

$P_3N_3F_5NPF_2NPF_2NPF_5^{2-}$: a Cyclophosphazene with a Phosphazene Side-chain Dianion by F^- -induced Ring-opening of $P_3N_3F_6$

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$[(Me_2N)_3S^+]_2 [P_3N_3F_5NPF_2NPF_2NPF_5]^{2-}$ is prepared from the reaction of $(Me_2N)_3S^+Me_3SiF_2^-$ and $P_3N_3F_6$ and its X-ray crystal structure determined.

Recently, we reported the addition of fluoride ion to sulfanuric fluoride $[NS(O)F]_3$ by $(Me_2N)_3S^+Me_3SiF_2^-$, (TASF), to give $TAS^+ [(NS(O)F)_2(NS(O)F_2)]^-$.¹ Reactions of the isoelectronic cyclophosphazene $(NPF_2)_3$ with fluoride ion are described in the literature: with CsF opening of the ring system probably occurs, leading to formation of $Cs^+NPF_2NPF_2NPF_3^-$.² With NaF similar results were obtained, but subsequent degradation of the primary product was observed.³ Characterization of the product was based mainly on IR spectroscopy and from the complexity of the (unassigned) ^{19}F NMR spectrum of the primary product the authors suggested the above-mentioned acyclic structure of the anion.²

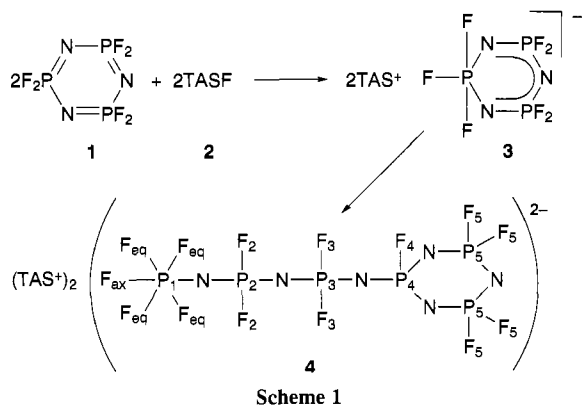
Different results are obtained when fluoride ion is added to $(NPF_2)_3$,⁴ **1** by TASF,⁵ **2** in homogeneous solution.

The reaction between $P_3N_3F_6$ and TASF occurs at 235 K in MeCN to give $TAS^+ P_3N_3F_7^-$ **3** (Scheme 1). This species was identified by ^{31}P and ^{19}F NMR spectroscopy.† The ^{31}P NMR spectrum at 235 K shows a well-resolved octet ($J_{PF} = 258$ Hz) at $\delta -5$ and the ^{19}F NMR spectrum a corresponding quartet at $\delta -46$. This coupling is significantly smaller than $^1J_{PF}$ in **1** (868 Hz) and is due to an averaging of $^1J_{PF}$ and $^3J_{PF}$. Only one resonance for **3** in both the ^{31}P and ^{19}F NMR spectra is observed indicating that the anion is undergoing exchange and since we observe P–F couplings this must be an intramolecular exchange process.

At this temperature the ^{31}P and ^{19}F NMR spectra show signals corresponding to the dianion $P_3N_3F_5NPF_2NPF_2NPF_5^{2-}$ **4** and on slight warming the signals due to **3** disappear and only signals due to **4** are observed.

Apart from the clear resonance of the NPF_5 group at $\delta -137$, the ^{31}P NMR spectrum of **4** is difficult to assign as the ring and chain phosphorus resonances all occur in the region $\delta +40$ to $\delta -70$ as broad, unresolved multiplets.

The ^{19}F NMR spectrum of **4** is easier to assign, with the expected 6 F resonances clearly observed. An AB_4X system is seen for the NPF_5 group at $\delta_{F_{eq}} -43.8$ and $\delta_{F_{ax}} -53.5$. The four equivalent ring-fluorine atoms, F_5 are observed as a complicated multiplet at $\delta -68.8$, F_4 the fifth ring-fluorine is assigned from the resonance intensity at $\delta -47.2$. Unfortunately, although both NPF_2 groups could be identified, $\delta -61.5$ and $\delta -63.5$, it was not possible to distinguish which is due to F_2 and which to F_3 .



4 was isolated quantitatively as a stable, colourless solid (mp 64 °C) and single crystals were grown by diffusion of diethyl ether into a MeCN solution. The X-ray structure‡ of the anion is presented in Fig. 1. The average P–N bond length to the phosphorus centres in the phosphazene side-chain is approximately 154 pm, the P(1)–N(1) distance to the hexacoordinated phosphorus is significantly longer [169.4(9) pm]. Contrary to planar cationic oligochlorophosphazenes⁶ and poly-fluorophosphazenes $(NPF_2)_n$,⁷ the phosphazene side chain in **4** is puckered. P(1), P(2) and P(3) deviate from the N(1)–N(2)–N(3) plane by +19, +44 and +40 pm, respectively.

