

A Planar, Cyclic Sulphur–Nitrogen Anion: the X-Ray Crystal and Molecular Structure of $[\text{Bu}_4\text{N}]^+[\text{S}_3\text{N}_3]^-$

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Summary An X-ray crystallographic analysis of $[\text{Bu}_4\text{N}]^+[\text{S}_3\text{N}_3]^-$ shows that the S_3N_3^- anion is a planar, six-membered ring; this anion plays a central role in the reduction of S_4N_4 and the deprotonation of $\text{S}_4\text{N}_4\text{H}_4$.

We recently reported the synthesis of caesium and tetraalkylammonium salts of the novel S–N anion, S_3N_3^- , from S_4N_4 and azides.¹ The vibrational spectra of these salts suggested a six-membered ring structure for S_3N_3^- in contrast to the five-membered ring structure established for the isoelectronic cation² $\text{S}_3\text{N}_2\text{Cl}^+$ and for a number of S_3N_3 derivatives.³ A puckered ring conformation (C_{3v}) was proposed for S_3N_3^- in the caesium salt.¹ In view of the central significance of S_3N_3^- in the development of a theory of aromaticity for S–N ring systems,⁴ we have determined the structure of $[\text{Bu}_4\text{N}]^+[\text{S}_3\text{N}_3]^-$ by X-ray crystallography and report the results here.

Crystal data: $[\text{Bu}_4\text{N}][\text{S}_3\text{N}_3]$, $M = 380.68$, monoclinic, space group $P2_1/n$, $a = 9.075(5)$, $b = 15.901(12)$, $c = 15.389(6)$ Å, $U = 2193$ Å³, $Z = 4$, $D_c = 1.152$ g cm⁻³. A total of 3374 independent reflections [$I > 3\sigma(I)$] were collected with an Enraf-Nonius CAD 4 diffractometer employing the θ - 2θ technique with graphite-monochromated radiation. The structure was solved by direct methods and Fourier techniques and refined with anisotropic temperature factors to an R value of 0.097. The positions of the protons were not determined.†

The X-ray crystal structure determination of $[\text{Bu}_4\text{N}]^+[\text{S}_3\text{N}_3]^-$ confirms the proposed six-membered ring structure for S_3N_3^- . Bond lengths and angles are indicated in the Figure. The average S–N bond length (1.60 Å) is comparable to the average S–N bond distance in S_4N_4 (1.62 Å)⁵ and S_4N_5^- (1.63 Å).⁶ The S_3N_3^- ring is essentially planar, the maximum deviation from the least-squares plane through the three sulphur atoms being 0.06 Å for N₃. The intra-ring S–S distances are 2.80–2.82 Å, compared to

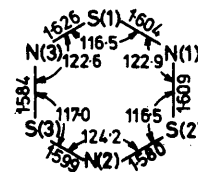


FIGURE. Principal dimensions of the S_3N_3^- anion in $[\text{Bu}_4\text{N}]^+[\text{S}_3\text{N}_3]^-$. Bond lengths are in Å with e.s.d.s of 0.012 Å; bond angles are in degrees with e.s.d.s of 0.7° at sulphur and 0.8° at nitrogen.

2.83 Å in the puckered ring of $\text{S}_3\text{N}_3\text{Cl}_3$,⁷ and so transannular S ··· S interactions may be an important feature of the bonding in S_3N_3^- .⁸ The growing list of planar S–N rings now includes examples of four (S_2N_2),⁹ five (S_3N_2^+),¹⁰ six (S_3N_3^-), seven (S_4N_3^+),¹¹ eight ($\text{S}_4\text{N}_4^{2+}$),¹² and ten (S_5N_5^+)¹³ atom systems. All these species, except S_3N_2^+ , are $(4n + 2)\pi$ electron systems according to Banister's classification of 'electron-rich aromatics'.⁴

Recently, it has been proposed that S_4N_5^- plays a central role among S–N anions.^{6,14} We find that S_3N_3^- also figures prominently in S–N chemistry, for example, in the reduction of S_4N_4 and in the deprotonation of $\text{S}_4\text{N}_4\text{H}_4$.¹⁵ Yellow crystals of $\text{K}^+\text{S}_3\text{N}_3^-$ can be isolated in 30% yield from the reaction of S_4N_4 with potassium metal in dimethoxyethane at 23 °C and, surprisingly, in 26% yield from the deprotonation of $\text{S}_4\text{N}_4\text{H}_4$ with potassium hydride in a 5:4 molar ratio in tetrahydrofuran. The vibrational spectra of $\text{K}^+\text{S}_3\text{N}_3^-$ are consistent with a structure of D_{3h} symmetry for the anion since only 4 bands at 925s, 645vs, 390m, and 180br cm⁻¹ are observed in the i.r. spectrum. The first three of these bands have coincidences in the Raman spectrum. The three weak bands observed in the i.r. spectrum of $\text{Cs}^+\text{S}_3\text{N}_3^-$ are absent in the i.r. spectrum of the potassium salt. It is possible that anion–cation interactions lead to distortion of the S_3N_3^- ring in the caesium salt, as in $\text{S}_4\text{N}_4^{2+}$.¹⁰

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Complete vibrational assignments for the $S_3N_3^-$ ion will be reported elsewhere.

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