Derivatives of *cis*-$NPCl_2(NSOCl)_2$ and $(NPCl_2)_2NSOCl$, IV[1]
Isothiocyanato Derivatives of *cis*-$NPCl_2(NSOF)_2$

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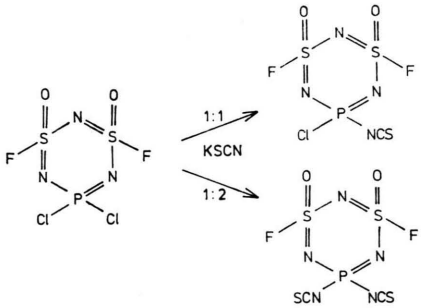
Dioxo-difluoro-chloro-isothiocyanato-cyclo-phospha-dithia-triazene, Dioxo-difluoro-bis(isothiocyanato)-cyclo-phospha-dithia-triazene, Preparation, Spectral Characteristics

The compounds $NPClNCS(NSOF)_2$ and $NP(NCS)_2(NSOF)_2$ are prepared by reaction of *cis*-$NPCl_2(NSOF)_2$ with KSCN. The mono(isothiocyanato) derivative obtained is a colourless liquid, consisting of two isomers in a ratio of 1:3.8; the bis(isothiocyanato) compound is a white crystalline solid.

The reaction of $(NPCl_2)_3$ with KSCN (molar ratio 1:6) in acetonitrile (or acetone) yields the compound $[NP(NCS)_2]_3$ [2,3]. The tetrameric phosphonitrilic isothiocyanate can be prepared analogously [3]. The isothiocyanate structure was first assigned on the basis of IR and Raman spectra [2,4] and later established by X-ray structural determinations [5,6]. Preparing the bis(isothiocyanato) derivative of $(NPCl_2)_3$ Dieck and Moeller [7] showed, that substitution by isothiocyanato groups proceeds *via* a geminal pathway. In this communication we report the preparation and characterization of two isothiocyanato derivatives of the cyclic compound *cis*-$NPCl_2(NSOF)_2$ [8,9] *viz.* $NPClNCS(NSOF)_2$ and $NP(NCS)_2(NSOF)_2$.



Reactivity

In polar media *cis*-$NPCl_2(NSOF)_2$ is very reactive towards KSCN and is very readily substituted to $NP(NCS)_2(NSOF)_2$. The preparation of $NPClNCS(NSOF)_2$ encounters more difficulties, since this product reacts rapidly to give $NP(NCS)_2(NSOF)_2$. The highest yields of $NPClNCS(NSOF)_2$ are obtained by reaction of *cis*-$NPCl_2(NSOF)_2$ and KSCN (molar ratio 1:1) in media of relatively low polarity such as pentane-acetonitrile (volume ratio 5:1), and at low temperature. The behaviour of $NPClNCS(NSOF)_2$ towards KSCN is comparable with that of $N_3P_3Cl_5F$ towards KF, where the mono-fluorophosphazene reacts very smoothly to gem-$N_3P_3Cl_4F_2$ [10]. As may be seen from the Experimental Part two isomers (a and b) $NPClNCS(NSOF)_2$ are formed. The two compounds probably differ in the position of the NCS group with respect to the other ligands. In addition to $NP(NCS)_2(NSOF)_2$ and $NPClNCS(NSOF)_2$ a yellow polymeric material was obtained (identical with the polymer formed by the reaction of $NP(NCS)_2(NSOF)_2$ with KSCN in molar ratio 1:2), which does not possess SF bonds. Obviously, replacement of the F atoms by NCS groups results in the formation of this polymeric material.

