvent is readily substracted. For a more concentrated solution (1.15 × 10⁻³ M), it was found that at a given wavelength the absorbance is significantly higher than in the pure solvent or than in a very dilute solution, but it is found that the temperature dependence of the band is the same as in pure liquid ammonia. The contribution of the solvent to the absorbance of the solution is then taken into account in the following way: the absorbance of pure ammonia is multiplied by a numerical factor to become identical with the absorbance of the solution in the wavelength range in which the absorbance is due to ammonia. For the 1.15 × 10⁻³ M solution, the absorbance around 225 nm is 2.4/1.7 times higher than in pure ammonia. Consequently, the contribution of the solvent is assumed to be 2.4/1.7 times that of the pure solvent. It was noted that this numerical factor is also equal to the ratio 1.15 × 10⁻³/0.82 × 10⁻³ of the concentration of the solution to that of the very dilute solution for which the absorption band of the solvent is not shifted relative to that of pure ammonia. For more concentrated solutions, the absorbance is very strong in the 225-nm range and prevents the observation of the shift of the absorption band toward high wavelengths when the temperature decreases. In these cases, if the concentration of the solution is C, the contribution of the solvent to the absorbance is assumed to be equal to $C/0.82 \times 10^{-3}$ times that of the pure ammonia. This empirical procedure was found to take satisfactorily into account the contribution of the solvent in Li_2S_6–NH_3 solutions and in other polysulfides solutions.

The examination of the absorption spectra when the contribution of the solvent has been taken into account suggests that five or six bands are involved. However the resolution of the spectra with five bands was not satisfactory for all temperatures and concentrations.

The resolution of the absorption spectrum of the most dilute solution studied (0.82 × 10⁻³ M) is shown for three different temperatures in Figure 2. In Figure 2a,b six absorption bands were found located at 610, 440, 330, 288, 268, and 244 nm. The absorbance of the bands at 610 and 268 nm decreases when the temperature decreases, and these bands are no longer observed at temperatures close to 200 K (Figure 2c). Since it has been shown that the concentration of S_3^- decreases when the temperature decreases, both bands at 610 and 268 nm are assigned to the S_3^- radical. The absorbance of the other bands (440, 330, 288, and 244 nm) increases when the temperature decreases, and these bands are consequently assigned to S_6^{2-}. To check these assignments, let us first write the relations between the absorbance of the bands of S_6^{2-} and that of S_3^-.

Let C_0 be the total concentration of the solute in solution. It is the concentration of S_6^{2-} at 200 K when S_3^- is completely dimerized into S_6^{2-}. For temperatures higher than 200 K, the concentration of S_6^{2-} and of S_3^- are related by
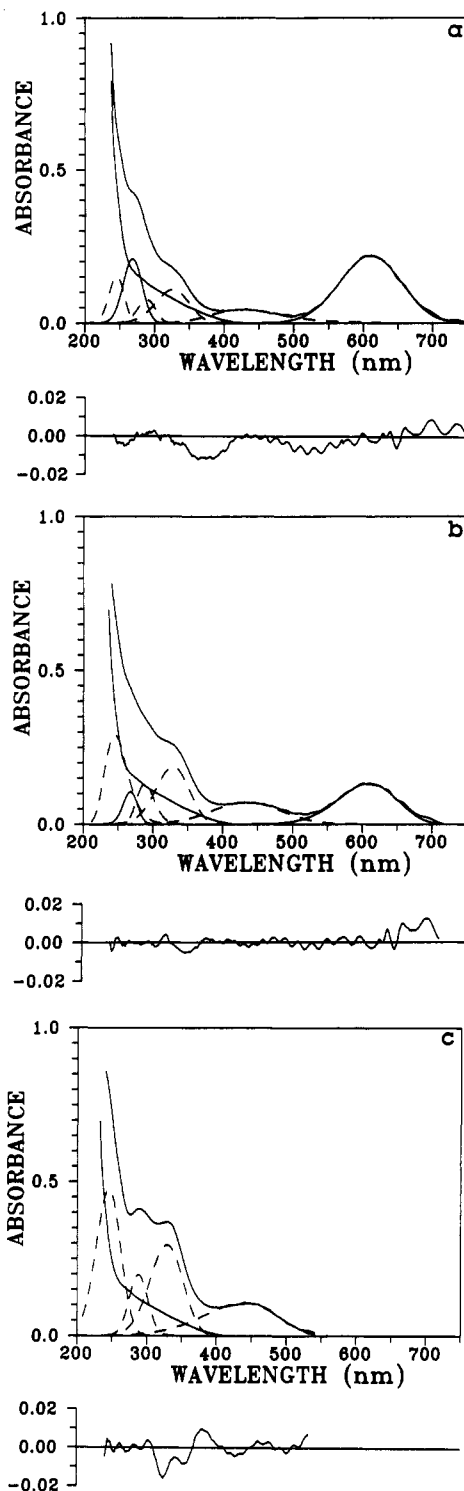
$$C_0 = [S_6^{2-}] + \frac{1}{2}[S_3^-] \qquad (4)$$

