

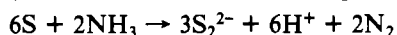
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Raman Spectroscopic Identification of the S_4N^- and S_3^- Ions in Blue Solutions of Sulfur in Liquid Ammonia

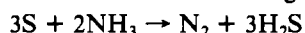
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It is well-known that elemental sulfur dissolves in liquid ammonia to give colored solutions which are green or blue at room temperature and red at lower temperatures.¹⁻³ Although a variety of physical techniques has been applied to this system, the identities of the chromophores in these solutions are still a matter of controversy. In 1967, Nelson and Lagowski reported that liquid ammonia solutions of sulfur (10^{-3} – 10^{-4} M) at -35°C exhibit absorption maxima at 580, 430, and 297 nm. These authors observed that the intensity of the 580-nm band decreases with a decrease in temperature while the other two bands increase and concluded that at least two different species are in equilibrium in sulfur–ammonia solutions.² On the basis of conductivity measurements, Zipp and Evers found that sulfur behaves as a fairly strong electrolyte in liquid ammonia but inferred that a large fraction of the dissolved sulfur is present in nonconducting forms.⁴ Kerouanton and co-workers reported that a 0.1 M solution of sulfur in liquid ammonia at room temperature exhibits no esr signal. They also observed adsorption maxima at 585 and 440 nm but found that a new band appeared at 610 nm as the solution aged. On the basis of this data together with electrochemical and cryoscopic measurements, these authors concluded that the sulfur chromophores in liquid ammonia are S_2NH_3 (red) and SNH_3 (blue). The overall reaction was represented as³



In contrast, Guiraud and co-workers interpreted their electrochemical results in terms of the following transformation:⁵



Solutions of sulfur in liquid ammonia have found application in organic syntheses. For example, the reaction of 4-chloronitrobenzene with sulfur in liquid ammonia was found to produce 4-nitrobenzenethiosulfenamide. $O_2NC_6H_4SSNH_2$, a result which led to the suggestion that nucleophilic species such as H_2NS^- and H_2NSS^- are present in liquid-ammonia solutions of sulfur.⁶

By contrast, we have shown that bubbling ammonia into a slurry of sulfur in hexamethylphosphoric triamide produces a deep blue solution of the S_4N^- ion,⁷ and in a review article published in 1977 one of us suggested that the S_4N^- was the blue chromophore in sulfur–ammonia solutions.⁸

While the current work was in progress, Meyer and co-workers published the results of a detailed study of the reactions of sulfur dioxide with ammonia.⁹ As part of this investigation they briefly reported the Raman spectrum of a solution of sulfur in liquid ammonia and tentatively concluded that "several singly charged radical ions, such as S_3^- , S_4^- , and S_4N^- might be present".¹⁰

Table I. Raman and Electronic Spectra of S_x , S_x^- , S_y^{2-} , and S_zN^-

	raman spectra, cm^{-1}	UV-visible spectra, nm	ref
S_2	716–718		14, 15
S_3	583	400	16
S_4	674 m, 653 w, m, 352 s ^a	530	13, 16a
S_2^-	585–595 s	400	13, 18
S_3^-	535 s, 233	~610	11, 13, 19
S_4^-	518 w, 439 m, 384 s	510	13, 19
S_2^{2-}	473 (BaS_2) or 451 ($\beta\text{-Na}_2S_2$)		20, 21
S_3^{2-}	466 s, 238 m (K_2S_3) or 476 s, 458 m, 238 w (Na_2S_3 , BaS_3)		21
S_4^{2-}	482 s, 445 m	420–430	22, 23
S_5^{2-}	496 m, 432 s, 252 m		21
S_6^{2-}	453 m, 373 s, 358 m		21
S_3N^-	894 m, 686 s, 574 vs	465	24
S_4N^-	892 w, 710 vs, 592 s, 570 s	582	12

^a Brown and co-workers¹⁷ assign Raman bands at 440, 601, and 668 cm^{-1} to the S_4 molecule. The different Raman bands reported for S_4 may correspond to different geometrical forms of the molecule.¹³

We have previously characterized both the S_3^- (λ_{max} ca. 610 nm)¹¹ and the S_4N^- (λ_{max} ca. 580 nm)¹² by Raman spectroscopy, a technique which is well suited to the identification of polysulfur species in solution. In order to settle the controversy over the identity of the colored species present in sulfur–ammonia solutions, we have investigated this system by Raman spectroscopy and we report the experimental details and our conclusions here.

