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Phosphorus Nitrides

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Pentacoordinate Phosphorus in a High-Pressure Polymorph of Phosphorus Nitride Imide $P_4N_6(NH)$**

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

Abstract: *Coordination numbers higher than usual are often associated with superior mechanical properties. In this contribution we report on the synthesis of the high-pressure polymorph of highly condensed phosphorus nitride imide* $P_4N_6(NH)$ *representing a new framework topology. This is the first example of phosphorus in trigonal-bipyramidal coordination being observed in an inorganic network structure. We were able to obtain single crystals and bulk samples of the compound employing the multi-anvil technique.* γ-$P_4N_6(NH)$ *has been thoroughly characterized using X-ray diffraction, solid-state NMR and FTIR spectroscopy. The synthesis of* γ-$P_4N_6(NH)$ *gives new insights into the coordination chemistry of phosphorus at high pressures. The synthesis of further high-pressure phases with higher coordination numbers exhibiting intriguing physical properties seems within reach.*

Unusually high coordination numbers of cations, particularly in covalent network structures, are often associated with interesting physical properties. These properties include high density, enhanced bulk modulus, and extraordinary mechanical hardness, all of which are of particular relevance for engineering applications.[1,2] According to the pressure-coordination rule, high coordination numbers are likely to occur in high-pressure polymorphs.[3] Therefore, explorative high-pressure synthesis is a highly valuable tool for the discovery of novel materials with intriguing properties.[4] Perhaps one of the most notable examples of an increase in coordination number at high pressures is observed in the case of SiO_2, which transforms to the six-coordinated stishovite structure type at pressures exceeding 9 GPa.[5,6] This phase has long been considered the hardest known oxide[7] and has only recently been surpassed by cotunnite-type TiO_2.[8] Recent investigations show that above 46 GPa silica analogous $AlPO_4$ adopts a $CaCl_2$-like structure containing PO_6-octahedra.[9] Similar phase transformations take place in Earth's mantle, most prominently in magnesium silicate $MgSiO_3$. High-pressure studies show that this mineral undergoes phase transitions to perovskite[10] and post-perovskite[11] structures at extreme pressures, both of which contain hexacoordinate Si atoms. Knowledge of these phase transitions greatly supports understanding of processes in planetary interiors. Increased coordination numbers also lead to interesting properties in nitride materials. Cubic boron nitride already enjoys widespread application as a high-temperature abrasive owing to its extreme hardness.[12,13] Silicon nitride Si_3N_4 is of high technological importance due to its mechanical and thermal properties.[14] It can be converted into its cubic high-pressure polymorph γ-Si_3N_4 at elevated pressures.[15] This high-pressure polymorph crystallizes in a spinel-type structure composed of SiN_4-tetrahedra as well as SiN_6-octahedra and displays a remarkably high hardness, which even surpasses that of stishovite.[16] In the case of phosphorus nitrides, an increased coordination number has to date only been observed in γ-P_3N_5, which also shows an increased hardness compared to the ambient-pressure phase.[17] In this high-pressure phase chains of edge-sharing quadratic PN_5-pyramids are linked by PN_4-tetrahedra to form a three-dimensional network. Even though a trigonal bipyramidal coordination is expected to be close in energy to a pyramidal one, no example for this coordination type has been found in inorganic network structures yet. Molecular species displaying this coordination geometry include PF_5,[18,19] $P(N_3)_5$[20] as well as phosphazenes.[21] It has also been proposed to occur in the theoretically predicted high-pressure polymorph δ'-P_3N_5.[22] Herein we report a new high-pressure polymorph of phosphorus nitride imide $P_4N_6(NH)$, which contains phosphorus in trigonal-bipyramidal coordination. To date only the ambient-pressure polymorph α-$P_4N_6(NH)$[23] as well as the high-pressure phase β-$P_4N_6(NH)$,[24] both of which contain only PN_4-tetrahedra, have been reported. Since this is the third reported polymorph of this compound we propose the name γ-$P_4N_6(NH)$.

We were able to synthesize γ-$P_4N_6(NH)$ by the reaction of P_3N_5 and NH_4Cl. The starting materials were treated at approximately 1200 °C for 120 min at a pressure of 14 GPa. The synthesis conditions were achieved using a modified Walker-type multi-anvil assembly and a 1000 t hydraulic press.[25] The product was obtained as an air-stable colorless crystalline solid. The product contained crystals large enough to be suitable for single-crystal X-ray diffraction. The formation of single crystals can be attributed to the presence of NH_4Cl acting as a mineralizer during the synthesis. This property has previously been utilized in the synthesis of the phosphorus nitrides β-HPN_2[26] and β-$P_4N_6(NH)$.[24] The

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product was successively washed with deionized water, ethanol, and acetone to remove excess NH_4Cl.

The composition of the obtained sample was analyzed using energy-dispersive X-ray (EDX) spectroscopy. The analysis confirmed the atomic ratio P:N of 4:7 and other than trace amounts of oxygen showed no signs of other elements being present in the sample. Details of the EDX results can be found in the supporting information.

