**N,P Clathrates**

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# A Nitridic Clathrate: $P_4N_4(NH)_4(NH_3)$**

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In molecular and solid-state chemistry, some phosphorus- and nitrogen-containing compounds exhibit specific similarities and analogies to silicon–oxygen compounds. This resemblance is explained by the isolobal relation between P–N and Si–O bonds.[1,2] Simple examples are phosphorus nitride imide, PN(NH),[3,4] and phosphorus oxide nitride, PON,[5] which are both isoelectronic with silica, $SiO_2$. Accordingly, both compounds crystallize in β-cristobalite-analogous network structures and are made up of corner-sharing $PX_4$ tetrahedra (X = O, N). The ternary nitridophosphates $NaPN_2$ and $LiPN_2$[6–9] have filled isoelectronic $[PN_2]^-$ network structures and are structurally related to PON and PN(NH), as they adopt the chalcopyrite structure type. More complex silica analogues are represented by the class of nitridosodalites[10–13] and related oxonitridosodalites.[14] Recently, we synthesized and identified the first oxonitridic zeolite,[15] namely, $Li_xH_{12-x-y+z}[P_{12}O_yN_{24-y}]X_z$ with X = Cl, Br.[16] The $[P_{12}O_yN_{24-y}]$ framework of this new framework type (NPO[17]) contains large 12-ring channels and is solely made up of 3-rings (i.e., rings composed of 12 or 3 corner-sharing tetrahedra, respectively) as fundamental building units (FBUs).[16] The specific topology of the framework type NPO has been identified previously as a possible candidate structure for microporous $SiO_2$,[18] but this prediction has not been proven by experiment so far.

Besides the diverse and manifold substance class of zeolites[19] and zeosils,[20] another group of microporous solids is formed by clathrasils and clathralites[20,21] (generic term: clathrate). Usually these compounds contain uncharged $SiO_2$ framework structures of corner-sharing $SiO_4$ tetrahedra with neutral molecules (or nothing) in their cagelike pores. Herein we report on the first nitridic clathrate $[P_4N_4(NH)_4](NH_3)$ (**1**), which is based on a novel PN(NH) framework structure.

$[P_4N_4(NH)_4](NH_3)$ (**1**) was obtained by a high-pressure high-temperature reaction[22–25] at 600 °C and 11 GPa in a Walker-type multianvil assembly starting from a mixture of ammonium azide $NH_4N_3$[26] and $P_3N_5$[27] [Eq. (1)]. In the past,

$$21\,NH_4N_3 + 16\,P_3N_5 \rightleftharpoons 12\,P_4N_4(NH)_4(NH_3) + 28\,N_2 \qquad (1)$$

we have employed the multianvil technique for the synthesis and investigation of the high-pressure behavior of silica-analogous phosphorus nitrides[9,22,25] and recently we synthesized the high-pressure polymorph γ-$P_3N_5$.[28] We have frequently used high $N_2$ partial pressures, generated in situ by thermolysis of azides, in our synthetic approaches to metal-containing nitridophosphates starting from the respective metal azide and $P_3N_5$. Thereby, phosphorus nitride $P_3N_5$ (thermal decomposition > 850 °C at normal pressure[22]) is prevented from dissociation into the elements [Eq. (2)] at the

$$P_3N_5 \rightarrow 3\,PN + N_2 \rightarrow {}^3\!/_4\,P_4 + {}^5\!/_2\,N_2 \qquad (2)$$

high reaction temperatures[22] above 1000 °C that are usually necessary for the crystallization of the desired metal nitridophosphates.

In the current work we utilized the thermolysis of ammonium azide $NH_4N_3$ under high pressure and high temperature to provide the high partial pressures of both $N_2$ and $NH_3$ which are concurrently necessary for an ammonolysis reaction and thermal stabilization of $P_3N_5$ [cf. Eq. (1)]. Under normal pressure $NH_4N_3$ decomposes into $NH_3$ and $HN_3$ at 133 °C.[26] Above approximately 300 °C highly exothermic explosive decomposition occurs frequently and nitrogen is formed as well [Eq. (3)]. At moderate pressures (ca. 2–

$$3\,NH_4N_3 \rightarrow 4\,NH_3 + 4\,N_2 \qquad (3)$$

3 MPa) and temperatures around 580 °C ammonolysis of $P_3N_5$ [Eq. (4)] made available crystalline phosphorus nitride imide PN(NH) (**2a**).[3]

$$P_3N_5 + NH_3 \rightleftharpoons 3\,PN(NH) \qquad (4)$$

Under the extreme synthesis conditions of $P_4N_4(NH)_4(NH_3)$ (**1**), $NH_3$ apparently is incorporated into the growing PN(NH) framework structure and therefore acts as a template molecule. Thus, in contrast to nonintercalated **2a**, a topologically different host lattice of PN(NH) and formation of the clathrate $P_4N_4(NH)_4(NH_3)$ (**1**) with $NH_3$-filled cages is observed. In addition, we found that pure PN(NH) (**2a**) forms a high-pressure (hp) polymorph hp-PN(NH) (**2b**) that is still structurally related to the β-cristobalite-type normal-pressure phase **2a**. This displacive phase transition occurs between 7 and 11.5 GPa.[29]

