

P-N Compounds: From the Single Tetrahedral Cation to Framework Structures

Alfred Schmidpeter

Institut für Anorganische Chemie, Universität München, D-80333 München, Germany

Stefan Horstmann and Wolfgang Schnick

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany

The element combination PN is isoelectronic to SiO (Fig. 1). How much practical impact is connected to this statement?

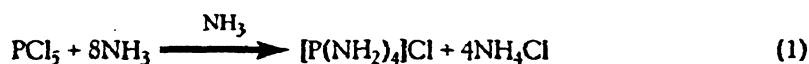
Like the hydrolysis of SiCl₄, the ammonolysis of PCl₅ is accompanied by a condensation. The complexity of this reaction already was realized when it was first investigated:

"Thatsache ist, wenn Chlorphosphor mit Ammoniak zusammenkommt, so entsteht positiv Salmiak in grosser Menge. Seine Bildung setzt nothwendig die Bildung von Amiden voraus; allein die Zusammensetzung der Chlorphosphore ist so, dass sich kein einfaches Amid bilden kann" [1].

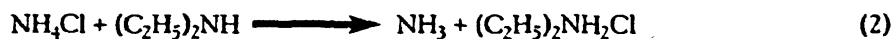
Justin Liebig wrote this in a letter [2] dated November 12, 1832 to Friedrich Wöhler.

The condensation (Fig. 2) [3] leads to cyclic oligomers and linear polymers (phosphazenes) and ends with a product of the empirical composition HPN₂. It was described [4] and named phospham as early as 1846. It is isoelectronic with silicon dioxide and in fact resembles the latter in its high chemical stability, but only now the structural analogy of the two has been proven [5].

By using excess liquid ammonia for the ammonolysis, the condensation can be suppressed and only the product of substitution, the tetraaminophosphoniumchloride, is obtained (Equation 1) [6, 7].



The pure product is obtained by reacting the byproduct, ammonium chloride, with diethylamine and removing the formed diethylamine hydrochloride.



An alternative preparation starts from phosphoro/thionic triamide SP(NH₂)₃ and thus avoids any risk

of condensation. A two step sequence leads to tetraaminophosphonium iodide (Equation 3) [8, 9].

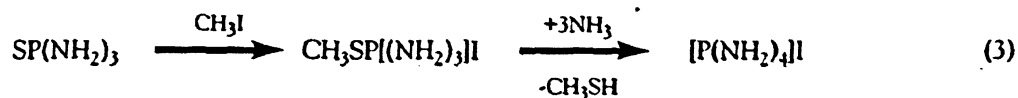
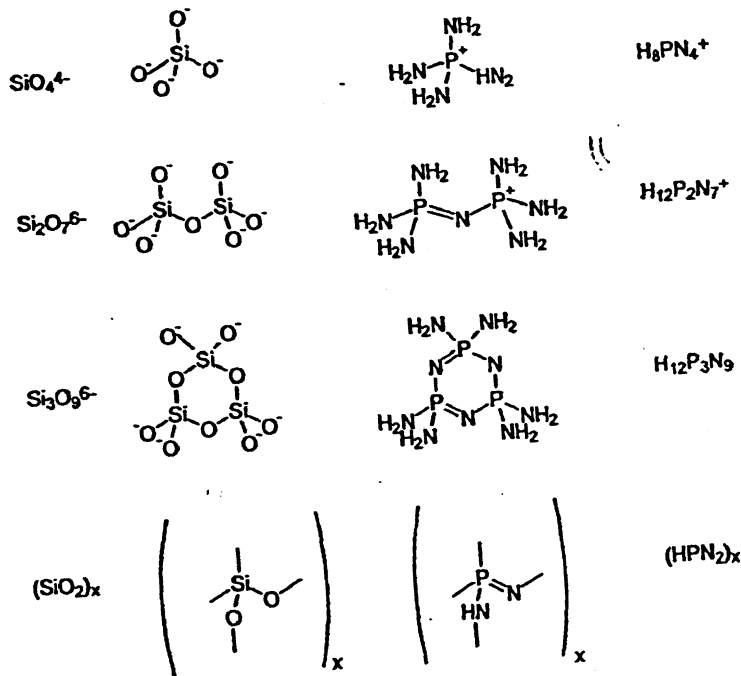