Substitution of fluorine atoms in $P_3N_3F_6$ by amino groups is reported to increase the average endocyclic P–N bond distances,^{8,9} similar results are obtained for the $P_3N_3F_5$ -fragment in **4**. More pronounced than for $P_3N_3F_5NH_2$,⁸ and 2,2- $P_3N_3F_3(NH_2)_2$,⁹ the P–N bond lengths adjacent and opposite to the substituted phosphorus centre increase compared to $P_3N_3F_6$ (P–N = 152.1 pm).¹⁰ The bonding situation in the $P_3N_3F_5$ -fragment of **4** might be described as in Fig. 2, with a high negative charge at N(5).

Cyclophosphazenes are starting materials for poly-phosphazenes,¹¹ ring-opening is observed at high temperatures and is catalysed by Lewis acids.¹² The anion in **4** might be considered as the first step in a base induced polymer formation from cyclic precursors.

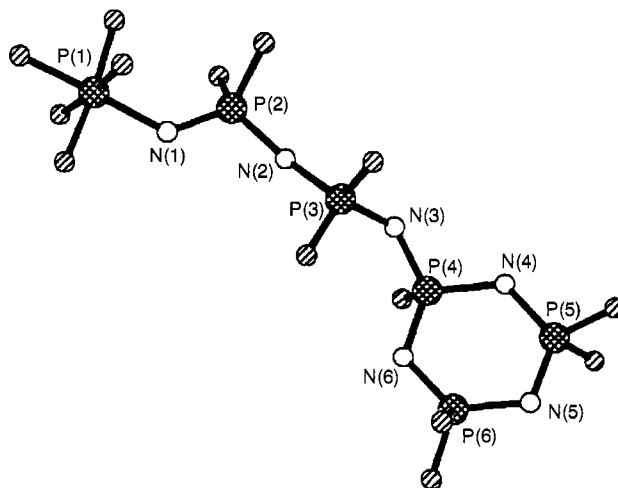


Fig. 1 The molecular structure of $P_3N_3F_5NPF_2NPF_2NPF_5^{2-}$. P–N bond lengths (pm) are: P(1)–N(1) 169.4(9), N(1)–P(2) 152.4(8), P(2)–N(2) 154.1(9), N(2)–P(3) 156.8(10), P(3)–N(3) 152.0(11), N(3)–P(4) 155.1(10), P(4)–N(4) 161.0(9), N(4)–P(5) 152.9(10), P(5)–N(5) 161.5(10), N(5)–P(6) 156.3(10), P(6)–N(6) 153.4(10), N(6)–N(4) 164.1(11). Approximate P–F bond lengths are: P(1)–F 164.1, P(2)P(3)–F 155.1, P(4)–F 158.2(9), P(5)–P(6)–F 156.1.

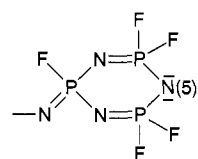


Fig. 2

Neutral cyclophosphazenes with phosphazene side-chains are known $P_3N_3F_5NPF_2(NPCl_2)_2Cl$, e.g. is formed in a multistep synthesis from $P_3N_3F_6$, $(Me_3Si)_2NH$, PF_3Cl_2 , and PCl_5 , respectively.¹³

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Footnotes

† NMR data [ref. 85% H_3PO_4 (for ^{31}P) and CCl_3F (for ^{19}F)]. ^{31}P and ^{19}F NMR data for **3**: $\delta_P -5$, $\delta_F -48$, $J_{PF} 258$ Hz. ^{31}P and ^{19}F NMR data for **4**: $\delta_{P1} -137$, $\delta_{F_{eq}} -43.8$, $\delta_{F_{ax}} -53.5$, $\delta_{F_{2,F3}} -61.5$ and -63.5 , $\delta_{F_4} -47.2$, $\delta_{F_5} -68.8$ $^1J_{P1F_{eq}} 714$, $^1J_{P1F_{ax}} 660$, $^1J_{P1F_{eq}} 714$, $^1J_{P2,3F_{2,3}} 939$, ≈ 900 , $^1J_{P4F_4}$ ca. 800 $^1J_{P5F_5}$ (Higher order resonance, unable to be assigned), $^2J_{F_{eq}F_{ax}}$ 36, $^3J_{P2F_{eq}}$ 29, $^4J_{F_{eq}F_2}$ 4 Hz.

‡ Crystal data: $C_{12}H_{36}F_{14}N_{12}P_6S_2$, crystal dimensions $0.80 \times 0.60 \times 0.05$ mm, $M = 864.47$, $T = 173$ K, triclinic, $a = 859.8(2)$, $b = 1005.0(2)$, $c = 2196.4(4)$ pm, $\alpha = 91.76(3)^\circ$, $\beta = 96.42(3)^\circ$, $\gamma = 109.77(3)^\circ$, $U = 1770.1(6)$ Å³, space group $P\bar{1}$, $Z = 2$, $D_c = 1.622$ Mg m⁻³, Mo-K α radiation, $\lambda = 0.71073$ Å, $\mu(Mo-K\alpha) = 5.24$ cm⁻¹, $F(000) = 880$. $R =$

0.0747, $wR_2 = 0.1652$ for 4610 independent diffractometer reflections out of 5070 measured ($0 \leq h \leq 9$, $-11 \leq k \leq 10$, $-24 \leq l \leq 24$, $2.54 \leq \theta \leq 22.5^\circ$). Atom coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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