Reactions of Tetrasulphur Tetranitride with Halides. Part VI.[1] The Preparation and Structure of Cyclopentathiazenium Pentachloro(phosphoryl chloride)stannate(IV)

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Tetrasulphur tetranitride, sulphuryl chloride, and tin tetrachloride react in phosphoryl chloride to give $S_4N_4{\cdot}POCl_3{\cdot}SnCl_4$ and the new cyclopentathiazenium salt $[S_5N_5][SnCl_5(OPCl_3)]$. *X*-Ray diffraction studies of the latter show that the cation has an azulene-type structure as found in $[S_5N_5][S_3N_3O_4]$. The reactions of $S_3N_2Cl_2$, $(SNCl)_3$, S_4N_3Cl, S_4N_4, and $(S_4N_4)_2SnCl_4$ with $POCl_3$ have also been studied.

CYCLOPENTATHIAZENIUM, $[S_5N_5]^+$, salts have been prepared by three methods: (*i*) from tetrasulphur tetranitride and a metal chloride (as a mixture or as an adduct) in thionyl chloride;[2] (*ii*) from S_4N_4, trichlorocyclotrithiazene $(SNCl)_3$, and a metal chloride in $SOCl_2$;[1] and (*iii*) from the reaction between $S(NSiMe_3)_2$ and $SF(NSO)O_2$ in methylene chloride.[3] The disadvantage of $SOCl_2$ is that it participates in side reactions with S_4N_4. We have therefore investigated the possibility of using phosphoryl chloride as an alternative solvent for the formation of cyclopentathiazenium salts.

We report the synthesis of the adduct $S_4N_4{\cdot}POCl_3{\cdot}SnCl_4$ and of $[S_5N_5][SnCl_5(OPCl_3)]$ from S_4N_4, tin tetrachloride, and sulphuryl chloride (1 : 1 : 1) in $POCl_3$. We also

$$\tfrac{1}{4}S_4N_4 \xrightarrow{SO_2Cl_2} \frac{1}{x}(SNCl)_x \xrightarrow{S_4N_4} S_5N_5Cl \xrightarrow{SnCl_4-POCl_3} [S_5N_5][SnCl_5(OPCl_3)] \quad (1)$$

report the action of $POCl_3$, at temperatures up to 105 °C, on each of the compounds S_4N_4, $(S_4N_4)_2SnCl_4$, $S_3N_2Cl_2$, S_4N_3Cl, and $(SNCl)_3$. An examination of crystals of $[S_5N_5][SnCl_5(OPCl_3)]$ by *X*-ray diffraction has shown that the cation has an azulene-type structure (as in $[S_5N_5]$-$[S_3N_3O_4]$)[4] rather than the heart-shaped arrangement reported[5] for $[S_5N_5][AlCl_4]$. The anion is a new species with an oxygen bridge between the phosphorus and metal atoms as found[6] in the isoelectronic adduct $SbCl_5(OPCl_3)$.

EXPERIMENTAL

Infrared spectra (250—4 000 cm^{-1}), of Nujol mulls prepared under nitrogen, were recorded using KBr plates and a Perkin-Elmer 457 prism grating spectrophotometer. Mass spectra were obtained on an A.E.I. MS9 mass spectrometer at 70 eV with an accelerating potential of 8 keV.† Samples were directly inserted into the ion source at 40 °C.

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† 1 eV ≈ 1.60×10^{-19} J.

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The compound $[S_5N_5][SnCl_5(OPCl_3)]$ crystallised with a monoclinic cell, $a = 8.272(1)$, $b = 12.834(2)$, $c = 18.515(3)$ Å, $Z = 4$, space group $P2_1/c$. The intensity data were collected on a Hilger and Watts four-circle diffractometer using zirconium-filtered Mo radiation and employing a θ—2θ scan. Within the range $0 < \theta \leqslant 25°$, 3 440 reflections were recorded and 2 054 of these were considered to be observed having net counts $\geqslant 2.5\ \sigma$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods to R 0.06 for the 2 054 observed reflections.

