Reactions of Tetrasulphur Tetranitride with Halides. Part IV.[1] The Formation of Cyclopentathiazenium Salts in Thionyl Chloride

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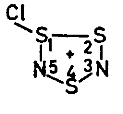
Tetrasulphur tetranitride reacts with thionyl chloride in the presence of ferric or aluminium chloride to give a mixture of the tetrachlorometallates (MCl_4^-, M = Fe or Al) of the cations $S_3N_2Cl^+$, $S_4N_3^+$, and the new species $S_5N_5^+$; their i.r. spectra are discussed. These three cations appear to be members of a potentially large class of inorganic aromatic SN species.

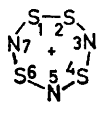
In the reaction between tetrasulphur tetranitride and thionyl chloride,[2] alternating SN sequences of 7 and 5 atoms are preserved in the products $S_4N_3^+Cl^-$ and $S(NSO)_2$ respectively. The reaction is slow at room temperature, and precipitation of S_4N_3Cl occurs during several hours. The S_4N_4–$SOCl_2$ mixture is therefore a potential source of SN fragments in solution. We have attempted to isolate new SN species by investigating ternary systems S_4N_4–$SOCl_2$–metal chloride. The Lewis acid MCl_x was added to modify the course of the reaction (i) by providing new reaction sites (*e.g.* for the donor S_4N_4 molecules) and/or (ii) by 'intercepting' and stabilising reactive SN intermediates.

Exploratory experiments[3] in the S_4N_4–$SOCl_2$–MCl_x system (MCl_x = metal or metalloid chloride) indicated that chlorides of many main group elements [Be, B, Al, Ga, In, Sn^{IV}, Sb^{V}, Se^{I}, and Te^{IV}] and transition metals [Groups IVB, VB, VIB, and Mn^{II}, Fe^{III}, Co^{II}, Zn^{II} and Hg^{II}] react with tetrasulphur tetranitride in thionyl chloride. Reactions involving Se_2Cl_2;[2] $BeCl_2$, $SbCl_5$, $CrCl_3$, $MnCl_2$, $FeCl_3$, $CoCl_2$, $ZnCl_2$, and $ZrCl_4$[4] have already been described. We now describe studies on the systems S_4N_4–$SOCl_2$–MCl_x [MCl_x = $AlCl_3$ or $FeCl_3$] and the isolation of tetrachlorometallate [(a) $AlCl_4^-$ (b) $FeCl_4^-$] salts of the cations (I)—(III).

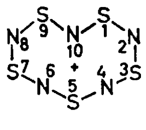
The cation (I) is already known as the chloride;[5] numerous salts of cation (II) have been prepared[5] though not including $S_4N_3AlCl_4$. Cation (III) is a new species and has been described in a preliminary communication.[6]



(I) $S_3N_2Cl^+$



(II) $S_4N_3^+$



(III) $S_5N_5^+$

EXPERIMENTAL

I.r. spectra of Nujol mulls prepared under nitrogen were recorded on Grubb–Parsons Spectromaster (400—4000 cm^{-1}) and DM2/DB3 (475—200 cm^{-1}) prism grating spectrophotometers. U.v. spectra, of solutions prepared in a dry box, were recorded on a Unicam SP 800 spectrophotometer. Acetonitrile was dried over phosphorus pentoxide and purified by distillation.[7] Formic acid was dried over boric oxide and anhydrous copper sulphate and purified by distillation.[7] Tetrasulphur tetranitride was prepared by the method described by Jolly.[8] Thionyl chloride was purified by fractional distillation from triphenyl phosphite.[9]

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[2] A. J. Banister and J. S. Padley, *J. Chem. Soc.* (*A*), 1967, 1437.

[3] A. J. Banister, P. J. Dainty and J. S. Padley, unpublished results.

[4] A. J. Banister and J. S. Padley, *J. Chem. Soc.* (*A*), 1969, 658.

[5] I. Haiduc, 'The Chemistry of Inorganic Ring Systems,' Wiley–Interscience, London, 1970.

[6] A. J. Banister, P. J. Dainty, A. C. Hazell, R. G. Hazell, and J. G. Lomborg, *Chem. Comm.*, 1969, 1187.

[7] A. Weissberger, 'Technique of Organic Chemistry, vol. VII Organic Solvents,' Interscience, New York, 2nd edn., 1955.

[8] W. L. Jolly, 'Synthetic Inorganic Chemistry,' Prentice Hall International, London, 1960, p. 166.

[9] L. Friedman and W. P. Wetter, *J. Chem. Soc.* (*A*), 1967, 36.