The crystal structure of $P_4N_4(NH)_4(NH_3)$ (**1**) was determined on the basis of powder X-ray diffraction analysis (Figure 1) by direct methods and refined by the Rietveld method.[30] The reflections of the powder pattern of **1** were indexed in the tetragonal crystal system[31] and space group $P\bar{4}n2$ was derived unambiguously.

Nitridic clathrate **1** has an unprecedented PN(NH) framework structure of corner-sharing $PN_4$ tetrahedra that form 4-rings and 8-rings as FBUs (Figures 2 and 3). According to the literature[32] the formula of **1** can be written as $|(NH_3)_2|$

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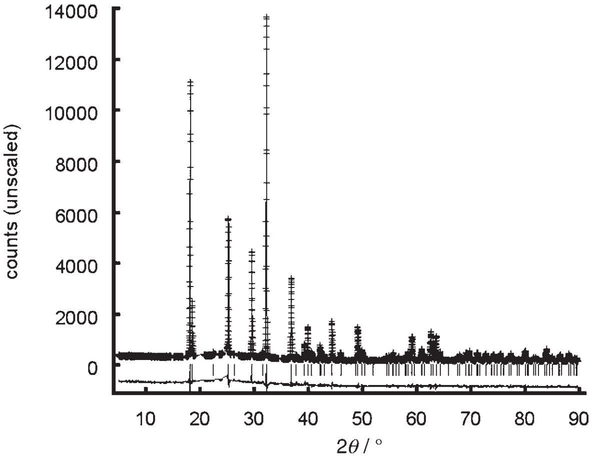


***Figure 1.*** Observed (crosses) and calculated (line) X-ray powder diffraction pattern as well as the difference profile of the Rietveld refinement of **1**. Allowed peak positions are marked by vertical lines.

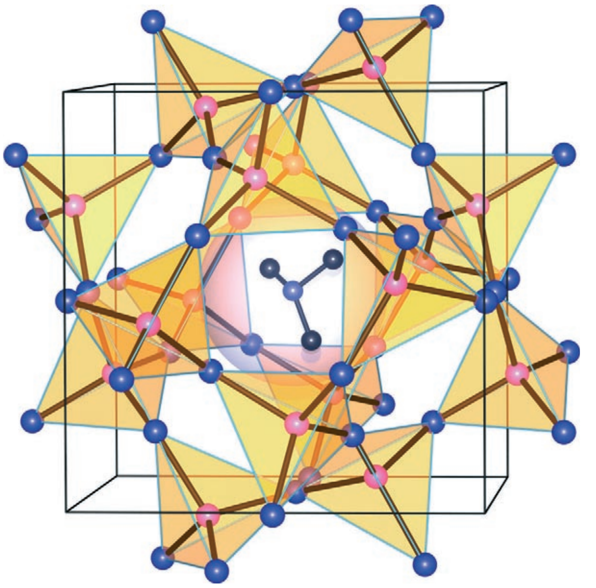


***Figure 2.*** Crystal structure of **1**, viewed approximately along [001]; blue N, pink P, dark gray H. The enclosed and rotationally disordered $NH_3$ molecule with its center of gravity on the site [000] is surrounded by a sphere representing the van der Waals radius of $NH_3$ (3.1 Å). The cavity is built up from one 8-ring (in the image plane) and two 4-rings (above and below the image plane).

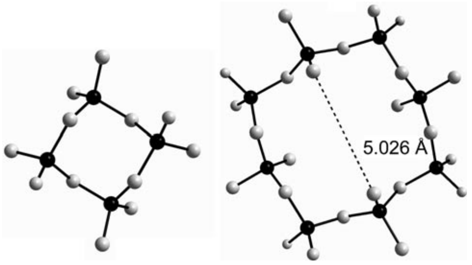


***Figure 3.*** Ball-and-stick model of the 4-ring and the 8-ring, viewed along [001]. The diameter of the 8-ring (between two opposite N atoms) is indicated by a dotted line.

