

Fig. 5. Projektion des Tetraederraumnetzes längs [100].

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The Crystal and Molecular Structure of (NPCl₂)₂NSOCl at -140°C

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Crystals of (NPCl₂)₂NSOCl are orthorhombic, space group *P2₁2₁2₁* with *a* = 7.461 (5), *b* = 8.359 (4) and *c* = 16.228 (8) Å at -140°C. The unit cell contains four molecules (NPCl₂)₂NSOCl. The structure was solved by conventional Patterson and Fourier techniques. The coordinates and anisotropic temperature factors were refined by a full-matrix least-squares analysis of 2309 independent reflexions, measured by an Enraf-Nonius CAD-4 diffractometer (Mo *K*α radiation) at -140°C. The *R* index is 5.0%. The molecules contain a six-membered ring of P, N and S in the sequence -P-N-P-N-S-N-. The ring has a boat conformation. Mean bond lengths with the standard deviation for the individual values in parentheses are: N-S 1.557 (3), S-Cl 2.048 (1), S-O 1.422 (3), P-Cl 1.976 (1) Å. The N-P bond lengths in the segment P-N-P have a mean value of 1.574 (3) Å; in the segment P-N-S the mean N-P bond length is 1.606 (3) Å. The π bonding system of (NPCl₂)₂NSOCl is discussed in comparison with that of NPCl₂(NSOCl)₂ and a comparison of the molecular arrangements in the structures of these compounds and NPCl₂(NSOCl)₂ is given.

Introduction

Within the scope of our investigations on the structure and reactivity of ring systems containing P, S and N atoms we recently prepared a compound with formula (NPCl₂)₂NSOCl (Baalmann, Velvis & van de Grampsel, 1972). From the close resemblance of the infrared spectrum of this compound with that of NPCl₂(NSOCl)₂ we arrived at a cyclic structure, consisting of two

NPCl₂ groups and one NSOCl group. In order to verify this assumption a determination of the crystal structure of (NPCl₂)₂NSOCl was undertaken.

Experimental

(NPCl₂)₂NSOCl was prepared by thermal decomposition of the mixture obtained by reaction of [Cl₃P=N-PCl₃]⁺[PCl₆]⁻ with sulphamic acid (Baalmann *et al.*,

1972). Suitable crystals were obtained by recrystallization from dry n-pentane. The unit-cell dimensions and the intensities of 2542 independent reflexions with $\theta \leq 35^\circ$ (zirconium-filtered molybdenum radiation) were measured at -140°C with an Enraf-Nonius CAD-4 diffractometer, applying a $\theta/2\theta$ scan technique. The crystal (approximate dimensions $0.3 \times 0.4 \times 0.6$ mm) used in data collection was mounted in a glass capillary. Unit-cell dimensions and some other crystallographic data are given in Table 1. The cooling apparatus applied has been described by van Bolhuis (1971).

Table 1. *Crystal data of* $(\text{NPCl}_2)_2\text{NSOCl}$

$(\text{NPCl}_2)_2\text{NSOCl}$ M.W. 329.3 m.p. $60-62^\circ\text{C}$
 Orthorhombic
 $a = 7.461$ (5), $b = 8.359$ (4), $c = 16.228$ (8) Å (-140°C)
 $V = 1012.1$ Å³
 Systematic absences: $h00$ when h is odd, $0k0$ when k is odd and $00l$ when l is odd
 Space group $P2_12_12_1$ $Z = 4$
 $F(000) = 640$
 $\mu(\text{Mo } K\alpha) = 18.9$ cm⁻¹ $\lambda(\text{Mo } K\alpha) = 0.71069$ Å

The observed intensities were corrected for Lorentz and polarization effects and for absorption (maximum and minimum absorption correction factor 1.83 and 1.45 respectively). Of the reflexions measured 2309 were used in the refinement; 197 reflexions with zero intensity ($I \leq 0$) and 36 reflexions with $I \leq \sigma(I)$ were given zero weight.

Determination of the structure

The four molecules lie in general positions in the unit cell. From a three-dimensional Patterson synthesis the approximate coordinates of the P, S, N and Cl atoms could be found. The position of the O atom was determined from a difference synthesis.

