Reactions of Tetrasulphur Tetranitride with Halides. Part V.[1] The Preparation of Cyclopentathiazenium ($S_5N_5^+$) Salts and Some Observations on the Structure of the Cyclopentathiazenium Cation

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The cyclopentathiazenium salts, $S_5N_5^+A^-$ ($A^- = AlCl_4^-, FeCl_4^-, SbCl_6^-$), are readily prepared in high yield from tetrasulphur tetranitride, trichlorocyclotrithiazene $(NSCl)_3$, and the metal chloride: $AlCl_3$, $FeCl_3$, or $SbCl_5$. Other salts can be prepared by metathesis in anhydrous formic acid. The nature of the bonding in the cation is discussed with respect to its unusual stability.

THE sulphur–nitrogen cations $S_3N_2Cl^+$, $S_4N_3^+$, and $S_5N_5^+$ are Hückel species with 6, 10, and 14 π-electrons respectively.[1,2] Salts of the first two cations are readily prepared from their chlorides ($S_3N_2Cl_2$ and S_4N_3Cl) by metathesis[3] or by reaction with a Lewis acid which can accept chloride ion.[1,3] Hitherto, salts of the planar heart-shaped cation $S_5N_5^+$ have been obtainable only after tedious separation from a mixture with $S_3N_2Cl^+$ and $S_4N_3^+$ salts produced simultaneously. Pure $S_5N_5^+FeCl_4^-$, $S_5N_5^+AlCl_4^-$, and $S_5N_5^+SbCl_6^-$ are now easily prepared in thionyl chloride solution from tetrasulphur tetranitride, trichlorocyclotrithiazene $(NSCl)_3$, and the iron(III), aluminium or antimony(V) chloride. The probable mechanism for the reactions is discussed. Other salts may also be prepared from $S_5N_5^+FeCl_4^-$ and $S_5N_5^+AlCl_4^-$, by metathesis. The nature of the bonding

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[1] Part IV, A. J. Banister and P. J. Dainty, preceding paper.

[2] D. B. Adams, A. J. Banister, D. T. Clark, and D. Kilcast, *Internat. J. Sulfur Chem.*, A, 1971, **1**, 143.

[3] M. Becke-Goehring and H. P. Latscha, *Z. anorg. Chem.*, 1964, **333**, 181.

in the cation is discussed with regard to the unusual chemical stability of pentathiazenium salts (for instance, warm concentrated nitric acid merely converts $S_5N_5^+$-$AlCl_4^-$ to the nitrate).

EXPERIMENTAL

I.r. spectra of Nujol mulls prepared under nitrogen, were recorded on a Grubb–Parsons Spectromaster (400—4000 cm^{-1}) prism grating spectrophotometer. U.v. spectra were recorded on a Unicam SP 800 spectrophotometer. Formic acid was dried over boric oxide and purified by fractional distillation.[4] Trichlorocyclotrithiazene was prepared [5] from $S_3N_2Cl_2$, and sulphuryl chloride; tetrasulphur tetranitride was prepared by the method described by Jolly.[6] Thionyl chloride was purified by fractional distillation from triphenyl phosphite.[7] Aluminium chloride was purified by sublimation and ferric chloride by heating with refluxing thionyl chloride for 1 h, antimony pentachloride was freshly distilled at reduced pressure under nitrogen.

The cyclopentathiazenium salts were slightly moisture sensitive and so were manipulated under nitrogen or in a dry box. Nitrogen was analysed by the standard micro-Kjeldahl method. In the analysis for (i) chlorine and (ii) sulphur, oxygen flask combustion was followed by (i) potentiometric titration of chloride ion with 0·01M-silver nitrate solution and, with a separate aliquot, (ii) titration *vs.* 0·01M-barium perchlorate solution using Sulphonazo III as indicator.[8] Aluminium and iron were analysed using a Perkin-Elmer 403 Atomic Absorption Spectrophotometer.