IR spectra

The characteristic strong isothiocyanato absorptions are found at 1925 and 1080 cm^{-1} for $NP(NCS)_2(NSOF)_2$ and at 1945 and 1077 cm^{-1} for $NPClNCS(NSOF)_2$. Both compounds give absorptions due to ring vibrations in the region 1150–1250 cm^{-1} (compare: *cis*-$NPCl_2(NSOF)_2$ 1215 and 1183 cm^{-1} [8]). The bands at 1375 cm^{-1} for

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$NP(NCS)_2(NSOF)_2$ and 1380 cm^{-1} for

$NPClNCS(NSOF)_2$

can be assigned to SO stretching modes. In conformity with the spectrum of *cis*-$NPCl_2(NSOF)_2$ [8] the absorption at 885 cm^{-1} (for $NP(NCS)_2(NSOF)_2$) and 884 cm^{-1} (for $NPClNCS(NSOF)_2$) can be ascribed to a SF vibration.

Mass spectra

From the mass-spectral data the larger strength of the S–F bond compared with that of the P–NCS bond in $NPClNCS(NSOF)_2$ and $NP(NCS)_2(NSOF)_2$ is reflected by the observation that under the experimental conditions of the mass spectrometer the ion $(M–F)^+$ has a much lower intensity than the ion $(M–NCS)^+$. In the mass spectrum of

$NPClNCS(NSOF)_2$

(isomeric mixture) the ion $(M–NCS)^+$ is more abundant than the ion $(M–Cl)^+$, whereas the abundance of the ions $(M–Cl)^+$ and $(M–F)^+$ is about the same. These observations indicate a decreasing bond strength in the sequence $SF \approx PCl > PNCS$. Correspondingly, it is observed that among the degradation products of $NPClNCS(NSOF)_2$ the intensity of the ion PCl^+ (13%) is greater than that of $PNCS^+$ (4%).

The metastable peaks in the two mass spectra (Table I) show that not only fragments NCS or Cl are lost, but also NS, NSF or NOF units. The remarkable fragmentation reactions

$NPCl(NSOF)_2^+ \rightarrow NPClNSOFS^+ + NOF$ and

$NPNCS(NSOF)_2^+ \rightarrow NPNCNSOFSO^+ + NSF$

obviously involve endocyclic nitrogen atoms. The loss of a NOF unit has also been observed in the mass spectrum of *cis*-$NPCl_2(NSOF)_2$ [8].

NMR spectra

As may be seen from Table II the ^{31}P NMR spectrum of $NPClNCS(NSOF)_2$ shows two singlets (—0.05 and + 0.85 ppm; relative intensities 1:3.8), belonging to the PClNCS unit in isomer a and b,

Table I. Metastable peaks and corresponding degradations in the mass spectra of $NPClNCS(NSOF)_2$* and $NP(NCS)_2(NSOF)_2$.

* $NPClNCS(NSOF)_2$.

Found *m/e*	Calcd	Reaction
234	234.1	$NP\,^{35}ClNCS(NSOF)_2^+ \rightarrow NPNCS(NSOF)_2^+ + {}^{35}Cl$
197	197.1	$NP\,^{37}ClNCS(NSOF)_2^+ \rightarrow NP\,^{37}Cl(NSOF)_2^+ + NCS$
195	195.2	$NP\,^{35}ClNCS(NSOF)_2^+ \rightarrow NP\,^{35}Cl(NSOF)_2^+ + NCS$
156	155.8	$NP\,^{37}Cl(NSOF)_2^+ \rightarrow NP\,^{37}ClNSOFS^+ + NOF$
155	154.7	$NP\,^{35}Cl(NSOF)_2^+ \rightarrow NP\,^{35}ClNSOFS^+ + NOF$

* Mixture of isomers.

