A Bicyclic S–N Cation: The Synthesis and Crystal Structure of S_4N_5Cl

By Tristram Chivers* and Lee Fielding

(*Department of Chemistry, The University of Calgary, Calgary* T2N 1N4, *Alberta, Canada*)

Summary An *X*-ray crystallographic study of S_4N_5Cl, prepared from $S_3N_3Cl_3$ and $Me_3SiNSNSiMe_3$, has revealed a predominantly ionic structure involving the new S–N cation, $S_4N_5^+$.

Current interest in binary S–N cations with planar, monocyclic structures, *e.g.* $S_3N_2^+$,[1,2] $S_5N_5^+$,[3,4] and $S_4N_4^{2+}$,[5] and in halogenated derivatives of polymeric sulphur nitride[6] prompts us to report the synthesis and *X*-ray structural determination of a new S–N halide, S_4N_5Cl, which contains the first reported bicyclic S–N cation, $S_4N_5^+$.

Equimolar amounts (3·88 mmol) of $S_3N_3Cl_3$ and $Me_3SiNSNSiMe_3$ at 23 °C in carbon tetrachloride (55 ml) produced golden-brown crystals of S_4N_5Cl in 63% yield after 12 h.† Complete elemental analyses were in excellent agreement with the empirical formula. The mass spectrum (70 eV) exhibited a very weak molecular ion peak, *m/e* 233 ($S_4N_5{}^{35}Cl^+$), and a strong peak at *m/e* 198 ($S_4N_5^+$). The i.r. spectrum (Nujol) showed bands at 1140w, 1050vs, 1023s, 966vs, 800w, 720w, 697s, 628w, 584s, 481m, 462m, 422s, 408m, and 308w cm^{-1}. The Raman spectrum had bands at 1114vw, 1015vs, 958s, 716w, 688w, 587m, 474m, 457sh, 398w, 304m, 199vs, and 173m cm^{-1}. Molecular weight determinations by vapour-phase osmometry in CS_2 suggested a monomeric structure in solution (found: 222, 2·17 mg ml^{-1}; 228, 4·07 mg ml^{-1}; calc: 233·7). An *X*-ray crystal structure determination, however, unexpectedly revealed a polymeric predominantly ionic structure in which $S_4N_5^+$ cations are symmetrically bridged by Cl^- ions (see Figure).

Crystal data: S_4N_5Cl, $M = 233\cdot74$, orthorhombic, space-group *Pnma*, $a = 17\cdot491(17)$, $b = 7\cdot819(2)$, $c = 4\cdot838(4)$ Å, $U = 661\cdot7\ (5)$ Å^3, $Z = 4$, $D_c = 2\cdot346$ g cm^{-3}. A total of 1162 independent reflections $[I > 3\sigma(I)]$ 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 *R*-factor of 0·066. The cation is bisected by a crystallographic mirror plane through S(1) S(2) and N(1); other mirror planes at *y* 0·25 and 0·75 pass through the cations and anions.