$[P_8^{+V[8]}N_8^{-III[2]}(N_8^{-III[2]}H_8)]_h\{3[4^28^4]\}_p\{0[4^28^4](P\bar{4}n2)\}$ to emphasize the topology of the pores and the host network. The cycle class sequence of this framework (i.e., the relative frequency of occurrence of $[P_nN_n]$ ring sizes in the network of **1** for $n = 1, 2, 3 \ldots$) was calculated with the program TOPOLAN[33] and amounts to {–, 0, 0, 4, 0, 0, 0, 36, 0, 168, …}. The characteristic cages of this novel clathrate structure are formed by bent 8-rings which adopt the boat form and are capped by two 4-rings situated above and below the ring plane of the 8-rings. Each 8-ring is connected to two neighboring 4-rings through two tetrahedral corners (Figure 4). The thus-formed cages each contain one $NH_3$ molecule, which is presumably rotationally disordered. The inclusion of ammonia in **1** was proved both by temperature-programmed mass spectrometry and FTIR spectroscopy (see Experimental Section). The diameter of the cavities is about 5 Å considering the centers of the atoms, and about 3.5 Å with respect to their van der Waals radii. According to its mean van der Waals radius of 3.1 Å[34] the $NH_3$ molecule fits quite well into the cavities (see Figure 2). The topology of porous structures can be illustrated clearly by simply connecting the tetrahedral centers of the framework (here the P atoms), and such a representation for **1** is displayed in Figure 5.

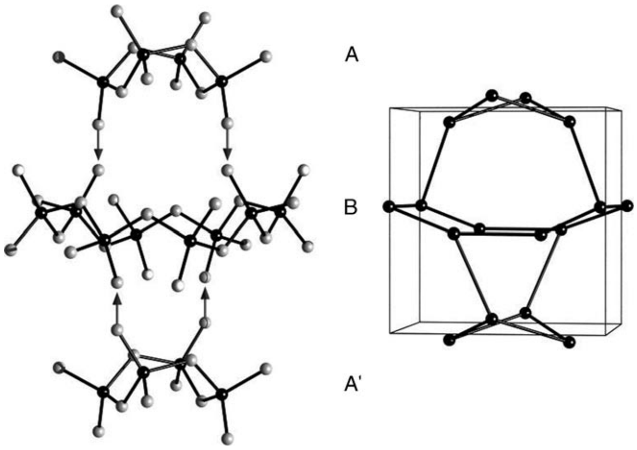
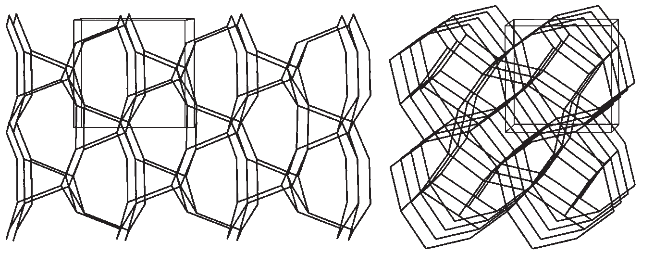


***Figure 4.*** Exploded view of the framework structure in **1**, viewed approximately along [010]. The upper and lower 4-rings (A and A′) are both connected through two P-N-P bridges to the middle 8-ring. On the right, the resulting framework topology in the unit cell of **1** is illustrated by simply connecting the tetrahedral centers (P) in **1**. For clarity, the intercalated $NH_3$ molecule is omitted in both drawings. The pore symbol[40] for **1** is$[4^28^4]$.

The $P_4N_4(NH)_4$ framework of **1** has not been observed in any porous structure or clathrate so far. However, its topology was already predicted theoretically by Bell et al.[35] and Treacy et al.,[36] who adopted the tiling theorem in a systematic search for structure candidates of hitherto unknown zeolites and clathrasils. However, during those investigations the specific framework structure realized in **1** was assumed to be unstable in the case of a silica ($SiO_2$) framework, while nitridic frameworks were not taken into account at that time. Presumably, the bond angles T-X-T (T = Si, P; X = O, N) in this framework type are unfavorably small[37] in the case of the hypothetical $SiO_2$ polymorph (theoretically refined values: Si-



View along *a* View along *c*

***Figure 5.*** Framework topology of **1**. For clarity, the N, NH groups, and $NH_3$ molecules are omitted and the tetrahedral centers (P) are directly connected.

