

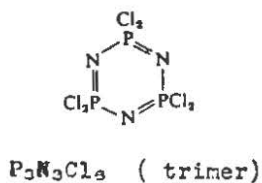
## Cyclophosphazene Chemistry

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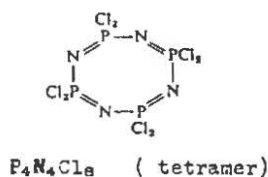
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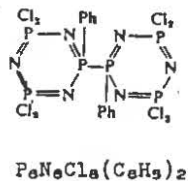
Cyclophosphazenes are heteroatom ring compounds which contain the repeating unit  $-(N=PRR')-$ , where R and R' can be halogens, amino groups or organic radicals. The first cyclophosphazene to be reported was the cyclic trimer,  $(PNCl_2)_3$  (a). Its preparation was described in 1834 by Liebig and Wohler, making cyclophosphazenes one of the earliest known inorganic heterocyclic compounds [1]. Many other structural types have been reported including the cyclic tetramer (b), the bridged dimer (c), and a fused ring tricyclic compound (d) [1]. The synthesis of an interesting compound having a closed structure and phosphazene character,  $K_6[P_{12}S_{12}N_{14}]$ , was described by Fluck in 1976 [2]. This molecule consists of 12 fused 6-membered rings containing both divalent and trivalent nitrogen atoms (e).



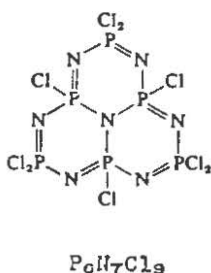
(a)



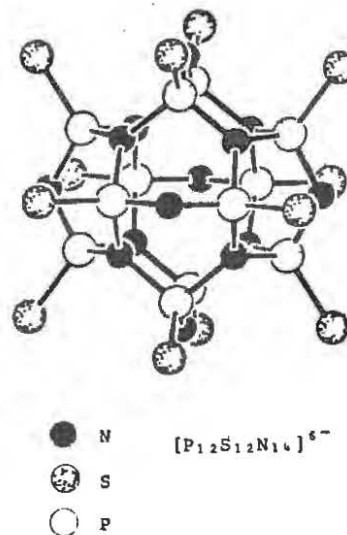
(b)



(c)



(d)



(e)

The simple cyclic phosphazenes can be made in a very complex reaction between  $NH_4Cl$  and  $PCl_5$  [1]. The mechanism of this reaction has been carefully studied by several workers [3]. The trimer can be extracted from the product mixture with acid, but separation of the other cyclic products is difficult. The synthesis of the bridged dimer is straightforward as it is a major product of the reaction between the trimer and methyl or phenyl magnesium chloride in THF [4]. No direct route has been reported for the synthesis of  $P_6N_7Cl_9$ . It can be made in low yield from polymerization then depolymerization of a mixture of low molecular weight cyclophosphazenes [5]. The  $P_{12}S_{12}N_{14}$  anion is more cooperative and forms in good yield when  $P_4S_{10}$  is added to molten  $KSCN$  [2].

The chemistry of the trimer has been extensively investigated [6]. It undergoes aminolysis, hydrolysis, and metathetical exchange reactions. The trimer also reacts with alkoxides, aryl oxides, and thiolates to form a variety of products including spirocyclic compounds [7]. Some of these spirocyclic cyclophosphazenes form molecular inclusion compounds with small organic molecules [8]. Several cyclophosphazene complexes have been reported which contain transition metals bound to the trimer [9], tetramer [10], and the hexamer [11]. Coordination to the metal can occur at the ring phosphorus [9] or nitrogen atom, or using ring and exocyclic nitrogen atoms [10]. Another interesting complex reported by Allcock contains an icosahedral carborane unit bound to the trimer through a phosphorus-carbon bond [12]. Recently, Allcock and Harris have explored the reaction of the trimer with carbanions [13]. Allcock has proposed a metal-halogen exchange mechanism to explain the interaction of the trimer with organocuprate complexes. The chemistry of the higher order cyclophosphazenes ( $[NPX_2]_n$  where  $n=4-8$ ) has not been investigated as thoroughly, but they appear to undergo some of the same reactions as the trimer [6]. The bridged dimer reacts with sodium alkoxides and aryl oxides to give substituted bicyclop phosphazenes and monomers [14]. The chemistry of  $P_6N_7Cl_9$  is very limited as substitution of the chlorines for more electron withdrawing groups causes collapse of the trimeric structure [5]. However, dimethylamine reacts to form an octakisdimethylamine derivative in which only one of the bonds to the central nitrogen is cleaved. The reaction chemistry of the  $P_{12}S_{12}N_{14}$  anion has not been reported, this may be due to low solubility in organic solvents.