The crystal structure of γ-$P_4N_6(NH)$ was solved from single-crystal X-ray diffraction data in the monoclinic space group $C2/c$ (no. 15) using direct methods.[27] All the heavy-atom positions could be found during structure solution and were refined anisotropically. Owing to its low scattering power and the small crystal size the H atoms could not be located. The crystal structure shows that γ-$P_4N_6(NH)$ is composed of a three-dimensional network of PN_4-tetrahedra and trigonal PN_5-bipyramids (Figure 1). The PN_5-bipyramids are connected by shared edges to form infinite strands along [110] and $[1\bar{1}0]$. These are arranged in a mesh-like pattern and are mutually interconnected by bowtie-like P_2N_7 double tetrahedra.

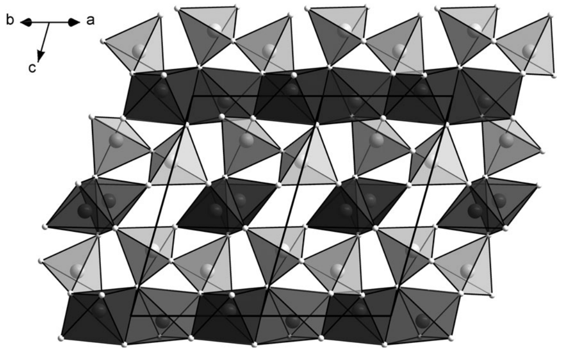

Figure 1. Crystal structure of γ-$P_4N_6(NH)$. View along [110] (P: larger light/dark gray spheres; N: small white spheres).

The framework topology can be unambiguously described with the point symbol $(3^2.4^6.5^6.6)(3^4.4^8.5^7.6^2)$ as determined with the TOPOS software package.[28] Owing to the different coordination numbers of the P atoms, the network topology is different to those of the other polymorphs. Therefore the phase transition leading to γ-$P_4N_6(NH)$ is necessarily a reconstructive one. The phase transition is associated with a considerable change in the crystal density. The change in density for the transition from β- to γ-$P_4N_6(NH)$ results in a much higher difference in densities (18.9%) than the transition from α- to β-$P_4N_6(NH)$ (5.5%). This behavior is expected as a result of the change in phosphorus coordination during the former transition.

The bonds around the tetrahedrally coordinate phosphorus atom (Figure 2) vary in the range between 156 and 169 pm which is consistent with the values found in other nitridophosphates. Owing to its higher coordination number, the bonds to the threefold coordinated nitrogen atoms N2 and N4 are about 10 pm longer than those to the doubly bridging nitrogen atoms N1 and N3. Tetrahedral angles (102–111°) show a slight deviation from the regular value. As would be expected,[29] the bonds around the trigonal bipyramidal phosphorus show a larger variation, with the axial bonds (182 pm) being markedly longer than the equatorial ones (163–167 pm). In the equatorial plane the bond to N1 is shorter than those to the triply coordinated N4 and N2. The equatorial N atoms form an almost equilateral triangle with no N-P-N angle deviating more than 0.7° from the regular value of 120°. However, the axial nitrogen ligands display a distinct kink in the N-P-N arrangement, as evidenced by the angle of 170.5(2)°. This effect is presumably caused by the high steric demand of this very dense network structure. While the location of the imidic H atom could not be directly determined from the structure analysis, crystal chemical considerations show that it is likely bound to N1. N2 and N4 already link three P atoms in a trigonal-planar arrangement, thus it is unlikely that they are NH groups. The bond P1–N1 is 2.9 pm longer than that to N3, which is likely due to the proton being bound to N1. Detailed information on bond lengths and angles can be found in the supporting information.

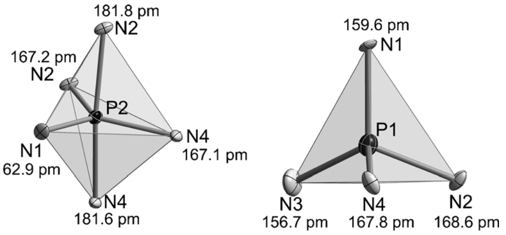

Figure 2. Coordination polyhedra and bond lengths around the two crystallographically distinct P atoms; thermal ellipsoids are set at 90% probability.

To verify the electrostatic consistency of the structure model, lattice-energy calculations were performed using the program MAPLE (Madelung part of lattice energy).[30] The overall MAPLE value for γ-$P_4N_6(NH)$ is in excellent agreement with that of β-$P_4N_6(NH)$, differing by less than 0.02%. The partial MAPLE values of the atomic sites ($P = 17\,030$–$16\,537$; $N = 4910$–$5673\ kJ\,mol^{-1}$) are in the range found in other nitridophosphates. The MAPLE values for N show a marked difference between $N^{[2]}$ and $N^{[3]}$, similar to what has been reported in literature.[31] The imidic N1 displays the lowest partial MAPLE value. The same pattern has been observed in β-$P_4N_6(NH)$, further corroborating our hypothesis on the location of the proton.

The accuracy of the structure model as well as the phase purity of the sample has further been established by means of Rietveld refinement of the powder pattern (Figure 3). The results corroborate the established crystal structure and show that other than 0.45(4) weight percent of the crucible material BN, no side phases are present.

