Preparation and *X*-Ray Structure of Sulphur–Nitrogen Oxides

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Summary The compounds $[S_5N_5]^+[S_3N_3O_4]^-$ and $S_4N_4O_2$ have been prepared from the same reaction; the crystal structures show that the shape of the $[S_5N_5]^+$ cation differs from that previously reported and that $[S_3N_3O_4]^-$ and $S_4N_4O_2$ contains S–N rings with exocyclic oxygen atoms.

ALTHOUGH S_4N_4[1] was first prepared 150 years ago, oxides of S_4N_4 were not known until the recent report[2] of the synthesis of $S_4N_4O_4$. In the course of further investigations of inorganic ring systems, two compounds with the general composition $S_4N_4O_2$ have been isolated. Their preparation and properties are now described.

Both compounds were prepared by the reaction between $Me_3Si–N=S=N–SiMe_3$ and $FSO_2N=S=O$ in CH_2Cl_2 solution. Removal of the volatile products and of the solvent followed by treatment of the liquid residue with CH_2Cl_2 gave a solution which deposited violet-black crystals (I) after several days. When a small amount of solvent was removed, yellow needles (II) were produced. Cryoscopic

molecular weight measurements and elemental analysis yielded results in good agreement with the formulation of both compounds as $S_4N_4O_2$.

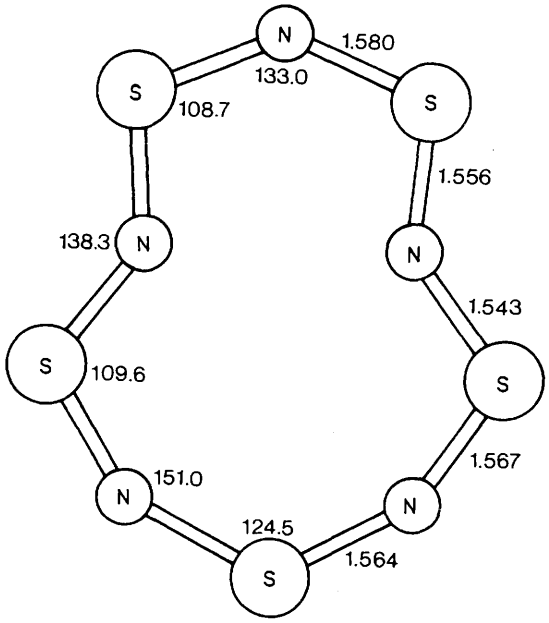

FIGURE 1. The $[S_5N_5]^+$ cation. E.s.d.'s in bond lengths are *ca.* 0·003 Å.

Compound (I) crystallises with a monoclinic cell, with $a = 8{\cdot}873$, $b = 11{\cdot}299$, $c = 13{\cdot}112$ Å, $\beta = 97{\cdot}27°$, space group $P2_1/c$ and four units of $[S_5N_5]^+[S_3N_3O_4]^-$ per cell. The *X*-ray intensity data were collected on a Hilger and Watts four-circle diffractometer using Zr-filtered radiation and a θ–2θ scan. The structure was solved by the symbolic addition procedure and the atomic parameters were refined by full-matrix least-squares methods. The final *R* was 0·030 for the 1915 reflections within the range $\theta \leqslant 26°$ and having net counts $\geqslant 3\sigma$.

The compound is ionic and the shape of the $[S_5N_5]^+$ cation (Figure 1) differs greatly from the heart-shaped ion reported[3] for $[S_5N_5]^+[AlCl_4]^-$. The ring is almost planar (within $\pm 0{\cdot}06$ Å) and the bond distances across the ring are the same within experimental error. The S–N bond lengths are normal for a delocalised S–N system and lie in the range 1·543—1·580 Å, compared with values of 1·465—1·590 Å in the $[S_5N_5]^+$ ring in $[S_5N_5]^+[AlCl_4]^-$ and 1·548—1·566 Å in the $[S_4N_3]^+$ ion.[4]

The $[S_3N_3O_4]^-$ anion has not previously been reported. As shown in Figure 2, it contains an S_3N_3 ring with two terminal oxygens on two of the sulphur atoms. Within experimental error, the ion shows *m* symmetry. The nitrogen atom situated between the two SO_2 groups is displaced by 0·64 Å out of the mean plane of the rest of the ring (planar within $\pm 0{\cdot}01$ Å) as a consequence of the nearly tetrahedral angles at these two sulphur atoms. The bond distances to this nitrogen atom indicate some multiple bonding and suggest that the negative charge is delocalised over the SO_2–N–SO_2 system. The bond distances in the di-imide N–S–N unit are very short, indicating substantial multiple bonding in this part of the ring whereas the bond joining this unit to the SO_2–N–SO_2 portion of the ring lie within the range of S–N single bonds.

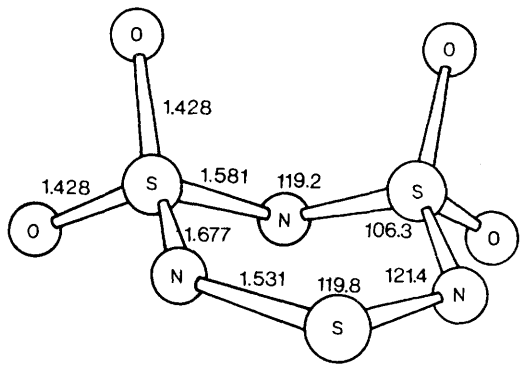

FIGURE 2. The $[S_3N_3O_4]^-$ anion. E.s.d.'s in bond lengths are *ca.* 0·003 Å.

In compound (II), the molecules contain an eight-membered S_4N_4 ring with both oxygens attached to the same sulphur atom. Owing to imperfections in the crystals, the structural parameters were determined with low accuracy and a full report will appear elsewhere. A feature of considerable interest is the formation of three different types of S–N rings in the same reaction.

(*Received, 2nd April* 1975; *Com.* 370.)

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