Aluminium chloride was purified by sublimation, and ferric chloride by heating with refluxing thionyl chloride for 1 h.

In all S_4N_4–$SOCl_2$–MCl_x reactions the molar proportions S_4N_4:MCl_x were 1 : 1 and mixtures were stirred continuously under an atmosphere of dry nitrogen. Solutions of tetrasulphur tetranitride (*ca.* 0·15M) in thionyl chloride were freshly prepared unless otherwise stated; the solubility of tetrasulphur tetranitride in thionyl chloride at 20° is *ca.* 25 g l^{-1}. Reactions were terminated when further heating for 1 h did not affect appearance (solution finally red–green, dichroic).

The crude products were obtained by concentrating the solution under reduced pressure, redissolving precipitated solid at the b.p. of the solvent and allowing the solution to cool slowly. Purification was by repeated sequences (up to *ca.* 6 times) of hand-sorting of crystals in a dry box (all compounds are sensitive to moisture) followed by recrystallisation from thionyl chloride, until a constant m.p. was obtained.

The 1-*Chloro*-1,2,4-*trithia*-3,5-*diazacyclopentahetranenium Salts* * (Ia, b).—The salts were formed [with compounds (II) and (III)] on treating a solution or suspension of metal chloride in thionyl chloride at 60°, with tetrasulphur tetranitride in thionyl chloride. Crystallisation [to constant melting point (Ia), 89° and (Ib), 83°] is slow. A similar reaction with $TaCl_5$ (at 40° for 2 days) gave one product only (m.p. 137°); analyses and the i.r. spectrum indicated that the structure was probably $S_3N_2Cl^+TaOCl_4^-$. It was also prepared by the action of thionyl chloride at 40° on the adduct [10] $S_4N_4,TaCl_5$.

Properties of cyclopentathiazenium compounds

	Analytical data									
	Found (%)				Required (%)					
Compound	Cl	N	S	Metal	Cl	N	S	Metal	M.p./°	I.r. spectrum (cm^{-1})
$S_5N_5^+AlCl_4^-$	34·1	17·1	39·5	6·0	35·5	17·5	40·2	6·8	181	1144s, 1048w, 1023w,sh, 976vw,sh, 733m, 722m,sh, 687w, 613w, 529s, 497vs,sh, 483vs, 327m.
$S_5N_5^+FeCl_4^-$	33·0	15·9	36·6	14·2	33·1	16·4	37·5	13·1	181	1143s, 1047w, 1017vw,sh, 731m, 721m,sh, 685m, 608m, 528s, 370s, 327s.
$S_5N_5^+GaCl_4^-$ *									171	1146s, 1049w, 1020w,sh, 988vw,sh, 733w, 722w, 712w,sh, 687w, 608w, 529s. No far i.r. recorded

* M.p. and i.r. spectrum obtained on single crystals from a slighly impure sample of the compound.

Salts (Ia, b) were also obtained by stirring the adducts [10] $S_4N_4,2AlCl_3$ and $S_4N_4,2FeCl_3$ with an excess of thionyl chloride (40°, *ca.* 1 h) until there was no further change in the final red–green dichroic colour of the solution. A third route is by reaction of $S_3N_2Cl_2$ ($S_3N_2Cl^+Cl^-$) with the metal trichloride.[11] A 1 : 1 molar ratio mixture of $S_3N_2Cl_2$ and ferric chloride suspended in thionyl chloride at 20° was stirred for 24 h and the precipitated product was recrystallised from thionyl chloride and characterised from its m.p. and i.r. spectrum.[11] U.v.–visible (225—700 nm) absorptions of $S_3N_2FeCl_5$ occur in acetonitrile (0·0315) at 237·5 (ε 16,000), 311·5 (ε 15,000), and 359 nm (ε 11,000). Molar extinction coefficients are approximate as the solutions slowly decompose.

I.r. Spectra.—$S_3N_2Cl^+AlCl_4^-$: 1170vw, 1059vw,sh, 1033w, 1012w, 988vw, 967w, 942vs, 784vw,sh, 765m, 745s, 716s, 695w, 685w, 574m, 571m, 529s,sh, 508vs,sh, 489vs, 477vs, 461vs, 423s, 381s, 319m, and 306s cm^{-1}. $S_3N_2Cl^+FeCl_4^-$: 1156vw, 1091vw, 1037vw, 1008vw, 938vs, 891vw, 759w, 742s, 717s, 574s, 463s, 458m,sh, 418vs, 379vs, 331m, 324m, and 304s cm^{-1}; $S_3N_2Cl^+TaOCl_4^-$: 1156w, 1110w, 1017w, 997w, 941vs, 762w, 746m,sh, 742m, 721m,sh, 715m, 570m, 534w, 522w, 466m, 460w,sh, 432s,sh, 418s, 376m, 316vs, 279s,sh, 253w, 246vw, and 224w cm^{-1}.

