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The Thio Analogue of Peroxynitrite, $[SSNS]^-$: Preparation, Electronic Structure, Resonance Raman Spectrum, and Formation of Complexes with Nickel and Cobalt

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Abstract: The reaction of triphenylphosphine with $PPN^+S_4N^-$ (or $Ph_4As^+S_4N^-$) in acetonitrile produces the corresponding salts of the S_3N^- ion. The S_3N^- ion is unstable with respect to the formation of S_4N^- in solution or in the solid state on heating or under pressure. The vibrational spectra of the ^{15}N-labeled anion, $S_3{}^*N^-$ ($^*N$ = 30% ^{15}N), suggest an unbranched arrangement of atoms $[SSNS]^-$ but do not distinguish between cis, trans, or helical conformations. Ab initio Hartree–Fock–Slater SCF calculations show that the statistical energy of the cis conformation is lower than that of the trans by ca. 10–20 kcal mol^{-1}. The calculations also show that the ground-state electronic structure of S_3N^- is a 6π-electron system. The strong absorption at 465 nm in the visible spectrum is assigned to a $\pi^* \rightarrow \pi^*$ transition. The resonance Raman spectrum of S_3N^- shows overtone progressions for all three fundamental stretching vibrations and several series of combination bands. The ^{15}N NMR chemical shift of S_3N^- is observed at +617.6 ppm (relative to NH_3(l)). Reaction of $PPN^+S_3N^-$ with $NiBr_2$ or $CoBr_2$ in acetonitrile produces complexes containing the $S_2N_2H^-$ ligand in addition to $M(S_3N)_2$ (M = Ni, Co).

We have recently reported the synthesis and structural characterization of the sulfur–nitrogen anions $S_3N_3^-$, a planar six-membered ring,[1] and S_4N^-, a planar cis–trans chain.[2] In addition, $S_4N_5^-$, first prepared by Scherer and Wolmershäuser,[3] has been shown to have a bicyclic cage structure.[4] These are the only well-characterized binary sulfur–nitrogen anions, although the square-planar complex $(S_4N_3)PtCl$, which is formally a complex of platinum(II) with the terdentate ligand $(SNSNSNS)^-$, has recently been structurally characterized.[5] Complexes of the S_3N^- anion with transition-metal ions of the type $M(S_3N)_2$ (where M = Ni,[6,7] Co,[7,8] Pd,[7,8] Pt,[7,9,10]) have been prepared, and the isolation and structure of $Co(NO)_2(S_3N)$ have been reported.[11] In this complex and in $Pd(S_3N)_2$[12] the S_3N^- ligand is coordinated to the metal in a bidentate fashion via sulfur atoms.

Preliminary attempts to prepare the S_3N^- anion by the reaction of n-$Bu_4N^+S_4N^-$ with triphenylphosphine in THF at room temperature led to the conclusion that the S_3N^- ion is unstable under these reaction conditions.[13] Subsequently, Bojes observed that this reaction produces a solution with a visible absorption band at 470 nm.[14] The deprotonation of S_7NH with sodium hydride also gives the 470-nm species together with S_4N^- (λ_{max} 580 nm) and $S_3N_3^-$ (λ_{max} 360 nm), and it was suggested that this species is a binary anion, $S_xN_y^-$ (where $1 < x/y < 4$).[14]

The discovery that large cations, e.g., PPN^+ ($PPN = Ph_3P{=}N{=}PPh_3$)[1], stabilize binary S–N anions, e.g., $S_4N_5^-$, $S_3N_3^-$, and S_4N^-, has enabled us to isolate the 470-nm species as a crystalline salt and to identify it as the S_3N^- anion.[15] We report here full details of the preparation and infrared, resonance Raman, and ^{15}N NMR spectra of the S_3N^- ion together with the characterization of the products of the reaction of S_3N^- with $NiBr_2$ and $CoBr_2$. In addition, we have carried out ab initio Hartree–Fock–Slater (HFS) SCF calculations for S_3N^- in order to (a) obtain an MO description of the ground-state electronic structure, (b) determine the conformation of lowest energy for this ion, and (c) assign the intense absorption in the visible spectrum to the appropriate electronic transition.

Experimental Section

Materials. S_4N_4[16] and $PPN^+N_3^-$[17] were prepared according to the literature method. Triphenylphosphine (Eastman), $NiBr_2$ and $CoBr_2$ (Alfa, ultrapure), and diethyl ether (Malinckrodt, anhydrous) were commercial samples used as received.

Acetonitrile (reagent grade) was dried by distillation from P_2O_5 followed by distillation from CaH_2. Methylene chloride was freshly distilled from P_2O_5. All distillations of solvents and all reactions were carried out under an atmosphere of nitrogen (99.99% purity) passed through Ridox an silica gel.

The preparation of $PPN^+S_4N^-$ described in the literature[1] was modified and the details are given below.

Elemental analyses were performed by MHW Laboratories, Phoenix, AZ.

