Salt of a Hydroxy-derivative of a Ring System containing the Phosphazene Unit; *X*-Ray Structure of $[(NSOCl)_2NPClO]^-[Me_4N]^+$

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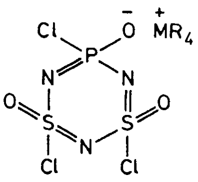
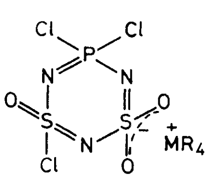
Summary Reactions of the ring system *cis*-$(NSOCl)_2NPCl_2$ with water in the presence of $[Me_4N]Cl$ or $[Ph_4As]Cl$ convert it into salts containing the $N_3PS_2O_3Cl_3^-$ anion; ^{31}P n.m.r. and *X*-ray structural data demonstrate that substitution takes place at the phosphorus centre.

ALTHOUGH numerous examples of hydroxy-substituted cyclophosphazenes are known,[1] little attention has been paid to the controlled hydrolysis of the parent chlorocyclophosphazenes.[2] In this report we show that the problem of the instability of the partly hydrolysed products can be avoided by the *in situ* preparation of salts of these acidic compounds.

Reactions of *cis*-$(NSOCl)_2NPCl_2$ with tetraphenylarsonium chloride hydrate or tetramethylammonium chloride–water in acetonitrile readily afford compounds which, according to their elemental analyses, can be described as $N_3PS_2O_3Cl_3$-MR_4 (**1**) and (**2**). Their ^{31}P n.m.r. signals, δ $-9{\cdot}2$ p.p.m. for (**1**) and $-8{\cdot}5$ p.p.m. for (**2**) (in CD_3CN solution at $40{\cdot}5$ MHz), show a considerable upfield shift compared with the usual values for PCl_2 groupings in cyclophosphazenes and related ring systems. This suggests a structure for these compounds in which the introduced oxygen ligand is attached to phosphorus, structure (A). Examples of compounds of this type are known from previous work.[3] However, as the influence of the introduced negative charge is not known, structure (B) cannot be excluded completely. Moreover, structures closely related to (B) are known to be readily formed under similar conditions.[4] In order to establish its structure definitely an *X*-ray structure de-



(A)



(B)

(1) M = As, R = Ph

(2) M = N, R = Me

termination of (**2**) was undertaken, using crystals grown from an acetonitrile–ether mixture. The crystals tend to decompose under radiation conditions.

Crystal data: $[(NSOCl)_2NPClO]^-[Me_4N]^+$, m.p. 178 °C (decomp.), monoclinic, space group $P2_1/c$, $a = 9{\cdot}849(10)$, $b = 13{\cdot}326(10)$, $c = 11{\cdot}010(10)$ Å, $\beta = 93{\cdot}56(3)^\circ$, $U = 1442{\cdot}2$ Å^3, $Z = 4$, $D_c = 1{\cdot}68$ g cm^{-3}. Intensity data were collected with a CAD-3 diffractometer using graphite monochromated Mo-K_α radiation. 1584 reflections had $I > 3\sigma(I)$ and were considered to be observed. Correction for Lorentz and polarization factors was applied but not for absorption. The structure was solved by direct methods and refined by full-matrix least-squares procedures. The final R factor was 0·068.†

The structure of the anion is shown in the Figure. The phosphorus and sulphur atoms, which are in principle indistinguishable in this case, were assigned from consideration of the observed molecular geometry (see bond lengths and angles in the Figure caption). The structure consists of distinct $[(NSOCl)_2NPClO]^-$ and $[Me_4N]^+$ ions. The ring in the anion has a slight chair conformation, the oxygen ligands all in equatorial positions. As in *cis*-$(NSOCl)_3$,[5] which is isoelectronic with the anion, these oxygen ligands are all at the same side of the ring plane. The shortness of the P–O bond strongly suggests that the negative charge is not localized on the oxygen atom, but is spread over the ring. This is compatible with the tautomerization observed for (neutral) hydroxycyclophosphazenes.[6]

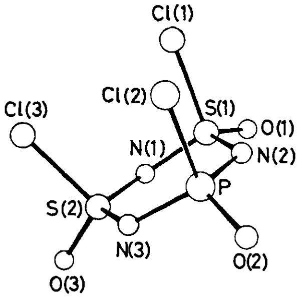


FIGURE. Structure of the anion of (**2**). Some bond distances are: S(1)–N(1), 1·568(7); N(1)–S(2), 1·546(8); S(2)–N(3), 1·529(8); N(3)–P, 1·591(8); P–N(2), 1·591(8); N(2)–S(1), 1·530(8); S(1)–O(1), 1·426(8); S(2)–O(3), 1·405(8); P–O(2), 1·438(9); mean N–C (cation), 1·504(6); some angles: N–P–N, 111·7(4); mean N–S–N, 114·8(7): S–N–S, 121·7(5); mean P–N–S, 123·5(7); Cl–P–O, 107·5(3); mean Cl–S–O, 104·4(5); mean C–N–C (cation), 109·5(3).

The method of preparation of these salts is applicable also to other ring systems containing the $NPCl_2$ unit. Under more forcing conditions $[$*trans*$\text{-}(NSOPh)_2NPClO]^-[Ph_4As]^+$ and $[(NPCl_2)_2NPClO]^-[Ph_4As]^+$ have also been prepared.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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