Phosphoryl chloride, sulphuryl chloride, and tin tetrachloride were purified by distillation. Tetrasulphur tetranitride was prepared by the method described by Jolly,[7] and $(SNCl)_3$ was obtained from it by the action of SO_2Cl_2;[8] $S_3N_2Cl_2$ was prepared from ammonium chloride and disulphur dichloride.[9] The adduct $(S_4N_4)_2SnCl_4$ was prepared by adding $SnCl_4$ to a solution of S_4N_4 in carbon tetrachloride.[10] Reagents and products were manipulated under nitrogen. Methods of analysis have been reported previously.[1]

Preparation of Cyclopentathiazenium Pentachloro(phosphoryl chloride)stannate(IV), $[S_5N_5][SnCl_5(OPCl_3)]$.—A mixture of $SnCl_4$ (0.90 cm^3, 1.99 g; 0.0076 mol) and SO_2Cl_2 (0.62 cm^3, 1.03 g; 0.0076 mol) in a round-bottomed flask (100 cm^3) was poured *via* a 15-cm glass connecting tube into a second flask (250 cm^3) containing a slurry of S_4N_4 (1.40 g, 0.0076 mol) in $POCl_3$ (20 cm^3). Transparent crystals of (I) formed on the lower part of the connecting tube. The solution, on stirring at room temperature, quickly turned red and purple-brown $(S_4N_4)_2SnCl_4$, (II), precipitated. A small amount of the adduct was withdrawn and characterised by its i.r. spectrum.[11] The upper flask and connecting tube were replaced by a water condenser. Both the solution and the solid became brown as the temperature was raised to the boiling point. During refluxing for 2 h (oil-bath, 105 °C), the solution and precipitate lightened to red. A brown powder, (III), adhered to the upper part of the flask above the liquid level. Yellow crystals of the $[S_5N_5]^+$ salt, (IV), separated out on cooling. The mixture was filtered and, after pumping dry, the yellow platelets were separated by hand in a glove-box from the brown powder, (III), to give the $[S_5N_5]^+$ salt, (IV) (1.5 g, 30% yield based on S_4N_4) (Found: Cl, 41.55; N, 10.4; S, 23.7, Sn, 17.75. $Cl_8N_5OPS_5Sn$ requires Cl, 41.75; N, 10.3; S, 23.6; Sn, 17.45%). Major mass-spectral peaks were found at *m/e* (relative intensities and assignments are given): 307—301(3) $[SnCl(OPCl_3)]^+$; 270—268(2) $[Sn(OPCl_3)]^+$; 266—256(16)$[SnCl_4]^+$; 233—217(100) $[SnCl_3]^+$; 192—186(3) $[SnCl_2]^+$; 184(2) $[S_4N_4]^+$; 157—151(6) $[SnCl]^+$; 156—152(3) $[POCl_3]^+$; 138(2) $[S_3N_3]^+$; 124(2) $[S_3N_2]^+$; 122—116(6) $[Sn]^+$; 119—117(6) $[POCl_2]^+$; 92(8) $[S_2N_2]^+$; 78(5) $[S_2N]^+$; 64(2) $[S_2]^+([SO_2]^+)$; and 46(15) $[SN]^+$. I.r. spectrum: 1 210vs; 1 112s; 1 050w; 1 020s; 980w(sh); 804m; 731m; 619vs; 542m; and 476w cm^{-1}.

The colourless crystals, (I), taken from the connecting tube had an i.r. spectrum identical to that of $SnCl_4(POCl_3)_2$ prepared by the method of Garner and Sugden.[12] The brown powder, (III), was recrystallised from $POCl_3$ to give very small orange-brown crystals (1.1 g) (Found: Cl, 41.25; N, 9.7; S, 21.9; Sn, 18.9. $Cl_7N_4POS_4Sn$ requires Cl, 41.5; N, 9.35; S, 21.45; Sn, 19.85%). I.r. spectrum: 1 285vs; 1 166s; 1 022m; 970w(sh); 800m; 722s; 672w; 585vs; 536s; and 470w cm^{-1}.

The Action of $POCl_3$ *on* S_4N_4, $(S_4N_4)_2SnCl_4$, $(SNCl)_3$, *and* $S_3N_2Cl_2$.—A mixture of S_4N_4 (0.1 g) and $POCl_3$ (20 cm^3) was heated under reflux (105 °C). Visible reaction (conversion into yellow S_4N_3Cl) occurred as the temperature rose above 80 °C and was complete after boiling for 10 min. A mixture of $(S_4N_4)_2SnCl_4$ (1.3 g) and $POCl_3$ (20 cm^3) was heated under reflux for 1 h. The i.r. spectrum of the filtered solid showed that there had been no significant reaction. Trichlorocyclotrithiazene $(SNCl)_3$ (1.0 g dissolved in 20 cm^3 of $POCl_3$) was heated at 60 °C for 2 h. No reaction was observed. A sample of the solution was evaporated to dryness and an i.r. spectrum of the residue corresponded to $(SNCl)_3$. The solution was then heated at 80 °C for 2 h; S_4N_3Cl slowly precipitated. The cooled mixture was filtered. On evaporation the filtrate gave a little red-green dichroic oil which was not investigated further.