Instrumentation. Infrared spectra were recorded as Nujol mulls (CsI windows) on a Perkin-Elmer 467 grating spectrophotometer. UV–vis spectra were obtained with a Cary 219 spectrophotometer. Raman spectra were recoreded on a Jarrell-Ash Model 25-100 double monochromator calibrated with carbon tetrachloride. A Coherent Radiation CR3 argon ion laser was used to produce exciting lines at 457.9, 488.0, and 514.5 nm. Samples were mounted in a 6-cm diameter stainless steel ring on a bed of dry KBr, which was rotated at about 1000 rpm to prevent thermal decomposition. The ^{15}N NMR spectrum was recoreded at 20.266 MHz on a Varian XL-200 spectrometer, using a solution of $PPN^+S_3N^-$ (4×10^{-2} M) containing $Cr(acac)_3$ (ca. 10^{-1} M).[18]

Modified Preparation of $PPN^+S_4N^-$. A slurry of $PPN^+N_3^-$ (1.50 g, 2.58 mmol) and S_4N_4 (0.476, g, 2.58 mmol) in acetonitrile (45 mL) was stirred vigorously for 1.5 h to give a very dark blue-green solution, which was heated at reflux for a further 2 h. The hot, royal blue solution was cooled to −20 °C for ca. 1 h, filtered to remove sulfur, and reduced in

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(1) Chivers, T.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1979**, 752. Chivers, T.; Laidlaw, W. G. Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1980**, *102*, 5773.

(2) Bojes, J.; Chivers, T. *J. Chem. Soc., Chem. Commun.* **1978**, 391. Bojes, J.; Chivers, Laidlaw, W. G.; Trsic, M. *J. Am. Chem. Soc.* **1979**, *101*, 4517.

(3) Scherer, O. J.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 485.

(4) Flues, W.; Scherer, O. J.; Weiss, J.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 379.

(5) Endres, H.; Galantai, E. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 653.

(6) Piper, T. S. *J. Am. Chem. Soc.* **1958**, *80*, 30.

(7) Woollins, J. D.; Grinter, R.; Johnson, M. K.; Thomson, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1910.

(8) Weiss, J.; Thewalt, U. *Z. Anorg. Allg. Chem.* **1966**, *346*, 234.

(9) Haworth, D. T.; Lin, G. Y. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1838.

(10) Butler, I. S.; Sawai, T. *Can. J. Chem.* **1977**, *55*, 3838.

(11) Herberhold, M.; Haumaier, L.; Schubert, U. *Inorg. Chim. Acta* **1981**, *49*, 21.

(12) Weiss, J.; Neubert, H. S. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1966**, *21B*, 286.

(13) Chivers, T.; Drummond, I. *Inorg. Chem.* **1974**, *13*, 1222.

(14) Bojes, J. Ph.D. Thesis, University of Calgary, 1978.

(15) For a preliminary communication of part of this work, see: Bojes, J.; Chivers, T. *J. Chem. Soc. Chem. Commun.* **1980**, 1023.

(16) Villena-Blanco, M.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 98.

(17) Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84.

(18) Chivers, T.: Oakley, R. T.; Scherer, O. J.; Wolmershäuser, G. *Inorg. Chem.* **1981**, *20*, 914.

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volume to ca. 15 mL. The solution was then kept at ca. −20 °C to complete the precipitation of $PPN^+S_4N^-$. The cold slurry was quickly filtered in air on a medium-porosity glass frit, and the purple, microcrystalline produce was washed with toluene (2 × 80 mL) and *n*-pentane (2 × 80 mL) and stored under nitrogen. The yield of $PPN^+S_4N^-$ was 1.35 g (77% based on S).

Preparation of $PPN^+S_3N^-$. Triphenylphosphine (0.728 g, 2.78 mmol) was added to a stirred, royal blue solution of $PPN^+S_4N^-$ (1.35 g, 1.98 mmol) in acetonitrile (30 mL). Within 2 min the color of the solution became orange. Slow addition of diethyl ether (ca. 150 mL) precipitated a bright orange microcrystalline solid, which was washed with CH_3CN/Et_2O (1:5, 20 mL) and then Et_2O (25 mL) to give analytically pure $PPN^+S_3N^-$ (0.73 g, 1.13 mmol). Anal. Calcd for $C_{36}H_{30}N_2P_2S_3$: C, 66.64; H, 4.67; N, 4.32; P, 9.55; S, 14.82. Found: C, 66.50; H, 4.52; N, 4.23; P, 10.06; S, 14.10.

$Ph_4As^+S_3N^-$ was prepared from $Ph_4As^+S_4N^-$ and triphenylphosphine by a similar procedure. Anal. Calcd for $C_{24}H_{20}AsNS_3$: C, 58.40; H, 4.09; N, 2.84. Found: C, 58.17; H, 3.91; N, 2.61.

Crystals of $PPN^+S_3N^-$ or $Ph_4As^+S_3N^-$ suitable for X-ray crystallography were grown by cooling solutions in CH_3CN/Et_2O (1:4) to −20 °C for 2–4 h in the presence of triphenylphosphine sulfide. If the solutions were left to stand for a longer time, or in the absence of Ph_3PS, the blue color of S_4N^- beecame apparent.

$PPN^+S_3{*}N^-$ (*N = 30% ^{15}N) was prepared from $PPN^+S_4{*}N^-$[18] and triphenylphosphine by the same procedure as described above for the unlabeled compound.