Experimental Section

Preparation of Samples for Raman Spectra. Sublimed sulfur (Fisher Scientific Co.) was used without further purification. Ammonia (Matheson, 99.95%) was stored in a glass container and distilled under vacuum directly onto an accurately weighed amount of sulfur at -78°C in a weighed Pyrex glass tube of 4-mm outside diameter and 1-mm thickness. The glass tube was sealed off under vacuum and reweighed to obtain the weight of ammonia.

Instrumentation. Raman spectra were recorded on a Jarrell-Ash model 25-100 double monochromator calibrated with carbon tetrachloride. The detection system consisted of an ITT model FW130 phototube and an SSR model 1105 photon counter made by Princeton Applied Research Corp. A Coherent Radiation CR3 argon ion laser and a dye laser were used to produce the exciting lines at 514.5 (200 mW) and 600 nm (50 mW), respectively. The spectra were measured with a slit width of 4 cm^{-1} and a scan speed of 1.0 $\text{cm}^{-1} \text{ s}^{-1}$. Band positions are reported with an accuracy of $\pm 3 \text{ cm}^{-1}$.

Results and Discussion

The species to be considered as possible candidates for the chromophores in sulfur–ammonia solutions include small sulfur allotropes S_x or polysulfur radical anions S_x^- ($x = 2$ –4), polysulfide anions S_y^{2-} ($y = 2$ –6), and binary sulfur–nitrogen anions S_zN^- ($z = 3, 4$). All of these species have been well characterized by their Raman spectra and, in most cases, by their UV–visible spectra (see Table I). In addition, some of these species, e.g., S_3^- ,^{11,13} S_3N^- ,²⁴ and S_4N^- ,¹² exhibit char-

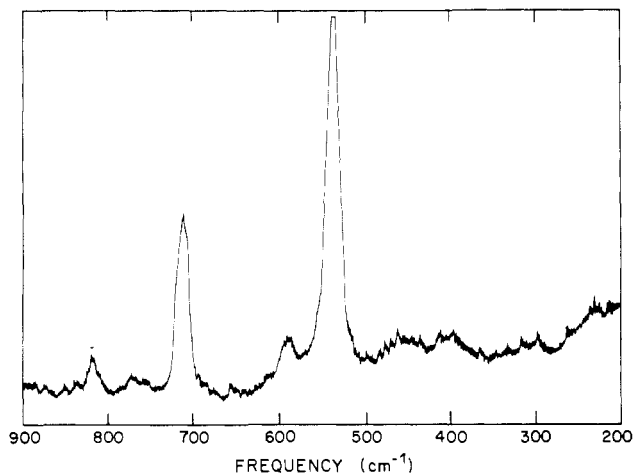
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Table II. Assignments of the Bands Observed in the Resonance Raman Spectra of Sulfur-Ammonia Solutions

Raman band, cm^{-1}			assign
9.4×10^{-3} M	1.3×10^{-1} M	7.7×10^{-1} M	
230 w	230 w		$\nu_2(\text{S}_3^-)$
	396 s ^a	396 s ^a	S_y^{2-}
	442 m ^a	442 m ^a	S_y^{2-}
535 vs	535 w		$\nu_1(\text{S}_3^-)$
571 sh, w	571 sh, m	571 sh, m	$\nu(\text{S-S}_4\text{N}^-)$
592 w	592 s	592 s	$\nu(\text{S-S}_4\text{N}^-)$
710 m	710 vs	710 vs	$\nu_s(\text{SNS}_4\text{N}^-)$
894 w	894 w	894 w	$\nu_{as}(\text{SNS}_4\text{N}^-)$
1070 m ^b			$2\nu_1(\text{S}_3^-)$

