Synthesis and Spectroscopic Characterization of the S_3N^- Ion

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Summary The reaction of S_4N^- with triphenylphosphine in acetonitrile produces S_3N^- which reacts with $NiCl_2$ to give $Ni(S_3N)_2$, vibrational spectra of $S_3{}^*N^-$ ($^*N = 30\%$ ^{15}N) suggest an $^-S{-}N{=}S{=}S$ arrangement of atoms in the anion

THREE binary sulphur–nitrogen anions have been structurally characterized the bicyclic cage, $S_4N_5{}^-$,[1] the planar six-membered ring, $S_3N_3{}^-$,[2] and the planar *cis–trans* chain, S_4N^- [3] We have found that the reaction of S_4N^- with triphenylphosphine in acetonitrile produces the S_3N^- anion We report here the synthesis and spectroscopic characterization of this new binary sulphur–nitrogen anion

When $PPN^+S_4N^-$ [0 500 mmol, PPN = $(Ph_3P)_2N$] is treated with triphenylphosphine (1·00 mmol)† in acetonitrile (10 ml) at 23 °C the deep blue solution immediately becomes orange Slow addition of diethyl ether (40 ml) to the reaction mixture followed by cooling to −20 °C for 6 h produces orange crystals of $PPN^+S_3N^-$ (0·26 mmol, 52%) ‡ $Ph_4As^+S_3N^-$ can be prepared in a similar manner Removal of solvent from the filtrate followed by extraction with diethyl ether yields pure triphenylphosphine sulphide

The u v -vis spectrum of solutions of S_3N^- in CH_2Cl_2 shows a smooth absorption band at 465 nm but the solutions rapidly become dark blue owing to the formation of S_4N^- (λ_{max} *ca* 580 nm) [3] This conversion of S_3N^- into S_4N^- was also observed in the solid state during the preparation of KBr discs for the rotating Raman sample holder when the pressure exceeded 4×10^7 Pa

The vibrational spectra of S_3N^- are informative in comparison with the corresponding spectra of S_4N^-, which show bands at *ca* 890, 710, 590, and 565 cm^{-1} [3] Since the strong bands at 590 and 565 do not exhibit satellites in the Raman spectrum of $S_4{}^*N^-$ ($^*N = 30\%$ ^{15}N), they have been attributed to stretching vibrations of the unequal S–S bonds in this anion [3] The S_3N^- anion has bands at 893vs, 666s, and 564s cm^{-1} in the i r spectrum and at 894 m, 686s, and 574vs cm^{-1} in the Raman spectrum The former two bands show satellites owing 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 an S–S vibration (see the Figure) Thus, in contrast with the well established branched structure

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† In an attempt to determine the exact stoicheiometry of the reaction a solution of Ph_3P in MeCN was titrated against a solution of $PPN^+S_4N^-$ in MeCN Taking the persistence of an orange colour as the end point values of the molar ratio in the range 1 27—1 45 1 were obtained We attribute the need to use an excess of Ph_3P to the slow reaction of S_3N^- with Ph_3P

‡ Complete analytical data are in good agreement with this formula

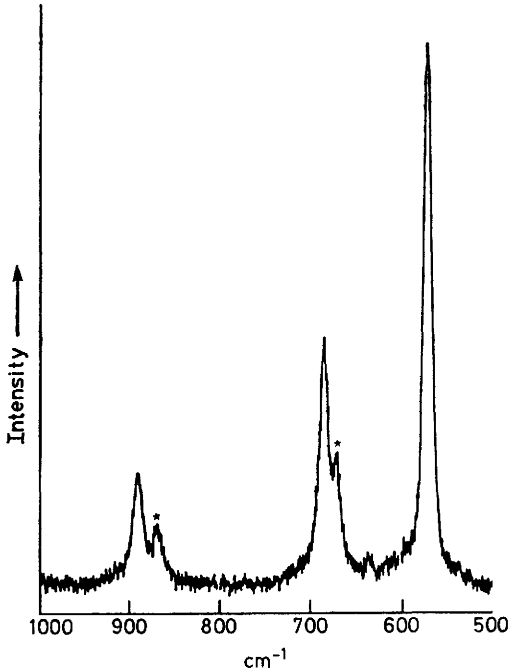
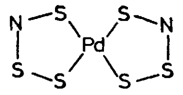


FIGURE Raman spectrum of $Ph_4As^+S_3{}^*N^-$ ($^*N$ = 30% ^{15}N) obtained using 488 nm excitation on a pressed solid sample mounted on KBr in a 6 cm stainless steel ring which was rotated at *ca* 1000 r p m to prevent thermal decomposition Bands marked with an asterisk are not observed in the Raman spectrum of $Ph_4As^+S_3N^-$

(D_{3h}) of the isoelectronic $CS_3{}^{2-}$ ion,[4] the vibrational spectra of S_3N^- suggest an unbranched arrangement of atoms, $^-S{-}N{=}S{=}S$, consistent with the cleavage of one S–S bond in S_4N^- by triphenylphosphine[5]

Transition-metal complexes of the type $M(S_3N)_2$ (M=Ni,[6] Co,[7] Pd,[7] or Pt[8]) have been obtained in *very low* yields[6,7] from the reactions of metal halides with S_4N_4 An *X*-ray structural determination of the palladium derivative (**1**) shows that two bidentate *cis*-S_3N^- ligands are bonded to the metal in this complex[9] Whether a *cis* or *trans* conformation is adopted in the free ion must await the results of an *X*-ray structural determination[10] It is noteworthy, however, that the reaction of $PPN^+S_3N^-$ with $NiBr_2$ in MeCN at reflux produces $Ni(S_3N)_2$ with i r bands at 980m, 730s, 715vs, and 525m cm^{-1} (*cf* ref 6)



(1)

In conclusion, the bidentate chelating ligand S_3N^- is readily prepared from S_4N^- and triphenylphosphine This synthesis should provide a convenient route for the study of transition-metal complexes of the S_3N^- anion

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[3] T Chivers and R T Oakley, *J Chem Soc Chem Commun* , 1979 752 T Chivers W G Laidlaw, R T Oakley, and M Trsic, *J Am Chem Soc* 1980, **102**, 5773

[4] G Gattow and W Behrendt 'Carbon Sulphides and Their Inorganic and Complex Chemistry,' ed A Senning, Georg Thieme, Stuttgart, 1977 p 167

[5] *Ab initio* Hartree–Fock–Slater self consistent field calculations of *cis*- and *trans*-S_3N^- using the geometry found for S_4N^- [3] show the *cis*-conformation to be *ca* 20 kcal lower in energy W G Laidlaw, personal communication

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[7] J Weiss and U Thewalt *Z Anorg Allg Chem* , 1966 **346** 234 report the preparation of 340 mg of $Pd(S_3N)_2$ from S_4N_4 (21 g) and $PdCl_2$ (17 g)

[8] D T Haworth and G Y Lin, *J Inorg Nucl Chem* , 1977 **39** 1838 identify $Pt(S_3N)$ on the basis of the i r spectrum I S Butler and T Sawai *Can J Chem* , 1977, **55** 3838 report mass spectroscopic evidence for the presence of $Pt(S_3N)_2$ in a mixture

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[10] Attempts to determine the single crystal *X*-ray structure of $PPN^+S_3N^-$ and Ph_4As^+ S_3N^- have failed owing to disorder problems, C Day, personal communication