

Isolation of the Geminal Bis(amido) Derivative, $N_4P_4(NH_2)_2Cl_6$, from the Reaction of $N_4P_4Cl_8$ with Ammonia

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Geminal Bis(amido)hexachlorocyclotetraphosphazene, Aqueous Ammonia Synthesis, ^{31}P NMR

The geminal isomer of $N_4P_4(NH_2)_2Cl_6$ is obtained from the reaction of the octachloride, $N_4P_4Cl_8$, with aqueous ammonia in diethyl ether in the presence of anhydrous sodium sulphate. The compound is characterised by ^{31}P NMR spectroscopy and by conversion to its dimethylamino derivative, $N_4P_4(NH_2)_2(NMe_2)_6$.

The reaction of octachlorocyclotetraphosphazene, $N_4P_4Cl_8$, with gaseous ammonia in diethyl ether was studied by de Ficquelmont [1]. Bis- and tetrakis-amido derivatives, $N_4P_4(NH_2)_2Cl_6$ m.p. 217–218 °C, and $N_4P_4(NH_2)_4Cl_4$ m.p. 161–162 °C were isolated. In a subsequent report [2], Lehr showed that the bis derivative has a 2,6-nongeminal disposition of the amido substituents; the tetra compound has the 2,2,6,6-structure.

We have investigated the reaction of $N_4P_4Cl_8$ with aqueous ammonia in diethyl ether in the presence of anhydrous sodium sulphate and isolated a bis(amido) derivative (m.p. 86–89 °C), which is different to the one described previously [1, 2]. Its $^{31}P\{^1H\}$ NMR spectrum is asymmetrical [Fig. (a)] and arises from an A_2BX spin system. This observation is compatible only with a geminal disposition of the amido substituents in the new bis(amido)-cyclotetraphosphazene; non-geminal bis derivatives of $N_4P_4Cl_8$ exhibit symmetrical A_2B_2 or $AA'BB'$ line patterns in their ^{31}P NMR spectra [3]. The compound is sensitive to moisture and deteriorates on storage. It has been further characterised by conversion to its dimethylamino derivative, $N_4P_4(NH_2)_2(NMe_2)_6$. The ^{31}P NMR spectrum of this derivative is also asymmetrical and of the A_2BC type [Fig. (b)]. Its 270 MHz 1H NMR spectrum shows two doublets for the $-NMe_2$ protons (2.62, 2.61 δ ; $^3J(P-H) = 11.0, 10.5$ Hz).

The reaction of the hexachloride, $N_3P_3Cl_6$, with ammonia gives a single bis substituted product and

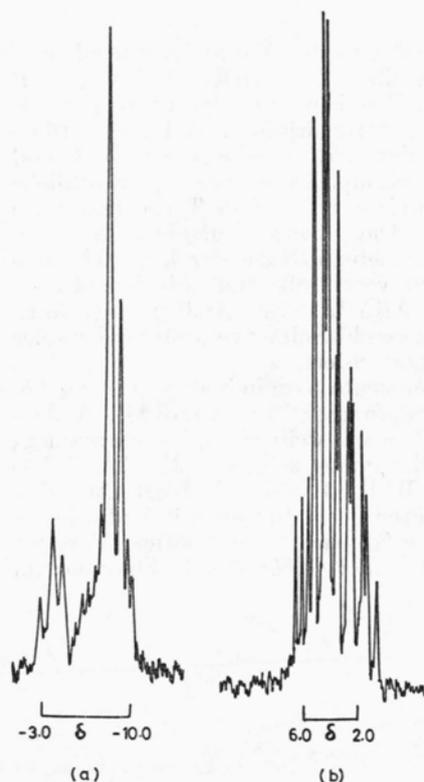


Figure. The $^{31}P\{^1H\}$ NMR spectrum (36.43 MHz, $CDCl_3$) of

(a) 2,2:4,4,6,6,8,8- $N_4P_4(NH_2)_2Cl_6$;
(b) 2,2:4,4,6,6,8,8- $N_4P_4(NH_2)_2(NMe_2)_6$.

this derivative has the geminal structure [4]. The initial replacement of the chlorine atoms of $N_3P_3Cl_6$ by primary amines depends on the reactivity of the nucleophile. Exclusive geminal replacement is observed with *t*-butylamine; reactive amines such as methylamine or ethylamine give rise almost entirely to nongeminal bis(amino)derivatives [3]. Analogous reactions of the octachloride have been explored in detail only recently. Reactive amines give 2,6-bis(amino) derivatives, $N_4P_4(NHR)_2Cl_6$, whereas sluggishly reactive amines yield both 2,4- and 2,6-substituted products [5]. Geminal compounds are not obtained. Hence, the isolation of the geminal bis(amido) hexachloro derivative, $N_4P_4(NH_2)_2Cl_6$, is somewhat unexpected. This compound provides the first authenticated example of geminal replacement at the bis stage in any aminolysis reaction of $N_4P_4Cl_8$. Its formation is probably partially due to the low reactivity of ammonia but more particularly to the use of aqueous ammonia: the water present could function as a base and promote the proton abstraction mechanism which favours geminal substitution [3].

The reaction of $N_4P_4Cl_8$ with aqueous ammonia in diethyl ether also yields a tris(amido) derivative,

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$N_4P_4(NH_2)_3Cl_5$ m.p. 271 °C, which probably has a 2,2,6-structure. In addition, large amounts of resins are obtained presumably because of facile intermolecular condensation reactions. Thus, the possibility of the formation of the 2,6-non-geminal product characterised earlier [2] cannot be discounted. A systematic investigation of this complex reaction is in progress.

Experimental

Anhydrous Na_2SO_4 (75 g) was suspended in a solution of $N_4P_4Cl_8$ (0.012 mole) in diethyl ether (250 cm³) at 0 °C. The suspension was stirred vigorously and aqueous ammonia (3.5 cm³, sp.gr. 0.88; 0.048 mole) mixed with diethyl ether (50 cm³) was added dropwise (1 h). The mixture was immediately filtered and the solvent was evaporated *in vacuo*. The residue was extracted with hot light petroleum (b.p. 60–80 °C) (2 × 30 cm³) under anhydrous conditions. The extract was transferred to a stoppered flask. After 12 h, powdery crystals of 2,2-bis(amido)-4,4,6,6,8,8-hexachlorocyclotetraphos-

phazatetraene, m.p. 86–89 °C (16% yield) were obtained. [Mass spectrum: Molecular ion at $m/e = 422$ corresponding to $(H_4^{35}Cl_6N_6P_4)^+$; IR spectrum: $\nu(P=N)$ 1315 cm⁻¹, $\nu(PCl_2)$ 605, 525.] A stirred solution of the bis(amido) derivative (0.0023 mole) in diethyl ether (150 cm³) was treated with an excess of Me_2NH (0.3 mole) at 0 °C. The mixture was allowed to attain room temperature, heated under reflux (4 h) and left overnight. After filtration and removal of the solvent, an oil was obtained which was characterised as 2,2-bis(amido)-4,4,6,6,8,8-hexakis(dimethylamino)cyclotetraphosphazatetraene (72% yield) [Mass spectrum: molecular ion at m/e 476 corresponding to $C_{12}H_{40}N_{12}P_4$].

Calcd	C 30.3	H 8.4	N 35.3,
Found	C 30.5	H 8.4	N 34.8.

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