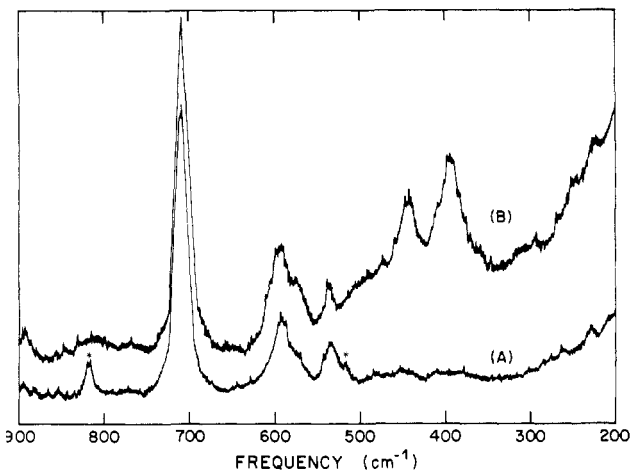
^a Not observed with 600-nm excitation. ^b Only observed with 600-nm excitation.

**Figure 1.** Raman spectrum of a solution of sulfur in liquid ammonia (9.4×10^{-3} M) with 600-nm excitation. Bands due to the laser are marked with an asterisk.

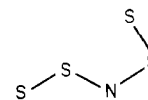
acteristic resonance Raman (RR) spectra.

The Raman spectra of solutions of sulfur in liquid ammonia were recorded at ambient temperature for solutions of varying concentrations (9.4×10^{-3} , 1.3×10^{-1} , and 7.7×10^{-1} M) at excitation wavelengths of 514.5 and 600 nm. These solutions were blue at 23 °C but turned red on cooling to -78 °C. The spectral data are summarized in Table II, and typical spectra are illustrated in Figures 1 and 2. The Raman spectrum of liquid ammonia shows no bands in the region of interest (900–400 cm^{-1}) for identifying polysulfur species.²⁵

As shown in Figure 1, the predominant band in the Raman spectrum of dilute solutions (9.4×10^{-3} M) at 535 cm^{-1} corresponds to the symmetric stretching vibration (ν_1) of S_3^- .^{11,13} For 600-nm excitation, the characteristic overtone progression of this vibration is observed at 1070 cm^{-1} ($2\nu_1$), 1600 cm^{-1} ($3\nu_1$), etc.¹³ A weak band at 230 cm^{-1} can be assigned to the symmetric bending mode (ν_2) of S_3^- .^{11,13} In addition to the bands attributable to S_3^- , a medium intensity band at 710 cm^{-1} and a weak band at 592 cm^{-1} can be assigned

**Figure 2.** Raman spectra of a solution of sulfur in liquid ammonia (1.3×10^{-1} M) with (A) 600-nm and (B) 514.5-nm excitation. Bands due to the laser are marked with an asterisk.

to the S_4N^- ion.¹² These bands correspond to the symmetrical SNS and SS stretching vibrations of this ion, respectively.



For the more concentrated solutions, the intensity of these bands increases dramatically relative to those attributed to S_3^- (see Figure 2), and the latter are absent in the Raman spectrum of the 7.7×10^{-1} M solution (see Table II).

To confirm the above assignments, we obtained the Raman spectrum of $[\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3]^+\text{S}_4\text{N}^-$ in liquid ammonia. In addition to the expected bands at 894 w, 710 s, and 590 m cm^{-1} , a medium intensity band at 692 cm^{-1} was observed and the intensity of the band at ca. 570 cm^{-1} relative to the 590- cm^{-1} band was strongly enhanced compared to its normal intensity in S_4N^- . The S_3N^- anion exhibits Raman bands at 894 m, 686 s, and 574 vs cm^{-1} , and so it appears that this species is formed in ammonia solutions of S_4N^- (cf. formation of S_3N^- by nucleophilic cleavage of one S–S bond in S_4N^- by triphenylphosphine).²⁴ There was no evidence from the Raman spectra, however, for the presence of S_3N^- in sulfur-ammonia solutions. Furthermore, the characteristic Raman bands at 475 m and 218 s cm^{-1} for $c\text{-S}_8^{26}$ were not observed.