FIGURE 1
Isoelectronic SiO and PN species



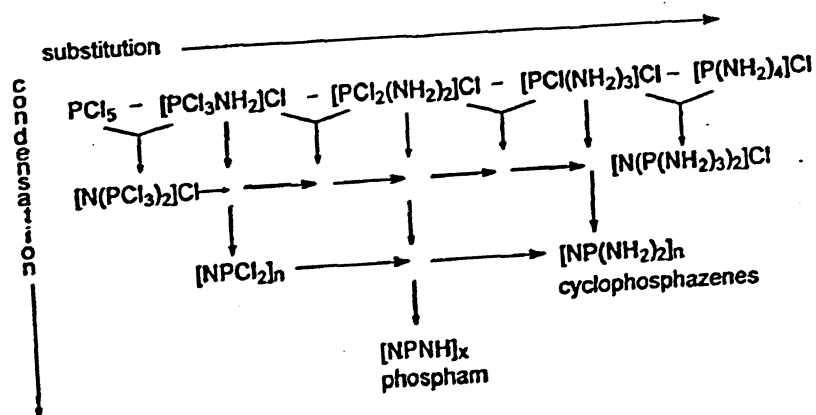
Justin Liebig



Friedrich Wöhler



FIGURE 2
The product pattern of the ammonolysis of PCl_5

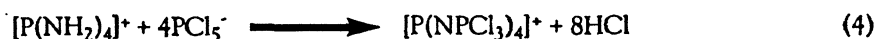


According to the X-ray structure determination, both salts contain the tetraaminophosphonium ion. In the cation, phosphorus and nitrogen form a markedly distorted tetrahedron, with a P-N distance of 160.7(2) pm being the shortest P-NH₂ bond ever reported.

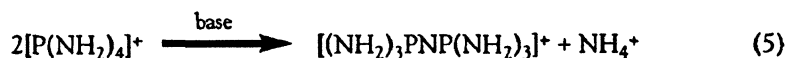
In the iodide, a CsCl analogous coordination of cations and anions is found (Fig. 3) [10]. Contrary to this, in [P(NH₂)₄]Cl, a mutual coordina-

tion number of 7 is realized, resembling a TII-analogous structure (Fig. 4). An essential feature for the arrangement of the cations in both structures is the formation of N-H...X hydrogen bonds.

The reaction of the tetraaminophosphonium ion with phosphorus pentachloride gives access to doubly branched phosphazenes (Equation 4) [6].

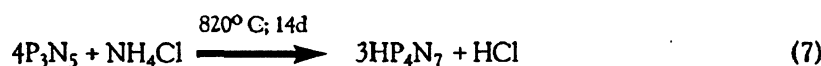
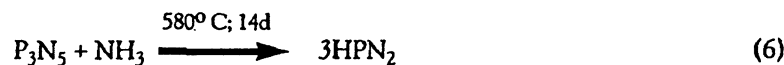


By the influence of bases, the tetraaminophosphonium salts condense to triaminophosphazo-triaminophosphonium salts (Equation 5) [6].



Thermal condensation of [P(PNH₂)₄]X-salts leads to phosphorus-nitride-imides with different hydrogen content, such as HPN₂ or HP₄N₇ [10].

These compounds are also obtained by heterogenous ammonolysis reactions (Equations 6 and 7) of pure and crystalline P₃N₅ [11].



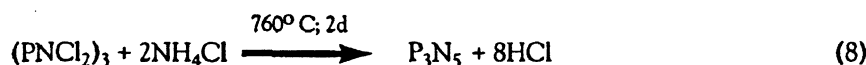
Both compounds are built up by three-dimensional framework structures of corner sharing PN₄-tetrahedra [11].

The structure of HPN₂ [5], which is isoelectronic to SiO₂, corresponds to the β-cristobalite type (Fig. 5), the high temperature modification of SiO₂.

The structure of HP₄N₇ can be regarded as a shear variant of the HPN₂ structure, which results by eliminating one NH₃ from four formula units of

HPN₂. The valences of the P-N framework are saturated by nitrogen which are bonded to three phosphorus atoms according to the formula $\frac{2}{3}[\text{P}_4^{[4]}\text{N}_5^{[2]}\text{N}_2^{[3]}]$.

The hydrogen-free phosphorus(V) nitride P₃N₅ is obtained in a pure and microcrystalline form by reacting (PNCl₂)₃ with ammonium chloride, according to Equation 8 [11].



