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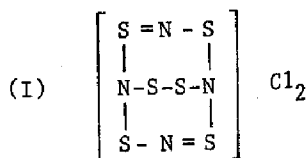
THE STRUCTURE OF THIODITHIAZYL CHLORODISULPHATE,  $S_3N_2S_2O_2Cl$  AND ITS PREPARATION  
FROM THIODITHIAZYL MONOCHLORIDE,  $S_3N_2Cl$

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Thiodithiazyl monochloride,  $S_3N_2Cl$ , has been known since 1880<sup>(1)</sup>, and although it is one of the most accessible inorganic sulphur-nitrogen compounds very little is known of its chemistry. It can be prepared from  $S_4N_4$  and  $S_2Cl_2$  in the cold<sup>(2)</sup>,  $S_4N_4$  and  $NOCl$ <sup>(2)</sup>,  $(NSCl)_3$  and  $NO$ <sup>(2)</sup>, or more conveniently from  $S_3N_2Cl_2$  either by heating (80-90°) in vacuo for 2-3 hours<sup>(3)</sup>, or by reduction with anhydrous formic acid (this paper). Thiodithiazyl monochloride is obtained as a deep green powder insoluble in most organic solvents and in water, by which it is rapidly hydrolysed.

Glemser<sup>(4)</sup> has suggested that  $S_3N_2Cl$  may be polymeric. Heal<sup>(5)</sup> and Becke-Geohring<sup>(6)</sup> have proposed (monocyclic<sup>(5)</sup> and bicyclic<sup>(6)</sup>(I)) ionic structures containing the  $S_6N_4^{2+}$  cation. An ionic structure is supported by recent chlorine n.q.r. data<sup>(7)</sup>. In contrast to  $S_3N_2Cl^+Cl^-$  which shows



chlorine n.q.r. frequencies [29.02 MHz ( $^{35}Cl$ ) and 22.91 MHz ( $^{37}Cl$ ) at 77°K] in the region expected for chlorine covalently bound to sulphur, no signal was detected for  $S_3N_2Cl$  in the frequency range 13.0 to 44.0 MHz<sup>(7)</sup>.

We have studied the reactions of  $S_3N_2Cl$  with chloride ion acceptors ( $AlCl_3$  and  $FeCl_3$ ) and with anhydrous acids ( $H_2SO_4$  and  $HSO_3Cl$ ). The chlorodisulphate,  $S_3N_2S_2O_6Cl$ , was obtained in low yield from  $S_3N_2Cl$  and chlorosulphuric acid and an examination of a single crystal by X-ray diffraction revealed a unique type of structure. The compound is essentially ionic ( $S_6N_4$ )<sup>2+</sup>( $ClSO_3 \cdot O \cdot SO_3^-$ )<sub>2</sub>. The cation (Figure 1) is of a new type; it consists of a pair of planar  $S_3N_2$  rings related by a centre of symmetry. The SS bonds in adjacent rings are parallel and the SS distances (3.027 Å) between the rings are well below the usual van der Waals separation (~ 3.7 Å). Each  $S_3N_2$  ring has a closely associated  $S_2O_6Cl^-$  ion.

