

The Crystal and Molecular Structure of $\text{NPCl}_2(\text{NSOF})_2$ at -160°C

BY P. A. TUCKER* AND J. C. VAN DE GRAMPPEL

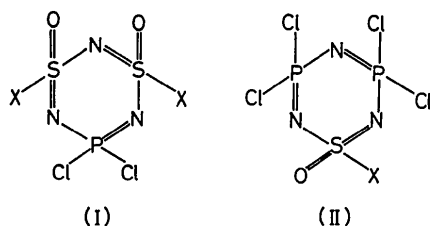
Departments of Structural and Inorganic Chemistry, University of Groningen, Zernikelaan, Paddepoel, Groningen, The Netherlands

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Cyclo-tri- μ -nitrido-dichlorophosphorusbis(oxofluorosulphur), $\text{NPCl}_2(\text{NSOF})_2$, is monoclinic, space group $P2_1/c$, with $a=7.728$ (3), $b=7.664$ (3), $c=14.097$ (4) Å, $\beta=96.01$ (2)° at -160°C . The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares analysis of 1624 counter intensities measured at -160°C to a final R of 0.107. Mean bond lengths are P–N 1.596 (8), P–Cl 1.956 (4), S–F 1.570 (7) and S=O 1.420 (8) Å. The N–S bonds in the S–N–S section of the ring have a mean value of 1.568 (9) Å. The mean length of the other N–S bonds is 1.527 (9) Å. The six-membered ring has a twisted chair conformation with the oxygen atoms *cis* with respect to the ring plane. The molecular dimensions are compared with those in related compounds.

Introduction

Recently the six-membered rings (I; X=Cl) and (II; X=Cl) have been synthesized (van de Gramppe & Vos, 1963; Baalman, Velvis & van de Gramppe, 1972) and a number of derivatives prepared (Baalman & van de Gramppe, 1973*a, b*; Klingebiel, Lin, Buss & Glemser, 1973; Heider, Klingebiel, Lin & Glemser, 1974). A structure determination of (I; X=Cl) (van de Gramppe & Vos, 1969) showed that the N–S bond lengths in the S–N–P–N–S section differ slightly from those in the S–N–S section of the ring and that the N–P bonds are relatively long. On this basis van de Gramppe & Vos (1969) suggested that the d orbitals of sulphur in a SOCl group are more involved in the $p_\pi-d_\pi$ bonding in the ring than the d orbitals of phosphorus in a PCl_2 group. As replacement of chlorine in the SOCl group by the more electronegative fluorine should increase the effects observed for (I; X=Cl), it seemed of interest to determine the structure of (I; X=F). Furthermore we wished to see if the substitution of fluorine for chlorine increases the degree of ring planarity as it does in the case of cyclic phosphazenes.



Experimental

Colourless single crystals of $\text{NPCl}_2(\text{NSOF})_2$ were grown by vacuum sublimation at room temperature

* Present address: Department of Chemistry, The University, Leicester LE1 7RH, England.

for a period of several hours after the sample was initially warmed to initiate crystal growth. In view of the apparent reactivity of the compound with common adhesives and the ease of sublimation at room temperature, crystals were 'jammed' into thin-walled glass capillaries which were then sealed. The cell dimensions at 20 – 25°C and at -160°C were measured from zero-layer Weissenberg photographs with Ni-filtered Cu radiation. Sodium chloride reflexions were superimposed for calibration. The crystallographic data are given in Table 1.

Table 1. Crystal data

$\text{NPCl}_2(\text{NSOF})_2$	M.W.	278.0
Monoclinic	$Z=4$	
-160°C	20 – 25°C	
$a=7.728$ (3) Å	7.838 (8) Å	
$b=7.664$ (3)	7.758 (6)	
$c=14.097$ (4)	14.249 (14)	
$\beta=96.01$ (2)°	95.69 (3)°	
$V=830.3$ Å ³	862.2 Å ³	
$F(000)=528$	$\lambda(\text{Mo } K\alpha)=0.71069$ Å	
$\mu(\text{Mo } K\alpha)=14.2$ cm ⁻¹	$\lambda(\text{Cu } K\alpha_1)=1.54051$ Å	
Space group $P2_1/c$	$\lambda(\text{Cu } K\alpha_2)=1.54433$ Å	

Systematic absences: $h0l$ when l is odd and $0k0$ when k is odd $a(\text{NaCl})=5.6403$ Å (21°C), $a(\text{NaCl})=5.5991$ Å (-160°C).