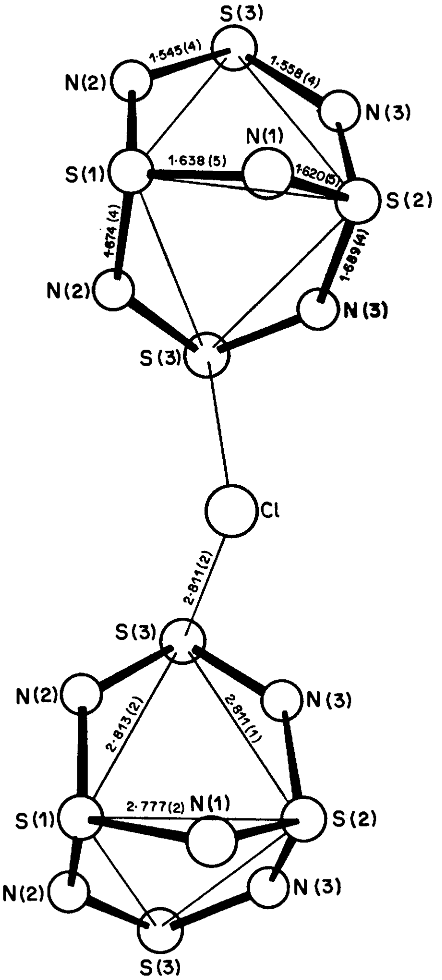

Figure. *X*-Ray structure of S_4N_5Cl. Interatomic distances are in Å. E.s.d.'s are shown in parentheses. Principal bond angles are ∠S(1)–N(1)–S(2), 117·0(3); S(1)–N(2)–S(3), 121·7(2); S(2)–N(3)–S(3), 119·9(2); N(1)–S(1)–N(2), 107·1(2); N(1)–S(2)–N(3), 108·7(2); N(2)–S(3)–N(3), 119·5; S(3)–Cl–S(3), 85·39(6)°.

In contrast to the isoelectronic species $S_4N_5O^-$, in which the exocyclic oxygen atom is connected to a sulphur which is bonded to three nitrogen atoms,[7] the chlorine atoms in S_4N_5Cl symmetrically bridge S_4N_5 units *via* the sulphur atoms bonded to two nitrogens. The S(3)–Cl distance is 2·811(2) Å compared to 2·084 and 2·150 Å for $S_3N_3Cl_3$[8] and 2·168 Å in $S_3N_2Cl^+$.[9] Significantly, the Cl^- ion in $S_3N_2Cl^+Cl^-$ is at distances in the range 2·90—3·04 Å from the three sulphur atoms of the cation.[9] Thus, it seems reasonable to view S_4N_5Cl as consisting of $S_4N_5^+$ cations bridged by Cl^- ions. This conclusion is further supported by the preparation of $S_4N_5^+SbCl_6^-$ as a yellow powder from S_4N_5Cl and antimony pentachloride in methylene chloride. The positions and intensities of the i.r. bands of the cation in this salt are virtually identical to those in S_4N_5Cl. In addition, a very strong band at 342 cm^{-1}, attributable to ν_3 of $SbCl_6^-$, is observed. The short S–N(3) distance in $S_4N_5^+$ and the long-range interactions with Cl^- suggest some preferential localisation of cation charge on these sulphur atoms [compared with S(1) and S(2)]. The *average* S–N bond length (1·62 Å) is very close to that observed for S_4N_4 (1·62 Å)[10] and $S_4N_5^-$ (1·63 Å),[11] but significantly longer than found in planar, monocyclic S–N cations, *e.g.* $S_3N_2^+$ (1·58 Å),[1] $S_4N_3^+$ (1·55 Å),[12] and $S_5N_5^+$ (1·54—1·56 Å).[3,4]

Within each $S_4N_5^+$ cage, there are five S · · · S separations in the narrow range 2·78—2·81 Å and the sixth pair of

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† *CAUTION:* S_4N_5Cl may explode under the influence of heat or pressure *e.g.* during m.p. determination or preparation of an i.r. mull.

sulphur atoms S(3) is 4·01 Å apart. These values compare with $S\cdots S$ distances of 2·63—2·74 Å for $S_4N_5O^-$,[7] 2·58—2·70 Å in S_4N_4,[10] and 2·71—2·75 Å in $S_4N_5^-$.[11] The structure of $S_4N_5^-$, *i.e.* a regular tetrahedron of sulphur atoms in which five of the edges are bridged by nitrogen,[11] can be rationalized using Banister's approach.[13] The 50 valence electrons can be accommodated by allocating a lone pair to each atom, a pair of electrons to each S–N bond, and an electron pair of higher energy to each $S\cdots S$ interaction in the S_4 tetrahedron. Thus, in $S_4N_5^+$, with two electrons less, the existence of only five $S\cdots S$ interactions is to be expected.

The easy preparation of S_4N_5Cl provides an alternative to $S_4N_5^-$ salts[14] for the synthesis of other derivatives of the S_4N_5 cage. Such reactions are being studied.

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