Derivatives of cis-NPCl₂(NSOCl)₂ and (NPCl)₂NSOCl, IV¹

Isothiocyanato Derivatives of eis-NPCl₂(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 NPCINCS(NSOF)₂ and NP(NCS)₂(NSOF)₂ are prepared by reaction of cis-NPCl₂(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 with KSCN (molar ratio 1:6) in acetonitrile (or acetone) yields the compound [NP(NCS)]₀⁻². The tetrameric phosphonitrilic iso-thiocyanate can be prepared analogously.⁵ The isothiocyanate structure was first assigned on the basis of IR and Raman spectra²,⁴ and later established by X-ray structural determinations⁵,⁶. Preparing the bis(isothiocyanato) derivative of (NPCl)₂ DIECK and MOELLER⁷ 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-NPCl₂(NSOF)₂, viz. NPCINCS(NSOF)₂ and NP(NCS)₂(NSOF)₂.

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 NPCINCS(NSOF)₂. Both compounds give absorptions due to ring vibrations in the region 1150–1250 cm⁻¹ (compare: cis-NPCl₂(NSOF)₂ 1215 and 1183 cm⁻¹). The bands at 1375 cm⁻¹ for

Reactivity

In polar media cis-NPCl₂(NSOF)₂ is very reactive towards KSCN and is very readily substituted to NP(NCS)₂(NSOF)₂. The preparation of NPCINCS(NSOF)₂ encounters more difficulties, since this product reacts rapidly to give NP(NCS)₂(NSOF)₂. The highest yields of NPCINCS(NSOF)₂ are obtained by reaction of cis-NPCl₂(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 NPCINCS(NSOF)₂ towards KSCN is comparable with that of N₂P₂Cl₄F towards KF, where the mono-fluorophosphazene reacts very smoothly to gem-N₂P₂Cl₄F. As may be seen from the Experimental Part two isomers (a and b) NPCINCS(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 NPCINCS(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 NPCINCS(NSOF)₂. Both compounds give absorptions due to ring vibrations in the region 1150–1250 cm⁻¹ (compare: cis-NPCl₂(NSOF)₂ 1215 and 1183 cm⁻¹). The bands at 1375 cm⁻¹ for
NP(NCS)$_2$(NSOF)$_2$ and 1380 cm$^{-1}$ for NPINCNS(NSOF)$_2$
can be assigned to SO stretching modes. In conformity
with the spectrum of cis-NPCl$_2$(NSOF)$_2$ the absorption at 885 cm$^{-1}$ (for NP(NCS)$_2$(NSOF)$_2$) and
884 cm$^{-1}$ (for NPINCNS(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 NPINCNS(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 NPINCNS(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

density in the sequence SF ≈ PCl > PNCS. Correspondingly, it is observed that among the degradation products of NPINCNS(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

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\text{NPCl(NSOF)$_2^+$} \rightarrow \text{NPCINSOFS+} + \text{NOF} \quad \text{and} \quad \text{NOPCNCS(NSOF)$_2^+$} \rightarrow \text{NPNCINSOFSO+} + \text{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)$_2$.

**NMR spectra**

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


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respectively. For NP(NCS)$_2$(NSOF)$_2$ a resonance signal is observed at $\pm 29.1$ ppm. Comparing these values with $\delta_F$ in cis-NPCl$_2$(NSOF)$_2$ ($\pm 30.9$ ppm) we observe that the signal shifts to higher field by about 30 ppm in the sequence PCl$_3$, PCINCS and P(NCS)$_2$. Hence replacement of a chlorine atom by the more electronegative NCS group results in an increase of electron charge on the phosphorus atom. In the $\text{^19}F$ NMR spectrum of NPCINCS(NSOCl)$_2$ we observe two singlets ($\pm 73.2$ and $\pm 73.5$ ppm; intensity ratio 1:3.8) belonging to the isomers a and b. Comparing the values of $\delta_F$ 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 discis 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 AET 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. FOOKENS (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% $\text{H}_3\text{PO}_4$ ($^{31}P$) and CFCl$_3$ ($^{19}F$).

1. **Preparation of NPCINCS(NSOF)$_2$**

At $-78^\circ$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 reaction mixture was raised to room temperature. After a total reaction time of 3.5 hours the temperature. After a total reaction time of 3.5 hours the temperature. After a total reaction time of 3.5 hours the temperature.

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

At $-18^\circ$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 $-30^\circ$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:**

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 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 w, 620 w, 530 m, 501 w, 461 w, 440 vw, $m/e$: 302 (M$^{+}$PCl)+ 4%, 300 (M$^{+}$Cl)+ 12%, 283 (M$^{+}$Cl)+ 0.5%, 281 (M$^{+}$Cl)+ 1.5%, 265 (M$^{+}$Cl)+ 2.5%, 244 (M$^{+}$PCl-NCS)+ 3%, 242 (M$^{+}$Cl-NCS)+ 9%, 46 NS$^{+}$ 100%.

**Analysis:**

Calcd Cl 7.43 N 21.66 S 39.68.

Found Cl 7.43 N 21.66 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 w, sh, 664 vw, sh, 567 vw, 548 w, 520 m, 505 w, br, 482 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 $-18^\circ$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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