Reaction between Trichlorocyclotrithiazene and Iron(III), *Aluminium and Antimony*(V) *Chloride.*—Iron(III) chloride was added in the molar ratio 1 : 1 to a stirred solution (at 20 °C) of trichlorocyclotrithiazene, $(NSCl)_3$, in thionyl chloride [*ca.* 10 ml of solvent per g of $(NSCl)_3$]. Precipitation of a bright red adduct was complete after *ca.* 2 h. The supernatant thionyl chloride solution was deep red. Addition of further iron(III) chloride to give an $(NSCl)_3$: $FeCl_3$ molar ratio of 1 : 2, gradually converted the bright red 1 : 1 adduct into the rust coloured $(NSCl)_3,2FeCl_3$, which is an intermediate in the $S_5N_5FeCl_4$ synthesis. A small amount of unchanged iron(III) chloride remained even after several days. Further iron(III) chloride, added in excess of the ratio 1 : 2 remained undissolved. Addition of a molar equivalent of $(NSCl)_3$ to the 1 : 2 adduct converted it back (in *ca.* 30 min), into the bright red 1 : 1 adduct. An equimolar quantity of tetrasulphur tetranitride was found to react with a vigorously stirred suspension of either of these adducts, or with the 1 : 3 mixture, and cyclopentathiazenium tetrachloroferrate was gradually precipitated. Similar adducts were formed with aluminium chloride and with antimony(V) chloride. The $(NSCl)_3$–$AlCl_3$ adducts were red (1 : 1) and yellow-orange (1 : 2). All the adducts were very moisture sensitive. Three adducts of antimony(V) chloride: $(NSCl)_3,xSbCl_5(x = 1, 2, \text{or } 3)$ have already been described.[9]

Cyclopentathiazenium Tetrachloroferrate, $S_5N_5FeCl_4$.—Trichlorocyclotrithiazene, anhydrous iron(III) chloride, and tetrasulphur tetranitride were allowed to react in the molar ratio 1 : 3 : 3. The iron(III) chloride was added to a solution of trichlorocyclotrithiazene in thionyl chloride [*ca.* 15 ml of $SOCl_2$ per g of $(NSCl)_3$] and the mixture was stirred (20° *ca.* 1 h) until the rust-brown adduct $(NSCl)_3,2FeCl_3$ was precipitated. On adding the tetrasulphur tetranitride, and stirring vigorously, the adduct and undissolved iron(III) chloride dissolved rapidly to give a very dark solution, from which the rust-brown $S_5N_5FeCl_4$ slowly precipitated (during *ca.* 1 h). Recrystallisation from thionyl chloride gave dark orange crystals; yield 55% (80% of crude product), m.p. 181 °C (decomp.) (Found: S, 37·3; N, 16·3; Fe, 13·6; Cl, 32·5. Calc. for $S_5N_5FeCl_4$: S, 37·5; N, 16·4; Fe, 13·0; Cl, 33·1%).

Cyclopentathiazenium Tetrachloroaluminate and Hexachloroantimonate(V).—Similar reactions occur with (i) aluminium chloride and with (ii) antimony(V) chloride.

(i) The intermediate solid adduct $(NSCl)_3,2AlCl_3$ appears a little more slowly than $(NSCl)_3,2FeCl_3$. The yellow $S_5N_5AlCl_4$ after recrystallisation from thionyl chloride has m.p. 181° (decomp.) [1] (Found: S, 39·1; N, 17·4; Al, 6·6; Cl, 34·7. Calc. for $S_5N_5AlCl_4$: S, 40·2; N, 17·5; Al, 6·8; Cl, 35·5%). Cyclopentathiazenium tetrachloroaluminate dissolves in concentrated nitric acid (70% w/w) at room temperature with evolution of hydrogen chloride. The $S_5N_5^+$ cation decomposes slowly in nitric acid solution; for the visible absorption at 427 nm, ε values for a 0·00054M solution were 2500 (freshly prepared); 1600 (after 19 h at 20°); 360 (after 18 h, at 20° and 1 h at 60°). The salt also dissolves with evolution of hydrogen chloride in anhydrous formic and concentrated sulphuric acids. Decomposition of the solution again occurs very slowly, in sulphuric acid during a matter of weeks.