The reaction is carried out in sealed glass ampules and the size of the batch is limited by the pressure caused by formation of hydrogen chloride. The

decomposition of tetraaminophosphoniumchloride (Equation 9) [7] is without these limits.

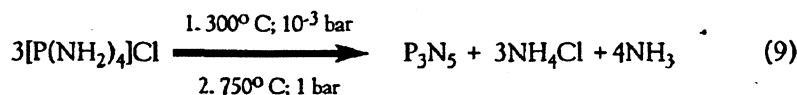


FIGURE 3
The coordination of the tetraaminophosphonium ion in $[P(NH_2)_4]^+$

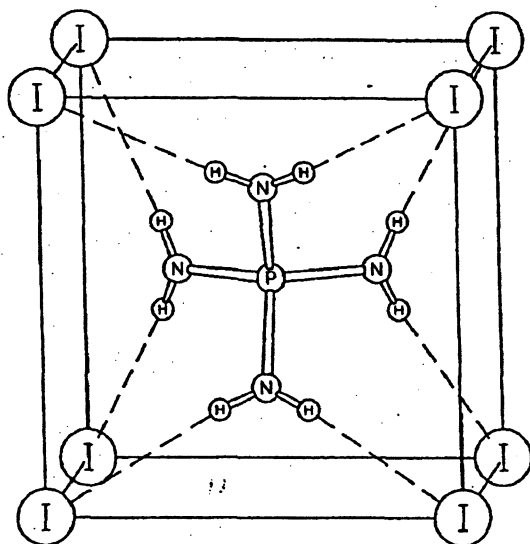
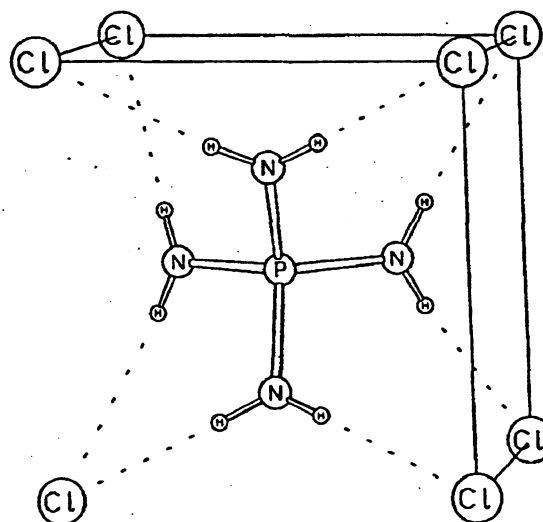


FIGURE 4
The coordination of the tetraaminophosphonium ion by chloride in $[P(NH_2)_4]Cl$.



According to the formula $\frac{2}{3}[P_3^{4-}N_3^{2-}N_2^{3-}]$, the solid contains two types of nitrogen atoms, with 3/5 bonded to two phosphorus atoms and 2/5 bonded to three atoms. The structure is dominated by a stacking disorder, as demonstrated by HRTEM investigations [11].

By reaction of P_3N_5 with Li_3N ternary phosphorus nitrides with P-N anions are accessible.

In the quasi-binary system Li_3N/P_3N_5 , $LiPN_2$ is the compound with the highest P content. It has a three-dimensional framework structure $\frac{2}{3}[PN_{4/2}]$ which is isotypic to HPN_2 or β -cristobalite [12]. In $Li_{12}P_3N_9$, the anion $[P_3N_9]^{12-}$ (Fig. 6) corresponds to the cyclotrisilicate anion $[Si_3O_9]^{6-}$ [13]. In Li_7PN_4 , isolated $[PN_4]^{7-}$ tetrahedra isoelectronic to ortho-silicate anions are found (Fig. 7) [14]. A compound containing the anion $[H_4PN_4]^{3-}$ isoelectronic to H_4SiO_4 is obtained from the reaction of P_3N_5 and $CsNH_2$ [15].

$Li_5P_2N_5$ contains no $\frac{2}{3}[P_2N_5^{5-}]$ layers, but isolated $[P_4N_{10}]^{10-}$ anions have been found (Fig. 8) [16]. A compound containing the anion $[H_6P_4N_{10}]^+$ has been obtained from the reaction of P_3N_5 and $NaNH_2$ [17]. These anions are isosteric to molecular phosphorus pentoxide P_4O_{10} or to silicic esters $Si_4O_6(OR)_4$ with bulky substituents R. An analogue to layer-silicates has not been found yet.