Reaction of $PPN^+S_3N^-$ with Nickel(II) Bromide. A clear, orange solution of $PPN^+S_3N^-$ was generated from $PPN^+S_4N^-$ (1.00 g, 1.47 mmol) and triphenylphosphine (0.540 g, 2.06 mmol) in acetonitrile (30 mL). Solid $NiBr_2$ (0.55 g, 2.52 mmol) was added to this solution, which immediately became royal blue and then turned dark red after stirring for several min. After 2 h at reflux, solvent was removed in vacuo from the reddish-black solution to give a dark oily residue, which was extracted with toluene (ca. 500 mL).

The toluene solution was reduced in volume to ca. 25 mL, and the products were separated by chromatography on a silica gel column (60–200 mesh; 50 × 3.5 cm). A green and a red fraction were obtained with toluene as the eluant, and a third, purple fraction was eluted with $CH_2Cl_2/MeOH$ (1:1).

Removal of solvent from the green solution produced feathery, black crystals of $Ni(S_3N)_2$ (0.065 g, 0.23 mmol, 31% based on N) identified by its infrared and visible spectra. The infrared spectrum showed bands at 989 s, 730 s, 717 vs, 537 m, 525 s, 506 w, 493 vw, 395 vw, 361 vw, 330 s, 311 w, 299 vw, 290 vw, 271 w cm^{-1}, in good agreement with the values reported in the literature.[7] The visible spectrum (cyclohexane) showed bands at ca. 720, 645, and 420 sh nm (cf. lit. 720, 651, 425 sh nm).[6]

Removal of solvent from the red solution gave $Ni(S_2N_2H)(S_3N)$ (0.015 g, 0.06 mmol), which had bands in the infrared spectrum at 3160 m, 1220 w, 1042 sh, 1035 m, 968 m, 961 m, 885 m, 723 vs, 710 vs, 630 w, 600 w, 527 ss, 502 w, 465 vw, 395 w, 332 m, 320 vw, 316 vw, 297 w, 285 w cm^{-1}, in excellent agreement with the literature values.[7] The visible spectrum (EtOH) showed bands at 725, 540, and 467 nm (cf. lit. 540 and 467 nm).[6]

Removal of solvent from the purple fraction gave a sticky dark black solid (0.034 g), which was difficult to purify. The visible spectrum (EtOH) showed bands at 561 and 403 nm (cf. lit. values of 563 and 405 nm for $Ni(S_2N_2H)_2$.[6]

Reaction of $PPN^+S_3N^-$ with Cobalt(II) Bromide. Solid $CoBr_2$ (0.50 g, 2.29 mmol) was added to a stirred orange solution of $PPN^+S_3N^-$ prepared from $PPN^+S_4N^-$ (1.16 g, 1.70 mmol) and triphenylphosphine (0.626 g, 2.39 mmol) in acetonitrile (30 mL). The solution, which became a dark green-black color immediately, was heated at reflux for 1 h. Solvent was removed in vacuo, and the sticky black residue was extracted with toluene (ca. 500 mL) to give a dark green solution. The volume of this solution was reduced to ca. 20 mL and TLC revealed the presence of three components: olive green, bright green, and violet. Chromatography on a silica gel column (60–200 mesh, 50 × 3.5 cm), with toluene as the eluant, gave two green fractions, but the violet fraction decomposed on the column.

Removal of solvent from the olive green fraction gave black crystals of $Co(S_3N)_2$ (ca. 7 mg) identified by its infrared spectrum, which showed bands at 960 sh, 947 m, 719 sh, 704 s, 530 sh, 523 w, 515 w, 382 w, 332 w, 324 w, 315 sh, 308 sh, 281 w cm^{-1}, in close agreeent with the values reported in the literature.[7] The visible spectrum (toluene) exhibited a broad band at ca. 600 nm with a shoulder at ca. 700 nm, consistent with the spectrum given in the literature.[7]

The second green fraction yielded insufficient material for a proper identification. However, previous workers have identified the second green and violet fractions obtained from the chromatographic separation of the products of the S_4N_4/cobalt(II) halide reaction in methanol as $Co(S_2N_2H)(S_3N)$ and $Co(S_2N_2H)_2$, respectively.[7,19]

Table I. Vibrational Frequencies (cm^{-1}) and Tentative Assignments for the S_3N^- and S_4N^- Ions[a]

S_3N^-		S_4N^-		
IR[b]	Raman[c]	IR[b]	Raman[c]	assignments
*893 vs	*894 m	*893 w	*892 w	ν_{as}(SNS)
*666 s	*686 s	*711 m	*710 vs	ν_s(SNS)
		594 s	592 s	ν(S–S)
564 s	574 vs	567 vs	570 s	ν(S–S)

[a] Bands marked with an asterisk show satellites resulting from the presence of ^{15}N in the spectra of $PPN^+S_3{*}N^-$ and $PPN^+S_4{*}N^-$ (*N = 30% ^{15}N). [b] Infrared spectra were recorded as Nujol mulls. [c] Raman spectra were measured on solid samples prepared as KBr disks mounted in a 6-cm stainless steel rim and rotated at 1000 rpm.