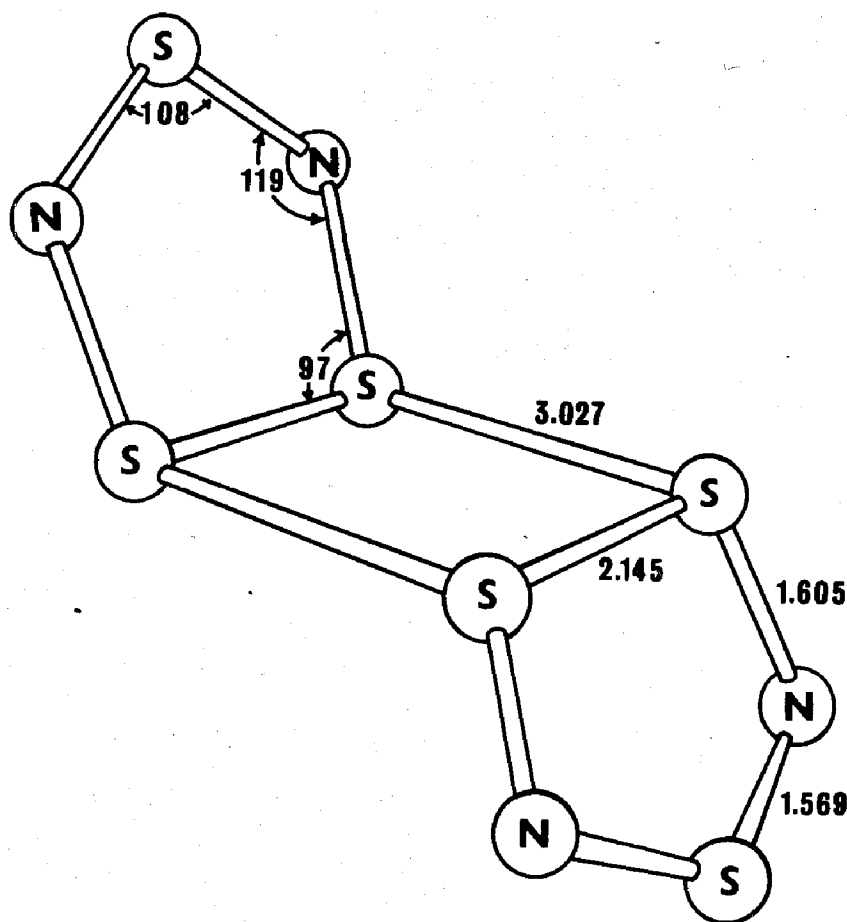


FIG. The  $S_6N_4^{2+}$  ion in  $S_6N_4(S_2O_6Cl)_2$

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### Experimental

I.r. spectra (Nujol mulls) were recorded on a Grubb Parsons GS2A or a Spectromaster prism grating spectrometer ( $4000-400\text{cm}^{-1}$ ). U.v./visible spectra were recorded on a Unicam SP800 spectrometer (190-700 nm). Thiodithiazyl monochloride,  $\text{S}_3\text{N}_2\text{Cl}$ , was prepared by heating  $\text{S}_3\text{N}_2\text{Cl}_2$  in vacuo at  $80-90^\circ$  for about 30 minutes<sup>(3)</sup>. Chlorosulphuric acid was freshly distilled under reduced pressure. Sulphur dioxide was dried in a cold trap over  $\text{P}_2\text{O}_5$  before distilling into the reaction flask. Formic acid was dried over boric oxide and anhydrous copper sulphate and purified by distillation<sup>(8)</sup>.

#### Reduction of thiodithiazyl dichloride to the monochloride with anhydrous formic acid.

Powdered thiodithiazyl dichloride (5 g.) was stirred at room temperature with anhydrous formic acid (ca. 50ml.). The orange  $\text{S}_3\text{N}_2\text{Cl}_2$  gradually turned dark green and when the evolution of gas had ceased (after ca. 2 h.), the precipitate ( $\text{S}_3\text{N}_2\text{Cl}$ ) was filtered and pumped dry in vacuo. The product was identified from its i.r. and u.v. spectra. Yield ca. 80%. Analysis figures showed that the purity of the product was usually inferior to that of the  $\text{S}_3\text{N}_2\text{Cl}$  obtained by heating  $\text{S}_3\text{N}_2\text{Cl}_2$  in vacuo<sup>(3)</sup>. I.r. and u.v. spectra were obtained using samples obtained by the latter method.

Thiodithiazyl monochloride dissolves in concentrated sulphuric acid with evolution of HCl. In the u.v./visible region  $\lambda_{\text{max}}$  (and  $\epsilon$ ) values were: 219 ( $3.5 \times 10^3$ ), 248.5 ( $4.7 \times 10^3$ ) and 356m ( $9 \times 10^2$ ); the molecular formula was taken as  $\text{S}_3\text{N}_2\text{Cl}$ . Since the solutions decompose rapidly on standing, spectra were recorded immediately, and molar extinction coefficients are only approximate. I.r. (Nujol mull) absorptions occurred ( $\text{cm}^{-1}$ ) at: 964s, 944vs, 745w, 716sh,s, 708vs, 699sh,s, 583s, 569w, 456w, 431m.

### Preparation of thiodithiazyl chlorodisulphate.

Thiodithiazyl monochloride (2.56 g., 0.016 mole) was added to chlorosulphuric acid (ca. 50ml.) in a round-bottomed flask under nitrogen. A rapid reaction ensued, HCl was evolved for a few minutes and the solution turned dark brown; there was no precipitate. The solution was allowed to stand under nitrogen at room temperature for 4-5 days, with occasional pumping to remove solvent. During this time, very deep green (virtually black) crystals formed at the bottom of the flask, together with a yellowish powder. The solid mixture was filtered and as much solvent as possible was removed in vacuo. The solid was washed with liquid SO<sub>2</sub>, pumped dry in vacuo and hand sorted, into crystals and powder, in a dry box. The powder was discarded. The crystals were further hand sorted to find those suitable for the X-ray studies. The overall yield was about 1%.