By the use of Beer's law, the concentrations of $[S_6^{2-}]$ and $[S_3^-]$ are expressed by

$$[S_6^{2-}] = \frac{A(S_6^{2-})}{l \ \epsilon(S_6^{2-})} \qquad [S_3^-] = \frac{A(S_3^-)}{l \ \epsilon(S_3^-)} \qquad (5)$$

where A is the absorbance, ϵ the molar extinction coefficient, and l the optical path length. These relations are valid for all the absorption bands of S_6^{2-} and of S_3^-, respectively. Equation 4 can then be replaced by

$$A(S_6^{2-}) = -\frac{1}{2} \frac{\epsilon(S_6^{2-})}{\epsilon(S_3^-)} A(S_3^-) + \epsilon(S_6^{2-}) l C_0 \qquad (6)$$

(20) Schultz, L. D.; Koehler, W. H. *Inorg. Chem.* **1987**, *26*, 1989.

Figure 2. Resolution of the absorption spectrum of a Li_2S_6–NH_3 solution (0.82 × 10⁻³ M) at three temperatures: (a) 285 K; (b) 260 K; (c) 200 K. For each panel are plotted the experimental signal and absorption bands of NH_3, S_3^- (—), and S_6^{2-} (- -). The sensitivity is 6 times higher for the residuals than for the absorption spectrum. The optical path length is 0.05 cm.

Since the absorption band at 610 nm is assigned unambiguously to S_3^-, the absorbance of the bands of S_6^{2-} can be expressed versus the absorbance of S_3^- at 610 nm by

$$A(S_6^{2-}) = -\frac{1}{2} \frac{\epsilon(S_6^{2-})}{\epsilon(S_3^-)} A(610) + \epsilon(S_6^{2-}) l C_0 \qquad (7)$$

This equation shows that the absorbance of each band of S_6^{2-} varies linearly with the absorbance of S_3^- at 610 nm. The second term of the right member allows the determination of $\epsilon(S_6^{2-})$, and the

Table I. Molar Extinction Coefficients Deduced from the Experimental Data Reported in Figure 3

	band, nm			
	440	330	288	244
ϵ, M^{-1} cm^{-1}	2205	6136	4190	9757
$\epsilon(610)$, M^{-1} cm^{-1}	4890	4568	5068	4545

slope gives $\epsilon(610)$. Obviously, the molar extinction coefficient, $\epsilon(610)$, of the absorption band at 610 nm must have the same value whichever absorption band of S_6^{2-} is considered. At 200 K, the absorbance, $A(610)$, is zero, and eq 7 can be written

$$A(S_6^{2-}) = \epsilon(S_6^{2-}) \, l C_0 \qquad (8)$$

Consequently, the absorbance of the various bands of S_6^{2-} increases linearly, at 200 K, with the concentration, C_0, of the solution; i.e., Beer's law is obeyed. The absorption bands of S_3^-, which can be observed only at temperatures higher than 200 K, do not follow Beer's law. Let $K(T)$ be the equilibrium constant for the equilibrium between S_6^{2-} and S_3^-, defined by

$$K(T) = \frac{[S_3^-]^2}{[S_6^{2-}]} = K_0 \exp\left(-\frac{\Delta H}{RT}\right) \qquad (9)$$