Theoretical Method. The single determinant closed-shell description of S_3N^- has been obtained by using the HFS procedure with the frozen core option ($1s^2$ for nitrogen and $1s^22s^22p^6$ for sulfur) as described by Baerends and co-workers.[20] The double Slater type basis set described by Clementi and Roetti was employed, augmented with a 3d orbital on sulfur.[21]

Results and Discussion

Preparation of S_3N^-. The reaction of triphenylphosphine with $PPN^+S_4N^-$ or $Ph_4As^+S_4N^-$ in acetonitrile proceeds rapidly at room temperature to give a clear orange solution, from which pure $PPN^+S_3N^-$ or $Ph_4As^+S_3N^-$ is precipitated by the addition of diethyl ether. However, the reaction is not as straightforward as eq 1 would suggest.

$$Ph_3P + S_4N^- \rightarrow Ph_3PS + S_3N^- \qquad (1)$$

The optimum molar ratio for maximizing the yield of S_3N^- was found to be ca. 1.4:1 (Ph_3P/S_4N^-), and all of the triphenylphosphine was converted to triphenylphosphine sulfide. Thus it appears that S_3N^- itself reacts slowly wiith triphenylphosphine, but we have been unable to identify the S–N product of this reaction. Furthermore, it was observed that redissolving $PPN^+S_3N^-$ in acetonitrile led to the formation of blue solutions (λ_{max} 580 nm) even at −50 °C, presumably due to the reaction of S_3N^- with itself to form S_4N^-. Indeed, it was only possible to grow crystals of $PPN^+S_3N^-$ (or $Ph_4As^+S_3N^-$) from solutions in acetonitrile *containing Ph_3PS*.

In the solid state, $PPN^+S_3N^-$ exhibits moderate air and thermal stability. For example, only a trace of sulfoxy anions could be detected by infrared spectroscopy after a sample of $PPN^+S_3N^-$ was exposed to air for several hours. On heating the sample darkens at 80–100 °C and becomes royal blue at ca. 150 °C due to the formation of S_4N^-. The transformation of S_3N^- to S_4N^- can also be brought about by subjecting solid samples to high pressures (vide infra).

Vibrational Spectra of S_3N^-. Various structural alternatives for the S_3N^- ion should be considered, e.g., branched chain (**1**) (cf. the isoelectric CS_3^{2-} ion[22]), planar open-chain (cis (**2**) or trans (**3**)), nonplanar open-chain (helical (**4**)), and cyclic (planar (**5**) or bent (**6**)). The vibrational spectra of S_3N^- and the ^{15}N-labeled ion $S_3{*}N^-$ (*N = 30% ^{15}N) are helpful in narrowing down these possibilities.

The observed vibrational frequencies are compared in Table I with the corresponding data for S_4N^- and $S_4{*}N^-$.[1] Bands are

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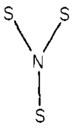
(19) Daum, K. W.; Goehring, M.; Weiss, J. *Z. Anorg. Allg. Chem.* **1955**, *278*, 260.

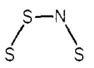
(20) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. (b) Baerends, E. J.; Ros, P. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1978**, *12*, 169.

(21) (a) Clementi, E.; Roetti, C. *At. Data Nucl. Data Tables* **1974**, *14*, 177. (b) Laidlaw, W. G.; Trsic, M. *Chem. Phys.* **1979**, *36*, 323.

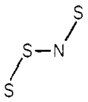
(22) Gattow, G.; Behrendt, W. "Carbon Sulphides and Their Inorganic Complex Chemistry"; Senning, A., Ed.; Georg Thieme Publishers: Stuttgart, **1977**; p 167.



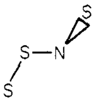
1, D_{3h}



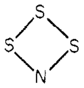
2, C_s



3, C_s



4, C_1



5, C_{2v}

6, C_s

observed at ca. 890, 710, 595, and 570 cm^{-1} in the infrared and Raman spectra of S_4N^-. The strong bands at 595 and 570 cm^{-1} do not exhibit satellites in the Raman spectrum of $S_4{}^*N^-$ ($^*N$ = 30% ^{15}N) and have therefore been assigned to stretching vibrations of the unequal S–S bonds in the anion. The S_3N^- anion has bands at 893 vs, 666 s, and 564 s cm^{-1} in the infrared spectrum and at 894 m, 686 s, and 574 vs cm^{-1} in the Raman spectrum.[23] The former two bands show satellites due to the presence of ^{15}N in the Raman spectrum of $S_3{}^*N^-$ and are thus attributed to S–N vibrations while the very strong band at 574 cm^{-1} remains as a single peak, which can be assigned to a S–S vibration, consistent with the cleavage of one S–S bond in S_4N^- by triphenylphospine.

Thus the vibrational spectra appear to rule out structures **1**, **5**, and **6** and suggest an SSNS$^-$ arrangement of atoms, i.e., the S_3N^- ion should be regarded as the thio analogue of peroxynitrite.[24] However, these data do not allow a distinction to be made between the alternatives **2**, **3**, or **4**.[25]

Electronic Structure and Bonding in S_3N^-. To continue the characterization of S_3N^-, we normally carry out HFS SCF molecular orbital calculations by using the geometry as determined by X-ray crystallography. However, in the present case attempts to obtain a single-crystal analysis of S_3N^- have been thwarted by disorder problems. At best the Ph_4As^+ salt has yielded to analysis only in terms of a model in which the S_3N^- anion exists in a nearly planar cis conformation, which exhibits 4-fold disorder.[26] Unforntunately, refinement of the model has not yielded accurate structural parameters. In the absence of accurate structural parameters for the cis conformer, we have assumed values for bond lengths and angles similar to those for S_4N^-, viz., d(S–N) = 1.60 Å; d(S–S) = 1.90 Å; SSN = 110°; SNS = 120°.[1,27] Table II and Figure 2 contain the results of our HFS SCF calculations for this system.[28]