An arrangement analogous to chain-silicates is realized in the calcium phosphorus nitride Ca_2PN_3 (Fig. 9) [18]. The synthesis is analogous to that of the Li-salts by reacting the basic metal nitride Ca_3N_2 with the acidic non-metal nitride P_3N_5 (Equation 10).

FIGURE 5
The structure of HPN_2

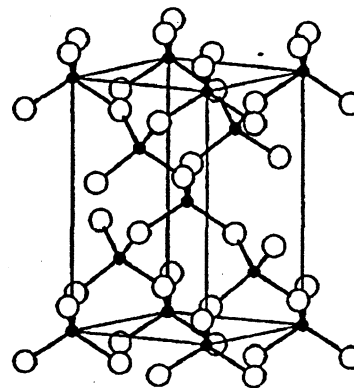
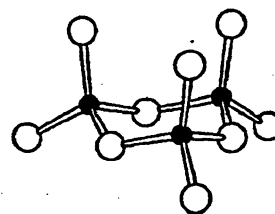
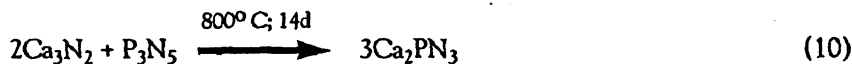


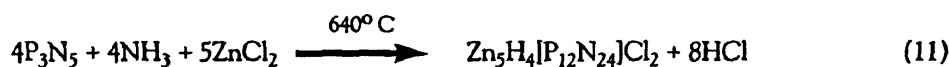
FIGURE 6
The structure of the anion $P_3N_9^{12-}$ in $Li_{12}P_3N_9$



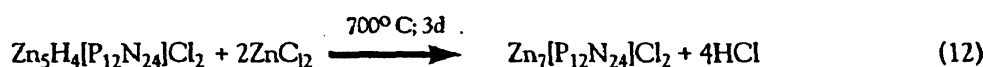


Because most of the ternary phosphorus nitrides contain structural analogues to the silicates, it seemed to be a promising task to search for P-N frameworks with zeolite-like structures.

The synthesis of a P-N zeolite succeeded by treating P_3N_5 and volatile metal halide with ammonia at 640°C (Equation 11) [19].

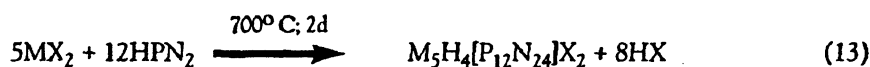


In a subsequent reaction with additional zinc chloride, a complete exchange of the hydrogen is possible (Equation 12).



The cubic compound is isostructural to sodalite, $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$. The aluminosilicate framework is replaced by a nitrido phosphate framework (Fig. 10). In the center of the β -cage, a Cl^- ion is found which

is tetrahedrally surrounded by metal cations Zn^{2+} . A more elegant method for preparation of P-N sodalites is the direct reaction of metal dihalides with phosphorus nitride imide (Equation 13) [11].

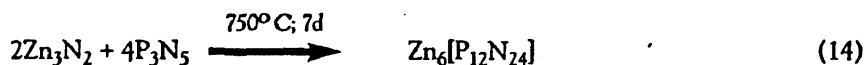


A large number of compounds has been realized in this manner containing, for example, Mg^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} or Pb^{2+} as cations and F^- , Cl^- , Br^- or I^- as anions.

A striking feature of several P-N sodalites is their intense color. The cobalt and nickel containing

compounds are blue, the iron containing brown and Cr and Ti containing materials are green.

A P-N sodalite without a central halide ion is accessible by reaction of zinc nitride with phosphorus nitride (Equation 14) [20].



The P-N framework in this compound is the same as in $\text{Zn}_7[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$, but the zinc atoms are disordered. Indications have been found that $\text{Zn}_6[\text{P}_{12}\text{N}_{24}]$ might be useful as a hydrogen storage material.

As shown in this overview, several examples for the structural analogy between Si-O and P-N

compounds do exist. Typical silicate building blocks and the corresponding P-N isosteres show different formal charges, as $\text{SiO}_4^{4-}/\text{PN}_4^{7-}$, $\text{Si}_3\text{O}_9^{6-}/\text{P}_3\text{N}_9^{12-}$ or $\text{SiO}_2/\text{PN}_2^-$, but in ternary and higher compounds, the P-N substructures correspond to the respective silicate structures.