The intensities were measured on a Nonius AD3 diffractometer at -160°C with a crystal of approximate dimensions $0.02 \times 0.03 \times 0.01$ cm. The cooling apparatus has been described by van Bolhuis (1971). The intensities of 2578 reflexions with $\theta \leq 30^\circ$ were measured with a $\theta/2\theta$ scan technique and Zr-filtered Mo radiation. They were corrected for Lorentz and polarization effects but not for absorption. Of the measured reflexions 1624 with $\sigma(F) \leq \frac{1}{3}[\langle \sigma^2(F) \rangle]^{1/2}$ were used in the refinement. $\langle \sigma^2(F) \rangle$ was computed over all measured intensities.

Scattering factors were taken from Cromer & Waber (1965). The atomic coordinates of three of the Cl, P and S atoms were deduced from a Patterson synthesis.

The positions of the remaining atoms were found from successive difference syntheses. Because of the initial difficulty of distinguishing between oxygen and fluorine both were given scattering factors for oxygen until the molecular geometry was sufficiently accurately determined to resolve any ambiguity.

Four cycles of block-diagonal least-squares refinement with isotropic temperature factors reduced R to 0.127. In subsequent cycles the weighting scheme $w = (6.0 + |F_o| + 0.02|F_o|^2)^{-1}$ was introduced in order to make $w\Delta^2$ approximately independent of $|F_o|$. Anomalous dispersion corrections (Cromer, 1965) for the Cl, P and S atoms were applied. Five further cycles reduced R to 0.107 [$R_w = \sum w(|F_o| - |F_c|) / \sum w|F_o| = 0.119$]. The large R is probably due to the inclusion in its computation of a considerable number of reflexions with intensities bordering on significance. The maximum shift in the final cycle was 0.1σ .* The final atomic parameters with estimated standard deviations derived from the least-squares treatment are listed in Tables 2 and 3. No satisfactory interpretation of the anisotropic thermal parameters could be obtained by treating the entire molecule as a rigid body (Pawley, 1963).

* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30572 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Fractional atomic coordinates with standard deviations (in parentheses)

	x/a	y/b	z/c
P	0.1365 (3)	0.1471 (3)	0.1231 (2)
Cl(2)	-0.0902 (3)	0.1173 (4)	0.1718 (2)
Cl(1)	0.2467 (3)	-0.0827 (3)	0.1364 (2)
S(1)	0.1991 (3)	0.3521 (3)	-0.0300 (2)
S(2)	0.3577 (3)	0.4249 (3)	0.1477 (2)
F(1)	0.3512 (8)	0.2615 (9)	-0.0762 (4)
F(2)	0.5374 (8)	0.3347 (8)	0.1367 (5)
O(1)	0.1002 (11)	0.4410 (11)	-0.1061 (5)
O(2)	0.3973 (10)	0.5706 (10)	0.2078 (5)
N(1)	0.1059 (11)	0.2004 (12)	0.0130 (6)
N(2)	0.2943 (11)	0.4830 (12)	0.0426 (6)
N(3)	0.2472 (10)	0.2843 (11)	0.1893 (5)

Table 3. Anisotropic thermal parameters (\AA^2) with standard deviations (in parentheses)

The temperature factor is in the form: $\exp[-\frac{1}{2}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{23}klb^*c^* + 2B_{13}hla^*c^* + 2B_{12}hka^*b^*)]$.

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
P	1.72 (9)	1.30 (10)	1.13 (9)	0.19 (7)	0.46 (6)	-0.11 (8)
Cl(1)	2.44 (10)	0.93 (9)	2.70 (11)	-0.01 (7)	-0.09 (8)	0.11 (7)
Cl(2)	1.95 (9)	2.52 (11)	1.64 (9)	0.14 (8)	0.84 (7)	-0.35 (8)
S(1)	1.74 (9)	1.80 (10)	0.90 (8)	0.10 (7)	0.54 (6)	-0.20 (7)
S(2)	1.57 (9)	1.35 (9)	1.07 (8)	-0.03 (7)	0.46 (6)	0.06 (7)
F(1)	2.5 (3)	3.3 (3)	1.6 (2)	-0.5 (2)	1.1 (2)	0.0 (2)
F(2)	1.8 (2)	2.5 (3)	2.3 (2)	0.1 (2)	0.7 (2)	0.5 (2)
O(1)	3.2 (3)	3.1 (4)	1.5 (3)	0.8 (3)	-0.2 (2)	-0.7 (3)
O(2)	2.7 (3)	1.9 (3)	1.3 (2)	-0.1 (2)	0.5 (2)	-0.1 (2)
N(1)	2.1 (3)	1.8 (3)	1.2 (3)	-0.2 (3)	0.5 (2)	-0.6 (3)
N(2)	2.4 (3)	1.7 (3)	1.6 (3)	0.3 (3)	0.4 (2)	-0.4 (3)
N(3)	2.0 (3)	1.8 (3)	0.7 (2)	0.0 (2)	0.2 (2)	-0.2 (2)