As the results in Table II indicate, there are three σ bonding orbitals, 1a′, 2a′, 3a′, and two σ antibonding orbitals, 4a′ and 9a′. The antibonding character of the HOMO, 9a′, is particularly strong in the region of the central bond, $N-S_2$, and as a result the overlap population (0.17) implies a rather weak ($^1/_3$) σ bond for this linkage whereas the overlap populations (0.33 and 0.40) suggest a more significant ($^2/_3$) σ bond character for the S_1-N and S_2-S_3 linkages, respectively. In addition there are two well-developed lone pairs, 5a′ and 8a′, on the terminal sulfurs and two essentially nonbonding orbitals, 6a′ and 7a′, associated with the central $N-S_2$ linkage.

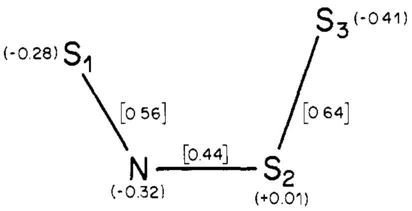


Figure 1. Overlap populations in brackets and atomic charges in parentheses for *cis*-S_3N^-.

The characteristics of the π orbitals are what one might expect: the lowest, 1a$_1''$, is strongly bonding to the central $N-S_2$ linkage, the next π orbital, 2a″, is strongly bonding to the two terminal bonds and mildly antibonding to the central bond, while the highest occupied π MO, 3a″, plays an opposite role to 2a″, being mildly bonding to the central region and rather strongly antibonding to the terminal bonds, particularly S_2-S_3. The resulting π overlap populations of 0.23 and 0.27 suggest a $^1/_2\pi$ bond for each of the S_1-N and $N-S_2$ linkages,[25] whereas the overlap population of 0.14 indicates a much weaker π contribution to the S–S linkage. The lowest unoccupied π orbital, 4a″, is, of course, antibonding to all linkages and, unlike the 3a″, there is as heavy involvement of the nitrogen center.

In summary, the S–S linkage in S_3N^- is primarily a σ bond whereas there is a strong π contribution to the S_1NS_2 region. The total overlap populations are similar to those found for the S–S and S–N linkages in S_4N^-,[1] although the value for the internal SN linkage of 0.45 is significantly less than the 0.53–0.55 found in S_4N^- and indicates a slightly weaker bond.

The charge distribution calculated for the cis conformer (Figure 1) shows that the terminal sulfurs both carry a significant negative charge whereas the internal sulfur is essentially neutral.[29] As expected the nitrogen center is also negative. Perhaps the most striking feature is the relatively large value of the negative charge on S_1(–0.28) and on the adjacent nitrogen (–0.32). This is in contrast to the charge alternation found for S_4N^-,[1] and reflects on the one hand the propensity of the terminal sulfurs to carry a portion of the excess charge[30] and on the other hand the ability of nitrogen to accommodate electron density. As in S_4N^-, the polarity of the S–S bond in S_3N^- is consistent with the relatively high intensity of the S–S stretching vibration in the infrared spectrum (vide supra).

The charge associated with each center can be partitioned into σ and π contributions. As a reference we assume that each of the terminal sulfurs would normally contribute only one electron to the π network, with the remaining five valence electrons being associated with the σ network or remaining as lone pairs on sulfur. Further one would also assert that the internal sulfur would contribute two electrons to the π network and would retain four valence electrons for the σ network or as lone pairs. With this in mind it is clear from the calculated charges (see Table II) that the terminal sulfurs have lost σ electrons to the central linkage (e.g., for S_1 the loss is 5 – 4.76 = 0.24; for S_3 the loss is 5 – 4.75 = 0.25) while for S_2 there is a gain (given by 4 – 4.33 = –0.33). At the same time it is evident that the terminal sulfurs are carrying an excess of π charge (e.g., for center S_1 the excess is given by 1 – 1.52 = –0.52; for center S_3 the excess is 1 – 1.66 = –0.66, while for center S_2 there is a formal loss of π electrons given by 2 – 1.66 = +0.33). In summary, there is a strong (over 0.5 electron) movement of π electrons toward the terminal sulfurs while there is a weaker (0.25 electron) movement of σ nonbonding electrons in the opposite direction. Consequently the net charge on sulfur centers is a balance of opposing trends; without the

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[23] A simple rationalization of the displacement of the 666- and 564-cm^{-1} bands in the infrared spectrum to respectively 686 and 574 cm^{-1} in the Raman is not apparent to us.

[24] Johnson, D. K.; Wasson, J. R. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 891. On the basis of semiempirical extended Hückel MO calculations, these authors concluded that S_3N^- with D_{3h} geometry would only exist as a transient intermediate.

[25] The helical structure (**4**) cannot be discounted on the basis of the vibrational spectra. however, the *planar* structures (**2** or **3**) are considered to be more likely alternatives by analogy with S_4N^-. Certainly, as pointed out in the analysis of bonding (cf. section Electronic Structure and Bonding), the strong π bonding of the central NS linkage would be lost on going to a nonplanar structure.