$NP(NCS)_2(NSOF)_2$

Found *m/e*	Calcd	Reaction
217	217.4	$NP(NCS)_2(NSOF)_2^+ \rightarrow NPNCS(NSOF)_2^+ + NCS$
151	150.9	$NPNCS(NSOF)_2^+ \rightarrow NPNCNSOFSO^+ + NSF$
90	90.4	$NPNNSNSF^+ \rightarrow NPNNSF^+ + NS$

Table II. Chemical shifts δ and coupling constants $^3J_{P-F}$ in the ^{31}P- and ^{19}F NMR spectra for *cis*-$NPCl_2(NSOF)_2$, $NPClNCS(NSOF)_2$ and $NP(NCS)_2(NSOF)_2$ (solvent $CDCl_3$).

	cis-$NPCl_2(NSOF)_2$	$NPClNCS(NSOF)_2$	$NP(NCS)_2(NSOF)_2$
^{31}P	$\delta = -30.9$ ppm	$\delta_a = -0.05$ ppm $\delta_b = +0.85$ ppm	$\delta = +29.1$ ppm
^{19}F	$\delta = -73.2$ ppm	$\delta_a = -73.2$ ppm $\delta_b = -73.5$ ppm	$\delta = -74.7$ ppm
$^3J_{P-F}$	1 Hz	not observed	not observed

respectively. For $NP(NCS)_2(NSOF)_2$ a resonance signal is observed at +29.1 ppm. Comparing these values with δ_P in *cis*-$NPCl_2(NSOF)_2$ (—30.9 ppm) we observe that the signal shifts to higher field by about 30 ppm in the sequence PCl_2, PClNCS and $P(NCS)_2$. Hence replacement of a chlorine atom by the more electronegative NCS group[11] results in an increase of electron charge on the phosphorus atom. In the ^{19}F NMR spectrum of NPClNCS$(NSOF)_2$ we observe two singlets (—73.2 and —73.5 ppm; intensity ratio 1:3.8) belonging to the isomers a and b. Comparing the values of δ_F for the three compounds given in Table II it can be concluded that the introduction of a NCS group results in a slight decrease of electron density on the fluorine atom.

Experimental

All experiments were carried out under dry nitrogen. Solvents were purified and dried by conventional methods. The elemental analyses were carried out at the Microanalytical Department of this University under supervision of Mr. A. F. HAMMINGA. The IR spectra were recorded as nujol mulls between KBr discs by a Hitachi EPI-G spectrophotometer. Calibration was carried out by means of polystyrene film bands. The mass spectra were obtained by Mr. A. KIEWIET (Department of Organic Chemistry of this University) on an AEI MS9 mass spectrometer at 70 eV, using an accelerating voltage of 8 kV. The ^{31}P and ^{19}F NMR spectra were recorded by Mr. R. H. FOKKENS (NMR Department, University of Amsterdam) on a Varian XL-100 FT spectrometer at 40.5 MHz and 94.1 MHz respectively. Chemical shifts were determined relative to the external standards 85% H_3PO_4 (^{31}P) and $CFCl_3$ (^{19}F).

1. Preparation of NPClNCS(NSOF)$_2$

At — 78 °C a solution of KSCN (880 mg, 9.07 mmole) in 20 ml of dry acetonitrile was added slowly to a stirred solution of *cis*-$NPCl_2(NSOF)_2$ (2.52 g, 9.06 mmole) in 100 ml of dry pentane. When the addition was complete the temperature of the reaction mixture was raised to room temperature.

After a total reaction time of 3.5 hours the pentane and acetonitrile layer were separated and evaporated to dryness under vacuum. The product from the pentane layer was an almost colourless liquid. The yellow oily residue from the acetonitrile layer was extracted twice with 40 ml of dry ether (the remaining precipitate is KCl). The combined yellow ether fractions were evaporated to dryness and the resulting yellow oily product was extracted twice with 30 ml of dry pentane. The residue consisted of polymeric material. The combined pentane fractions were evaporated to dryness. The product obtained was combined with the liquid already obtained from the pentane layer. Total yield 1800 mg. G.L.C.-mass spectrometry experiments at 140 °C (steel 6 ft × 1/8 inch column, 10% UCW 98, 80–100 WAW-DMCS) on a Hewlett Packard 7620 A Research Chromatograph showed that this liquid contained four compounds, *cis*-$NPCl_2(NSOF)_2$, NPClNCS$(NSOF)_2$ (isomer a), NPClNCS$(NSOF)_2$ (isomer b) and $NP(NCS)_2(NSOF)_2$ in a ratio of 4.2:1:3.8:4.2 with relative retention times 1:4.4:4.9:15.4.