(ii) The intermediate adduct with antimony(V) chloride precipitates immediately. Since this reaction is quite strongly exothermic, slow addition is advisable. The $S_5N_5SbCl_6$ is only sparingly soluble in thionyl chloride. Solvent extraction with thionyl chloride yields a yellow powder m.p. 188° (decomp.) (Found: S, 28·3; N, 12·3; Sb, 21·8 (by difference); Cl, 37·6. Calc. for $S_5N_5SbCl_6$: S, 28·4; N, 12·4; Sb, 21·6; Cl, 37·6%). Cyclopentathiazenium hexachloroantimonate is insoluble in water; i.r. spectra revealed slight decomposition after contact with water at 20° for 12 h.

The order of addition of the reagents is important. Tetrasulphur tetranitride reacts in thionyl chloride with antimony(V) chloride to give the 1 : 1 adduct, and this does not react with trichlorocyclotrithiazene. Each cyclopentathiazenium salt shows the characteristic i.r. absorptions of the $S_5N_5^+$ cation.[1]

Cyclopentathiazenium Reineckate, $S_5N_5[Cr(NH_3)_2(NCS)_4]$.—$S_5N_5FeCl_4$ was stirred at room temperature with a molar equivalent of $NH_4[Cr(NH_3)_2(NCS)_4]$, (Reinecke's salt), in anhydrous formic acid, (*ca.* 20 ml of formic acid per g $S_5N_5FeCl_4$). A brownish precipitate was gradually formed (*ca.* 1 h), and was washed with fresh, cold formic acid. Analysis, i.r. and u.v. data indicated that the product was $S_5N_5^+[Cr(NH_3)_2(NCS)_4]^-$. The tetraphenylborate, $S_5N_5^+$-BPh_4^-, was prepared similarly from $S_5N_5FeCl_4$ and $NaBPh_4$.

DISCUSSION

The reactions between tetrasulphur tetranitride, trichlorocyclotrithiazene, and metal chloride were suggested

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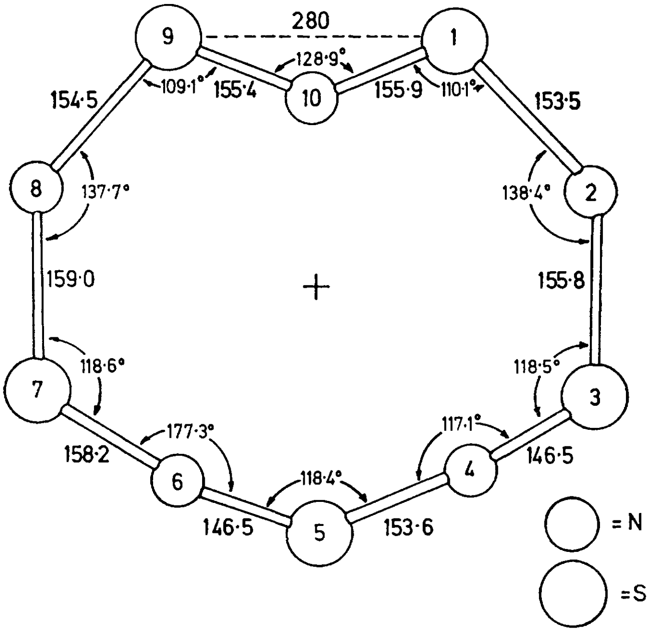
by the results of reactions between iron(III) chloride or aluminium chloride and tetrasulphur tetranitride in thionyl chloride.[1] The reaction sequence proposed[1] can be summarised:

$$S_4N_4 \xrightarrow{SOCl_2} NSCl \xrightarrow{FeCl_3} [NS^+FeCl_4^-] \xrightarrow{S_4N_4} S_5N_5^+FeCl_4^-$$

