A New Cationic S–N Ring System, $S_4N_4^{2+}$. The Crystal Structure of Cyclotetrathiazyl Bis hexachloroantimonate(V), $[S_4N_4][SbCl_6]_2$, and Cyclotetrathiazyl Hexafluoroantimonate(V) Tetradecafluorotriantimonate, $[S_4N_4][SbF_6][Sb_3F_{14}]$

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Summary An *X*-ray crystallographic study has shown that the new cyclic cation $S_4N_4^{2+}$ has different structures in the compounds $[S_4N_4][SbCl_6]_2$ and $[S_4N_4][SbF_6][Sb_3F_{14}]$ which were prepared by the reactions of S_4N_4 or $S_3N_3Cl_3$ with $SbCl_5$ and of S_4N_4 with SbF_5, respectively.

In an investigation of the reactions of S_4N_4 with Lewis acids, we have previously shown that AsF_5 reacts with S_4N_4 in a 3 : 1 mole ratio to give the salt $[S_3N_2]^+AsF_6]^-$.[1] In a continuation of this work we have found that the reaction of S_4N_4 with $SbCl_5$ in a 1 : 3 mole ratio in SO_2 solution, gives the yellow crystalline product $[S_4N_4][SbCl_6]_2$ [reaction (1)].

$$S_4N_4 + 3SbCl_5 \longrightarrow [S_4N_4][SbCl_6]_2 + SbCl_3 \qquad (1)$$

The same product is obtained from the reaction of $S_3N_3Cl_3$ with $SbCl_5$ in a 1 : 2 mole ratio in SO_2 solution. This reaction is complex as there was at least one unidentified product. In the reaction of S_4N_4 with SbF_5 in a 1 : 6 mole ratio, the compound $[S_4N_4][Sb_3F_{14}][SbF_6]$ was obtained. The apparent overall reaction corresponds to a 1 : 4 mole ratio, *i.e.*, reaction (2). Intensity data for crystals of $[S_4N_4][SbCl_6]_2$ and $[S_4N_4][SbF_6][Sb_3F_{14}]$ were collected on a Syntex P1 automatic diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0{\cdot}7169$ Å).

$$S_4N_4 + 4SbF_5 \longrightarrow [S_4N_4][SbF_6][Sb_3F_{14}] \qquad (2)$$

Crystal data: $[S_4N_4][Sb_4F_{20}]$: $M = 1051{\cdot}4$, monoclinic, space group $P2_1/n$, $a = 16{\cdot}382(8)$, $b = 16{\cdot}200(8)$, $c = 8{\cdot}454(6)$ Å, $\beta = 109{\cdot}3(7)°$, $U = 2116{\cdot}0$ Å^3, $Z = 4$, $D_c = 3{\cdot}30$ g cm^{-3}. The structure was solved by direct methods and Fourier techniques to give an *R*-factor of 0·10 for 1944 observed reflections [$I > 3\sigma(I)$]. Refinement is being continued. The cell contains two crystallographically non-equivalent $S_4N_4^{2+}$ ions.

$[S_4N_4][SbCl_6]_2$: $M = 528{\cdot}5$, orthorhombic, space group *Pbcn*, $a = 12{\cdot}873(8)$, $b = 12{\cdot}602(7)$, $c = 13{\cdot}557(8)$ Å, $U = 2198{\cdot}9$ Å^3, $Z = 4$, $D_c = 1{\cdot}60$ g cm^{-3}. The structure was solved by conventional Patterson and Fourier techniques to give an *R*-factor of 0·073 for 855 observed reflections [$I > 3\sigma(I)$]. Each site of the cation consists of an equal mixture of sulphur and nitrogen. The disordering appears to arise from a random occupation of the molecular sites by two orientations of the molecule which are related by a C_2 operation about an axis perpendicular to the S_4 axis of the molecule.

Figure 1 shows the structures of $S_4N_4^{2+}$ in $[S_4N_4][Sb_4F_{20}]$ and the third structure found in $[S_4N_4][SbCl_6]_2$. Structure (A) is planar and has equal bond lengths and bond angles, structure (B) is also planar but has alternating bond lengths, while structure (C) is non-planar, has S_4 symmetry and a very pronounced alternation in bond lengths while the bond angles are all equal. However, equality of the bond angles is a necessary consequence of the disordering.

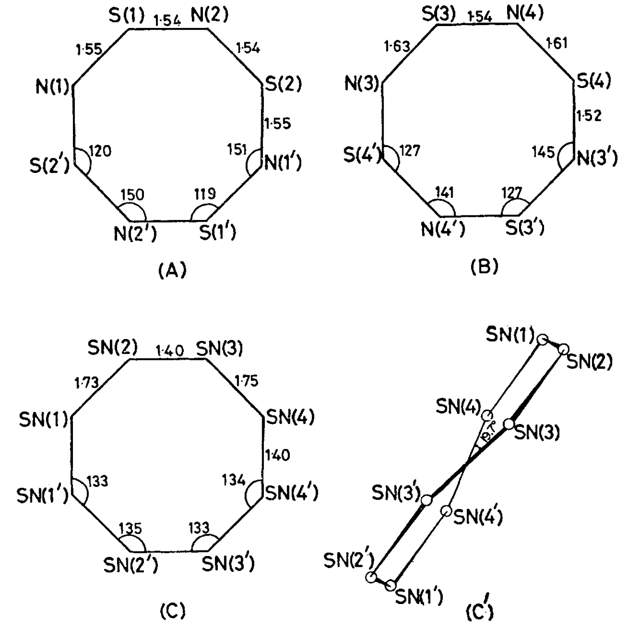
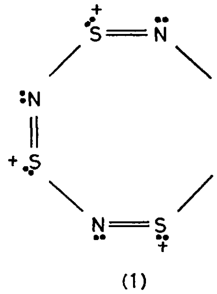
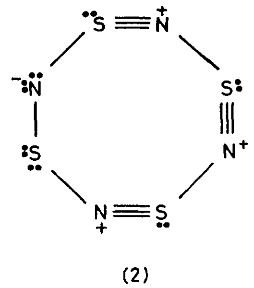