The trimer is essentially a planar ring when it is symmetrically substituted having substituents extending above and below the plane [15]. The tetramer and the higher rings have different conformations in solid state depending on their substituents [16,17], but the  $^{31}P$  NMR spectrum in solution usually shows the phosphorus atoms to be equivalent for symmetrically substituted derivatives [18]. The structure of  $P_6N_7Cl_9$  is interesting as the rings are made up of two almost planar segments, one containing the trivalent central nitrogen, the other bent down from the central plane at a  $25^\circ$  angle [5]. The 6-membered rings in  $P_{12}S_{12}N_{14}^{6-}$  are even more contorted due to the presence of two trivalent nitrogen atoms in each ring, and the restriction of forming a closed structure [2]. The structure of the  $P_{12}S_{12}N_{14}$  anion, which has  $T_h$  symmetry, can best be visualized by looking at the various closed geometric figures it contains. The triply bridging nitrogen atoms form a cube, the doubly bridging nitrogen atoms are arranged in an octahedron, and the sulfur atoms describe a slightly distorted icosahedron. Finally, the phosphorus and triply bridging nitrogen atoms are at the vertices of a pentagonal dodecahedron.

References

1. Heal, H. G. "The Inorganic Chemistry of Sulfur, Nitrogen, and Phosphorus"; Academic Press: New York, 1980; pp 214-49.
2. Fluck, E. F.; Lang, M.; Horn, F.; Hadricke, G. M.; Sheldrick, G. M. Z. Naturforsch. B. 1976, 31b, 419-26.
3. Emsley, J.; Udy, P. B. J. Chem. Soc. (A) 1970, 3025-9.
4. Harris, P. J.; Desorcie, J. L.; Allcock, H. R. J. Chem. Soc., Chem. Comm. 1981, 852-3.
5. Oakley, R. T.; Paddock, N. L. Can. J. Chem. 1973, 51, 520-8.
6. Krishnamurthy, S. S.; Sau, A. C.; Woods, M. "Advances in Inorganic Chemistry and Radiochemistry", Vol. 21; Academic Press: New York, 1978; pp. 41-112.
7. Allcock, H. R.; Kugel, R. L. J. Am. Chem. Soc. 1969, 91, 5452-6.
8. Allcock, H. R. Acc. Chem. Res. 1978, 11, 81-7.
9. Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. Inorg. Chem. 1981, 20, 716-22.
10. Calhoun, H. P.; Paddock, N. L.; Trotter, J. J. Chem. Soc., Dalton 1973, 2708-12.
11. Marsh, W. C.; Trotter, J. J. Chem. Soc. (A) 1971, 1482-6.
12. Allcock, H. R.; Scopelianos, A. G.; O'Brien, J. P.; Bernheim, M. Y. J. Am. Chem. Soc. 1981, 103, 350-7.
13. Allcock, H. R.; Harris, P. J.; Connolly, M. S. Inorg. Chem. 1981, 20, 11-6.
14. Allcock, H. R.; Connolly, M. S.; Harris, P. J. J. Am. Chem. Soc. 1982, 104, 2482-90.
15. Bullen, G. J. J. Chem. Soc. (A) 1971, 1450-3.
16. McGeachin, H. McD.; Tromans, F. R. J. Chem. Soc. 1961, 4777-83.
17. Wagner, A. J.; Vos, A. Acta. Cryst. 1968, B24, 707-13.
18. Keat, R.; Shaw, R.; Woods, M. J. Chem. Soc., Dalton 1976, 1582-9.