[26] Cordes, A. W.; Sweptson, P. N. Department of Chemistry, University of Arkansas, Fayetteville, AR, private communication.

[27] Burford, N.; Chivers, T.; Cordes, A. W.; Oakley, R. T.; Pennington, B.; Swepston, P. N. *Inorg. Chem.* **1981**, *20*, 4430.

[28] We have also performed some calculations on a trans conformer with the same bond lengths and angles. We find that the energy of this system is some 10–20 kcal mol^{-1} higher than that of the cis conformer—adding to the X-ray evidence that cis is the preferred conformer. A word of caution is necessary though, since this energy difference may well be near the limit of accuracy of the method employed.

[29] The charges calculated for the trans conformer are similar, viz. $q_{S_1} = -0.32$, $q_N = -0.33$, $q_{S_2} = 0.08$, $q_{S_3} = -0.43$, as are the overlap populations $P_{S_1N} = 0.48$, P_{NS_2} 0.40, $P_{S_2S_3} = 0.65$.

[30] Laidlaw, W. G.; Trsic, M. *Int. J. Quant. Chem.* **1980**, *17*, 969.

Table II. Overlap Populations for *cis*-S_3N^- [a]

designation (C_s symmetry)	principal MO function	orbital overlap populations				self-atom orbital overlap populations			
		ϵ_j, au	NS_1	NS_2	S_2S_3	N	S_1	S_2	S_3
1a′	σ_{NS_2}	−0.654	0.061	0.104	0.015	0.376	0.057	0.160	0.015
2a′	$\sigma_{S_2S_3}$	−0.497	0.067	−0.026	0.113	0.120	0.124	0.307	0.196
3a′	σ_{NS_2}	−0.392	0.019	0.076	0.018	0.138	0.259	0.152	0.260
4a′	σ^*	−0.239	−0.044	−0.044	−0.036	0.171	0.335	0.380	0.365
5a′	$1pS_1$	−0.173	0.003	−0.001	0.011	0.224	0.429	0.159	0.143
1a″	π_{NS_2}	−0.148	0.038	0.071	0.029	0.261	0.077	0.308	0.038
6a′	nb	−0.144	0.021	0.039	0.005	0.208	0.075	0.331	0.231
7a′	nb	−0.052	0.011	−0.036	−0.003	0.346	0.225	0.314	0.204
2a″	$\pi_{S_2S_3}$, π_{NS_1}	−0.045	0.050	−0.033	0.075	0.159	0.233	0.210	0.284
8a′	$1pS_3$	0.009	0.002	0.001	0.012	0.137	0.015	0.068	0.788
3a″	$\pi^*_{S_2S_3}$	0.032	−0.031	0.029	−0.069	0.045	0.409	0.239	0.466
9a′	$\sigma^*_{NS_2}$, $\sigma^*_{NS_1}$	0.058	−0.058	−0.069	−0.011	0.251	0.854	0.200	0.070
4a″	π^*	0.111	−0.071	−0.075	−0.069	0.437	0.355	0.367	0.238
			total overlap			electrons (net charges)			
	π		0.23	0.27	0.14	1.16 (−0.16)	1.52 (−0.52)	1.66 (+0.34)	1.66 (−0.66)
	σ		0.33	0.17	0.40	4.16 (−0.16)	4.76 (+0.24)	4.33 (−0.33)	4.75 (+0.25)
	total σ and π		0.56	0.44	0.54	5.32 (−0.32)	6.28 (−0.28)	5.99 (+0.01)	6.41 (−0.41)

[a] See Figure 1 for numbering scheme.

"back-donation" of the σ network, the charge due to the more labile π electrons would be much more pronounced. Nitrogen, as expected, carries an excess of *both* π electrons ($1 - 1.16 = -0.16$) and σ nonbonding electrons ($4 - 4.16 = -0.16$).

Before leaving this discussion of charge, we should remark that judging strictly from distribution of electrons one should assert that the π electrons of the S–S linkage are not polarized (there are 1.66 π electrons on both center S_2 and center S_3). However, as the foregoing analysis shows, this π distribution is certainly distorted from the reference point of 2 π electrons on S_2 and 1 π electron on S_3. Thus, the final π distribution for S_2–S_3 is symmetrical (i.e., not polarized), but this should not be taken to imply that there has been no redistribution of the electrons. The π electron distribution for the S_1N and S_2N region are both polarized toward the terminal sulfur, but care must be exercised in interpreting this as paralleling the redistribution of π electrons.

The oscillator strength for the $\pi^* \rightarrow \pi^*$ transition (3a″ → 4a″) and for the $n \rightarrow \pi^*$ (9a′ → 4a″) transition were calculated,[31] and the former is favored by a factor of 10^5. We might also remark that the oscillator strengths for the $\pi^* \rightarrow \pi^*$ transition in S_3N^- is about half that calculated for this transition in S_4N^-, a result supported by the fact that the measured absorption is less intense in S_3N^- than it is for S_4N^-. By use of a method proposed by Ziegler et al.,[32] λ_{max} of the $\pi^* \rightarrow \pi^*$ transition, depicted in Figure 2, was calculated to be 468 nm while λ_{max} for the same transition of the trans conformer was found to be 515 nm. Certainly the experimental λ_{max} of 465 nm lies quite close to that calculated for the cis conformer.