As shown in Figure 2, no Raman bands were observed in the 400–500- cm^{-1} region when 600-nm excitation was used. For an exciting frequency of 514.5 nm, however, bands at 442 m and 396 s cm^{-1} were present. By comparison with the Raman spectra of sulfur dissolved in primary amines²⁷ and with the spectra of polysulfide solutions in electron-pair donor solvents,^{13,19} these bands can be tentatively assigned to polysulfides, e.g., S_6^{2-} , S_4^{2-} , and/or S_4^- . It should be noted, however, that the UV-visible spectra of sulfur-ammonia solutions exhibit a band at 430–440 nm but not at ca. 510 nm.^{2,3} On this basis, these Raman bands are more likely due to S_6^{2-} and/or S_4^{2-} rather than S_4^- (see Table I). The assignment of the red species as polysulfide ions S_x^{2-} is consistent with the observation that the 430–440-nm band increases in intensity at low temperatures,^{2,3} since the radical anion S_3^- is known to dimerize on cooling.^{8,19}

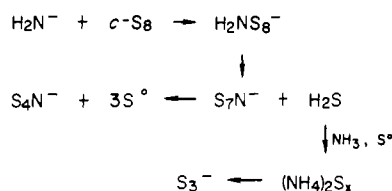
From these results we conclude that the blue color of sulfur-ammonia solutions is due to the presence of both S_4N^- (λ_{max} 580 nm) and S_3^- (λ_{max} ca. 610 nm). The relative importance of these ions is concentration dependent. The for-

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mation of the radical anion, S_3^- , is favored in dilute solutions in which it is undoubtedly formed by dissociation or disproportionation of polysulfides, e.g., S_4^{2-} or S_6^{2-} .⁸ The lack of an ESR signal for S_3^- in more concentrated solutions (10^{-1} M)³ is probably due to dimerization of the radical anions.⁸

In order to explain the formation of the anionic species identified by Raman spectroscopy in this investigation, we propose the following scheme.



The initial step in the cleavage of $c\text{-S}_8$ by nucleophiles (e.g., CN^- , S^{2-} , or Ph_3P)²⁸ is ring opening, and we suggest a similar step for the reaction of $c\text{-S}_8$ with the nucleophile NH_2^- formed by self-ionization of ammonia. Further degradation of the intermediate chain species, H_2NS_8 , by NH_2^- could produce intermediates of the type proposed by Sato and co-workers, i.e., H_2NS_x^- ($x = 1, 2$),⁶ but there is no direct evidence for these species from our spectroscopic studies. We propose that H_2NS_8^- loses H_2S to give the binary sulfur-nitrogen anion S_7N^- , which is known to rearrange to form S_4N^- .¹⁰ Support for this suggestion comes from the observation that S_7NH is formed, albeit in low yield, by the hydrolysis of blue solutions formed by passing ammonia into solutions of sulfur in HMPA.⁷ In the presence of ammonia and sulfur, the H_2S eliminated will form ammonium polysulfides and hence, by dissociation or disproportionation, the radical anion S_3^- .^{8,13,19}

Finally, it seems reasonable to conclude that the S_4N^- ion is one of the reactive nucleophiles in reactions of sulfur-ammonia solutions with organic substrates. Since salts of S_4N^- have recently been prepared and isolated,¹² the nucleophilic behavior of this anion can now be tested.

Acknowledgment. We thank Dr. J. Bojes for a gift of $\text{PPN}^+\text{S}_4\text{N}^-$ and the NSERC (Canada) for financial support.