Discussion

The molecular shape, atom numbering and orientation of the thermal ellipsoids are shown in Fig. 1. The six-membered ring has a twisted-chair conformation analogous to that reported for (I; X=Cl) (van de Grampel & Vos, 1969). The distances of the ring atoms from their mean plane (Table 4) are only slightly less for (I; X=F) than for (I; X=Cl). Therefore the substitution of fluorine for chlorine does not appear to have the same marked effect on ring planarity as it has in cyclophosphazenes. The molecule has approximate mirror symmetry with the mirror plane through P, Cl(1), Cl(2) and N(2) (Table 4). The deviation from m symmetry is probably due to the same non-bonded interaction as in (I; X=Cl) (see below).

Bond lengths

Bond lengths compared with those in (I; X=Cl) are shown in Fig. 2. Bond angles with estimated standard deviations are listed in Table 5. Van de Grampel & Vos (1969) have compared the variation of ring bond lengths in (I; R=Cl) with those in the geminally substituted cyclophosphazenes $\text{N}_3\text{P}_3\text{Cl}_4\text{Ph}_2$ and $\text{N}_3\text{P}_3\text{Cl}_2\text{Ph}_4$ (Mani, Ahmed & Barnes, 1965, 1966). The rationalization of the ring bonding given by van de Grampel & Vos may also be applied to (I; X=F). Comparing the molecular dimensions of (I; X=F) and (I; X=Cl) (Fig. 2) the substitution of chlorine by the more electronegative fluorine slightly increases the difference between

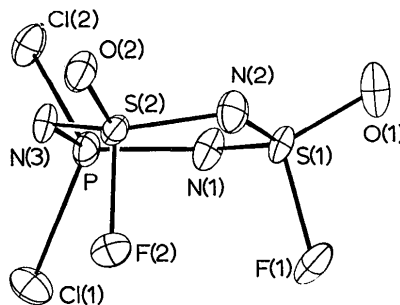


Fig. 1. Molecular shape and atom numbering in $\text{NPCl}_2(\text{NSOF})_2$ with thermal ellipsoids scaled to include 50% probability

Table 4. Equations of mean planes through sets of atoms and distances (Å) of atoms from the plane

Coordinates in Å are referred to orthogonal axes a' , b and c .

Mean plane of the ring: P, N(1), S(1), N(2), S(2), N(3)
 $0.8149x - 0.5570y - 0.1601z = -0.218$

[P 0.026; N(1) -0.016; S(1) 0.072; N(2) -0.138; S(2) 0.147; N(3) -0.091]

Approximate molecular mirror plane: P, Cl(1), Cl(2), N(2)
 $0.3117x + 0.2423y + 0.9188z = 2.134$

[P -0.003; Cl(1) 0.001; Cl(2) 0.001; N(2) 0.001; N(1) -1.344; N(3) 1.340; S(1) -1.373; S(2) 1.351; O(1) -2.391; O(2) 2.436; F(1) -1.749; F(2) 1.480]

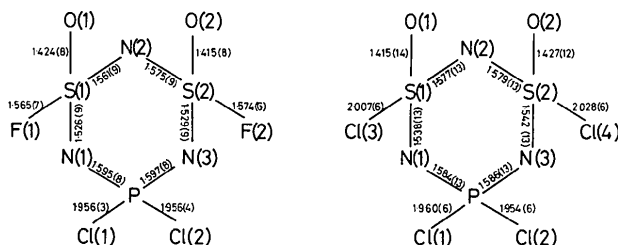


Fig. 2. A comparison of molecular dimensions in $\text{NPCl}_2(\text{NSOF})_2$ and $\text{NPCl}_2(\text{NSOCl})_2$