The concentration $[S_6^{2-}]$ is expressed versus $[S_3^-]$ and C_0 from eq 4. The concentration $[S_3^-]$ is then the solution of a second-degree equation and is expressed by

$$[S_3^-] = \frac{K(T)}{4}\left[\left(1 + \frac{16C_0}{K(T)}\right)^{1/2} - 1\right] \qquad (10)$$

The experimental absorbance of the bands of S_3^- must follow this equation versus concentration, C_0, and temperature. Consequently, the experimental data deduced from the resolution of the absorption spectra must obey eqs 7, 8, and 10.
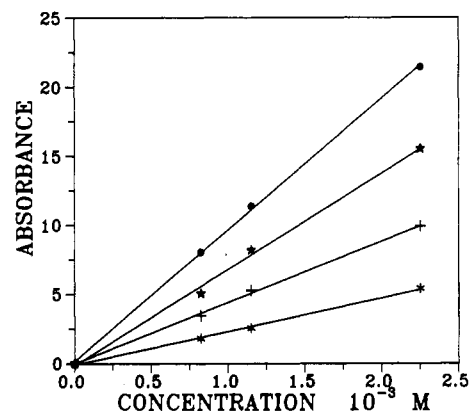
In Figure 3 the variations of the absorbance of the various bands are plotted versus the absorbance at 610 nm for a 0.82×10^{-3} M solution. Linear variations are found, as expected from eq 7. The molar extinction coefficients of these bands and of the 610-nm band, deduced from these data, are reported in Table I. The bands at 330, 288, 244, and 440 nm lead to rather close values for $\epsilon(610)$, and these four bands are, therefore, assigned to S_6^{2-}.

The variations of absorbance at 268 nm, $A(268)$, versus the absorbance at 610 nm, $A(610)$, are linear (Figure 3). This band at 268 nm has, therefore, the same variations as that at 610 nm: it increases when the temperature decreases. Therefore, it is concluded that the band at 268 nm must also be assigned to S_3^-. The slope of $A(268)$ versus $A(610)$ is slightly smaller than 1; the molar extinction coefficients of both bands of S_3^- are, therefore, quite close.

The above mentioned results have been deduced from the experimental data obtained for a $Li_2S_6-NH_3$ solution at various temperatures. Other dilute $Li_2S_6-NH_3$ solutions have also been investigated (1.15×10^{-3} and 2.25×10^{-3} M). Linear variations quite similar to that of Figure 3 have been obtained. For the three investigated solutions, it is shown that at 200 K, the absorbance of each band assigned to S_6^{2-} varies linearly with the concentration (Figure 4), as expected from Beer's law expressed by eq 8. The linear least-squares fit for the data reported in Figure 4 allows the best determination of the extinction coefficient of the bands of S_6^{2-}; these values are $\epsilon(440) = 2410 \pm 90$ M^{-1} cm^{-1}, $\epsilon(330) = 6960 \pm 280$ M^{-1} cm^{-1}, $\epsilon(288) = 4425 \pm 120$ M^{-1} cm^{-1}, and
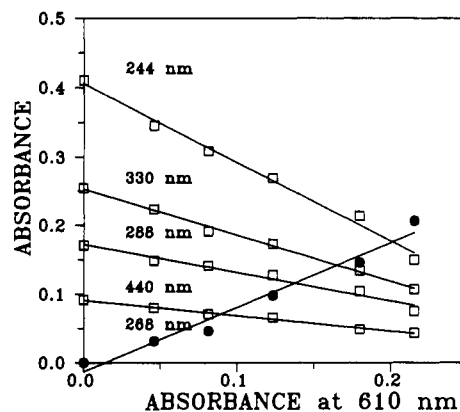
Figure 3. Plot of the absorbance for the various absorption bands versus the absorbance of S_3^- at 610 nm for a $Li_2S_6-NH_3$ solution (0.82×10^{-3} M). ($\square$) S_6^{2-} bands; ($\bullet$) S_3^- band.