The 1,2,4,6-*Tetrathia*-3,5,7-*triazacycloheptahetranenium Salts* (IIa, b).—The S_4N_4–$SOCl_2$–MCl_3 (M = Al or Fe) reactions produce small quantities of S_4N_3,MCl_4; the yield improves (up to *ca.* 40% based on nitrogen) on treating the solution or suspension of MCl_3 (M = Al or Fe) in thionyl chloride at 40—45° with an S_4N_4–$SOCl_2$ solution which has been set aside at room temperature for 20—25 min (to produce S_4N_3Cl in solution). Compounds (I) and (II) in the mixed product are not readily distinguished by eye and have similar solubility in thionyl chloride; considerable enrichment was obtained however on recrystallisation, and the characteristic i.r. absorptions were located. Compound (IIb) was also prepared by stirring (24 h) a 1 : 1 molar ratio mixture of the corresponding chloride (II) and ferric chloride suspended in thionyl chloride at 20°. The insoluble product was recrystallised from thionyl chloride. It has been prepared previously in formic acid.[12] The i.r. spectrum is identical to that of product (IIb) from S_4N_4–$SOCl_2$–$FeCl_3$.

I.r. Spectra.—$S_4N_3^+AlCl_4^-$: 1176m, 1139w, 1035s, 743vw, 722vw, 676m, 667w,sh, 616vw, 570m, 563w,sh, 522m,sh, and 495vs,br cm^{-1}; $S_4N_3^+FeCl_4^-$: 1178m, 1139w, 1094vw, 1032vs, 1020s,sh, 751vw, 723vw, 676s, 670m,sh, 647vw, 616w, 570ms, 564m,sh, 517m, 486vs,br and 469s,br.

The Cyclopentathiazenium (1,3,5,7,9-*Pentathia*-2,4,6,8,10-*penta-azacyclodecahetranenium*) *Salts* (IIIa, b).—These salts were prepared by treating solid tetrasulphur tetranitride with a solution or suspension of MCl_3 (M = Al or Fe) in thionyl chloride. Maximum yields of $S_5N_5MCl_4$ (estimated 65% based on nitrogen) were obtained in reactions close to 35° (M = Al) or *ca.* −15° (M = Fe). Compounds (I), which were always generated simultaneously, were removed during the hand-sorting and recrystallisation procedure; they appear as relatively dull yellow to yellow-brown crystals. Crude $S_5N_5AlCl_4$ and $S_5N_5FeCl_5$ appear as orange and black crystals respectively. Pure $S_5N_5AlCl_4$ and $S_5N_5FeCl_4$ are obtained as yellow needles and brown plates respectively. Analyses, m.p.s, and i.r. absorptions are given in the Table.

Acetonitrile, anhydrous formic acid, and concentrated

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* In view of the difficulty of naming some of the compounds prepared in this work by established rules of nomenclature, we have, on the advice of the Director of Publications, adopted a system at present under consideration by the I.U.P.A.C. authorities. This system provides the most satisfactory names for heteroaromatic structures without emphasising the supremacy of carbon as in organic nomenclature. The basic principles are those of replacement nomenclature.

[10] G. G. Alange and A. J. Banister, unpublished results.

[11] Experimental work by H. G. Clarke.

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

(18·3M) sulphuric acid solutions of $S_5N_5AlCl_4$ absorb, in the region 225—700 nm, 327 (ε 35,000) and 426 nm (ε 2,500).[11] Molar extinction coefficients were measured in formic and sulphuric acids since the solid dissolves slowly in acetonitrile and the solutions slowly decompose. Hydrogen chloride is evolved during the dissolution in formic or sulphuric acid but this is due to decomposition of the $AlCl_4^-$ anion only; the absorption wavelengths in the three solvents are identical.

Exploratory investigations of the S_4N_4–$SOCl_2$–$GaCl_3$ system, again showed three products with spectra characteristic of compounds of types (I), (II), and (III). It was concluded that they were similar to the analogous aluminium and iron compounds described above and so were not isolated pure in any quantity by the necessarily tedious fractional crystallisation. The i.r. frequencies and m.p. of $S_5N_5GaCl_4$ are given in the Table.