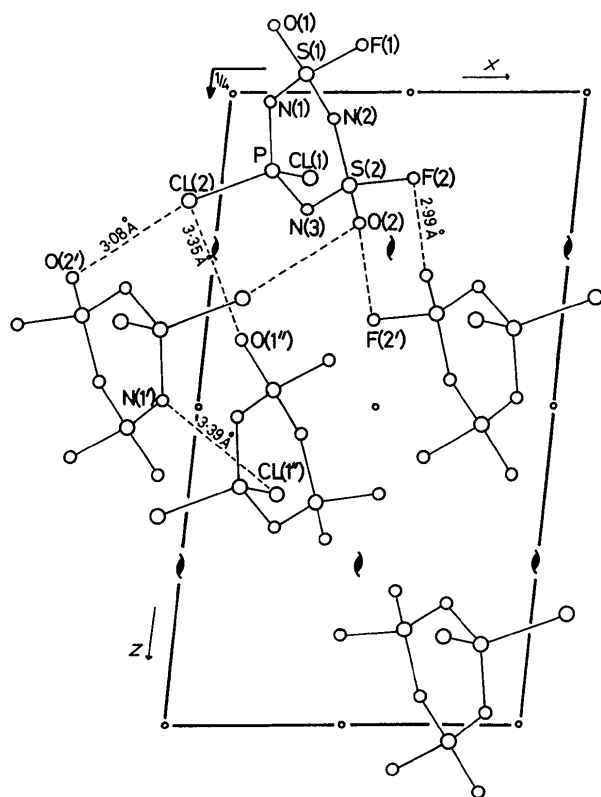


Fig. 3. A projection of the structure of $\text{NPCl}_2(\text{NSOF})_2$ along the b axis.

the lengths of the P-N and shorter S-N bonds. However the differences between corresponding bond lengths for (I; X=F) and (I; X=Cl) are of the same order as the standard deviations.

Table 5. Bond angles ($^\circ$) with estimated standard deviations in parentheses

N(3)-P-N(1)	114.5 (4)	O(1)-S(1)-F(1)	105.4 (5)
P-N(1)-S(1)	123.6 (5)	O(1)-S(1)-N(2)	111.4 (5)
N(1)-S(1)-N(2)	116.0 (5)	O(1)-S(1)-N(1)	115.2 (5)
S(1)-N(2)-S(2)	120.9 (6)	F(1)-S(1)-N(2)	103.6 (4)
N(2)-S(2)-N(3)	115.4 (4)	F(1)-S(1)-N(1)	103.5 (4)
S(2)-N(3)-P	121.8 (5)	O(2)-S(2)-F(2)	105.5 (5)
Cl(2)-P-Cl(1)	104.9 (2)	O(2)-S(2)-N(2)	111.5 (5)
Cl(2)-P-N(1)	108.9 (3)	O(2)-S(2)-N(3)	114.9 (4)
Cl(2)-P-N(3)	108.4 (3)	F(2)-S(2)-N(2)	102.9 (4)
Cl(1)-P-N(1)	110.0 (4)	F(2)-S(2)-N(3)	105.2 (4)
Cl(1)-P-N(3)	109.7 (3)		

In Table 6 the $\text{P}(\text{Cl}_2)\text{-N}$ and P-Cl lengths in (I; X=F) are compared with those in other six-membered rings having the same pseudo mirror symmetry. The tabulated values indicate that the shorter the $\text{P}(\text{Cl}_2)\text{-N}$ bond the longer the P-Cl bond. However, the differences between individual compounds are of the same order of magnitude as the standard deviations. The observed trend is consistent with a larger degree of exocyclic $d_\pi\text{-p}_\pi$ bonding as the π bonding in the ring becomes weaker.

Table 6. A comparison of the mean values of the $\text{P}(\text{Cl}_2)\text{-N}$ and P-Cl bond lengths in (I; X=F), (I; X=Cl) (van de Grampsel & Vos, 1969), $\text{N}_3\text{P}_3\text{Cl}_6$ (Bullen, 1971), $\text{N}_3\text{P}_3\text{Cl}_2(\text{NH}^i\text{Pr})_4 \cdot \text{HCl}$ (Mani & Wagner, 1971) and $\text{N}_3\text{P}_3\text{Cl}_2\text{Ph}_4$ (Mani, Ahmed & Barnes, 1966)

Individual estimated standard deviations are given in parentheses.