The product NPClNCS$(NSOF)_2$ (isomers a and b together) was separated by preparative G.L.C. at 140 °C (glass 6 ft × 1/4 inch column, 10% UCW 98, 60–80 WAW-DMCS). The colourless liquid obtained was distilled at 60 °C/0.10 mm Hg. Yield 160 mg (0.53 mmole, 5.9%).

Analysis: NPClNCS$(NSOF)_2$ (300.65)

Calcd	Cl 11.79	N 18.64	S 32.00,
Found	Cl 11.97	N 18.57	S 31.74.

As the difference in retention time of the isomers a and b is very small no attempts were made to separate the two compounds.

IR: 1945 vs, 1380 vs, 1210 vs, 1177 vs, 1109 m, 1077 s, 884 s, 843 vs, 751 s, 706 m, 670 m, 640 m, 567 vw, sh, 542 m, 520 s, 501 w, 461 w, 440 vw.

m/e: 302 $(M\ ^{37}Cl)^+$ 4%, 300 $(M\ ^{35}Cl)^+$ 12%, 283 $(M\ ^{37}Cl–F)^+$ 0.5%, 281 $(M\ ^{35}Cl–F)^+$ 1.5%, 265 $(M–Cl)^+$ 2.5%, 244 $(M\ ^{37}Cl–NCS)^+$ 3%, 242 $(M\ ^{35}Cl–NCS)^+$ 9%, 46 NS^+ 100%.

2. Preparation of NP(NCS)$_2$(NSOF)$_2$

At —18 °C a solution of *cis*-$NPCl_2(NSOF)_2$ (900 mg, 3.24 mmole) in 40 ml of dry acetonitrile was added slowly to a stirred solution of KSCN (630 mg, 6.49 mmole) in 30 ml of dry acetonitrile. When the addition was complete the temperature of the reaction mixture was raised to room temperature. After a total reaction time of 3.5 hours the reaction mixture was evaporated to dryness and the yellow oily residue was extracted twice with 30 ml of dry ether (the remaining precipitate is KCl). The combined yellow ether fractions were evaporated to dryness and the resulting yellow oily product was extracted twice with 50 ml of dry hexane. The residue consisted of polymeric material. After evaporation of the combined hexane fractions to about the half of the original volume and cooling the solution at —30 °C white crystals of $NP(NCS)_2(NSOF)_2$ (m.p. 25.5–26.5 °C) separated. Yield 270 mg (0.84 mmole, 25.8%).

Analysis: $NP(NCS)_2(NSOF)_2$ (323.28)

Calcd	C 7.43	N 21.66	S 39.68,
Found	C 7.43	N 21.83	S 39.79.

IR: 2000 m, 1925 vs, 1375 vs, 1212 vs, 1181 s, 1080 s, br, 885 m, 837 vs, 749 m, 706 m, 678 m, br, 670 vw, sh, 664 vw, sh, 567 vw, 548 w, 520 m, 505 w, br, 462 vw.

m/e: 323 M^+ 4%, 304 $(M–F)^+$ 0.5%, 265 $(M–NCS)^+$ 5.5%, 46 NS^+ 100%.

3. Reaction of $NP(NCS)_2(NSOF)_2$ with KSCN

The reaction of $NP(NCS)_2(NSOF)_2$ with KSCN (molar ratio 1:2) in dry acetonitrile at —18 °C yielded after a total reaction time of 3.5 hours a yellow polymeric material and an almost quantitative amount of KF. The IR spectrum of the polymeric material did not contain a band in the range 860–910 cm^{-1}, indicating the absence of SF bonds.

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