^{31}P solid-state NMR spectroscopy (Figure S1 in the Supporting Information) shows two signals, which can be attributed to the two distinct atomic environments in γ-$P_4N_6(NH)$. The signal at $\delta = -17.4$ ppm is in a range typical for tetrahedrally coordinate phosphorus nitrides. The second signal is at a distinct chemical shift of $\delta = -103.0$ ppm. The only other example of a chemical shift in this range for phosphorus nitrides has been found in the case of γ-P_3N_5, where the signal was attributed to tetragonal pyramidally

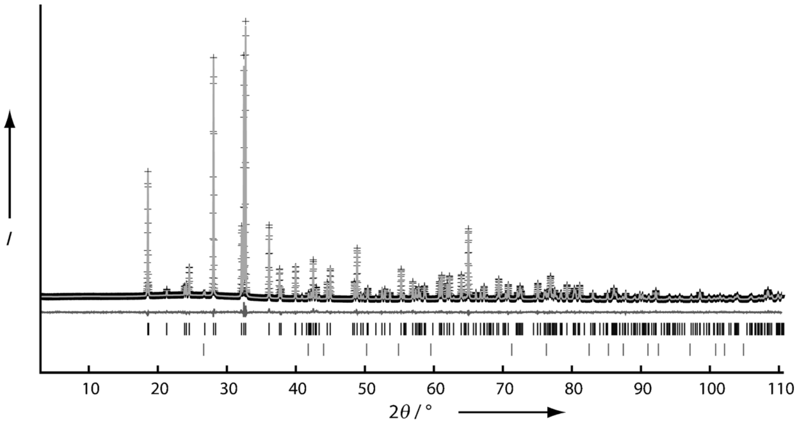

Figure 3. Observed (crosses) and calculated (light gray line) powder diffraction pattern of γ-P_4N_6(NH) as well as difference profile (dark gray line). Black vertical bars represent the positions of Bragg reflections of γ-P_4N_6(NH) and gray vertical bars the Bragg reflections of hexagonal BN.

coordinate phosphorus. Thus the general trend seems to be that higher coordination numbers shift the ^{31}P signals significantly upfield. To gain more insight into the location of the hydrogen atom, a ^{1}H solid-state NMR spectrum (Figure S2) was collected. It displays one single sharp peak at $\delta = 10.6$ ppm, corresponding to a single hydrogen site in the crystal structure.

The FTIR spectrum of the sample is reminiscent of that of the other polymorphs, as well as the less condensed phosphorus nitride imide PNNH.[32] A broad absorption around 3000 cm^{-1} can be attributed to the N–H valence bond. Additionally, two groups of bands can be seen below 1500 cm^{-1}. The group in the range 1400–1200 cm^{-1} is caused by asymmetric P-N-P stretching modes. The second group between 600 and 1200 cm^{-1} can be attributed to symmetric P-N-P stretching modes.

With γ-P_4N_6(NH), we obtained the first inorganic network structure containing phosphorus in trigonal-bipyramidal coordination and only the second one with pentacoordinate phosphorus at all. We were able to thoroughly characterize this compound by means of single-crystal and powder X-ray diffraction as well as solid-state NMR and FTIR spectroscopy. The location of the H atom can be inferred with reasonable certainty. These results shows that in the pressure range attainable with the multi-anvil technique structures containing higher coordinate phosphorus are accessible. Therefore similar structures of related nitridophosphates, such as MP_4N_7[33] and $M_3P_6N_{11}$ (M = Na, K, Rb, Cs)[34–36] should be accessible. Similarly, this gives an indication that silica analogous phosphorus oxonitride PON could have a high-pressure polymorph containing pentacoordinate phosphorus, potentially representing a new AB_2-type net. These findings could indicate that even compounds containing hexacoordinate phosphorus could be accessible in macroscopic amounts using multi-anvil techniques. Likely candidates are the theoretically predicted δ-P_3N_5 and δ′-P_3N_5[22] as well as spinel type BeP_2N_4.[37]

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[27] Crystal data for γ-P_4N_6(NH): crystal size: $0.011 \times 0.026 \times 0.026$ mm, space group *C*2/*c* (no. 15), $a = 6.8018(4)$, $b = 7.2204(5)$, $c = 8.9572(6)$ Å, $\beta = 111.231(2)°$, $V = 410.05(5)$ Å^3, $Z = 4$, $\rho_{\text{diffrn}} = 3.612$ gcm^{-3}, Bruker D8 Venture, Mo-K_α-radiation

(71.073 pm), multi-scan absorption correction, 5565 reflections, 628 independent reflections, $R_{\mathrm{int}} = 0.0273$, least-squares refinement on F^2, R-values (all data/$F_o^2 \geq 2\sigma(F_o^2)$): $R_1 = 0.0301/0.0252$, $wR_2 = 0.0814/0.0788$, GooF = 1.197 for 555 observed reflections ($F_o^2 \geq 2\sigma(F_o^2)$) and 51 parameters. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-427650.

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