On adding powdered thiodithiazyl dichloride (4 g) to $POCl_3$ (40 cm$_3$) in a round-bottomed flask, the orange-brown $S_3N_2Cl_2$ remained largely undissolved, but on warming to 60 °C reaction occurred giving a green precipitate and a red solution. A sample of the precipitate was withdrawn; its i.r. spectrum corresponded to that of S_3N_2Cl.[13] On further heating and refluxing at 105 °C for 3 h the precipitate became yellow and the solution became orange. The i.r. spectra of the precipitate and evaporated solvent corresponded to S_4N_3Cl[14] and impure S_4N_3Cl respectively.

RESULTS AND DISCUSSION

The Structure and Bonding in $[S_5N_5][SnCl_5(OPCl_3)]$.—The cation, which consists of a ten-membered ring of alternate sulphur and nitrogen atoms, is a 14-π-electron member of the series of aromatic thiazenes.[15] The bond distances and bond angles are very similar to those in $[S_5N_5][S_3N_3O_4]$.[4] In both $[S_5N_5][SnCl_5(OPCl_3)]$ and $[S_5N_5][S_3N_3O_4]$ there is less variation in S–N bond distances and in nitrogen bond angles than in $[S_5N_5][AlCl_4]$; the mean values also differ significantly (Table 1).

TABLE 1

Some bond distances (pm) and bond angles (°) in $[S_5N_5]^+$ salts

	$[S_5N_5][AlCl_4]$	$[S_5N_5][S_3N_3O_4]$	$[S_5N_5][SnCl_5(OPCl_3)]$
SN bond lengths	146.5—159.0	154.3—158.0	149.7—158.7
(av. value)	153.9	156.0	155.8
N bond angles	129—177	133—151	132—153
(av. value)	151.9	142.4	142.6

The anion $[SnCl_5(OPCl_3)]^-$ contains a central metal atom with one oxygen and five chlorine atoms co-ordinated in an approximately octahedral arrangement

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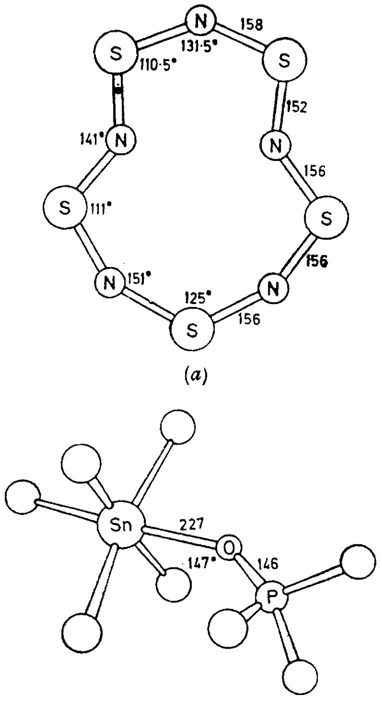
as found in the isoelectronic adduct $SbCl_5(OPCl_3)$.[6] The Sn–O distance [227(1) pm] is close to the mean value [228(3) pm] found in $SnCl_4(POCl_3)_2$.[16] The P–O distance [146(1) pm] is not significantly larger than that [144.8(5) pm] found in free $POCl_3$,[17] and is the same, within experimental error, as that in $SbCl_5(POCl_3)$ [147(2) pm] and $SnCl_4(POCl_3)_2$ [145(5) pm]. The Sn–O–P angle [147.3(6)°] also does not differ significantly from the angle at oxygen in $SbCl_5(POCl_3)$ [145.0(1.6)°] and in $SnCl_4(POCl_3)_2$ [148.2(2.7)°].



Structure of the cation (*a*) and the anion (*b*) in $[S_5N_5][SnCl_5(OPCl_3)]$ (Bond lengths in pm.)