O1-Si 125°, Si-O2-Si 134°, and Si-O3-Si 134°),[35,36] while the experimentally observed angles in **1** (P-N1-P 121.4(3)°, P-N2-P 123.4(2)°, P-N3-P 153.8(3)°) fit well into the usual range observable in phosphorus nitrides and imides.[3,7,9,22,25] The same holds for the P–N bond lengths in **1** (1.59(2)–1.67(2) Å).[3,7,9,22,25]

Nitridic clathrate **1** exhibits remarkable thermal stability with respect to evolution of ammonia. According to temperature-programmed mass spectrometry (see Experimental Section*)* the intercalated $NH_3$ in **1** is not expelled below 550 °C. At such temperatures **1** transforms presumably into a crystalline phase of normal-pressure PN(NH) [Eq. (5)].

$$P_4N_4(NH)_4(NH_3) \rightarrow 4\,PN(NH) + NH_3 \qquad (5)$$

Above 810 °C condensation of the thus-formed PN(NH) framework with further evolution of $NH_3$ is observed in mass chromatograms, which essentially represents the reverse of the ammonolysis reaction of $P_3N_5$ [Eq. (4)]. This finding compares well with the condensation (with evolution of $NH_3$) of crystalline PN(NH) (**2a**) that we observed in mass chromatograms at 860 °C. Amorphous and relatively undefined PN(NH) (**2c**) is much more sensitive towards condensation to $P_3N_5$, which already starts at temperatures as low as 100 °C (see Experimental Section). In accordance with our previous results[22] we finally observed thermolysis of the thus-formed amorphous $P_3N_5$ into the constituting elements [cf. Eq. (2)] above 890 °C.

At first glance, the high-pressure approach seems to be quite unusual for the synthesis of porous compounds, as these conditions are expected to destabilize less dense framework structures, which usually have lower density than related phases of higher thermodynamic stability. The success of this approach for the synthesis of **1** may be rationalized by assuming that the increase in density (**1** vs. **2b** + $NH_3$) is the driving force of the high-pressure reaction in a closed system. The density of **1** (2.642 $g\,cm^{-3}$) is comparable to that of 2.67 $g\,cm^{-3}$ for hp-PN(NH) (**2b**),[29] but for a quantitative estimation of the driving force for pressure-driven formation of **1** (as compared with the possibly competing formation of hp-PN(NH) + $NH_3$), the respective temperature- and pressure-dependent values for **1** and **2b**, as well as the contribution of $NH_3$, must be considered; however, these are not available as yet. Further experimental and theoretical investigations are planned to shed light on this issue and to further broaden this novel high-pressure approach to hitherto unknown porous structures.

## *Experimental Section*

$P_4N_4(NH)_4(NH_3)$ (**1**) was synthesized from the starting materials $NH_4N_3$[26] and $P_3N_5$[27] by high-pressure high-temperature synthesis in a similar way as outlined in the literature[22] in a Walker-type multianvil[24,38] module. Octahedra with an edge length of 14 mm (Ceramic Substrates, Isle of Wight) were used, and the sample was placed into a capsule made of hexagonal boron nitride (Henze, Kempten). The mixture was heated over 10 min to 600 °C at 11 GPa, the temperature was maintained for 15 min, and the reaction was finally quenched by cooling to room temperature. About 0.5 $mm^3$ of **1** were obtained per batch as a colorless and crystalline powder.

The thermal behavior of **1** was investigated by temperature-dependent mass spectroscopy on a JEOL M-station J-MS 700 mass spectrometer. The sample was heated by an electric furnace to 900 °C in an evacuated silica glass tube connected to the gas inlet of the mass spectrometer (heating rate 10 °C $min^{-1}$). The mass chromatograms exhibit two discrete peaks which are indicative of formation of $NH_3$ ($m/z$ 17): The first peak, at 565 °C, represents evolution of intercalated $NH_3$ [Eq. (5)]. The second peak, at 810 °C, represents evolution of $NH_3$ from condensation of the PN(NH) framework to yield phosphorus(V) nitride $P_3N_5$ [Eq. (4)]. The last peak, observed at 890 °C for $m/z$ 28 ($N_2$), comes from the thermolysis of $P_3N_5$ [Eq. (2)]. The setup of our apparatus did not allow for the detection of low-volatility phosphorus(III) nitride PN as an intermediate. However, small amounts of $P_4$ ($m/z$ 124) were identified in the mass spectrum at 900 °C [Eq. (2)].

The experiment was repeated with crystalline PN(NH) (**2a**) as reference.[3,4] Condensation of **2a** has been observed at 860 °C, whereas the condensation of amorphous PN(NH) (**2c**) already starts at approximately 80 °C.

The FTIR spectrum[39] of **1** exhibits a significant band at 1091 $cm^{-1}$ for the $\delta_s$(H-N-H) deformation mode and at 1635 $cm^{-1}$ for the $\delta_{as}$(H-N-H) mode originating from the intercalated $NH_3$ molecule. The PN(NH) framework only shows N–H valence modes because of the absence of $NH_2$ groups. The observed N–H valence modes result from both imide groups of the framework and N–H vibrational modes of the ammonia molecules and they resemble those of crystalline PN(NH).[3,29]

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