DISCUSSION

Structures of the Three Classes of Products.—Type (I) *compounds* ($S_3N_2Cl^+$ *salts*). In the absence of reproducible analyses, structures for type (I) compounds were assigned as follows. The combination of the chloride (I), $S_3N_3Cl^+Cl^-$, and iron(III) chloride in thionyl chloride to give a compound identical to (Ib), indicated an ionic structure $S_3N_2Cl^+FeCl_4^-$. The presence of $FeCl_4^-$ was confirmed by the u.v. absorptions of (Ib) which are typical of tetrachloroferrate(III) salts.[13] An *X*-ray structural study [14] of the S_4N_4–$SOCl_2$–$FeCl_3$ product (Ib) showed that it contained $FeCl_4^-$ and the cation $S_3N_2Cl^+$ as found [15] in $S_3N_2Cl_2$. The very similar near-i.r. spectra of $S_3N_2AlCl_5$, $S_3N_2TaOCl_5$, and the similarly obtained gallium compound, indicated that these are salts of the same $S_3N_2Cl^+$ cation *viz.* $S_3N_2Cl^+AlCl_4^-$, $S_3N_2Cl^+TaOCl_4^-$, and $S_3N_2Cl^+GaCl_4^-$.

The similarity in the i.r. spectra of $S_3N_2Cl_2$ and compounds (I) is to be expected. However, the 1017 cm^{-1} absorption of $S_3N_2Cl_2$ is much weaker in the salts with larger anions resulting in a remarkable spectral similarity to S_4N_4. This emphasises the structural relationship between S_4N_4 and $S_3N_2Cl^+$. The latter consists of planar S_2N_2 with the third S atom (with attached Cl) out of the local plane [Figure (b)]. The S_4N_4 molecule can be regarded as consisting of two fused S_3N_2 rings with a common S–S axis and a further S–S link, and again each S_3N_2 ring has a planar S_2N_2 portion. The average SN distances differ little in $S_3N_2Cl^+FeCl_4^-$ (159 pm) [14] and S_4N_4 (162 pm).[16] Since compounds (I) are still formed using S_4N_4 adducts instead of separate S_4N_4 and metal chloride, a possible function of the metal chloride may be to act as a template during the attack of thionyl chloride on tetrasulphur tetranitride [Figure (a)]. Retention of an S_3N_2 ring has also been described for reactions of S_4N_4 with acetylenes.[17]

It is now clear that many reactions in ternary systems S_4N_4–$SOCl_2$–metal chloride give mixtures of products which are difficult to separate by recrystallisation. For instance i.r. spectra of the compounds reported [4] as $S_2N_2FeCl_3$ and $S_3N_3SbCl_6$ indicate that they were substantially $S_3N_2Cl^+FeCl_4^-$ and $S_3N_2Cl^+SbCl_6^-$. The spectra of these two $S_3N_2Cl^+$ salts are very similar.

Type (II) *compounds* ($S_4N_3^+$ *salts*). The i.r. spectra of the type (II) compounds from the $AlCl_3$, $GaCl_3$, and $FeCl_3$ reactions are closely similar to one another and to that of S_4N_3Cl.[2] The iron compound has also been prepared from S_4N_3Cl and $FeCl_3$. We therefore conclude that they are salts $S_4N_3^+X^-$ ($X = AlCl_4$, $GaCl_4$, and $FeCl_4$).

Type (III) *compounds* ($S_5N_5^+$ *salts*). It has been shown by *X*-ray diffraction [6,18] that $S_5N_5AlCl_4$ contains the planar heart-shaped cation $S_5N_5^+$ (III). The close similarity of i.r. spectra (Table) indicates that the other type (III) compounds from S_4N_4–$SOCl_2$–$GaCl_3$ or $FeCl_3$ are $S_5N_5^+GaCl_4^-$ and $S_5N_5^+FeCl_4^-$. These salts are the only sulphur–nitrogen–metal compounds isolated from S_4N_4–$SOCl_2$–MCl_n reactions which give clear yellow or orange thionyl chloride solutions. All other such compounds are either (i) highly insoluble or (ii) readily dissolved to give intensely coloured red–green dichroic solutions. The compounds of type (III) readily crystallise on account of the appreciable differences in solubility at room temperature and at the b.p. of thionyl chloride. This is in contrast to the $S_3N_2Cl^+$ salts described above which have a relatively high solubility in thionyl chloride at room temperature and may take several days to crystallise.