The present results indicate that again an intermediate thiazyl chloride adduct [in this instance, of the trimer $(NSCl)_3$] is a potential source of NS^+, which is abstracted by S_4N_4 as $S_5N_5^+$. The fact that $(NSCl)_3$ does not react with the adduct $S_4N_4,SbCl_5$ is also consistent with the proposed mechanism. The recommended reactant ratios 1 : 3 : 3, $(NSCl)_3 : S_4N_4 : FeCl_3$, $AlCl_3$ or $SbCl_5$, are the same as the reaction stoicheiometry.



Excess of tetrasulphur tetranitride is avoided, as it reacts[10] with the solvent, to give S_4N_3Cl. In the case of the $FeCl_4^-$ salt, excess of iron(III) chloride is avoided as it is sparingly soluble. It is important to avoid simultaneous excess of $(NSCl)_3$ and metal halide, as these combine to form a sparingly soluble and highly air-sensitive adduct.

As found for $S_4N_3^+Cl$, $S_5N_5^+FeCl_4^-$ undergoes metathetical reactions in formic acid, *e.g.* with $NaBPh_4$ and Reinecke's salt, $NH_4[Cr(NH_3)_2(NCS)_4]$. This appears to be a general method for preparing other $S_5N_5^+$ salts.

Bonding in $S_5N_5^+$.—Structural parameters are shown in the Figure. The $S_5N_5^+$ ion is almost planar, and heart-shaped but without a mirror plane perpendicular to the ring.[11] It is a 14-π-electron system[2] and so the total complement of 54 valence electrons $[(5 \times 6) + (5 \times 5) - 1]$ can be regarded as being composed, essentially, of the following types of electron pairs: $10\sigma + 7\pi + 10$ ' non-bonding ' (one per atom).

The structure of $S_5N_5^+$ is unusual in several ways: (i) The wide bond angles at the nitrogen atoms (between 137 and 178°) indicate extensive in-plane lone-pair delocalisation. This has been confirmed by a recent all-valence electron SCFMO treatment.[2] The 10 ' non-bonding ' electron pairs are therefore not entirely non-bonding.

(ii) The shortest SN ring distances known (146·5 pm) are shown by the almost-linearly co-ordinated nitrogen atoms [N(4) and N(6)] of $S_5N_5^+$. Thus, each of these nitrogen atoms has two multiple NS bonds, the distance of one being close to that (144·6 pm)[12] of N≡S–F.

(iii) The ring distances are so short (average $d_{SN} = 154$ pm) that the sulphur atoms on either side of each nitrogen atom are closer than the sulphur van der Waals diameter of *ca.* 370 pm.[13] The shortest ' non-bonded ' SS distance (280 pm) is $d(S_1—S_9)$. Ring distances are also short in the 10π system $S_4N_3^+$ (average $d_{SN} = 155$ pm)[14] which is the only other planar SN species known.

The short ring distances in $S_4N_3^+$ and $S_5N_5^+$ are less surprising when one calculates the average number, n, of σ and π electrons per SN bond [$7\sigma + 5\pi$ pairs in $S_4N_3^+$, $n = (14 + 10)/7 = 3{\cdot}43$. $10\sigma + 7\pi$ pairs in $S_5N_5^+$, $n = (20 + 14)/10 = 3{\cdot}40$]. Thus each ring atom in $S_5N_5^+$ exercises an apparent covalency (on average) of 3·40. This is remarkable for the nitrogen atoms which all carry a negative charge.[2]

The extensive π delocalisation and the high bond orders in $S_4N_3^+$ and $S_5N_5^+$ no doubt contribute to the striking chemical stability (under acid conditions) of the salts. A further important consequence is that satisfactory sets of canonical structures cannot be written. This perhaps explains why $S_4N_3^+$ was not earlier recognised as being one member of a potentially large class of sulphur–nitrogen aromatic species.

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