The coordinates and anisotropic temperature factors were refined by a full-matrix analysis of the 2309 observed reflexions.

Use was made of the X-RAY System of Crystallographic Programs (1972). Scattering factors were taken

from Cromer & Mann (1968). Six cycles of refinement reduced the weighted R index to 3.7% with individual weights [$w = 1/\sigma^2(F_o)$] derived from the counting statistics. At this stage of the refinement the weighting scheme $w = 1/[\sigma^2(F_o) + 4 \times 10^{-4}F_o^2]$ was introduced. After three cycles the weighted R index was 5.0%. No significant changes in the atomic parameters were observed on introducing the new weighting scheme. The maximum shift in the last cycle was 0.2σ . The variation of $w\Delta^2$ over ranges of $|F_o|$ was quite satisfactory. The final atomic parameters and their standard deviations as calculated by the least-squares program are listed in Tables 2 and 3.*

Table 2. *Fractional atomic coordinates with standard deviations in units of the last decimal position*

	<i>x</i>	<i>y</i>	<i>z</i>
P(1)	0.3165 (1)	0.2895 (1)	0.1189 (1)
P(2)	0.0773 (1)	0.4539 (1)	0.2165 (1)
S	0.3262 (1)	0.6179 (1)	0.1238 (1)
Cl(1)	0.2506 (1)	0.1932 (1)	0.0115 (1)
Cl(2)	0.4974 (1)	0.1388 (1)	0.1611 (1)
Cl(3)	0.0751 (1)	0.4367 (1)	0.3379 (1)
Cl(4)	-0.1770 (1)	0.4854 (1)	0.1860 (1)
Cl(5)	0.1769 (2)	0.6686 (1)	0.0212 (1)
N(1)	0.1455 (4)	0.2944 (4)	0.1760 (2)
N(2)	0.1895 (4)	0.6141 (3)	0.1961 (2)
N(3)	0.4188 (4)	0.4551 (4)	0.1043 (2)
O	0.4504 (4)	0.7462 (4)	0.1311 (2)

Discussion of the structure

Molecular structure

The molecular structure of $(\text{NPCl}_2)_2\text{NSOCl}$ is shown in Fig. 1. The molecule consists of two dichlorophosphazene units and one oxochlorothiazene unit, together forming a six-membered ring. The bond lengths and angles are listed in Table 4. The ring contains a non-crystallographic pseudo mirror plane

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31382 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Thermal parameters* U_{ij} (10^{-4} Å²)

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

Standard deviations are given in parentheses.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	122 (3)	173 (3)	161 (3)	28 (3)	-7 (3)	-13 (3)
P(2)	117 (3)	139 (3)	158 (3)	-8 (3)	11 (3)	-12 (3)
S	168 (3)	162 (3)	168 (3)	-4 (3)	26 (3)	26 (2)
Cl(1)	297 (4)	450 (6)	225 (4)	47 (5)	-78 (4)	-140 (4)
Cl(2)	192 (3)	250 (4)	284 (4)	86 (3)	-7 (3)	57 (3)
Cl(3)	261 (4)	228 (4)	157 (3)	-50 (3)	15 (3)	21 (3)
Cl(4)	124 (3)	287 (4)	268 (4)	19 (3)	-21 (3)	-79 (3)
Cl(5)	369 (5)	381 (5)	173 (3)	161 (5)	-18 (4)	45 (3)
N(1)	154 (11)	160 (12)	300 (13)	-1 (10)	61 (10)	-44 (10)
N(2)	176 (11)	159 (11)	174 (10)	-21 (10)	32 (10)	6 (9)
N(3)	157 (11)	198 (12)	246 (12)	27 (11)	51 (10)	15 (10)
O	265 (13)	238 (12)	338 (14)	-105 (11)	72 (11)	34 (11)

through the atoms S, Cl(5), O and N(1), the deviations from symmetry m being small (Table 5). The planes $\text{P}(1)\text{Cl}(1)\text{Cl}(2)$, $\text{P}(2)\text{Cl}(3)\text{Cl}(4)$ and $\text{S}\text{Cl}(5)\text{O}$ make angles of 84.0 , 84.6 and 89.3° respectively with the plane $\text{P}(1)\text{P}(2)\text{S}$. The six-membered ring of $(\text{NPCl}_2)_2\text{NSOCl}$ is not planar, but has a boat configuration; the Cl atom linked to S is in an axial position, the O atom in an equatorial position (Table 6).