Registry No. S_8 , 10544-50-0; NH_3 , 7664-41-7; S_3^- , 12597-04-5; S_4N^- , 74273-17-9.

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Enantioselective Displacement Reaction of PPh_3 by Chiral Diphosphines in $(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_2)_2$

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It is believed that chiral complexes containing optically active ligands in which the metal is a chirality center are important in determining the stereochemical course of homogeneous asymmetric reactions catalyzed by transition-metal complexes.¹⁻³ Optically active organometallic compounds of the above type were identified more than a decade ago.⁴

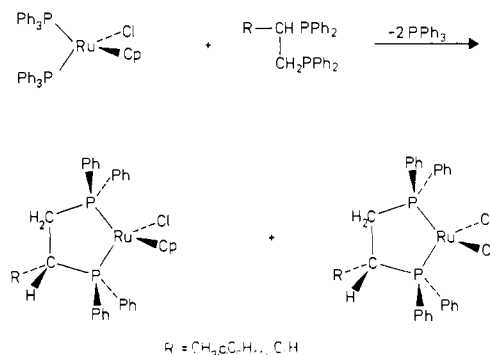
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Table I. ^1H and ^{31}P NMR Data for the Complexes Examined in Toluene- d_8 as the Solvent

complex	δ			$J_{\text{P}_1\text{P}_2}$, Hz	
	$\eta^5\text{-C}_5\text{H}_5^a$	P_1^b	P_2^b		
$\eta^5\text{-CpRuCl}(\text{PPh}_3)_2$	4.05	38.8			
$\eta^5\text{-CpRuCl}(\text{dpe})$	4.55 ^c	79.7			
$\eta^5\text{-CpRuCl}(\text{chiraphos})$	4.29 ^d	84.6	66.5	39.3	
$\eta^5\text{-CpRuCl}(\text{prophos})$ {	d_1^e	4.26	80.9	74.1	30.2
	d_2	4.30	86.4	61.3	36.7
$\eta^5\text{-CpRuCl}(\text{phephos})$ {	d_1	4.18	83.9	66.4	35.7
	d_2	4.13	90.2	58.1	40.0
$\eta^5\text{-CpRuCl}(\text{cyphos})$ {	d_1	4.30	71.0	67.4	36.8
	d_2	4.31	90.0	61.9	36.8

^a $(\text{CH}_3)_4\text{Si}$ as the internal standard. ^b H_3PO_4 85% as the external standard; downfield is positive. ^c In CD_2Cl_2 (see ref 7). ^d In CD_2Cl_2 . ^e $d = \text{diastereomer}$.

Scheme I



However, there are not many examples of kinetic control of the asymmetric induction in the formation of such organo-transition-metal compounds.³

It has recently been reported that 1,2-bis(diphenylphosphino)ethane (dpe) is able to displace triphenylphosphine from $(\eta^5\text{-cyclopentadienyl})\text{chlorobis}(\text{triphenylphosphine})\text{ruthenium(II)}$ (**1**) in boiling benzene^{5,6} or toluene.⁷ In view of our interest in the use of chiral homologues of dpe in asymmetric reactions such as hydroformylation⁸ and cross-coupling^{9,10} and our search for the mode of transmission of the chiral information from the ligand to the substrate, we have studied the displacement reaction of triphenylphosphine from **1** by (+)-(*R*)-1,2-bis(diphenylphosphino)propane (prophos),¹¹ by (-)-(*R*)-1-phenyl-1,2-bis(diphenylphosphino)ethane (phephos),¹² and by (-)-(*S*)-1-cyclohexyl-1,2-bis(diphenylphosphino)ethane (cycphos).¹³ Furthermore, the reaction of **1** with dpe and with (-)-(*2S,3S*)-2,3-bis(diphenylphosphino)butane (chiraphos)¹⁴ has also been investigated as a comparison.

The reactions were carried out in NMR tubes either under vacuum or under nitrogen, with equimolecular amounts of both reagents in toluene- d_8 as the solvent. Products were monitored

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