	$\text{P}(\text{Cl}_2)\text{-N}$ (Å)	P-Cl (Å)
I(X=F)	1.596 (8)	1.956 (4)
I(X=Cl)	1.585 (13)	1.957 (6)
$\text{N}_3\text{P}_3\text{Cl}_6$	1.581 (3)	1.993 (2)
$\text{N}_3\text{P}_3\text{Cl}_2(\text{NH}^i\text{Pr})_4 \cdot \text{HCl}$	1.558 (5)	2.000 (3)
$\text{N}_3\text{P}_3\text{Cl}_2\text{Ph}_4$	1.556 (9)	2.017 (5)

The S-F length is 0.040 Å shorter than in $\text{N}_3\text{S}_3\text{F}_3$ (1.610 Å; Krebs, Pohl & Glemser, 1972; Krebs & Pohl, 1973). A similar shortening (0.048 Å) is observed in $\text{CINS}(\text{O})\text{F}_2$ (1.548 Å; Oberhammer, 1973) relative to CINSF_2 (1.596 Å; Haase, Oberhammer, Zeil, Glemser & Mews, 1970). This shortening may reflect a contraction of the bonding orbitals on the sulphur atom due to the strongly electronegative oxygen atom. The S=O lengths in (I; X=Cl), $(\text{NSOCl})_3$ and (I; X=F) are not significantly different. This is surprising in view of the difference in 'S-O stretching' frequency between the first two compounds and the last (Baalmann & van de Grampsel, 1973a).

The angles at phosphorus are similar to those generally found in cyclotriphosphazenes (e.g. $\text{N}_3\text{P}_3\text{Cl}_6$; Bullen, 1971) but with a slightly smaller N-P-N angle, reflecting the smaller N-P double-bond character

(Schlueter & Jacobson, 1968), and a slightly larger Cl–P–Cl angle. The angles subtended at sulphur by pairs of bonds would seem to depend on the electron density in those bonds. Thus, for example, the O(1)–S(1)–N(1) and O(2)–S(2)–N(3) angles are equal within experimental error and are significantly larger than the O(1)–S(1)–N(2) and O(2)–S(2)–N(2) angles, reflecting the greater double-bond character of the S(1)–N(1) and S(2)–N(3) compared with the S–N(2) bonds.

Molecular arrangement

The molecular packing projected along **b** is shown in Fig. 3. The way in which the molecules are arranged parallel to **c** is identical with the arrangement found parallel to $[\bar{1}01]$ in (I; X=Cl). Indeed the repeat distances at $20\text{--}25^\circ\text{C}$ along $[001]$ in (I; X=F) and along $[\bar{1}01]$ in (I; X=Cl) are 14.25 and 14.42 Å respectively. The short non-bonded contact (3.09 Å) observed in (I; X=Cl) between one of the phosphorus-bonded chlorine atoms and oxygen is also present in (I; X=F) [$\text{Cl}(2)\cdots\text{O}(2')$; 3.08 Å]. As suggested in the case of (I; X=Cl) (van de Grampel & Vos, 1969), this interaction is probably responsible for the deviation from molecular *m* symmetry. The second short contact in (I; X=Cl) between sulphur-bonded chlorine and oxygen is not replaced by a short $\text{F}\cdots\text{O}$ non-bonded contact. The shorter of the remaining intermolecular contacts, all greater than the sum of the van der Waals radii (Pauling, 1960), are marked on Fig. 3.

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Structure Cristalline du *trans*- $\text{Fe}(\text{CO})_3[\text{P}(\text{OCH}_3)_3]_2$

PAR DARIA GINDEROW

Laboratoire de Chimie Appliquée de l'Etat Solide, Ecole Nationale Supérieure de Chimie de Paris,
11 rue Pierre et Marie Curie, 75005 Paris, France

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trans- $\text{Fe}(\text{CO})_3[\text{P}(\text{OCH}_3)_3]_2$ crystallizes in space group $C2/c$, with cell constants $a=11.964$, $b=11.208$, $c=13.406$ Å, $\beta=108.80^\circ$ and $Z=4$. The structure was solved by the heavy-atom method. Refinement was carried out by the full-matrix least-squares procedure, with 1193 observed reflexions; the final *R* value is 4.4%. The molecule has a twofold axis collinear with the iron atom and one carbonyl group. The ligand $\text{P}(\text{OCH}_3)_3$ has internal asymmetry.

Introduction

Le composé *trans*- $\text{Fe}(\text{CO})_3[\text{P}(\text{OCH}_3)_3]_2$ fait partie de la série des dérivés de métal carbonylé étudiés par Reck-

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