In summary, the ab initio HFS calculations indicate that S_3N^- is a six π-electron system; the cis conformation is lower in energy than the trans,[28] the internal S–N bond is somewhat weaker than in the related S_4N^- system, and finally the 465-nm band observed in the visible spectrum appears to be a $\pi^* \rightarrow \pi^*$ transition of lower intensity than the band observed at 580 nm for S_4N^-.

Resonance Raman Spectrum of S_3N^-. The Resonance Raman (RR) spectrum of $PPN^+S_3N^-$ is illustrated in Figure 3. An interesting result of this study was the detection of S_4N^- formed from S_3N^- in the solid state under pressure, via the RR technique. Samples of $PPN^+S_3N^-$ for Raman studies were prepared as KBr disks. When a pressure of ca. 1 ton was used, a bright orange disk, which displayed only S_3N^- Raman lines, was obtained. However, if the pressure significantly exceeded 1 ton, dark spots were observed in the orange disk, and the Raman spectrum exhibited bands due to to the S_4N^- ion whose relative intensity (compared to the S_3N^- bands) was greatly enhanced when 600-nm excitation was employed due to the RR effect. Thus, the RR technique can be used to detect the presence of small amounts

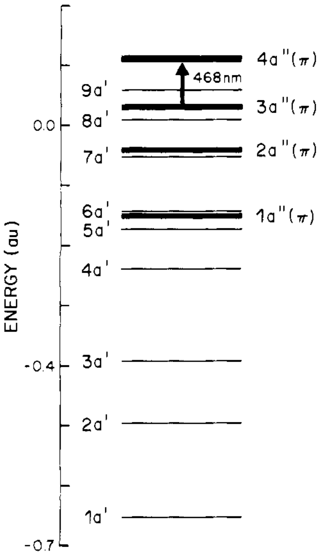

Figure 2. Orbital energy level diagram for *cis*-S_3N^- showing the π^*(3a″) → π^*(4a″) transition. The π orbitals are represented by thick lines. The HOMO is 9a′ and the LUMO is 4a″.

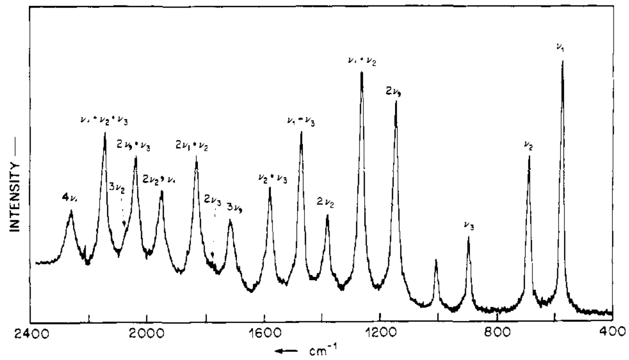

Figure 3. Resonance Raman spectrum of $PPN^+S_3N^-$ obtained with 488-nm excitation. The fundamental vibrations ν_1, ν_2, and ν_3 are tentatively assigned to ν(S–S), ν_s(SNS), and ν_{as}(SNS), respectively.

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(31) Trsic, M.; Ziegler, T.; Laidlaw, W. G. *Chem. Phys.* **1976**, *15*, 383.

(32) Ziegler, T.; Rauk, A.; Baerends, E. J. *Theor. Chim. Acta* **1977**, *46*, 1.

of S_4N^- (λ_{max} 585 nm) in the presence of S_3N^- (λ_{max} 465 nm) by choosing the appropriate excitation frequency. This result is reminiscent of RR studies of polysulfur radical anions, which allow the detection of S_2^- (λ_{max} ~400 nm) in the presence of S_3^- (λ_{max} ~600 nm).[33]

As indicated in Figure 3, the RR spectrum of S_3N^- is characterized by overtone progressions for all three fundamental stretching vibrations of the anion. For the S–S stretching vibration at 570 cm^{-1}, the progression can readily be observed up to the fourth overtone. These results suggest that the electronic transition at 465 nm is to a molecular orbital that is delocalized over all four atoms of the S_3N^- anion, as indeed is the case for the LUMO, 4A″ (see Table II). In addition to the overtone progressions, a number of combination bands are observed in the RR spectrum of S_3N^-.

^{15}N NMR Spectrum of S_3N^-. The ^{15}N NMR spectrum of $S_3{}^*N^-$ ($^*N$ = 30% ^{15}N) exhibits a signal at +617.6 ppm (ref $NH_{3(l)}$ at 25 °C. The corresponding values for other binary sulfur–nitrogen anions are 138.7 (4 N) and 53.3 (1 N) ($S_4N_5^-$), 148.4 ($S_3N_3^-$) and 244.2 ppm (S_4N^-).[18,34] The remarkable difference in shifts for the S_3N^- and S_4N^- ions is worthy of comment, but it should be noted that the internal nitrogen in $Ph_3P{=}NS{\it N}SS$ is also strongly deshielded (σ = +472.0 ppm).[18]