FIGURE 7
The structure of the anion PN_4^{7-} in Li_7PN_4

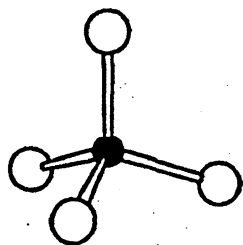
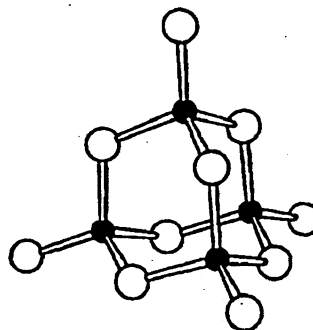


FIGURE 8
The structure of the anion $\text{P}_4\text{N}_{10}^{10-}$ in $\text{Li}_{10}\text{P}_4\text{N}_{10}$



Using this structural analogy, it should also be possible to obtain phosphorus nitrides analogous to nanoporous zeolites or layered silicates which might be materials with promising technical relevance. ❖

References and notes

1. From W. Lewicki, "Wöhler and Liebig—Briefe von 1829–1873," J. Cromm Verlag, Göttingen, p. 63 (1982).
2. "When chlorophosphorus and ammonia are brought together, much ammonium chloride is formed. This necessitates the formation of amides; the composition of chlorophosphorus is such however, that no simple amide can form."
3. A. Schmidpeter et al., *Z. Naturforsch.*, B24, 799 (1969) and literature cited there.
4. M.C. Gerhardt, *Ann. Chim. Phys.*, 18, 188 (1846); *C.R. Acad. Sci.*, 22, 858 (1846).
5. W. Schnick and J. Lücke, *Z. Anorg. Allg. Chem.*, 610, 21 (1992).
6. A. Schmidpeter and C. Weingand, *Angew. Chem.*, 81, 573 (1969); *Angew. Chem. Int. Ed. Engl.*, 8, 615 (1969).
7. S. Horstmann and W. Schnick, unpublished results.
8. A. Schmidpeter and C. Weingand, *Angew. Chem.*, 80, 234 (1968); *Angew. Chem. Int. Ed. Engl.*, 7, 210 (1968).
9. W. Schnick et al., *Angew. Chem.*, 106, 818 (1994); *Angew. Chem. Int. Ed. Engl.*, 33, 785 (1994).
10. S. Horstmann and W. Schnick, *Z. Naturforsch.*, (in press).
11. W. Schnick, *Angew. Chem.*, 105, 846 (1993); *Angew. Chem. Int. Ed. Engl.*, 32, 806 (1993).
12. W. Schnick and J. Lücke, *Z. Anorg. Allg. Chem.*, 588, 19 (1990).
13. U. Berger and W. Schnick, unpublished results.
14. W. Schnick and J. Lücke, *J. Solid State Chem.*, 87, 101 (1990).
15. H. Jacobs and F. Golinski, *Z. Anorg. Allg. Chem.*, 620, 531 (1994).
16. W. Schnick and U. Berger, *Angew. Chem.*, 103, 857 (1991); *Angew. Chem. Int. Ed. Engl.*, 30, 830 (1991).
17. H. Jacobs et al., *Z. Anorg. Allg. Chem.*, 620, 1213 (1994).
18. W. Schnick and V. Schultz-Coulon, *Angew. Chem.*, 105, 308 (1993); *Angew. Chem. Int. Ed. Engl.*, 32, 280 (1993).
19. W. Schnick and J. Lücke, *Angew. Chem.*, 104, 208 (1992); *Angew. Chem. Int. Ed. Engl.*, 31, 213 (1992).
20. F. Wester and W. Schnick, unpublished results.

FIGURE 9
The structure of the anion $[\text{PN}_3^{4-}]_n$ in Ca_2PN_3

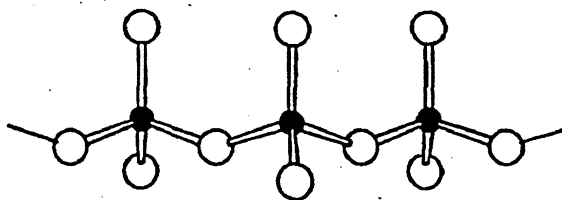


FIGURE 10
The β -cage of $\text{Zn}_7[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$