Figure 4. Plot of the absorbance at 440, 330, 288, and 244 nm versus the concentration C_0 at 200 K. The path length is 1 cm. The slope of the linear variations is equal to the molar extinction coefficient of the related band (Beer's law).

$\epsilon(244) = 9520 \pm 160$ M^{-1} cm^{-1}.

The absorption spectrum of $Li_2S_6-NH_3$ solutions between 800 and 230 nm can be studied only for very dilute solutions, and the study of moderately dilute solutions would require a very short optical path length. However, these solutions have been studied between 800 and ca. 230 nm and, in this case, the variations of $A(440)$ can be plotted versus $A(610)$, and $\epsilon(440)$ and $\epsilon(610)$ can be determined. The value of $\epsilon(610)$ has, therefore, been obtained for eight sets of data related to different concentrations. The average value of $\epsilon(610)$ was found equal to 4330 ± 200 M^{-1} cm^{-1}. It was then deduced that $\epsilon(268) = 4000 \pm 400$ M^{-1} cm^{-1}. These values are reported in Table II, together with the other parameters of each band deduced from the resolution calculations.
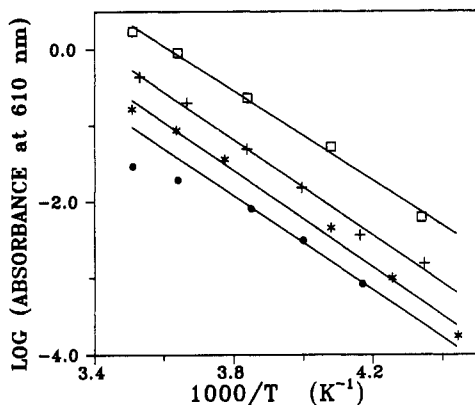
The variations of the absorbance of S_3^- at 610 nm versus temperature allowed, from eq 10, the determination of the equilibrium constant of the dissociation equilibrium between S_6^{2-} and S_3^-. From this equation, the absorbance at 610 nm is given by

$$A(610) = \frac{l \, K(T) \, \epsilon(610)}{4}\left[\left(1 + \frac{16C_0}{K(T)}\right)^{1/2} - 1\right] \qquad (11)$$

It has been shown[5] that, at 290 K, the equilibrium constant,

Table II. Parameters of the Absorption Bands in $Li_2S_6-NH_3$ Solutions

band, nm	band, 10^3 cm^{-1}	width, 10^3 cm^{-1}	asymmetry	ϵ, M^{-1} cm^{-1}
610 (S_3^-)	16.40 ± 0.06	2.5 ± 0.2	0.23 ± 0.02	4330 ± 200
440 (S_6^{2-})	22.7 ± 0.3	5 ± 0.5 ($T \geqslant 260$ K)	0.20 ± 0.05	2410 ± 90
		6 ± 0.5 ($T < 260$ K)	0.4 ± 0.1	
330 (S_6^{2-})	30.3 ± 0.3	4.5 ± 0.5	0.25 ± 0.02	6960 ± 280
288 (S_6^{2-})	34.7 ± 0.3	3.5 ± 0.5	0.10 ± 0.05	4425 ± 120
268 (S_3^-)	37.3 ± 0.3	3.5 ± 0.5	0.15 ± 0.05	4000 ± 400
244 (S_6^{2-})	41.0 ± 0.7	6 ± 1	0.15 ± 0.05	9520 ± 160