Table 4. Intramolecular distances and angles

The estimated standard deviations are given in parentheses. For the numbering of the atoms see Fig. 1.

$\text{N}(1) - \text{P}(1)$	1.577 (3) Å	$\text{N}(1) - \text{P}(1) - \text{N}(3)$	116.8 (2)°
$\text{N}(1) - \text{P}(2)$	1.571 (3)	$\text{N}(1) - \text{P}(2) - \text{N}(2)$	116.7 (2)
$\text{N}(2) - \text{P}(2)$	1.613 (3)	$\text{N}(2) - \text{S} - \text{N}(3)$	115.2 (2)
$\text{N}(2) - \text{S}$	1.555 (3)	$\text{P}(1) - \text{N}(1) - \text{P}(2)$	122.0 (2)
$\text{N}(3) - \text{P}(1)$	1.598 (3)	$\text{P}(2) - \text{N}(2) - \text{S}$	120.8 (2)
$\text{N}(3) - \text{S}$	1.559 (3)	$\text{P}(1) - \text{N}(3) - \text{S}$	121.0 (2)
$\text{P}(1) - \text{Cl}(1)$	1.982 (1)	$\text{Cl}(1) - \text{P}(1) - \text{Cl}(2)$	102.5 (1)
$\text{P}(1) - \text{Cl}(2)$	1.969 (1)	$\text{Cl}(3) - \text{P}(2) - \text{Cl}(4)$	104.6 (1)
$\text{P}(2) - \text{Cl}(3)$	1.975 (1)	$\text{Cl}(5) - \text{S} - \text{O}$	105.5 (1)
$\text{P}(2) - \text{Cl}(4)$	1.979 (1)	$\text{N}(1) - \text{P}(1) - \text{Cl}(1)$	109.0 (1)
$\text{S} - \text{Cl}(5)$	2.048 (1)	$\text{N}(3) - \text{P}(1) - \text{Cl}(1)$	109.9 (1)
$\text{S} - \text{O}$	1.422 (3)	$\text{N}(1) - \text{P}(1) - \text{Cl}(2)$	111.5 (1)
$\text{P}(1) \cdots \text{P}(2)$	2.754 (1)	$\text{N}(3) - \text{P}(1) - \text{Cl}(2)$	106.2 (1)
$\text{P}(1) \cdots \text{S}$	2.747 (1)	$\text{N}(1) - \text{P}(2) - \text{Cl}(3)$	111.0 (1)
$\text{P}(2) \cdots \text{S}$	2.756 (1)	$\text{N}(2) - \text{P}(2) - \text{Cl}(3)$	105.6 (1)
$\text{N}(1) \cdots \text{N}(2)$	2.712 (4)	$\text{N}(1) - \text{P}(2) - \text{Cl}(4)$	108.6 (1)
$\text{N}(1) \cdots \text{N}(3)$	2.704 (4)	$\text{N}(2) - \text{P}(2) - \text{Cl}(4)$	109.6 (1)
$\text{N}(2) \cdots \text{N}(3)$	2.629 (4)	$\text{N}(2) - \text{S} - \text{Cl}(5)$	105.1 (1)
		$\text{N}(3) - \text{S} - \text{Cl}(5)$	104.9 (1)
		$\text{N}(2) - \text{S} - \text{O}$	112.3 (2)
		$\text{N}(3) - \text{S} - \text{O}$	112.8 (2)

Table 5. Distances to the best plane through S, Cl(5), O and N(1)

The equation of the plane is $-0.6540X + 0.5029Y + 0.5651Z = 2.1414$ Å with X , Y and Z in Å.

$\text{P}(1)$	-1.378 Å	$\text{Cl}(1)$	-2.447 Å
$\text{P}(2)$	1.375	$\text{Cl}(2)$	-2.507
S	-0.001	$\text{Cl}(3)$	2.426
$\text{N}(1)$	0.000	$\text{Cl}(4)$	2.469
$\text{N}(2)$	1.313	$\text{Cl}(5)$	0.000
$\text{N}(3)$	-1.315	O	0.000

Table 6. Distances to the plane $\text{P}(1)\text{P}(2)\text{S}$

The equation of the plane is $0.6463X - 0.0389Y + 0.7621Z = 2.9030$ Å with X , Y and Z in Å.