The reaction between S<sub>3</sub>N<sub>2</sub>Cl and HSO<sub>3</sub>Cl (using molar ratio 1:1) was also carried out in liquid SO<sub>2</sub> as solvent (in which S<sub>3</sub>N<sub>2</sub>Cl is slightly soluble). The precipitate which had formed after a few hours was solvent extracted with liquid SO<sub>2</sub> to give crystals of S<sub>3</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub>Cl; however these were mostly twinned or complex and unsuitable for X-ray work. The overall yield was again of the order of 1%.

### Other reactions of S<sub>3</sub>N<sub>2</sub>Cl.

The reactions of S<sub>3</sub>N<sub>2</sub>Cl with AlCl<sub>3</sub> and FeCl<sub>3</sub> were studied in various solvents in an attempt to prepare S<sub>3</sub>N<sub>2</sub>MCl<sub>4</sub> (M = Al, Fe). The reactions in nitrobenzene, chlorobenzene, acetyl chloride or carbon tetrachloride gave mixtures which appeared to consist of starting materials, hydrolysis products and (in the case of acetyl chloride) a complex (CH<sub>3</sub>CO<sup>+</sup>MC<sub>4</sub><sup>-</sup>, cf. CH<sub>3</sub>CO<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>)<sup>(9)</sup> with the solvents. In liquid sulphur dioxide, insoluble powders were obtained; analyses and spectra showed that they were mixtures and probably contained the required AlCl<sub>4</sub><sup>-</sup> or FeCl<sub>4</sub><sup>-</sup> salt, but they were too insoluble in liquid SO<sub>2</sub> to allow recrystallisation. In thionyl chloride,

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$S_3N_2Cl$  reacted (1:1) with  $AlCl_3$  or  $FeCl_3$  to give crystalline products but i.r. and u.v. spectra and analyses showed that they were  $AlCl_4^-$  and  $FeCl_4^-$  salts of the  $S_3N_2Cl^+$  cation already known (10,11).

### Structural Studies

The crystals obtained from the reaction between  $S_3N_2Cl$  and chlorosulphuric acid, crystallised in a triclinic cell with  $a = 7.689$ ,  $b = 10.726$ ,  $c = 6.614\text{\AA}$ ,  $\alpha = 101.00$ ,  $\beta = 114.43$ ,  $\gamma = 90.35^\circ$ , space group  $P\bar{1}$  and two units of  $S_3N_2S_2O_6Cl$  per cell. The intensity data were collected on a four circle diffractometer, using Zr-filtered Mo radiation, to a limit of  $\theta = 25^\circ$ . A total of 1707 reflections was recorded, and, of these, 1337 reflections were considered to be observed having net counts  $\geq 3$  e.s.d.'s. The structure was solved using the Patterson function and refined by full matrix least squares methods. The final R-value was 0.031 for the observed reflections.

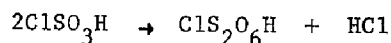
In the crystal, the cation consists of two planar  $S_3N_2$  rings, related to one another by a centre of symmetry. The isolated  $S_3N_2$  units, which show  $C_{2v}$  symmetry within the limits of experimental error, have an SS distance of  $2.145\text{\AA}$  and two distinct SN distances (mean values  $1.569\text{\AA}$  and  $1.605\text{\AA}$ ). The  $S_3N_2$  rings which lie in parallel planes  $2.884\text{\AA}$  apart are separated from one another by SS distances of  $3.027\text{\AA}$ .

In the anion,  $ClSO_3 \cdot O \cdot SO_3^-$ , the SO bridge distances are  $1.552$  and  $1.718\text{\AA}$ ; the shorter distance involves the sulphur atom attached to chlorine. The terminal SO distances lie between  $1.396$  and  $1.438\text{\AA}$ , and the SCl distance is  $1.986\text{\AA}$ . All the terminal oxygen atoms approach closely (in the range  $2.68$ – $3.04\text{\AA}$ ) to the sulphur atoms of the cations.

### Discussion

The reactions of  $S_3N_2Cl$  with  $AlCl_3$  and  $FeCl_3$  did not produce any useful products except in liquid  $SO_2$ . In this case the product was contaminated with starting material. Recrystallisation was not attempted because the reaction of  $S_3N_2Cl$  with chlorosulphuric acid produced crystals suitable for X-ray analysis.