Figure 5. Variation of log (absorbance at 610 nm) versus $1/T$ for various $Li_2S_6-NH_3$ solutions: 10^{-2} M ($\square$); 4×10^{-3} M (+); 2.25×10^{-3} M (✳); 8.2×10^{-4} M (●). The slope of the linear variations is equal to $-\Delta H/2R$.
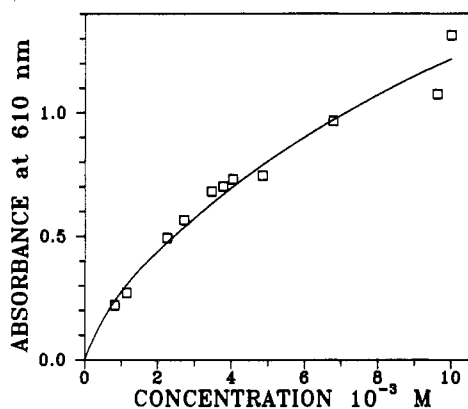
Figure 6. Variation of the absorbance of S_3^- at 610 nm versus C_0 at 290 K. The experimental data ($\square$) are given for an optical path length equal to 0.5 mm. The full line is the theoretical absorbance given by eq 11, with $\epsilon = 4300$ M^{-1} cm^{-1}, $K(290) = 4.4 \times 10^{-3}$ M, and $l = 0.05$ cm.

$K(290)$, is close to 4×10^{-3} M. When C_0 is large enough, $16C_0$ is much larger than $K(T)$, and eq 11 can be approximated by

$$A(610) \simeq l\ \epsilon(610)\ [C_0\ K(T)]^{1/2} \qquad (12)$$

In this case, the variations of log $A(610)$ versus $1/T$ are expected to be linear with a slope $-\Delta H/2R$. Such variations have been found as shown in Figure 5. It is also shown in Figure 5 that,

for the more dilute investigated solution, the high-temperature data deviate from the linear variation found at lowest temperatures; this results from the breakdown of the approximation required to obtain eq 12: $16C_0$ is not much larger than $K(T)$.

The slope of the linear variations shown in Figure 5 allows the determination of $\Delta H/R$ yielding 5900 ± 200 K. The variations of $A(610)$ versus C_0 at 290 K are then fitted (Figure 6) to the variations given by eq 11 by a nonlinear least-squares procedure, using $\epsilon = 4300$ M^{-1} cm^{-1} and $\Delta H/R = 5900$ K; the best fit is obtained for $K(290) = 4.4 \times 10^{-3}$ M.

Conclusion

The absorption spectra of $Li_2S_6-NH_3$ solutions have been resolved between 800 and 230 nm. It is shown that S_6^{2-} has four bands and S_3^- two bands in this range. A previous study had already given an indication of an absorption band of S_3^- in the UV range.[2] The absorption spectrum of a Na_2S_6-HMPA solution displays an intense absorption band at 620 nm assigned to S_3^-, a weak band at 450 nm assigned to S_6^{2-}, and another unassigned intense band at 277 nm.[2] The present work suggests that this band could be assigned to S_3^-, but study of the thermal variations of this absorption spectrum are needed to confirm this assignment. It must also be mentioned that a theoretical study of the electronic structure of S_3^- by Cotton et al. has suggested the possible existence of an absorption band in the UV range, but the experimental location of this band is rather different from the theoretical prediction.[21]

The present resolution of the absorption spectra of $Li_2S_6-NH_3$ confirms that the only reduced forms of sulfur in these solutions are S_6^{2-} and S_3^-. The equilibrium constant has been determined accurately, and results confirm previous determinations. The activation energy ΔH is found equal to 49.1 ± 1.7 kJ mol^{-1}; this is in good agreement with previously reported values: 48 kJ mol^{-1} in NH_3[5] and 47.4 kJ mol^{-1} in DMF.[3]

Registry No. NH_3, 7664-41-7; Li_2S_6, 115681-11-3; LiS_3, 132774-34-6.

(21) Cotton, F. A.; Harmon, J. B.; Hedges, R. M. *J. Am. Chem. Soc.* **1976**, *98*, 1417.