$\text{N}(1)$	-0.121 Å	$\text{Cl}(3)$	1.496 Å
$\text{N}(2)$	0.236	$\text{Cl}(4)$	-1.614
$\text{N}(3)$	0.259	$\text{Cl}(5)$	-2.006
$\text{Cl}(1)$	-1.615	O	0.648
$\text{Cl}(2)$	1.443		

In the related compound $\text{NPCl}_2(\text{NSOCl})_2$, where the ring has a chair form, both O atoms are in equatorial positions. This causes the non-bonded $\text{Cl} \cdots \text{Cl}$ distances on the other side of the ring to be much shorter in $\text{NPCl}_2(\text{NSOCl})_2$ (where one $\text{Cl} \cdots \text{Cl}$ distance is even shorter than the sum of the van der Waals radii, 3.60 Å) than in $(\text{NPCl}_2)_2\text{NSOCl}$ (Table 7).

It is reasonable to suppose that these $\text{Cl} \cdots \text{Cl}$ approaches can affect the pattern and mechanism of substitution reactions. Assuming a nucleophilic attack at the side of the O atom it can be shown from the molecular geometry that for $(\text{NPCl}_2)_2\text{NSOCl}$ an $S_{\text{N}}2$ type transition state with five-coordinated P can be easily realized.

For $\text{NPCl}_2(\text{NSOCl})_2$, however, the formation of such a transition state is hindered by $\text{Cl} \cdots \text{Cl}$ repul-

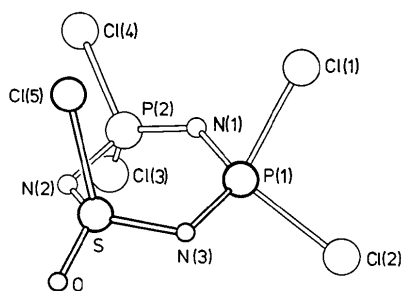


Fig. 1. Molecular structure of $(\text{NPCl}_2)_2\text{NSOCl}$.

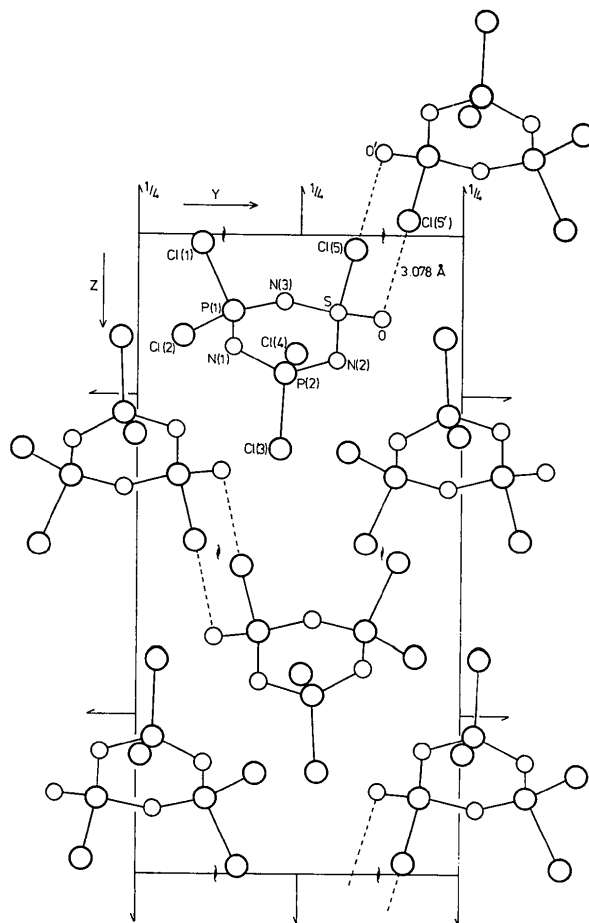


Fig. 2. Projection of the structure of $(\text{NPCl}_2)_2\text{NSOCl}$ along the a axis.