Both  $S_4N_3Cl$  and  $S_3N_2Cl$  are soluble in chlorosulphuric acid;  $S_4N_3Cl$  gives the chlorosulphate<sup>(12)</sup>, but on standing with occasional pumping the solution of  $S_3N_2Cl$  slowly deposits crystals of the chlorodisulphate. Some hydrogen chloride was probably removed during the pumping, with formation of chlorodisulphuric acid:



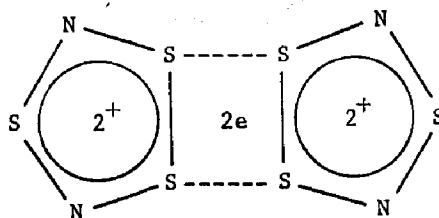
The chlorodisulphate is presumably less soluble than the chlorosulphate in chlorosulphuric acid.

The type of structure found for the cation is without precedent. The cation can be regarded as bicyclic  $S_6N_4^{2+}$  with a unique type of 4 centre interaction between pairs of sulphur atoms in two identical  $\pi$  delocalised  $S_3N_2$  rings (Figure 1). The SN distances (mean values  $1.569\text{\AA}$  and  $1.605\text{\AA}$ ) are typical of the distances found in  $\pi$  delocalised SN rings (cf.  $S_3N_2Cl^+$ ,  $1.543$ - $1.617$ , mean  $1.589\text{\AA}$ <sup>(10)</sup>;  $S_4N_3^+$ ,  $1.493$ - $1.582$ , mean  $1.550\text{\AA}$ )<sup>(13)</sup>. The SS distance ( $2.145\text{\AA}$ ) in each ring is close to that in  $S_3N_2Cl^+$  ( $2.136\text{\AA}$ )<sup>(10)</sup> and  $S_4N_3^+$  ( $2.064\text{\AA}$ )<sup>(13)</sup>. The  $S_3N_2$  rings are separated from one another by SS distances ( $3.03\text{\AA}$ ) which are appreciably shorter than van der Waals contact (e.g.  $3.64\text{\AA}$  in solid tetrasulphur tetranitride<sup>(14)</sup> and  $3.69\text{\AA}$  in orthorhombic sulphur)<sup>(15)</sup>. Sulphur-sulphur distances close to  $3\text{\AA}$  (viz.  $2.86$ ,  $2.94$ ,  $3.00$ ,  $3.07$ ,  $3.09\text{\AA}$  etc.)<sup>(16)</sup> have also been found in  $S_8^{2+}$  and these short cross-ring distances have been interpreted as resulting

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from multicentre bonding<sup>(17)</sup>. Since  $S_3N_2^{2+}$  would be a  $6\pi$  Hückel ring, it appears that the  $S_6N_4^{2+}$  cation can be regarded as consisting of two aromatic 1,2-dithiolium cations linked via pairs of sulphur atoms in a 4 centre 2 electron bond:



The anion was found to be the chlorodisulphate ion,  $ClSO_3 \cdot O \cdot SO_3^-$ , and this is the first reported structure determination of this species. The most noticeable features of the anion are the asymmetry of the oxygen bridge and the remarkably long bridge SO distance ( $1.718\text{\AA}$ ) involving the sulphur atom attached to oxygen only. It is a rare example of an SO bond longer than the "single bond" distance calculated from either Pauling's covalent radii ( $1.70\text{\AA}$ )<sup>(18)</sup> or the Schomaker-Stevenson rule ( $1.69\text{\AA}$ )<sup>(19)</sup>. A similar value of  $1.72\text{\AA}$  has been reported in  $(NO_2^+)_2S_3O_{10}^{2-}$  but the accuracy of this determination is low (e.s.d's about  $0.05\text{\AA}$  for the SO bonds)<sup>(20)</sup>. The other SO bridge distance ( $1.552\text{\AA}$ ) in  $S_6N_4^{2+}(S_2O_6Cl)^{2-}$  can be compared with that in  $HO-SO_3^-$  ( $1.56\text{\AA}$ , in  $KHSO_4$ )<sup>(21)</sup> and  $CH_3O-SO_3^-$  ( $1.58\text{\AA}$ )<sup>(22)</sup>. The terminal SO distances ( $1.396-1.438\text{\AA}$ ) are close to those in the disulphate ion,  $S_2O_7^{2-}$  (mean SO =  $1.437\text{\AA}$ )<sup>(23)</sup>. The SCl distance ( $1.986\text{\AA}$ ) is similar to those in  $S_2Cl_2$  ( $1.99\text{\AA}$ )<sup>(24)</sup> and  $SO_2Cl_2$  ( $2.011\text{\AA}$ )<sup>(25)</sup>. The structure of  $S_6N_4^{2+}(S_2O_6Cl)^{2-}$  will be discussed in further detail elsewhere.

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