Preparation and Crystal Structure of a New Sulphur Nitride, S_5N_6; a Molecular Basket

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Summary An *X*-ray crystallographic study has shown that S_5N_6, prepared from $Bu_4N^+S_4N_5^-$ and bromine in methylene chloride, has a structure in which an –N=S=N– unit bridges two sulphur atoms of an S_4N_4 cradle.

The preparation and structural characterization of anionic, $S_4N_5^-$,[1] and cationic, $S_4N_5^+$,[2] cages closely related to S_4N_4 have recently been described. During an investigation of the reactions of these ions, we have observed the unexpected formation of pentasulphur hexanitride, S_5N_6, on several occasions. Here we report the details of an easy synthesis and the crystal structure of this novel sulphur nitride.

A solution of bromine (0·40 mmol) in dry methylene chloride (30 ml) was added (20 min) to a solution of $Bu_4N^+S_4N_5^-$ (0·65 mmol) in methylene chloride (20 ml) at 0 °C. After 5·5 h, the orange solution was filtered and slow removal of the solvent from the filtrate below 0 °C led to the precipitation of S_5N_6 in 73% yield [after washing with cold methylene chloride (5 ml)]. The orange crystals of S_5N_6 are stable for long periods at 20 °C under an inert atmosphere, but turn black immediately on exposure to air. S_5N_6 sublimes without significant decomposition at 45 °C and 10^{-2} mmHg and decomposes at 130 °C during a m.p. determination. The u.v.–visible spectrum (in CH_2Cl_2) showed two smooth bands with λ_{max} 375 (ϵ *ca.* 5 × 10^3) and 250 nm (ϵ *ca.* 6 × 10^4 l mol^{-1} cm^{-1}). The i.r. spectrum (Nujol)† of S_5N_6 showed bands at 1088sh, 1066s, 1030s, 968w, 938s, 852s, 835w, 694m, 648s, 621w, 573s, 554m, 500s, 463w, 433m, 418w, and 388s cm^{-1}. Crystals suitable for an *X*-ray structural determination were obtained by recrystallization from methylene chloride followed by slow evaporation of a solution of S_5N_6 in carbon disulphide.

Crystal data: S_5N_6, M = 244·36, monoclinic, space group $C2/c$, a = 8·787(2), b = 11·190(2), c = 7·427(2) Å, U = 700·3(5) Å^3, Z = 4, D_c = 2·317 g cm^{-3}. A total of 781 independent reflections [$I \geqslant 3\sigma(I)$] were collected with an Enraf–Nonius CAD 4 diffractometer employing the θ–2θ technique with graphite-monochromated Mo-K_α radiation. The structure was solved by direct methods and Fourier techniques and all atoms were refined anisotropically to give an unweighted R-factor of 0·033.

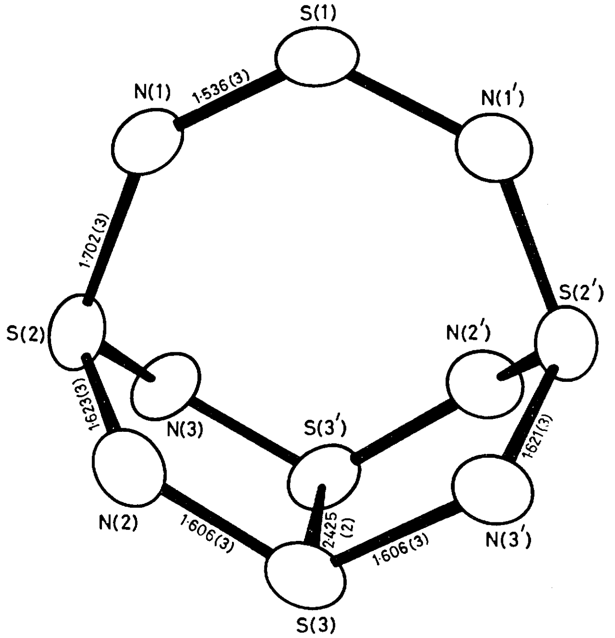

Figure. *X*-Ray structure of S_5N_6. Symmetry related atoms are labelled with primes. Interatomic distances are in Å. E.s.d.'s are shown in parentheses. Principal bond angles are N(1)–S(1)–N(1′), 126·3(2); N(2)–S(2)–N(3), 105·7(2); N(1)–S(2)–N(2), 109·2(2); N(1)–S(2)–N(3), 108·6(2); N(2)–S(3)–N(3)′, 118·5(2); N(2)–S(3)–S(3′), 92·7(1); N(3′)–S(3)–S(3′), 92·9(1); S(1)–N(1)–S(2), 137·1(2); S(2)–N(2)–S(3), 121·7(2); S(2)–N(3)–S(3′), 120·6(2)°.

The structure of S_5N_6 has twofold symmetry (see Figure) and resembles a basket in which an –N=S=N– unit [S(1)–N(1) = 1·54 Å] is the handle which bridges two sulphur atoms of an S_4N_4 cradle *via* S–N single bonds [S(2)–N(1) = 1·70 Å].[3] The average S–N bond distance in the cradle, 1·61 Å, does not differ significantly from that observed for S_4N_4 (1·62 Å),[4] but the S–S distances are notably affected by the introduction of a bridge. Thus, the S(2)–S(2′) separation is now 3·94 Å, while the S(3)–S(3′) distance has shortened to 2·43 Å (*cf.* 2·58 Å in S_4N_4).[4]

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† *CAUTION*: Minor explosions have occurred during the grinding of samples for i.r. mulls.

The four other S–S separations in the cradle are in the range 2·80—2·82 Å, close to the values found for $S_4N_5^+$ (2·78—2·81 Å).[2] The S(1)–S(2) distances are 3·01 Å.

Using Banister's approach to bonding in S–N cages,[5] the 44 electrons of the S_4N_4 cage in S_5N_6 can be accommodated by allocating a lone pair to each atom, a pair of electrons to each S–N bond in the cage, one electron to each of the bonds to the –N=S=N– bridge, and an electron pair of higher energy to each of the five S–S interactions (*cf.* $S_4N_5^+$).[2] The incipient formation of five-membered S_3N_2 rings in S_5N_6, as a result of the shortening of the S(3)–S(3′) separation, is noteworthy in view of the mechanism proposed for the formation of $S_3N_2^+$ in the oxidation of S_4N_4 by AsF_5[3] and the production of various cyclic S_3N_2 derivatives from S_4N_4.[6]

We have also observed the formation of S_5N_6 (in addition to S_4N_4 and $S_3N_2O_2$) in the reaction of Na^+ $S_4N_5^-$ with thionyl chloride. In contrast, the $S_4N_5^-$ ion reacts smoothly with chlorine in methylene chloride to give S_4N_5Cl in good yield, while the reaction with sulphuryl chloride produces S_5N_6 *and* S_4N_5Cl, separable by sublimation.

The unexpected discovery of S_5N_6 suggests that other hitherto unpredicted S–N cage species, *e.g.* $S_5N_7^-$ or $S_4N_6^{2-}$, are possible.[7] Attempts to prepare such ions are in progress.

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