It is well-known that the contribution of the dominant paramagnetic term, σ_p, to ^{15}N chemical shifts is very sensitive to changes in electronic structure.[35,36] This term will contribute to the deshielding of the nitrogen nucleus if (a) low-lying excited states involving electrons at nitrogen are available, (b) electrons are in orbitals with larger σ character, or (c) multiple bonding to nitrogen is present, leading to an increased charge density on nitrogen. Certainly conditions a and c are met for both S_3N^- and S_4N^-. however is is evident from previous NMR data for S–N compounds that a simple correlation of ^{15}N chemical shift is not to be expected.[18]

Reactions of S_3N^- with Transition-Metal Halides. The reaction of transition-metal halides with S_4N_4 in methanol at reflux produces very low yields of complexes of the type $M(S_3N)_2$ (M = Ni,[6] Pd[8]). Recently, improvements in the preparative and purification procedures were described,[7] but the yields of nickel and palladium complexes were still low.[7] The cobalt and platinum complexes could not be obtained pure by this route but were prepared by disproportionation of $M(S_2N_2H)(S_3N)$ complexes.[7] The latter, together with $M(S_2N_2H)_2$, are the major products of the reaction of S_4N_4 with transition-metal halides in methanol.[6–10]

The isolation of salts of the S_3N^- ion allows the possibility of preparing $M(S_3N)_2$ complexes by the direct reaction of these salts with transition-metal halides. We have investigated this possibility for the transition metals Ni, Co, Pd, and Pt, for which $M(S_3N)_2$ complexes are known. The reaction of $PPN^+S_3N^-$ with nickel(II) bromide in acetonitrile was carried out under a variety of reaction conditions, and the optimum yield of $Ni(S_3N)_2$ was ca. 30%, which represents a significant improvement over existing syntheses.[7] The reactions of $PPN^+S_3N^-$ with other transition-metal halides (Co, Pd, Pt) were less successful. In the case of cobalt, the complex $Co(S_3N)_2$ was formed and identified spectroscopically (infrared and visible spectra), but it was not possible to obtain an analytically pure sample. For palladium and platinum, however, we found no evidence for the formation of $M(S_3N)_2$ complexes.

Recently, we have reported the preparation of the following complexes of Cu(I) with the S_3N^- ion: $PPN^+[Cu(S_3N)_2]^-$, $PPN^+[ClCu(S_3N)]^-$, and $(Ph_3P)_2\,Cu(S_3N)$ by the direct reaction of $PPN^+S_3N^-$ with copper halides in acetonitrile.[38] The S_3N^- ligand in these complexes is coordinated to the metal in a cis bidentate fashion through sulfur atoms, cf. $Pd(S_3N)_2$[12] and $Co(NO)_2(S_3N)$[11].

A surprising feature of this investigation of the reactions of S_3N^- with nickel and cobalt halides was the isolation or detection of complexes of the $S_2N_2H^-$ ion, viz., $M(S_2N_2H)(S_3N)$ and $M(S_2N_2H)_2$. These products are obtained in much lower yields than in the S_4N_4 transition-metal halide reactions[5–9] (vide supra), but their formation suggests that the S_3N^- ion is the source of $S_2N_2H^-$ in these systems. We are attempting to verify this proposal by experiments designed for the isolation of salts of $S_2N_2H^-$ with large cations.

Conclusions

The novel anion S_3N^- is readily obtained as a PPN^+ or Ph_4As^+ salt by the reaction of S_4N^- with triphenylphosphine in acetonitrile. Vibrational spectra suggest that the anion has an unbranched structure $[SSNS]^-$. MO calculations indicate a cis conformation for the ion for which the ground-state electronic configuration is a 6π-electron system. Complexes containing the $S_2N_2H^-$ ligand are formed, in addition to $M(S_3N)_2$, when S_3N^- reacts with certain transition-metal halides in acetonitrile.

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Registry No. $PPN^+S_3N^-$, 76468-84-3; $Ni(S_3N)_2$, 13782-36-0; $Co(S_3N)_2$, 13782-15-5; $PPN^+S_4N^-$, 74273-18-0; $Ph_4As^+S_3N^-$, 76341-49-6; S_4N_4, 28950-34-7; $PPN^+N_3^-$, 38011-36-8; $Ph_4As^+S_4N^-$, 79233-89-9.

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[33] Clark, R. J. H.; Cobbold, D. G. *Inorg. Chem.* **1978**, *17*, 3169 and references cited therein.

[34] The ^{15}N chemical shift of S_4N^-, measured in CH_3CN, is 244.2 ppm; the value of 212.8 ppm quoted in ref 18 is in error: Oakley, R. T., private communication.

[35] Mason, J. *Chem. Rev.* **1981**, *81*, 205.

[36] Levy, G. C.; Lichter, R. L. "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy"; Wiley-Interscience: New York, 1979.

[37] The yields of these complexes, as described in ref 7, are as follows: S_4N_4 (10 g) + $NiCl_2$ (12 g) $\rightarrow$ $Ni(S_3N)_2$ (0.009 g); S_4N_4 (14 g) + $PdCl_2$ (10 g) + NH_4Cl (5 g) $\rightarrow$ $Pd(S_3N)_2$ (0.065 g).

[38] Bojes, J.; Chivers T.; Codding, P. W. *J. Chem .Soc., Chem. Commun.* **1981**, 1171.