

Ca₂PN₃: A New Phosphorus(v) Nitride with One-Dimensional Infinite Chains of Corner-Sharing PN₄ Tetrahedra**

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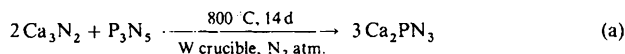
The systematic investigation of binary and higher phosphorus(v) nitrides has uncovered a variety of P–N substructures which, despite the comparatively small number of known compounds, show clear structural analogies to silicates and phosphates.^[1–6] The characteristic structural elements found in all the phosphorus(v) nitrides are PN₄ tetrahedra which may be connected by common vertices showing differing degrees of condensation: Isolated PN₄^{7–} anions are found in Li₇PN₄,^[1] whereas in Li₁₂P₃N₉ three PN₄ units form P₃N₉^{12–} anions, analogously to cyclotrisilicates.^[2] The smallest imaginable cage structure that can be formed from corner-sharing PN₄ tetrahedra has been found in Li₁₀P₄N₁₀,^[3] which contains the P₄N₁₀^{10–} anion, the nitrido analogue of molecular phosphorus(v) oxide. HPN₂, LiPN₂,^[4, 5] and Zn₇[P₁₂N₂₄]Cl₂^[6] each exhibit three-dimensional infinite network structures of corner-sharing PN₄ tetrahedra, $\frac{3}{2}$ [PN_{4/2}], which can be considered as the topological equivalent of β -cristobalite or of the sodalite framework, respectively. Low-dimensional structures of corner-sharing PN₄ tetrahedra have not yet been proven for phosphorus(v) nitrides. Like silicate compounds with chain or layer structures the analogous phosphorus nitrides are expected to have

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P:N ratios of 1:3 or 2:5. In contrast, lithium phosphorus nitrides with these ratios contain “dreier” rings or P₄N₁₀^{10–} cages, respectively.

By the reaction of stoichiometric amounts of the binary nitrides Ca₃N₂ and P₃N₅ [Eq. (a)] we have now successfully



synthesized pure calcium phosphorus(v) nitride Ca₂PN₃^[7] and elucidated its crystal structure.^[8] In the solid one-dimensional infinite “zweier” chains exist running parallel [100] (Fig. 1). These chains exhibit a periodicity of two PN₄ tetrahedra and an extreme stretching factor $f_s = 1.0$ similar to that found in johannsenite, CaMn[Si₂O₆], ($f_s = 0.98$).^[9] The P–N bond lengths to the terminal nitrogen atoms (average value: 162.5 pm) are shorter than those within the chains (167.4 pm). This finding corresponds qualitatively with the bonding in Li₁₂P₃N₉ and Li₁₀P₄N₁₀ and can be explained by an increased double bond character or by polar bonding contributions. The Ca²⁺ ions in Ca₂PN₃ are coordinated in a distorted pentagonal bipyramidal manner by the nitrogen atoms of the PN₃ chains, whereby one Ca²⁺ ion connects three chains with one another.^[10] The Ca–N contact distances (242–300 pm) lie approximately in the region of the sum of the ionic radii.

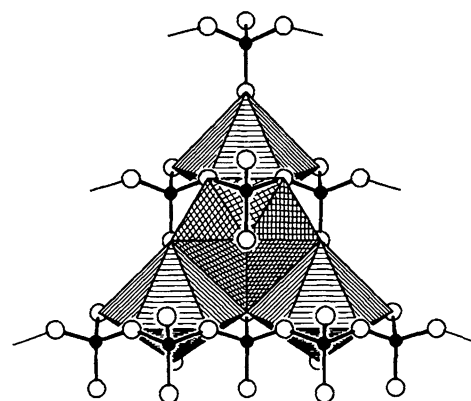


Fig. 1. Crystal structure of Ca₂PN₃ (view along [001]). The PN₃ chains along [100] are clearly visible. The two crystallographically independent Ca atoms are each coordinated in a distorted pentagonal-bipyramidal fashion by nitrogen atoms of the PN₃ chains. The coordination spheres around the Ca²⁺ ions are shown as closed polyhedra. Phosphorus: black, nitrogen: white.

Despite the observed topological similarity of the P–N substructures in this compound (as in other phosphorus(v) nitrides) with isosteric silicate anions, it appears that the structure rules as formulated by Liebau for silicates^[11] cannot be applied directly to phosphorus(v) nitrides: cyclic silicate anions are less stable than chainlike arrangements due to electrostatic repulsive forces between the oxygen atoms. In the case of phosphates, this difference is leveled out due to lower charge densities on the PO₄^{3–} units. In contrast, for phosphorus(v) nitrides (PN₄^{7–}), this repulsive effect is expected to be significantly enhanced due to the higher charges. In addition, a significant destabilization of cyclic and branched silicate anions is observed due to the influence of hard electropositive counterions (Li⁺, Mg²⁺), whereas with soft cations (Ca²⁺, Na⁺, K⁺) the opposite effect occurs.

