

The Preparation and Structure of Pentathiazyl Tetrachloroaluminate, $S_5N_5AlCl_4$

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Summary The preparation of a stable salt of the pentathiazyl ion, $S_5N_5^+$, is described; the ion has been shown by X-ray diffraction to be a planar, heart-shaped ring.

THE sulphur nitrides S_2N_2 , S_4N_4 , and $(SN)_x$ polymer can be regarded as members of the series: SN^+ , S_2N_2 , $S_3N_3^+$, S_4N_4 , $S_5N_5^+$, S_6N_6 $(SN)_x$. The title compound contains $S_5N_5^+$, the first cation of this series to be definitely characterised as a stable salt.

The pentathiazyl salt was obtained by adding solid tetrasulphur tetranitride (1 mole) to a thionyl chloride solution of aluminium chloride (1 mole) at 35°, stirring for 48 hr. at this temperature, and fractionally crystallising from the mixed product obtained on concentrating the solution. The salt was recrystallised from thionyl chloride to constant melting point (181°). The crystals are pale-yellow prisms bounded by {102} and terminated by {011}.

X-Ray diffraction shows the crystals to be orthorhombic with $a = 9.412$, $b = 13.647$, and $c = 20.761$ Å. The space group is $Pnma$, $Z = 8$.

A least-squares refinement using isotropic temperature factors gave an R -value of 0.19 for 1288 reflections. The data were collected on a linear diffractometer of the Arndt-Phillips design¹ using graphite monochromatized Mo- K_α radiation. Further refinement of the structure is in progress.

¹ U. W. Arndt and D. C. Phillips, *Acta Cryst.*, 1961, **14**, 807.

² N. C. Baenziger, *Acta Cryst.*, 1951, **4**, 216.

The structure consists of discrete $S_5N_5^+$ and $AlCl_4^-$ ions. The $S_5N_5^+$ ion forms a ten-membered ring which is almost planar and approximates to the symmetry $mm2$. The mean

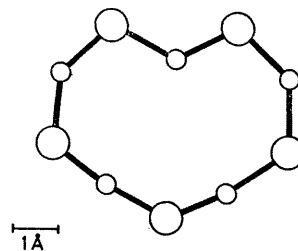


FIGURE. The $S_5N_5^+$ ion projected on to the least-squares best plane through the ring. The large circles represent sulphur atoms, the small circles nitrogen atoms.

S-N distance is 1.55 Å which indicates considerable double-bond character, and the large values of the S-N-S angles are probably associated with a large contribution of the nitrogen lone-pair electrons to the bonding. The dimensions and angles of the $AlCl_4^-$ ions are similar to those found in $NaAlCl_4$.²

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