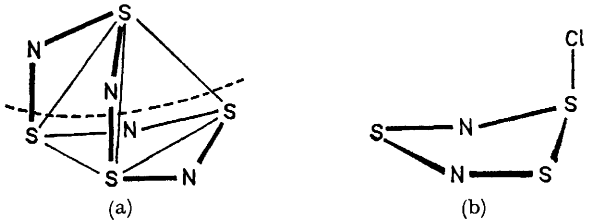

FIGURE (a) The ring fission of tetrasulphur tetranitride, in the presence of ferric or aluminium chloride. (b) The structure of $S_3N_2Cl^+$

One interesting aspect of the preparation of $S_5N_5^+$ salts is that, in the presence of the stated metal halides, the 8-membered ' ring ' (in fact a cage) of tetrasulphur tetranitride can be expanded to a 10-membered ring (the largest sulphur–nitrogen ring known). The only other reactions of tetrasulphur tetranitride involving change in ring size are ring contractions [*e.g.* chlorine [19] and sulphuryl chloride [1] give trichlorocyclotrithiazene $(NSCl)_3$, and disulphur dichloride gives [5] the chloride of (II) S_4N_3Cl]. It seems likely that the thionyl chloride attacks tetrasulphur tetranitride with the formation of $S_3N_2Cl_2$ and NSCl [*via* S_3N_2 and SN_2 fragments as shown in Figure (a)], and that the latter with ferric

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chloride provides incipient $NS^+FeCl_4^-$; ($NS^+AsF_6^-$ is already known [20]). The sulphur nitride then abstracts the NS^+ as $S_5N_5^+$.

Aromaticity of $S_3N_2Cl^+$, $S_4N_3^+$, *and* $S_5N_5^+$.—From Hückel MO calculations, Johnson, Blyholder, and Cordes [21] concluded that the electronic spectra of $S_4N_3^+$ were consistent with a 10-π-electron system. This suggests that in addition to the σ framework electrons (2 per atom) and the lone-pair electrons (2 per atom), each nitrogen provides 1 π-electron and each sulphur atom provides 2 π-electrons. Similarly $S_3N_2Cl^+$ and $S_5N_5^+$ are seen to be 6- and 14-π-electron species, and the three cations appear to compose an aromatic series.

Johnson *et al.*[21] assumed, from the SS bond distance (206 pm), that the π system does not bridge the two atoms. However, Lindqvist [22] proposed that with zero *s* character an SS single bond can be as long as 258 pm (in S_4N_4). This introduces the possibility of significant π bonding across the SS bond of $S_4N_3^+$. The genuine aromatic character of $S_3N_2Cl^+$, $S_4N_3^+$, and $S_5N_5^+$ has now been proved by all-valence electron SCF/MO calculations.[23] In the cation of $S_4N_3NO_3$, the p_π–p_π and p_π–d_π bond overlap populations,[24] for the SS bond and for one of the two neighbouring SN bonds, are:

	p_π–p_π	p_π–d_π
SS bond (206·4 pm)	0·30	*ca.* 0·4
SN bond (158·2 pm)	0·41	*ca.* 0·5

Thus the p_π–p_π and p_π–d_π interactions are of a comparable order of magnitude in the two bonds. The d_π components are upper limits as *d* orbital contributions are overestimated in a CNDO treatment.[23] For both bonds it is expected that p_π–p_π exceeds p_π–d_π overlap.

If sulphur consistently provides 2 π-electrons in other heterocycles, then $S_3N_2Cl^+$, $S_4N_3^+$, and $S_5N_5^+$ are seen to be members of an extensive and largely unexplored class of Hückel species which can be subdivided as follows:

(i) Neutral molecules: S_2N_2 (already known [5]), S_3N_4, S_4N_6, *etc.* Molecules with a great excess of nitrogen are expected to be explosive.

(ii) Cations: *e.g.* $S_2N_3^+$, $S_3N_5^+$ (both unknown) and doubly-charged species such as $S_6N_4^{2+}$ [present in S_3N_2Cl (ref. 5)?].

(iii) Anions: it is not known if an anionic charge (*e.g.* as in $S_3N_3^-$) has a serious destabilising effect on sulphur d_π bonding, as no planar anions have been prepared.

Many more SN Hückel structures are generated by inserting a group which provides no further π electrons; for instance, inserting Cl–S$^+$ into S_2N_2 gives $S_3N_2Cl^+$.

This systematisation must remain largely tentative until efforts are made to synthesise new species, especially those containing NN bonds.

We thank Ferodo Ltd. for the provision of a studentship (to P. J. D.) and Mr. R. Coult for analyses and technical assistance.

[1/2396 *Received*, 13*th December*, 1971]

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