Although any generalization is difficult owing to the small number of phosphorus(v) nitrides known to date, the appearance of $\frac{1}{2}$ [PN₂N_{2/2}] chains in the calcium compound and [P₃N₉^{12–}] “dreier” rings in the lithium compound is nev-

ertheless surprising. Also, the existence of $[\text{P}_4\text{N}_{10}^{10-}]$ cages in $\text{Li}_{10}\text{P}_4\text{N}_{10}$, for which no isosteric silicate anion is known, is a further example of the divergent structural behavior of phosphorus(v) nitrides compared to silicates. Possible reasons for this could be, in particular, in comparison to the Si–O bonds, the higher covalent character of the P–N bonds, longer P–N bond lengths and, related to this, the larger P–P distances between neighboring tetrahedral centers and a preference for smaller bond angles at the bridging nitrogen atoms. Thus, P–N bonds are on average about 10 pm longer than Si–O bonds of comparable bond strength.^[12] A simple estimation of the degree of covalency of the P–N bonds based on the occurring differences in electronegativity (Pauling)^[13] gives a distinctly higher value than that found for the more polar Si–O bonds (P–N: 78%, Si–O: 50% covalent). These two factors result in a smaller electrostatic repulsion between centers of neighboring tetrahedra for the phosphorus(v) nitrides. Consequently, for the P–N–P bond angles an average value of about 120° is observed which is significantly smaller than the ideal value for the Si–O–Si bond angles in silicates (140°) as given by Liebau.^[14, 15]

The coordinative requirements of the Ca^{2+} ions in Ca_2PN_3 could be responsible for the formation of the PN_3 "zweier" chains found in this compound. Likewise, in Mg_2PN_3 , which crystallizes in an ordered wurtzite superstructure variant,^[16] infinite chains of corner-sharing PN_4 tetrahedra are probably present. We are currently working on a more accurate determination of the structural data for this compound.

Experimental Procedure

Stoichiometric amounts of the binary nitrides Ca_3N_2 (synthesized from pure alkaline earth metal in a flow of nitrogen gas, 950°C, 1 h, heating rate 150°C h⁻¹) and P_3N_3 were homogenized in a micro-ball mill under an argon atmosphere (glove box, MBRAUN, Garching (FRG); $\text{O}_2 < 0.4$ ppm, $\text{H}_2\text{O} < 0.1$ ppm). The reaction mixture was sealed under a pure nitrogen atmosphere in a tungsten crucible in a quartz ampoule and finally allowed to react at 800°C (14 days). Under these conditions, Ca_2PN_3 was obtained in a pure form as a light beige microcrystalline powder.

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 [7] Elemental analyses were performed by first dissolving the product obtained in dilute H_2SO_4 at 180°C and 10 bar. The amount of calcium was determined by complexometric titration with EDTA, phosphorus photometrically as molybdovanadatophosphate, and nitrogen photometrically as indophenol. Parallel to this, the solid product was analyzed by energy dispersive and wavelength dispersive X-ray microanalyses (EDX: Ca, P and WDX: absence of oxygen). The presence of hydrogen (as N–H groups) was excluded by use of IR spectroscopy.
 [8] Ca_2PN_3 ; *Cmca*, $a = 519.14(4)$, $b = 1031.60(8)$, $c = 1128.91(10)$ pm; $Z = 8$, Stoe-Stadi/P-transmission powder diffractometer, $\text{Cu}_{\text{K}\alpha 1}$ radiation, germanium monochromator, linear position-sensitive detector (Stoe-Mini-PSD), capillary measurement, number of data points: 4001, measurement range: $10^\circ \leq 2\theta \leq 90^\circ$, total measurement time: 12 h, structure determination: direct methods (Mulan) and difference Fourier (program package C.S.D. from STOE, Darmstadt (FRG)); structure refinement: modified Rietveld method, number of observed reflections: 138, number of refined parameters: 14, number of refined positional and temperature parameters: 17, R factors: $R_p = 0.049$, $R_{wp} = 0.0636$, $R_{\text{int}, \text{hkl}} = 0.0939$. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD-56915, the names of the authors, and the journal citation.

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 [10] Ca_2PN_3 is isotypical with Rb_2TiO_3 (see W. Schartau, R. Hoppe, *Z. Anorg. Allg. Chem.* 1974, 408, 60) and with alkali metal cobaltates(IV) $[\text{M}_2\text{CoO}_3]$ where $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ (see M. Jansen, R. Hoppe, *Z. Anorg. Allg. Chem.* 1974, 408, 75).
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 [15] The P–N–P bond angles at the bridging nitrogen atoms observed to date in phosphorus nitrides vary from 116° to 148° from which the largest value observed is from the "zweier" chains present in Ca_2PN_3 with maximum stretching factor $f_s = 1.0$. The observed range of bond angles at nitrogen for phosphorus(v) nitrides is about the same as the corresponding range in molecular phosphazenes. (H. R. Allcock, *Phosphorus-Nitrogen Compounds*, Academic Press, New York, 1972, p. 44f.).
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