Reactions.—The adduct $(S_4N_4)_2SnCl_4$ (which is unaffected by boiling $POCl_3$) and some excess of $SnCl_4$ were treated with a solution of SO_2Cl_2 in $POCl_3$. Sulphuryl chloride is known[18] to react with S_4N_4 to give $(SNCl)_3$ and so the course of the reaction may well be somewhat similar to that between S_4N_4 and metal chlorides in $SOCl_2$ [equation (2)]. The co-ordinated

$$S_4N_4 \xrightarrow{SOCl_2} NSCl \xrightarrow{MCl_3} [SN][MCl_4] \xrightarrow{S_4N_4} [S_5N_5][MCl_4] \quad (2)$$

S_4N_4 was probably chlorinated by the SO_2Cl_2 to form an oligomer of SNCl, or perhaps $S_4N_4Cl_2$ (as yet unknown), which remains co-ordinated to the $SnCl_4$. Rearrangement then takes place involving solvent $POCl_3$ which enters the anion. The overall reaction is (3). The

$$2\tfrac{1}{2}S_4N_4 + SO_2Cl_2 + 2SnCl_4 + 2POCl_3 \longrightarrow 2[S_5N_5][SnCl_5(OPCl_3)] \quad (3)$$

product could, no doubt, be prepared by method (*ii*) described in the introduction [*viz*. $S_4N_4 + (SNCl)_3 + SnCl_4$ in $POCl_3$]; the chosen method, (*i*), avoids the preparation of $(SNCl)_3$. There was also the possibility in our method that the co-ordinated S_4N_4 ring would remain intact during chlorination [Nelson and Heal[18] showed that $(SNCl)_4$ is probably an intermediate in the reaction between chlorine and S_4N_4 in carbon disulphide]. This could lead to the formation of the hitherto unknown $(10\,\pi)$ cyclotetrathiazenium(2+) ion as $[S_4N_4][SnCl_6]$, but no evidence for its presence was found in the products.

The reaction yielded two other products in addition to yellow platelets of $[S_5N_5][SnCl_5(OPCl_3)]$. Transparent crystals of $SnCl_4(POCl_3)_2$ were formed during the early part of the reaction. Mass and i.r. spectra were identical to those of a sample prepared from $POCl_3$ and $SnCl_4$.[12] The brown powder, (III), which from i.r. and mass spectra and analyses was shown to be $S_4N_4{\cdot}POCl_3{\cdot}SnCl_4$, is a new adduct which has similarities in its i.r. spectrum to both $(S_4N_4)_2SnCl_4$ and $SnCl_4(POCl_3)_2$. Other possible side reactions are as follows. Trichlorocyclotrithiazene, $(SNCl)_3$, forms numerous air-sensitive adducts with Lewis acids including a 1 : 1 adduct with $SnCl_4$.[19] This adduct was either not formed or was consumed during the reaction.

The studies of the action of hot $POCl_3$ on S_4N_4, $(S_4N_4)_2SnCl_4$, $(SNCl)_3$, and $S_3N_2Cl_2$ showed that $POCl_3$ has potential as a non-participating solvent for the formation of other sulphur–nitrogen cations. The compounds S_4N_4 and $(SNCl)_3$ can be used without decomposition providing the temperature is kept below *ca*. 60 °C. Table 2 shows all possible 2 : 1 adducts of Cl^-, $POCl_3$, and S_4N_4 with $SnCl_4$. It is interesting to note that with the formation of the new species (III) ($S_4N_4{\cdot}POCl_3{\cdot}SnCl_4$) and $[SnCl_5(OPCl_3)]^-$, only one species, $S_4N_4{\cdot}[SnCl_5]^-$, remains to be synthesised to complete the Table.

TABLE 2

Possible 2 : 1 adducts of Cl^-, $POCl_3$, and S_4N_4 with $SnCl_4$

	Cl^-	$POCl_3$	S_4N_4
Cl^-	$[SnCl_6]^{2-}$		
$POCl_3$	$POCl_3{\cdot}[SnCl_5]^-$ [a]	$SnCl_4(POCl_3)_2$ [b]	
S_4N_4	$S_4N_4{\cdot}[SnCl_5]^-$ [c]	$S_4N_4{\cdot}POCl_3{\cdot}SnCl_4$ [a]	$(S_4N_4)_2SnCl_4$ [d]

[a] This work. [b] Ref. 12 and this work. [c] Unknown. [d] Ref. 11 and this work.

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