Table 7. Intramolecular distances between chlorine atoms *trans* to oxygen in $(\text{NPCl}_2)_2\text{NSOCl}$ and $\text{NPCl}_2(\text{NSOCl})_2$

$(\text{NPCl}_2)_2\text{NSOCl}$		$\text{NPCl}_2(\text{NSOCl})_2^*$	
Cl(1)···Cl(4)	4·916 Å	Cl(1)···Cl(3)	4·342 Å
Cl(1)···Cl(5)	4·015	Cl(1)···Cl(4)	3·893
Cl(4)···Cl(5)	4·058	Cl(3)···Cl(4)	3·507

* van de Grampel & Vos (1969).

sion. The results of substitution reactions with bulky primary and secondary amines, using acetonitrile as solvent, are in agreement with this picture. In the case of $(\text{NPCl}_2)_2\text{NSOCl}$ the first substitution takes place at a P atom, whereas $\text{NPCl}_2(\text{NSOCl})_2$ mainly gives a mono amino derivative with formula $\text{NPCl}_2\text{NSOCINSOAm}$ (Am = amino) (Baalmann, Keizer & van de Grampel, 1976; van den Berg, Klei, de Ruiter & van de Grampel, 1976).

Bond lengths

The N–P and N–S bond lengths (Table 4) are all shorter than the lengths of the single N–P and N–S bonds in H_3NPO_3^- (1·77 Å, Cruickshank, 1964) and in H_3NSO_3 (1·76 Å, Sass, 1960), respectively. The double-bond character of the ring bonds can be ascribed to a $d\pi$ – $p\pi$ overlap of d orbitals (P, S) with $p(sp^2)$ orbitals of N (Craig & Paddock, 1962; Cruickshank, 1961; Dewar, Lucken & Whitehead, 1960).

The N–P bonds in the islands $\text{Cl}_2\text{P–N–SOCl}$ differ from those in the island $\text{Cl}_2\text{P–N–PCl}_2$. An analogous phenomenon has been observed in the ring system $\text{NPCl}_2(\text{NSOCl})_2$ (van de Grampel & Vos, 1969). In the latter the N–S bonds in the islands $\text{Cl}_2\text{P–N–SOCl}$ are shorter than those in the island SOCl–N–SOCl . This difference has been ascribed to the greater ability of the d orbitals of the S atom for forming π bonds than the d orbitals of the P atom.

The same concept can be applied to the difference between the N–P bonds in $(\text{NPCl}_2)_2\text{NSOCl}$. In the island $\text{Cl}_2\text{P–N–SOCl}$ the N–P double-bond character will decrease in favour of the N–S bond. In the island $\text{Cl}_2\text{P–N–PCl}_2$ the electron density is equally shared by the two N–P bonds, leading to a stronger N–P bond than in the island $\text{Cl}_2\text{P–N–SOCl}$ and, therefore, to a shorter N–P distance.

Arrangement of the molecules

In Fig. 2 the projection of the structure along the x axis is given. The molecules are arranged in two

chains around $[x, \frac{3}{4}, 0]$ and $[x, \frac{1}{4}, \frac{1}{2}]$ respectively. The interaction between the molecules in these chains is probably effected by short non-bonded contacts between Cl and O [$\text{Cl}(5) \cdots \text{O}' = 3\cdot078$ (3) Å; sum of the van der Waals radii 3·20 Å]. Between the chains no such interactions are present.

It is remarkable that the relatively low-melting compounds $\text{NPCl}_2(\text{NSOCl})_2$ (56·5–58·5°C; Baalmann & van de Grampel, 1973; Tucker & van de Grampel, 1974) and $(\text{NPCl}_2)_2\text{NSOCl}$ (60–62°C; Baalmann *et al.*, 1972) have short non-bonded contacts with two neighbouring molecules, whereas the relatively high-melting compound $\text{NPCl}_2(\text{NSOCl})_2$ (94·9–95·9°C; van de Grampel & Vos, 1963) possesses short $\text{Cl} \cdots \text{O}$ contacts (3·05, 3·09 Å) with four neighbours (van de Grampel & Vos, 1969). This suggests for this class of compounds a relationship between the number of intermolecular contacts and the melting point.

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