FIGURE 1. (A) Structure of ring (A) in $[S_4N_4][SbF_6][Sb_3F_{14}]$; (B) Structure of ring (B) in $[S_4N_4][SbF_6][Sb_3F_{14}]$; (C) structure of ring (C) in $[S_4N_4][SbCl_6]_2$ viewed down the S_4 axis; (C′) structure of ring (C) viewed down the pseudo-C_2' axis.

It is remarkable that the removal of two electrons from S_4N_4 causes the structure to change from a three-dimensional cage to a flat, or almost flat, ring. A rationalisation of the difference in structure between a postulated planar $S_4N_4^{2+}$ and the neutral S_4N_4 molecule has recently been given in terms of a simple molecular orbital description.[2] Structure (A), with equal bond lengths, clearly closely resembles $S_4N_3^+$ [3] and $S_5N_5^+$.[4,5] Indeed, the average bond lengths are essentially the same in the three ions and the average bond angles, at nitrogen and at sulphur, are also similar. The mean S–N bond length corresponds to a bond order of approximately two.[1] No conventional description of the bonding in these rings is completely satisfactory. However, if each atom is assumed to have a lone-pair of electrons and there is one localised bond between each pair of atoms, then there are 10 remaining electrons in both $S_4N_3^+$ and $S_4N_4^{2+}$, and 14 remaining electrons in $S_5N_5^+$, which can be described as 10π- and 14π-electron aromatic systems, respectively. This would however imply a bond order of substantially less than 2. A valence-bond description seems even more unsatisfactory. As a basis of such a description sixteen resonance structures of type (**1**) must be postulated corresponding to a bond order of < 1·5. Sixteen additional resonance structures of type (**2**) may also be postulated which would give a bond order closer to 2. The large bond angles at nitrogen for structures (A) and (B) are consistent with a contribution from structures of type (**2**), as no lone-pair is present on three of the nitrogen atoms in these structures. We note, however, that the involvement of nitrogen lone-pair electrons in the bonding is inconsistent with the 10π-electron molecular orbital description. The very artificial nature of these valence-bond structures is also evident from the presence of charges on many of the atoms.



(1)



(2)

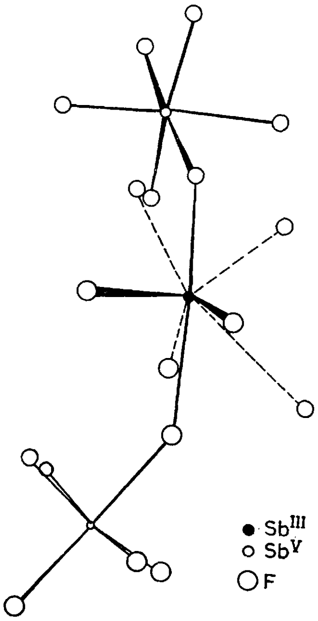


FIGURE 2. The $Sb_3F_{14}^-$ anion. – – – long contacts to neighbouring F atoms.

The bonding diagrams (**1**) and (**2**) and the 10π-electron molecular orbital description suggest possible resonance stabilisation of the molecule in its planar form. However, such a resonance stabilisation is clearly quite unimportant as the flat planar form is obviously readily distorted to structure (B) and to the non planar form (C) with strongly alternating bond lengths. Clearly all three forms have similar energies and the presumably weak interactions with neighbouring ions in the crystal lattice appear to be sufficient to cause a rather drastic change in the structure of the cation. It seems that we do not yet have a satisfactory description of the bonding in S–N systems.

In $[S_4N_4][Sb_3F_{14}][SbF_6]$ the previously unreported $Sb_3F_{14}^-$ anion (Figure 2) is present. This may be described as consisting of an SbF_2^+ ion linked by two *trans* asymmetric fluorine bridges, [Sb^{III}–F(bridge) 2·30 Å, Sb^V–F(bridge) = 1·95 Å] to two SbF_6^- anions giving the Sb^{III} atom an AX_4E configuration.[6] The Sb^{III}–F (terminal) distances of 1·90 Å are, as expected, longer than all the Sb^{V}–F (terminal) distances, mean 1·84 Å. The Sb^{III} atom also has four long contacts surrounding the lone pair giving it a similar overall configuration to the iodine atom in $[IF_4]^+[Sb_2F_{11}]^-$.[7]

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